Република Србија
МИНИСТАРСТВО ЗА НАУКУ И
ТЕХНОЛОШКИ РАЗВОЈ
Комисија за стицање научних звања

Број:06-00-69/996
14.04.2010. године
Београд

На основу члана 22. става 2. члана 70. став 6. Закона о научноистраживачкој делатности ("Службени гласник Републике Србије", број 110/05 и 50/06 - исправка), члана 2. става 1. и 2. тачке 1 – 4.(прилози) и члана 38. Правилника о поступку и начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача ("Службени гласник Републике Србије", број 38/08) и захтева који је поднео

Институт за хемију технологију и металургију у Београду

Комисија за стицање научних звања на седници одржаној 14.04.2010.. године, донела је

ОДЛУКУ
О СТИЦАЊУ НАУЧНОГ ЗВАЊА

Др Томислав Тришовић

стиче научно звање

Виши научни сарадник

у области природно-математичких наука - хемија

ОБРАЗЛОЖЕЊЕ

Институт за хемију технологију и металургију у Београду

утврдио је предлог број 1834 од 16.12.2009. године на седници научног већа Института и поднео захтев Комисији за стицање научних звања број 1841 од 17.12.2009. године за доношење одлуке о испуњености услова за стицање научног звања ***Виши научни сарадник***.

Комисија за стицање научних звања је по предходно прибављеном позитивном мишљењу Матичног научног одбора за хемију на седници одржаној 14.04.2010. године разматрала захтев и утврдила да именовани испуњава услове из члана 70. став 6. Закона о научноистраживачкој делатности ("Службени гласник Републике Србије", број 110/05 и 50/06 - исправка), члана 2. става 1. и 2. тачке 1 – 4.(прилози) и члана 38. Правилника о поступку и начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача ("Службени гласник Републике Србије", број 38/08) за стицање научног звања ***Виши научни сарадник,*** па је одлучила као у изреци ове одлуке.

Доношењем ове одлуке именовани стиче сва права која му на основу ње по закону припадају.

Одлуку доставити подносиоцу захтева, именованом и архиви Министарства за науку и технолошки развој у Београду.

ПРЕДСЕДНИК КОМИСИЈЕ
Др Станислава Стошић-Грујичић,
научни саветник

МИНИСТАР
Божидар Ђелић

Прилог 1: Награде и признања

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Gold Medal with Nicola Tesla's Face

ЗЛАТНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

**М. Гвозденовић, Б. Гргур, Л. Рафаиловић, Б. Југовић,
С. Пашалић, Т. Тришовић
ИНСТИТУТ ТЕХНИЧКИХ НАУКА – САНУ
из области нових технологија за**

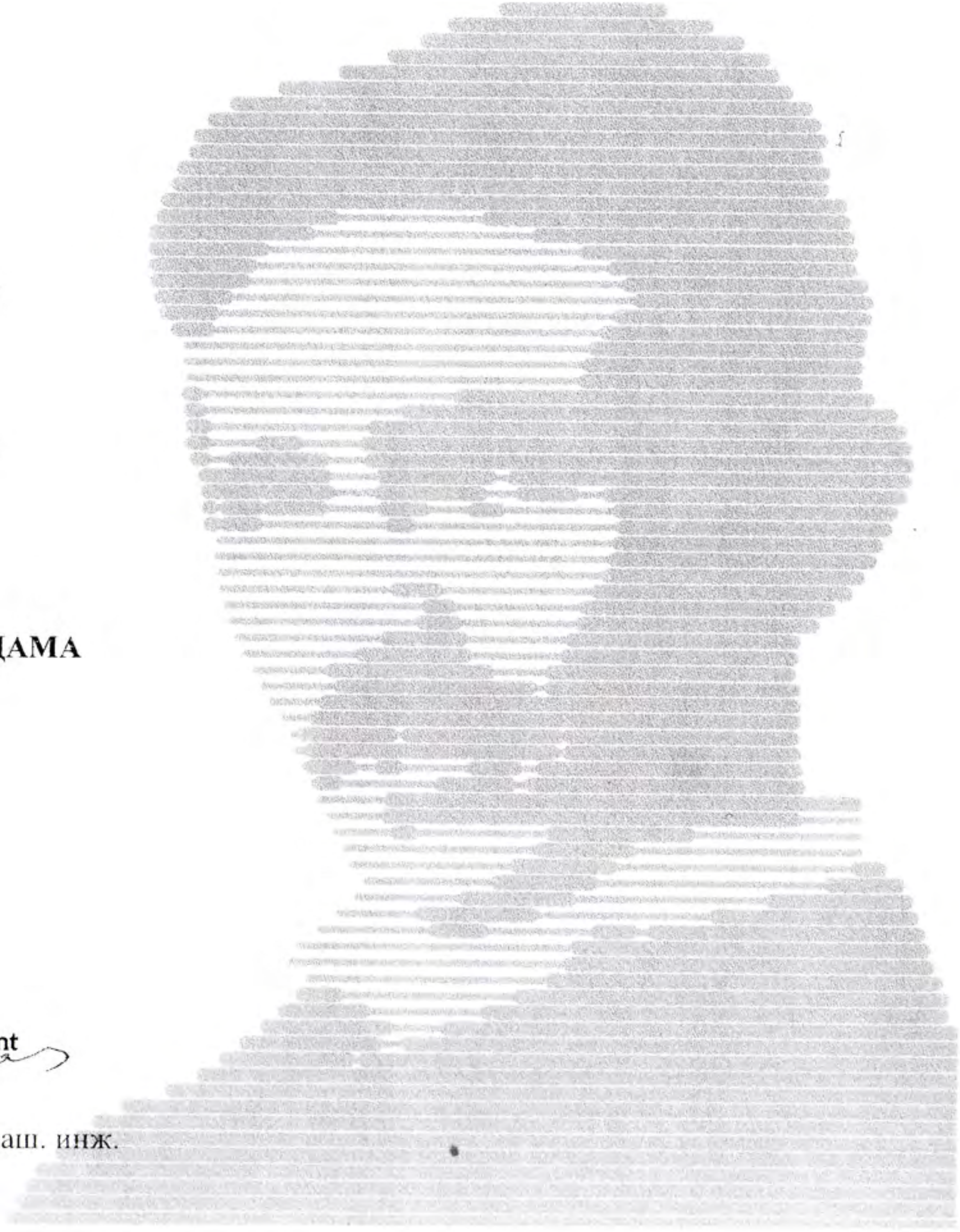
**АУТОМАТСКИ УРЕЂАЈ ЗА ТРЕТМАН ВОДА У ХИДРОМАСАЖНИМ КАДАМА
И БАЗЕНИМА СА ВИШЕСТЕПЕНИМ РЕВЕРЗНИМ СТРУЈНИМ
РЕЖИМИМА**

«ПРОНАЛАЗАШТВО – БЕОГРАД 2011»

Број 72-11
Београд / Belgrade
27. маја 2011.

Председник / President

мр Ђуро Борак, дипл. маш. инж.



Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Silver Medal with Nicola Tesla's Face

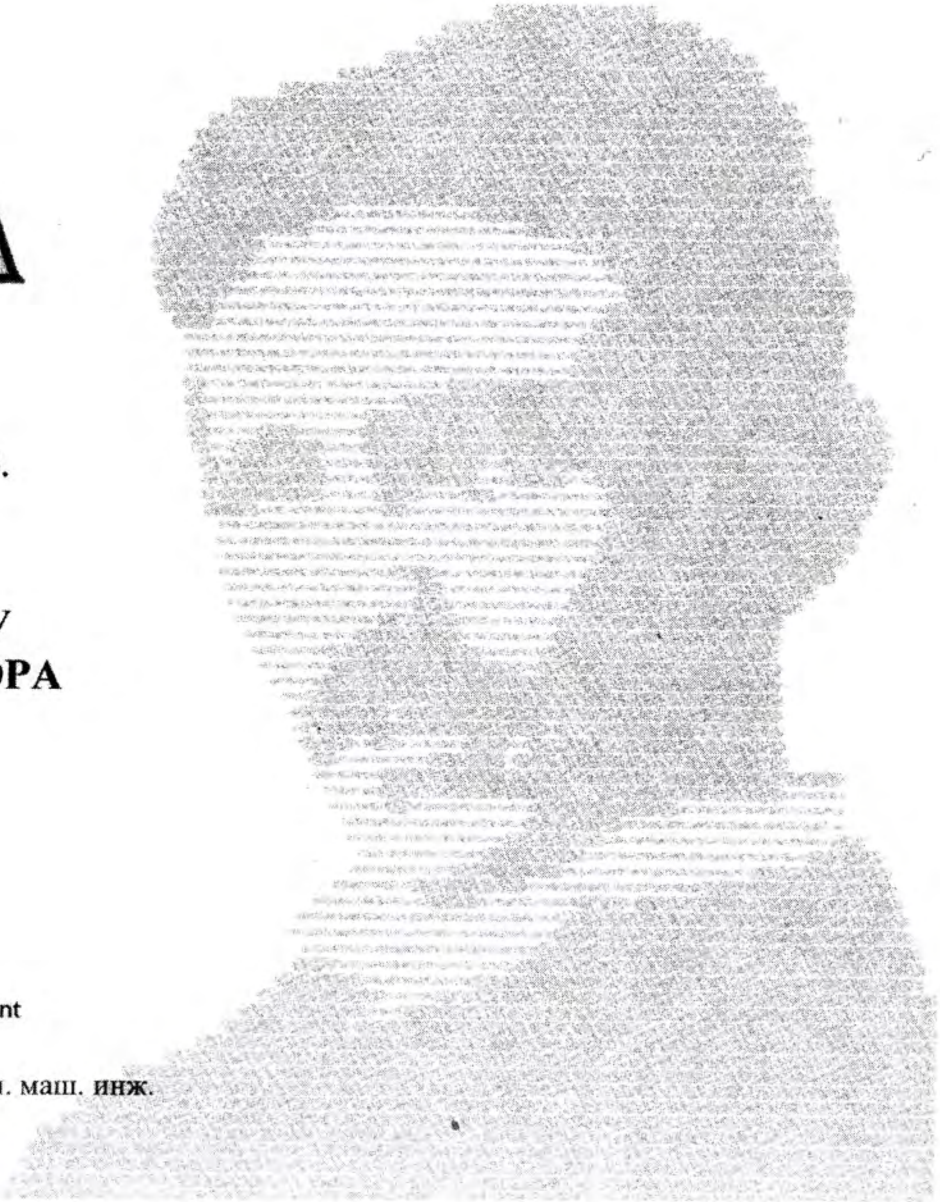
СРЕБРНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

М. Гвозденовић, Б. Гргур, Т.Тришовић, Л. Рафаиловић, Б. Југовић - Институт техничких наука САНУ, Београд
из области проналазака за

ЦЕВНИ ЕЛЕКТОЛИЗЕР ЗА ЕЛЕКТОХЕМИЈСКУ СИНТЕЗУ БРАУНОВОГ ГАСА И АКТИВНОГ ХЛОРА

«ПРОНАЛАЗАШТВО – БЕОГРАД 2012»



Број 51
Београд / Belgrade
25. маја 2012.

Председник / President

мр Ђуро Борак, дипл. маш. инж.

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Golden Plaquette

ЗЛАТНА ПЛАКЕТА

СА ВЕЛИКОМ ЗЛАТНОМ МЕДАЉОМ НИКОЛЕ ТЕСЛЕ

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ - Београд
за патентно решење

УРЕЂАЈ ЗА ФОТОКАТАЛИТИЧКИ И ЕЛЕКТОХЕМИЈСКИ ТРЕТМАН ПИЈАЋИХ ВОДА

Аутори: Милица Гвозденовић, Др Бранимир Југовић, Проф. Др Бранимир Гргур, Др. Јасмина Стевановић, Др Томислав Тришовић,

«ПРОНАЛАЗАШТВО – БЕОГРАД 2009»

Број: 081-09

Београд / Belgrade

22. 05. 2009.

Председник / President

Мр. Ђуро Борак, дипл. инж. маш.

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Special Recognation

СПЕЦИЈАЛНО ПРИЗНАЊЕ

СА ЗЛАТНОМ МЕДАЉОМ САВЕЗА ПРОНАЛАЗАЧА БЕОГРАДА

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ
за нове технологије

МУЛТИФУНКЦИОНАЛНА ЕЛЕКТРОХЕМИЈСКА ЋЕЛИЈА
И
УРЕЂАЈ ЗА ЕЛЕКТРОХЕМИЈСКУ ПРОИЗВОДЊУ АКТИВНОГ ХЛОРА СА ЦЕВНИМ РЕАКТОРОМ И ПОДХЛАЂИВАЊЕМ РЕАКЦИОНОГ РАСТВОРА

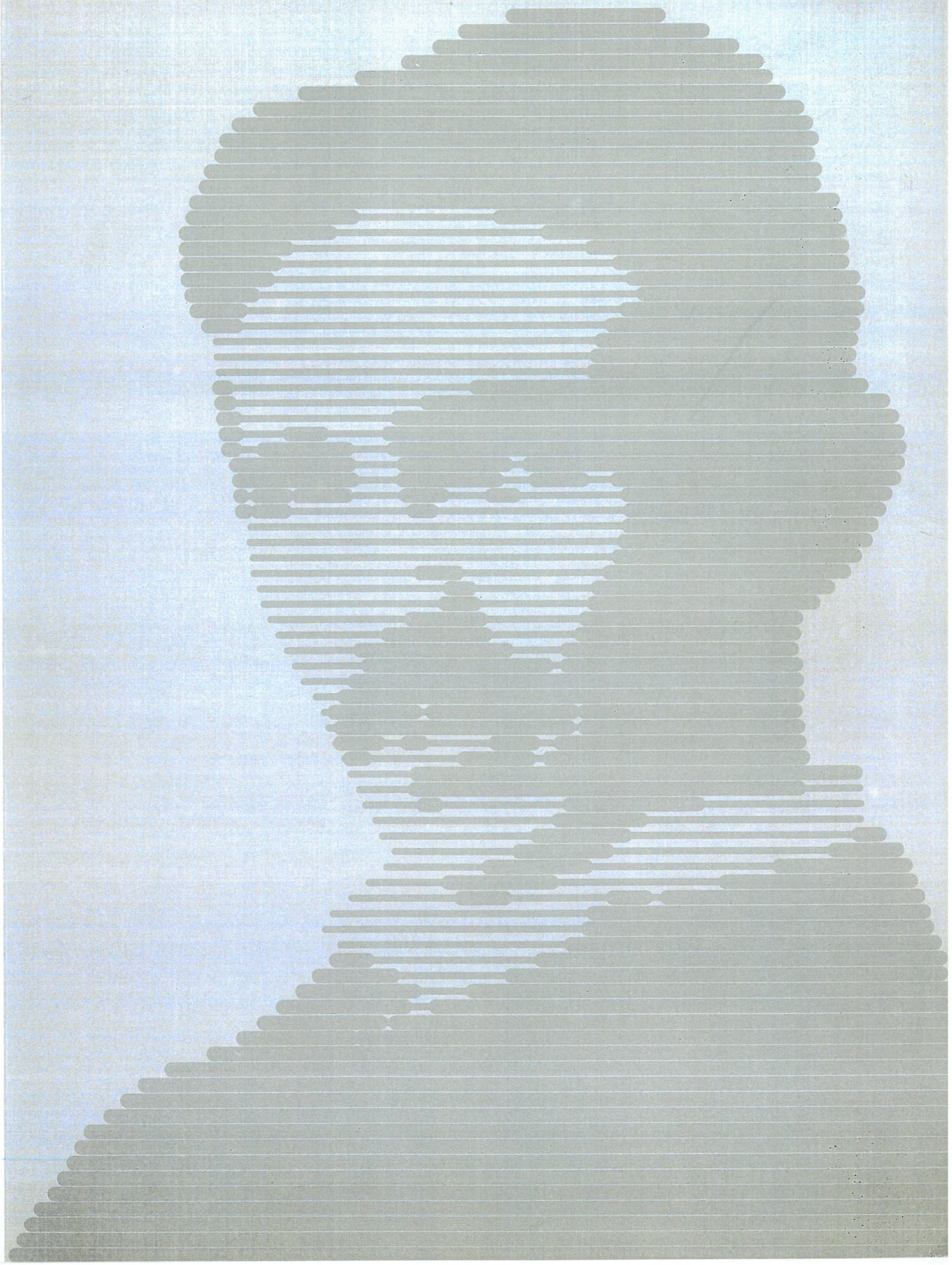
Аутори: Лидија Рафаиловић, Драгослав Шумарац, Бранимир Гргур и Томислав Тришовић

«ПРОНАЛАЗАШТВО – БЕОГРАД 2008»

Број: 010-08

Београд / Belgrade
09. 05. 2008.

Председник / President
Мр. Ђуро Борак, дипл. инж. маш.



ПРИВРЕДНА КОМОРА БЕОГРАДА

ДОДЕЉУЈЕ

Годишњу награду

др ТОМИСЛАВУ ТРИШОВИЋУ, дипл. инж. технологије

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ

за проналазак

ЕЛЕКТРОХЕМИЈСКИ УРЕЂАЈ ЗА ПРОИЗВОДЊУ И ДОЗИРАЊЕ ДЕЗИНФЕКЦИОНИХ СРЕДСТАВА

остварен у 2004/2005. години

Председник жирија
др Зоран Радојевић

Београд,

Председник
Привредне коморе Београда

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Golden Plaquette

ЗЛАТНА ПЛАКЕТА

Лидија Рафаиловић, дипл. физ. хем., проф. др Мирослав Спасојевић, дипл. инж., проф. др Бранимир Гргур, дипл. инж., доцент др Томислав Тришовић, дипл. инж.

за проналазак

УРЕЂАЈ ЗА ИСТОВРЕМЕНУ ПРОИЗВОДЊУ И ДОЗИРАЊЕ СРЕДСТАВА ЗА ДЕЗИНФЕКЦИЈУ ИНДУСТРИЈСКОГ КАПАЦИТЕТА

ИЗЛОЖБА «ПРОНАЛАЗАШТВО – БЕОГРАД 2006»

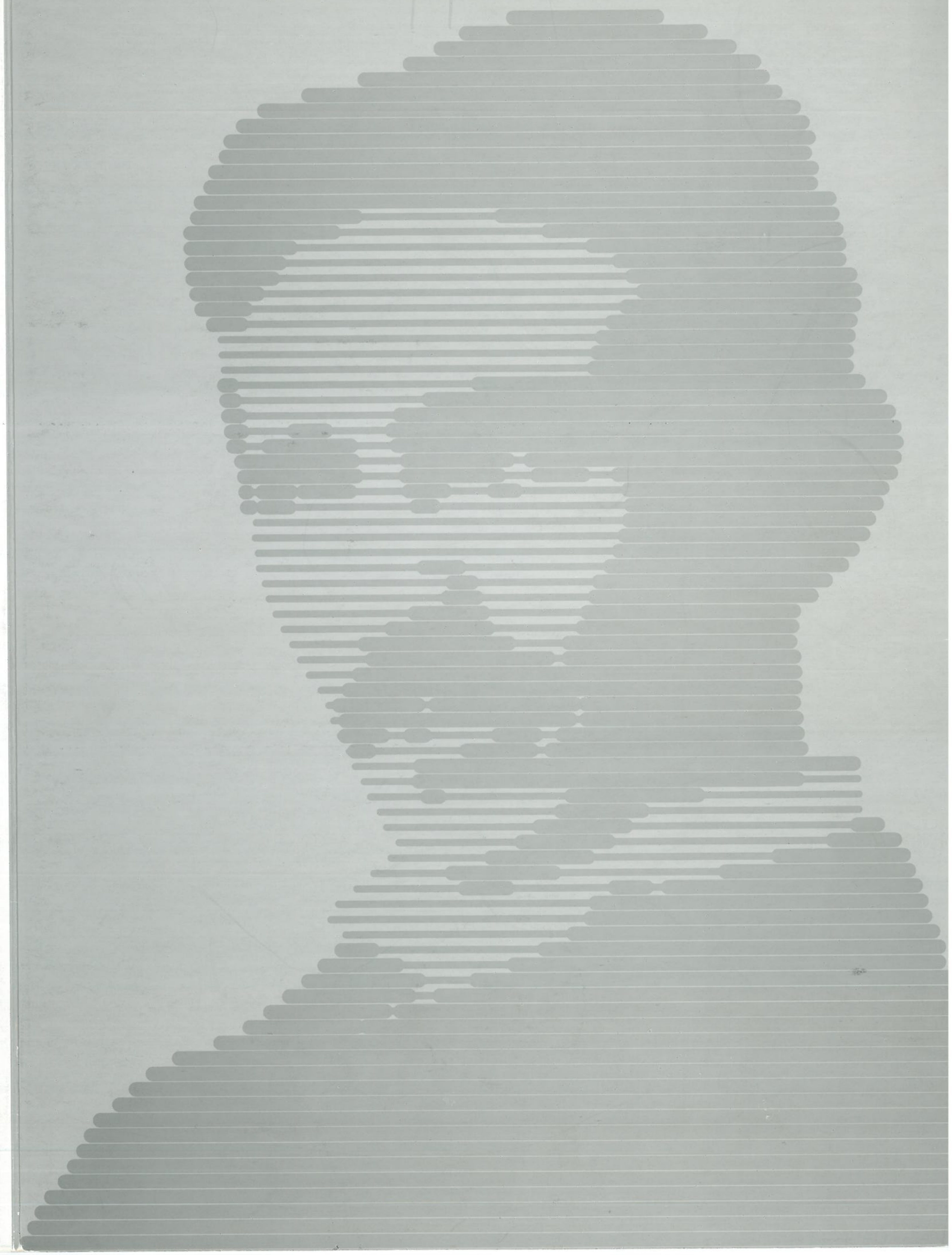
Број: 039-06

Београд / Belgrade

02. 06. 2006.

Председник / President

Мр. Ђуро Борак, дипл. маш. инж.



Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Special Recognation

СПЕЦИЈАЛНО ПРИЗНАЊЕ

СА ЗЛАТНОМ МЕДАЉОМ САВЕЗА ПРОНАЛАЗАЧА БЕОГРАДА

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ
за нове технологије

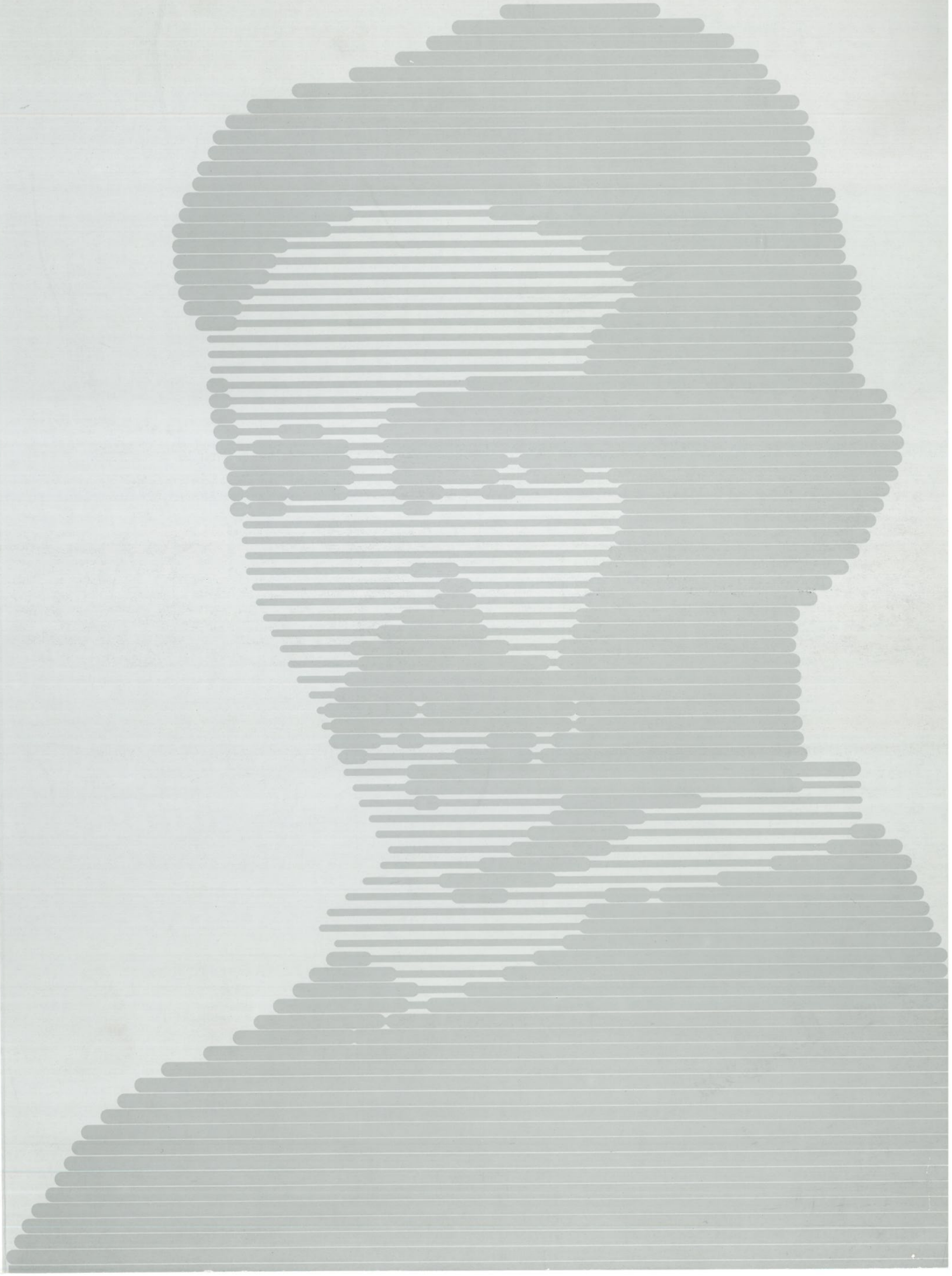
МУЛТИФУНКЦИОНАЛНА ЕЛЕКТРОХЕМИЈСКА ЋЕЛИЈА
И
УРЕЂАЈ ЗА ЕЛЕКТРОХЕМИЈСКУ ПРОИЗВОДЊУ АКТИВНОГ ХЛОРА СА ЦЕВНИМ РЕАКТОРОМ И ПОДХЛАЂИВАЊЕМ РЕАКЦИОНОГ РАСТВОРА

Аутори: Лидија Рафаиловић, Драгослав Шумарац, Бранимир Гргур и Томислав Тришовић

«ПРОНАЛАЗАШТВО – БЕОГРАД 2008»

Број: 010-08
Београд / Belgrade
09. 05. 2008.

Председник / President
Мр. Ђуро Борак, дипл. инж. маш.



КЊИЖЕВНОСТ
МУЗИКА
ЛИКОВНО СТВАРАЛАШТВО
НОВИНАРСТВО
ДРУШТВЕНЕ НАУКЕ
ПРОНАЛАЗАШТВО
ОБРАЗОВАЊЕ
ПОЗОРИШТЕ
ФИЛМ
МЕДИЦИНА
СПОРТ
ПРИРОДНЕ НАУКЕ
АРХИТЕКТУРА
СТВАРАЛАШТВО МЛАДИХ

Скупштина града Београда

Награда града Београда

ЗА ОБЛАСТ НАУКЕ-ПРОНАЛАЗАШТВА ЗА 2004. ГОД.

ДР. ЉИЉАНИ ГАЈИЋ-КРСТАЈИЋ
МР НАТАШИ ТРИШОВИЋ
ПРОФ. ДР. НЕДЕЉКУ КРСТАЈИЋУ
ДР. ТОМИСЛАВУ ТРИШОВИЋУ

у Београду
17. АПРИЛ 2005. ГОДИНЕ

Дани Београда

Градоначелник
града Београда

Председник Скупштине
града Београда
Милорад Перовић

Председник Комисије

ПРИВРЕДНА КОМОРА БЕОГРАДА
11000 Београд, Кнеза Милоша 12
телефон: 381 011/ 641-355; факс: 642-029
интернет: www.kombeg.org.yu
ПИБ: 100045959

Наш знак: 01-54/1 Ваш знак: Београд, 13.01.2006.

Poštovani gospodine Trišoviću,

Zadovoljstvo nam je da Vas obavestimo da je Žiri za dodelu godišnjih nagrada Privredne komore Beograda za najbolje pronalaske, tehnička unapređenja i dizajnerska rešenja, doneo odluku da Vam dodeli Godišnju nagradu Privredne komore Beograda za pronalazak «ELEKTROHEMIJSKI UREĐAJ ZA PROIZVODNJU I DOZIRANJE DEZINFEKCIONIH SREDSTAVA».

O datumu uručenja diplome i novčane nagrade bićete blagovremeno obavešteni.

Čestitamo Vam na dobijenoj nagradi i želimo sve najbolje u Novoj godini.

Prilog:

-Odluka Žirija

PREDSEDNIK
PRIVREDNE KOMORE BEOGRADA

Milan Janković

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Gold Medal with Nicola Tesla's Face

ЗЛАТНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

ТЕХНОЛОШКО МЕТАЛУРШКИ ФАКУЛТЕТ из Београда
Проф. др Бранимиру Гргуру, Горану Бабићу и др Томиславу Тришовићу
за област нових технологија

ПОСТУПАК ЗА ЕЛЕКТРОХЕМИЈСКУ ПРОИЗВОДЊУ

ПОВИДОН - ЈОДА

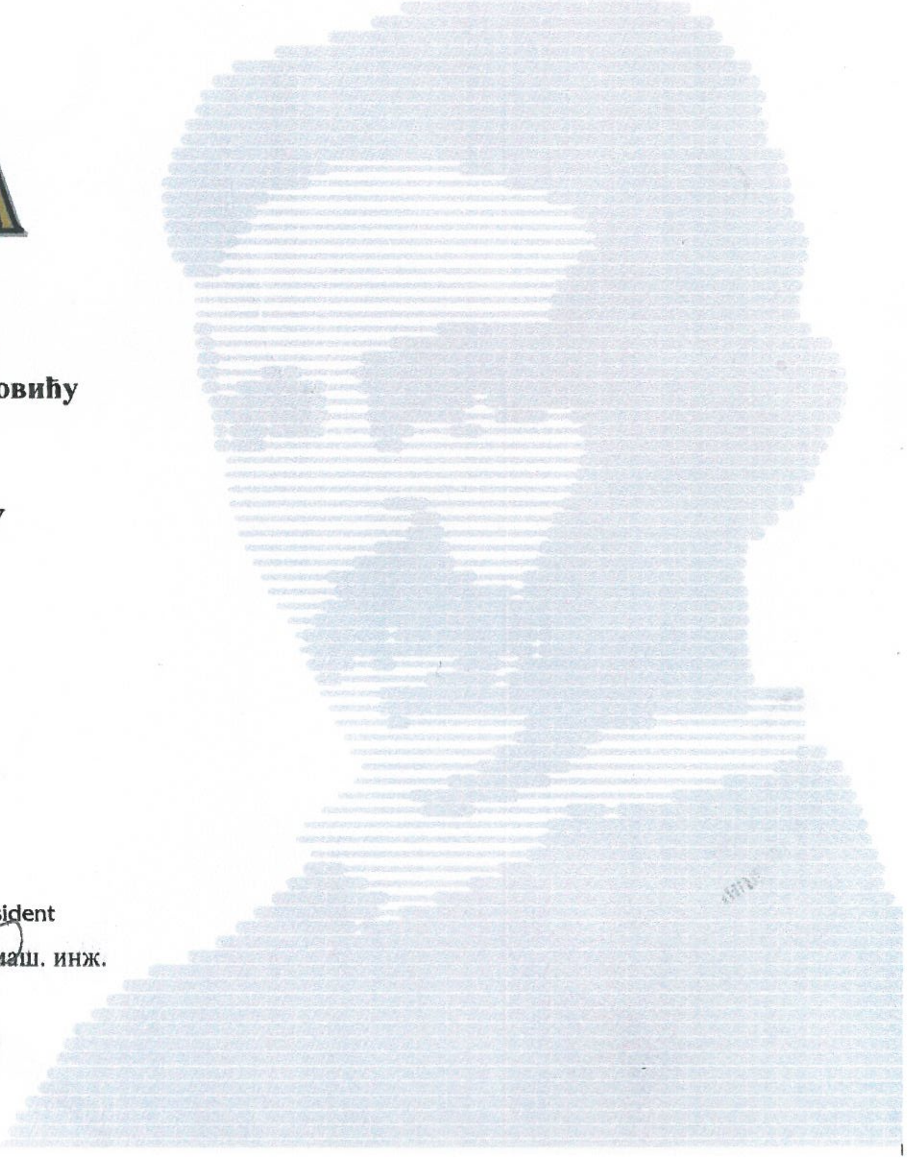
«ПРОНАЛАЗАШТВО – БЕОГРАД 2009»

Број 085-09

Београд / Belgrade

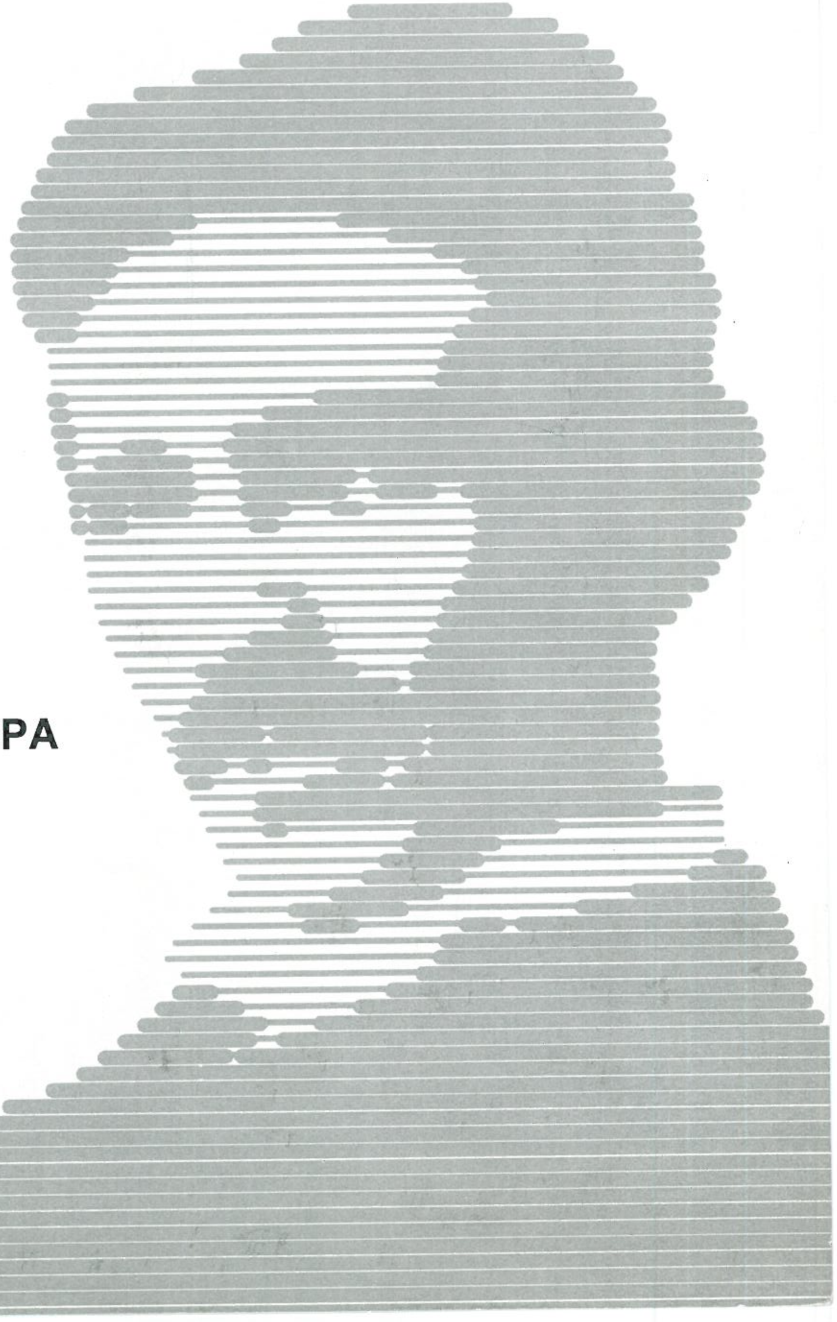
22. маја 2009

Председник / President
мр Ђуро Борак, дипл. маш. инж.



Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Silver Medal with Nicola Tesla's Face



СРЕБРНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

др Томислав Тришовић

ЗА ПРОНАЛАЗАК

УРЕЂАЈ ЗА ЕЛЕКТРОХЕМИЈСКУ ПРОИЗВОДЊУ АКТИВНОГ ХЛОРА

НА ИЗЛОЖБИ «ПРОНАЛАЗАШТВО – БЕОГРАД 2004»

Број: 083/04
Београд / Belgrade
21. 05. 2004.

Председник / President
Мр. Ђуро Борак, дипл. маш. инж.

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Bronze Medal with Nicola Tesla's Face

БРОНЗАНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

Томислав Тришовић

У ОБЛАСТИ НОВИХ ТЕХНОЛОГИЈА

**УНИВЕРЗАЛНИ УРЕЂАЈ ЗА ЕЛЕКТРОХЕМИЈСКУ СИНТЕЗУ
СА МОДУЛАРНИМ РЕАКТОРИМА ПРОТОЧНОГ ТИПА**

НА ИЗЛОЖБИ «ПРОНАЛАЗАШТВО – БЕОГРАД 2007»

Број: 001
Београд / Belgrade
01. 06. 2007.

Председник / President
Мр. Ђуро Борак, дипл. маш. инж.

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Gold Medal with Nicola Tesla's Face

ЗЛАТНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

М. Гвозденовић, Б. Гргур, Л. Рафаиловић, Б. Југовић, С. Пашалић, Т. Тришовић
ИНСТИТУТ ТЕХНИЧКИХ НАУКА – САНУ
из области нових технологија за

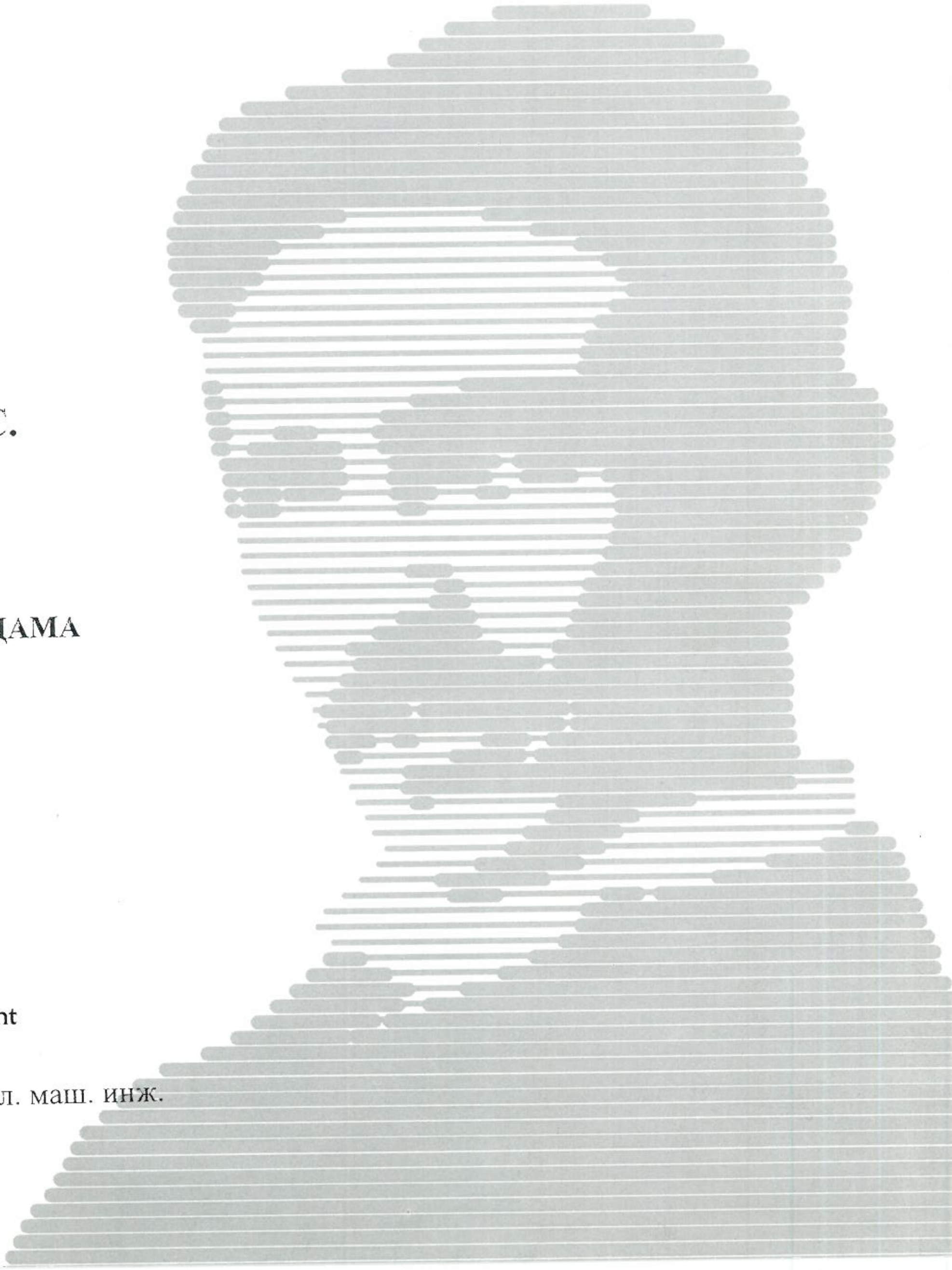
АУТОМАТСКИ УРЕЂАЈ ЗА ТРЕТМАН ВОДА У ХИДРОМАСАЖНИМ КАДАМА И БАЗЕНИМА СА ВИШЕСТЕПЕНИМ РЕВЕРЗНИМ СТРУЈНИМ РЕЖИМИМА

«ПРОНАЛАЗАШТВО – БЕОГРАД 2011»

Број 72-11
Београд / Belgrade
27. маја 2011.

Председник / President

мр Ђуро Борак, дипл. маш. инж.



Drugi mednarodni sejem inovacij v Sloveniji

2nd International Exhibition of Inventions in Slovenia

organized by Inovatorski center ASI

Ljubljana, May 17 to 18, 2010

GOLD PRIZE

is hereby awarded to

dr. TOMISLAV TRIŠOVIĆ

for the invention

AUTOMATIC DEVICE FOR PHOTOCATALYTICAL AND ELECTROCHEMICAL DRINKING WATER TREATMANT

Ljubljana, May 18, 2010

Tomaž Pevc,
director

Pevc

Prvi mednarodni inovacijski sejem v Sloveniji

1st International Exhibition of Inventions in Slovenia

Organizator / organized by: Inovatorski center ASI

Celje, 9.-16. september / September 9 to 16, 2009

SREBRNA MEDALJA
SILVER PRIZE

Prejme jo inovator
is hereby awarded to
dr. Tomislav Trišović

za inovacijo
for the invention
MULTIFUNKCIJSKA NAPRAVA ZA FIZIKALNO-KEMIČNO OBDELAVO VODE

Celje, 15.9.2009

Tomaž Pevc,
direktor ASI
Pevc

DIPLOMA

THIS DOCUMENT IS TO CERTIFY THAT

Dr. T. Trišović

IS AWARDED THE ASSOCIATION OF HUNGARIAN INVENTORS'

GENIUS MEDAL

FOR THE INVENTION

Automatic device for photocatalytical and electrochemical drinking water treatment

2ND INTERNATIONAL INVENTION EXHIBITION – LJUBLJANA

ON THIS 18TH DAY OF MAY IN THE YEAR OF 2010

GYÖRGY GÁL
MEMBER OF PRESIDIUM

ДИПЛОМ

Министерство образования и науки Российской Федерации

награждает

Ph.D.Tomislav Trišović, M.Sc. Goran Babić
Prof Ph.D.Branimir Grgur, Prof. Ph.D. Hans
Peter Karnthaler, M. Sci. Lidija Rafailović

за высокий научно-технический уровень
разработки, представленной на
Международной выставке изобретений "GENIUS"

г. Будапешт, Венгрия, ноябрь 2007 г.

Заместитель Министра образования
и науки Российской Федерации

Фридлянов В.Н.

THE GENIUS - BUDAPEST - THE INNOVATION BRIDGEHEAD

GENIUS - BUDAPEST
International Invention Fair

DIPLOMA

This document is to certify that during the **GENIUS-BUDAPEST** International Inventions Fair out of 300 items from 20 countries

Lidija Rafailovic, Dr. Miroslav Spasojevic,
Dr. Branimir Grgur, Dr. Tomislav Trisovic

SYSTEM FOR ELECTROCHEMICAL PRODUCTION AND DOSING ACTIVE CHLORINE HIGH CAPACITY

is awarded this prestigious

GENIUS MEDAL

On the 11th day of September in the year of 2006
Budapest, Hungary

Dr. Szántay Csaba
President

MAGYAR FELTALÁLÓK EGYESÜLETE
GENIUS

Dr. Vedres András
Secretary General

ARCA 2006.

4. međunarodna izložba inovacija, novih ideja, proizvoda i tehnologija

dodjeljuje se

POSEBNO PRIZNANJE

Trisovic T. dr. et al

Modular eletrochemical generator

Zagreb, rujan 2006.

Predsjednik Udruge inovatora Hrvatske
dr. sc. Stanislav Čajavec

S. Čaj

HRVATSKA
ZAJEDNICA
TEHNIČKE
KULTURE

UDRUGA
INOVATORA
HRVATSKE

Zagrebački
Velesajam

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Gold Medal with Nicola Tesla's Face

ЗЛАТНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

др Томислав Тришовић

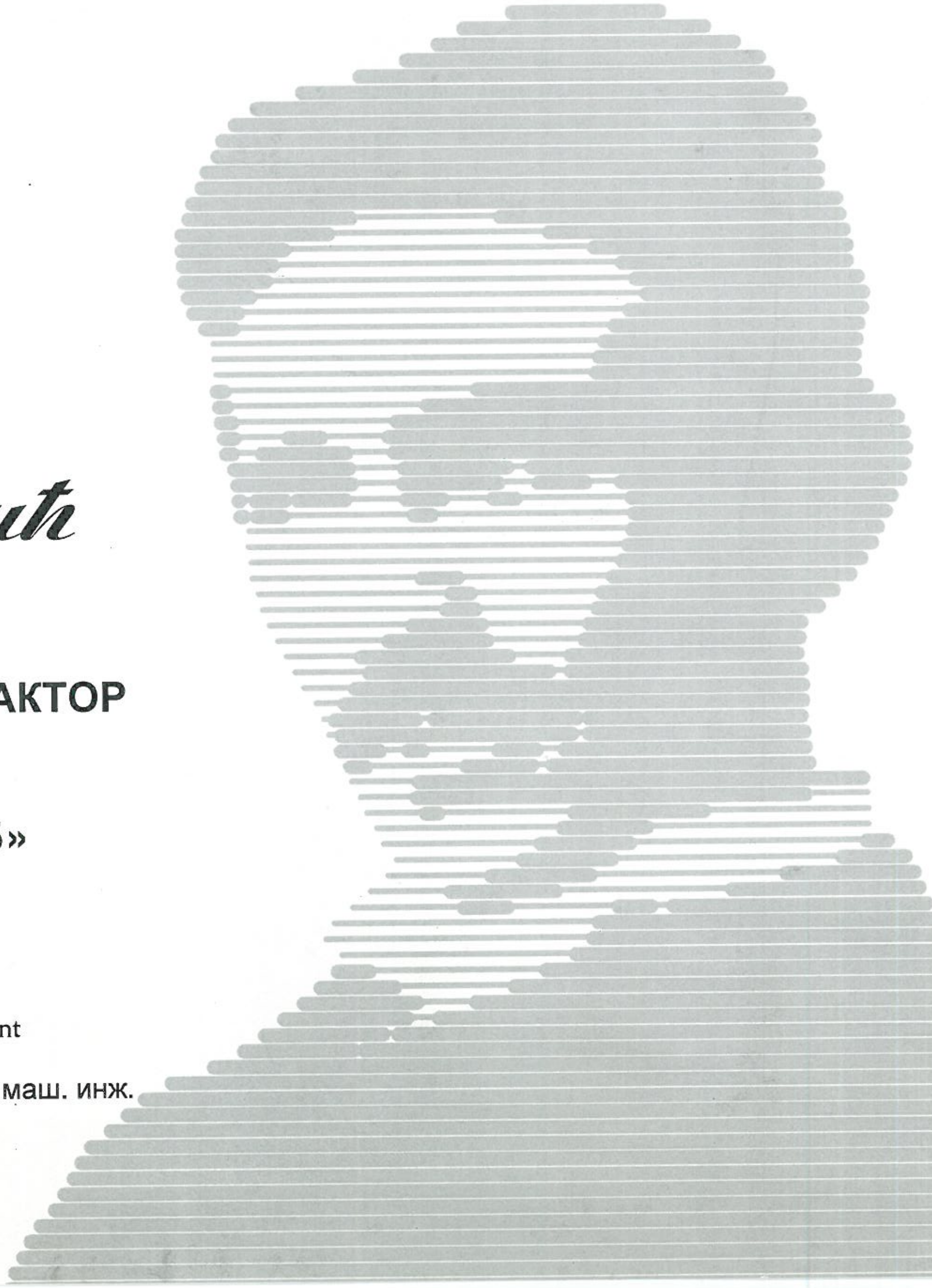
ЗА ПРОНАЛАЗАК

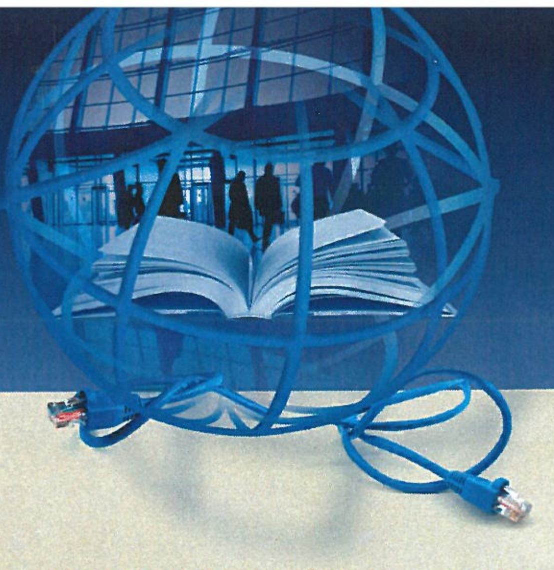
МОДУЛАРНИ ПРОТОЧНИ ЕЛЕКТРОХЕМИЈСКИ РЕАКТОР

НА ИЗЛОЖБИ «ПРОНАЛАЗАШТВО – БЕОГРАД 2005»

Број: 086/05
Београд / Belgrade
27. 05. 2005.

Председник / President
Мр. Ђуро Борак, дипл. маш. инж.





POSLOVNO-TEHNOLOŠKI INKUBATOR
TEHNIČKIH FAKULTETA BEOGRAD

POVODOM PET GODINA USPEŠNOG RADA

DODELJUJE

Plaketu

za

Uspešan transfer znanja iz istraživanja i pokretanje proizvodnje

AQUA Crystal d.o.o.

Beograd, 17.12.2012.godine

Direktor
Gordana Danilović Grković

ИТФ
БЕОГРАД

POSLOVNO-TEHNOLOŠKI
INKUBATOR
TEHNIČKIH FAKULTETA - Beograd d.o.o.

СПАТУМ **UIATIM**

Сојузот на пронаоѓачите и авторите на техничките унапредувања на Македонија

Доделува:

ЗЛАТЕН МЕДАЛ

На

д-р ТОМИСЛАВ ТРИШКОВИЌ
Институт техничких наука САНУ
Београд

на 25-та Интернационална изложба на пронајдоци, технички унапредувања, нови производи и творештво на млади

“МАКИНОВА 2005“

1980 МАКИНОВА СКОПЈЕ ***2005***

за пронајдокот:

Електрохемиски уред за производство на активен хлор

Скопје, _18-23.10.2005 *г.*

Претседател
проф. д-р Мито Златаноски

Савез проналазача и аутора техничких унапређења Београда

Belgrade Association of Inventors and Authors of Technical Improvements
Award Gold Medal with Nicola Tesla's Face

ЗЛАТНА МЕДАЉА

СА ЛИКОМ НИКОЛЕ ТЕСЛЕ

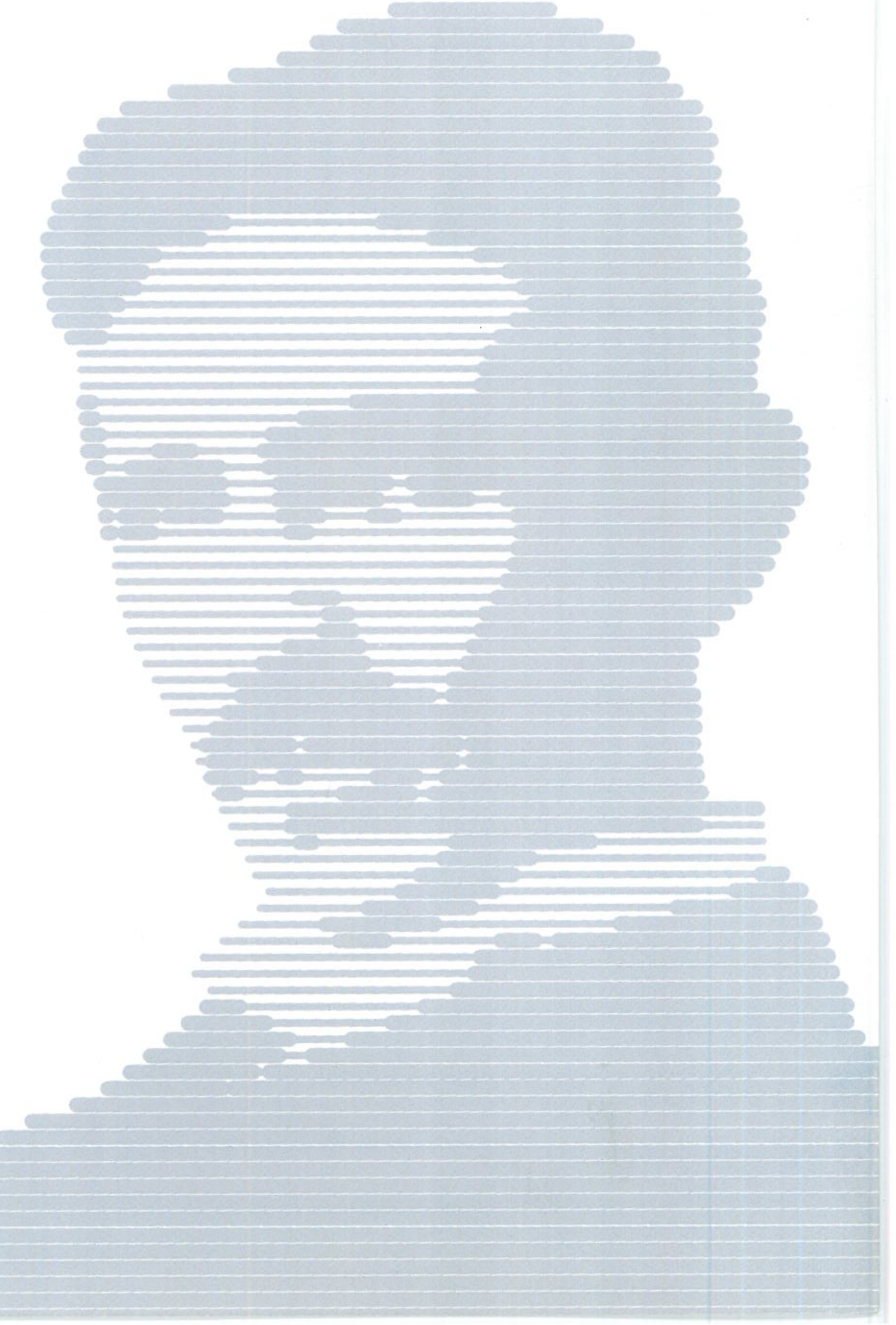
Аутори:Томислав Тришовић, Бранимир Југовић, Милица Гвозденовић, Лидија Рафаиловић, Бранимир Гргур,
AQUA CRYSTAL DOO – БЕОГРАД
из области проналазака за
за (for)

СИСТЕМ ЗА АУТОМАТСКУ ДЕЗИНФЕКЦИЈУ ВОДЕ УПРАВЉАН ПОТЕНЦИОМЕТРИСКОМ ЕЛЕКТОДОМ
'HE SYSTEM FOR AUTOMATIC WATER DISINFECTIONS DRIVEN BY THE POTENTIOMETER ELECTRODE

„ПРОНАЛАЗАШТВО – БЕОГРАД 2013"

Број 038-ПБ
Београд / Belgrade
29. маја 2013.

Председник / President
мр Ђуро Борак, дипл. маш. инж.



Poslovna
Savršenost

Certificate

Tomislav Trišović

pohađao/la je i uspešno završio/la kurs

Marketing na internetu

U Beogradu 27.09.2013. godine

Miroslav Zorić PR
AGENCIJA ZA OBRAZOVANJE
POSLOVNA SAVRŠENOST
BEOGRAD (RAKOVICA)

Прилог 2: Рецензије пројеката за Министарство просвете науке и технолошког развоја

Република Србија
МИНИСТАРСТВО ПРОСВЕТЕ
И НАУКЕ
Број: 011-00-2/2011-14
Датум: 28.03.2011.
Београд
Немањина 22-26

LETTER OF APPRECIATION

We gratefully acknowledge your contribution to voluntary participate in the evaluation of national Serbian project proposals.

The Ministry of Education and Science (Former Ministry of Science and Technological Development) of the Republic of Serbia launched on May 23rd 2010 a Call for proposals for the new 4-year project cycle in basic research, applied research (technology development) and priority research fields (multidisciplinary integrated research). The proposals were evaluated by international experts during the period July-December 2010. The Ministry will fund 780 projects, out of 878 that applied. The success rate in this call was 89%. In the next four years, 11615 scientists will be supported through the Ministry.

In this process, the support of international evaluators was crucial. The proposals were evaluated by 1585 foreign evaluators. This task had two objectives, to promote atmosphere of competitiveness among Serbian researchers, and to promote Serbian research potential among their colleagues abroad.

We would like to express our gratitude for helping Serbian research community to receive a more objective and international validation of their proposals.

Thank you for committing your time and expertise.

Assistants Minister:

Prof. Dr. Viktor Nedović

....

Prof. Dr. Tibor Sabo

....

Dr. Radosav Cerović

....

State Secretary:

Prof. Dr. Radivoje Mitrović

....

На основу члана 36. Закона о иновационој делатности ("Службени гласник РС", бр. 110/05), сагласно Правилнику о условима конкурисања, критеријумима за избор реализатора пројеката и условима финансирања пројеката или изградње инфраструктуре намењене реализацији иновационих пројеката ("Службени гласник РС", бр. 59/06), на основу Одлуке број 401-00-00006/2010-02 од 01.03.2010. године, а у вези са спровођењем поступка оцењивања предлога иновационих пројеката пријављених на јавни позив објављен дана 10.06.2009. године у дневном листу „Политика“, уговорне стране:

1. **Република Србија - Министарство за науку и технолошки развој, Београд, Немањина 22-26, ПИБ 105002818, матични број: 17693794** (у даљем тексту: Министарство), и
2. **Институт техничких наука САНУ, Кнез Михаилова 35/IV,Београд, ПИБ 100039438, матични број: 07011016 у којој су рецензенти запослени/остварили право на пензију** (у даљем тексту: Организација),

закључују

УГОВОР
о исплати рецензентима накнаде за оцењивање предлога иновационих пројеката пријављених по јавном позиву објављеном дана 10.06.2009. године у дневном листу „Политика“

Члан 1.

Овим уговором утврђују се међусобна права и обавезе уговорних страна везано за исплату накнаде за оцену предлога иновационих пројеката извршену у периоду од 01.10.2009. до 19.02.2010. године:
1. од стране рецензента Оливере Милошевић за 1 иновациони пројекат;
2. од стране рецензентаТомислава Тришовића за 3 иновациона пројекта;
3. од стране рецензента Бранимира Југовића за 1 иновациони пројекат;

Члан 2.

За оцењивање предлога иновационих пројеката наведених у члану 1. овог Уговора, одређени су оцењивачи Оливера Милошевић, Томислав Тришовић и Бранимир Југовић који су запослени/пензионери код Организације.

За рецензију сваког од иновационих пројеката наведених у члану 1. Министарство уплаћује:
2.1. рецензенту Оливери Милошевић накнаду у износу од по 6.000,00 динара нето по извршеној рецензији, што чини укупно 6.000,00 динара за уплату рецензенту ;
2.2. рецензенту Томиславу Тришовићу накнаду у износу од по 6.000,00 динара нето по извршеној рецензији, што чини укупно 18.000,00 динара за уплату рецензенту ;
2.3. рецензенту Бранимиру Југовићу накнаду у износу од по 6.000,00 динара нето по извршеној рецензији, што чини укупно 6.000,00 динара за уплату рецензенту ;
Укупан износ накнаде на име извршених рецензија од стране горе наведених рецензената износи 45.180,00 динара бруто, од ког ће износа Организација, у року од седам дана од дана пријема уплате Министарства, исплатити рецензенте у укупном износу као у ставу 2. овог члана, а након уплате:
- пореза на доходак грађана (20%),
- доприноса за ПИО на терет примаоца прихода (22%), и
- нормираних трошкова (20%).

Члан 3.

На овај Уговор се примењују одредбе Закона о облигационим односима.
За евентуалне спорове по овом Уговору надлежан је Привредни суд у Београду.

Члан 4.

Овај Уговор је сачињен у 7 (седам) истоветних примерака, од којих три за Министарство, а по један за Организацију и оцењиваче пројеката.

У Београду, 01.04.2010.године
Евиденциони број уговора: 401-00-00006/2010-02-43

УГОВОРНЕ СТРАНЕ:

1) за Министарство
по овлашћењу

Проф. др Милош Недељковић

2) за Организацију

Проф. др Драгољуб Ускоковић

ИНСТИТУТ ТЕХНИЧКИХ НАУКА
СРПСКЕ АКАДЕМИЈЕ НАУКА И УМЕТНОСТИ
Бр. 226/1
30.04. 2010. год.
Кнез Михајлова 35/IV, Београд ПФ 315
Тел. 636-994, 185-437; Фах. 185-263

УНИВЕРЗИТЕТ У КРАГУЈЕВЦУ
ТЕХНИЧКИ ФАКУЛТЕТ
Број LXIV - 916/16
5. 05. 2010. год.
ЧАЧАК

На основу члана 77. Статута Техничког факултета, чл. 20. Правилника о уџбеницима и другим наставним публикацијама бр. XXIV-1600/15 од 9. јула 2008. год., на предлог Катедре за мехатронику бр. 923. од 4. маја 2010. год., Наставно-научно веће, на седници одржаној 5. маја 2010. год., донело је

ОДЛУКУ
о именовању рецензената

Именују се рецензенти за техничко решење под називом **"Побољшана технологија за сушење воћа и поврћа енергетске ефикасности и заштите животне средине",** а настало је као резултат рада на пројекту "Развој и примена логистичких система за коришћење биомаса и отпадног дрвета као енергената у домаћинствима у индустрији", чији је аутор **др Срећко Ћурчић, ванр. проф., Технички факултет, Чачак,** у следећем саставу:

1. **Др Радомир Стевановић, доцент,** Агрономски факултет, Чачак,
научна област: Инжењерски процеси,
2. **Др Томислав Тришовић, доцент,** Агрономски факултет, Чачак,
научна област: Инжењерски процеси.

Доставити:
- именованима,
- аутору,
- архиви ННВ.

ДЕКАН
ТЕХНИЧКОГ ФАКУЛТЕТА
Проф. др Јерослав М. Живанић, дипл. инж. ел.

ИНСТИТУТ ЗА
ВОЋАРСТВО
ЧАЧАК
Број: 119/2
Датум: 1. 03. 2010.

INSTITUT ZA VOĆARSTVO – ČAČAK
FRUIT RESEARCH INSTITUTE – ČAČAK

На основу члана 59 Закона о научноистраживачкој делатности (Сл. Гласник РС бр. 110/05), члана 36 Статута Института и Правилника о поступку и начину вредновања, и квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник бр. 38/2008) – Прилог 2, Научно веће Института за воћарство на редовној 22. седници од 1. 03. 2010. године је донело следећу

ОДЛУКУ

ПОКРЕЋЕ СЕ поступак верификације научноистраживачког резултата оствареног на Пројекту Министарства за науку и технолошки развој РС, ТР - 20013А – *Стварање и проучавање нових генотипова воћака и увођење савремених биотехнологија гајења и прераде воћа*: **„Вишеслојан проструjни модел за испитивање процеса сушења воћа - шљиве“**, у оквиру категорије *Ново експериментално постројење* (М83).

За евалуацију резултата предлажу се рецензенти-експерти:

1. доц. др Томислав Тришовић

2. доц. др Радомир Стевановић

в. д. председника Научног већа

др Ђурђина Ружић

Доставлјено:
- Ауторима резултата,
- Рецензентима,
- Архиви НВ.

32000 Čačak, Srbija, Kralja Petra I, br. 9; Tel: 032/221-375, 221-413, Fax: 032/221-391; Direktor: 032/222-625; Prodaja sadnica i voća: 032/228-125; Komercijala: 032/225-457; e-mail: institut-cacak@eunet.yu

32000 Čačak, Serbia, Kralja Petra I 9; Tel: +381 (0) 32 221 375, 221 413, Fax: +381 (0) 32 221 391; Director: +381 (0) 32 222 625; Sale of Nursery Stock, Fruit: +381 (0) 32 228 125; Commercal Office: +381 (0) 32 225 457; e-mail: institut-cacak@eunet.yu

Прилог 3: Чланство у комисијама за дипломске и мастер радове

УНИВЕРЗИТЕТ У КРАГУЈЕВЦУ
АГРОНОМСКИ ФАКУЛТЕТ У ЧАЧКУ
Дана 03.10.2014.године

Списак студената основних академских студија код којих је др Томислав Тришовић био ментор дипломског (завршног) рада

Студент	Наслов рада	Датум одбране
1. Марија С. Чворовић	«Технологија производње и смрзавања домаћих пита у хладњачи Моравица»	12.11.2007.год.
2. Јасмина М. Јовановић	«Технологија производње и смрзавања пецива у хладњачи-Мооравица»	05.05.2008.год.
3. Даница М. Попадић	« Индустријски начин производње замрзутог теста»	26.04.2013.год

Списак студената основних академских студија код којих је др Томислав Тришовић био члан Комисије за одбрану завршног рада

Студент	Наслов рада	Датум одбране
1. Миљојка Д. Мијаиловић	«Производња дестилата шљиве као основе за ракију шљивовицу»	23.09.2013.год.
2. Слађана Д. Новитовић	«Ефекат технолошких параметара на садржај HCN у дестилату шљиве Пожегаче»	31.03.2014.год.

ZAPISNIK

O ODRŽANOJ JAVNOJ ODBRANI

MAGISTARSKE TEZE

Dana 13.05.2008. održana je javna odbrana magistarske teze magistranta **ALEKSANDRE B. PETROVIĆ, dipl. inž.** pod nazivom: *„UTICAJ GVOŽĐA NA ELEKTROHEMIJSKE KARAKTERISTIKE NIKAL-OKSIDNE ELEKTRODE KADMIJUM/NIKAL-OKSID AKUMULATORA“.*

Po zaključenju javne odbrane utvrđuje se da je **ALEKSANDRA (Borivoje) PETROVIĆ**, dipl. inž. odbranila magistarsku tezu.

Beograd, 13.05.2008.

KOMISIJA

Grgur B.

1. Dr Branimir Grgur, van. prof. TMF

M. Maksimović

2. Dr Miodrag Maksimović, red. prof. TMF

Snežana Gojković

3. Dr Snežana Gojković, red. prof. TMF

4. Dr Tomislav Trišović, naučni saradnik
ITN-SANU, Beograd

Прилог 4: Потврда о учешћу у комисији за одбрану докторске дисертације

ZAPISNIK

sa odbrane doktorske disertacije Mr BRANIMIRA JUGOVIĆA

Komisija za odbranu doktorske disertacije **Mr Branimira Jugovića** odredjena na sednici Nastavno-naučnog veća Tehnološko-metalurškog fakulteta u Beogradu održanoj dana **17.07.2008.** godine u sastavu:

1. **Dr Branimir Grgur, van. prof. TMF**
2. **Dr Miodrag Maksimović, red. prof. TMF**
3. **Dr Jasmina Stevanović, naučni savetnik IHTM, Beograd**
4. **Dr Tomislav Trišović, naučni saradnik ITN-SANU, Beograd**

sastala se na dan **25.12.2008.** godine **u** **16,00 sati** i konstatovala sledeće:

1. Na temu koju je predložilo NNV TMF-a na svojoj sednici od **21.10.2005.** godine Veće naučnih oblasti Univerziteta je dalo saglasnost na sednici od **26.01.2006.** godine čime je **Mr Branimiru Jugoviću** odobrena izrada doktorske disertacije pod nazivom:

„ELEKTROHEMIJSKI IZVORI ENERGIJE SISTEMA METAL|ELEKTROPROVODNI POLIMER NA BAZI VODENIH RASTVORA“

2. Veće Tehnološko-metalurškog fakulteta na sednici od **17.07.2008.** godine imenovalo je Komisiju za ocenu i odbranu doktorske disertacije Mr Branimira Jugovića u sastavu:
    1. **Dr Branimir Grgur, van. prof. TMF**
    2. **Dr Miodrag Maksimović, red. prof. TMF**
    3. **Dr Jasmina Stevanović, naučni savetnik IHTM, Beograd**
    4. **Dr Tomislav Trišović, naučni saradnik ITN-SANU, Beograd**

3. Veće Tehnološko-metalurškog fakulteta na svojoj sednici od **25.09.2008.** godine prihvatilo je Izveštaj o oceni doktorske disertacije **Mr Branimira Jugovića** i donelo odluku da se izveštaj sa primerkom disertacije stavi na uvid javnosti, a po isteku roka od 30 dana, dostavi na saglasnost Veću naučnih oblasti Univerziteta.

4. Veće naučnih oblasti Univerziteta, na sednici održanoj **27.11.2008.** godine donelo je odluku kojom se daje saglasnost na izveštaj o uradjenoj doktorskoj disertacije **Mr BRANIMIRA JUGOVIĆA** pod nazivom: **„ELEKTROHEMIJSKI IZVORI ENERGIJE SISTEMA METAL|ELEKTROPROVODNI POLIMER NA BAZI VODENIH RASTVORA“**, čime su se stekli zakonski uslovi da se doktorant pozove na javnu odbranu svoje doktorske disertacije.
   Javna odbrana disertacije zakazana je za **25.12.2008.** godine u **16,00 sati** u Sali za sednice Tehnološko-metalurškog fakulteta.

5. Članovi komisije pred kojom se vrši odbrana disertacije odlučili su da odbrani predsedava **Dr Branimir Grgur**

Predsednik Komisije, **Dr Branimir Grgur** u zakazano vreme otvorio je sednicu, izneo biografske podatke o doktorantu i njegovoj dosadašnjoj naučnoj i stručnoj delatnosti, pročitao spisak objavljenih i saopštenih radova kao i odluke Veća Tehnološko-metalurškog fakulteta koje su se odnosile na prijavu, ocenu i odbranu disertacije. Zatim je pozvao **Mr BRANIMIRA JUGOVIĆA** da pristupi izlaganju svoje disertacije.

Doktorant je izneo bitne postavke doktorske disertacije, ciljeve i puteve rešavanja postavljenih problema, izneo do kojih je zaključaka došao na osnovu izvršenih merenja, eksperimentalnih i teorijskih ispitivanja. Na osnovu izvedenih zaključaka doktorant je pokazao da ova doktorska disertacija predstavlja originalan doprinos nauci.

Po završenom izlaganju doktoranta članovi Komisije su izneli svoje ocene disertacije i postavili doktorantu pitanja u vezi sa obrazloženjem i odbranom naučnih postavki iznetih u disertaciji. Na sva postavljena pitanja doktorant je dao konkretne odgovore koje su članovi Komisije u potpunosti prihvatili.

Posle javne odbrane Komisija se povukla da bi razmotrila i prodiskutovala izlaganje doktoranta, odgovore i odbranu disertacije. Razmotrivši sve činjenice, Komisija je donela jednoglasno odluku da je **Mr BRANIMIR JUGOVIĆ** odbranio svoju doktorsku disertaciju sa temom: **„ELEKTROHEMIJSKI IZVORI ENERGIJE SISTEMA METAL|ELEKTROPROVODNI POLIMER NA BAZI VODENIH RASTVORA“** i time stekao pravo na promociju u naučni stepen **DOKTORA TEHNIČKIH NAUKA iz oblasti: HEMIJA I HEMIJSKA TEHNOLOGIJA.**

Predsednik Komisije **Dr Branimir Grgur** javno je saopštio odluku Komisije pred kojom je doktorant odbranio doktorsku disertaciju i zaključio zasedanje u 17 sati.

U Beogradu, 25.12.2008. godine

ČLANOVI KOMISIJE:

1. Dr Branimir Grgur, van. prof. TMF

2. Dr Miodrag Maksimović, red. prof. TMF

3. Dr Jasmina Stevanović, naučni savetnik IHTM

4. Dr Tomislav Trišović, naučni saradnik ITN-SANU

Прилог 5. Доказ о ангажовању на Агрономском факултету у Чачку (Универзитет у Крагујевцу)

УНИВЕРЗИТЕТ У КРАГУЈЕВЦУ
АГРОНОМСКИ ФАКУЛТЕТ
Број: 344 **/1**
Ч а ч а к, 23.02.2011.год.

На основу чл. 65. Закона о високом образовању, чл. 30. и 33. Закона о раду (Сл.гласник РС бр. 24/05 и 61/05), чл. 3. Посебног колективног уговора за високо образовање (Сл.гласник РС 12/09) и чл. 8. Правилника о раду закључује се

УГОВОР О РАДУ

ИЗМЕЂУ

1. Агрономског факултета у Чачку, Универзитета у Крагујевцу, кога заступа декан, проф.др Мирослав Спасојевић с једне стране и
2. **др Томислав Тришовић,** са пребивалиштем у Београду, Ул.Миријевски венац бр. 6/22, по занимању доктор техничких наука, с друге стране.

Члан 1.

Уговорне стране констатују да је **др Томислав Тришовић**, одлуком Стручног већа за техничко-технолошке науке Универзитета у Крагујевцу **бр. 28/5 од 12.01.2011.године,** изабрана **у звање ванредни професор за ужу научну област: Инжењерски процеси са непуним радним временом од 20%, на период од пет година.**

Члан 2.

Запослени има VIII степен стручне спреме и по занимању је доктор техничких наука.

Члан 3.

Запослени ће обављати послове **ванредни професоср за ужу научну област: Инжењерски процеси**, утврђене Правилником о систематизацији послова и радних задатака запослених на Агрономском факултету у Чачку.

Именовани ће обављати послове из става 1. на Агрономском факултету у Чачку, ул.Цара Душана бр.34.

Члан 4.

Избор у звање и заснивање радног односа **на одређено време, на период од пет година, за именованог тече од 23.02.2011. год. до 22.02.2016.године.**

Члан 5.

Запослена је дужна да ступи на рад дана **23.02.2011.године.**

Члан 6.

Запослени заснива радни однос са непуним радним временом, односно са радним временом од 20%, што дневно износи 1,6 часова или 8 часова недељно.

Члан 7.

Запосленом се утврђује основна зарада за послове које обавља у висини од **14.565,20** динара у бруто износу **(за 20% радног времена)**, а обрачунава се по коефицијенту **28,01** утврђеним Уредбом о измени Уредбе о нормативима и стандардима услова рада универзитета и факултета за делатности које се финансирају из буџета (Сл.гласник РС бр. 110/07) .

Зараду запосленог чини зарада коју оствари за обављени рад и време проведено на раду, увећана зарада, накнада зараде и остала примања. По основу минулог рада зарада се увећава за 0,4% за сваку навршену годину радног стажа..

Запослени има право на накнаду путних трошкова и право на друга примања у складу са Законом о раду, колективним уговором и Правилником о раду.

Члан 8.

Факултет може запосленом да **откаже уговор о раду** ако за то постоји оправдани разлог који се односи на радну способност запосленог, његово понашање и потребе Факултета, и то:

1. ако је утврђено да запослени **не остварује резултате рада,** односно да **нема потребна знања и способности за** послове на којима ради;
2. ако не **поштује радну дисциплину**: неоправдано узастопно изостајање са рада 3 радна дана или 5 радних дана са прекидима у току три месеца, закашњава на посао или напушта рад пре краја радног времена, ако је на одсуству или годишњем одмору без решења и др.; **односно ако је његово понашање** такво да не може да настави рад на Факултету и то: ометање запослених да раде, туча, свађа, долазак на посао у пијаном стању, употреба алкохола за време рада што је довело до пијанства, самовољни прекид рада и др.;
3. ако запослени **својом кривицом учини повреду радне** обавезе утврђене Правилником о раду, и то:

- неизвршавање или несавесно, неблаговремено и немарно извршавање радних обавеза,
- ако незаконито располаже средствима Факултета,
- ако повреди прописе о заштити од пожара, експлозије, елементарних непогода и других штетних деловања, као и непридржавања мера о безбедности и здрављу на раду,
- ако злоупотреби радну обавезу у намери да за себе или другог прибави имовинску корист веће вредности (преко 30.000 динара), односно свако друго незаконито и неовлашћено понашање са наведеном намером,
- изазивање националне или верске нетрпељивости организовањем студената у политичке сврхе,
- неостваривање наставног плана и програма Факултета ,
- одбијање извршавања послова или радних налога декана или продекана, ако за то не постоје оправдани разлози,
- давање нетачних података, ако је то било од битног утицаја на доношење одлуке на Факултету,
- ако злоупотреби положај и прекорачи овлашћења,
- ако ода пословну, службену или другу тајну утврђену законом или општим актом Факултета,
- ако нецелисходно и неодговорно користи средства рада,
- ако проневери или украде имовину Факултета,
- неовлашћена послуга средствима повереним запосленом за обављање послова,
- неоправдано неприсуствовање седницама органа Факултета,

4. ако учини **кривично дело** на раду и у вези са радом;

5. ако се запослени **не врати на рад** на Факултет у року од 15 дана од дана истека рока за неплаћено одсуство или мировање радног односа у смислу овог Правилника;

6. ако запослени **злоупотреби право на одсуство због привремене спречености** за рад;

7. ако запослени **одбије закључивање анекса уговора о раду**, у случајевима прописаним законом,

8. ако услед **технолошких, економских** или организационих промена престане потреба за обављањем одређеног посла или дође до смањења обима посла.

Члан 9.

Послодавац је дужан да обезбеди безбедност и заштиту здравља на раду у складу за Законом о раду, другим законом и општим актом.

Запослени је дужан да се придржава прописаних мера заштите на раду.

Члан 10

Послодавац се обавезује да благовремено уплаћује доприносе за пензијско, инвалидско и здравствено осигурање у складу са Законом.

Члан 11.

Запослени и послодавац прихватају да се на сва права, обавезе и одговорности која нису утврђена овим Уговором, примењују одговарајуће одредбе Закона о раду, колективног уговора и Правилника о раду.

Члан 12.

Послодавац је дужан да запосленом у случају повреде на раду или штете на раду или у вези са радом, надокнади штету у складу са одредбама Закона.

Члан 13.

Свака од уговорних страна може да откаже овај Уговор под условима и у случајевима утврђеним Законом и општим актом.

Члан 14..

Овај Уговор сачињен је у 4 истоветна примерка од којих свака уговорна страна задржава по 2 примерка.

У Чачку, дана 23.02.2011.г

ЗА ПОСЛОДАВЦА
ДЕКАН
Проф.др Мирослав Спасојевић

ЗАПОСЛЕНИ
др Томислав Тришовић

Прилог 6. Педагошки рад

Универзитет у Крагујевцу
Агрономски факултет
Чачак, Србија

Университет в Крагуевце
Агрономический факультет
Чачак, Сербия

University of Kragujevac
Faculty of Agronomy
Čačak, Serbia

Universitè de Kragujevac
Faculte des sciences agronomiques
Čačak, Serbia

Цара Душана 34, 32000 Чачак, Србија
Cara Dušana 34, 32000 Čačak, Serbia
Тел/Tel: +381 32/30 34 00 или/or +381 32/30 34 10 Fax: +381 32/30 34 01 www.afc.kg.ac.rs, afdekanat@kg.ac.rs

Датум 10.10.2014. године

Број 2229/1

Потврда

којом се потврђује да је др Томислав Тришовић дизајнирао пет апаратура за експерименталне вежбе из Термодинамике и Технологије хлађења. То су:

1. Апаратура за мерење хидростатичког притиска,
2. Апаратура за производњу дезинфицијенса – активног хлора,
3. Апаратура за одређивање заптивености коморе,
4. Апаратура за демонстрацију основних елемената расхладне инсталације,
5. Апаратура за мерење влажности ваздуха.

Потврда се издаје на лични захтев као доказ о реализованим активностима.

С поштовањем,

Агрономски факултет у Чачку
Декан

проф. др Владета Стевовић

Прилог 7: Билатерални пројекат

	A	B	C	D	E
1		PRILOG 2/PRILOGA 2			
2		**Odobreni projekti izmedju Republike Srbije i Republike Slovenije za 2012-2013** **Sprejeti projekti med Republiko Slovenijo in Republiko Srbijo v letih 2012-2013**			
3		**Naslov projekta v slovenščini**	**Naslov projekta na srpskom jeziku**	**Evidencioni broj projekta**	**Naziv raziskovalne organizacije v Sloveniji**
4	1	Ohranjevalci, različne operatorske in matrične enačbe ter njihova uporaba	Očuvanja i razne operatorske i matrične jednačine sa primenama	451-03-1251/2012-09/01	Inštitut za matematiko, fiziko in mehaniko
5	2	Srčna funkcija in natriuretični peptidi pri bolnikih z akutnim poslabšanjem KOPB	Srčana funkcija i natriuretski peptidi u bolesnika sa akutnim pogoršanjem hronične opstruktivne bolesti pluća	451-03-1251/2012-09/02	Bolnišnica Golnik, Klinični oddelek za pljučne bolezni in alergijo
6	3	Spektroskopija in hitra senčna fotografija lasersko povzročene plazme	Spektroskopija i brza fotografija senke laserski uzrokovane plazme	451-03-1251/2012-09/03	Univerza v Ljubljani, Fakulteta za strojništvo
7	4	Ideje o Evropi in evropeizaciji v primerjalni perspektivi: Slovenija in Srbija	Ideje o Evropi i evropeizaciji u komparativnoj perspektivi: Slovenija i Srbija	451-03-1251/2012-09/04	Znanstvenoraziskovalni center Slovenske akademije znanosti in umetnosti
8	5	Visoko energijski ortosilikatni katodni materiali za litijeve ionske akumulatorje	Visoko energijski ortosilikatni katodni materijali za litijum jonske	451-03-1251/2012-09/05	Kemijski inštitut
9	6	Oblikovanje nanostrukturiranih multifunkcionalnih in sintranih funkcionalno gradientnih električnih in bioloških materialov	Nanostrukturno dizajniranje višefunkcionalnih i sinterovanih funkcionalno gradijentnih električnih i bioloških materijala	451-03-1251/2012-09/06	Institut "Jožef Stefan"
10	7	Umetnostna izmenjava in ustvarjanje jugoslovanske identitete v vizualni kulturi 1848-1990: Srbija-Slovenija/Slovenija-Srbija	Umetnička razmena i kreiranje jugoslovenskog identiteta u vizuelnoj kulturi od 1848-1990: Srbija-Slovenija/Slovenija-Srbija	451-03-1251/2012-09/07	Znanstvenoraziskovalni center Slovenske akademije znanosti in umetnosti
11	8	Radonski indeks v zdraviliščih in speleoterapevtskih centrih v Sloveniji in Srbiji	Radonski indeks pojedinih banjskih lečilišta i speleološko-terapijskih centara u Sloveniji i Srbiji	451-03-1251/2012-09/08	Institut "Jožef Stefan"
12	9	Narečna leksika srbskega in slovenskega jezika - komparativni aspekt	Dijalekatska leksika srpskog i slovenačkog jezika – komparativni aspekt	451-03-1251/2012-09/09	Znanstvenoraziskovalni center Slovenske akademije znanosti in umetnosti
13	10	Uporaba umetne inteligence pri trajnostnem razvoju obdelovalnih postopkov	Primena veštačke inteligencije u održivom razvoju	451-03-1251/2012-09/10	Univerza v Ljubljani, Fakulteta za strojništvo
14	11	Sistem evalvacije vernakularne arhitekture JV Evrope: sistem, dokumentiranje, znanstvena	Sistem evaluacije vernakularne arhitekture na teritoriji jugostočne Evrope Sistematizacija,	451-03-1251/2012-09/11	Univerza v Ljubljani, Fakulteta za arhitekturo
15	12	Raziskovanje regionalne strukture slovenskih in srbskih obmejnih območij s Hrvaško in Madžarsko	Istraživanje regionalne strukture pograničnih područja Slovenije i Srbije prema Hrvatskoj i Mađarskoj	451-03-1251/2012-09/12	Univerza v Ljubljani, Filozofska fakulteta
16	13	Jadransko-balkanska regionalna povezava: blaženje ogroženosti družbe in okolja s plazenjem tal.	Mreža zemalja Adria-Balkan regiona: Smanjenje rizika od klizišta i uticaja na društvo i okolinu	451-03-1251/2012-09/13	Univerza v Ljubljani, Fakulteta za gradbeništvo in geodezijo
17	14	Problematika raziskovanja, soočenja in vrednotenja komunistične zapuščine / Izkušnja Slovenije in Srbije	Problematika raziskovanja, soočenja in vrednotenja komunistične zapuščine / Izkušnja Slovenije in Srbije	451-03-1251/2012-09/14	Univerza v Ljubljani, Filozofska fakulteta
18	15	Antioksidativni in antiapoptotični učinek ekstrakta borovnic (Vaccinium myrtillus L.): in vivo ter in	Anti –oksidativni i anti-apoptični efekat ekstrakta borovnice (Vaccinium myrtillus L.): in vivo i in vitro	451-03-1251/2012-09/15	Univerza v Ljubljani, Biotehniška fakulteta
19	16	Potencialni zdravstveni učinki funkcionalne hrane na bazi depurizirane sirotke	Potencialni zdravstveni benefit funkcionalne hrane bazirane na depurinizovanoj surutki	451-03-1251/2012-09/16	Univerza v Mariboru, Medicinska fakulteta

	F	G	H	I	J	K	L	M	N	O	P
1											
2											
3	**Ime in priimek odgovornega raziskovalca v Sloveniji**	**Ime i prezime rukovodioca projekta u Srbiji**	**Naziv institucije u Srbiji**	**Sredstva v Sloveniji v letu 2012 (EUR)**	**Sredstva u Srbiji za godinu 2012**	**Sredstva v Sloveniji v letu 2013 (EUR)**	**Sredstva u Srbiji za godinu 2013**				
4	Peter Šemrl	Dragan S. Djordjević	Prirodno-matematički fakultet, Univerzitet u Nišu	1500	1500	1500	1500				
5	Mitja Lainščak	Aleksandar N. Nesković	Klinički centar u Zemunu	1500	1500	1500	1500				
6	Janez Možina	Marinković Bratislav	Institut za fiziku, Zemun	1500	1500	1500	1500				
7	Tanja Petrović	Ildiko Erdei	Filozofski fakultet, Univerzitet Beograd	1500	1500	1500	1500				
8	Robert Dominko	Dragana Jugović	Institut tehničkih nauka SANU, Beograd	1500	1500	1500	1500				
9	Srečo Davor Škapin	Smilja Marković	Institut tehničkih nauka SANU, Beograd	1500	1500	1500	1500				
10	Barbara Murovec	Nenad Makuljević	Filozofski fakultet, Univerzitet Beograd	1500	1500	1500	1500				
11	Janja Vaupotič	Zora S. Žunić	Institut za nuklearne nauke "Vinča"	1500	1500	1500	1500				
12	Metka Furlan	Jasna Vlajić Popović	Institut za srpski jezik SANU,Beograd	1500	1500	1500	1500				
13	Janez Kopač	Milenko Sekulić	Fakultet tehničkih nauka, Univerzitet Novi Sad	1500	1500	1500	1500				
14	Borut Juvanec	Biljana Arandjelović	Gradjevnsko-arhitektonski fakultet, Univerzitet Niš	1500	1500	1500	1500				
15	Jernej Zupančič	Lazar Lazić	Prirodno-matematički fakultet, Univerzitet Novi Sad	1500	1500	1500	1500				
16	Matjaž Mikoš	Biljana Abolmasov	Rudarsko-geološki fakultet, Univerzitet Beograd	1500	1500	1500	1500				
17	Mitja Ferenc	Momčilo Pavlović	Institut za savremenu istoriju, Beograd	1500	1500	1500	1500				
18	Nataša Poklar Ulrih	Dušan Sokolović	Medicinski fakultet, Univerzitet Niš	1500	1500	1500	1500				
19	Avrelija Cencič	Gordana Kocić	Medicinski fakultet, Univerzitet Niš	1500	1500	1500	1500				

	A	B	C	D	E
20	17	Mikrostrukturne preiskave materialov za shranjevanje vodika v korelaciji z desporcijskimi lastnostmi	Ispitivanje mikrostrukture materijala za skladištenje vodonika i korelacija sa desorpcionim osobinama	451-03-1251/2012-09/17	Institut "Jožef Stefan"
21	18	Vloga neotipljivega kapitala za gospodarsko rast in prestrukturiranje v državah Zahodnega Balkana in Sloveniji	Uloga neopipljivog kapitala za privredni rast u perspektivi država zapadnog balkana i Slovenije	451-03-1251/2012-09/18	Univerza v Ljubljani, Ekonomska fakulteta
22	19	Minerali kot prekurzorji za napredne tehnologije	Minerali kao prekursori za savremene tehnologije	451-03-1251/2012-09/19	Institut "Jožef Stefan"
23	20	Avtomatizirana fotokemična naprava z elektrokemičnim generatorjem za dezinfekcijo vode in situ	Automatski uređaj za in situ tretman voda sa fotoelektrohemijskim i elektrohemijskim generatorima dezinficijenasa	451-03-1251/2012-09/20	Univerza v Mariboru, Fakulteta za kemijo in kemijsko tehnologijo
24	21	Oksidi prehodnih kovin perovskitnega tipa z multiferoičnimi lastnostmi	Perovskiti prelaznih metala sa multiferroičnim svojstvima	451-03-1251/2012-09/21	Inštitut za matematiko, fiziko in mehaniko
25	22	Srbi in Slovenci: migranti, manjšina, kolektivne identitete in spomini	Srbi i Slovenci: Migranti, manjina, kolektivni identiteti i pamćenje	451-03-1251/2012-09/22	Znanstvenoraziskovalni center Slovenske akademije znanosti in umetnosti
26	23	Uporaba tehnologije upravljanja poslovnih procesov v e-izobraževalnih sistemih	Primena tehnologija sistema za upravljanje tokovima rada u sistemima za	451-03-1251/2012-09/23	Institut "Jožef Stefan"
27	24	Tehnologija izdelave Au nano delcev	Tehnologija proizvodnje i ispitivanje biokompatibilnosti Au nano-čestica	451-03-1251/2012-09/24	Univerza v Mariboru, Fakulteta za strojništvo
28	25	Strukturni prehodi proteinov in njihovo prepoznavanje z majnhimi molekulami: Termodinamika v povezavi s funkcijo	Strukturalni prelazi proteina i njihovo prepoznavanje sa manjim molekulima	451-03-1251/2012-09/25	Univerza v Ljubljani, Fakulteta za kemijo in kemijsko tehnologijo
29	26	Prilagoditev gospodarjenja z gozdovi pričakovanim podnebnim spremembam	Prilagodjavanje šumske ekonomije očekivanim klimatskim promenama	451-03-1251/2012-09/26	Univerza v Ljubljani, Biotehniška fakulteta
30	27	Hemoglobin iz obnovljivih virov kot izhodni material za hem-železo, proizvod za preventivo in	Hemoglobin iz obnovljivih sirovina kao osnov za preparat	451-03-1251/2012-09/27	BIA podjetje za laboratorijsko in procesno opremo d.o.o. Ljubljana
31	28	Zagotavljanje kakovosti univerzitetnega študija: vloga in odgovornost študentov in učiteljev	Zagotavljanje kakovosti univerzitetnega študija: vloga in odgovornost študentov in učiteljev	451-03-1251/2012-09/28	Univerza v Ljubljani, Filozofska fakulteta
32	29	Uporaba alternativnih cenovno ugodnih materialov za izboljšanje kvalitete pitne vode	Upotreba alternativnih jeftinih materijala za poboljšanje kvaliteta pijaće vode	451-03-1251/2012-09/29	Kemijski inštitut
33	30	Geokemične lastnosti onesnaženih območij in geokemične lastnosti preteklih katastrofičnih geoloških dogodkov	Geohemijske karakteristike zagađenih područja i geohemijski pokazatelji katastrofalnih događaja u geološkoj prošlosti	451-03-1251/2012-09/30	Geološki zavod Slovenije
34	31	Modeliranje termomehanskih pogojev in dimenzioniranje reaktorjev za hidrolizo	Modeliranje termo-mehaničkih uslova i konstruisanje reaktora za hidrolizu ligno-celuloznih	451-03-1251/2012-09/31	Univerza v Mariboru, Fakulteta za strojništvo
35	32	Potrebe in poti malih gospodarstev za povečanje mednarodne konkurenčnosti v pokriznem	Potrebe i načini unaprdjenja medjunarodne konkurentnosti malih ekonomija u post kriznom	451-03-1251/2012-09/32	Univerza v Ljubljani, Fakulteta za družbene vede
36	33	Depozicija zračnih onesnažil v mahovih: kovine, dušikove spojine in PAH-i.	Depozicija atmosferskih polutanata u mahovinama: teški metali, azot i PAH	451-03-1251/2012-09/33	Univerza v Ljubljani, Biotehniška fakulteta
37	34	Projektna zrelost podjetij in razvoj novih izdelkov	Projektna zrelost i razvoj novih proizvoda	451-03-1251/2012-09/34	Univerza v Mariboru, Fakulteta za strojništvo
38	35	Multivariatna analiza biodiverzitete in kakovost travnikov zahodnega Balkana kot osnova za	Multivarijaciona analiza biodiverziteta i kvalitet prirodnih travnjaka zapadnog Balkana kao osnova	451-03-1251/2012-09/35	Znanstvenoraziskovalni center Slovenske akademije znanosti in umetnosti
39	36	Medkulturni odnosi na območju bivše Jugoslavije	Međukulturni odnosi na prostoru bivše Jugoslavije	451-03-1251/2012-09/36	Univerza na Primorskem, Fakulteta za humanistične študije Koper

	F	G	H	I	J	K	L	M	N	O	P
20	Sašo Šturm	Ljiljana Matović	Institut za nuklearne nauke Vinča, Beograd	1500	1500	1500	1500				
21	Janez Prašnikar	Božidar Cerović	Ekonomski fakultet u Beogradu, Univerzitet Beograd	1500	1500	1500	1500				
22	Nina Daneu	Branko Matović	Institut za nuklearne nauke Vinča, Beograd	1500	1500	1500	1500				
23	Marjana Simonič	Tomislav Trišović	Institut tehničkih nauka Srpske akademije nauka i umetnosti	1500	1500	1500	1500				
24	Marko Jagodič	Zorica Marinković-Stanojević	Institut za multidisciplinarne studije, Beograd	1500	1500	1500	1500				
25	Maja Godina Golija	Lada Stevanović	Etnografski institut SANU Beograd	1500	1500	1500	1500				
26	Tanja Arh	Miroslav Trajanović	Mašinski fakultet, Univerzitet Niš	1500	1500	1500	1500				
27	Rebeka Rudolf	Miodrag Čolić	Medicinski fakultet, Univerzitet Niš	1500	1500	1500	1500				
28	Jurij Lah	Uroš Andjelković	Institut za hemiju, tehnologiju i metalurgiju, Beograd	1500	1500	1500	1500				
29	Andrej Bončina	Milan Medarević	Šumarski fakultet, Univerzitet Beograd	1500	1500	1500	1500				
30	Aleš Podgornik	Vesna Ilić	Institut za medicinska istraživanja, Beograd	1500	1500	1500	1500				
31	Jasna Mažgon	Nataša Vujisić Živković	Filozifski fakultet, Univerzitet Beograd	1500	1500	1500	1500				
32	Nataša Novak Tušar	Nevenka Rajić	Tehnološko Metalurški Fakultet, Univerzitet Beograd	1500	1500	1500	1500				
33	Gorazd Žibret	Vladica Cvetković	Rudarsko - geološki fakultet, Univerzitet Beograd	1500	1500	1500	1500				
34	Aleksandra Lobnik	Mirko Komatina	Mašinski fakultet, Univerzitet Beograd	1500	1500	1500	1500				
35	Matija Rojec	Slavica Penev	Institut ekonomskih nauka, Beograd	1500	1500	1500	1500				
36	Franc Batič	Aneta Sabovljević	Biološki fakultet,Univerzitet Beograd	1500	1500	1500	1500				
37	Iztok Palčič	Danijela Lalić	Fakultet tehnićkih nauka, Univerzitet Novi Sad	1500	1500	1500	1500				
38	Urban Šilc	Zora Dajić Stevanović	Poljoprivredni fakultet Univerzitet Beograd	1500	1500	1500	1500				
39	Blaž Lenarčič	Ivan Kovačević	Filozofski fakultet, Univerzitet Beograd	1500	1500	1500	1500				

	A	B	C	D	E
40	37	Vzpostavitev slovensko-srbske kolekcije zrnatih stročnic za zagotovitev trajnostne uporabe v kmetijskih sistemih	Obrazovanje i korišćenje srpkso slovenačke zbirke znanih mahunarki u cilju poboljšanja održivosti obeju zemlje	451-03-1251/2012-09/37	Kmetijski inštitut Slovenije
41	38	Inteligentno pridobivanje podatkov s pomočjo ontologij	Inteligetno pretrazivanje informacija bazirano na ontologijama.	451-03-1251/2012-09/38	Univerza v Ljubljani, Fakulteta za računalništvo in informatiko
42	39	Izolacija in karakterizacija bakteriofagov specifičnih za bakterijo Acinetobacter baumanii	Izolacija i karakterizacija *Acinetobacter baumannii* specifičnih bakteriofaga	451-03-1251/2012-09/39	Univerza v Ljubljani, Biotehniška fakulteta
43	40	Alternativne rastline v ekološki pridelavi: razširitev ponudbe prehranskih proizvodov na tržišču	Alternativne kulture u organskoj proizvodnji u ulozi proširenja ponude prehrambenih proizvoda na	451-03-1251/2012-09/40	Univerza v Mariboru, Fakulteta za kmetijstvo in biosistemske vede
44	41	Ugotavljanje nekaterih onesnaževalcev okolja, ki imajo v prehranski verigi pomembno vlogo pri zagotavljanju varne in kvalitetne hrane	Monitoring određenih kontaminenata životne sredine značajnih za bezbednost i kvalitet hrane u lancu ishrane	451-03-1251/2012-09/41	Univerza v Ljubljani, Veterinarska fakulteta
45	42	Celostni pristop k raziskavi kakovosti zelenjave	Holistički pristup proučavanju Kvaliteta voća	451-03-1251/2012-09/42	Univerza v Ljubljani, Biotehniška fakulteta
46	43	Vpliv procesnih parametrov na proces granulacije s talinami v vrtinčno slojnih plasteh	Optimizacija granulacije topljenjem u uređaju tipa fluidizirajućeg sistema	451-03-1251/2012-09/43	Univerza v Ljubljani, Fakulteta za farmacijo
47	44	Eksperimentalne in teoretične raziskave absorpcije vodika v sistemih Mg-Zr-Fe-Ni in Ti-Fe-Ni	Eksperimentalno i teorijsko ispitivanje sorpcije vodonika u Mg-Zr-Fe-Ni i Ti-Fe-Ni sistemima	451-03-1251/2012-09/44	Institut "Jožef Stefan"
48	45	Karakterizacija senzoričnih in fizikalnokemijskih lastnosti zaščitenih tradicionalnih sušenih mesnin iz Slovenije in Srbije	Karakterizacija senzornih i fizičkohemijskih atributa zaštićenih tradicionalnih fermentisanih suvih proizvoda od mesa iz Slovenije i Srbije.	451-03-1251/2012-09/45	Univerza v Ljubljani, Biotehniška fakulteta
49	46	Vpliv pridelovalnih sistemov v poljedelstvu na pridelek, kakovost in varstvo okolja	Uticajproizvodnih sisstema u ratastvu na kvalitet i prinos	451-03-1251/2012-09/46	Univerza v Mariboru, Fakulteta za kmetijstvo in biosistemske vede
50	47	Spektroskopska in LC-MS/MS določitev bioflavonoidov v živilih in farmacevtskih pripravkih	Spektroskopsko i LC-MS/MS odredjivanje biofilingog u hrani i farmacetskih oblicima	451-03-1251/2012-09/47	Univerza v Ljubljani, Fakulteta za kemijo in kemijsko tehnologijo
51	48	Diagnostična vrednost novih kazalcev zgodnjega odkrivanja ateroskleroze pri bolnikih z ledvično odpovedjo pri kronični ledvični bolezni	Dijagnostička vrednost novih biomarkera u ranom otkrivanju aterosklezore kod pacijenata sa termalnim stadijumom renalne bolesti	451-03-1251/2012-09/48	Univerza v Ljubljani, Fakulteta za farmacijo
52	49	Morfološke, funkcionalne, genetske in farmakološke lastnosti arterij možganskega Willisovega kroga pri človeku: vrednotenje in primerjava z živalskimi modeli	Morfološke, funkcionalne, genetska obeležja i farmakološka evaluacija prekobrojnih arterija u humanom moždanom arterijskom prstenu evaluacija i poredjenje sa životinjskim modelom	451-03-1251/2012-09/49	Univerza v Ljubljani, Medicinska fakulteta
53	50	Trajnost in energetska učinkovitost mehanskih sistemov v intralogistiki in energetiki	Održivost i energetska efikasnost mašinskih sistema u intralogistici i energetici	451-03-1251/2012-09/50	Univerza v Ljubljani, Fakulteta za strojništvo
54					
55					
56					
57					

	F	G	H	I	J	K	L	M	N	O	P
40	Jelka Šuštar Vozlič	Mirjana Vasić	Institut za povrtarstvo i ratarstvo, Novi Sad	1500	1500	1500	1500				
41	Marko Bajec	Boško Nikolić	Elelktrotehnički fakultet, Univerzitet Beograd	1500	1500	1500	1500				
42	Rok Kostanjšek	Petar Knežević	Prirodno-matematički fakultet, Univerzitet Novi Sad	1500	1500	1500	1500				
43	Martina Bavec	Marija Bodroža-Solarov	Istraživačko-razvojni institut za prehrambene tehnologije, Novi Sad	1500	1500	1500	1500				
44	Anton Vengušt	Dragan R. Milićević	Institut za higijenu i tehnologiju mesa, Beograd	1500	1500	1500	1500				
45	Dragan Žnidarčič	Žarko M. Ilin	Poljoprivredni fakultet, Univerzitet Novi Sad	1500	1500	1500	1500				
46	Stane Srčič	Jelena Parojčić	Farmaceutski fakultet, Univerzitet Beograd	1500	1500	1500	1500				
47	Andraž Kocjan	Vasil Koteski	Institut za Nuklearne Nauke Vinča	1500	1500	1500	1500				
48	Božidar Žlender	Vladimir Tomović	Tehnološki fakultet, Univerzitet Novi Sad	1500	1500	1500	1500				
49	Franc Bavec	Jovan Crnobarac	Poljoprivredni fakultet, Univerzitet Novi Sad	1500	1500	1500	1500				
50	Helena Prosen	Predrag T. Đurđević	Fakultet inzenjerskih nauka, Univerzitet Kragujevc	1500	1500	1500	1500				
51	Darko Černe	Zorana Jelić-Ivanović	Farmaceutski fakultet, Univerzitet Beograd	1500	1500	1500	1500				
52	Gorazd Drevenšek	Ljiljana Vasović	Medicinski fakultet, Univerzitet Niš	1500	1500	1500	1500				
53	Boris Jerman	Nenad Zrnić	Mašinski fakultet Univerzitet Beograd	1500	1500	1500	1500				
54											
55											
56											
57											

Прилог 8: Потврда руководиоца пројекта

University of Belgrade
Faculty of
Technology
and Metallurgy

У оквиру пројекта “**Модификација металних и неметалних материјала електропроводним полимерима за примену у новим технологијама**“, са редним бројем Х 142044, 2005-2010. год. и “**Електрохемијска синтеза и карактеризација наноструктурираних функционалних материјала за примену у новим технологијама**“, са редним бројем ОН172046, 2010- год., финансираног од стране Министарства просвенте, науке и технолошког развоја, др Томисла Тришовић руководи радним задацима повезаним са пројектима.

У Београду, 09.10.2014.

Руководилац пројекта:

Др Бранимир Гргур, ред. проф. ТМF-а
e-mail: BNGrgur@tmf.bg.ac.rs
Tel/fax: 3303-681

Прилог 9: Сепарати радова

M 14

4

Electrochemical Polymerization of Aniline

Milica M. Gvozdenović[1,*], Branimir Z. Jugović[2], Jasmina S. Stevanović[3],
Tomislav Lj. Trišović[2] and Branimir N. Grgur[1]
[1]Department of Physical Chemistry and Electrochemistry,
Faculty of Technology and Metallurgy, University of Belgrade, Belgrade,
[2]Institute of Technical Sciences, Serbian Academy of Science and Arts,
[3]Center for Electrochemistry, Institute of Technology and Metallurgy, Belgrade
Serbia

1. Introduction

From its revolutionary discovery, up to day electroconducting polymers attracts attention of researchers along scientific community. Among numerous known electroconducting polymers, polyaniline and its derivates are probably the most investigated. Such popularity, in both theoretical and practical aspects, is a consequence of its unique properties: existence of various oxidation states, electrical and optical activity, low cost monomer, red/ox reversibility, environmental stability etc. (Inzelt, 2008; Horvat-Radošević & Kvastek, 2006; Gospodinova & Terlemezyan, 1998). These diverse and important features seem to be promising in vide area of practical applications in: rechargeable power sources (Gvozdenović et al., 2011; Jugović et al., 2006; Jugović et al., 2009), sensors (Bezbradica et al., 2011; Dhaoui, 2008; Grummt et al. 1997, Gvozdenović et al., 2011; Mu & Xue, 1996), magnetic shielding, electrochemical capacitors (Xu et al., 2009), electrochromic devices (Kobayashi et al. as cited in Mu, 2004; Wallace et al., 2009), corrosion protection etc. (Biallozor & Kupniewska, 2005; Camalet et al., 1996, 1998, 2000a, 2000b; Gvozdenović & Grgur, 2009; Gvozdenović et al., 2011; Kraljić et al., 2003; Popović & Grgur, 2004; Popović et al. 2005, Grgur et al., 2006; Özylimaz et al., 2006). Polyaniline is commonly obtained by chemical or electrochemical oxidative polymerization of aniline (Elkais et al., 2011; Jugović et al., 2009; Lapkowski, 1990; Stejskal & Gilbert, 2002; Steiskal at al., 2010) although photochemically initiated polymerization (Kim et al., 2001 as cited in Wallace et al., 2009; Teshima et al., 1998) and enzyme catalyzed polymerization were also reported (Bhadra et al., 2009; Nagarajan et al., 2000).

Polyanilne obtained by electrochemical polymerization is usually deposited on the electrode, however electrochydrodinamic route was also developed resulting in polyaniline colloids of specific functionalities (Wallace et al., 2009). Electrochemical polymerization of aniline is routinely carried out in strongly acidic aqueous electrolytes, through generally accepted mechanism which involves formation of anilinium radical cation by aniline oxidation on the electrode (Hussain & Kumar, 2003). Electrochemical polymerization of aniline is proved to be auto-catalyzed (Mu & Kan, 1995; Mu et al., 1997). The experimental conditions, such as: electrode material, electrolyte composition, dopant anions, pH of the

---

[*] Corresponding Author

electrolyte etc., all have strong influence on the nature of the polymerization process (Camalet et al., 2000; Ćirić Marjanović et al., 2006; Córdova et al., 1994; Duić & Mandić, 1992; Giz et al., 2000; Gvozdenović & Grgur, 2009; Inzlet, 2008; Lippe & Holze, 1992; Mu & Kan, 1998; Mun & Kan, 1998; Nunziante & Pistoia, 1989; Okamoto & Kotaka, 1998a, 1998b, 1999; Popović & Grgur, 2004; Pron et al., 1993; Pron & Rannou, 2010; Wallace et al., 2009). The low pH is almost always needed for preparation of the conductive polyaniline in the form of emeraldine salt, since it is evidenced that at higher pH, the deposited film is consisted of low chain oligomeric material (Stejskal et al., 2010). The doping anion incorporated into polymer usually determines the morphology, conductivity, rate of the polyaniline growth during electrochemical polymerization, and has influence on degradation process (Córdova et al., 1994; Lippe & Holze, 1992; Mandić et al., 1997; Okamoto & Kotaka, 1999, Pron & Rannou, 2010). The electrochemical polymerization of aniline is practically always carried out in aqueous electrolytes, although polymerization in organic solvents such is acetonitrile was also reported. Recently it was observed that ionic liquids electrolytes might be used for successful preparation of conductive polyaniline (Heinze et al., 2010; Wallace et al., 2009). Finally, electrochemical polymerization and co-polymerization of numerous substituted aniline derivates, resulted in polymer materials with properties different from the parent polymer, were also investigated (Karyakin et al. 1994; Kumar, 2000; Mattoso & Bulhões, 1992; Mu, 2011; Zhang, 2006)

Since there is a still growing interest for the research in the field of conducting polymers with polyaniline as the most representative, the aim of this paper is to review the extremely rich literature attempting to describe all important aspects of electrochemical polymerization of aniline.

2. Polyaniline

Polyaniline is probably the eldest known electroconducting polymer, since it was used for textile coloring one century ago (Sayed & Dinesan, 1991; Wallace et al., 2009).The great interest in research of polyaniline is connected to discovery of its conductivity in the form of emeraldine salt and existence of different oxidation forms (Inzelt, 2008; MacDiarmid et al., as cited in Wallace et al., 2009; Syed & Dinesan, 1991).

2.1 Different oxidation states of polyaniline

Unlike other know electroconducting polymers, polyaniline can exist, depending on degree of oxidation, in different forms, known as: leuoemeraldine, emeraldine and perningraniline. Leucoemeraldine, eg. leucoemeraldine base, refers to fully reduced form; emeraldine, eg. emeraldine base, is half-oxidized, while perningraniline, eg. perningraniline base, is completely oxidized form of polyaniline. The only conducting form of polyaniline is emeraldin salt, obtained by doping or protonation of emeraldine base (Fedorko et al., 2010; MacDiarmid et al., 1987, Pron & Rannou, 2002).

The unique feature of mentioned polyaniline forms is ease of its mutual conversions by both chemical and electrochemical reactions as it can be seen in Fig.1. (Gospodinova & Terlemezyan, 1998; Kang et al., 1998; Stejskal et al.,1996).

Apart from the changes in oxidation levels, all the transitions among polyaniline forms are manifested by color and conductivity changes (Stejskal et al., 1996). The conducting protonated emeraldine in the form of green emeraldine salt, obtained as a product of electrochemical polymerization of aniline in acidic electrolytes, can be easily transformed by further oxidation to fully oxidized dark blue perningraniline salt, which can be treated by alkali to form violet perningraniline. Emeraldine salt can also be reduced to transparent leucoemeraldine, or can be transformed by alkali to blue non conducting emeraldine. The two blue forms of polyanilne, perningranilne salt and emeraldine have different shades of blue (Stejskal et al., 1996). Both reduction of emeraldine salt to leucoemeraldine and oxidation to perningraniline states are followed by decrease in conductivity (Stejskal et al., 2010).

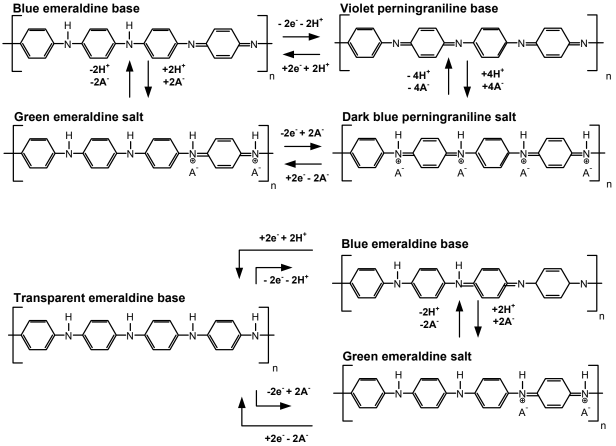


Fig. 1. Different forms of polyaniline

2.2 Polyaniline conductivity

The mechanism of polyaniline conductivity differs from other electroconducting polymers, owing to the fact that nitrogen atom is involved in the formation of radical cation, unlike most of the electroconducting polymers whose radical cation is formed at carbon. On the other hand, nitrogen is also involved in the conjugated double bonds system. Therefore, electrical conductivity of polyaniline is dependent both on the oxidation and protonation degrees (Fedorko et al., 2010; Genies at al., 1990; Pron & Rannou, 2002; Wallace et al., 2009).

As mentioned before, polyaniline is characterized by existence of various oxidation forms. Polyaniline in the form of emeraldine base can be doped (protonated) to conducting form of emeraldine salt. Emeraldine base, half oxidized form, is consisted of equal amount of amine (-NH-) and imine (=NH-) sites. Imine sites are subjected to protonation to form bipolarone or dicatione (emeraldine salt form). Bipolarone is further dissociated by injection of two electrons both from electron pairs of two imine nitrogen, into quinodiimine ring, and the third double bond of benzenoid ring is formed (Stejskal, 2010).

Unpared electrons at nitrogen atoms are cation radicals, but essentially they represent polarons. The polaron lattice, responible for high conductivity of polyaniline in the form of emeraldine salt is formed by redistribution of polarons along polymer chain, according to shematic representation given in Fig. 2. (Wallace et al., 2009)

Although both bipolaron and polaron theoretical models of emeraldine salt conductivity were proposed (Angelopulus et al., as cited in Wallace et al., 2009; Tanaka et al., 1990), it was lately confirmed that, beside from the fact that few of spineless bipolarons exist in polyaniline, formation of polarons as charge carriers explained high conductivity of polyaniline (Mu et al., 1998; Patil et al., 2002). As mentioned, unique property of polyaniline is conductivity dependence on the doping (proton) level (Chiang et al., 1986; Wallace et al., 2009). The maximal conductivity of polyaniline is achieved at doping degree of 50%, which corresponds to polyaniline in the form of emeraldine salt (Tanaka et al., 1989). For higher doping degrees some of the amine sites are protonated, while lower doping degrees means that some of the imine sites were left unprotonated (Wallace et al., 2009), explaining why, in the light of the polaron conductivity model, reduction of emeraldine salt to leucoemeraldine and oxidation to perningraniline states decrease the conductivity. The order of magnitude for conductivity varies from 10^{-2} S cm^{-1}, for undoped emeraldine, up to 10^{3} S cm^{-1} for doped emeraldine salt (Inzelt, 2008; Wallace et al., 2009).

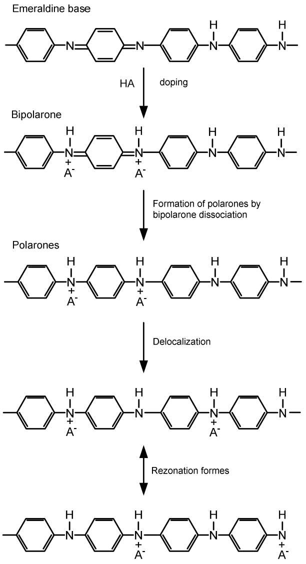


Fig. 2. Schematic presentation of polyaniline conductivity

Beside the fact that doping degree has the pronounced effect on the conductivity, various other factors such as: moisture amount (Kahol et al., 1997; Patil et al., 2002), morphology (Monkman & Adams, 1991; Zhou et al., 2007), temperature (Probst & Holze, 1995) etc. were also found to had influence on the polyaniline conductivity.

3. Mechanism and kinetics of the electrochemical polymerization of aniline

Generally, electroconducting polymers are obtained by either chemical or electrochemical oxidative polymerization, although reductive polymerization was also reported (Heinze et al., 2010; Inzlet et al., 2000; Yamamoto & Okida, 1999;Yamamoto, 2003, as cited in Inzelt, 2008). Chemical polymerization is used when large quantity of polymer is requested. Electrochemical polymerization is favorable, since in the most cases the polymer is directly deposited on the electrode facilitating analysis. On the other hand, electrochemical polymerization is especially useful if polymer film electrode is needed. By proper design of the electrochemical experiment, polymer thickness and conductivity can be easily controlled. It is believed that electrochemical polymerization is consisted of three different steps, in first, oxidation of the monomer at anode lead to formation of soluble oligomers in the diffusion layer, in the second, deposition of oligomers occurs through nucleation and growth process, and finally, the third step is responsible for chain propagation by solid state polymerization (Heinze et al., 2010). Unfortunately, a general mechanism of electrochemical polymerization could not be established, since it was evidenced that various factors had influence. However, it was observed that first step of the electrochemical polymerization was formation of reactive cation radicals (Heinze et al., 2010; Kankare, 1998). The next step, strongly dependent on the experimental conditions, is believed to be essential for the polymer growth (Inzelt, 2008). The knowledge on the kinetics of the nucleation and growth process during electrochemical synthesis of electroconducting polymers is also of great interest, since it would be useful in control of the morphology, density, crystallinity etc. of the desired polymer.

3.1 Mechanism

Both the mechanism and the kinetics of the electrochemical polymerization of aniline were extensively investigated (Andrade et al. 1998; Arsov et al. 1998; Carlos et al. 1997; Hussain & Kumar, 2003; Inzelt et al., 2000, Bade et al. 1992; Lapkowski, 1990; Malinauskas et Holze, 1998; Mandić et al., 1997; Mu & Kan, 1995; Mu et al., 1997). Electrochemical, similarly to chemical, polymerization of aniline is carried out only in acidic electrolyte, since higher pH leads to formation of short conjugation oligomeric material, with different nature (Wallace et al., 2009).

As stated before, it is generally accepted that the first step of the polymerization process of aniline involves formation of aniline cation radicals, by anodic oxidation on the electrode surface, which is considered to be the rate-determining step (Zotti et al., 1987, 1988). The existence of aniline radical cation was experimentally confirmed, by introducing molecules, (resorcinol, hydroquinone, benzoquinine etc.), capable of retarding or even stopping the reaction, which evidenced a radical mechanism (Mu et al., 1997). The oxidation of the aniline monomer is an irreversible process, occurring at higher positive potentials than redox potential of the polyaniline (Inzelt, 2008).

The following step is dependent on numerous factors such as: electrolyte composition, deposition current density, or potential scan rate, nature and state of the anode material, temperature etc. (Inzelt, 2008). There is a request for relatively high concentration of radical cations near the electrode surface. Radical cations can be involved, depending on reactivity, in different reactions. If it is quite stable, it may diffuse into the solution and react to form soluble products of low molecular weights. On the other hand, if is very unstable, it can react rapidly with anion or the solvent, in the vicinity of the electrode and form soluble products with low molecular weights (Park & Joong, 2005). In favorable case, coupling of the anilinium radicals would occur, followed by elimination of two protons and rearomatization leading to formation of dimer (lately oligomer). The aniline dimer, or oligomer, is further oxidized on the anode together with aniline. The chain propagation is achieved by coupling radical cations of the oligomer with anilinium radical cation. Finally, the counter anion originating from the acid, normally present in the electrolyte, dopes the polymer, meeting the request of electroneutrality. The mentioned mechanism of aniline electrochemical polymerization is schematically presented in Fig. 3 (Hussain & Kumar 2003, Wallace et al. 2009).

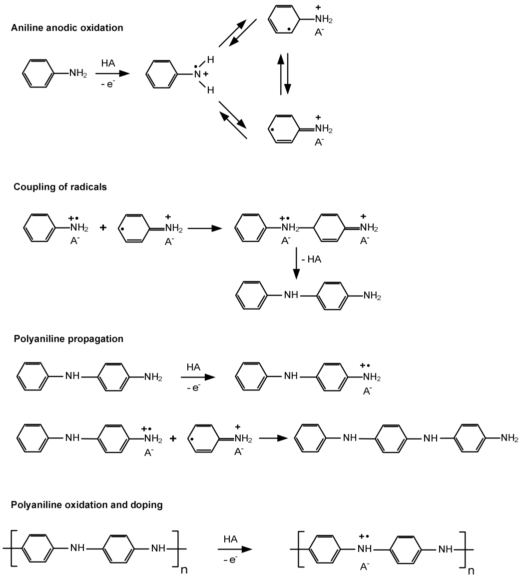


Fig. 3. Schematic presentation of mechanism of electrochemical polymerization of aniline.

It was evidenced that electrochemical polymerization of aniline is an autocatalytic process (Inzelt, 2008; Mu & Kan, 1996; Mu et al.,1997; Stilwell & Park, 1996; Wallace et al., 2009). It was observed that current increased over time, at constant potentials higher than 0.80 V and that anodic peak potentials shifted to more negative values upon increasing cycle number (Mu et al., 1997). Generally, it means that the more polymer formed on the anode, the higher the rate of the electrochemical polymerization.

3.2 Nucleation and growth of polyaniline

Explanation of the kinetics of the nucleation and growth process during electrochemical synthesis of electroconducting polymers is usually relaying on the metal deposition theory (Heinze et al., 2010; Kankare, 1998). According to the theory, two kinds of nucleation process exist, instantaneous and progressive, with three types of growth refering to: one- (1D), two- (2D), and three- (3D) dimensional processes. Instantaneous nucleation implies constant number of nuclei, growing without the further formation of nuclei. In the case of progressive nucleation, nuclei are constantly generated. 1D growth implies growth in only one direction, e.g. perpendicular to the electrode surface. In the 2D growth, the nuclei has preference to grow parallel to the electrode surface, while the 3D growth is characterized by the similar rates for these processes perpendicular and parallel to the electrode are quite similar (Heinze et al., 2010).

It was shown, mostly base on potentiostatic experiments, that several stages of polyaniline growth during electrochemical polymerization of aniline were involved, proceeding through different mechanism (Mandić et al.,1997). Cyclic voltammetry studies indicated that polyaniline growth was strongly dependent on type and concentration of anion in the electrolyte (Zotti et al.,1988). Studies on the early stages of the polyaniline growth indicate progressive nucleation of the polyaniline film, with 2D or 3D growth mechanism or 3D instantaneous nucleation, depending on electrolyte concentration and composition (Bade et al., 1992; Córdova et al., 1994; Mandić et al., 1997). The mass transfer controlled early stage of the polyaniline growth leads to formation of a compact layer (Inzlet 2010). In the case of perchloric acid, depending on monomer concentration, the nucleation process proceeds from progressive, at lower, to instantaneous nucleation at higher concentration (Mandić et al., 1997). At advanced stage, characterized by exponential current increase, 1D growth was assumed, resulted in continual branching and formation of the open structure (Cruz & Ticianelli, 1997)

3.3 Factors affecting electrochemical polymerization of aniline

Electrochemical synthesis of electroconducting polymers is strongly dependent on numerous parameters involved, such as: nature of the doping anion (affecting morphology, order of the polymer rate growth, nature and the composition of the solvent (to nucleofilic solvent would react with cation radicals formed by monomer oxidation on the anode) electrode material (depending on its surface energy controls the ease of the desired polymer deposition), temperature of the electrochemical polymerization etc. (Heinze et al., 2010; Inzelt, 2008; Pron & Rannou, 2002; Pruneanu et al., 1998; Wallce et al., 2009).

3.3.1 Doping anions

Electrochemical polymerization of aniline, as mentioned before, is practically always carried out in strong acidic aqueous electrolytes. Doping anions incorporated in polyaniline originate from the acid, and represent its conjugated base. The dopant anions are inserted during electrochemical polymerization fulfilling the request of electroneutrality, and therefore their concentrations are on the stoichiometric levels, for its reasonable that their presence have strong influence on, polyanilne morphology, conductivity, and electrochemical activity and the polymerization process itself (Arsov et al., 1998; Cordova et al,. 1994; Dhaoui et al., 2008; Koziel, 1993, 1995; Lapkowski, 1990, 1993; Lippe & Holze, 1992; Okamoto & Kotaka, 1998; Pron et al., 1992; Pron & Rannou, 2002).

It was experimentally confirmed that polyanilne obtained in the presence of so called "large dopant anions", originated from hydrochloride acid, sulfuric acid, nitric acid, *p*-toluensulfonic acid, and sulfosalicylic acid promoted formation of more swollen and open structured film, while the presence of "small ions" such is ClO_4^- or BF_4^-, resulted in formation of a more compact structure (Nunziante & Pistoria, 1989; Pruneanu et al., 1998; Zotti et al., 1988). The order of the polyaniline growth was also proved to increase with the size of the dopant anion (Inzelt et al., 2000). It was shown that addition of polyelectrolytes in polymerization electrolyte resulted in insertion of these molecules as dopants (Hyodo & Nozaki 1988, as cited in Wallace et al. 2009). It was also possible to obtain optically active polyaniline by electrochemical polymerization in the presence of (+) or (-) camphorsulfonic acid, leading to insertion of chiral dopants (Majidi et al., 2009).

3.3.2 Electrolyte composition

As mentioned previously, electrochemical polymerization of aniline is usually performed in aqueous electrolytes. There is limited number of studies referred to electrochemical polymerization in non-aqueous solvents (Genies & Lapkowski, 1987; Lapkowski, 1990; Pandey & Singh, 2002; Şahin et al., 2003). In the early studies acetronitrlie was mostly used as solvent, for example Watambe et al. (Miras et al. 1991; Watambe et al. 1989, as cited in

Wallace et al., 2009) made first electrochemical polymerization of aniline in acetonitrile solution containing lithium perchlorate, the resulted polymer exhibited similar redox properties as “ordinary” prepared polyaniline.

Lately, apart from acetonitrile, the studies involved use of: dichlormethane, nitrobenzene with various electrolytes such as: sodium tetraphenylborate, tetraethilammonium tetrafluoroborate and tetraetilammoniumperchlorate and resulted films showed different microstructures and electrochemical activity (Pandey & Singh, 2002). Other studies referred to electrochemical polymerization of aniline and fluoro- and chloro- substituted anilines and their coopolymers with aniline in acetonitrile containing tetrabutilammonium perchlorate and perchloric acid. The obtained polymers exhibited similar electrochemical and UV-behavior to “ordinary” polyaniline, but their conductivities were remarkably lower, explained by the steric effects of the substituent (Şahin et al. 2003). Various alkyl substituted anilines were electrochemically polymerized in both acetonytrile and dimethiylsulfoxide, their conductivities were also very low suggested that there were not in the typical state of the emeraldine salt (Yano et al., 2004). Successful electrochemical co-polymerization of aniline and pyrrole was also carried out in acetonitrile.

Finally, electrochemical polymerization of aniline was performed in various ionic liquids (Heinze et al., 2010; Innis et al., 2004; Li et al., 2005; Mu, 2007). For example, using IR and NMR spectroscopy Mu showed that the ionic liquid, namely 1-ethyl-3-methylimidazolium ethyl sulfate was incorporated in polyaniline during electrochemical polymerization. It was also observed that resulted polyaniline had exhibited good electrochemical activity in solutions with pH 12, and also considerably wider window of the detectable color changes at higher pH values, this effect was explained by the fact that used ionic liquid possessed high buffer capacity, which improved the redox activity and the electrochemical activity in broader pH range (Mu, 2007). Apart from the strong influence of the solvent, the presence of other components in the electrolyte solution, used for electrochemical polymerization of aniline, also had influence, primarily, on the morphology of the deposit (Inzelt, 2008). It was shown that presence of alcohols in the electrolyte would lead to polyaniline in the form of nanofibres agglomerated into interconnected network, FTIR spectra of the resulted polymer revealed strong interactions between alcohol and polyaniline molecules (Zhou et al., 2008).

3.3.3 Electrode material

Electrochemical polymerization of aniline is easily performed at so called inert electrodes, such as: platinum, gold, various graphite, carbons or indium-tin-oxide glasses, according to previously described mechanism. But the fact that relatively high electrode potential is required for oxidation of aniline, restricts the usage of other materials. The electrochemical polymerization of aniline on active metals is usually considered for application in corrosion protection (Biallozor & Kupniewska, 2005; Tallman et al., 2002). The problem connected to electrochemical polymerization onto active metals is either dissolution, or formation of non-conducting passive layer, on the potentials necessary for oxidation of aniline.

In the case of iron and steel the potential at which polymerization starts is in the region of active dissolution, leading to lost of the metal and contamination of the electrolyte, therefore it necessary to find a suitable electrolyte that would enable strong passivation of the metal without suppressing further electrochemical polymerization. The most common electrolyte used to electrochemical deposition of polyaniline on steel and aluminum is oxalic acid (Camalet et al., 1996, 2000a, 2000b; Martyak et al., 2002). The use of oxalic acid permitted formation of passive layer consisted of iron oxalate, on which aniline polymerize. It was also showed that *p*-toluen sulfonic acid can be used for electrochemical polymerization of aniline, the deposition occurred after passivation. The passive film, in contrast to oxalic acid, was consisted mainly of iron oxide (Camalet et al., 1998). Other approach involves the pretreatment of the steel surface by polypyrrole, which can be easily formed electrochemically on iron and steel, with low extent of the metal dissolution, after this treatment aniline is easily electrochemically polymerized (Lacroix et al., 2000). The problem with electrochemical polymerization of aniline on aluminum is occurrence of two simultaneous processes electrochemical polymerization and passivation of the electrode by very stable protective oxide (Biallozor & Kupniewska, 2005). The studies of electrochemical polymerization on aluminum and its alloys involved pretreatment of the metal, and further polymerization (Huerta-Vilca et al., 2005; Wang & Tan, 2006). Similarly to steel, oxalic acid and *p*-toluen sulfonic acid electrolytes were used to grow polyaniline on aluminum (Conroy & Breslin, 2005; Karpagam et al., 2008). It was shown that sodium benzoate could be used to electrochemically polymerize aniline, without need for pretreatment, on steel, copper and aluminum (Gvozdenović & Grgur, 2009; Gvozdenović et al. 2011; Popović & Grgur, 2004). Electrochemical polymerization of substituted anilines on various metals and alloys were also carried out (Chaudhari & Patil 2007; Chaudhari et al., 2009; Pawar et al., 2007).

3.4 Experimental performance

Generally, experimental set-up for electrochemical synthesis of electroconducting polymers in laboratory conditions is simple. It involves, in majority of cases, standard three-electrode electrochemical cell, although in some cases of galvanostatic polymerization, two electrode cell can be used (Wallace et al., 2009). The polymer obtained by this procedure is deposited directly on the electrode. Novel experimental set-up, enabling electrochemical generation of polyaniline colloids, using flow-through electrochemical cell, was also reported (Aboutanos et al., 1999; Innis et al., 1998). In this novel electrochemical cell, anode was separated from two and cathodes by ion exchange membrane. The anodic and cathodic electrolytes were passed through electrode compartments at specified flow, while polymerization was achieved at constant potential.

The most common experimental techniques used for electrochemical polymerization of aniline are: cyclic voltammetry (potentiodynamic), galvanostatic and potetntiostatic techniques. Polymerization using cyclic voltammetry is characterized by cyclic regular change of the electrode potential and the deposited polymer is, throughout the experiment, changing between its non-conducting and conducting (doped) state, followed by exchange of the electrolyte through polymer (Heinze et al., 2010). At the end of polymerization the obtained polymer is in its non-conducting form, moreover, cyclic voltammetry favors formation of disordered chains and open structure (Heinze et al., 2010) As stated before, relatively high potential is required for electrochemical oxidation of aniline monomer, therefore at first 2 – 10 cycles, the upper potential limit is high, but owing to autocatalytic nature of aniline electropolymerization, the upper potential limit can be decreased to avoid degradation resulted from over oxidation of perningranilin form of polyaniline (Inzelt, 2008). Recently, it was shown that cyclic voltammetry can even be useful for formation of nanostructure polyaniline . It was shown that different sized polyaniline nanofibres were electrochemicaly polymerized, by different scan rates, in the presence of ferrocensulfonic acid (Mu & Yang, 2008).

Galvanostatic polymerization, owing to current control, enables reaction to proceed at constant rate. Galvanostatic synthesis permits estimation of the polymer mass deposited on the electrode (Kankare, 1998). On the other hand, galvanostatic polymerization leads to formation of polyaniline in its conductive form.

Electrochemical polymerization of aniline on graphite electrode from hydrochloride acid electrolyte, obtained by cyclic voltammetry (numbers on the figure refers to cycle number) given in Fig. 4., while in the insert of the Fig.4, hronopotnetiometric curve of galvanostatic polymerization from the same electrolyte is shown (Gvozdenović et al., 2011; Jugović, PhD thesis, 2009; Jugović et al., 2009)

Electrochemical polymerization of aniline proceeds together with insertion of chloride anions (dopant) from the electrolyte, according to:

$$(\mathrm{PANI})_n + \mathrm{n}y\mathrm{Cl}^- \rightarrow [\mathrm{PANI}^{y+}(\mathrm{Cl}^-)]_n + \mathrm{n}y\mathrm{e}^-$$

Where y refers to doping degree, ration between the number of charges in the polymer and the number of monomer units (Kankare, 1998).

As seen on cyclic voltammograms in Fig.4., doping of chloride ions started at potential of ~ -0.1 V (SCE), the first well defined anodic peak, situated at potential of 0.2 V (SCE) indicate transition of leucoemeraldine form of polyaniline to emeraldine salt, followed by the changes of y between 0 and 0.5.

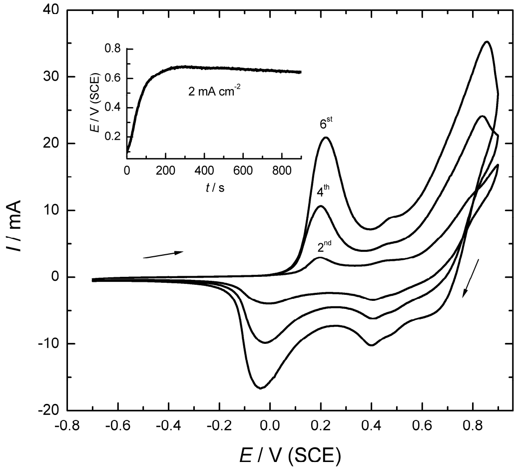


Fig. 4. Cyclic voltammograms of electrochemical polymerization of aniline on graphite electrode from aqueous solution of 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline, at scan rate of 20 mV s^{-1}. Insert: Chronopotentiometric curves of aniline polymerization at constant current density of 2.0 mA cm^{-2}.

Second anodic peak, occurred at potenial of ~ 0.5 V (SCE) denotes formation of fully doped perningraniline salt (y = 1).

The potentiostatic technique of electrochemical polymerization is characterized by pronounced changes in the current i.e. polymerization rate, and similarly to galvanostatic polymerization obtained polymer is in its doped form (Heinze et al., 2010). It was observed that potentiostatic method could be useful in obtaining polyaniline nanowiers (Gupta & Miura, 2007). Modified potentiostatic techniques were also reported.

Some of the researches used pulse potentiostatic technique to obtained polyaniline electrochemically (Tang et al., 2000; Tsakova et al., 1993; Zhou et al., 2007). The potentiostatic pulse technique implies application of periodic cathodic and anodic pulses, with important parameters, lower (cathodic) and upper (anodic) limit potentials with additional cathodic and anodic pulses duration, during given time. It was observed (Zhou et al., 2007) that mentioned parameters had strong influence on the morphology of polyaniline, thus on its electrochemical activity.

3.5 Electrochemical co-polymerization of aniline and aniline derivates

Owing to its conductivity and redox activity, polyaniline is considered for practical application in various fields. Unfortunately, beside its unique properties, application of polyaniline in biochemical systems is limited as a consequence of the lost of activity at pH above 4 (Karyakin et al., 1994; Malinauskas, 1999; Mu 2011). This problem might be overcome by introduction of so- called pH functional groups into polyaniline chain (Mu, 2011). This could be achieved either by sulfonation (Wei et al., 1996) or by co-polymerization, which is more efficient way to alter the properties of parent polymer. Electrochemical polymerization of aniline and aniline derivates with pH functional groups, sulpho, carboxyl or hydroxyl was reported. It was observed that self-doped polyanilines, obtained by electrochemical co-polymerization of aniline with: *o*-aminobenzoic acid, *m*-aminobenzoic acid, or *m* – aminobenzensulfonic acid had exhibited redox activity at high pH (Karyakin et al., 1996).

Apart from aniline and aniline derivate, electrolyte solution also contains acid necessary for protonation of nitrogen atom. The obtained co-polymers are often called self-doped polyanilines, since the introduced negatively charged functional groups plays role of an intermolecular dopant which is able to compensate the charge on positively charged nitrogen atoms of the polymer. The presence of intermolecular anion alters properties of "ordinary" polyaniline, and has influence on the polymerization process as well. It was shown that upper switching potential limit had important influence on self-doping, the limit of 0.9 V was proven to be optimal, and while in the case of un- substituted aniline, upper limit was lower.

The problem related to electrochemical activity of self-doped polyaniline is its rapid lost. Recently, it was showed that electrochemical polymerization of aniline and 5-aminosalycylic acid, which nears two acidic functional groups, had lead to co-polymer with satisfactory redox activity (Mu, 2011).

4. Conclusion

Although polyaniline is among the first know electroconductive polymers, the interest in this field of study still exist, since its diverse and unique properties can be useful in various practical applications. Electrochemical polymerization of aniline and aniline derivates were intensively investigated. Various factors such as: electrode material, dopant anions, electrolyte composition, monomer type, pH etc. were proven to exhibit influence in the electropolymerization process and properties of the desired polymer. The electrochemical synthesis of polyaniline, similar to chemical, is practically always performed in strong acidic electrolytes, according to radical mechanism, and the polymer is deposited on anode, permitting easy way for further analysis. It was also proved that, using inconvenient experimental setup, polyaniline colloids can also be obtained electrochemically. Finally, studies of electrochemical co-polymerization of aniline and its derivates with acidic functional groups were also performed, leading to so called self-doped polyanilines, with benefit of being electrochemically active even in high pH solutions.

5. Acknowledgment

This work was supported by the Ministry of Education and Science, Republic of Serbia, under Contract No. 172046

6. References

Aboutanos V.; Barisci J.; Kane-Maguire L. & Wallace G. (1999). Electrochemical preparation of chiral polyaniline nanocomposites. *Synthetic Metals*, Vol. 106, No. 2, (October 1999), pp. 89-95, ISSN0379-6779

Andrade G.; Aguirre M. & Biaggi S.(1998). Influence of the first potential scan on the morphology and electrical properties of potentiodynamically grown polyaniline films. *Electrochimica Acta*, Vol. 44, No. 4, (September 1998), pp. 633-642, ISSN0013-4686

Arsov Lj.; Plieth W. & Koβmehl. (1998). Electrochemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline. *Journal of Solid State Electrochemistry,* Vol. 2, No. 5, (August 1998), pp. 355-361, ISSN1432-8488

Bade K.; Tsakova V. & Schultze J. (1992). Nucleation, growth and branching of polyaniline from microelectrode experiments. *Electrochimica Acta,* Vol. 37, No. 12, (September 1992), pp. 2255-2261, ISSN0013-4686

Bernard M.-C.; Cordoba de Torresi S. & Hugot-Le Goff A.(1999). In situ Raman study of sulfonate-doped polyaniline. *Electrochimica Acta*, Vol. 44, No. 12, (January 1999), pp. 1989-1997, ISSN0013-4686

BezbradicaD.; Jugović B.; Gvozdenović M.; Jakovetić S. & Knežević-Jugović Z. (2011). Electrochemically synthesized polyaniline as support for lipase immobilization. *Journal of Molecular Catalysis B: Enzymatic*, Vol. 70, No. 1-2, (June 2011), pp. 55-60, ISSN1381-1177

Bhadani, S.; Gupta M. & Sen Gupta S. Cyclyc Voltammetry and Conductivity Investigations of Polyaniline. (1993), *Journal of Applied Polymer Science*, Vol. 49, No. 3 (July 1993), pp. 397-403, ISSN0021-8995

Bhadra S.; Khastgir D.; Singha N. & Lee J. (2009). Progress in preparation, processing and applications of polyaniline. *Progress in Polymer Science*, Vol. 34, No. 8, (August 2009), pp. 783-810, ISSN0079-6700

Biallozor S. & Kupniewska A. (2005). Conducting polymers electrodeposited on active metals. *Synthetic Metals*, Vol. 155, No. 3, (December 2005), pp. 443-449, ISSN0379-6779

Camalet J.; Lacroix J.; Aeiyach S. & Lacaze P.(1998). Characterization of polyaniline films electrodeposited on mild steel in aquous *p*-toluensulfonic acid solution. *Journal of Electroanalytical Chemistry,*Vol. 445, No.1-2 (March 1998) pp. 117-129, ISSN1572-6657

Camalet J.; Lacroix J.; Aeiyach S.; Chane-Ching K. & Lacaze P. Electrodeposition of protective polyaniline films on mild steel. *Journal of Electroanalytical Chemistry*, Vol. 416, No. 1-2, (November 1996), pp. 179-182, ISSN1572-6657

Camalet J.; Lacroix J.; Aeiyach S.; Chane-Ching K.; Petit Jean J.; Chauveau E. & Lacaze P. (2000). Aniline electropolymerization on mild steel and zinc in a two-step process. *Journal of Electroanalitical Chemistry,*Vol. 481, No.1 (January 2000) pp. 76-81 ISSN1572-6657

Camalet J.; Lacroix J.; Ngyen T.; Aeiyach S.; Pham M.; Petit Jean J. & Lacaze P.-C. (2000). Aniline electropolymerization on platinum and mild steel from neutral aqueous media. *Journal of Electroanalytical Chemistry,* Vol. 485, No.1 (May 2000) pp. 13-20, ISSN1572-6657

Chaudhari S. & Patil P. (2007). Corrosion protective poly(*o*-ethoxyaniline) coatings on copper. *Electrochimica Acta*, Vol. 53, No. 2, (December 2007), pp. 927-933, ISSN0013-4686

Chaudhari S.; Gaikwad A. & Patil P.(2009). Poly(*o*-anisidine) coatings on brass: Synthesis, characterization and corrosion protection. *Current Applied Physics*, Vol. 9, No. 1, (January 2009), pp. 206-218, ISSN1567-1739

Chiang J. & MacDiarmid A. (1986). Polyaniline: Protonic acid doping of the emeraldine form to the metallic regime. *Synthetic Metals,* Vol. 13, No. 1-3, (January 1986), pp. 193-205, ISSN0379-6779

Ćiric-Marjanović G.; Marjanović N., Popović M.; Panić V.& Mišković-Stanković V. (2006). Anilinium 5-sulfosalicylate electropolymerization on mild steel from an aqueous solution of sodium 5-sulfosalicylate/disodium 5-sulfosalicylate. *Russian Journal of Electrochemistry,* Vol. 42, No. 12, (December 2006), pp. 1358-1364, ISSN1023-1935

Conroy K. & Breslin C.(2003).The electrochemical deposition of polyaniline at pure aluminium: electrochemical activity and corrosion protection properties. *Electrochimica Acta*, Vol. 48, No. 6, (February 2003), pp. 721-732, ISSN0013-4686

Córdova R.; del Valle M.; Arratia A.; Gómez H. Schrelber R. (1994). Effects of anions on the nucleation and growth mechanism of polyaniline. *Journal of Electroanalytical Chemistry,* Vol. 377, No. 1-2, (October 1994), pp. 75-83, ISSN1572-6657

Cruz C. & Ticianelli E. (1997).Electrochemical and ellipsometric studies of polyaniline films grown under cycling conditions. *Journal of Electroanalytical Chemistry*, Vol. 428, No. 1-2, (May 1997), pp. 185-192, ISSN1572-6657

Dalmolin C.; Canobre S.; Biaggio S.; Rocha-Filho R.; Bocchi N. Electropolymerization of polyaniline on high surface area carbon substrates. *Journal of Electroanalytical Chemistry*, Vol. 578, No. 1, (April 2005), pp. 9-15, ISSN1572-6657

Dhaoui W.; Bouzitoun M.; Zarrouk H.; Ouada H. & Pron A. (2008). Electrochemical sensor for nitrite determination based on thin films of sulfamic acid doped polyaniline deposited on Si/SiO_2structures in electrolyte/insulator/semiconductor (E.I.S.) configuration. *Synthetic Metals*, Vol. 158, No.17-18, (October 2008), pp. 722-726, ISSN0379-6779

Duić Lj. & Mandić Z. (1992). Counter-ion and pH effect on the electrochemical synthesis of polyaniline. *Journal of Electroanalytical Chemistry,* Vol. 335, No. 1-2, (September 1992), pp. 207-221 , ISSN1572-6657

Elkais A.; Gvozdenović M.; Jugović B.; Stevanović J.; Nikolić N.; Grgur B. (2011). Electrochemical synthesis and characterization of polyaniline thin film and polyaniline powder, *Progress in Organic Coatings*, Vol. 71, No. 1, (May 2011) pp. 32-35, ISSN0300-9440

Fedorko P.; Trznadel M.; Pron A.; Djurado D.; Planès J. & Travers J. (2010). New analytical approach to the insulator–metal transition in conductive polyaniline. *Synthetic Metals,* Vol. 160, No. 15-16, (August 2010), pp. 1668-1671, ISSN0379-6779

Ferreira V.; Cascalheira A. & Abrantes L. (2008). Electrochemical preparation and characterisation of Poly(Luminol–Aniline) films. *Thin Solid Films*, Vol. 516, No. 12, (April 2008), pp. 3996-4001 ISSN0040-6090

Genies E.; Boyle A.; Lapkowski M. & Tsintavis. (1990). Polyaniline: A historical survey. *Synthetic Metals*, Vol. 36, No. 2, (June 1990), pp. 139-182, ISSN0379-6779

Giz M.; de Albuqurque Maranhão S. & Torresi R. (2000). AFM morphological study of electropolymerized polyaniline films modified by sufracant and large anions. *Electrochemistry Communications,* Vol.2, No. 6, (June 2000), pp. 377-381, ISSN1388-2481

Gospodinova N. & Terlemezyan L. Conducting polymers prepared by oxidative polymerization: polyaniline. (1998). *Progress in Polymer Science*, Vol. 23, No. 8, (December 1998), pp. 1443-1484, ISSN0079-6700

Grgur B.; Gvozdenović M.; Mišković-Stanković V. & Kačarević-Popović Z. (2006). Corrosion behavior and thermal stability of electrodeposited PANI/epoxy coating system on mild steel in sodium chloride solution. *Progress in Organic Coatings*, Vol. 56, No. 2-3, (July 2006), pp. 214-219, ISSN0300-9440

Grummt U.; Pron A.; Zagorska M. & Lefrant S. (1997).Polyaniline based optical pH sensor. *Analytica Chimica Acta*, Vol. 357, No. 3, (December 1997), pp. 253-259, ISSN0003-2670

Gupta V. & Miura N. (2005).Large-area network of polyaniline nanowires prepared by potentiostatic deposition process. *Electrochemistry Communications*, Vol. 7, No. 10, (October 2005), pp. 995-999, ISSN1388-2481

Gvozdenović M. & Grgur B. (2009). Electrochemical polymerization and initial corrosion properties of polyaniline-benzoate film on aluminum. *Progress in Organic Coatings*, Vol. 65, No. 3, (July 2009), pp. 401-404, ISSN0300-9440

Gvozdenović M.; Jugović B.; Stevanović J.; Grgur B.; Trišović T. & Jugović Z. (2011). Electrochemical synthesis and corrosion behavior of polyaniline-benzoate coating on copper, *Synthetic Metals*, Vol. 161, No. 13-14, July 2011, pp 1313-1318, ISSN0379-6779

Gvozdenović M.; Jugović B.; Bezbradica D.; Antov M. Knežević-Jugović Z. & Grgur B. (2011). Electrochemical determination of glucose using polyaniline electrode modified by glucose oxidase. *Food Chemistry*, Vol. 124, No.1, (January 2011), pp. 396-400, ISSN0308-8146

Gvozdenović M.; Jugović B.; Trišović T.; Stevanović J. & Grgur B. (2011). Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte. *Materials Chemistry and Physics*, Vol. 125, No. 3, (February 2011), pp. 601-605, ISSN0254-0584

Heinze J.; Frontana-Uribe B. & Ludwigs S. (2010). Electrochemistry of Conducting Polymers-Persistent Models and New Concepts. *Chemical Reviews,* Vol.110, No.8, (June 2010), pp. 4724-4771 ISSN0009-2665

Horvat-Radošević V. & Kvastek K. Role of Pt-probe pseudo-reference electrode in impedance measurements of Pt and polyaniline (PANI) modified Pt electrodes. (2006). *Journal of Electroanalytical Chemistry*, Vol. 591, No. 2, (June 2006), pp. 217-222, ISSN1572-6657

Huerta-Vilca D.; de Moraes S. & de Jesus Motheo A. (2005). Aspects of polyaniline electrodeposition on aluminium. *Journal of Solid State electrochemistry,* Vol. 9, No. 6 (June 2005), pp. 416-420, ISSN1432-8488

Hussain A. & Kumar A. (2003). Electrochemical synthesis and characterization of chloride doped polyaniline. *Bulletin of Material Science,* Vol. 26, No. 3, (April 2003), pp. 329-334 ISSN0250-4707

Innis P.; J. Mazurkiewicz J.; Nguyen T.; Wallace G. & MacFarlane D. (2004). Enhanced electrochemical stability of polyaniline in ionic liquids. *Current Applied Physics*, Vol. 4, No. 2-4, (April 2004), pp. 389-393, ISSN1567-1739

Innis P.; Norris I.; Kane-Maguire L. & Wallace G.(1998).Electrochemical Formation of Chiral Polyaniline Colloids Codoped with (+)- or (−)-10-Camphorsulfonic Acid and Polystyrene Sulfonate. *Macromolecules*, Volume 31, No. 19, (September 1998), pp 6521–6528 ISSN0024-9297

Inzelt G.; Pineri M.; Schultze J. & Vorotyntsev M. Electron and proton conducting polymers: recent developments and prospects. *Electrochimica Acta*, Vol. 45, No. 15-16, (May 2000), pp. 2403-2421 ISSN0013-4686

Inzelt G.(2008). *Conducting Polymers – A New Era in Electrochemistry,* Springer-Verlag, ISBN 978-3-540-75929-4, Berlin, Heidelberg

Jugović B.; Trišović T.; Stevanović J.; Maksimović M. & Grgur B. (2006). Novel electrolyte for zinc–polyaniline batteries, *Journal of Power Sources*, Vol. 160, No. 2, (October 2006), pp. 1447-1450 ISSN0378-7753

Jugović B.; Gvozdenović M.; Stevanović J.; Trišović T. & Grgur B. (2009). Characterization of electrochemically synthesized PANI on graphite electrode for potential use in electrochemical power sources . *Materials Chemistry and Physics*, Vol. 114, No. 2-3, (April 2009), pp. 939-942, ISSN0254-0584

Kahol P.; Dyakonov A.; & McCormick B. (1997). An electron-spin-resonance study of polymer interactions with moisture in polyaniline and its derivatives. *Synthetic Metals*, Vol. 89, No. 1, (July 1997), pp. 17-28, ISSN0379-6779

Kang E; Neoh K. & Tan K. Polyaniline: A polymer with many interesting intrinsic redox states , *Progress in Polymer Science,* Vol.23, No. 2, (1998), pp. 277-324, ISSN0079-6700

Kankare J. (1998). Electronically Conducting Polymers: Basic Methods of Synthesis and Characterization, In: *Electrical and Optical Polymer Systems: Fundamentals: Methods, and Applications,* Ed. by: Wise D.; Wnek G.; Trantolo D.; Cooper J. & Gresser D. , pp. 167-199, Marcel Dekker, ISBN 0824701186, New York

Karpagam V.;Sathiyanarayanan S. & Venkatachari G. (2008).Studies on corrosion protection of Al2024 T6 alloy by electropolymerized polyaniline coating *Current Applied Physics*, Vol. 8, No. 1, (January 2008), pp. 93-98, ISSN1567-1739

Karyakin A.; Strakhova A. & Yatsimirsky A. (1994). Self-doped polyanilines electrochemically active in neutral and basic aqueous solutions.: Electropolymerization of substituted anilines. *Journal of Electroanalytical Chemistry*, Vol. 371, No. 1-2, (June 1994), pp. 259-265, ISSN1572-6657

Koziel K. & Lapkowski M.(1993). Studies on the influence of the synthesis parameters on the doping process of polyaniline. *Synthetic Metals*, Vol. 55, No. 2-3, (March 1993), pp. 1011-1016, ISSN0379-6779

Koziel K.; Lapkowski M. & Lefrant S. (1995). Spectroelectrochemistry of polyaniline at low concentrations of doping anions. *Synthetic Metals*, Vol. 69, No. 1-3, (March 1995), pp. 137-138, ISSN0379-6779

Kraljić M.; Mandić Z. & Duić Lj. (2003). Inhibition of steel corrosion by polyaniline coatings. *Corrosion Science*, Vol. 45, No. 1, (January 2003), pp. 181-198, ISSN0010-938X

Kumar D.(2000). Synthesis and characterization of poly(aniline-co-o-toluidine) copolymer *Synthetic Metals*, Vol. 114, No. 3, (September 2000), pp. 369-372 ISSN0379-6779

Lacroix J.; Camalet J.; Aeiyach S.; Chane-Ching K.; Petitjean J.; Chauveau E. & Lacaze P. (2000). Aniline electropolymerization on mild steel and zinc in a two-step process. *Journal of Electroanalytical Chemistry*, Vol. 481, No.1, (January 2000), pp. 76-81, ISSN1572-6657

Lapkowski M. (1990). Electrochemical synthesis of linear polyaniline in aqouos solutions. *Synthetic Metals,* Vol. 35, No. 1-2, (February-March 1990), pp. 169-182 ISSN0379-6779

Li M.; Ma C.; Liu B. & Jin Z. (2005). A novel electrolyte 1-ethylimidazolium trifluoroacetate used for electropolymerization of aniline. *Electrochemistry Communications*, Vol. 7, No. 2, (February 2005), pp. 209-212, ISSN1388-2481

Macdiarmid A.; Chiang J.; Richter A. & Epstein A. (1987). Polyaniline: a new concept in conducting polymers. *Synthetic Metals*, Vol. 18, N. 1-3, (February 1987), pp. 285-290, ISSN0379-6779

Majidi M.; Kane-Maguire L. & Wallace G. (1994).Enantioselective electropolymerization of aniline in the presence of (+)- or (−)-camphorsulfonate ion: a facile route to conducting polymers with preferred one-screw-sense helicity. *Polymer,* Vol. 35, No. 14, (July 1994), pp. 3113-3115, ISSN0032-3861

Malinauskas A. & Holze R. (1997). Suppression of the "first cycle effect" in self-doped polyaniline. *Electrochimica Acta*, Vol. 43, No. 5-6, (November 1997), pp. 515-520, ISSN0013-4686

Malinauskas A. (1999). Electrocatalysis at conducting polymers. *Synthetic Metals*, Vol. 107, No. 2, (November 1999), pp. 75-83 ISSN0379-6779

Mandić Z.; Duić Lj. & Kovačiček F. (1997). The influence of counter-ions on nucleation and growth of electrochemically synthetized polyaniline film. *Electrochimica Acta,* Vol. 42, No. 9, (1997), pp. 1389-1402, ISSN0013-4686

Martyak N.;McAndrew P.; McCaskie J.& Dijon J. (2002). Electrochemical polymerization of aniline from an oxalic acid medium. *Progress in Organic Coatings*, Vol. 45, No. 1, (September 2002), pp. 23-32, ISSN0300-9440

Mattoso L. & Bulhões L. (1992). Synthesis and characterization of poly(*o*-anisidine) films. *Synthetic Metals*, Vol. 52, No. 2, (October 1992), pp. 171-181, ISSN0379-6779

Mažeikiené R.; Niaura G. & Malinauskas A. (2003). Voltammetric study of the redox processes of self-doped sulfonated polyaniline. *Synthetic Metals*, Vol. 139, No. 1, (August 2003), pp. 89-94, ISSN0379-6779

Miras M.; C. Barbero C. & Haas O. (1991). Preparation of polyaniline by electrochemical polymerization of aniline in acetonitrile solution. *Synthetic Metals*, Vol. 43, No. 1-2, (June 1991), pp. 3081-3084, ISSN0379-6779

Monkman A. & Adams P. (1991). Optical and electronic properties of stretch-oriented solution-cast polyaniline films. *Synthetic Metals*, Vol. 40, No.1, (March 1991), pp. 87-96, ISSN0379-6779

Mu S. & Kan J. (1996). Evidence for the autocatalitic polymerization of aniline, *Electrochimica Acta,* Vol.4, No.10, (November 1996), pp. 1593-1599, ISSN0013-4686

Mu S. & Kan J. The effect of salts on the electrochemical polymerization of aniline. *Synthetic Metals*, Vol. 92, No. 2, (January 1998), pp. 149-155, ISSN0379-6779

Mu S. & Xue H. (1996). film. *Sensors and Actuators B: Chemical*, Vol. 31, No. 3, (March 1996), pp.155-160 ISSN0925-4005

Mu S. & Yang Y. (2008). Spectral Characteristics of Polyaniline Nanostructures Synthesized by Using Cyclyc Voltammetry. *Journal of Physical Chemistry B*. Vol. 112, No. 37, (September 2008), pp. 11558-11563 ISSN1520-6106

Mu S. &Kan J. (1998). The effect of salts on the electrochemical polymerization of aniline. *Synthetic Metals,* Vol. 92, No. 2 (January 1998), pp.149-155, ISSN0379-6779

Mu S. (2004). Electrochemical copolymerization of aniline and *o*-aminophenol. *Synthetic Metals,* Vol.143, No. 3, (June 2004), pp. 259-268, ISSN0379-6779

Mu S. (2007). Pronounced effect of the ionic liquid on the electrochromic property of the polyaniline film: Color changes in the wide wavelength range. *Electrochimica Acta*, Vol. 52, No. 28, (November 2007), pp. 7827-7834, ISSN0013-4686

Mu S. (2011). Synthesis of poly(aniline-*co*-5-aminosalicylic acid) and its properties. *Synthetic Metals*, Vol. 161, No. 13-14, (July 2011), pp. 1306-1312, ISSN0379-6779

Mu S. (2011). Synthesis of poly(aniline-*co*-5-aminosalicylic acid) and its properties. *Synthetic Metals*, Vol. 161, No. 13-14, (July 2011), pp. 1306-1312, ISSN0379-6779

Mu S.; Chen C. & Wan J. (1997). The kinetic behavior for the electrochemical polymerization of aniline in aqueous solution, *Synthetic Metals,* Vol.88, (April 1997), pp. 249-254, ISSN0379-6779

Mu S.; Kan J.; Lu J. & Zhuang L. (1998). Interconversion of polarons and bipolarons of polyaniline during the electrochemical polymerization of aniline. *Journal of Electroanalytical Chemistry*, Vol. 446, No. 1-2, (April1998), pp.107- 112, ISSN1572-6657

Nagarajan R.; Tripathy S; Kumar J.; Bruno F. & Samuelson L. (2000). An Enzymatically Synthesized Conducting Molecular Complex of Polyaniline and Poly(vinylphosphonic acid). *Macromolecules*, Vol. 33, No. 262, (November 2000), pp. 9542–9547 ISSN0024-9297

Nunziante P. & Pistoia G. (1989). Factors affecting the growth of thick polyaniline films by the cyclic voltmmetry technique. *Electrochimica Acta,* Vol. 34, No. 2, (February 1989), pp. 223-228, ISSN0013-4686

Okamoto H. Okamoto M. & Kotaka T. (1998). Structure and properties of polyaniline films prepared via electrochemical polymerization. II: Structure and properties of polyaniline films prepared via electrochemical polymerization. *Polymer,* Vol. 39, No. 18, (1998), pp. 4359-4367 ISSN0032-3861

Okamoto H. & Kotaka T. (1998). Structure and properties of polyaniline films prepared via electrochemical polymerization. I: Effect of pH in electrochemical polymerization media on the primary structure and acid dissociation constant of product polyaniline films. *Polymer,* Vol. 39, No. 18, pp. 4349-4358, ISSN0032-3861

Okamoto H. & Kotaka T.(1998). Structure and properties of polyaniline films prepared via electrochemical polymerization. III: Effect of counter ions in electrochemical polymerization media on the structure responses of the product polyaniline films. *Polymer,* Vol. 40, No. 2, (1989), pp. 407-417, ISSN0032-3861

Özyılmaz A.; Erbil M. & Yazıcı B. (2006). The electrochemical synthesis of polyaniline on stainless steel and its corrosion performance. *Current Applied Physics*, Vol. 6, No. 1, (January 2006), pp. 1-9, ISSN1567-1739

Pandey P. & Singh G. (2002). Electrochemical Polymerization of Aniline in Proton-Free Nonaqueous Media, Dependence of Microstructure and Electrochemical Properties of Polyaniline on Solvent and Dopant. *Journal of Electrochemical Society*, Vol. 149, No. 4, (April 2002) pp. D51-D56, ISSN0013-4651

Park S. & Joong H. (2005). Recent Advances in Electrochemical Studies of π-Conjugated Polymers. *Buillten of the Korean Chemical Society,* Vol. 26, No. 5, (May 2005), pp. 697-706 ISSN0253-2964

Patil R.; Harima Y.; Yamashita K.; Komaguchi K.; Itagaki Y. & Shiotani M. (2002). Charge carriers in polyaniline film: a correlation between mobility and in-situ ESR meausurements. *Journal of Electroanalytical Chemistry,* Vol. 518, No. 1, (January 2002), pp. 13-19, ISSN1572-6657

Pawar P.; Gaikwad A. & Patil P. (2007). Corrosion protection aspects of electrochemically synthesized poly(o-anisidine-co-o-toluidine) coatings on copper. *Electrochimica Acta*, Vol. 52, No. 19, (May 2007), pp. 5958-5967, ISSN0013-4686

Popović & Grgur B. (2004). Electrochemical synthesis and corrosion behavior of thin polyaniline-benzoate film on mild steel. *Synthetic Metals*, Vol. 143, No. 2, (June 2004), pp. 191-195, ISSN0379-6779

Popović M.; Grgur B. & Mišković–Stanković V. (2005). Corrosion studies on electrochemically deposited PANI and PANI/epoxy coatings on mild steel in acid sulfate solution . *Progress in Organic Coatings*, Vol. 52, No. 4, (April 2005), pp. 359-365, ISSN0300-9440

Probst M. & Holze R. (1995). Time- and temperature-dependent changes of the *in situ* conductivity of polyaniline and polyindoline. *Electrochimica Acta*, Vol. 40, No. 2, (February 1995), pp. 213-219, ISSN0013-4686

Proń A.; Laska J.; Österholm J-E. & Smith P. (1993). Processable conducting polymers obtained via protonation of polyaniline with phosphoric acid esters. *Polymer,* Vol. 34, No. 20, (October 1993), pp. 4235-4240 ISSN0032-3861

Pron A. & Rannou P. (2002). Processible conjugated polymers: from organic semiconductors to organic metals and superconductors. *Progress in Polymer Science,* Vol. 27, No. 1, (February 2002), pp. 135-190, ISSN0079-6700

Pruneanu S.; Csahók E.; Kertész V. & Inzelt G. (1998). Electrochemical quartz crystal microbalance study of the influence of the solution composition on the behaviour of poly(aniline) electrodes. *Electrochimica Acta*, Vol 43. No. 16-17, (May 1998), pp. 2305-2323, ISSN0013-4686

Şahin Y.; Perçin P.; Şahin M. & Özkan G. (2003). Electrochemical preparation of poly (2-bromoaniline) and poly (aniline-*co*-2-bromoaniline) in acetonitrile. *Journal of Applied Polymer Science,* Vol. 90, No. 9, (November 2003), pages 2460–2468, ISSN0021-8995

Spinks G.; Dominis A. Wallace G. & Tallman D (2002). Electroactive conducting polymers for corrosion control. Part 2. Ferrous metals. *Journal of Solid State Electrochemistry,* Vol. 6, No. 2, (February 2002), pp. 85-100, ISSN1432-8488

Stejskal J. & Gilbert R. (2002). Polyaniline. Preparation of a conducting polymer (IUPAC Technical Report). *Pure and Applied Chemistry,* Vol. 74, No. 5, (2002), pp. 857-867 doi:10.1351/pac200274050857

Stejskal J.; Kratochvíl & Jenkins A. (1996). The formation of polyaniline and nature of its structures. *Polymer,* Vol. 37, No. 2, pp. 367-369, (February 1996), ISSN0032-3861

Stejskal J.; Sapurina I. & Trchová M. (2010). Polyaniline nanostructures and the role of aniline oligomers in their formation. *Progress in Polymer Science*, Vol. 35, No. 12, (December 2010), pp. 1420-1481, ISSN0079-6700

Syed A. & Dinesan M. (1991). Polyaniline—A novel polymeric material, *Talanta*, Vol. 38, No. 8, (August 1991), pp. 815-837 ISSN0039-9140

Tallman D.; Spinks G.; Dominis A. & Wallace G. (2002). Electroactive conducting polymers for corrosion control. Part1. General introduction and review of non-ferrous metals. *Journal of Solid State Electrochemistry,* Vol. 6, No. 2, (February 2000), pp. 73-84, ISSN1432-8488

Tanaka J.; Mashita N.; Mizoguchi K. & Kume K. (1989). Molecular and electronic structures of doped polyaniline. *Synthetic Metals*, Vol. 29, No. 1, (March 1989), pp. 175-184, ISSN0379-6779

Tanaka K.; Wang S. & Yamabe T. (1990). Will bipolarons be formed in heavily oxidized polyaniline? *Synthetic Metals*, Vol. 36, No.1, (May 1990), pp. 129-135, ISSN0379-6779

Tang H.; Kitani A. & Shiotani M. (1996). Factors of anions on electrochemical formation and overoxidation of polyaniline. *Electrochimica Acta,* Vol. 41, No. 9, (June 1996) pp. 1561-1567 ISSN0013-4686

Tang Z.; Liu S.; Wang Z.; Dong S. & Wang E. (2000).Electrochemical synthesis of polyaniline nanoparticles . *Electrochemistry Communications*, Vol. 2, No.1, (January 2000), pp. 32-35, ISSN1388-2481

Tsakova V.; Milchev A. & Schultze J. (1993).Growth of polyaniline films under pulse potentiostatic conditions. *Journal of Electroanalytical Chemistry*, Vol. 346, No. 1-2, (March 1993), pp. 85-97, ISSN1572-6657

Wallace G.; Spinks G.; Kane-Maguire L. & Teasdale P. (2009). *Conductive Electroactive Polymers,* CRC Press, Taylor & Francis Group, ISBN 978-1-4200-6709-5, Boca Raton

Wang T.& Tan Y. (2006). Understanding electrodeposition of polyaniline coatings for corrosion prevention applications using the wire beam electrode method. *Corrosion Science*, Vol. 48, No. 8, (August 2006), pp. 2274-2290, ISSN0010-938X

Xu G.; Wang W.; Qu X.; Yin Y.; Chu L.; He B.; Wu H.; Fang L.; Bao Y. & Liang L. (2009). Electrochemical properties of polyaniline in *p*-toluene sulfonic acid solution. *European Polymer Journal*, Vol. 45, No. 9, (September 2009), pp. 2701-2707, ISSN0014-3057

Yano J.; Ota Y. & Kitani A. (2004). Electrochemical preparation of conductive poly(*N*-alkylaniline)s with long *N*-alkyl chains using appropriate dopant anions and organic solvents. *Materials Letters*, Vol. 58, No. 12-13, (May 2004), pp. 1934-1937 ISSN0167-577X

Zhang J.; Shan D. & Shaolin M. (2006). Electrochemical copolymerization of aniline with *m*-aminophenol and novel electrical properties of the copolymer in the wide pH range. *Electrochimica Acta*, Vol. 51, No. 20, (May 2006), pp. 4262-4270, ISSN0013-4686

Zhou H.; Wen J.; Ning X.; Fu C.; Chen J. & Kuang Y. (2007). Electrosynthesis of polyaniline films on titanium by pulse potentiostatic method. *Synthetic Metals*, Vol. 157, No. 2-3, (February 2007), pp. 98-103, ISSN0379-6779

Zhou S.; Wu T.; Kan J. Effect of methanol on morphology of polyaniline.(2007). *European Polymer Journal*, Vol. 43, No. 2, (February 2007), pp. 395-402, ISSN0014-3057

Zotti G; Cattarin S. & Comiss N. (1987). Electrodeposition of polythiophene, polypyrrole and polyaniline by the cyclic potential sweep method. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, Vol. 235, No. 1-2, (October 1987), pp. 259-273, ISSN1572-6657

Zotti G; Cattarin S. & Comiss N. (1988). Cyclic potential sweep electropolymerization of aniline: The role of anions in the polymerization mechanism. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, Vol. 239, No. 1-2, (January 1988). pp. 387-396, ISSN1572-6657

Journal of The Electrochemical Society, **157** (5) D295-D301 (2010)
0013-4651/2010/157(5)/D295/7/$28.00 © The Electrochemical Society

Study of the Dendritic Growth of Ni–Co Alloys Electrodeposited on Cu Substrates

L. D. Rafailović,[a,b,z] **D. M. Minić,**[c] **H. P. Karnthaler,**[a] **J. Wosik,**[b] **T. Trišović,**[d] **and G. E. Nauer**[b,e,*]

[a]*Physics of Nanostructured Materials and* [e]*Faculty of Chemistry, University of Vienna, A-1090 Vienna, Austria*
[b]*Center for Electrochemical Surface Technology, A-2700 Wiener Neustadt, Austria*
[c]*Faculty of Physical Chemistry, University of Belgrade, 11000 Belgrade, Serbia*
[d]*Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, 11000 Belgrade, Serbia*

Ni–Co alloy deposits and their parent metals were formed on Cu substrates by electrolysis under different current densities applied in the galvanostatic regime. A quantitative scanning electron microscopy technique was employed to study the morphology and surface roughness of the obtained deposits. The structure of the deposits is governed by the nature of depositing ions and quantity of evolved hydrogen. The cauliflower morphology and the highest mean surface roughness values are the results of electrodeposition from the Ni containing bath. The structure of the Co deposits formed under the same conditions and determined by the formation of the hexagonal close-packed phase results in a more uniform grain size distribution and formation of smoother platelet deposits. The mean surface values of the parent metals are independent of the current density. The dendritic growth is a special case of a structure formed only in the Ni–Co alloy deposition at selected, high current densities of 220 and 400 mA cm^{-2}. The dendrites obtained at a higher current density of 400 mA cm^{-2} have shown more developed structures with smaller dendrites that have more pronounced secondary branch and high order branches.

Manuscript submitted December 28, 2009; revised manuscript received February 1, 2010. Published April 8, 2010. This was Paper 2713 presented at the Vienna, Austria, Meeting of the Society, October 4–9, 2009.

The electrodeposition is one of the well-known approaches developed in recent years for the preparation of the nanostructured pure metals and alloys.[1,2] The Ni–Co alloys have been widely investigated due to their unique magnetic and electrical properties, which have found a potential application in different computer read/write heads and microelectromechanical systems.[3,4]

In general, electrolytic deposits can be compact or disperse.[5,6] The disperse deposits are formed under electrolysis conditions, which favor a complete diffusion control of the process. The electrodeposition represents an excellent tool for the formation of metal disperse deposits with a highly developed surface area, which can be successfully used as electrodes in electrochemical devices such as fuel cells, batteries, and sensors.[7] The basic characteristics of these electrodes, which should be fulfilled to be used for these purposes are the open porous structure, which enables the rapid transport of gas and liquid, and the extremely high surface area, which is desirable for electrochemical reactions. According to this, in the galvanostatic powder deposition, the initial deposition current density must be larger than the limiting diffusion current density.[8] The electrodeposition at overpotentials belonging to the plateau of the diffusion-limiting current density leads to the formation of dendritic deposits. The strong hydrogen codeposition leads to a stirring of the solution and changes the mass-transfer limitations at the electrode surface.[9] At the same time, the evolved hydrogen affects the mass- and heat-transfer, limiting the current density and ohmic resistance, leading to the formation of the open porous deposit structures with a high surface area.[9-11]

In this work, Ni–Co nanoscaled deposits were prepared and characterized using different techniques, with respect to elucidating the effect of the current density and electrolyte composition on the formation of the dendritic deposits.

Experimental

The Ni, Co, and Ni–Co nanostructured deposits were obtained in the galvanostatic regime at a current density range of 65–400 mA cm^{-2}. The electrolyses were performed from ammonium sulfate–chloride solutions for the concentration ratio $Ni^{2+}/Co^{2+} = 1$ of a solution composition as follows: total concentration 0.12 M ($NiSO_4 + CoSO_4$), 0.5 M NH_4Cl, and 3.5 M NH_4OH at pH 10. The parent metal deposits were prepared from the same supporting electrolyte with a total metal ion concentration of Co^{2+} or Ni^{2+} being 0.12 M. The reagents of the analytical purity and deionized water were used for the bath preparation. The temperature of the bath during deposition was maintained at 298 K. The Ni, Co, and Ni–Co deposits were prepared at the constant current density with a quantity of electricity of 0.043 Ah cm^{-2} and an average sample thickness of (25 ± 5) μm. The Cu electrodes placed in the center of the cell with a 1.0 cm^2 surface area and a 0.2 cm thickness were used as working electrodes. A Ti plate covered with RuO_2/TiO_2 (10 cm^2 geometric area), placed close and parallel to the Cu plate, was used as an anode [dimensionally stable anode (DSA)]. The schematic representation of the electrochemical cell used for the deposition is presented in Fig. 1.

The polarization measurements were carried out by a computer-controlled electrochemical system (PAR M 273A, software PAR M352/252, version 2.01) with a sweep rate of 1 mV s^{-1}. For the correction of the IR drop, the current-interrupt technique was used with a time of current interruption of 0.5 s. The polarization curves were measured in a three-electrode electrochemical cell at (298 ± 1) K (Fig. 1), where the DSA was replaced by a large-area platinum mesh. The Luggin capillary connecting the reference electrode [saturated calomel electrode (SCE)] to the electrolyte was positioned at a distance of 0.2 cm from the working electrode (copper rod embedded in resin, $d = 4$ mm). Before each experiment, the working electrode was highly polished with an alumina-paste (0.05 μm)-impregnated polishing cloth.

The average current efficiency for the hydrogen evolution reaction is determined by the measurement of the quantity of evolved hydrogen based on Faraday's law. The overall electrodeposition current was calculated as a function of the electrodeposition time. The thickness of the deposits was estimated based on their cross-section images.

The surface morphology was analyzed by XL 30 environmental scanning electron microscope (ESEM) with field emission gun (FEI Co., Netherlands). The profile and roughness measurements, as well as three-dimensional (3D) area analyses, directly from the stereoscopic images of the specimen surface were carried out using MeX software from Alicona (A). The cross-section alloy composition

---

* Electrochemical Society Active Member.
[z] E-mail: lidija.rafailovic@univie.ac.at

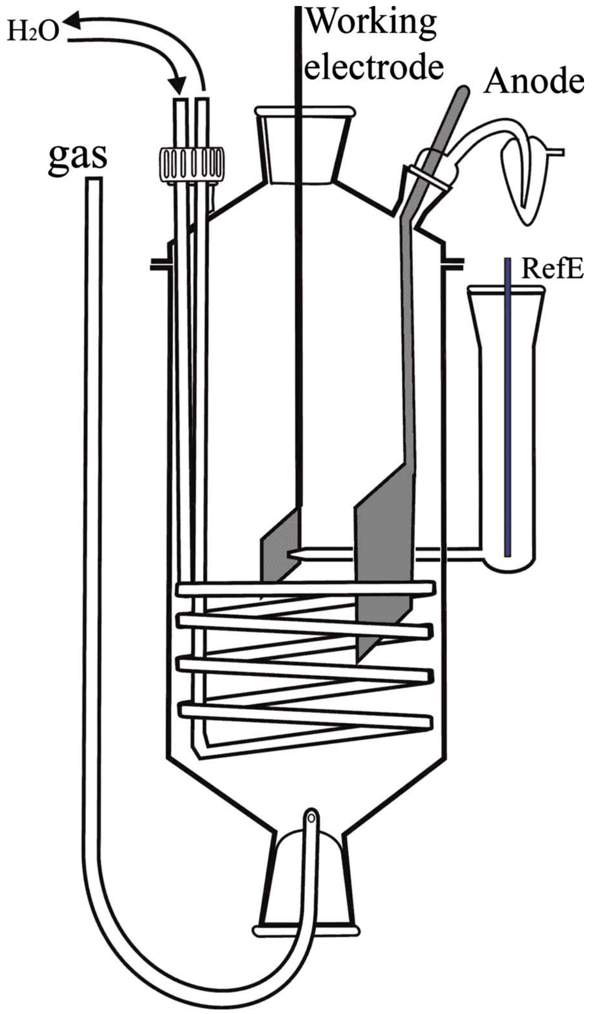


Figure 1. (Color online) Schematic representation of the electrochemical cell.

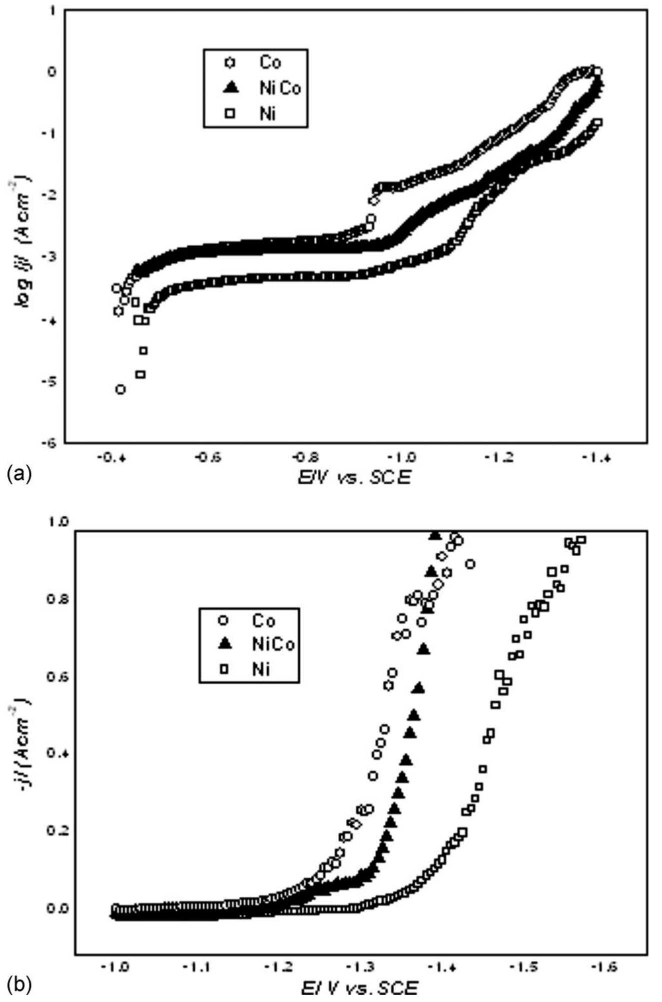


Figure 2. Polarization curves for galvanostatic Ni, Ni–Co, and Co deposition from the solution containing: □, 0.12 M $NiSO_4$; ▲, 0.12 M ($NiSO_4$ + $CoSO_4$) with concentration ratio $Ni^{2+}/Co^{2+} = 1$; and ○, 0.12 M $CoSO_4$ in 0.5 M NH_4Cl and 3.5 M NH_4OH measured with IR drop correction. Scan rate: 1 mV s^{-1}.

analyses of the deposited samples embedded in the resin were performed by ESEM using the energy dispersive X-ray analysis (EDX) technique (Genesis).

X-ray powder diffraction (XRD) analysis was carried out using an MPD diffractometer (Philips, NL) with Cu Kα radiation (40 kV/30 mA) in Bragg/Brentano geometry. The step scan mode was utilized with 0.03° in a 2θ/1.15 s step. The angular 2θ range investigated was 20–110°.

Results and Discussion

Cathode polarization and efficiency.— During the cathodic electrodeposition of the iron group metals from aqueous solutions, a competitive cathodic hydrogen evolution reaction occurs.[12] Because the formation of the disperse and powder deposits is enhanced by a small metal ion concentration and high deposition current density, polarization curves were measured with a correction for the IR drop. In this case, the plateau corresponding to the limiting current density cannot be established, as in the case for the electrodeposition performed from aqueous solutions containing an electropositive metal such as Cu due to the intensive hydrogen evolution reaction almost from the beginning of the deposition. At the end of this plateau and at larger overpotentials, the intensive hydrogen evolution takes place. Therefore, the polarization curves for the electrodeposition of Ni, Ni–Co, and Co are complex with the appearance of the limiting current density in a wide range of potential values (Fig. 2a), characterized by the electrodeposition currents that grew (Fig. 2b) with the increasing of the overpotential. The corresponding overpotential needed for the deposition is most positive for the deposition of Co, followed by the deposition of Ni–Co alloy and Ni.

The electrodeposition potentials of Ni, Ni–Co, and Co are very similar with the values of about −0.5 V vs SCE. The range of potentials of −0.6 to −1.0 V is the activation control region of the metal and alloy electrodeposition. The deposition at overpotentials higher than −1.1 V is characterized by a sharp increase in the current density, most probably as a consequence of the formation of dendritic deposit with more developed structures.

The hydrogen evolution reaction in the alkaline solution proceeds according to the three reaction mechanisms[13] resulting in the release of OH^- ions in the layer surrounding the electrode and, therefore, an increase in pH. However, the bath for the electrodeposition consists of NH_4Cl/NH_4OH used as a buffering agent for pH 10, and no significant increase in pH during deposition was observed.

The hydrogen overpotential can manifest itself through the cathodic current efficiency (Fig. 3). The hydrogen evolution during the deposition of the alloys diminishes the current efficiency, depending on the electrolyte composition and on the current density. These results agree well with the polarization measurements where the electrodeposition performed from bath with Co bath has a lower hydrogen overpotential and consequently a lower current efficiency.

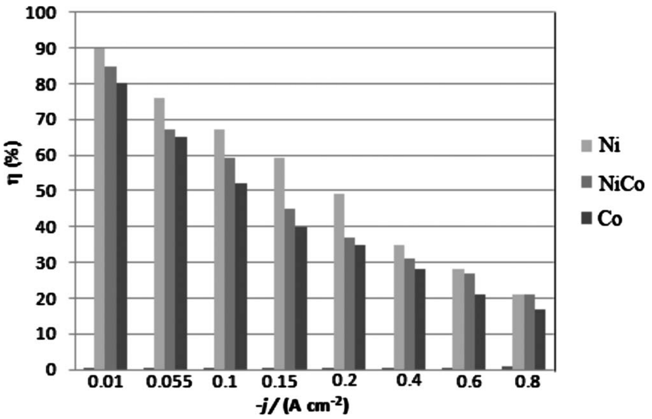


Figure 3. The dependence of the current efficiency on current density for Ni, Ni–Co, and Co electrodeposition (electrolyte composition: Ni–0.12 M $NiSO_4$, Ni–Co alloy–0.12 M ($NiSO_4$ + $CoSO_4$), $Ni^{2+}/Co^{2+} = 1$, and Co–0.12 M $CoSO_4$).

Also, the evolution of hydrogen provides some additional stirring effect and enhances the formation of disperse deposits with more developed structures. Deposition becomes dependent on hydrogen evolution because at current densities, $j \geq 200$ mA cm^{-2}, the hydrogen evolution is predominant in the overall cathodic process. The current efficiencies $\eta \leq 50\%$ (Fig. 3) for the Ni-containing electrolyte and $\eta \leq 40\%$ for the Co-containing electrolyte at a current density of 200 mA cm^{-2} were found. The hydrogen method used for the calculation of the current efficiency of the Ni, Co, and Ni–Co alloys results in slightly higher values in comparison with the current efficiency data obtained by the gravimetric method. An explanation is attributed to the fact that the formation of dendritic deposits at higher current densities can cause the fall of some amount of deposit into the solution, resulting in less weight values and, consequently, diminished values of the calculated current efficiency.

Growth of Ni, Co, and dendritic Ni–Co deposits on Cu substrates.— The needlelike deposits known as dendrites are usually obtained by electrodeposition at low cation concentrations. By definition, dendrite represents a skeleton of monocrystals and consists of stalk and branches resembling a tree.[8]

The scanning electron microscopy (SEM) of the Ni–Co deposit cross sections obtained on copper substrates has shown the gradual evolution of the dendritic formation (Fig. 4a-c). With an increasing current density, a detailed investigation of the deposits morphology has shown a formation of primary dendrites, which further grows with increasing current density. The sample obtained at a current density of 65 mA cm^{-2} revealed the formation of a rough deposit (Fig. 4a). The propagation of this structure by branching produces dendrites, as shown in Fig. 4b. The dendrites obtained at a higher current density of 400 mA cm^{-2} (Fig. 4c) have shown more developed structures with smaller dendrites that have more pronounced secondary branch and high order branches. A comparison with deposits obtained from pure Ni baths revealed a formation of a rough deposit only (Fig. 5a). In contrast, electrodeposition performed at the lowest value of the current density, i.e., 65 mA cm^{-2}, from a pure Co bath has shown a formation of dendritic growth (Fig. 5b). In the particular case of anisotropic Co deposition when the hexagonal close-packed (hcp) lattice is formed, the growth along the high index axis does not lead to a formation of low index planes. Therefore, the hcp lattice serves as a growth site for the dendrite formation because the development of protrusions along some axis in the direction of the increasing concentration is more favorable. Repeated nucleation results in the dendrite formation. Although deposits produced from simple solution salts without additives are often dendritic or treelike, real dendritic structures are formed only from Ni–Co baths ($Ni^{2+}/Co^{2+} = 1$), whereas with increasing current density, the dendritic growth is even more pronounced (Fig. 4b and c). In this range of concentrations, Ni and Co exhibit a mutual solid solubility. The deposition from bath with different Ni^{2+}/Co^{2+} concentration ratios, i.e., 0.25, 0.5, 2, and 4, results in more disperse than the dendritic growth.[14]

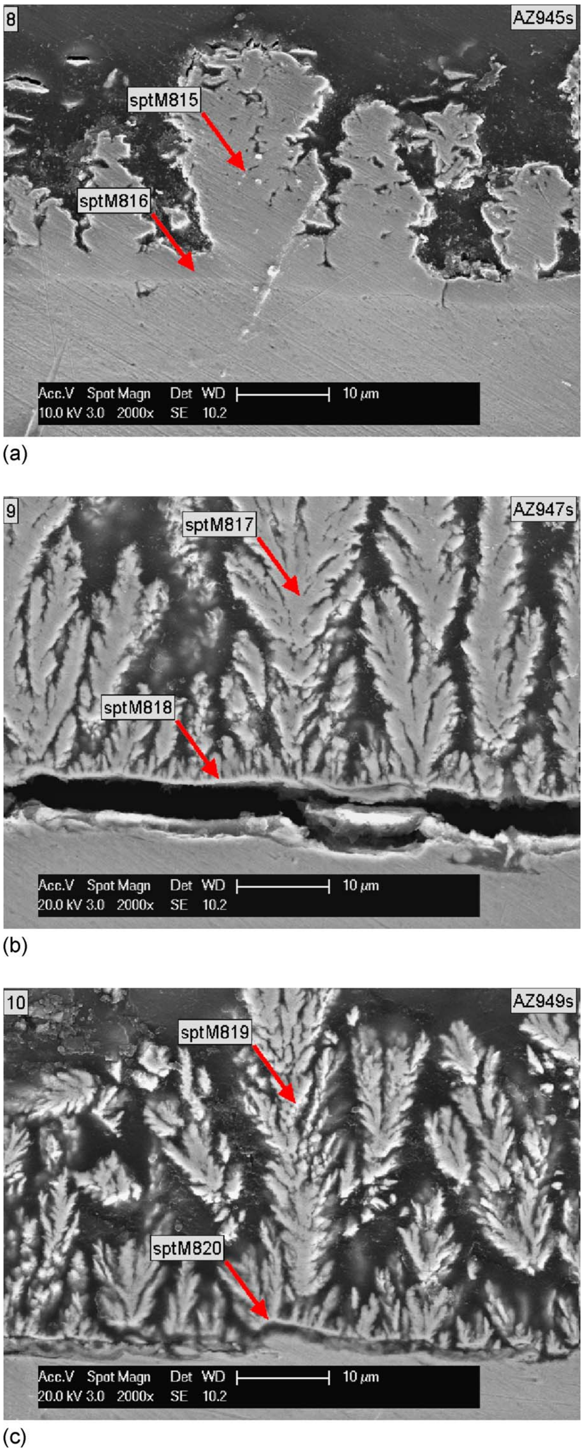


Figure 4. (Color online) Cross sections of Ni–Co deposits galvanostatically obtained from the solution containing 0.12 M ($NiSO_4$ + $CoSO_4$), $Ni^{2+}/Co^{2+} = 1$ at current density: (a) 65, (b) 220, and (c) 400 mA cm^{-2}.

EDX composition analysis of Ni–Co deposits.— The cross-section composition analysis of the alloys galvanostatically deposited from the solution containing the total concentration of

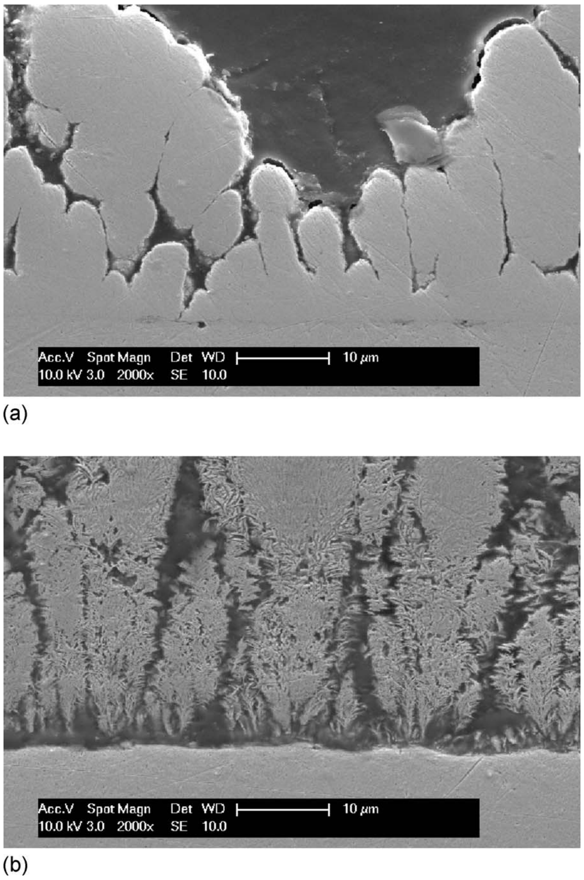


Figure 5. (a) Cross section of Ni deposit galvanostatically obtained from the solution containing 0.12 M $NiSO_4$ at current density of 65 mA cm^{-2}. (b) Cross section of Co deposit galvanostatically obtained from the solution containing 0.12 M $CoSO_4$ at current density of 65 mA cm^{-2}.

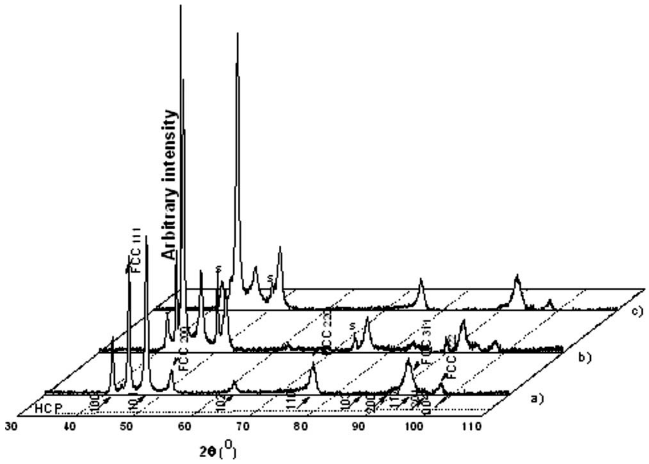


Figure 6. XRD of Ni–Co deposits galvanostatically obtained on Cu substrate from the solution containing 0.12 M ($NiSO_4 + CoSO_4$), $Ni^{2+}/Co^{2+} = 1$ at current density: (a) 65, (b) 220, and (c) 400 mA cm^{-2} (S-reflection attributed to the Cu substrate).

0.12 mol dm^{-3} of ion metal with a ratio $Ni^{2+}/Co^{2+} = 1$ is presented in Table I. The composition of the dendritic deposit samples near the electrode surface and in some distance is different (see Table I).

An EDX analysis revealed that at higher current densities, i.e., 220 and 400 mA cm^{-2}, the deposition of Co is enhanced near the electrode surface (~1 μm) due to the lower overpotential for the Co electrodeposition (sptM818, sptM820 in Fig. 4b and c), reaching values of the corresponding ions in the solution (sptM817, sptM819 in Fig. 4b and c). An explanation can be attributed to the fact that at high current densities, the hydrogen evolution is higher (Fig. 3), providing some stirring effect and leading to the more uniform distribution of Ni^{2+} and Co^{2+} ions in the diffusion layer and therefore resulting in a more uniform composition of the deposit. At high current densities, high growth velocities deplete the cations in the double layer, and the growth is controlled by mass transfer in the electrolyte. However, for a lower current density of 65 mA cm^{-2} (Fig. 4a), the deposition comes more under the activation control, so the deposition of Co is enhanced compared to Ni.

At a current density of 65 mA cm^{-2}, the content of Co in the deposit is higher than in the electrolyte, as a consequence of the lower overpotential for the Co^{2+} reduction compared to Ni^{2+}, as can also be seen from the polarization curves (Fig. 2). In the current density range 65–400 mA cm^{-2}, the current density increase results in an increase in the nickel content in the deposits. The phenomenon

Table I. Cross-section composition analysis of Ni–Co alloys galvanostatically deposited at different current densities.

Atom % Ni	Atom % Co	*j* (mA cm^{-2})	Spot position
40	60	65	Interface
22	78	65	Bulk
39	61	220	Interface
49.5	50.5	220	Bulk
37	63	400	Interface
49.5	50.5	400	Bulk

Table II. Phase composition, grain size, and cell parameters of the Ni–Co deposits galvanostatically obtained from solution containing 0.12 mol dm^{-3} ($NiSO_4 + CoSO_4$), ratio $Ni^{2+}/Co^{2+} = 1$ at current density: (a) 65, (b) 220, and (c) 400 mA cm^{-2}.

	Content of the phases (atom %)			Lattice parameters		
Current density (mA cm^{-2})	Amorphous	fcc/hcp	Grain size (±3 nm)	*a* (Å)	*c* (Å)	Cell volume (Å^3)
65		72	19	3.5291		43.953
	/	28	15	2.5053	4.0717	22.132
220		20	13	3.5296		43.972
	9	71	11	2.4987	4.0767	22.043
400		5	11	3.5329		44.095
	15	80	10	2.4947	4.1005	22.100

of the anomalous codeposition (characteristic of the electrodeposition of iron group metals) is very pronounced in the production of compact deposits. In the disperse deposits, the anomalous codeposition is much less pronounced, so that the composition of the deposits obtained at high current density is almost similar to the concentration of the metal ions in the electrolyte (Fig. 4c). Increasing the current density shifts the ratio of Ni and Co in the alloys closer to the value of the concentration of the corresponding ions in electrolyte.

Structural analysis of Ni–Co deposits.— The nanostructured dendritic deposits were analyzed by XRD (Fig. 6). The Rietveld refinement procedure[15] was used to determine the structure and the grain size of the deposits. For this purpose, Rietveld's refinement program TOPAS V3.0 (Bruker AXS GmbH, Germany) was used.[16] The quality of the refinement progress was controlled by monitoring the fit parameter R_{wp}, the goodness of fit, and the Durbin–Watson factor.

A detailed Rietveld's analysis revealed that Ni–Co alloys obtained by the galvanostatic deposition using the same electrolyte at different current densities consist of a mixture of solid solutions. The crystal structure obeys the phase diagram[17] because the obtained bulk deposits are in the range of concentrations where Ni and Co exhibit solid solubility (see Table I.)

The face-centered cubic (fcc) phase, whose structure is defined by the $Fm\bar{3}m$ space group, and hcp, whose structure is defined by the $P63/mmc$ space group, were identified. By increasing the current density, the structure and composition of the obtained deposits is progressively changed.

The increase in the current density leads to the increase in the content of the fcc phase, as well as the formation of significant amounts of the amorphous phase (Table II). Furthermore, the cell volume of the fcc phase increases slightly with increasing current density (Table II).

At a current density of 65 mA cm^{-2}, mainly the hcp phase, the equilibrium phase of Co stable at room temperature is generated, and it is in good correlation with the EDX results of the bulk material (Table I). At higher electrode polarization, i.e., far from equilibrium, at a current density of 220 mA cm^{-2}, the fcc phase growth preferentially on the polycrystalline FCC-structured Cu substrate. Still, an amount of 20% hcp phase (Co) calculated by the XRD Rietveld refinement is present (Table II). Taking into account the amount of an amorphous phase of 9%, this means that approximately 70% of the deposit is composed of the fcc solid solution.

In the deposition at a current density of 400 mA cm^{-2}, even further from equilibrium in comparison with deposits obtained at 220 mA cm^{-2}, the growth of the fcc phase is more pronounced (Table II.). As determined by TOPAS using the Rietveld method, the disperse deposits with more developed structures obtained at a high current density, i.e., 400 mA cm^{-2}, also contained an up to 15% amorphous phase. The amorphous phase content, attributed to the enhanced background intensity, was estimated by the determination of the integral area of the broad diffuse diffraction halo, which cannot be assigned to distinct diffraction maxima correlated with crystalline phases and by comparing with samples without an amorphous phase.

The classical expression[8] for the steady-state nucleation rate J is given by

$$J = K_1 \exp - \frac{K_2}{\eta^2} \qquad [1]$$

where K_1 and K_2 are practically overpotential-independent constants. The nucleus probability formation J is enhanced by the increase in the overpotential η. The electrochemical deposit formation at higher current densities is accompanied by higher overpotential values. Based on the equation, obviously, a further increase in the current density decreases the grain size of the deposits down to 10 nm (Table II).

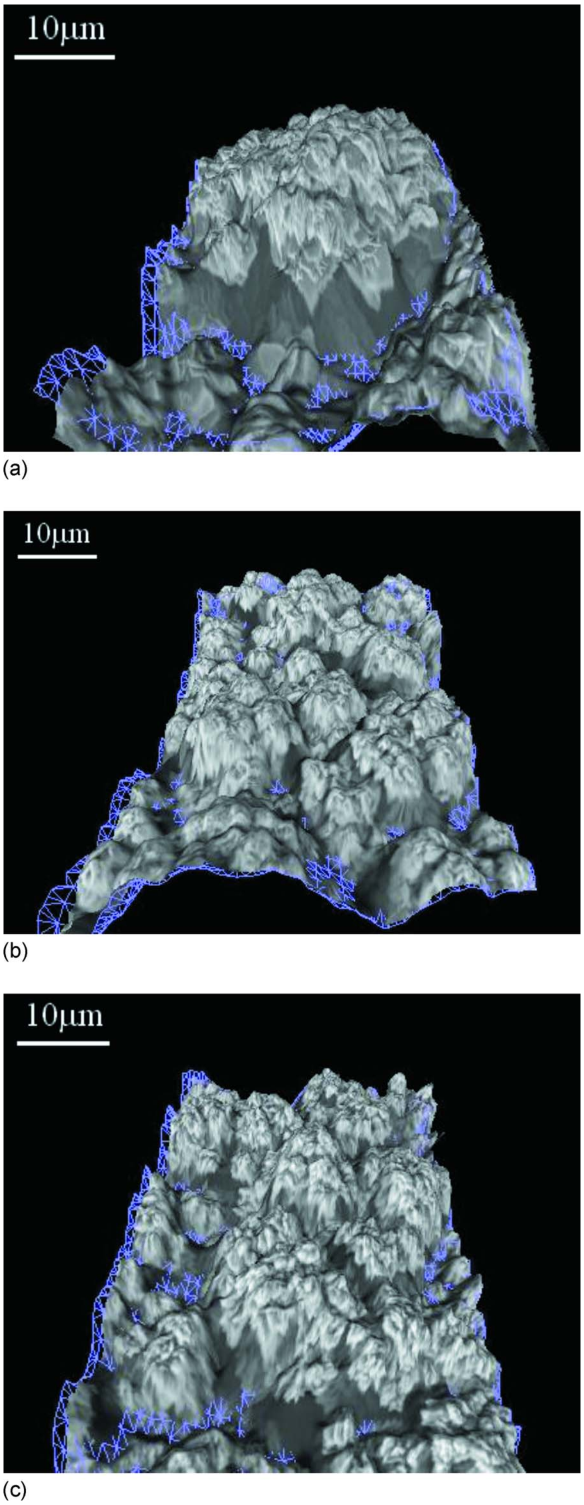


Figure 7. (Color online) 3D SEM reconstruction of the surfaces of Ni–Co deposits galvanostatically obtained at current densities: (a) 65, (b) 220, and (c) 400 mA cm^{-2}.

Surface morphology of Ni–Co deposits.— The nature and magnitude of the applied electric field across the counter-working electrode arrangement determines (*i*) grain size, (*ii*) surface roughness, and (*iii*) dendritic electrodeposit growth.

The surface roughness of the Ni–Co deposits was determined by the 3D SEM reconstruction of the specimen surface (Fig. 7a-c). Such a characterization gives quantitative results of the mean sur-

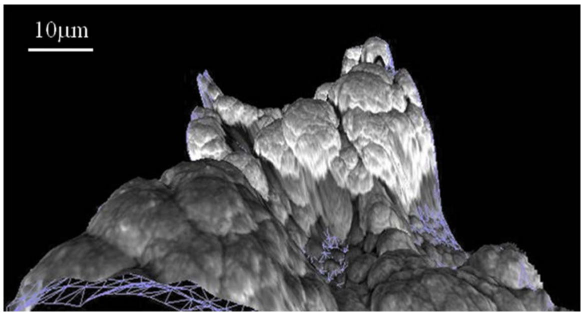


Figure 8. (Color online) 3D SEM reconstruction of the surface of Ni deposit galvanostatically obtained at current density of 400 mA cm^{-2}.

face roughness: $\sigma = 3$ μm in the deposit obtained at current density 65 mA cm^{-2} (Fig. 7a) and $\sigma = 1$ μm in the deposits obtained at current densities 220 and 400 mA cm^{-2} (Fig. 7b and c). The value σ represents a picture of local surface irregularities and gives the height deviation of the surface from the mean level. An increase in the current density results in a decrease in the mean roughness because at higher current densities, the amount of crystal nuclei on the surface is enhanced, causing a more homogeneous grain size distribution and, therefore, formation of a smoother deposit.

The effective surface roughness increases due to the increase in the coarseness of the deposit with increasing current density (Fig. 7b and c). This surface amplification leads to the initiation of the preferential growth of protrusions or dendrites. The Ni deposits obtained from simple solution salts are characterized by a cauliflower surface morphology and mean surface roughness values of $\sigma = 4$ μm for all analyzed deposits obtained at current densities of 65, 220, and 400 mA cm^{-2}. A typical 3D SEM reconstruction of the surface of the Ni deposit is presented in Fig. 8.

Co deposits have shown mean σ values of 1 μm, and the result of the deposition is the appearance of smoother deposits compared to the Ni deposits (Fig. 9). One of the consequences of hydrogen evolution is that H_2 bubbles are attached to the surface during deposition and therefore can cause growth of the deposit around the bubbles before they are released. Such impact of hydrogen during the codeposition of Ni can cause larger mean surface values of Ni deposits. The confirmation of these is the presence of craters or holes in the Ni deposit (Fig. 10a), clearly visible on the surface of one typical SEM micrograph. The bottoms of the holes consist of small Ni particles, while around them during codeposition, larger cauliflower particles are formed. A faster growth of the deposit around bubbles is caused by increasing current density because the overall current is concentrated around the bubbles, which are not conductive. This directly results in the formation of high surface area disperse deposit confirmed by 3D SEM results and the value of surface roughness of $\sigma = 4$ μm. A typical SEM micrograph of particles of the Co deposit (Fig. 10b) separated by boundaries is characterized by the platelet morphology with very fine nanosized crystallites growing on the surface during codeposition from the Co-containing bath. In both cases, the particles consist of smaller agglomerates of grains.

The surface morphology of the Ni–Co deposit is characterized by the formation of dendrites. Figure 10c shows the cauliflower-shaped

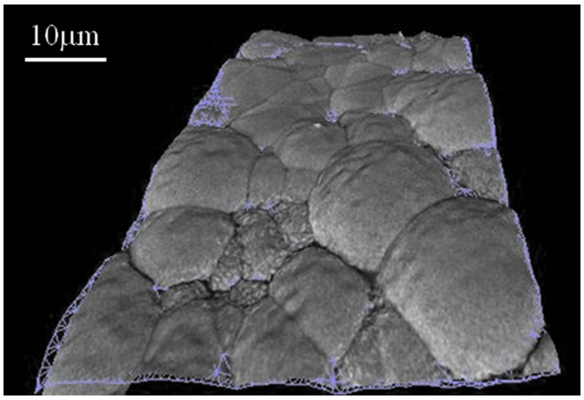


Figure 9. (Color online) 3D SEM reconstruction of the surface of Co deposit galvanostatically obtained at current density of 220 mA cm^{-2}.

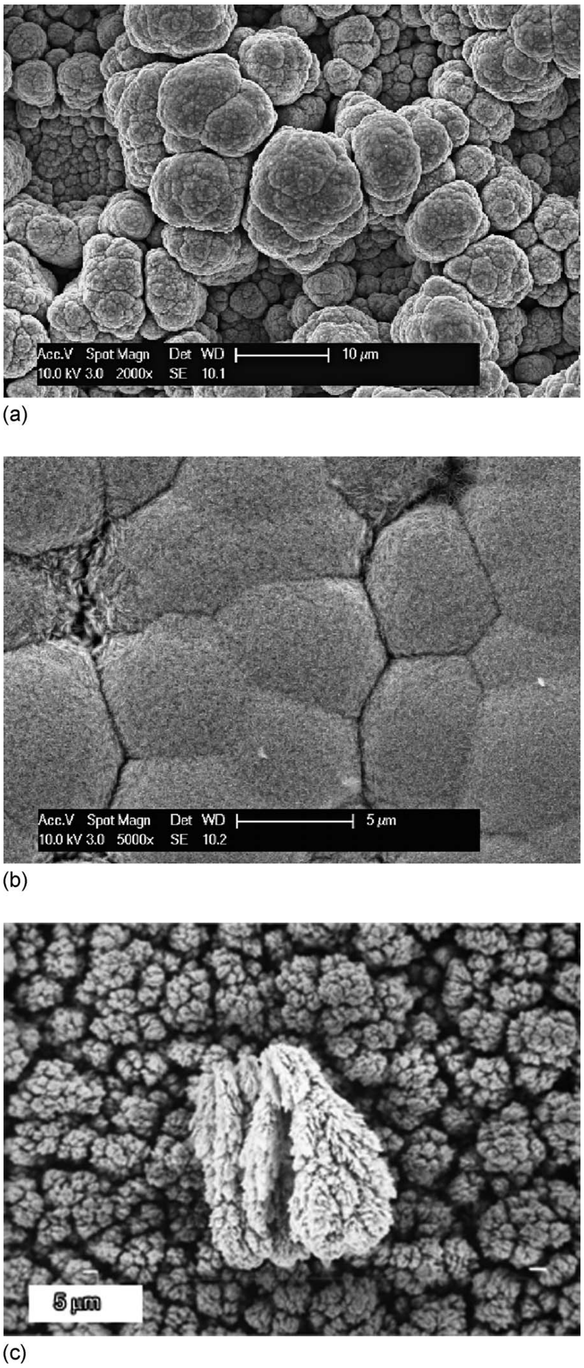


Figure 10. (a) SEM micrograph of Ni deposit formed by galvanostatic deposition at current density of 400 mA cm^{-2}. (b) SEM micrograph of Co deposit formed by galvanostatic deposition at current density of 220 mA cm^{-2}. (c) SEM micrograph of Ni–Co dendrites formed by galvanostatic deposition at current density of 400 mA cm^{-2}.

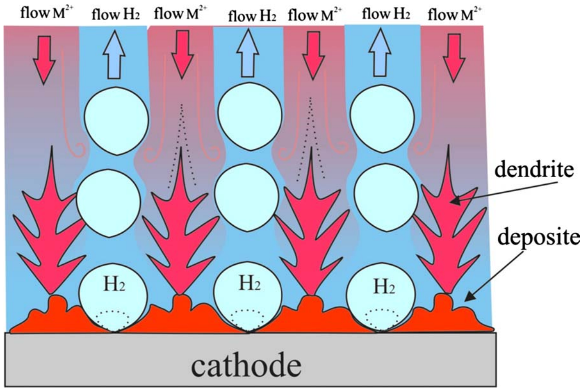


Figure 11. (Color online) Schematic representation of the dendrite formation.

particles with dendrites growing on its surface. Increasing the overpotential under a strong hydrogen codeposition leads to the dendritic deposits formation in the Ni–Co alloy deposition.

The basic cause of dendritic growth is the formation of the diffusion field of depositing ions that favors the development of protrusion in the direction of increasing concentration. Dendrite exhibits a highly ordered structure and grows and branches in well-defined directions.

The motion of the growing interface is controlled by a concentration of the diffusing particle and electric potential.[18] According to Fick's law, which satisfies the equation for a nonlocal growth process, such as electrodeposition, the low value of the growth velocity and the large value of the diffusion length enhance the deposition preferentially on protrusions.

Well-defined organizations, such as dendritic, are formed under such conditions. A schematic representation of the common effect of hydrogen and electrolysis conditions, which favor the dendrite formation, is shown in Fig. 11.

Apart from decreasing the concentration of the depositing ion, the formation of a dendritic deposit can also be enhanced by increasing the concentration of the supporting electrolyte, increasing the viscosity of the solution, decreasing the temperature, and decreasing the velocity of motion of the solution.[8]

Conclusion

The grain size of Ni–Co deposits is determined by the applied overpotential. Increasing current density results in finer grain deposits. The structure of Ni–Co deposits is characterized by a solid solution formation; increasing current density results in an increase in the volume fraction of the cubic phase. The morphology of Ni–Co is affected by conditions applied during electrolysis. Morphology is determined by the nature of depositing ions. The Ni deposit exhibits a spherical growth during deposition, which manifests itself by a typical cauliflower structure; the surface pattern of the Co deposit is characterized by a platelet structure. The composition of the alloy deposit is determined by the hydrodynamics conditions in the near electrode layer; with increasing current density, the hydrogen evolution is predominant, leading to the more uniform distribution of Ni and Co ions in the double layer, and, therefore, the composition of the deposits reaches the real value of the corresponding ions in the solution. The whole process determines the density of nucleation sites and the final morphology of the deposit. The formation of the dendritic Ni–Co alloy deposits is enhanced by increasing the current density and leads to a decrease in the mean roughness. The number of atoms in the nucleus having the critical radius declines with the overpotential square, resulting in a more rapid nucleation at higher current density and the formation of smaller crystals with the average grain sizes of 10 nm. The increase in the current density leads to an increase in the volume fraction of the cubic phase in the nanocrystalline alloy deposits with a corresponding decrease in the grain size.

Acknowledgments

This research was supported by the research project "Bulk Nanostructured Materials" within the research focus "Material Science" of the University of Vienna. The investigation was partially supported by the Ministry of Science and Environmental Protection of Serbia, under project 142025, and within the K plus program at CEST by the Austrian Research Promotion Agency (FFG) and the government of Lower Austria. L.D.R. is grateful for the support by the I.K. "Experimental Materials Science–Nanostructured Materials," a college for Ph.D. students at the University of Vienna.

University of Vienna assisted in meeting the publication costs of this article.

References

1. M. K. Roy, V. S. Subrahmanyam, and H. C. Verma, *Phys. Lett. A*, **328**, 375 (2004).
2. M. A. Meyers, A. Mishra, and D. J. Benson, *Prog. Mater. Sci.*, **51**, 427 (2006).
3. D. Kim, D.-Y. Park, B. Y. Yoo, P. T. A. Sumodjo, and N. V. Myung, *Electrochim. Acta*, **48**, 819 (2003).
4. D.-Y. Park, K. S. Park, J. M. Ko, D.-H. Cho, S. H. Lim, W. Y. Kim, B. Y. Yoo, and N. V. Myung, *J. Electrochem. Soc.*, **153**, C814 (2006).
5. V. Radmilović, K. I. Popov, M. G. Pavlović, A. Dimitrov, and S. Hadži Jordanov, *J. Solid State Electrochem.*, **2**, 162 (1998).
6. K. I. Popov, N. V. Krstajić, and M. I. Cekerevac, in *Modern Aspects of Electrochemistry*, Vol. 30, R. E. White, B. E. Conway, and J. O'M. Bockris, Editors, p. 261, Plenum, New York (1996).
7. H. C. Shin, J. Dong, and M. Liu, *Adv. Mater.*, **15**, 1610 (2003).
8. K. I. Popov, S. S. Djokić, and B. N. Grgur, *Fundamental Aspects of Electrometallurgy*, Kluwer Academic, New York (2002).
9. N. D. Nikolić, Lj. J. Pavlović, M. G. Pavlović, and K. I. Popov, *Electrochim. Acta*, **52**, 8096 (2007).
10. H. Vogt, *J. Appl. Electrochem.*, **25**, 764 (1995).
11. H. Vogt, *Electrochim. Acta*, **50**, 2073 (2005).
12. D. R. Gabe, *J. Appl. Electrochem.*, **27**, 908 (1997).
13. M. P. Marčeta Kaninski, V. M. Nikolić, G. S. Tasić, and Z. Lj. Rakočević, *Int. J. Hydrogen Energy*, **34**, 703 (2009).
14. L. D. Rafailović, H. P. Karnthaler, T. Trišović, and D. M. Minić, *Mater. Chem. Phys.*, **120**, 409 (2010).
15. H. Rietveld, *J. Appl. Crystallogr.*, **2**, 65 (1969).
16. Bruker AXS, *TOPAS V3: General Profile and Structure Analysis Software for Powder Diffraction Data*, Bruker AXS, Karlsruhe (2005).
17. T. B. Massalski, *Binary Alloy Phase Diagrams*, Vol. 2, p. 1215, ASM International, Materials Park, OH (1991).
18. J. Ebothé and S. Vilain, *J. Phys. D: Appl. Phys.*, **32**, 2342 (1999).

Materials Chemistry and Physics 120 (2010) 409–416

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Microstructure and mechanical properties of disperse Ni–Co alloys electrodeposited on Cu substrates

L.D. Rafailović[a], H.P. Karnthaler[a], T. Trišović[b], D.M. Minić[c,*]

[a] *University of Vienna, Physics of Nanostructured Materials, Faculty of Physics, Boltzmanngasse 5, 1090 Vienna, Austria*
[b] *Institute of Technical Sciences of Serbian Academy of Science and Arts, Knez Mihailova 35, Belgrade, Serbia*
[c] *University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12, 11000, Belgrade, Serbia*

ARTICLE INFO

Article history:
Received 12 April 2009
Received in revised form
10 November 2009
Accepted 19 November 2009

Keywords:
Alloys
Nanostructured materials
X-ray scattering
Microstructure

ABSTRACT

The nickel and cobalt disperse alloy deposits of five different compositions were obtained by electrodeposition on Cu substrates in the galvanostatic regime from an ammonium sulfate-chloride solution. The effect of cathodic current density and Ni^{2+}/Co^{2+} ions concentration ratio in the electrolyte on the composition, microstructure, morphology and mechanical properties of Ni–Co alloys were investigated. Conditions for formation of nanostrustured disperse deposits and surface roughness was determined by 3D SEM reconstruction of the specimen surface. It was established that formation of the disperse deposits with highly developed structures is favored from bath with equal Ni^{2+}/Co^{2+} ions concentration ratio in the electrolyte. Cathodic polarization diagrams determined for all investigated alloys have shown shift of the cathodic potential for alloy deposition to the more negative values with increasing Ni^{2+}/Co^{2+} ions concentration ratio in the electrolyte. An increase of in the cobalt content in the alloy was observed with decreasing the current density and increasing of the Co^{2+} ions concentration ratio in the bath. X-ray analyses of nanocrystalline Ni–Co deposits show formation of a single phase face-centered cubic (FCC), a single phase hexagonal-close packed (HCP) and mixture of FCC solid solutions and HCP phase depending on the current density applied and electrolyte composition. The increase of HCP phase content in the nanocrystalline deposits appears as a result of both, the increase in Co^{2+} ions concentration in the bath and decrease of deposition current density. The mechanical properties of nanocrystalline deposits have shown increase of the hardness with increasing Ni content in the alloy. The cross-section of the samples electrodeposited on Cu substrates from electrolytes with equal ion metal concentration at lower current density values revealed the beginning of a dendrite structure formation.

1. Introduction

The recent interest in the electrodeposition of iron-group metals (Ni, Co and Fe) and their alloys is due to their unique magnetic and thermophysical properties [1,2]. Electrodeposition is a process which is capable for depositing nanocrystalline metals and alloys [3] onto recessed and non-uniform surfaces, and therefore has found a role in microelectromechanical systems (MEMS) [2,4–7]. The hardness and strength of the electrolytic deposits are better than alloys prepared by conventional metallurgical processes [2]. One of the most important aspects of electrodeposition process is possibility for production of nanocrystalline materials which exhibit unique properties compared to the microcrystalline counterparts [3].

A metal powder represents a loose deposit which can spontaneously fall off from the electrode or can be removed by tapping or by other similar way [8–10]. The electrodeposition of the powders from the solutions, established by the work of Calusaru [11] possesses significant advantages over other methods for synthesis of nanocrystalline materials [3]. This method usually yields products of requested chemical composition and high purity, which can be well pressed and sintered [12–14]. The effect of operating conditions, electrolyte composition, temperature and pH on the Ni–Co composition and properties of obtained deposits are widely investigated [15–18]. On the other hand, electrodeposition at very high current density and high overpotential is only investigated for the case of the obtaining of powders [19–21].

However, electrochemical synthesis of disperse deposits on the substrate is insufficiently investigated [8]. Investigations of such Cu deposits formed at high current densities characterized by open and very porous structures with extremely high surface areas were initiated recently [22]. It has been stated that the open and porous structures of copper deposits obtained at high current densities were ideally suited for use as electrodes in electrochemical devices such as fuel cells, batteries and chemical sensors [22], while the extremely high surface area is relevant for evaluating

---

[*] Corresponding author.
E-mail addresses: dminic@ffh.bg.ac.rs, dminic2003@yahoo.com (D.M. Minić).

0254-0584/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2009.11.029

some electrochemical reactions [23]. Surface microstructure plays a crucial role in application such as a magnetic storage, printing devices and all other similar technological procedures, but correlation between surface morphology and roughness structure with deposition parameters is still open topic [24]. Three-dimensional (3D) characterization seems more adapted for applied research. Therefore, the aim of this study is investigation of the influence of deposition current density on microstructure of disperse Ni–Co deposits and correlation between electrolysis conditions for formation of such rough deposits on the substrates with morphology, surface roughness and mechanical properties.

2. Experimental

The deposits were obtained in an open glass electrochemical cell with a volume of 1 dm^3, thermostatically controlled at a temperature of 298 K. A Ti-plate covered with RuO_2/TiO_2 (10 cm^2 geometric area), placed close and parallel to the Cu plate, was used as an anode (DSA). The solutions were made from analytical grade chemicals and triple distilled water. The alloys were electrodeposited from mixed ammonium sulfate-chloride solutions of different Ni^{2+}/Co^{2+} ions concentration ratios of 0.25, 0.5, 1, 2 and 4 (total concentration of $NiSO_4 + CoSO_4$ was 0.12 mol $dm^{-3)}$ using 0.5 mol dm^{-3} NH_4Cl and 3.5 mol dm^{-3} NH_4OH as a buffering agent and a supporting electrolyte at pH 10. The electrodeposition was performed with a constant current regime ranging from 65 to 400 mA cm^{-2}. The deposition time was adjusted to the same quantity of electricity (43 mA cm^{-2}).

Polarization diagrams were recorded with the three-compartment standard electrochemical cell at a temperature of 298 K. The platinum foil counter electrode and the reference–saturated calomel electrode (SCE) were placed at separate compartments, connected to the working electrode by a Luggin capillary positioned at a distance of 0.2 cm from the working electrode surface. The working electrode was a copper electrode rod (d = 0.4 cm). Before each experiment the working electrode surface was polished using 0.05 μm alumina impregnated polishing cloths. The Ni–Co alloys were electrodeposited with same quantity of electricity (43 mAh cm^{-2}).

Polarization measurements were performed by a computer controlled electrochemical system (PAR M 273A) using the corrosion software (PAR M352/252, version 2.01) with a sweep rate of 1 mV s^{-1}. To obtain polarization curves corrected for the IR drop, current interrupt technique was used with the time of current interruption being 0.5 s.

The current efficiency of alloy deposits was determined at different current densities by measuring the mass of the deposit on the copper cathode which was used as a working electrode.

Surface morphology was examined using an XL 30 ESEM-FEG (environmental scanning electron microscope with field emission gun, FEI Company, NL). The 3D reconstruction of the specimen surface was characterized by SEM using MeX software from Alicona (A). It enables to carry out a 3D analysis directly from the digital images yielding profile and roughness measurements and also area analysis as well as volumetric measurements. An alloy composition analysis was performed by ESEM using the energy dispersive X-ray spectrometry (EDX) software Genesis (USA). X-ray powder diffraction (XRD) analysis was carried out using a MPD diffractometer (Philips, NL) with CuKα radiation (40 kV/30 mA). Step scan mode was utilized with 0.03° in 2θ per 1.15 s step.

The micro-hardness of the deposits was determined using a Vickers microhardness indenter with a load of 50 μN. Cross-sections of the Ni–Co samples deposited on the Cu substrates were performed for indentation measurements. The final value quoted for the hardness of the deposits was the average of 10 measurements. Optical micrographs of the sample cross-sections were obtained by optical microscope Olympus SZX 12 (JP).

3. Results and discussion

3.1. Current efficiency

Fig. 1 shows the polarization curves for different compositions of the electrolyte performed on a Cu cathode. The shape and position of the polarization curves strongly depend on the electrolyte composition. A decrease in the content of Co^{2+} as well as an increase in the content of Ni^{2+} shifts the position of the corresponding polarization curves towards negative values of the potentials corresponding to the potential of the Ni/Ni^{2+} deposition of pure nickel.

Metal and alloy deposition of the iron group from aqueous solutions, is accompanied by a concurrent hydrogen evolution reaction [25] which significantly affects the shape of the polarization curve and the morphology of the obtained deposits. According to the polarization diagrams, corrected for IR drop (which is indispensable because the galvanostatic deposition for production of disperse deposits is performed at high current densities using small ion metal concentration), the Ni–Co electrodeposition at overpotentials higher than – 1.2 V is characterized by sharp increase of the current density where disperse deposits with high developed structures are formed. Formation of the disperse deposits is dependant on hydrogen evolution since at current density higher than 200 mA cm^{-2}, the current efficiency is less than 50% (Fig. 2) for all investigated electrolyte compositions. Hydrogen provides some additional stirring effect and enhances formation of disperse deposits with more developed structures.

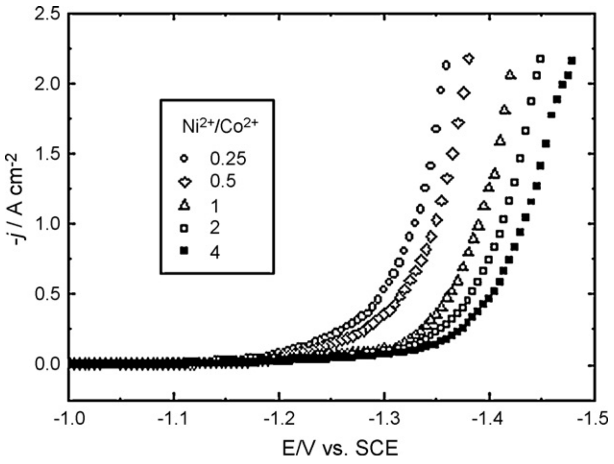


Fig. 1. Polarization curves for the cathodic process of Ni–Co deposition on copper cathode for different composition of the electrolyte: (○) Ni^{2+}/Co^{2+} = 0.25; (◊) Ni^{2+}/Co^{2+} = 0.5; (△) Ni^{2+}/Co^{2+} = 1, (□) Ni^{2+}/Co^{2+} = 2 and (■) Ni^{2+}/Co^{2+} = 4, corrected for IR drop. Scan rate 1 mV $^{-1}$.

The hydrogen evolution during the deposition of the alloys diminishes the current efficiency, depending on the electrolyte composition as well as on the current density. These results are in agreement with polarization measurements where alloys with less nickel content have lower hydrogen overpotential and consequently a lower current efficiency. In the current density range, where the disperse deposits were obtained, the current efficiency decreases with the increase of the current density and with the decrease of the Ni^{2+} concentration in the electrolyte.

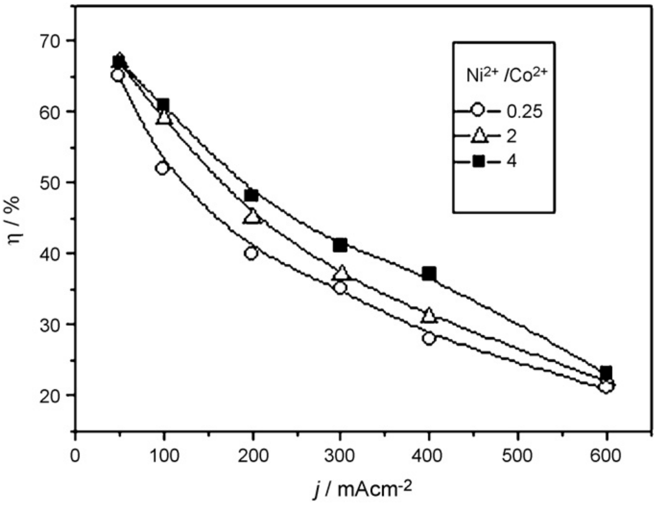


Fig. 2. Current efficiency of the Ni–Co deposition process for the different current densities and compositions of the electrolyte: (○) Ni^{2+}/Co^{2+} = 0.25; (△) Ni^{2+}/Co^{2+} = 1 and (■) Ni^{2+}/Co^{2+} = 4.

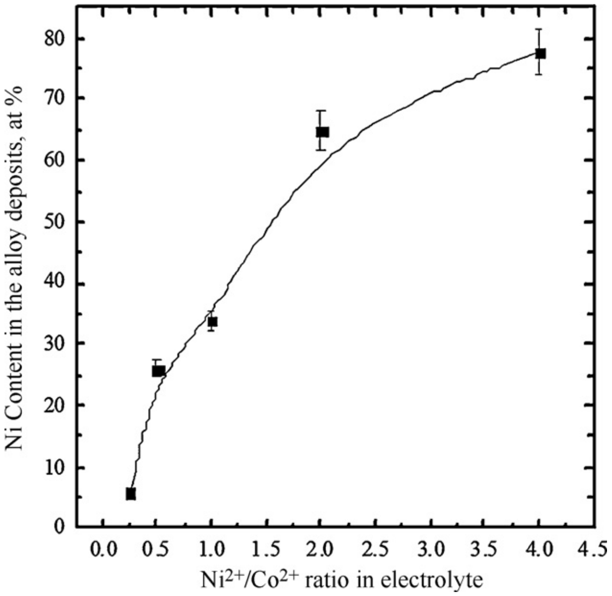


Fig. 3. Dependence of the alloy composition on Ni^{2+}/Co^{2+} ratio in the electrolyte at a current density 65 mA cm^{-2}.

3.2. *Composition of the Ni–Co alloys*

In order to define the influence of the electrolyte concentration on composition of the obtained disperse Ni–Co deposits, the electrodeposition from five electrolytes of different compositions at current density of 65 mA cm^{-2} was performed. The chemical composition of the alloys galvanostatically deposited was determined for alloy samples as an average of 3 measurements with surfaces of 10 μm^2 with an error of ±2%. Afterwards, current densities of 220 and 400 mA cm^{-2} were selected to define the effect of the current density on deposit composition for a chosen electrolyte composition.

According to the EDX analysis, the electrolyte composition (Ni^{2+}/Co^{2+} ions ratio) as well as the current density, affects the composition of the electrodeposited alloys remarkably, Figs. 3 and 4.

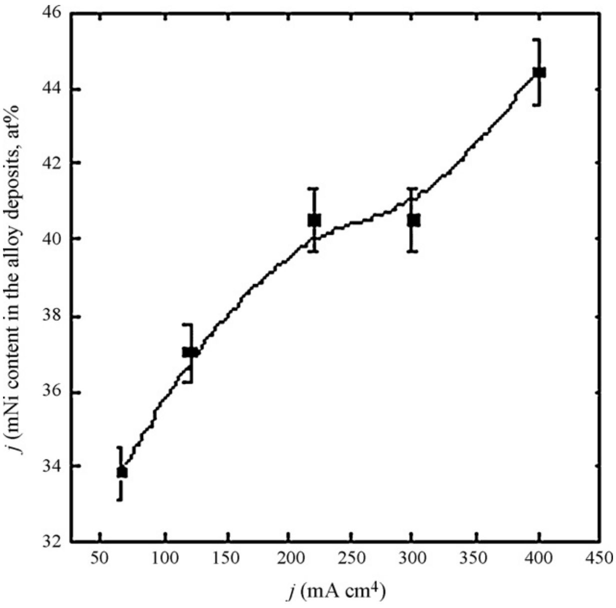


Fig. 4. Dependence of the alloy composition on current density from an electrolyte with concentration ratio $Ni^{2+}/Co^{2+} = 1$.

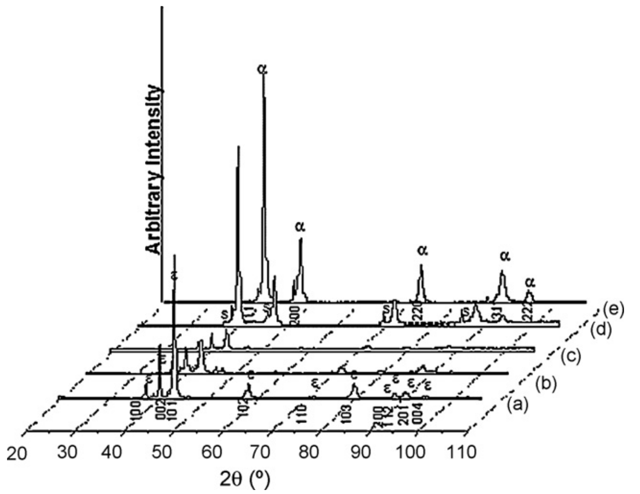


Fig. 5. X-ray diffraction patterns of alloys deposited from the electrolyte with different Ni^{2+}/Co^{2+} concentration ratio: (a) 0.25, (b) 0.5, (c) 1, (d) 2 and e) 4 at a current density 65 mA cm^{-2} (α-reflections attributed to the α-Ni; ε-reflections attributed to the ε-Co; S-reflection attributed to the Cu substrate).

However, the percentage of Ni in the deposit, especially for the deposit obtained from the electrolyte with $[Ni^{2+}]/[Co^{2+}] = 0.25$ was lower than in the electrolyte solution, Fig. 3. This indicates that the electrochemical alloying leads to an increase in the reaction rate of Co at relatively low current density of $j = 65$ mA cm^{-2} resulting in the higher content of cobalt in the alloy than in the electrolyte. Such behavior is in accordance with the term "anomalous co-deposition" as introduced by Brenner [25] which refers to the preferential deposition of the less noble metal, i.e. Co. Besides, with the increase of the Ni^{2+} concentration in the electrolyte, the Ni content in the alloys almost reaches its content in the electrolyte.

The difference between the electrolyte composition and the deposit composition (Fig. 4) is much less pronounced at high current density, i.e. $j = 400$ mA cm^{-2}. The composition of the obtained deposit is almost similar to the concentration of the metal ions in the electrolyte. In this case, the composition of the deposits is dependent on the current density, indicating that an increase of the current density is accompanied by a decrease of the cobalt content in the deposit. An increase of the current density leads to an increase of the overpotential which is combined by an increase of the activation of the electrode reaction. This results in an increase of the nickel content in the deposits.

3.3. *Microstructure of deposits-Influence of chemical composition of the electrolyte on microstructure*

Fig. 5 shows a series of XRD patterns for all five alloys electrodeposited from different bath compositions at a selected current density of $j = 65$ mA cm^{-2} with same quantity of electricity and with an average sample thickness of (25 ± 5) μm.

The X-ray analysis of the deposits shows the presence of solid solutions of Ni and Co with a structure which changes progressively with the change of their chemical composition depending on the used electrolyte. For the lowest content of Ni, a single phase deposit involves the hexagonal close-packed (HCP) phase also known as ε-phase (Fig. 5a). With the increase of nickel content in the deposit ranging to 30–40 at%, the mixture of face centered cubic (FCC) also known as α-phase and the HCP phase was found (Fig. 5b–d). With the further increase of Ni content in Ni deposit, only a single FCC phase is observed (Fig. 5e). The noticed diffraction peaks of Cu with low intensity belong to the substrate material. Deposits rich in Co and deposits rich in Ni (Fig. 5a and e) exhibit cell volumes comparable to the theoretical values of Co (22.1 Å^3) and Ni (43.8 Å^3), cf.

Table 1
Phase composition, grain size and cell parameters of the electrodeposited alloys.

Ni^{2+}/Co^{2+}/current density	Crystal structure/concentration (%)	Grain size (nm)	*a* (Å)	*c* (Å)	Cell volume (Å^3)
$Ni^{2+}/Co^{2+} = 0.25$/ 65 mA cm^{-2}	HCP/100	20	2.506	4.069	22.126
$Ni^{2+}/Co^{2+} = 0.5$ 65 mA cm^{-2}	FCC/27 HCP/73	11/9	3.533/2.505	4.076	44.114/22.153
$Ni^{2+}/Co^{2+} = 1$/ 65 mA cm^{-2}	FCC/28 HCP/72	19/15	3.529/2.505	4.072	43.955/22.127
$Ni^{2+}/Co^{2+} = 1$/ 220 mA cm^{-2}	FCC/71 HCP/21 amorphous phase/8	13/11	3.530/2.499	4.077	43.971/22.043
$Ni^{2+}/Co^{2+} = 1$/ 400 mA cm^{-2}	FCC/82 HCP/3 amorphous phase/15	11/10	3.533/2.495	4.100	44.096/22.100
$Ni^{2+}/Co^{2+} = 2$ 65 mA cm^{-2}	FCC/87 HCP/13	14/5	3.528/2.480	4.057	43.901/21.610
$Ni^{2+}/Co^{2+} = 0.25$/ 65 mA cm^{-2}	FCC/100	13	3.526		43.833

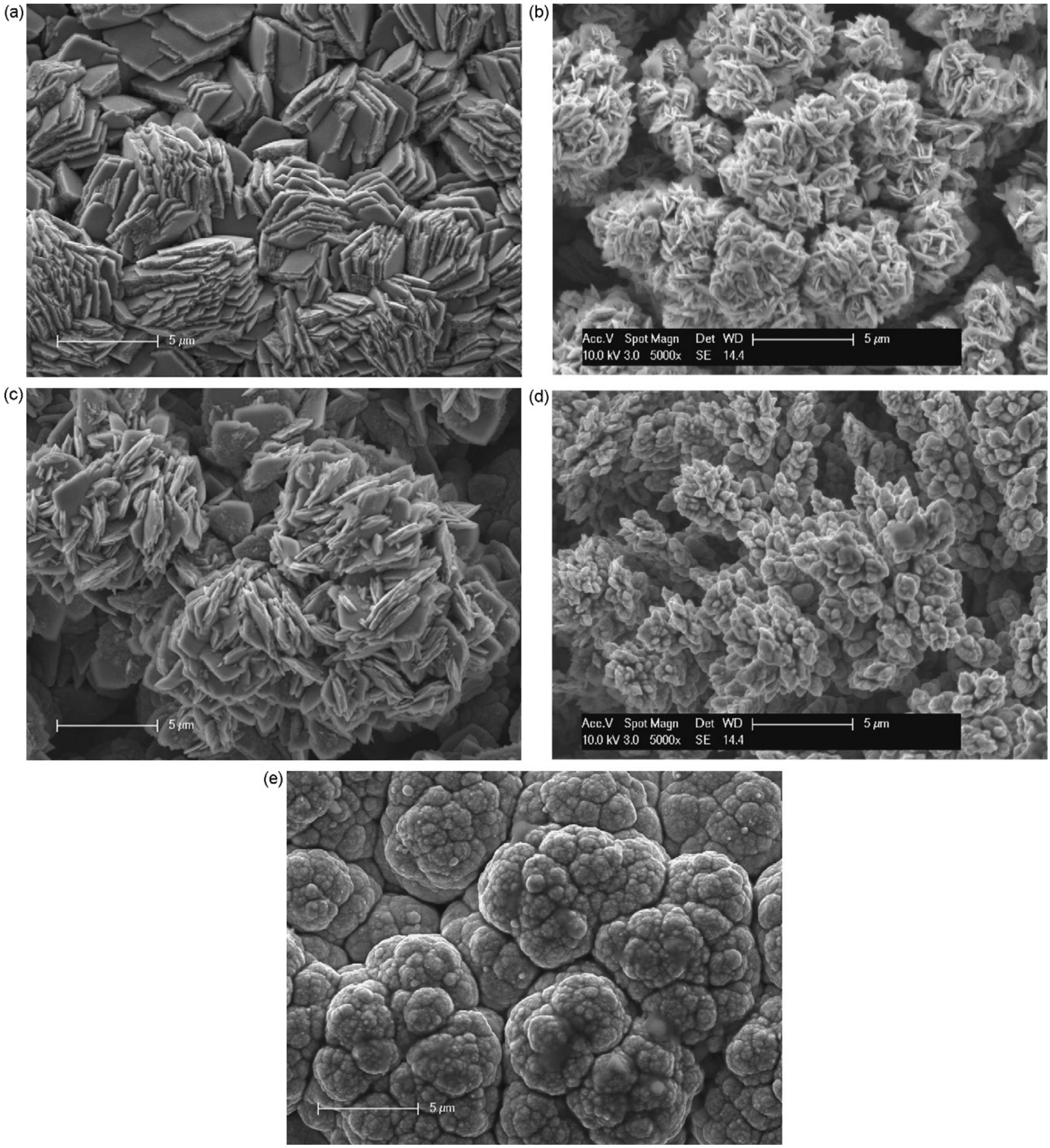


Fig. 6. SEM micrographs of Ni–Co deposits obtained at a current density 65 mA cm^{-2} from an electrolyte with different Ni^{2+}/Co^{2+} concentration ratio: (a) 0.25, (b) 0.5, (c) 1, (d) 2 and (e) 4.

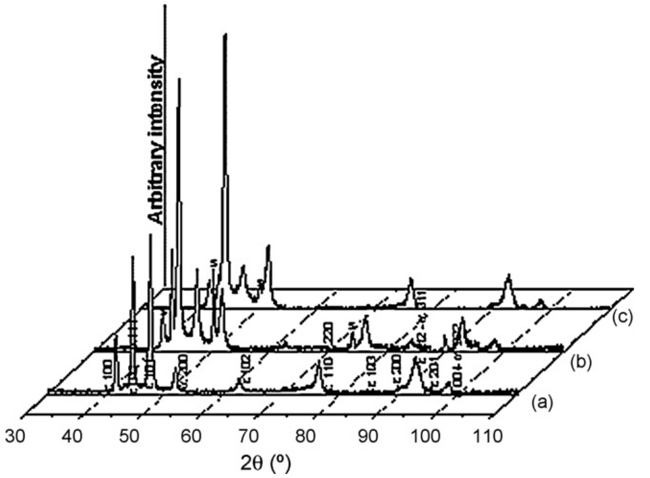


Fig. 7. X-ray diffraction patterns of alloys deposited from an electrolyte with concentration ratio $Ni^{2+}/Co^{2+} = 1$ at different current densities: (a) 65 mA cm^{-2}, (b) 220 mA cm^{-2} and (c) 400 mA cm^{-2} (α-reflections attributed to the α-Ni; ε-reflections attributed to the ε-Co; S-reflection attributed to the Cu-substrate).

Table 1.

The morphology of all Ni–Co deposits strongly depended on the chemical composition of the alloy deposit, i.e. the chemical composition of the electrolyte, Fig. 6. For the chosen current density of 65 mA cm^{-2} particles with a size varying from 5 to about 50 μm composed of fine nanosized crystallites of different morphology were obtained.

The morphology of the alloy deposited from electrolyte with the highest concentration of [Co^{2+}] ions in the electrolyte, at current density of 65 mA cm^{-2} is shown in Fig. 6a. This deposit possesses the platelet structure.

For the concentration ratio [Ni^{2+}]/[Co^{2+}] = 1 in the electrolyte, the morphology of the deposit is slightly changed and consists of cauliflower particles exhibiting a surface morphology based on preferred oriented platelets (Fig. 6c). Fig. 6b and d show enhanced dendritic growth with more disperse deposits obtained from the baths with the concentration ratio [Ni^{2+}]/[Co^{2+}] = 0.5 and 2, respectively. At one and the same current density of 65 mA cm^{-2}, more developed structures are formed leading an increase of the mean surface roughness. Finally, the particles deposited from the electrolyte with the highest content of Ni show cauliflower structure, Fig. 6e. The morphology of the deposits is similar to the morphology of the pure Ni obtained from the Wath's bath without addition of a surfactant substance [8,20].

The SEM micrographs show that the surface morphology of the deposit is determined by the nature of the electrochemically active ions or complexes and the kinetics of the electrocrystallization process.

3.4. Phase analysis of deposits-Influence of current density on microstructure

A detailed Rietveld's analysis revealed that the phase composition of the deposited Ni–Co solid solutions depends on the composition of the electrolyte bath as well as on the applied current density (Fig. 7). Rietveld's refinement procedure [26] is able to simulate the XRD pattern from given starting parameters. The purpose of this simulation is therefore to refine individual parameters, e.g. phase content, grain size, and crystal lattice parameters, to obtain a good fit. For this purpose Rietveld's refinement program TOPAS V3.0 (Bruker AXS GmbH, Germany) was used [27]. The quality of the refinement progress was controlled by monitoring the fit parameter R_{wp}, the goodness of fit (GOF), and the Durbin–Watson factor.

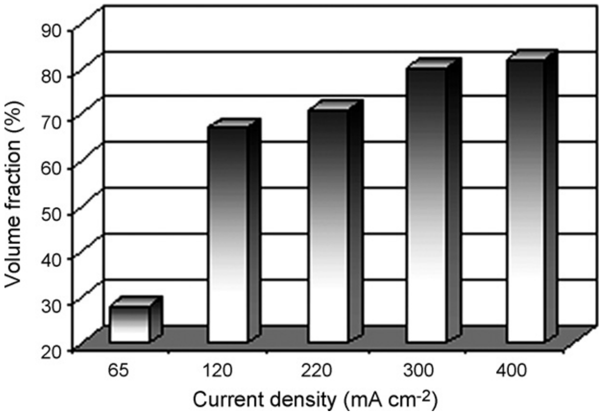


Fig. 8. Evolution of the FCC phase content in deposits as a function of current density from an electrolyte with concentration ratio $Ni^{2+}/Co^{2+} = 1$.

The deposits obtained from an electrolyte with a equal ion metal concentration ratio, [Ni^{2+}]/[Co^{2+}] = 1, have shown the formation of a mixture of both phases, HCP and FCC. The formation of solid solutions is a consequence of the mutual miscibility of Ni and Co in the range of concentration in the obtained deposits (Table 1) which is in accordance to the phase diagram [28]. The decrease of the current density results in pronounced crystallization and an increase of the size of crystallites as well as a higher HCP content in the alloys. Evolution of the FCC phase content from the same bath was achieved by the increase of current density (Fig. 8).

If the kinetics of the deposition process is fast, a disperse deposit can be obtained at low driving force, while a much larger driving force is needed for kinetically slow processes such as Ni and Co deposition [8] resulting in an electrodeposition process far from equilibrium conditions, i.e. at high overpotentials, and in the formation of the FCC phase. At low overpotentials, a higher amount of Co as the HCP phase is formed.

3.5. Grain size of Ni–Co alloy deposits

The electrolyte composition and the current density have a great effect on the grain size of the deposits. Average grain sizes were calculated from the peak broadening from XRD according to the Scherrer equation with the Rietveld refinement method [26]. Obtained alloy deposits were composed of fine nanosized crystallites (cf. Table 1).

The alloy electrodeposited at selected current density of 65 mA cm^{-2} from the electrolyte with the ratio [Ni^{2+}]/[Co^{2+}] = 0.25 (Fig. 5a), contains the ε-Co phase with hexagonal close-packed lattice and with an average grain size of 20 ± 2 nm. The average grain size in the deposits consisting single FCC phase was 13 ± 2 nm (Fig. 5e). In general, deposits with finer grain sizes are obtained with increasing [Ni^{2+}] concentrations in the electrolyte. With increasing Co content in the alloys (Table 1) the average size of crystallite increases ranging from 13 to 19 nm for the FCC phase and from 15 to 20 nm for the HCP phase. The mixture of two phases leads to a further grain size refinement of deposits.

A reduction of the grain size was also achieved by an increase of the current density. Increasing the current density leads to the increase of the overpotential, and therefore increases the nucleus formation probability resulting in smaller critical radii and the number of atoms constituting the nucleus. Hence, the increase of current density decreases the grain size of the Ni–Co deposits (Table 1). The formation of electrochemical deposits from electrolytes with a higher [Ni^{2+}]/[Co^{2+}] ratio is accompanied by higher overpotential values, therefore deposit with finer grains is formed

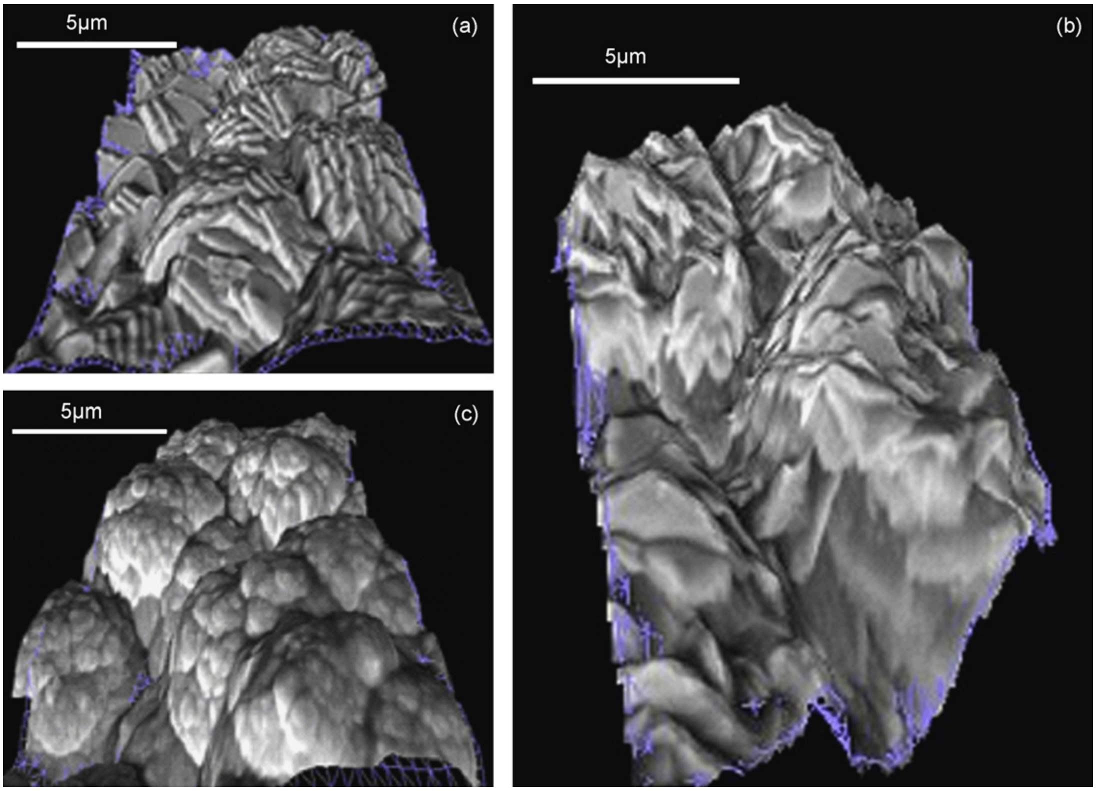


Fig. 9. 3D SEM reconstruction of the surfaces of Ni–Co deposits obtained at a current density 65 mA cm^{-2} from the electrolyte with different Ni^{2+}/Co^{2+} concentration ratios: (a) 0.25; (b) 1 and (c) 4.

from a bath containing a higher Ni^{2+} ions concentration (Table 1.). For the deposition of more disperse deposits composed from fine nanosized crystallites, the use of the overpotentials higher than 1.3 V are requested, specifically in the case of the deposits obtained from electrolyte with concentration ratio [Ni^{2+}]/[Co^{2+}] > 0.5.

3.6. Surface roughness of Ni–Co alloy deposits

The 3D dataset was deduced from two stereoscopic images obtained by tilting the sample stage in the ESEM at the eucentric point with an angle of 5°, Fig. 9a–c. The calculated roughness parameters are shown in Table 2.

The concentration ratios [Ni^{2+}]/[Co^{2+}] = 0.25 and 4 corresponding to a single-phase systems, led to a surface with similar mean roughness values in spite of different morphology, (Fig. 6a and e), respectively. In the case of a ions concentration [Ni^{2+}]/[Co^{2+}] = 1, involving more than one phase, the *Ra* values are almost 3 times higher, and the active surface increases in comparison to the specimens with ratios of 0.25 and 4. An increase in the current density results in a decrease in the mean roughness (Table 2), since at higher current densities the amount of crystal nuclei on the surface is enhanced. The larger the nucleation rate, the more homogenous is the grain size distribution leading to the formation of smoother deposits (see also, Fig. 6a and e). 3D SEM reconstruction experimental results confirmed the beginning of disperse deposits formation in galvanostatic deposition using current density, $j \geq 65$ mA cm^{-2}.

3.7. Mechanical properties of Ni–Co deposits

Nanoindentation test were performed to investigate the mechanical properties of the deposited samples. A load of 50 μN was applied on the cross-section of the samples (deposits on copper substrate). The low applied load is needed to make penetration depths small enough to avoid the influence of the substrate on the hardness measurements. The nanoindentation test demonstrated that nanocrystalline deposits have a higher hardness with an increase of the Ni content in the sample (Fig. 10). The hardness of the Ni–Co alloys deposited from the same bath composition but at different current densities shows a reduction of the hardness, not as significant as in the case of the hardness measured on the samples prepared from the different bath compositions.

Table 2
Roughness parameters of alloys deposited from electrolytes of different Ni^{2+}/Co^{2+} concentration ratio and at different current densities.

Ni^{2+}/Co^{2+} concentration ratio	Current densities (mA cm^{-2})	*Ra* (μm)	*Rz* (μm)	RS
0.25	65	0.7	4.7	1.64
0.5	65	1.3	5.2	1.34
1	65	3.0	13.1	1.98
1	220	1.1	5.2	1.38
1	400	1.0	6.5	1.62
2	65	2.1	9.2	1.37
4	65	1.0	4.7	1.64

Ra, mean roughness, *Rz*, the difference between the highest and the lowest point in the picture of defined scan, RS, active surface, the ratio of the real surface including topography to a projected surface of the measurements (a square with dimensions of 23 μm × 15 μm).

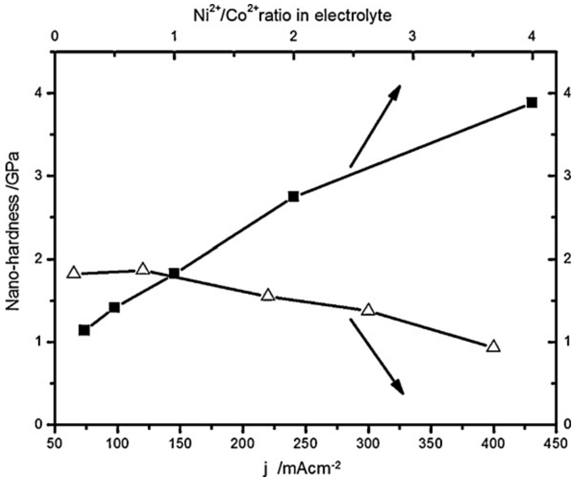


Fig. 10. Hardness of Ni–Co deposits as a function of current density and electrolyte composition: (△) concentration ratio $Ni^{2+}/Co^{2+} = 1$ at different current densities, (■) different concentration ratio Ni^{2+}/Co^{2+} at a current density 65 mA cm^{-2}.

In contrast to some authors [29], the hardness is increased with an increase of the Ni content in the deposits. According to the optical micrographs of the cross-sections of the deposits obtained on the Cu substrate presented in Fig. 11, two possible reasons can cause such behavior. One is the grain size and the second is porosity inside the deposit with high Co content (Fig. 11a). The release of hydrogen in the layer surrounding the electrode also affects the properties of the obtained deposits, causing the formation of craters in the deposit (Fig. 11c). The deposit obtained form the electrolyte with the highest concentration of Ni^{2+} are compact (Fig. 11c), while the deposits obtained at the same current density from the bath with the concentration ratio $Ni^{2+}/Co^{2+} = 1$ show a dendritic structure (Fig. 11b). It should be indicated that when the grain size is smaller than 10 nm, the grain refinement may cause softening of the nanocrystalline metals. In these measurements, differences in the grain size have not been so significant, but they still affect the large difference in the hardness value (Fig. 12).

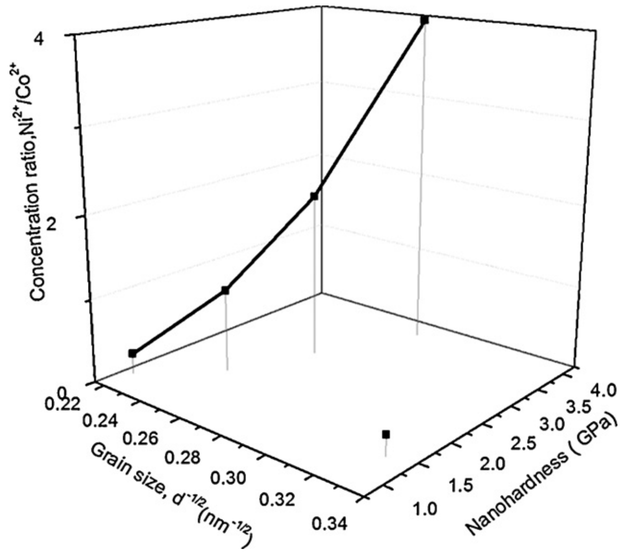


Fig. 12. Effect of the grain size on nanohardness of Ni–Co deposits performed from an electrolyte with different Ni^{2+}/Co^{2+} concentration ratio (*d*, average value of grains).

The hardness measurements performed on the Ni–Co deposits obtained from an electrolyte with a concentration ratio $[Ni^{2+}]/[Co^{2+}] = 1$ at different current densities have shown a reduction of hardness. The explanation can be attributed to the fact that at higher current densities a more disperse deposit with porous structure and very high surface area is formed. Nanohardness of deposits decreases with increasing current density since evolution of the dendritic structure occurred during deposition at higher current densities.

The grain size is the main parameter influencing the grain boundary hardening. Based on the Hall–Petch relationship, nanocrystalline material is expected to exhibit higher strength than their microcrystalline counterparts [30]. In the present study, the nanograin size did not affect the softening of the deposits formed from electrolytes with equal ion compositions, $Ni^{2+}/Co^{2+} = 1$ at different current densities, considering grain sizes of the deposits were in the range of 10 nm. Although the more dendritic deposits performed at higher current densities, are characterized by a reduce

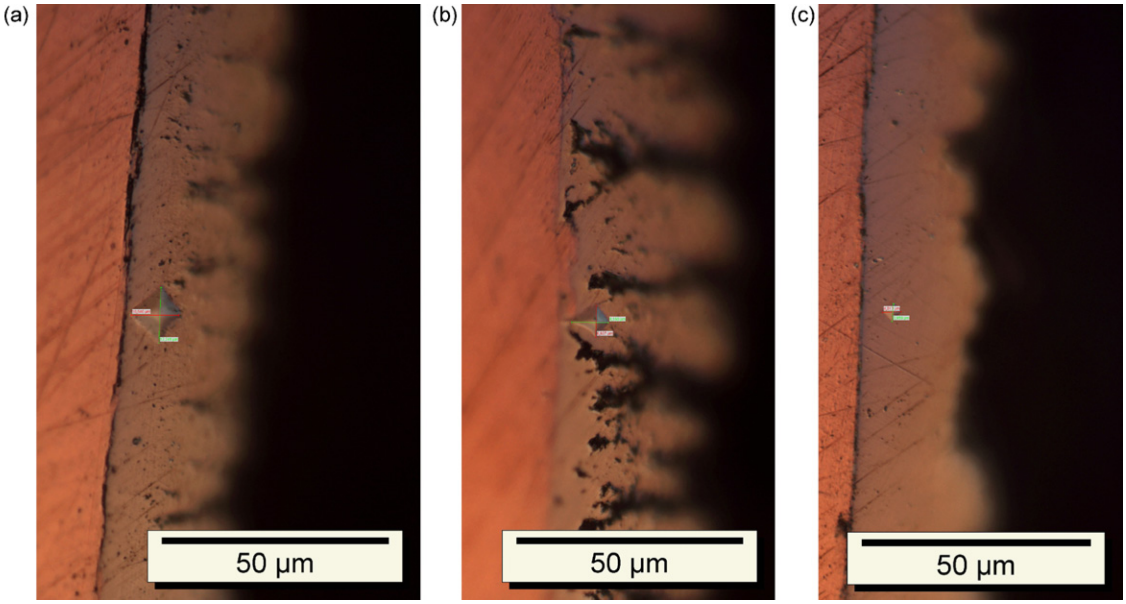


Fig. 11. Cross-section of Ni–Co deposits obtained on copper substrate from an electrolyte with concentration ratio Ni^{2+}/Co^{2+}: (a) 0.25; (b) 1 and (c) 4 at a current density 65 mA cm^{-2}.

grain size, the formation of the deposits with a very disperse dendritic structure has a decisive influence on the measurements.

4. Conclusions

The microstructure as well as the morphology of the Ni–Co alloy deposits electrochemically obtained from an ammonium sulfate-chloride solution depends on the deposition current density and the bath composition. With a decrease in the deposition current density the volume fraction of the HCP phase in the deposits increases accompanied by the crystal grain growth. The increase of HCP phase content in the nanocrystalline deposits appears as a result of both an increase in the Co^{2+} ions concentration in the bath and a decrease of the deposition current density. The increase of the current density and the decrease of the Co^{2+} ions concentration in the bath results in finer grain deposits. Surface morphology and mean roughness of the deposits depend on the concentration ratio in electrolyte; in the case of equal ions concentration of Ni^{2+}/Co^{2+} in the electrolyte, the mean roughness of the deposit is the highest. It is possible to achieve variety of microstructural properties by choosing the current density or the electrolyte composition appropriately.

Acknowledgments

This research was supported by the research project “Bulk Nanostructured Materials” within the research focus “Material Science” of the University of Vienna. The investigation was partially supported by the Ministry of Science and Environmental Protection of Serbia, under Project 142025 and within the K plus programme at CEST by the Austrian Research Promotion Agency (FFG) and the government of Lower Austria. L.R is grateful for the support by the I.K. “Experimental Materials Science – Nanostructured Materials”, a college for PhD students at the University of Vienna.

References

[1] D. Landolt, J. Electroanal. Chem. 149 (2002) S9.
[2] R. Orinakova, A. Turonova, D. Kladekova, M. Galova, R.M. Smith, J. Appl. Electochem. 36 (2006) 957.
[3] M.A. Meyers, A. Mishra, D.J. Benson, Prog. Mater. Sci. 51 (2006) 427.
[4] H. Li, F. Ebrahimi, Mater Sci. Eng. A 347 (2003) 93.
[5] N.V. Myung, K. Nobe, J. Electrochem. Soc. 148 (2001) 136.
[6] D.-Y. Park, K.S. Park, J.M. Ko, D.-H. Cho, S.H. Lim, W.Y. Kim, B.Y. Yoo, N.V. Myung, J. Electrochem. Soc. 153 (2006) 814.
[7] N.V. Myung, D.-Y. Park, B.-Y. Yoo, P.T.A. Sumodjo, J. Magn. Magn. Mater. 265 (2003) 189.
[8] K.I. Popov, M.G. Pavlović, Electrodeposition of metal powders with controlled particle grain size and morphology”, in: R.E. White, B.E. Conway, J.O.’M. Bockris (Eds.), Modern Aspects of Electrochemistry, vol. 24, Plenum Press, New York, 1993 (Chapter 6).
[9] K.I. Popov, N.V. Krstajić, M.I. Čekerevac, The mechanism of formation of coarse and disperse electrodeposits, in: R.E. White, B.E. Conway, J.O’M. Bockris (Eds.), Modern Aspects of Electrochemistry, 30, Plenum Press, New York, 1996, p. 261.
[10] K.I. Popov, S.S. Djokić, B.N. Grgur, Fundamental Aspect of Electrometallurgy, Kluwer Academic press, New York, 2002.
[11] A. Calusaru, Electrodeposition of Powders from Solutions, Elsevier, New York, NY, 1979.
[12] A. Maričić, M. Spasojević, L. Rafailović, V. Milovanović, L. Ribić-Zelenović, Mat. Sci. Forum 45 (2004) 411.
[13] L. Ribić-Zelenović, L. Rafailović, M. Spasojević, A. Maričić, Sci. Sintering 38 (2006) 145.
[14] L. Ribić-Zelenović, L. Rafailović, M. Spasojević, A. Maričić, Phys. B Cond. Matter. 403 (2008) 2148.
[15] E. Gómez, S. Pané, X. Alcobe, E. Vallés, Electrochim. Acta 51 (2006) 5703.
[16] Sh. Hassani, K. Raeissi, M.A. Golozar, J. Appl. Electochem. 38 (2008) 689.
[17] A. Bai, Ch-Ch. Hu, Electrochim. Acta 47 (2002) 3447.
[18] C. Lupi, D. Pilone, Miner. Eng. 14 (2001) 1403.
[19] A. Bianco, G. Gusmano, R. Montanari, G. Montesperelli, E. Traversa, Thermochim. Acta 269/270 (1995) 117.
[20] V.D. Jović, B.M. Jović, M.G. Pavlović, Electrochim. Acta 51 (2006) 5468.
[21] V.D. Jović, B.M. Jović, V. Maksimović, M.G. Pavlović, Electrochim. Acta 52 (2007) 4254.
[22] H.C. Shin, J. Dong, M. Liu, Adv. Mat. 15 (2003) 1610.
[23] N.D. Nikolić, K.I. Popov, Lj.J. Pavlović, M.G. Pavlović, Sensors 7 (2007) 1.
[24] J. Eboth, S. Vilain, J. Phys. D: Appl. Phys. 32 (1999) 2342.
[25] A. Brenner, Electrodeposition of Alloys I, Academic Press, New York, 1963.
[26] H. Rietveld, J. Appl. Crystal 2 (1969) 65.
[27] Bruker AXS, TOPAS V3: General profile and structure analysis software for powder diffraction data, Karlsruhe, 2005.
[28] T.B. Massalski, Binary Alloy Phase Diagrams, vol. 2, ASM International, Materials Park, OH, USA, 1991, p. 1215.
[29] L. Wang, Y. Gao, Q. Xue, H. Liu, T. Xu, Appl. Surf. Sci. 242 (2005) 326.
[30] S. Tao, D.Y. Li, Nanotechnology 17 (2006) 65.

Materials Chemistry and Physics 125 (2011) 601–605

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte

M.M. Gvozdenović[a], B.Z. Jugović[b,*], T.Lj. Trišović[b], J.S. Stevanović[c], B.N. Grgur[a]

[a] Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia
[b] Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia
[c] ICTM, Institute of Electrochemistry, Njegoševa 12, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 25 September 2009
Received in revised form
21 September 2010
Accepted 14 October 2010

Keywords:
Polymers
Electrochemical techniques
Electrochemical properties

ABSTRACT

Polyaniline electrode (PANI) was formed electrochemically at graphite electrode. Electrochemical polymerization was performed at constant current density of 2.0 mA cm^{-2} from aqueous solution of 1.0 mol dm^{-3} HCl with addition of 0.25 mol dm^{-3} aniline monomer. Electrochemical characterization of the PANI electrode in chloride and chloride/citrate electrolyte was performed using cyclic voltammetry and galvanostatic measurement in order to study the influence of citrate ions on charge/discharge capability and cycling efficiency. It was observed that, for anodic potential 0.32 V, higher electrode capacity of PANI electrode in chloride/citrate electrolyte was obtained, comparing to chloride electrolyte, indicating positive effect of citrate ions on cycling characteristics. On the other hand, for higher anodic potential limit of 0.50 V, faster decrease of the electrode capacity in chloride/citrate electrolyte was observed. It was suggested that influence of both chloride and citrate anions had exhibited influence on electrochemical behavior of PANI electrode in citrate containing electrolyte.

1. Introduction

Due to their unique properties, such as: mechanical strength, electrical conductivity, corrosion stability, possibility of chemical and electrochemical synthesis, electroconducting polymers (ECP) are considered in wide area of practical application such as: microelectronics, optoelectronics, active corrosion protection, sensors, electromagnetic shielding, and electrochemical power sources [1–8].

ECP can be synthesized by both chemical and electrochemical oxidative polymerization. However, electrochemical synthesis is favorable permitting the control over the reaction rate. On the other hand, electrochemical polymerization occurs together with doping by organic or inorganic ions in a single step.

Among large number of ECP, polyaniline (PANI) is the most investigated as possible cathode material for aqueous based electrochemical power sources [5–13]. Systems consisted of PANI cathode combined to some electronegative metal (mainly zinc) anode, are likely to accomplish most of the three E criteria: energy (high energy content with respect to volume and weight), economics (low manufacturing and maintenance costs, long service life) and environment (toxic free, safety, low energy consumption, easy to recycle) denoted as the determining factors of an electrochemical power system success [14,15]. However, these systems still have not been commercialized due to several reasons, related to the fact that PANI is degradable at potentials higher than 0.5 V [16,17]. The main reason is connected to zinc dendrite and solid phase formation [6,8,18]. Zinc deposits, obtained from common chloride electrolytes, are almost completely in the form of dendrites, even if the deposition was performed using low current densities.

Fast growing zinc dendrites can lead to shortcutting with cathode affecting poor efficiency and cycling life. Addition of some organic anions to metal deposition baths, due to formation of metal complexes, can lead to both higher quality metal deposits and to suppression of dendrite deposits [19].

It was shown previously, that addition of citrate anions to common chloride electrolyte had led to formulation of smooth zinc deposits without irregularities even at electrode edges. On the other hand, corrosion rate in citrate containing electrolyte was lowered to one order of magnitude comparing to chloride electrolyte [20]. Hence, the aim of this work was to investigate electrochemical characteristic of PANI electrode as possible cathode material in citrate containing electrolyte to be used combined to zinc anode in rechargeable electrochemical power sources.

2. Experimental

PANI electrode was formed by electrochemical synthesis on graphite electrode ($S = 0.64$ cm^2) from aqueous solution of 1.0 mol dm^{-3} HCl (p.a. Merck) containing 0.25 mol dm^{-3} aniline (p.a. Aldrich), at constant current density of 2 mA cm^{-2}.

---

* Corresponding author. Tel.: +381 11 3303695; fax: +381 11 3303695.
E-mail address: branimir.jugovic@itn.sanu.ac.rs (B.Z. Jugović).

0254-0584/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2010.10.011

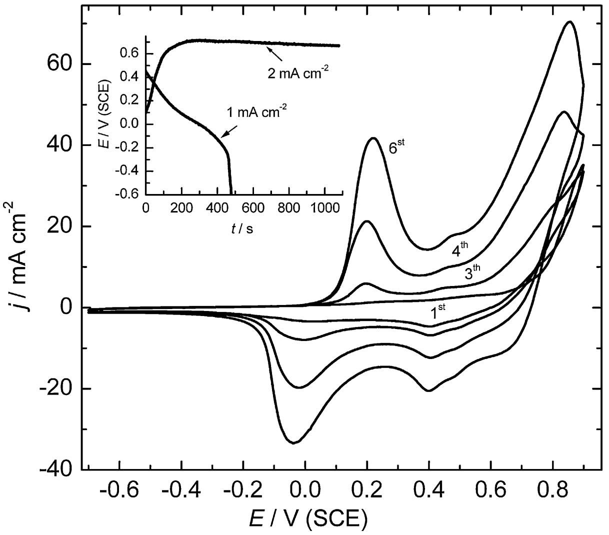


Fig. 1. Cyclic voltammogram of PANI electrode in 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline ($\nu = 20$ mV s^{-1}). Insert: Galvanostatic curve of electrochemical polymerization of aniline at graphite electrode in 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline, $j = 2.0$ mA cm^{-2}, and dedoping by $j = 1.0$ mA cm^{-1}.

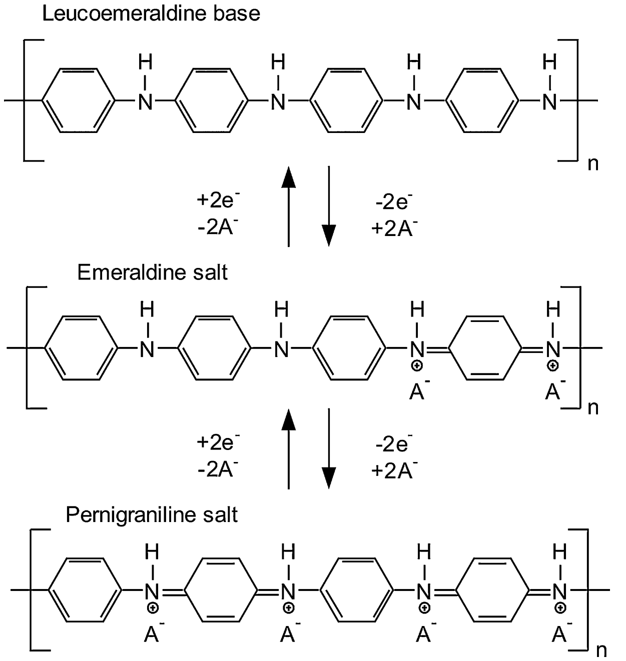


Fig. 2. Generalized scheme of various PANI oxidation forms.

After electrochemical polymerization, PANI electrode was galvanostatically discharged (dedoped) in the same solution with a current density of 1 mA cm^{-2} to the potential of −0.6 V, than rinsed in double-distilled water, and transferred into another electrochemical cell for further characterization. Prior to use, aniline was distilled under argon atmosphere. The working electrode, cylindrically shaped graphite inserted in Teflon holder, was first mechanically polished by fine emery papers (2/0, 3/0 and 4/0, respectively), and than by polishing alumina (1 μm, Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.). The traces of the polishing alumina were removed from the electrode surface in an ultrasonic bath during 5 min.

PANI electrode was characterized using cyclic voltammetry and chronopotentiometric measurements in chloride and chloride/citrate electrolytes. Chloride electrolyte was consisted of aqueous solution of 0.5 mol dm^{-3} NH_4Cl and 0.2 mol dm^{-3} $ZnCl_2$, while chloride/citrate electrolyte was consisted of 0.5 mol dm^{-3} NH_4Cl and 0.2 mol dm^{-3} $ZnCl_2$ with addition of 0.3 mol dm^{-3} Na-citrate. All experiments were performed in standard three compartment electrochemical cell at ambient temperature (22 °C). Saturated calomel electrode (SCE) was used as reference, while Pt wire served as counter electrode. The electrochemical measurements were carried out using PAR 273A potentiostat/galvanostat interfaced to PC.

3. Results and discussion

Chronopotentiometric curve of PANI electrochemical polymerization on graphite electrode from 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline at constant current density of 2.0 mA cm^{-2} during 1080 s is given in insert of Fig. 1. Aniline electrochemical polymerization occurs together with doping by chloride anions, according to:

$$(\mathrm{PANI})_n + ny\mathrm{Cl}^- \rightarrow [\mathrm{PANI}^{y+}(\mathrm{Cl}^-)]_n + ny\mathrm{e}^- \quad (1)$$

where y refers to doping degree (ratio between the number of charges in the polymer and the number of monomer units). After polymerization, PANI electrode was discharged (dedoped) galvanostatically with current density of 1 mA cm^{-2}, and transferred to another electrochemical cell for further investigation.

Six successive cyclic voltammograms ($\nu = 20$ mV s^{-1}) of the PANI electrode are shown in Fig. 1. Voltamogramms are characterized by constant charge increase resulted from the formation of insoluble PANI. The observed anodic and cathodic peaks correspond to different oxidation forms of PANI. First anodic peak, occurring at potential of ~0.2 V, is connected to doping of chloride anions indicating transition of leucoemeraldine ($y = 0$) form of PANI to emeraldine salt ($y = 0.5$). Further increase in potential, above ~0.50 V, refers to transition of emeraldine salt to perningraniline salt ($y = 1$) [20]. Between these well defined peaks, small peaks could be assigned to hydrolysis and degradation products of PANI [20-22]. Different forms of PANI oxidation states are schematically represented in Fig. 2 [20]. Leucemeraldine is fully reduced form of PANI, with doping degree, $y = 0$, conductive emeraldine salt is half oxidized form ($y = 0.5$), while perningraniline salt refers to fully oxidized form ($y = 1$).

As it could be seen in insert of Fig. 1, polymerization occurred at potentials ~0.7 V, meaning that PANI is mostly obtained in the form of perningraniline salt. Comparing the polymerization charge of 0.60 mAh cm^{-2} and discharge charge of ~0.14 mAh cm^{-2}, it could be concluded that only 23% of the total mass, was obtained in the form conducting of emeraldine salt and therefore available for the further charge exchange. The rest of the charge refers to formation of inactive PANI oligomers and degradation products [20].

Chronopotentiometric charge/discharge curves of the PANI electrode in chloride and chloride/citrate electrolyte, obtained by different current densities between 0.25 and 1.00 mA cm^{-2} are given in Fig. 3.

As it can bee seen in Fig. 3, in both chloride and chloride/citrate electrolyte, charging of PANI electrode started at potential of ~−0.1 V. In chloride electrolyte, potential almost linearly increased up to ~0.5 V. In chloride/citrate electrolyte, at potentials higher than 0.35 V, faster increase of the potential was observed. Such behavior is probably connected to appearance of degradation products, occurring at higher potentials. Discharge of the PANI electrode started at ~0.45 V in chloride, and ~0.3 V in chloride/citrate electrolyte, at potentials lower than ~0.1 V, sharp decrease of the potential in both electrolytes could be explained by diffusion limitations. Even though, the open circuit potential of the PANI electrode in chloride electrolyte was higher than in chloride/citrate electrolyte, chloride/citrate electrolyte exhibited better discharge characteristics, especially when lower current densities were used.

Dependences of charge/discharge capacities of PANI electrode in chloride and chloride/citrate electrolytes are given in Fig. 4. Charge/discharge characteristics of PANI electrode in both electrolytes were affected by the applied current density, probably as a consequence of chloride anion diffusion limitation trough the polymer film [23]. As it can be seen in insert of Fig. 4, columbic efficiency was higher in chloride/citrate electrolyte.

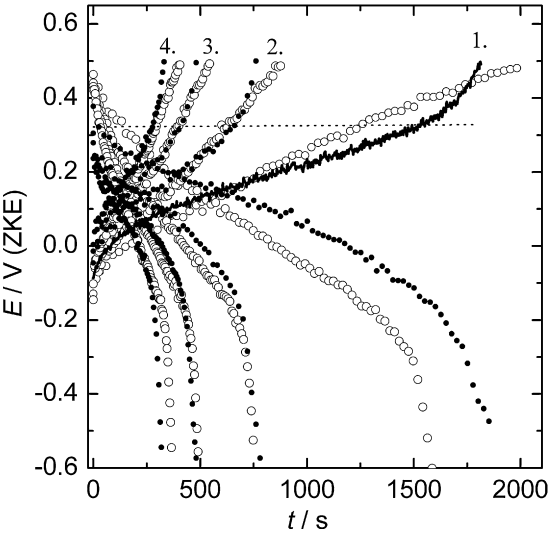


Fig. 3. Charge/discharge curves of PANI electrode in (○) chloride and (●) chloride/citrate obtained with current densities: (1) 0.25; (2) 0.50; (3) 0.75; (4) 1.00 mA cm^{-2}.

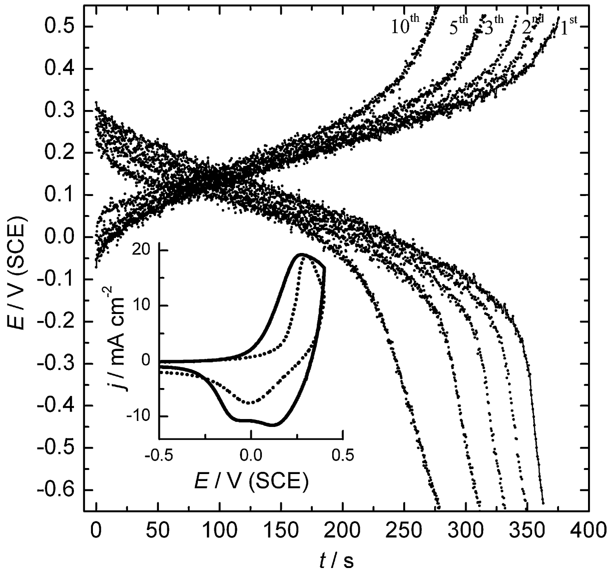


Fig. 5. Charge/discharge curves of PANI electrode during ten cycles, $j = 1$ mA cm^{-2} in chloride/citrate electrolyte for anodic potential limit of 0.50 V. Insert: cyclic voltammograms: (–) before and (. . .) after ten cycles, $\nu = 20$ mV s^{-1}.

It was previously showed that anodic potential limit had exhibited influence on charge/discharge characteristics of the PANI electrode, resulted in decrease of the electrode capacity during cycling [10]. On the other hand, it was observed that addition of citrate anions had enhanced characteristics of negative zinc electrode [19], in terms of both deceased corrosion rate and absence of zinc dendrite growth. For that reason, charge/discharge behavior of the PANI electrode was investigated in chloride/citrate electrolyte. In Figs. 5 and 6 chronopotentiometric charge/discharge curves of the PANI electrode in chloride/citrate electrode during ten cycles, obtained by current density of 1 mA cm^{-2} and different anodic potential limits of 0.5 and 0.32 V are given, respectively. Cyclic voltammograms taken before and after ten cycles of are given in inserts of both Figs. 5 and 6.

As seen in Figs. 5 and 6, anodic potential limit had great influence on charge/discharge behavior of PANI electrode in chloride/citrate electrode. For higher anodic potential limit of 0.5 V (Fig. 5) charge/discharge capacities constantly decreased over time. As seen in insert of Fig. 5, cyclic voltammograms taken before and after ten cycles showed capacity lost, suggesting that strong PANI degradation had occurred. For anodic potential limit of 0.32 V in Fig. 6 charge/discharge curves of the PANI electrode in chloride/citrate electrolyte were the same over ten cycles, meaning that electrode capacity remained practically constant. This funding indicates that degradation of PANI did not occurred. As seen in insert of Fig. 5, cyclic voltammograms of the PANI electrode before and after ten cycles remained the same, confirming again the fact that there was no PANI degradation during cycling. It is interesting to mention that charge/discharge capacities of the PANI electrode were almost two times higher in chloride/citrate than in chloride electrolyte (given in dot lines in Fig. 6).

The dependences of charge and discharge capacities of the PANI electrode, calculated by integration of anodic and cathodic parts of voltammograms from Figs. 5 and 6, on cycle number is given in Fig. 7.

As seen in Fig. 7, for anodic potential limit of 0.50 V, permanent lost (around 25%) of the capacity during ten cycles was observed

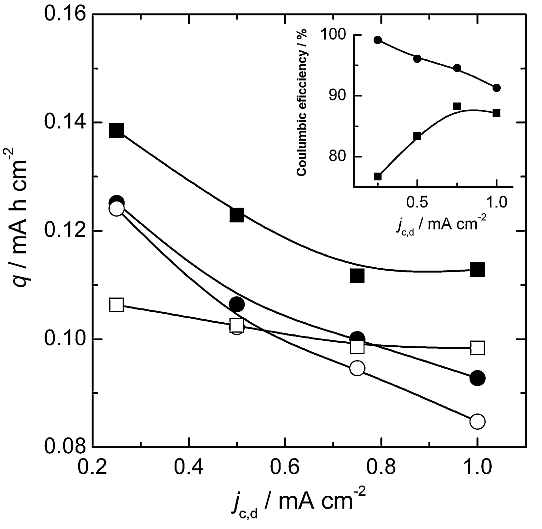


Fig. 4. Dependences of charge: (●) chloride/citrate; (■) chloride, and discharge: (○) chloride/citrate; (□) chloride, capacity of PANI electrode on current density. Insert: Columbic efficiency.

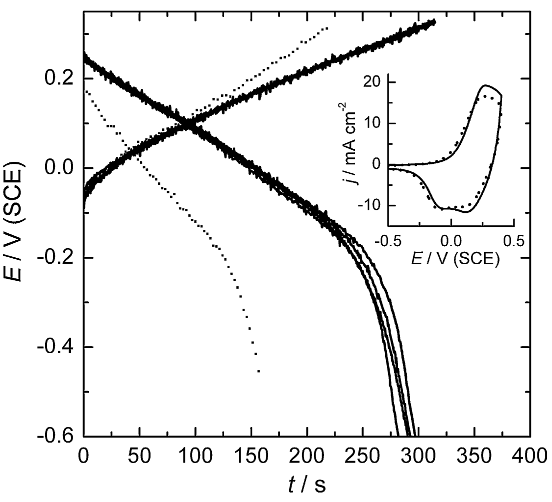


Fig. 6. Charge/discharge curves of PANI electrode during ten cycles, $j = 1$ mA cm^{-2} in chloride/citrate (full lines) and chloride electrolyte (dot lines), for anodic potential limit of 0.32 V, (dot lines) chloride. Insert: cyclic voltammograms: (–) before and (. . .) after ten cycles, $\nu = 20$ mV s^{-1}.

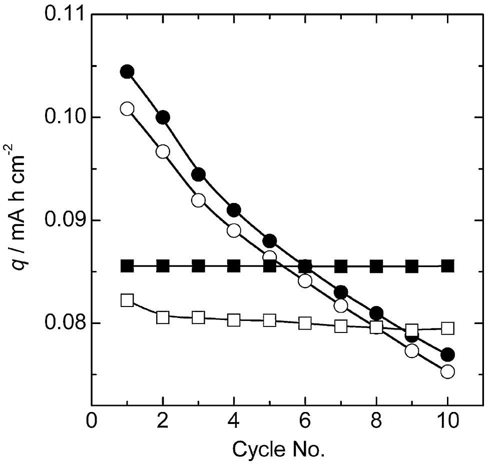


Fig. 7. Dependences of PANI electrode capacities on cycle number in chloride/citrate electrolyte, for anodic potential limit of 0.5 V: (●) charge; (○) discharge and 0.32 V: (■) charge; (□) discharge. Insert: Columbic efficiency for anodic potential limit of: (●) 0.5 V and (■) 0.32 V.

even though the initial capacity was higher, than one obtained for anodic limit of 0.32 V. On contrary, there was practically no capacity lost observed for the potential limit of 0.32 V. Since PANI was always polymerized under the same conditions, the decrease of the capacity for higher anodic potential limit of 0.5 V in chloride/citrate electrolyte could be connected to the presence of citrate anions. The effect of the doping anions, proposed by Yang et al. [24] could be attributed to the hydrophobic effect following the Hofmeister series [25]:

$$ClO_4^- > NO_3^- > I^- > Br^- > Cl^- > F^- > HPO_4^{2-} > SO_4^{2-} > \text{citrate}^{3-} \qquad (1)$$

According to this, perchlorate ions are the most hydrophobic, citrate ions are the most hydrophilic, while chloride are in the middle. So, it was expected that chloride ions would form relatively stabile ion pars in oxidized PANI film, therefore PANI degradation could be limited to certain degree by dissociation of the ion par, resulting in slower degradation kinetics of PANI in chloride than in chloride citrate electrolyte.

In Fig. 8 cyclic voltammograms of the PANI electrode in chloride, chloride/citrate and in pure citrate (0.3 mol dm^{-3} Na-citrate) are given.

As it can be seen in Fig. 8, doping process in chloride, chloride/citrate, and pure citrate electrolyte, started at potential of 0.15 V. Anodic peak potential connected to doping of leucoemeraldine to emeraldine salt in chloride and chloride/citrate electrolytes was observed at practically the same potential of 0.25 V, while the peak potential in pure citrate electrolyte was shifted for more than 100 mV in the positive direction. On the other hand, in chloride/citrate electrolyte, doping preceded through a broad peak, indicating that both chloride and citrate anions were involved in doping. It could be suggested that, at lower potentials doping by chloride occurred, while at higher potentials doping by citrate anions occurred. Comparing the values of the potentials in doping area for chloride and chloride/citrate electrolytes for the same value of current densities, it seams that doping reaction in chloride/citrate was shifted for about 30 mV in negative direction. This negative shift of the potential resulted in higher charge/discharge capacities obtained in chloride/citrate than in chloride electrolyte. On the other hand, in order to avoid fast PANI degradation and decrease in charge exchange ability, it is highly recommended that anodic potential limit during cycling should not exceed ~0.35 V.

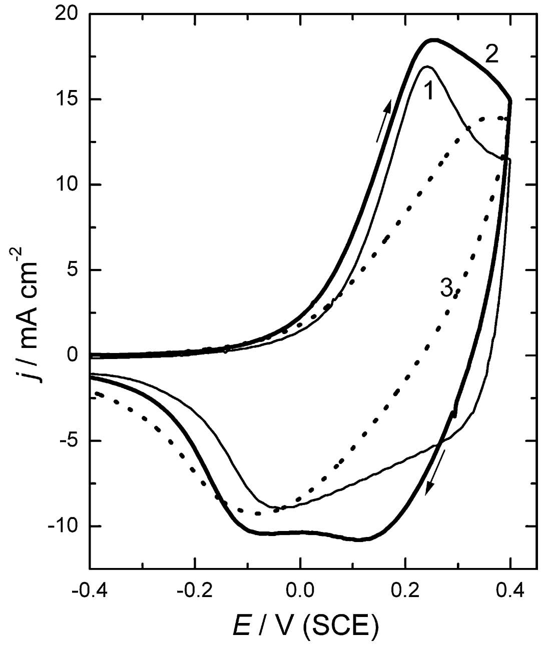


Fig. 8. Cyclic voltammograms of PANI electrode in: (1) chloride, (2) chloride/citrate and (3) citrate electrolyte, $\nu = 20\,\text{mV s}^{-1}$.

4. Conclusion

Electrochemical synthesis of PANI on graphite from aqueous solution of hydrochloric acid containing aniline monomer was performed under galvanostatic conditions. The polymerization charge was 0.60 mAh cm^{-2} while discharge charge was ~0.14 mAh cm^{-2}. It was concluded that only 25% of the total deposited PANI mass was obtained in the form of conducting emeraldine salt, and therefore available for charge exchange. The rest of the charge refers to formation of inactive PANI oligomers and degradation products. Based on electrochemical studies, it was concluded that in chloride/citrate electrolyte both citrate and chloride anions were engaged in doping. The faster decrease in charge/discharge capacity, for potential limit of 0.50 V, in chloride/citrate electrolyte compared to chloride electrolyte, was explained by hydrophilic effect of citrate ions. Higher charge/discharge capacities in chloride/citrate electrolyte were explained by negative doping potential shift of about 30 mV, enabling wider potential frame for doping/dedoping (charging/discharging). It was recommended that charging potential should not exceed 0.35 V.

Acknowledgment

This work is financially supported by the Ministry of Science and Technological Development, Republic of Serbia, Contract No. 172046.

References

[1] A. Malinauskas, J. Malinauskienė, A. Ramanavičius, Nanotechnology 16 (2005) R51.
[2] D.E. Tallman, G. Sprinks, A. Dominis, G.G. Wallace, J. Solid State Electrochem. 6 (2002) 73.
[3] S.K. Shukla, M.A. Quraishi, R. Prakash, Corros. Sci. 50 (2008) 2867.
[4] B. Jugović, M. Gvozdenović, J. Stevanović, T. Trišović, B. Grgur, Mater. Chem. Phys. 114 (2009) 939.
[5] M. Sima, T. Visan, M. Buda, J. Power Sources 56 (1995) 133.
[6] J. Kan, H. Xue, S. Mu, J. Power Sources 74 (1998) 113.
[7] B. Gupta, R. Prakash, Mater. Sci. Eng. 29 (2009) 1746.
[8] V. Singh, S. Mohan, G. Singh, P.C. Pandey, R. Prakash, Sens. Actuators. B: Chem. 132 (2008) 99.

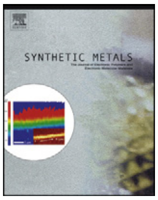
[9] B.Z. Jugović, T. Lj. Trišović, J. Stevanović, M. Maksimović, B.N. Grgur, J. Power Sources 160 (2006) 1447.
[10] B.Z. Jugović, T. Lj. Trišović, J. Stevanović, M. Maksimović, B.N. Grgur, Electrochim. Acta 51 (2006) 6268.
[11] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, H. Heli, Synth. Met. 155 (2005) 480.
[12] A. Mirmohseni, R. Solhjo, J. Eur. Polym. 39 (2003) 219.
[13] R. Mažeikiene, A. Malinauskas, Mater. Chem. Phys. 83 (2004) 184.
[14] P. Rüetschi, J. Power Sources 42 (1993) 1.
[15] F. Beck, P. Rüetschi, Electrochim. Acta 45 (2000) 2467.
[16] Lj. D. Arsov, W. Plieth, G. Koβmehl, J. Solid State Electrochem. 2 (1998) 355.
[17] H.N. Dinh, J. Ding, S.J. Xia, V.I. Birss, J. Electroanal. Chem. 459 (1998) 45.
[18] G. Mengoli, M.M. Musiani, D. Pletcher, S. Valcher, J. Appl. Electrochem. 17 (1987) 515.
[19] E. Erdem, M. Saçak, M. Karakişla, Polym. Int. 39 (1996) 153.
[20] B. Jugović, M. Gvozdenović, J. Stevanović, T. Trišović, B. Grgur, Mater. Design 30 (2009) 3291.
[21] N. Gospodinova, L. Terlemezyan, Prog. Polym. Sci. 23 (1998) 1443.
[22] J.Y. Lee, L.H. Ong, G.K. Chuah, J. Appl. Electrochem. 23 (1993) 1031.
[23] K. Ghanbaria, M.F. Mousavi, M. Shamsipur, H. Karami, J. Power Sources 170 (2007) 513.
[24] X. Yang, Q. Xie, S. Yao, Synth. Met. 143 (2004) 119.
[25] W. Kunz, J. Henle, B.W. Ninham, Curr. Opin. Colloid Interface Sci. 9 (2004) 19.

Synthetic Metals 161 (2011) 1313–1318

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Electrochemical synthesis and corrosion behavior of polyaniline-benzoate coating on copper

Milica M. Gvozdenović[a,*], Branimir Z. Jugović[b], Jasmina S. Stevanović[c], Branimir Grgur[a], Tomislav Lj. Trišović[b], Zvonimir S. Jugović[d]

[a] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[b] Insitute of Technical Science, Serbian Academy of Science and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia
[c] Institute of Chemistry Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia
[d] Technical Faculty Čačak, University of Kragujevac, Svetog Save 65, 32000 Čačak, Serbia

ARTICLE INFO

Article history:
Received 4 January 2011
Received in revised form 3 March 2011
Accepted 26 April 2011
Available online 25 May 2011

Keywords:
Electrochemical polymerization
Sodium benzoate
Polyaniline
Copper

ABSTRACT

Electrochemical polymerization of polyaniline (PANI) coating on copper electrode was performed galvanostatically in the current density range between 0.50 and 1.25 mA cm^{-2}, from aqueous solution of 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline. The corrosion behavior of PANI coated copper and copper electrode exposed to 0.5 mol dm^{-3} sodium chloride solution was investigated by potentiodynamic and electrochemical impedance spectroscopy techniques. It was observed that thin PANI (5 μm) coating had provided efficient protection (∼96%) to copper in 0.5 mol dm^{-3} sodium chloride solution. Unusual initial impedance behavior to that normally observed with conventional organic coatings was attributed to dedoping of benzoate anions from the polymer coating.

1. Introduction

The unique properties of electroconducting polymers (ECP), such as: electrochemical activity, environmental stability, eases of synthesis procedures both chemical and electrochemical [1–9], permits them to be considered in wide range of various practical applications: electronic devices, rechargeable power sources, sensors, biosensors, magnetic shielding and active corrosion protection as well [10–18].

Copper and large numbers of its alloys are widely used in industrial application such as process equipments, electrical and electronics devices, marine etc. Apart from high electrical and thermal conductivity and excellent formability, copper also exhibits good corrosion resistance; however it corrodes in variety of aggressive environments [18]. The corrosion protection strategy of copper is usually based on inhibition, using organic compounds mainly benzotriazoles, aminotriazole and its derivates [19–24]. Apart from good protective properties of inhibitors in variety of corrosive environments, they are quite toxic, hence application of electroconducting polymers (ECP) could be considered as possible environmental friendly procedure in corrosion protection of copper. Both chemical and electrochemical oxidative polymerization are used to obtain ECP. Electrochemical synthesis is favorable permitting direct polymer film synthesis on metal surface without oxidizing agent, followed by doping by organic or inorganic ions in a single step. The basic problem related to electrochemical polymerization of ECP on copper, in general, is the fact that two competitive processes occur on anode: electrochemical synthesis and deposition of ECP and dissolution of copper on potentials necessary to oxidize the monomer. Hence, it would be beneficial to work with electrolyte which can passivate copper and, on the other hand, permits electrochemical polymerization.

Most of the studies devoted to corrosion protection of copper by ECP are connected to use of polypirrole (Ppy). Recently, Bazzaoui et al. have used electrochemical synthesis of PPy on copper and brass from aqueous solution of sodium saccharinate and pyrrole solution, the obtained coating exhibited significant corrosion protection in both chloride and hydrochloride solutions [17]. Redondo and Breslin obtained homogenous PPy film electrodeposited on copper from pyrrole containing phosphate solution; the growth of the film was achieved on previously oxidized copper electrode in the phosphate solution. The coating effectively protected copper in a chloride solution [25,26]. Fenelon and Breslin also electrodeposited Ppy coating on Cu, CuZn and CuNi with good protective properties from sodium oxalate solution [27,28]. Herrasti et al. investigated electrochemical synthesis of PPy on previously passivated copper electrodes using different electrochemical techniques, they pointed out that chronopotentiometry seemed to produce best protective

---

[*] Corresponding author. Tel.: +381 11 3303695; fax: +381 11 3303695.
E-mail address: popovic@tmf.bg.ac.rs (M.M. Gvozdenović).

0379-6779/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2011.04.029

coating for long immersion times in chloride solution [28,29]. Tüken et al. performed electrochemical synthesis of polythiophene (PTh) on copper electrode previously coated with thin PPy film. They concluded that PPy/PTh coating on copper had provided good protection during long immersion in sodium chloride solution [30].

Apart from the fact that polyaniline (PANI), owing to the low price of its monomer, could be considered as most challengeable EPP for the purpose of corrosion protection in general, only few studies were dedicated to use of PANI in corrosion protection of copper. Brusic et al. investigated the possible use of PANI and its derivates for corrosion protection of copper and silver [31]. Unsubstituted PANI in both doped in the form of salt (doping with HCl or dodecylbenzensulfonic acid) and undoped in the form of base were investigated, together with substituted PANI with etoxy and propyl groups, were investigated. The polymers were applied on copper foils by spin coating procedure. It was observed that etoxy substituted PANI in the form of base had provided best corrosion protection, even better than benzotriazole. The protective function was connected to the inhibition of oxygen reduction.

Chaudhari and Patil obtained uniform and adherent film of poly (o-etoxyaniline) on copper from aqueous o-etoxyaniline and salicilate containing solution using cyclic voltammetry. They observed decrease of the corrosion rate compared to uncoated copper in sodium chloride solution for almost 140 times [32]. They also investigated corrosion protective features of electrochemically copolymerized poly (o-anididine-co-o-toluidine) coatings on copper and based on both potentiodynamic polarization and electrochemical impedance measurements, they observed increased corrosion protection of copolymer comparing to respective homopolymers [33]. The same authors also investigated electrochemical synthesis and corrosion protection of poly (o-anisidine) coatings on brass [34].

Özyilmaz et al. used cyclic voltammetry to perform electrochemical synthesis of PANI coating on nickel plated copper from oxalic acid and sodium oxalate solution [35,36].

It was observed that PANI obtained from both solutions had provided increased corrosion protection of nickel plated copper electrode in sodium chloride solution.

It can be concluded that there is constant interest in application of ECP in general for the corrosion protection of copper, although there is only few studies dedicated to the use of PANI in such systems.

Previously, we have shown that electrochemical syntheses PANI film on mild steel and aluminum from aqueous sodium benzoate solution [15,37] had resulted in homogenous and strongly adherent thin PANI film with increased corrosion protection properties. The aim of this paper was to investigate conditions for electrochemical synthesis of thin protective PANI film on copper from sodium benzoate solution containing aniline.

2. Experimental

2.1. Electrochemical polymerization of PANI on copper

Potentiodynamic anodic polarization curves of copper in 0.1–0.3 sodium benzoate with and without presence of 0.2 mol dm^{-2} aniline were recorded at scan rate of 0.5 mV s^{-1}.

Polyaniline (PANI) film on copper was obtained by electrochemical polymerization from aqueous solution of 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline under galvanostatic conditions in the current density range of 0.50–1.25 mA cm^{-2}.

Prior to use, aniline (p.a. Aldrich) was distilled under argon atmosphere. Electrolytes were prepared with distilled water. Copper sheet (S = 2.0 cm^2) served as working electrode. Before all experiments, working electrode was first mechanically abraded by fine emery papers (2/0, 3/0 and 4/0, respectively) and then by polishing alumina (1 μm, Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.). After mechanical polishing, the traces of the polishing alumina were removed from the electrode surface ultrasonically during 5 min.

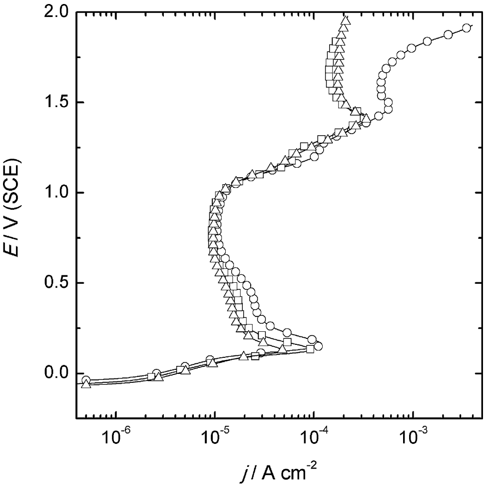


Fig. 1. Potentiodynamic anodic polarization (ν = 0.5 mV s^{-1}) curves of copper electrode in: (○) 0.1 mol dm^{-3}, (□) 0.3 mol dm^{-3} and (△) 0.5 mol dm^{-3} Na–benzoate.

The mass of the electrochemically polymerized PANI film was determined by measuring the mass difference of copper samples before and after dissolution of PANI in hot methanol/acetone (30/70) mixture.

2.2. Corrosion behavior

Corrosion behavior of copper electrode and PANI coated copper electrode in 0.5 mol dm^{-3} sodium chloride solution was investigated using potentiodynamic measurements and electrochemical impedance spectroscopy (EIS). The working surface area of the copper and PANI coated copper electrode used in potentiodynamic and EIS measurements was reduced to 0.5 cm^2, using Teflon holder in order to avoid the edge effects. The three compartment electrochemical cell was used in all experiments. Copper and PANI coated copper electrode served as working, standard calomel (SCE) as reference and platinum wire was used as counter electrode.

EIS measurements were performed at open circuit potentials in the frequency range between 50 mHz and 100 kHz, while below 5 Hz the fast Fourier technique (FFT) was used. All experiments were performed using instrumentation consisted of PC controlled PAR263A potentiostat/galvanostat connected to PAR frequency response detector FRD100.

Scanning electron microscope (SEM) micrographs of PANI coated copper taken before and after immersion in 0.5 mol dm^{-3} sodium chloride were made using scanning electron microscope – Jeol, JSM-5800.

3. Results and discussion

3.1. Electrochemical polymerization of PANI on copper

In order to obtain optimal concentration of sodium benzoate for electrochemical synthesis of PANI on copper, anodic polarization curves of copper electrode in different concentration of sodium benzoate were recorded, and presented in Fig. 1.

As it can be seen in Fig. 1, corrosion potential, E_{corr}, of copper electrode in sodium benzoate had value ~−0.10 V(SCE). At potentials more positive than 0.3 V(SCE), passivation of the electrode occurred, with critical passivity current density of 200, 90 and

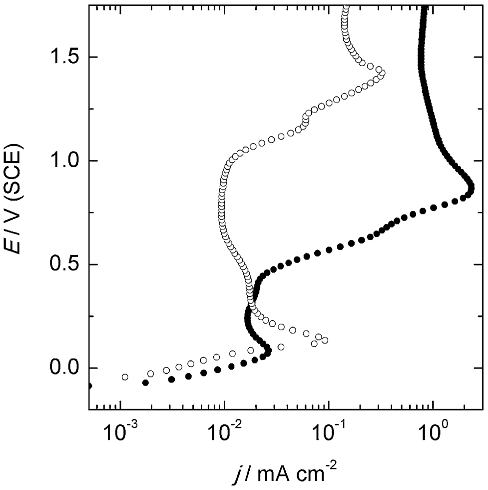


Fig. 2. Potentiodynamic anodic polarization ($v = 0.5\,\mathrm{mV\,s^{-1}}$) curves of copper in: (○) $0.3\,\mathrm{mol\,dm^{-3}}$ sodium benzoate and (●) $0.3\,\mathrm{mol\,dm^{-3}}$ sodium benzoate and $0.20\,\mathrm{mol\,dm^{-3}}$ aniline.

$40\,\mu\mathrm{A\,cm^{-2}}$ and the mean value of passivation current density of 25, 15 and $13\,\mu\mathrm{A\,cm^{-2}}$ for sodium benzoate concentration of 0.1, 0.3 and $0.5\,\mathrm{mol\,dm^{-3}}$, respectively. At potentials more positive than 1.3 V transpassive region probably connected to transformation in the structure of the passive layer followed by oxygen evolution reaction was observed. There is no significant difference in anodic polarization curves of the copper in different concentration of sodium benzoate, although the lowest value of the critical passivation current density was achieved in $0.5\,\mathrm{mol\,dm^{-3}}$ sodium benzoate, while almost the same value of the mean passivation current density was achieved in 0.3 and $0.5\,\mathrm{mol\,dm^{-3}}$ sodium benzoate solutions. In order to ensure good conductivity and solubility of sodium benzoate, concentration of $0.3\,\mathrm{mol\,dm^{-3}}$ was used in all further experiments.

In Fig. 2, anodic polarization curves of copper electrode in $0.3\,\mathrm{mol\,dm^{-3}}$ sodium benzoate with addition of $0.2\,\mathrm{mol\,dm^{-3}}$ aniline, are given for lower concentration of monomer, it was practically impossible to grow polymer film, similar observation could be find in literature for the growth of the polypyrrole on copper [29].

As it could be seen in Fig. 2, in the presence of aniline, corrosion potential was shifted for ~50 mV in the negative direction, connected to anodic inhibitory effect of absorbed aniline monomer [15]. After short passivation of copper, in aniline containing electrolyte, polymerization started at potentials more positive than 0.4 V(SCE) and proceeded up to the potential of 2.5 V(SCE). The observed pick at ~0.7 V(SCE) could be connected to the existence of polyaniline in the form of pernigraniline salt [38], at potentials more positive than ~2 V(SCE), slow oxygen reduction reaction was observed.

Chronopotentiometric (galvanostatic) curves of electrochemical polymerization of aniline on copper electrode from aqueous solution of $0.3\,\mathrm{mol\,dm^{-3}}$ sodium benzoate and $0.2\,\mathrm{mol\,dm^{-3}}$ aniline, obtained by different current densities during 1000s are given in Fig. 3, while in the insert of Fig. 3, chronopotenitometric curve for first 25 s of polymerization, with current density of $1.25\,\mathrm{mol\,dm^{-3}}$, is presented.

As it could be seen in Fig. 3 dissolution of copper was not observed, initial increase of the potential, observed during first 25 s of polymerization (insert of Fig. 3), is related to the formation of polyaniline layer on copper surface, while further slower increase of the potential could be connected to polymerization of aniline on already formed polymer on the metal surface.

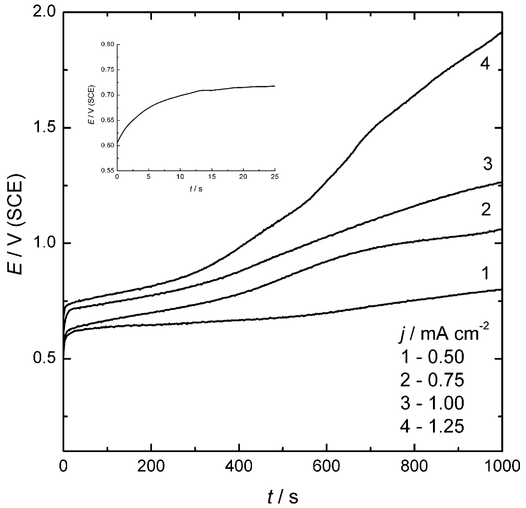


Fig. 3. Chronopotentiometric (galvanostatic) curves of Cu electrode in $0.3\,\mathrm{mol\,dm^{-3}}$ sodium benzoate and $0.2\,\mathrm{mol\,dm^{-3}}$ aniline solutions obtained by different current densities (as marked in the figure). Insert: chronopotentiometric curve obtained with $1.0\,\mathrm{mA\,cm^{-3}}$ during 25 s of polymerization.

Dependence of the experimentally determined PANI mass (full symbols) together with calculated theoretical mass of the PANI film (full line) on applied polymerization current density is given in Fig. 4. Insert of Fig. 4 shows dependence of the polymerization efficiency on the polymerization current density, given as a ratio of experimentally determined and calculated theoretical mass of PANI.

Theoretical mass, m_t ($\mathrm{mg\,cm^{-2}}$) of PANI film was calculated assuming 100% current efficiency, and taking into account average molar mass of aniline monomer unit in the polymer, according to equation [39]:

$$m_t = \frac{jt(M_m + yM_a)}{(2+y)F\rho} \tag{1}$$

where j ($\mathrm{A\,cm^{-2}}$) is polymerization current density over time, t (s); M_m and M_a, $\mathrm{g\,mol^{-1}}$, are molar mass of aniline monomer ($93.13\,\mathrm{g\,mol^{-1}}$) and inserted benzoate anions ($121.12\,\mathrm{g\,mol^{-1}}$), respectively, $F = 96{,}484\,\mathrm{C\,mol^{-1}}$ is Faraday constant, and y is doping degree. Due to the high polymerization potential, it was reasonably to assume that most of the PANI film was obtained in

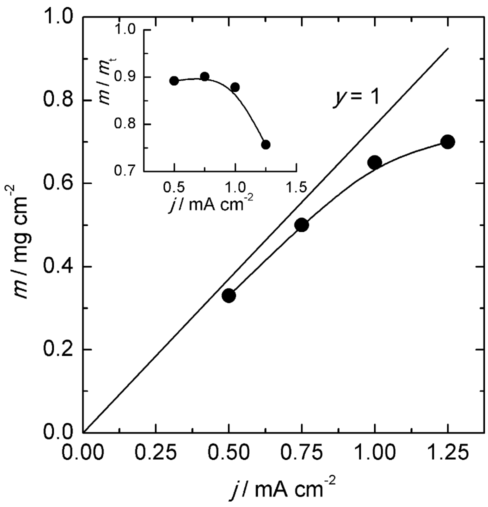


Fig. 4. Dependence of the experimentally determined mass of PANI film (●) and (□) theoretical PANI mass on current polymerization densities. Insert: polymerization efficiency.

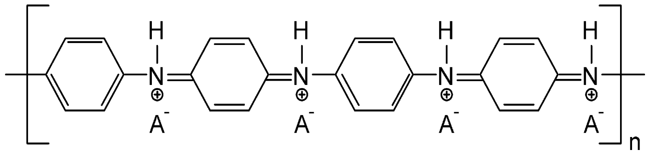


Fig. 5. Shematic presentation of PANI in the form of perningranilin salt (A–$C_6H_5COO^-$) [25].

perningranilin form referring to $y = 1$, schematically presented in Fig. 5.

As seen in Fig. 4, mass of the polymerized PANI on copper increased with increase of the current density, but polymerization efficiency, after having practically the same values for lower current densities, decreased for higher current densities. Such observation could be connected to the formation of polyaniline degradation and hydrolysis products [38], and oxygen evolution reaction. Since, the completely uniform PANI films were obtained for higher current densities and in order to achieve lower extent of degradation, polymerization current density of 1.0 mA cm^{-2} was used in further experiments. Using equation:

$$\delta = \frac{m}{\rho} \tag{2}$$

where m (g cm^{-2}) is experimental mass of the deposited PANI, and assuming that density of the benzoate doped PANI was similar to sulfate doped ($\rho = 1.3$ g cm^{-3}) [40], thickness of the PANI film, obtained with current density of 1.0 mA cm^{-2}, during 1000s, was estimated to be ~5.0 μm.

3.2. Corrosion behavior

3.2.1. Polarization measurements

Potentiodynmanic polarization curves ($\nu = 0.5$ mV s^{-1}) of copper and copper coated by electrochemically deposited PANI film, after 24 h of immersion in 0.5 mol dm^{-3} NaCl are given in Fig. 6.

As it can be seen in Fig. 6, anodic polarization curves of copper and PANI coated copper are under activation control, characterized by the Tafel slope of ~54 mV dec^{-1}, connected to anodic dissolution of copper, while cathodic polarization curves are under mixed activacion–diffusion control of oxygen reduction. The corrosion potential of pure copper was, $E_{corr} = -0.270$ V(SCE), while corrosion potential of PANI coated copper was $E_{corr} = -0.225$ V(SCE). Corrosion current densities were determined as intercept of anodic Tafel lines with corrosion potential. It was found that corrosion current densities for copper and PANI coated copper were $j_{corr,Cu} = 3.1$ and $j_{corr,Cu/PANI} = 0.19$ μA cm^{-3}. The protection efficiency of PANI expressed as:

$$E = \frac{j_{corr,Cu} - j_{corr,Cu/PANI}}{j_{corr,Cu}} \times 100\% \tag{3}$$

was estimated to 96%.

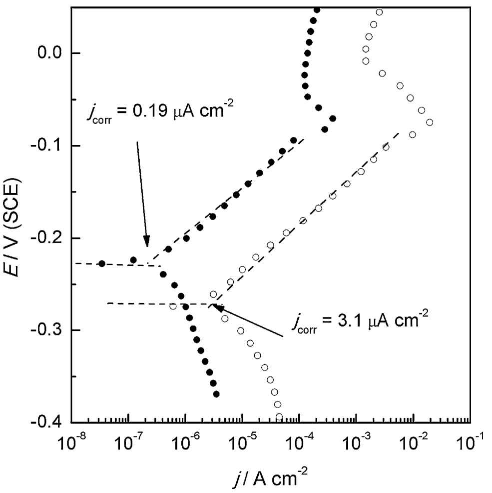


Fig. 6. Potentiodynamic ($\nu = 0.5$ mV s^{-1}) polarization curves of: (●) Cu and (○) PANI coated Cu in 0.5 mol dm^{-3} NaCl.

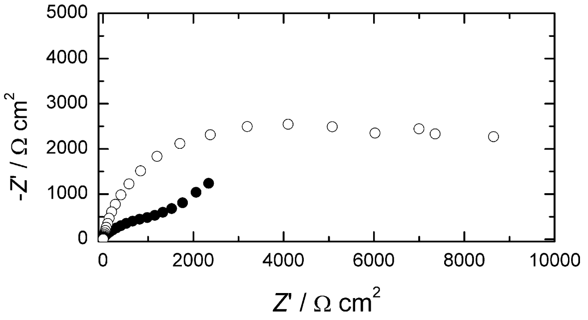


Fig. 7. Complex plane (Nyquist) impedance spectra of: (●) Cu and (○) PANI coated Cu in 0.5 mol dm^{-3} NaCl.

3.2.2. Electrochemical impedance spectroscopy (EIS)

EIS spectra in complex plane (Nyquist plot) of copper and PANI coated copper electrodes after 24 h of immersion in 0.5 mol dm^{-3} NaCl, are shown in Fig. 7.

As it can be seen in Fig. 7, without detailed analysis in the term of equivalent circuits and fitting procedure, the low frequency part of the impedance spectra for copper electrode, related to corrosion process, indicates mixed activation-diffusion control, while semi cycle at higher frequencies could be attributed to the formation of corrosion film products [19–21]. On the other hand, the impedance spectra of PANI coated copper is characterized by two slightly depressed overlapping semi cycles, with significantly higher value of the overall impedance comparing to pure copper, indicating protective features of the PANI film.

Complex plane spectra of PANI coated copper taken at different times of exposure in 0.5 mol dmmol dm^{-3} NaCl are given in Fig. 8, while insert of Fig. 8 shows the time dependences of the corresponding open circuit (corrosion) potential, at which the impedance spectra were taken.

As seen in Fig. 8, without detailed analysis, the overall impedance of PANI coated copper, unusually to conventional organic coatings, firstly increased, from the value of ~8 kΩ cm^2 at the beginning of immersion, to ~16 kΩ cm^2 after 540 h of immersion. The increase of the impedance might be a consequence of cathodic dedoping of benzoate anions from PANI film, according to:

$$(PANI^{y+}(C_6H_5COO^-)_y)_n + nye \rightarrow (PANI)_n + ny\,C_6H_5COO^- \tag{4}$$

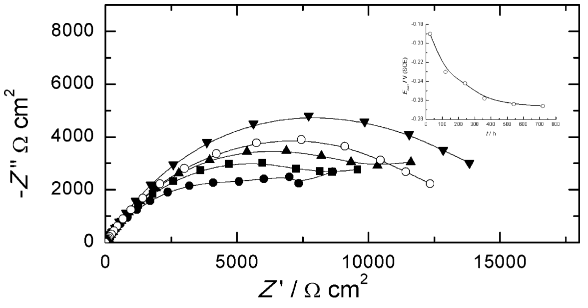


Fig. 8. Complex plane (Nyquist) impedance spectra of PANI coated Cu after: (●) 120 h, (■) 240 h, (▲) 360 h, (▼) 540 h and (○) 720 h of exposure to 0.5 mol dm^{-3} NaCl. Insert: time dependences of corresponding open circuit potentials.

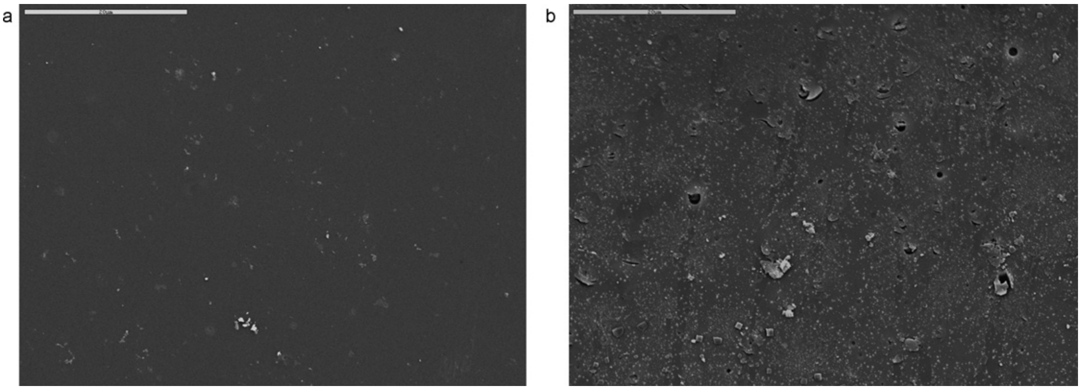


Fig. 9. SEM micrographs of PANI coated Cu (a) before and (b) after 7 days of immersion in 0.5 mol dm^{-3} NaCl.

Dedoping provoked the lost of the PANI film conductivity, reflected in the increase of the overall impedance. Since the shift of the open circuit potential to more negative values is characteristic of dedoped state [41], the observed decrease in corrosion potentials (insert of Fig. 8), also confirms the assumption of dedoping process. After observed increase, the overall impedance of PANI started to decrease slowly, meaning that PANI started to act as conventional organic coating enabling barrier corrosion protection of the metal surface.

3.2.3. Corrosion process of PANI coated copper

In order to observe the effects of corrosion media on surface morphology of PANI coating on copper, SEM micrographs were taken before and after immersion in NaCl, and given in Fig. 9(a) and (b), respectively.

As it could be seen in Fig. 9, before exposure to corrosion media, PANI coating was compact and uniformly deposited on copper surface. After immersion in NaCl, the development of pores in the coating was clearly observed.

It is well known from the literature [12,42] that corrosion process of copper in NaCl solutions can be explained by activation controlled anodic dissolution, according to:

$$Cu \rightarrow Cu^{+} + e^{-} \tag{5}$$

In further chemical reactions Cu^{+} reacts with Cl^{-} generating CuCl, which is then transformed to $CuCl_2{}^{-}$ and rate determining cathodic reaction under mixed activation-diffusion control of oxygen reduction, according to:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{6}$$

On the other hand, corrosion process of PANI coated copper exposed to NaCl solution can be explained by the same reactions of anodic dissolution and cathodic oxygen reduction (5) and (6) occurring on the metal surface in the pores of the PANI film and slow parallel cathodic reaction of benzoate anions dedoping (4), which is confirmed by the impedance data.

4. Conclusion

Electrochemical synthesis of PANI film on copper from aqueous solution of sodium benzoate containing aniline was investigated using potentiodynamic and galvanostatic experiments. Protective PANI coating was successfully obtained with high polymerization efficiency (~90%) under galvanostatic conditions using current density of 1.0 mA cm^{-2} from aqueous solution of 0.3 mol dm^{-3} sodium benzoate containing aniline.

Corrosion behavior of copper in the presence of thin (5 μm) PANI film in 0.5 mol dm^{-3} NaCl solution was investigated using potentiodynamic and electrochemical impedance spectroscopy techniques. It was observed that PANI thin coating had provided high protection efficiency to copper. Unusual impedance behavior to those observed with organic coatings, reflected in initial increase of the overall impedance, was connected to dedoping of benzoate ions from the PANI film, after which the values of the overall impedance started to decrease similar to those with classical organic coatings. Therefore, corrosion process of PANI coated copper in NaCl was explained by the same electrochemical reactions of copper anodic dissolution and cathodic oxygen reduction occurring in parallel with slow cathodic dedoping of the benzoate anions from the PANI film, after dedoping, PANI coating started to act like conventional organic coating.

Acknowledgment

This work was financially supported by the Ministry of Science and Technological Development, Republic of Serbia, under Contract H172046

References

[1] J.Y. Shimano, A.G. MacDiarmid, Synth. Met. 123 (2001) 251–262.
[2] C.M.S. Izumi, D.C. Ferreira, A.-M.D. Costa Ferreira, M.L.A. Temperini, Synth. Met. 159 (2009) 1165–1173.
[3] J.P. Lock, J.L. Lutkenhaus, N.S. Zacharia, S.G. Im, P.T. Hammond, K.K. Gleason, Synth. Met. 157 (2007) 894–898.
[4] B.R. Kim, H.K. Lee, E. Kim, S.-H. Lee, Synth. Met. 160 (2010) 1838–1842.
[5] S.S. Umare, B.H. Shambharkar, R.S. Ningthoujam, Synth. Met. 160 (2010) 1815–1821.
[6] C. Janáky, B. Endrődi, K. Kovács, M. Timko, A. Sápi, C. Visy, Synth. Met. 160 (2010) 65–71.
[7] M. Jain, S. Annapoorni, Synth. Met. 160 (2010) 1727–1732.
[8] M. Radoičić, Z. Šaponjić, J. Nedeljković, G. Ćirić-Marjanović, J. Stejskal, Synth. Met. 160 (2010) 1325–1334.
[9] H. Zhang, X. Wang, J. Li, F. Wang, Synth. Met. 159 (2009) 1508–1511.
[10] A. Wu, E.C. Venancio, A.G. MacDiarmid, Synth. Met. 157 (2007) 303–310.
[11] S. Sathiyanarayanan, S.S. Azim, G. Venkatachari, Synth. Met. 157 (2007) 205–213.
[12] S. Sathiyanarayanan, S.S. Azim, G. Venkatachari, Synth. Met. 157 (2007) 751–757.
[13] Y. Li, B. Ying, L. Hong, M. Yang, Synth. Met. 160 (2010) 455–461.
[14] N.D. Nghia, N.T. Tung, Synth. Met. 159 (2009) 831–834.
[15] M.M. Popović, B.N. Grgur, Synth. Met. 143 (2004) 191–195.
[16] D.E. Tallman, G. Springs, A. Dominis, G.G. Wallace, J. Solid State Electrochem. 6 (2002) 85–100.
[17] M. Bazzaoui, J.I. Martins, E.A. Bazzaoui, L. Martins, E. Machnikova, Electrochim. Acta 52 (2007) 3568–3581.
[18] J.J. Steppan, J.A. Roth, L.C. Hall, D.A. Jeanotte, C.P. Carbone, J. Electrochem. Soc. 134 (1997) 175–179.
[19] V. Brusic, M.A. Frisch, B.N. Eldrige, F.P. Novak, F.B. Kaufman, B.M. Rush, G.S. Frankel, J. Electrochem. Soc. 138 (1991) 2253–2259.
[20] C.A. Ferreira, S. Aeiyach, A. Couloud, P.C. Lacaze, J. Appl. Electrochem. 29 (1999) 259–263.
[21] A.M. Fenelon, C.B. Breslin, J. Appl. Electrochem. 31 (2001) 509–516.
[22] R.S. Goncalves, D.S. Azambuja, A.M.S. Lucho, Corros. Sci. 44 (2002) 467–479.
[23] C.K. Tan, D.J. Blackwood, Coross. Sci. 45 (2003) 545–557.

[24] T.K. Roth, G. Jha, A.K. Singh, N. Bondgopadhyay, O.N. Mohanty, Surf. Coat. Technol. 167 (2003) 16–21.
[25] M.I. Redondo, C.B. Breslin, Corros. Sci. 49 (2007) 1765–1776.
[26] A.M. Fenelon, C.B. Breslin, Electrochim. Acta 47 (2002) 4467–4476.
[27] A.M. Fenelon, C.B. Breslin, Corros. Sci. 45 (2003) 2837–2850.
[28] P. Herrasti, F.J. Recio, P. Ocón, E. Fatás, Prog. Org. Coat. 54 (2005) 285–291.
[29] P. Herrasti, A.I. del Rio, J. Recio, Electrochim. Acta (2007) 6496–6501.
[30] T. Tüken, B. Yazici, M. Erbil, Prog. Org. Coat. 53 (2005) 38–45.
[31] V. Brusic, M. Angelopus, T. Graham, J. Electrochem. Soc. 144 (1997) 436–443.
[32] S. Chaudhari, P.P. Patil, Electrochim. Acta 53 (2007) 927–933.
[33] P. Pawar, A.B. Gaikwad, P.P. Patil, Electrochim. Acta 52 (2007) 5958–5967.
[34] S. Chaudhari, A.B. Gaikwad, P.P. Patil, Curr. Appl. Phys. 9 (2009) 206–218.
[35] A.T. Özyilmaz, M. Erbil, B. Yazici, Appl. Surf. Sci. 252 (2005) 2092–2100.
[36] A.T. Özyilmaz, Prog. Org. Coat. 54 (2005) 127–133.
[37] M.M. Gvozdenović, B.N. Grgur, Prog. Org. Coat. 65 (2009) 401–404.
[38] N. Gospodinova, L. Terlemezyan, Prog. Polym. Sci. 23 (1998) 1443–1484.
[39] J. Kankare, in: D. Wise, G.E. Wenk, D.J. Trontolo, T.M. Cooper, J.D. Gresser (Eds.), Electrical and Optical Polymer Systems: Fundamentals, Methods and Applications, Marcel Dekker, New York, 1998 (Chapter 6).
[40] J. Steiskal, R.G. Gilbert, Purre Appl. Chem. 74 (2002) 857–867.
[41] B.N. Grgur, M.M. Gvozdenović, V.B. Mišković-Stanković, Prog. Org. Coat. 56 (2006) 214–219.
[42] E.M. Sherif, S.-M. Park, J. Electrochem. Soc. 152 (10) (2005) B428–B433.

Journal of Power Sources 217 (2012) 193–198

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Electrochemical characteristics of rechargeable polyaniline/lead dioxide cell

Branimir N. Grgur [a,*], Aleksandar Žeradjanin [b], Milica M. Gvozdenović [a], Miodrag D. Maksimović [a], Tomislav Lj. Trišović [c], Branimir Z. Jugović [c]

[a] *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11020 Belgrade, Serbia*
[b] *Ruhr-Universität Bochum, Universitätsstr. 150, NC 04/788, D-44780 Bochum, Germany*
[c] *Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11000 Belgrade, Serbia*

HIGHLIGHTS

- ► PANI and PbO_2 electrode was synthesized from sulfuric acid solution.
- ► Electrode was investigated for PANI/PbO_2 rechargeable cell.
- ► Electrochemical characteristic of the cell was determined.

ARTICLE INFO

Article history:
Received 27 April 2012
Received in revised form
21 May 2012
Accepted 5 June 2012
Available online 12 June 2012

Keywords:
Polyaniline
Lead dioxide
Rechargeable cell
Sulfuric acid
Ammonium sulfate

ABSTRACT

Electrochemically synthesized polyaniline (PANI) and lead dioxide have been investigated as electrode materials for PANI/1.1 M H_2SO_4; 0.5 M $(NH_4)_2SO_4/PbO_2$ rechargeable cell. At constant current charge/discharge of the cell, the average discharge potential of 1.1 V, specific capacity of 50 mA h g^{-1}, specific energy of 55 W h kg^{-1}, and self discharge rate of 2.2% per day have been obtained.

1. Introduction

Replacement the Pb negative electrode with polyaniline (PANI) could avoid some of the problems with negative Pb electrode compared to classical Pb/PbO_2 systems [1–3]. Additionally, both the specific energy and the specific power could increase significantly, owing to the much smaller mass of PANI electrode compared to classical Pb negative electrode. Moreover, lower concentration of sulfuric acid and decrease of lead content in such cell increase its ecological acceptability of such cell.

In our previous work, electrochemical characteristics of polyaniline (PANI) and lead dioxide (PbO_2) electrodes were investigated in 1.1 M H_2SO_4, aiming to characterize thin film PANI and PbO_2 electrode for the potential application in aqueous based PANI/H_2SO_4/PbO_2 cell. [1]. Considering electrochemical behavior, for different doping (oxidation) potential limits, and dedoping capacity of PANI electrode in 1.1 M H_2SO_4 it was suggested that doping potential should not exceed 0.4 V. The obtained specific electrode capacity of PANI electrode was 240 mAh g^{-1}. This value was obtained considering only the electroactive mass (0.48 g) of the total deposited PANI mass (2.1 mg). So, the realistic value of the specific electrode capacity will be around 50 mA h g^{-1}. By simulation of the charge/discharge characteristic, based on the half cell reactions, it was estimated that cell charging voltage would range between 1 and 1.9 V, while discharge would occur between 1.35 and ~0.8 V, with most of the charge delivered at above 1 V.

In the PANI/PbO_2 system, the half cell reaction for charge and discharge can be given as [1]:

$$\left[\mathrm{PANI}^{y+}\left(\mathrm{SO_4}^{2-}\right)_y\right]_n + 2nye \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} (\mathrm{PANI})_n + ny\mathrm{SO_4}^{2-} \qquad (1)$$

where y is doping degree, and:

---

* Corresponding author. Tel./fax: +381 11 3303 681.
E-mail address: BNGrgur@tmf.bg.ac.rs (B.N. Grgur).

0378-7753/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2012.06.025

$$PbSO_4 + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} PbO_2 + SO_4{}^{2-} + 4H^+ + 2e \quad (2)$$

The overall reaction in the cell would be:

$$nyPbSO_4 + 2nyH_2O + \left[PANI^{y+}\left(SO_4{}^{2-}\right)_y\right]_n \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} PbO_2 + (PANI)_n + 2nySO_4{}^{2-} + 4nyH^+ \quad (3)$$

It is very important to bear in mind that, according to given schema, during cell charging, PANI would be dedoped, on contrary, during cell discharge, PANI would be doped.

It is interesting to note that from early work on PANI, Pb and PbO_2 cells, by Kitani et al. [4], until now, practically no data on electroconducting polymers (ECP)/PbO_2 cells were provided in the literature. There were attempts to improve characteristics of negative, Pb electrode, and prevent grids corrosion by PANI coatings, conducted by Martha et al. and Cheraghi et al. [5–7].

After the reexamining of the results in 1.1 M H_2SO_4, it was concluded that PbO_2 electrode had poor cyclization characteristics and low coulombic efficiency in this electrolyte. In the present study we have used the novel electrolyte consisted of 1.1 M sulfuric acid and 0.5 M ammonium sulfate which has good buffer capacity and benefits to PbO_2 electrode [8].

Hence, the aim of this work was investigation of electrochemically synthesized polyaniline and lead dioxide as ~~the~~ electrode materials for PANI/1.1 M H_2SO_4; 0.5 M $(NH)_4SO_4$/PbO_2 cell.

2. Experimental

Thin film PANI electrode was electrochemically synthesized from aqueous 1.1 M sulfuric acid solution with addition of 0.25 M aniline monomer (p.a. Merck, previously distilled in argon atmosphere). The polymerization was performed on graphite electrode ($S = 18$ cm^2), galvanostatically at constant current of 36 mA, during 5000 s, with the total polymerization charge of 50 mA h. After polymerization, PANI electrode was discharged with the current of 18 mA to test the film quality, washed with bidistilled water and transferred into another electrochemical cell for further investigations.

The mass of PANI was determined by measuring the graphite electrode before and after electropolymerization, followed by overnight drying in vacuum.

Lead dioxide electrode was prepared on pure lead (99.95%) ($S = 18$ cm^2), according to Planté formation process described in detail by Petersson et al. [9,10]. In order to remove lead oxides, naturally formed in the air, the lead sample was dipped in 8 M HNO_3 for 30 s, and rinsed in bidistilled water prior to immersion in 0.5 M H_2SO_4 and 0.05 M $KClO_4$ (p.a. Merck) for the formation process. The lead electrode was initially pretreated cathodically at constant current of 36 mA during 25 min, and then oxidized and reduced galvanostatically in the same electrolyte at current of 36 mA. After formation process, the remains of perchlorate ions were removed from the electrode by rinsing in bidistilled water. Finally, the PbO_2 electrode was completely oxidized in pure 1.1 M H_2SO_4 with the current of 36 mA during 1500 s.

For all further electrochemical experiments electrolyte consisted of 1.1 M sulfuric acid and 0.5 M ammonium sulfate was used.

Prior to investigation, working electrode was mechanically polished firstly with fine emery papers (2/0, 3/0 and 4/0, respectively) and then with polishing alumina of 1 μm (Banner Scientific Ltd.) on the polishing cloths (Buehler Ltd.). After mechanical polishing the traces of the polishing alumina were removed from the electrode surface ultrasonically in ethanol during 5 min.

Electrochemical synthesis and characterization of PANI and PbO_2 electrodes were performed in a single compartment electrochemical cell with total volume of 100 cm^3. Platinum mesh ($S = 18$ cm^2) was used as counter, while saturated calomel electrode, SCE, ($E_r = 0.243$ V vs. SHE), served as reference electrode. For the characterization of the PANI/PbO_2 cell the same electrochemical cell, with electrode gap of 1 cm, was used.

The electrochemical measurements were carried out using PAR M273 potentiostat/galvanostat controlled by a computer, while voltage data was collected using ISO-Tech IDM 73 multimeter connected to the computer via RS 232.

3. Results and discussion

3.1. Synthesis and characterization of PANI electrode

Fig. 1 shows the chronopotentiometric curve of aniline polymerization on graphite electrode at constant current of 36 mA, during 5000 s with the polymerization charge, q_{pol}, of 50 mA h from aqueous solution of 1.1 M H_2SO_4 and 0.25 M aniline (ANI) monomer. Aniline polymerization, in sulfuric acid solution, proceeded in the potential range between 0.7 and ~0.52 V according to the equation:

$$n(ANI) + nySO_4{}^{2-} = \left[PANI^{y+}\left(SO_4{}^{2-}\right)_y\right]_n + 2nye \quad (4)$$

The mass of PANI deposited on graphite electrode, determined in a separate experiment after drying in vacuum overnight, was 0.0989 g. The corresponding thickens of PANI electrode, assuming the density of sulfate doped PANI of 1.43 g cm^{-3}, was estimated to ~40 μm [11].

Insert of Fig. 1 shows cyclic voltammogram of the PANI electrode in 1.1 M sulfuric acid and 0.5 M ammonium sulfate, for the anodic potential limit of 0.5 V. Doping of the PANI electrode with sulfate anions started at ~−0.1 V and proceeded up to the potential of 0.4 V. The well defined peak at 0.2 V, could be attributed to the changes of the doping degree of PANI between $y > 0$ and 0.5. It should be noted that at low negative potentials leucoemeraldine form ($y \approx 0$) could exist as well [12]. Above potentials of ~0.4 V the possibilities of formation the quinone-like degradation products is expected [1,13].

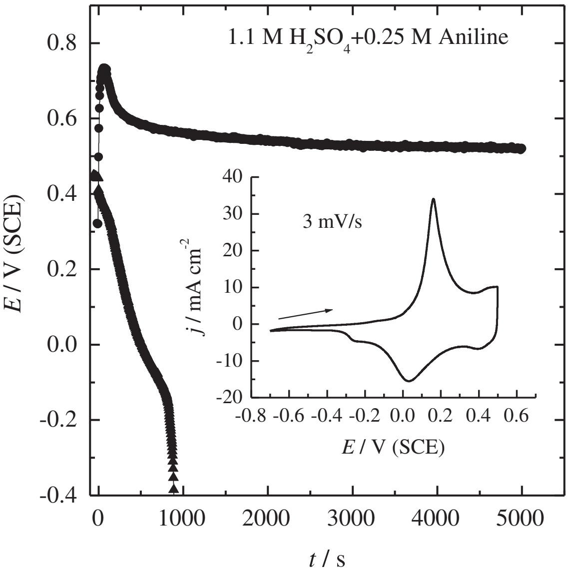


Fig. 1. Galvanostatic curves of aniline electropolymerization ($I = 36$ mA) and discharge ($I = 18$ mA). Insert: cyclic voltammogram of PANI electrode in 1.1 M sulfuric acid and 0.5 M ammonium sulfate.

In the cathodic scan, reduction of degradation products and emeraldine salt to leucoemeraldine proceeded in the potential range between 0.5 and −0.3 V.

Doping/dedoping curves of PANI electrode for different currents, and for doping potential limit of 0.4 V are shown in Fig. 2. Curves are characterized by constant increase/decrease of the potential which is connected to the changes of the emeraldine salt doping degree given by overall reaction:

$$[\mathrm{PANI}]_n + ny\mathrm{SO_4}^{2-} \underset{\text{dedoping}}{\overset{\text{doping}}{\rightleftarrows}} \left[\mathrm{PANI}^{y+}\left(\mathrm{SO_4}^{2-}\right)_y\right]_n + 2nye \tag{5}$$

Fig. 3 shows calculated values of doping/dedoping electrode capacity and specific capacity for different currents. As it can be seen electrode capacity was dependent on the applied current, and decreased from 7 (6.5) to 5.5 mA h, or from 70 (65) to 55 mA h g^{-1} with increasing the current. Decrease in the electrode capacity with increasing of the current, is connected with slow diffusion of sulfate anions through polymer film. Coulombic efficiency, shown in the insert of Fig. 3, for the current higher than 30 mA was ~100%, while for the current lower than 30 mA, was higher than 100% (103–108%). This unusual results, as pointed out in our previous paper, could be explained by the possibilities of hydrogen evolution reaction ($E_\mathrm{r} = -0.24$ V) or even more probably by formation of protonated leucoemeraldine at low current and negative potentials [1]. Such additional charge was, after current interruption, quickly discharged, at the PANI electrode open circuit potentials of −0.05 V and was not observed during charge.

As pointed out, the degradation of PANI could occur above ~0.4 V. So, behavior of PANI electrode during cyclization, at a constant current of 36 mA for charging potential limits of 0.35 and 0.45 V, was investigated, and shown in Fig. 4. As it can be seen in Fig. 4, during first ten cycles for charging with potential limit of 0.35 V, discharge time remained constant. Charging of the electrode to the potential of 0.45 V, during nine cycles, provoked some small decrease of the discharge times, inducing the additional decrease of the discharge time for potential limits of 0.35 V during twentieth cycle. Hence, it could be suggested that charging potential limits should not exceed 0.4 V.

3.2. Synthesis and characterization of PbO_2 electrode

Fig. 5 shows galvanostatic synthesis of PbO_2 on the oxide free lead electrode at constant current of 36 mA in aqueous solution of 0.5 M H_2SO_4 and 0.05 M $KClO_4$, according to the similar procedure described by Petersson et al. [9,10]. Initially, the electrode was treated cathodically for 1500 s at 36 mA and then oxidized and reduced galvanostatically in the same electrolyte. After current was applied, during 10 s, potential had the similar value as the open circuit potential, ~−0.52 V. This time could be assigned to the induction period, t_ind, of the $PbSO_4$ formation. When most of the lead surface was converted into $PbSO_4$, increase of the potential up to the ~1.7 V followed by a plateau at ~1.55 V, could be connected to transformation of $PbSO_4$ into PbO_2. After 700 s, electrode was discharged to ~0.7 V, with the same current. According to Fig. 5 the total time, which could be connected to the formation of PbO_2, was 700 s (or 7 mA h). Relying to Faradays law, and assuming formation process efficiency of 100% [9,10], the calculated mass and corresponding thickness of the PbO_2 electrode, were 31 mg and 1.85 μm respectively.

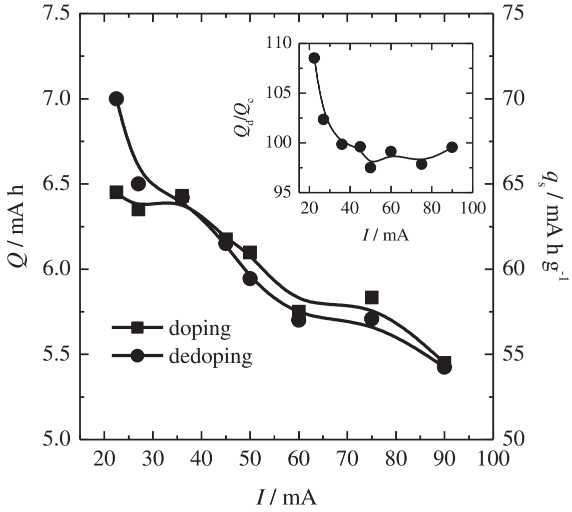


Fig. 3. Calculated values of PANI electrode capacity (Q) and specific capacity (q_s) for different currents. Insert: Coulombic efficiency.

Charge/discharge curves of PbO_2 electrode, for different currents, in 1.1 M sulfuric acid and 0.5 M ammonium sulfate are shown in Fig. 6. Charge of the electrode started at 1.4 or 1.5 V, depending on applied current, followed by slow increase of the potential. After that period of time, faster increase of the potential could be connected to oxidation of small amounts of $PbSO_4$

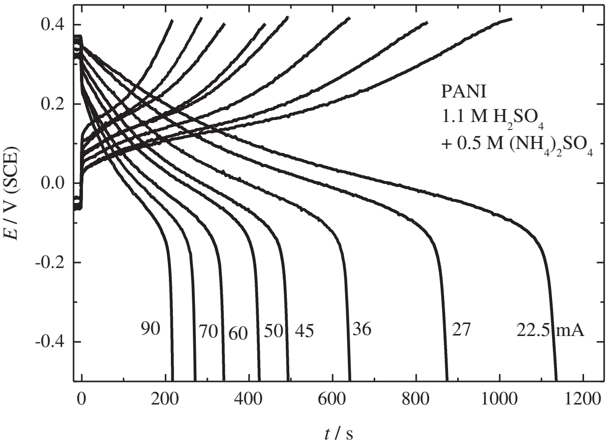


Fig. 2. Doping/dedoping curves of PANI electrode for different currents, marked in figure.

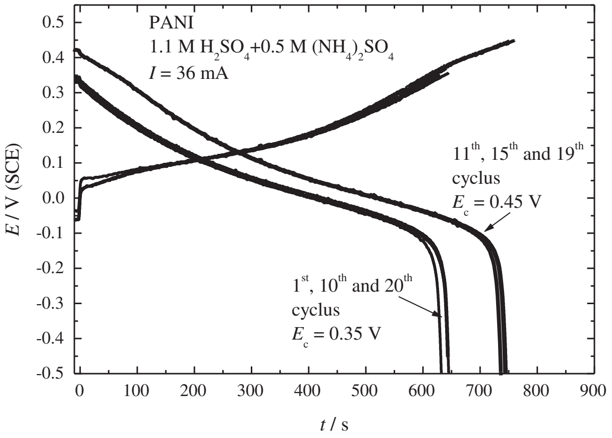


Fig. 4. Potential-current curves of PANI electrode during cyclization at a constant current of 36 mA for charging potential limits of 0.35 and 0.45 V.

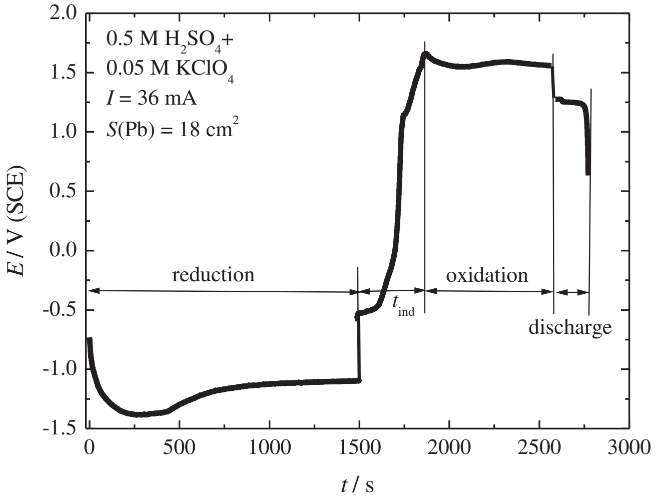


Fig. 5. Dependence of potential on time during galvanostatic formation of PbO_2 electrode.

remains, and oxygen evolution. Discharge of the PbO_2 occurred via one well defined potential plateau of 1.27 ± 0.01 V.

From Fig. 6 the capacities of charge/discharge processes were calculated and shown in Fig. 7. Charge capacity increased non-linearly from 8.5 to 9.7 mA h with increasing current. On contrary, discharge capacity of ~7 mA h was practically independent on applied current. Coulombic efficiency of charge/discharge, shown in the insert of Fig. 6, for the current lower than 30 mA, ranged from 81 to 82.5%, while for the current higher than 30, decreased from 82 to 73%.

During the cyclization of PbO_2 electrode (Fig. 8), small decrease of charging and increase of discharging potentials, and practically constant capacity were observed. Decrease of the peak during cyclization, was also observed for the first 100 s of the charging process, and could be connected to oxidation of $PbSO_4$ phase.

3.3. *Electrochemical characteristic of PANI/PbO_2 cell*

Comparing the results for PANI and PbO_2 electrode it can bee concluded that disbalance in the charge/discharge time, for the same current existed. In Fig. 9 charge/discharge curves for PbO_2 electrode at current 22.5 mA (j = 1.25 mA cm^{-2}) and 27.5 mA (j = 1.53 mA cm^{-2}), and for PANI electrode of 22.5 mA (j = 1.25 mA cm^{-2}) are shown. As it can be seen, charge/discharge times, were practically equal for the PbO_2 current of 27.5 mA and 22.5 mA for the PANI electrode. To avoid this problem we reduced the surface area of PbO_2 electrode to 14.7 cm^2. Now, for the overall cell current of 22.5 mA, current density for PbO_2 electrode was 1.53 mA cm^{-2}, and for PANI electrode 1.25 mA cm^{-2}.

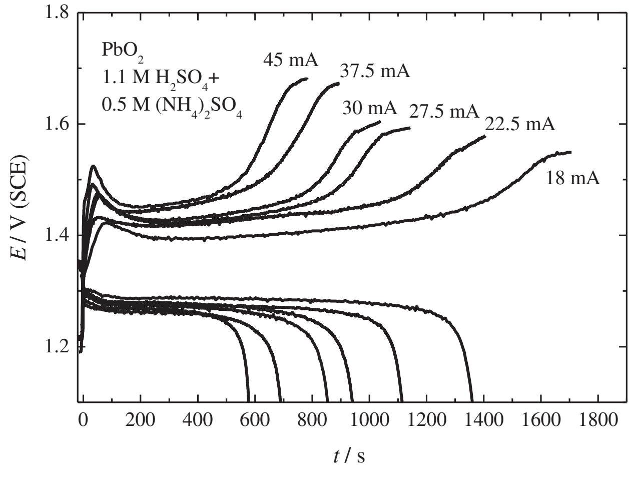


Fig. 6. Charge/discharge curve of PbO_2 electrode for different currents, marked in figure.

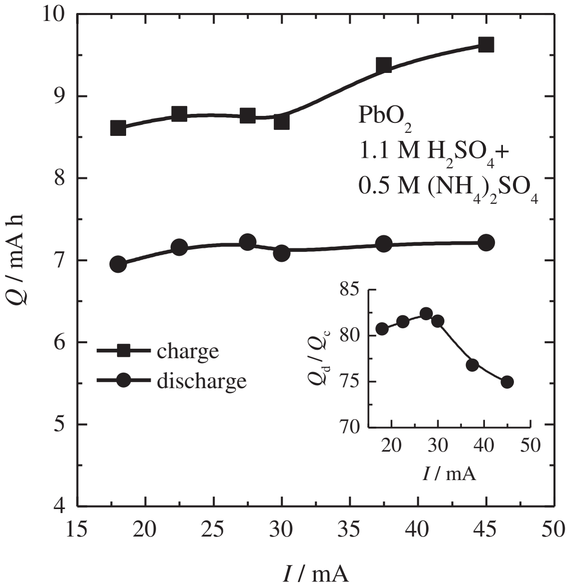


Fig. 7. Dependence of charge/discharge capacity of PbO_2 electrode for different current. Insert: Coulombic efficiency of charge/discharge.

With such surface reduced PbO_2 electrode, the charge/discharge characteristics of the complete cell, during ten cycles with current of 22.5 mA, were investigated and shown in Fig. 10. Charging of the cell started at ~0.85 V, followed by voltage increase up to 1.5 V. The shoulder in the potential range of 1.5–1.8 V could be associated to behavior of PbO_2 electrode, and sharp increase of the voltage above

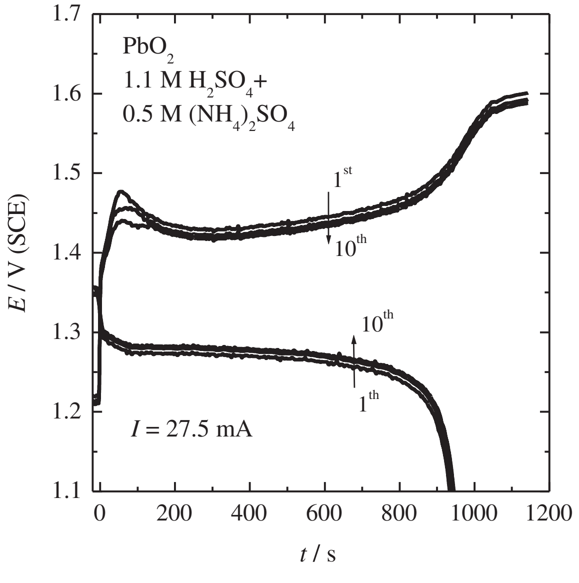


Fig. 8. Potential-current curves of PbO_2 electrode during cyclization at a constant current of 27.5 mA.

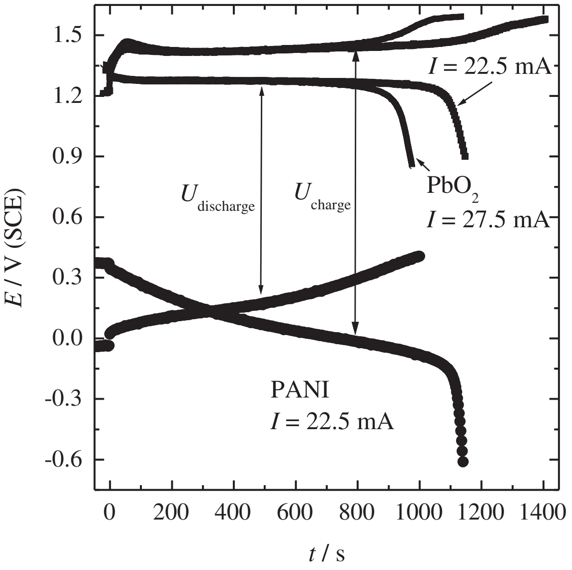


Fig. 9. Comparison of charge/discharge curves for PbO_2 and PANI electrode.

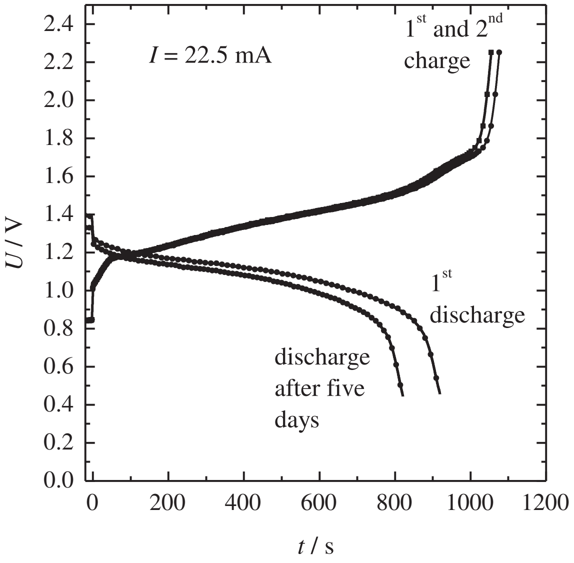


Fig. 11. Determination of the self discharge rate of PANI/PbO_2 cell.

1.8 V to PANI electrode. Open circuit voltage of charged cell was 1.4 V. Discharge of the cell occurred in the potential range of 1.4 to 0.8 V, followed by the sharp decrease of the voltage, which can be connected to behavior of PbO_2 electrode. Average discharge voltage was ~1.1 V, comparable to those of cadmium/nickel oxide and metal hydride/nickel oxide batteries. It should be noted that discharge of the cell below 0.4 V could affect PANI electrode, due to the possibilities of degradation. Decrease of the charge/discharge times during cyclization was most probably connected to some electrode capacity disbalance, rather than active mass degradation.

Self discharge rate was investigated after five days, and results are shown in Fig. 11. After five days, decrease of the open circuit potential from 1.4 V to 1.32 V, and discharge time of 11% were observed, giving self discharge rate of 2.2% per day. The reasons of such high self discharge rate were probably connected to both electrodes. Thin film PbO_2 was probably discharged due to the presence of the organic impurities form PANI electrode. Self discharge of PANI electrode, as proposed by Rahmanifar et al. [14], occurred as a consequence of the reaction of soluble hydroquinone (HQ) like species with pernigraniline salt form of PANI, giving protonated emeraldine, via simplified reaction:

$$\left[\mathrm{PANI}\left(\mathrm{SO_4}^{2-}\right)_4\right]_n + n\mathrm{HQ} + 2ne \xrightarrow{\text{self-discharge}} \left[\mathrm{PANI}\left(\mathrm{SO_4}^{2-}\right)_2\right]_n + n\mathrm{Q} + 2n\mathrm{SO_4}^{2-} \tag{6}$$

Based on the above given redox reaction, HQ is formed under the conditions at which PANI existed in the pernigraniline form, and then the resulting HQ reacted with the remaining pernigraniline and converted it to the emeraldine conductive form. This could be the main cause of the reduced open circuit potential and the capacity.

Knowing the masses of PANI (0.0989 g) and PbO_2 (25.4 mg, initial mass of PbO_2 reduced for 18%) it was possible to draw the diagram of charge/discharge over specific capacity of the cell. As it

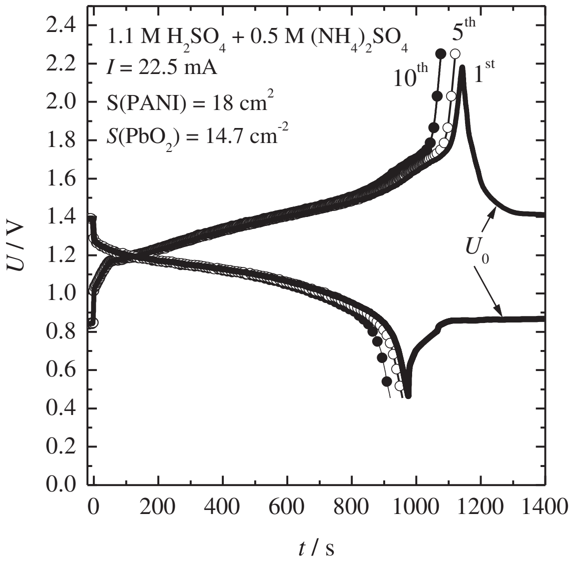


Fig. 10. Charge/discharge curves of PANI/PbO_2 cell during cyclization.

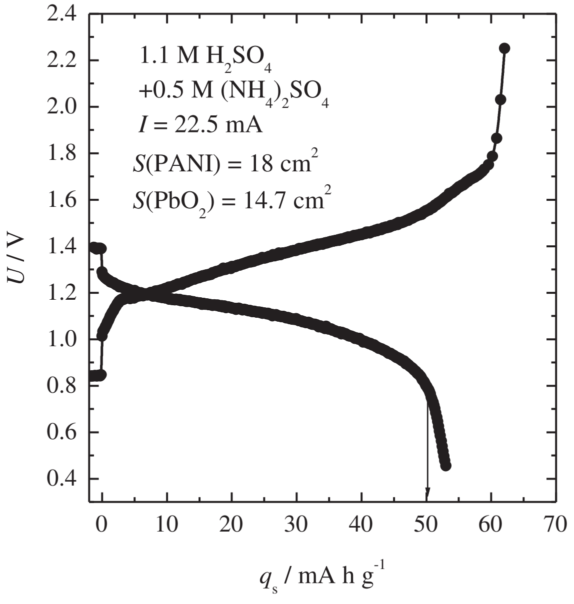


Fig. 12. Dependence of charge/discharge voltage on specific capacity of the PANI/PbO_2 cell.

can be seen in Fig. 12 available specific discharge capacity was 50 mA h g^{-1} of active electrode mass, with active mass utilization of 83%. For the average discharge voltage of 1.1 V, specific discharge energy of 55 W h kg^{-1} was calculated.

4. Conclusions

Polyaniline and lead dioxide electrode were successfully synthesized from sulfuric acid based solutions. Charge/discharge characteristic of the separate electrodes was investigated in 1.1 M sulfuric acid and 0.5 M ammonium sulfate electrolyte. Based on this results, electrodes were balanced and characteristics of polyaniline/lead dioxide cell were investigated. At the charge/discharge current of 22.5 mA the average discharge potential of 1.1 V, specific capacity of 50 mA h g^{-1}, specific energy of 55 W h kg^{-1}, and self discharge rate of 2.2% per day were obtained. High self discharge rate was connected to reaction of soluble hydroquinone like species formed during the polyaniline charging.

Acknowledgment

The work was supported by the Ministry of Education and Science of the Republic of Serbia under the research project: “Electrochemical synthesis and characterization of nanostructured functional materials for application in new technologies” (No. 172046).

References

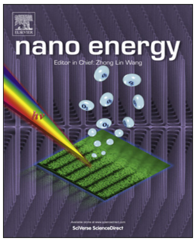
[1] B.N. Grgur, V. Ristić, M.M. Gvozdenović, M.D. Maksimović, B.Z. Jugović, J. Power Sources 180 (2008) 635–640.
[2] P. Ruetschi, J. Power Sources 127 (2004) 33–44.
[3] B. Culpin, D.A.J. Rand, J. Power Sources 36 (1991) 415–438.
[4] A. Kitani, M. Kaya, K. Sasaki, J. Electrochem. Soc. 133 (6) (1986) 1069–1073.
[5] S.K. Martha, B. Hariprakash, S.A. Gaffoor, A.K. Shukla, J. Appl. Electrochem. 36 (2006) 711–722.
[6] S.K. Martha, B. Hariprakash, S.A. Gaffoor, D.C. Trivedi, A.K. Shukla, J. Chem. Sci. 118 (1) (2006) 93–98.
[7] B. Cheraghi, A.R. Fakhari, S. Borhani, A.A. Entezami, J. Electroanal. Chem. 626 (2009) 116–122.
[8] D.B. Matthews, M.A. Habib, S.P.S. Badwal, Aust. J. Chem. 34 (1981) 247–269.
[9] I. Petersson, B. Berghult, E. Ahlberg, J. Power Sources 74 (1998) 68–76.
[10] I. Petersson, E. Ahlberg, B. Berghult, J. Power Sources 76 (1998) 98–105.
[11] J. Stejskal, I. Sapurina, M. Trchova, J. Prokes, I. Krivka, E. Tobolkova, Macromolecules 31 (1998) 2218–2222.
[12] N. Gospodinova, L. Terlemezyan, Prog. Polym. Sci. 23 (1998) 1443–1484.
[13] M. Gao, G. Zhang, G. Zhang, X. Wang, S. Wang, Y. Yang, Polym. Degrad. Stab. 96 (2011) 1799–1804.
[14] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, H. Heli, Synth. Met. 155 (2005) 480–484.

Nano Energy (2013) 2, 523-529

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

Enhanced oxygen evolution and reduction reactions of porous ternary NiCoFe foam electrodes prepared by dynamic hydrogen template deposition

Lidija D. Rafailović[a,b,*], **Christoph Gammer**[b], **Christian Rentenberger**[b], **Tomislav Trišović**[c], **Christoph Kleber**[a], **H. Peter Karnthaler**[b]

[a]*CEST, Center of Electrochemical Surface Technology, Viktor-Kaplan-Strasse 2, 2700 Wr. Neustadt, Austria*
[b]*University of Vienna, Physics of Nanostructured Materials, Boltzmanngasse 5, 1090 Vienna, Austria*
[c]*Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia*

Received 24 October 2012; accepted 25 December 2012
Available online 5 January 2013

KEYWORDS
Nanostructured energy materials;
Ternary NiCoFe electrodes;
Bifunctional catalyst;
Transmission electron microscopy;
Nanodendritic foam structures

Abstract

Electrodeposition at high current densities provides excellent means for the production of deposits with a high surface area. Porous deposits attract great interest due to their wide range of possible applications in electrocatalysis. In addition, an advanced porous electrode should have both, micro and nanoscaled features. We report the synthesis of a multiscale open porous foam of NiCoFe and its excellent electrocatalytic performance. At a current density of 1 A cm^{-2} a 3D dendritic structure with open pores is obtained with pore walls having a morphology that consists of 'cauliflower-like' particles containing open multiscaled dendritic structures. Cyclic voltammograms of a smooth NiCoFe electrode are compared with those of the achieved nanodendritic NiCoFe foam electrode. The catalytic activity of the NiCoFe foam is strongly enhanced for both, the cathodic reduction of oxygen and the anodic evolution of oxygen and shows a good reversibility. Therefore the presented new material is promising as bifunctional catalyst in electrochemical energy conversion and storage devices.

© 2013 Elsevier Ltd. All rights reserved.

Introduction

Electrodeposition at high current densities provides excellent means for the production of deposits with a high

---

[*] Corresponding author at: CEST, Center of Electrochemical Surface Technology, Viktor-Kaplan-Strasse 2, 2700 Wr. Neustadt, Austria. Tel.: +43 2622 22266 26.
E-mail addresses: lidija.rafailovic@cest.at, lidija.rafailovic@univie.ac.at (L.D. Rafailović).

2211-2855/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.nanoen.2012.12.004

surface area in the form of powders or in the form of disperse layers on the substrate [1,2]. Different processing parameters can change chemical composition, crystallite size and morphology of the deposit, which significantly alter its physical and chemical properties [1]. High surface area porous materials attract great interest due to their wide range of possible applications in electrocatalysis [3-6]. Still, the rate of electrochemical reactions is not related directly in a simple way to the surface area of the electrode since in the case of porous materials the active surface and therefore the reaction rate can be even reduced by a decrease in accessible surface area. Therefore, an advanced porous electrode should have both, micro- and nanoscaled features [3]. Recently, the production of multiscale porous materials with nanoramified dendritic walls was achieved by dynamic hydrogen templating [7]. During electrodeposition of metals at high current densities hydrogen bubbles are formed in a cathodic side reaction and serve as a template for multiscale porous structures allowing the synthesis of bulk foams without introducing additional processing steps or use of hazardous chemicals. Silver [8] and gold [9] metal foam electrodes have been achieved by deposition directly on the electrode surface. Recently, we showed that CoNi dendritic alloys exhibit promising results as catalysts for oxygen evolution reaction that is of particular interest for electrochemical conversion and storage devices [10].

In this paper we report the synthesis of a multiscale open porous foam of NiCoFe and its excellent electrocatalytic performance. Oxidized FeCoNi ternary alloys have shown enhanced battery performances when used as anode in Li batteries [11]. The higher conductivity of cobalt oxy compounds in comparison to the nickel compounds leads to a better reversibility when used as positive electrode material for alkaline batteries [12]. The low thermal expansion coefficient of NiCoFe alloys allows applications as high temperature alloy [13]. It is the aim of the present work to synthesize a novel dendritic NiCoFe alloy foam electrode by dynamic hydrogen templating showing favorable features on multiple length scales: from micrometer pores to nanodendritic structures to nanograins with a high density of catalytic sites.

Experimental

The ternary alloy structures were prepared by electrodeposition on polycrystalline Ti cathodes at a constant current density of $j = 1\ \mathrm{A\,cm^{-2}}$ in ammonium sulfate-chloride solution (0.09 M $NiSO_4$+ 0.03 M $FeSO_4$+ 0.053 M $CoSO_4$+0.4 M H_3BO_3+0.28 M NH_4Cl, at pH=2 adjusted with HCl) [14], at room temperature without stirring, using a Jaissle potentiostat, IMP 83 PC-10. For the synthesis of NiCoFe structures, Ti was used as a cathode and Ti/RuO_2, TiO_2 was used as an anode. The electrolyte solutions were made from analytical grade chemicals and high purity water. All samples were carefully treated to prevent oxidation that can be caused by their high surface area exposed to oxygen and moisture in the air [15].

The polarization measurements were carried out by a computer controlled electrochemical system (PAR M 273 A) in a three-electrode compartment electrochemical cell at (298 ± 1) K with a sweep rate of 1 mV s^{-1}. For the correction of the iR drop, a current interrupt technique was used with a time of current interruption of 0.5 s. The working electrode was a Ti rod with a diameter of 2 mm embedded in a resin. A Pt-mesh with large surface was used as a counter electrode. The electrochemical characterization of the oxygen reduction/oxidation performance for the NiCoFe electrodes was done by linear sweep voltammetry (LSV) at a scan rate of 10 mV s^{-1} in 0.1 M KOH at pH= 12.6.

The determination of the phase content and the crystallite size were conducted by X-ray diffraction in Bragg-Brentano geometry. The evaluation was done by Rietveld refinement [16] using the TOPAS software. The morphology was analyzed with a scanning electron microscope (SEM) equipped with a field emission gun. The profile and roughness measurements were carried out from stereoscopic images using MeX software (Alicona). To analyze the foam structures in detail transmission electron microscopy (TEM) studies were carried out at 200 kV in a CM200 (Philips). TEM bright field images and diffraction patterns were recorded from pieces of the sample that were transferred to a carbon grid. To determine the crystallite size from the electron diffraction patterns, the peak analysis using selected area diffraction (PASAD) software was used [17].

Results and discussion

Figure 1 shows the results on the electrochemical behavior of NiCoFe with a polarization curve of the ternary alloy. For comparison the polarization curves of the pure metals Ni, Co and Fe were obtained with the same concentration of the respective metal ions present in the solution. It is characteristic for the iron group metals (Ni, Co and Fe) and their alloys that electrodeposition from an aqueous electrolyte is accompanied by intensive hydrogen evolution, which is caused by their negative standard electrode potentials relative to hydrogen [18]. Therefore, it is necessary to correct all polarization measurements for the iR drop in the electrolyte during the process [19,20]. The standard redox potentials of Ni^{2+}, Co^{2+}, Fe^{2+} and H^+ are −0.50, −0.52, −0.68 and −0.24 V vs. a saturated calomel electrode (SCE), respectively. The linear sweep exhibits some similarities. As indicated in Figure 1, the potential shows at the beginning a region (i) of rather linear dependence on the logarithm of the current density up to a current density of about $10^{-2.5}\ \mathrm{A\,cm^{-2}}$; this is followed by a region (ii) with almost no dependence of the potential on current density until a limiting current density of about $10^{-0.5}\ \mathrm{A\,cm^{-2}}$ is reached. Thereafter, in region (iii) the potential decreases strongly with increasing log j. The different regions are indicated for NiCoFe in Figure 1. Region (i) can be explained as mixed electron transfer and diffusion control of the metal reduction reaction coinciding with limited hydrogen evolution. Region (i) can be explained as electron transfer and region (ii) as mixed electron transfer and diffusion control of the metal reduction reaction coinciding with hydrogen evolution. Region (iii) is indicative of significant hydrogen evolution. The relative overpotentials for the hydrogen evolution reaction, after iR correction, at around 0.1 A cm^{-2} at this pH, increase from Co > Fe > Ni.

Figure 2 shows the structure and morphology of NiCoFe deposits obtained at different current densities. At a current density of 0.1 A cm^{-2} (sample A) a compact smooth

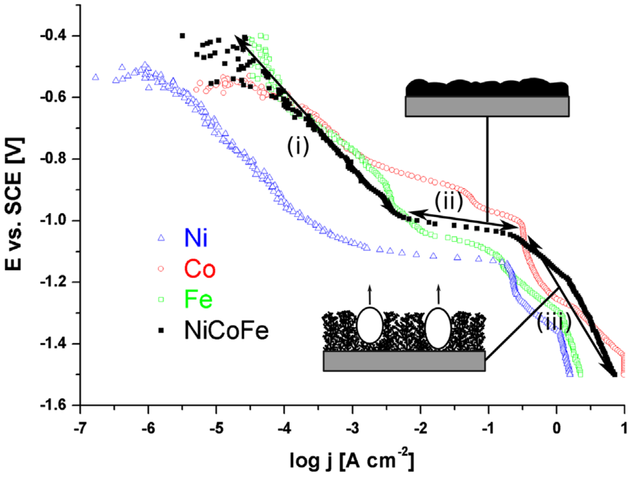


Figure 1 Linear sweep voltammograms for the electrodeposition of Ni, Co, Fe metal deposits and NiCoFe alloy deposits in ammonium sulfate-chloride solutions measured with an iR drop correction. In the case of NiCoFe, the different electrochemical regions are indicated with arrows marked (i), (ii) and (iii). Schematic representations of NiCoFe deposits obtained in region (ii) and (iii) at current densities of 0.1 and 1 A cm^{-2}, respectively, are shown.

deposit is formed (cf. Figure 2a). Only small protrusions are visible at higher magnification and the sample is completely dense (cf. insert Figure 2a). As shown in Figure 1 this current density represents the border between regions (ii) and (iii). Therefore mixed electron transfer and diffusion control is active leading to the formation of the smooth deposit. In contrast, at a current density of 1 A cm^{-2} (sample B) a 3D dendritic structure with open pores is obtained (Figure 2b). The pore walls have a finer morphology consisting of 'cauliflower-like' particles containing open multiscaled dendritic structures (as shown in the insert of Figure 2b). The pores and microstructure are a consequence of the vigorous hydrogen gas evolution and diffusion-limited metal deposition active in region (iii) as concluded from Figure 1. It should be noted that the morphology of the compact smooth deposit does not change when deposition time is increased until the same charge is passed compared to the dendritic foam structure ($t = 1800$ s).

The chemical composition was determined by energy dispersive X-ray spectroscopy yielding a composition of $Ni_{20}Co_{45}Fe_{35}$ in the case of the smooth deposit obtained at a current density of 0.1 A cm^{-2} (sample A). This indicates an anomalous co-deposition of the iron group elements [18] where the less noble metal is deposited preferentially to the nobler one. On the other hand in the case of the dendritic foam deposit obtained at a current density of 1 A cm^{-2} (sample B) a composition of $Ni_{50}Co_{30}Fe_{20}$, corresponding to that of the electrolyte is obtained. Intensive hydrogen evolution causes gas stirring, changing the mass transfer conditions in the double layer and hence the local electrolyte composition at the electrode surface. Under pure diffusion control the composition of the deposit is determined by the composition of the electrolyte.

Figure 2c shows the X-ray profiles corresponding to the deposits. In the case of the smooth deposit (sample A) broad peaks corresponding to a mixture of FCC and BCC structure

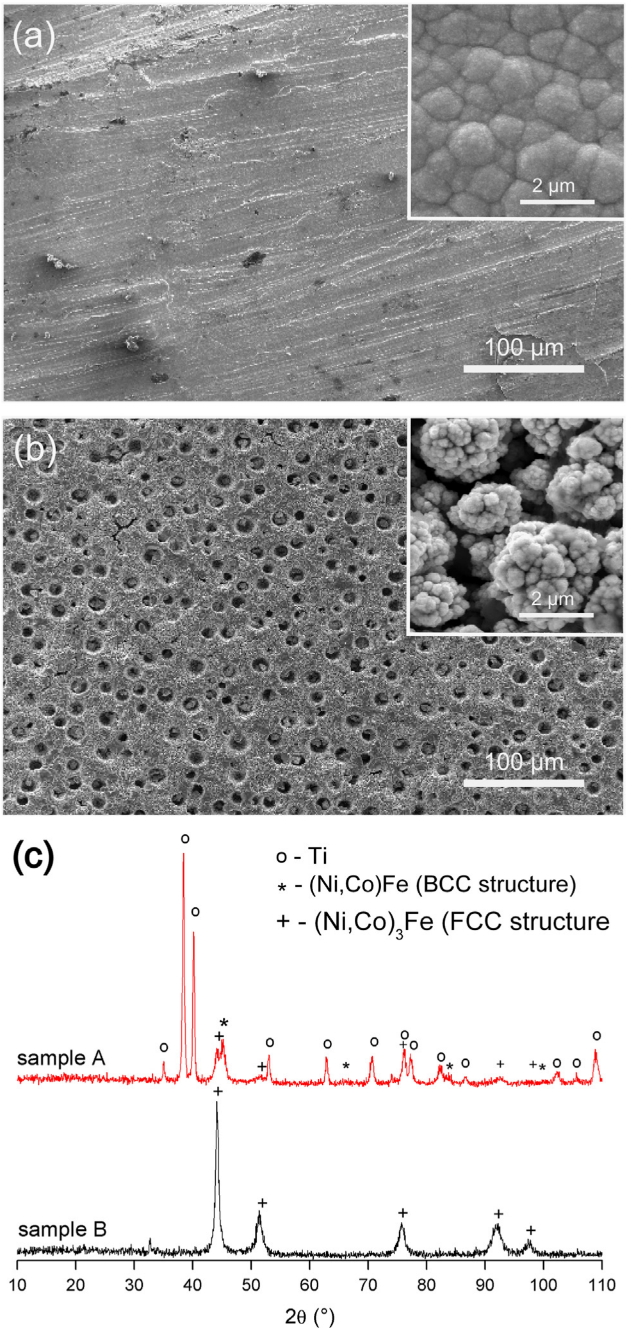


Figure 2 NiCoFe alloy deposits obtained by electrodeposition at different current densities on a Ti substrate (deposition time $t = 180$ s): (a) SEM image of the rather smooth deposit obtained at $j = 0.1$ A cm^{-2} characterized by a compact morphology; only at higher magnification soft hills are visible (sample A). (b) SEM image of a dendritic foam deposit obtained at $j = 1$ A cm^{-2} showing an open porous 'cauliflower-like' morphology (sample B). (c) Corresponding X-ray profiles; the smooth deposit (sample A) shows broad peaks resulting from a mixture of FCC and BCC structure of the nanocrystalline $Ni_{20}Co_{45}Fe_{35}$ deposit and sharp peaks from to the Ti substrate; the dendritic foam deposit (sample B) shows broad peaks resulting from a mixture of FCC and BCC structure of the nanocrystalline $Ni_{20}Co_{45}Fe_{35}$ deposit.

is observed. The BCC structure of (Ni, Co)Fe solid solution is expected from the phase diagram for the given composition

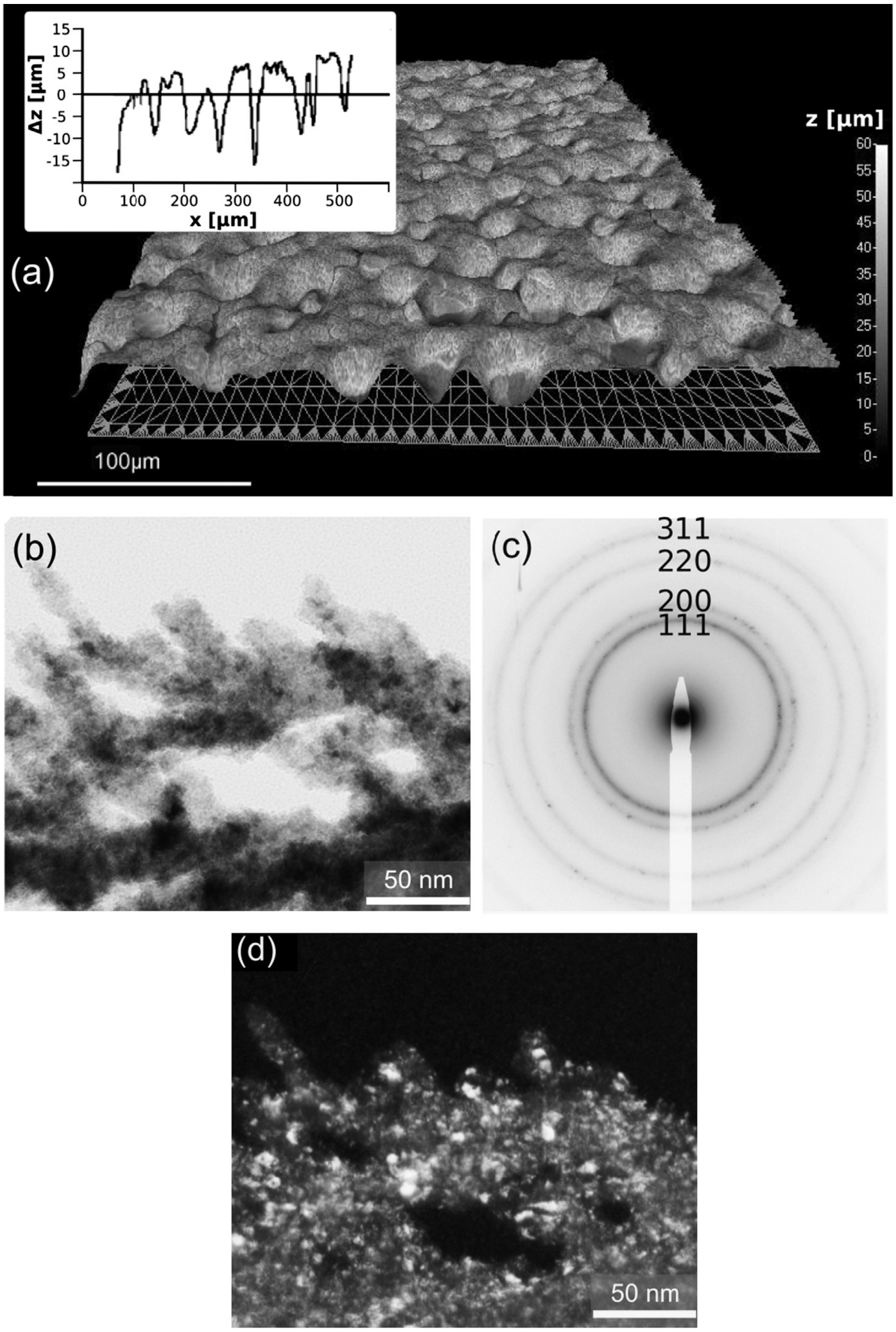


Figure 3 Open dendritic NiCoFe foam obtained by electrodeposition at a current density of $j = 1\ \mathrm{A\ cm^{-2}}$. (a) 3D SEM reconstruction of the surface showing the distribution of pores formed during hydrogen co-deposition. A roughness profile across the surface is shown as insert. (b) TEM bright-field image revealing a highly branched dendritic structure. The dendrites are very fine with branches down to 50 nm. (c) The corresponding TEM diffraction pattern shows FCC structure only. (d) TEM dark-field image of the same area as (b). The dendrites consist of a nanograined structure with crystallites smaller than 10 nm.

($Ni_{20}Co_{45}Fe_{35}$) [21]. In addition the reflections arising from the Ti substrate are visible because the deposit is very thin (around 1 µm). The dendritic foam deposit (sample B) shows peaks corresponding to the FCC structure of the $(Ni, Co)_3Fe$ solid solution in accordance with the significantly different composition obtained at the higher current density ($Ni_{50}Co_{30}Fe_{20}$). No reflections from the Ti substrate are visible because the deposit is thicker (around 20 µm). In the case of the smooth compact layers delimitation can occur during electrodeposition because of oxidation of Ti substrates. Nevertheless, Ti substrate represents an excellent choice for the deposition of the nanodendritic foam structure showing a uniform distribution of the deposit. The crystallite size was evaluated from the X-ray profiles by Rietveld refinement leading to an area weighted mean of 7.4 ± 1 and 6.5 ± 1 nm in the case of sample A and B, respectively. This can be correlated with the linear sweep voltammogram (cf. Figure 1). Deposition at a current density of 0.1 A cm^{-2} belongs to region (ii) with almost no dependence of the overpotential on current. Since from the nucleation theory, the crystallite size is mainly affected by the increase of overpotential [22], the crystallite size is not changed after reaching the plateau in the polarization diagram. The increase of the overpotential with increasing current after the plateau in region (iii) is connected with an increase in hydrogen bubble evolution only.

Figure 3 shows a detailed investigation of the dendritic foam deposit by methods of electron microscopy. The 3D SEM reconstruction of surface (Figure 3a) reveals pronounced circular depressions with about 20 μm diameter caused by the intensive gas bubble evolution. In addition a roughness on a smaller scale is encountered in the roughness profile shown as insert. Therefore to analyze the structure on an even finer length scale, a TEM investigation of the deposited FeCoNi foam was carried out. The resulting bright field image (cf. Figure 3b) reveals dendritic branches with sizes less than 50 nm containing nanocrystals smaller than 10 nm. The corresponding TEM diffraction pattern (cf. Figure 3c) is caused by a nanocrystalline FCC structure. The evaluation of diffraction patterns from different areas using the PASAD software [17] leads to the result that the deposit is homogenous in structure.

Recently, we investigated the morphology of NiCoFe powders obtained by electrodeposition. TEM methods yield the results that the particles have a highly branched dendritic structure extending from the micrometer scale to the nanoscale. Since the material is deposited far off the thermal equilibrium it contains a high density of stable defects such as grain boundaries and twin boundaries, as one nanograin contains about three twins [23]. All these defects provide active sites in the form of surface steps for electrochemical reactions [24]. Therefore, the achieved dendritic NiCoFe alloy foam provides in addition to the multiscaled high surface area also a high density of active sites.

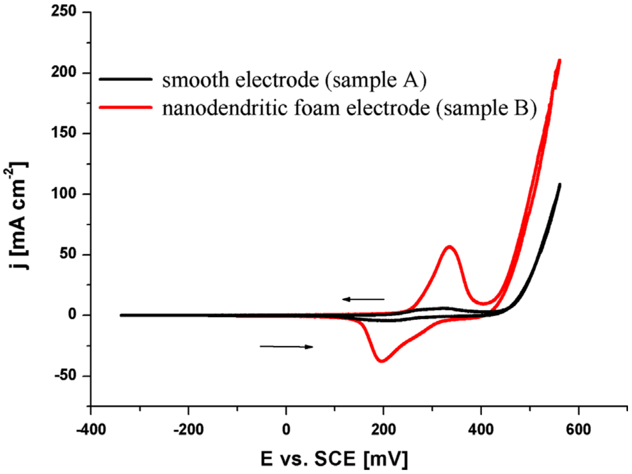


Figure 4 Cyclic voltammograms on smooth NiCoFe electrodes and dendritic NiCoFe foam electrodes recorded in 0.1 M KOH solution (scan rate of 10 mV s^{-1}). The nanodendritic foam electrode shows a significantly enhanced reaction rate attributed to the multiscale dendritic foam structure.

In Figure 4 cyclic voltammetry curves of both, the smooth electrode and the dendritic foam electrode are shown. The curves were recorded in a 0.1 M KOH solution at room temperature with a potential range from −400 mV to +600 mV vs. SCE at a sweep rate of 10 mV s^{-1}. The cyclic voltammograms show reversible redox processes; oxygen reduction in the cathodic region and oxidation of NiCoFe in the anodic region. The dendritic foam electrode demonstrates a significantly enhanced reaction rate when compared with the smooth electrode. Therefore the nanodendritic NiCoFe alloy foam is a promising candidate as bifunctional catalyst in alkaline solutions. The catalytic activity is enhanced for both, the cathodic reduction of oxygen and the anodic evolution of oxygen. In the case of fuel cells, the performance of a smooth electrode is limited by the significant anodic overpotential required for oxygen evolution due to the presence of an oxide layer that covers the entire surface [25,26]. The achieved dendritic NiCoFe alloy foam on contrary shows a good reversibility and a high activity in the cathodic region. This is linked to processes involving the redox reaction between the redox couple M^{III}/M^{II}. The reversibility of the electrocatalytic processes offers the possibility to use non-noble NiCoFe transition metals for the fast electron transfer reaction between the oxidized NiCoFe dendritic alloy in dilute alkaline media that are of considerable interest for practical applications.

For the dendritic foam electrode the oxygen evolution potential is slightly positively shifted as compared to the smooth electrode and shows a significantly increased rate. Integration of the peak in the anodic region from 250 mV to 400 mV vs. SCE gives a charge of 500 mC cm^{-2} for the dendritic foam electrode. The formation of $(Ni,Co,Fe)(OH)_2$, which is most probable at this pH, would require a charge of around 0.07 mC cm^{-2}. The enhancement in reaction rate due to the high surface area of the foam electrode can be expressed as an effective roughness factor indicating the effective surface over the geometrical area. In the present case a value of about 7000 is achieved that can be attributed to the multiscale dendritic foam structure plus taking into account in addition to the high surface area, the fact that the reaction rate is further enhanced by the presence of a high density of defects providing active sites.

Conclusion

In summary we demonstrated the excellent electrochemical features of nanodendritic NiCoFe foam. Its catalytic activity is strongly enhanced for both, the cathodic reduction of oxygen and the anodic evolution of oxygen and shows a good reversibility. Therefore it is a promising candidate as bifunctional catalyst in electrochemical conversion and storage devices. Ternary NiCoFe alloys were deposited at different current densities. At a current density of 0.1 A cm^{-2}, corresponding to mixed electron transfer and diffusion control, a smooth electrode is formed. In contrast to that during galvanostatic deposition at a high current density of 1 A cm^{-2} a multiscaled foam structure is achieved with pore sizes around 20 μm and nanodendritic walls. The dendritic branches are very fine with sizes less than 50 nm and consist of nanocrystals containing a high density of defects. The achieved dendritic NiCoFe foam electrodes show a significantly increased reaction rate for oxygen reaction when compared with the smooth NiCoFe electrode. The increase is ascribed to the multiscale 3D morphology and the defects formed during hydrogen template deposition. The resulting structure has a high surface area and a high density of active sites yielding a value of about 7000 for the effective roughness factor. In addition the composition of the achieved foam is in accordance to the chemical composition of the electrolyte, whereas the compact deposit obtained at a lower current density results in a distinct change of alloy composition content.

Acknowledgments

This research was supported by the research project "Bulk Nanostructured Materials" within the research focus "Material Science" of the University of Vienna and by the Austrian Science Fund (FWF): [S10403, P22440]. The work at CEST was supported within the COMET program by the Austrian Research Promotion Agency (FFG) and the government of Lower Austria.

References

[1] A. Marčić, M. Spasojević, L. Rafailović, V. Milovanović, L. Ribić-Zelenović, Materials Science Forum 453 (2004) 411.
[2] L.D. Rafailović, H.P. Karnthaler, T. Trišović, D.M. Minić, Materials Chemistry and Physics 120 (2010) 409.
[3] S. Cherevko, C. Chung, Electrochimica Acta 55 (2010) 6383.
[4] A. Kloke, C. Köhler, R. Gerwig, R. Zengerle, S. Kerzenmacher, Advanced Materials 24 (2012) 2916.
[5] J. Elias, M. Parlinska-Wojtan, R. Erni, C. Niederberger, F. Sauvage, M. Thevenin, J. Michler, L. Philippe, Nano Energy 1 (2012) 742.
[6] H.C. Shin, M.L. Liu, Advanced Functional Materials 15 (2005) 582.
[7] H. Shin, J. Dong, Advanced Materials 15 (2003) 1610.
[8] S. Cherevko, X. Xing, C. Chung, Electrochemistry Communications 12 (2010) 467.
[9] S. Cherevko, C. Chung, Electrochemistry Communications 13 (2011) 16.
[10] L.D. Rafailović, C. Gammer, C. Rentenberger, C. Kleber, A.H. Whitehead, B. Gollas, H.P. Karnthaler, Physical Chemistry, Chemical Physics 14 (2012) 972–980.
[11] G.F. Ortiz, J.L. Tirado, Electrochemistry Communications 13 (2011) 1427–1430.
[12] K.H. Kim, J.Y. Zheng, W. Shin., RSC Advances 2 (2012) 4759–4767.
[13] X.Z. Fu, Q.C. Xu, R.Z. Hu, B.X. Pan, J.D. Lin, D.W. Liao, Journal of Power Sources 164 (2007) 916–920.
[14] Y. Sverdlov, Y. Rosenberg, Y. Rozenberg, R. Zmood, R. Erlich, S. Natan, Y. Shacham-Diamand, Microelectronic Engineering 76 (2004) 258.
[15] M. Pavlovic, L. Pavlovic, I. Doroslovaki, N. Nikolic, Hydrometallurgy 73 (2004) 155.
[16] H. Rietveld, Journal of Applied Crystallography 2 (1969) 65.
[17] C. Gammer, C. Mangler, C. Rentenberger, H.P. Karnthaler, Scripta Materialia 63 (2010) 312.
[18] N. Zech, E. Podlaha, D. Landolt, Journal of the Electrochemical Society 146 (1999) 2886.
[19] V. Jović, B. Jović, M. Pavlović, Electrochimica Acta 51 (2006) 5468.
[20] L. Rafailović, D. Minić, H. Karnthaler, J. Wosik, T. Trisović, G. Nauer, Journal of the Electrochemical Society 157 (2010) 295.
[21] N. Nikolić, L. Pavlović, M. Pavlović, K. Popov, Electrochimica Acta 52 (2007) 8096.
[22] K. Popov, S. Djokić, B. Grgur, Fundamental Aspects of Electrometallurgy, Plenum Pub Corp, 2002.
[23] L.D. Rafailović, C. Gammer, C. Kleber, C. Rentenberger, P. Angerer, H.P. Karnthaler, Journal of Alloys and Compounds 543 (2012) 167–171.
[24] I. Kasatkin, P. Kurr, B. Kniep, A. Trunschke, R. Schlögl, Angewandte Chemie 119 (2007) 7465–7468.
[25] V. Bagotsky, Fuel Cells, Problems and solutions, Second edition, Wiley, 2011.
[26] N. Ramaswamy, S. Mukerjee, Advances in Physical Chemistry 491604 (2012) 1–17.

Lidija D. Rafailović graduated in Physical Chemistry at the University of Belgrade. She received her PhD in Physics as participant of the doctoral college "Experimental Materials Science - Nanostructured Materials" from the University of Vienna. Currently she holds a position as Senior researcher at the Center of Electrochemical Surface Technology. Her research interests include development of new electrode materials for energy storage and conversion, electrochemical synthesis of new carbon/metal materials and metallization of polymers.

Christoph Gammer obtained a diploma in mathematics from the University of Technology, Vienna and a master degree in Physics from the University of Vienna. He received his Ph.D. in Physics as participant of the doctoral college "Experimental Materials Science - Nanostructured Materials" from the University of Vienna. Currently he is working as a research fellow at the University of California, Berkeley. His research interests include transmission electron microscopy of nanocrystalline, amorphous and energy related materials.

Christian Rentenberger received his Ph.D. in Physics from the University of Vienna and his venia docendi in Materials Physics in the field of transmission electron microscopy of Intermetallics. He is currently Associate Professor at the University of Vienna. His research interests concern transmission electron microscopy of metastable, nanostructured and amorphous phases.

Tomislav Trišović graduated from the Faculty of Technology and Metallurgy in Belgrade and completed his MSc studies at the Centre for Multidisciplinary Studies of the University of Belgrade and Ph.D. degree at the Faculty of Technology and Metallurgy in Belgrade. Currently holds a position of Research Associate in the Institute of Technical Sciences of the Serbian Academy of Sciences and Arts. His fields of interest are electrochemical synthesis, industrial electrochemistry and electrochemical engineering.

Christoph Kleber received his Dipl-Ing. in Physical and Theoretical Chemistry from the University of Technology, Vienna and later his Ph.D. from the University of Technology, Vienna. He is currently scientific director of the Austrian Centre of Electrochemical Surface Technology in Wiener Neustadt. His main research interests are corrosion and in general the understanding of the structure/property relationships of materials.

Prof. Dr. H. Peter Karnthaler received his Ph.D. in physics from the University of Vienna. He is Prof. i.R. in Physics of Nanostructured Materials, University of Vienna, was head of the Institute of Materials Physics and president of the Austrian Society for Electron Microscopy. His recent research interests are: Investigations based on transmission electron microscopy of bulk nanostructured and amorphous alloys; energy related alloys; long range ordered intermetallic alloys; martensitic phase transitions; nanobiocrystals.

J Appl Electrochem (2009) 39:2521–2528
DOI 10.1007/s10800-009-9946-7

ORIGINAL PAPER

Citrate-based zinc–polyaniline secondary cell: part I: optimization of the citrate/chloride electrolyte

**B. Z. Jugović · T. Lj. Trišović · J. S. Stevanović ·
M. M. Gvozdenović · B. N. Grgur**

Received: 12 December 2008 / Accepted: 7 June 2009 / Published online: 19 June 2009

Abstract Electrochemical behavior of zinc and thin polyaniline (PANI) electrodes in citrate/chloride-contained electrolyte has been investigated by the means of electrolyte composition optimization. Electrolyte contained 0.8 M sodium citrate, 0.3 M ammonium chloride, and ~0.3 M zinc chloride has been found to be an optimum electrolyte for the further applications in the real zinc–polyaniline citrate/chloride-based secondary cell.

Keywords Polyaniline · Zinc · Batteries · Citrate · Chloride

1 Introduction

According to the three E′ criteria suggested by Rüetschi and Beck [1, 2], zinc–polyaniline (PANI) secondary cells have some potential advantages, in comparison with classical (protonic and aprotonic) cells, such as ecological acceptability, uses of water-based electrolytes, and relatively low manufacturing costs. The Zn | ammonium chloride, zinc chloride | PANI electrochemical system is one of the most investigated [3], and is based on the following half-cell reactions:

$$[\mathrm{PANI}]_n + ny\mathrm{Cl}^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} \left[\mathrm{PANI}^{y+}(\mathrm{Cl}^-)_y\right]_n + ny\mathrm{e} \quad \text{(Positive electrode)}, \tag{1}$$

where y is the doping degree, and

$$\mathrm{Zn}^{2+-} + 2\mathrm{e} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} \mathrm{Zn} \quad \text{(Negative electrode)}. \tag{2}$$

The reaction during charge/discharge of the complete cell can be given as follows:

$$2[\mathrm{PANI}]_n + 2ny\mathrm{Cl}^- + ny\mathrm{Zn}^{2+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} 2\left[\mathrm{PANI}^{y+}(\mathrm{Cl}^-)_y\right]_n + ny\mathrm{Zn}. \tag{3}$$

Such system has been investigated by different authors [3–14]. It was concluded that zinc passivation and dendrite formation, as well as degradation of PANI at higher potentials are the main reasons why this system has not been commercialized till now.

In our previous articles [15, 16], it was shown that citrate/chloride-based electrolyte at pH ~5 has some potential advantages in comparison with pure chloride electrolyte. Due to the complexation of the free zinc ions, citrate anions produce negative shift of the open circuit potentials for more than 100 mV.

On the other hand, decrease of exchange current density and increase of deposition overpotential in chloride/citrate-contained electrolyte lower dendrite formation and probably zinc corrosion rate. In the cycling regime for the anodic potential limit of ~0.35 V (SCE), citrate/chloride electrolytes show better characteristic (higher specific capacity and Columbic efficiency of the PANI electrode) than the

B. Z. Jugović · T. Lj. Trišović
Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihailova 35, Belgrade, Serbia

J. S. Stevanović
ICTM, Institute of Electrochemistry, Njegoševa 12, Belgrade, Serbia

M. M. Gvozdenović · B. N. Grgur (✉)
Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11020 Belgrade, Serbia
e-mail: BNGrgur@tmf.bg.ac.rs

pure chloride electrolyte. Faster decrease of specific capacity in cycling regime for the anodic potential limits of 0.5 V (SCE) in citrate/chloride than in pure chloride electrolyte has been explained by higher hydrophilic effect of citrate anions. In citrate/chloride electrolyte, it seems that both anions are involved in doping of the PANI film, producing the broad peak. It was suggested that at the less positive potentials, doping proceeds with chloride, and at the more positive potentials with citrate anions, where faster degradation can occur [15].

In this article, we further investigated the behavior of the zinc and PANI electrode in citrate/chloride-contained electrolytes, mainly by the means of the electrolyte composition optimization, with the aim to obtain necessary data for preparation of the real cell, the characteristic of which will be given in the second part of this article.

2 Experimental

The working electrodes, zinc plate ($S = 2$ cm^2), and cylindrically shaped graphite inserted in Teflon holder ($S = 0.64$ cm^2) were mechanically polished with fine emery papers (2/0, 3/0, and 4/0, respectively) and then with polishing alumina (0.05 μm, Banner Scientific Ltd.) on the polishing cloths (Buehler Ltd.). After mechanical polishing, the traces of polishing alumina were removed from the electrode surface in an ultrasonic bath in ethanol during 5 min. For all the experiments, three-compartment electrochemical cells, with platinum foil ($S = 2$ cm^2) as a counter and saturated calomel electrode, $E_r = 0.243$ V (SHE), were used as a reference electrode at room temperature. The electrochemical measurements were carried out using Gammry PC3 and PAR 386 potentiostat/galvanostat controlled by a computer via interface.

Corrosion rate of the zinc electrode was investigated by measuring the mass loss of the polished pure zinc plate ($S = 8$ cm^2) after exposure for over 120 h in 200 ml of the investigated solution.

The zinc deposition efficiency was determined by measuring the mass difference of the polished copper substrate 2 × 2 cm ($S = 8$ cm^2) after zinc deposition, and by applying the Faraday's law. In all the cases, the total deposition charge was the same (50 mA h cm^{-2}). For the current density of 5 mA cm^{-2}, the zinc deposition/dissolution efficiency was determined by measuring the potentials. Micrographs of the zinc deposits at different current densities were obtained with an optical microscope (LEICA-DC 150) connected to the computer.

Polyaniline thin film electrode was obtained from the 1 M hydrochloric acid solution with the addition of 0.25 M aniline monomer (p.a. Merck, previously distilled in the argon atmosphere), at a constant current density of 2 mA cm^{-2} for 1080 s. The total polymerization charge was 0.6 mA h cm^{-2}. After polymerization, the electrode with the current density of 1 mA cm^{-2} was discharged, washed with bidistilled water, and transferred into the second electrochemical cell for further investigations.

All the electrolytes were prepared from p.a. grade chemicals (Merck) and bidistilled water. pH of all the investigated electrolytes was ~5, adjusted by 2 M sodium hydroxide, 1 M hydrochloric, or 1 M citric acid.

3 Results and discussion

3.1 Zinc electrode

3.1.1 Polarization and corrosion measurements

Figure 1 shows the polarization curves for the zinc deposition/dissolution reaction in the electrolytes containing 0.8 M Na-citrate and 0.3 M NH_4Cl with the addition of 0.05, 0.10, 0.30, and 0.50 M $ZnCl_2$ in comparison with the electrolyte containing 0.20 M $ZnCl_2$ + 0.50 M NH_4Cl, at pH ~5.

The zinc deposition/dissolution reaction of the chloride-contained electrolyte was characterized with an open circuit potential of −1 V (SCE) or −0.76 V (SHE), single anodic and cathodic Tafel slopes of ±33 mV dec^{-1}, and exchange current density of ~1.5 mA cm^{-2}. These values provoke the growth of dendrites during deposition reaction, as it is shown in Fig. 2 and explained in more details in Jugović et al. [15].

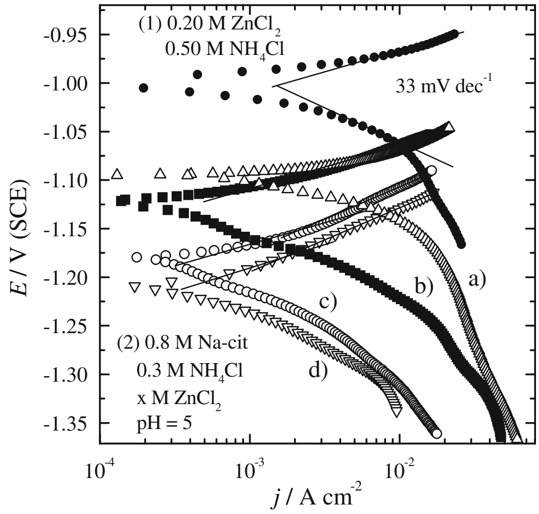


Fig. 1 IR-corrected polarization curve of the zinc electrode in the electrolytes containing (1) 0.5 M NH_4Cl + 0.2 M $ZnCl_2$ and (2) 0.8 M Na-citrate and 0.3 M NH_4Cl with the addition of (a) 0.5, (b) 0.3, (c) 0.1, and (d) 0.05 M $ZnCl_2$

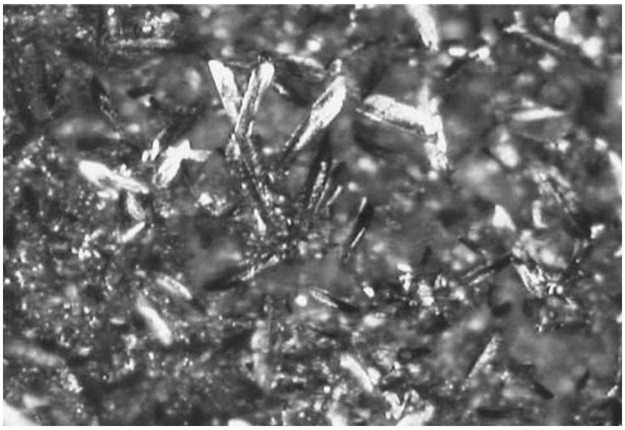


Fig. 2 Micrographs of the zinc deposits from 0.20 M $ZnCl_2$ + 0.50 M NH_4Cl. Deposition current density 3.5 mA cm^{-2}, deposition time 3 h, magnification 100×

Open circuit potential of the zinc electrode in citrate/chloride-contained electrolyte has more negative values in comparison with pure chloride electrolyte, which implies complexation of free zinc ions by citrate anions. For the same current density during polarization, it could be observed that anodic potentials (battery discharge) in citrate/chloride-contained electrolyte were significantly lower than that in the pure chloride electrolyte. This means that discharge voltage in citrate/chloride electrolyte will be higher. On the other hand, due to the more negative cathodic potentials (battery charge) in citrate/chloride electrolyte, charge voltage will be minimum 0.2 V higher than that in the pure chloride electrolyte.

Exchange current density was determined from the intercept of anodic Tafel line with open circuit potentials, since cathodic Tafel line was not well defined. In the separate experiments for all the citrate/chloride-contained electrolytes, the corrosion current density was determined as well. Determined values of equilibrium potentials, and exchange and corrosion current densities were summarized and shown in Table 1.

From the values given in Table 1, it can be observed that open circuit potential, and exchange and corrosion current densities decrease with decreasing zinc chloride concentration. Comparing the values of exchange and corrosion current densities, it can be concluded that the main reactions at the open circuit potential were deposition and dissolution reactions of zinc, while contribution of the corrosion was between 2% and 5%. From these results, it could be suggested that the low concentration of the zinc chloride will be beneficial from the anode point of view. However, on the other hand, under cathodic polarization, low concentration of the zinc chloride provokes relatively low value of the limiting current density. For example, in solution containing 0.05 M $ZnCl_2$, the limiting current density was ~10 mA cm^{-2}, while in the electrolyte containing 0.5 M $ZnCl_2$, the limiting current density was >50 mA cm^{-2}. Hence, based on the values of exchange, and limiting and corrosion current densities, as well as the value of the open circuit potential, the optimum zinc chloride concentration will be ~0.3 M.

Table 1 Determined values of open circuit potentials, and exchange and corrosion current densities of solid zinc electrode for different concentrations of zinc chloride in citrate/chloride-contained electrolytes

$c(ZnCl_2)$/M	E_r/V (SCE)	E_r/V (SHE)	j_0/mA cm^{-2}	j_{corr}/μA cm^{-2}
0.50	−1.094	−0.853	1.0	50
0.30	−1.122	−0.881	0.5	10
0.10	−1.180	−0.939	0.4	9
0.05	−1.209	−0.968	0.3	5

Polarization curve of the solid zinc electrode in the "optimum electrolyte" containing 0.8 M Na-citrate, 0.3 M NH_4Cl, and 0.3 M $ZnCl_2$ is shown in Fig. 3.

Anodic part of the polarization curve was characterized with the single Tafel slope of 60 mV dec^{-1} up to the current densities of 30 mA cm^{-2}. Cathodic part has few not well-defined waves, marked as (a–d), which could be connected with limiting currents. Hence, the value of cathodic Tafel line in this electrolyte cannot be determined. On the other hand, even the overpotential for the hydrogen evolution reaction on zinc is very high; some possibilities that hydrogen evolution could occur exist. At pH ~5, the concentration of the free hydrogen ion corresponds to a negligibly small diffusion limiting current density. However, in the presence of the protonated citrate species (such as $HCit^{2-}$) which could serve as a proton donor, the

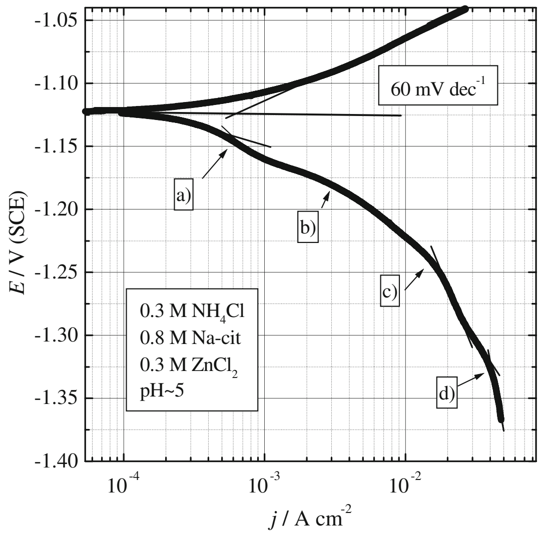


Fig. 3 IR-corrected polarization curve of the zinc electrode in the electrolyte containing 0.8 M Na-citrate, 0.3 M NH_4Cl, and 0.3 M $ZnCl_2$

limiting current density for hydrogen evolution could be significantly higher [17, 18].

For this reason, the influence of deposition current density and morphology on deposition current efficiency was investigated.

3.1.2 *Current efficiency and morphology of the zinc deposits*

Figure 4 shows determined current efficiency of zinc deposition reaction for the different deposition current densities. Copper substrate was applied to avoid possible oxidation of the zinc substrate which could affect the results, and to determine zinc deposition/dissolution efficiency. In all the cases, the total deposition charge was the same (50 mA h cm^{-2}).

Inset of Fig. 4 shows electrode potentials during zinc deposition. The electrode potentials were similar to the one obtained from polarization curves. For the same current density of 5 mA cm^{-2} dependence of the deposition and dissolution potentials of the zinc on copper over time was measured in order to obtain Columbic efficiency. It was observed that the Columbic efficiency for deposition/dissolution (charge/discharge) reaction was ~100%.

From Fig. 4, one can see that the current efficiency of zinc deposition reaction for low current densities of 2 mA cm^{-2} was relatively small (80%). By increasing the deposition current density to 5 mA cm^{-2}, the current efficiency increases up to 98%. Further increases of the current density provoked a small decrease of the current efficiency, from 97 to 94%.

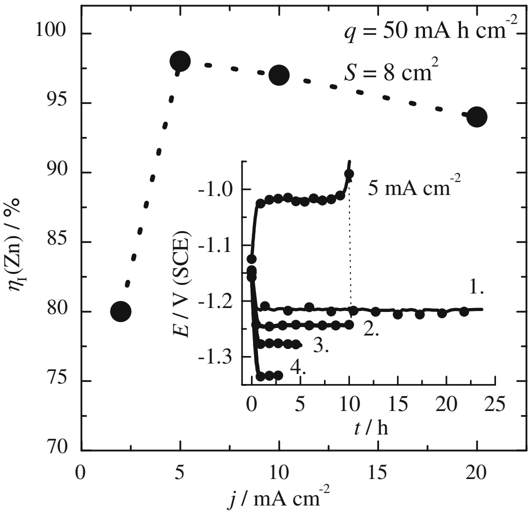


Fig. 4 Determined current efficiency of zinc deposition reaction on the copper electrode for the different deposition current densities. Inset: galvanostatic curves for zinc deposition at current densities of (1) 2, (2) 5, (3) 10, and (4) 20 mA cm^{-2} and for dissolution at a current density of 5 mA cm^{-2}

These results could be connected with the morphology of zinc deposits, shown in Fig. 5. A deposit obtained at a relatively small current density (2 mA cm^{-2}) was coarse and porous, with a lot of cavity induced by hydrogen evolution. Further increase of current density to 5 mA cm^{-2} and above, coarsens the deposit and decreases its porosity.

It should be noted that at the dendrite formation was not observed in any current density, even when the deposition charge was ~5 times higher than that in the pure chloride electrolyte (see Fig. 2).

3.1.3 *Mechanism of the zinc deposition reaction*

Considering the polarization measurements, deposition current efficiency, and morphology, the following mechanism for zinc deposition reaction could be suggested.

At pH ~5 in the presence of citrate in solution, zinc ion forms different types of complex with suggested species [19]:

$$Zn^{2+} + HCit^{2-} = ZnHCit \quad (pK_s = 3.0) \tag{4}$$

$$Zn^{2+} + Cit^{3-} = ZnCit^{-} \quad (pK_s = 4.8) \tag{5}$$

$$ZnCit^{-} + Cit^{3-} = ZnCit_2{}^{4-} \quad (pK_s = 1.7). \tag{6}$$

Due to the values of stability constants, it could be suggested that the main species in the solution was ZnCit^{-}, and the concentration of ZnHCit is considerably smaller, while the concentration of ZnCit$_2{}^{4-}$ and free zinc ions are rather low. Since deposition current density and potential depend on the concentration of the reacting species, decreasing the concentration provokes the decrease of the deposition current density, and at some point, the limiting current could be observed. Hence, the few waves in the cathodic part of the polarization curve (Fig. 3) could be assigned to the reduction of different species from the solution.

According to this analysis, it could be suggested that at relatively low current densities (~2 mA cm^{-2}), simultaneous deposition of zinc (~80%) from less stable complex or free zinc ion and hydrogen evolution (~20%) from protonated citrate species occurred, for example, via the following reactions:

$$2HCit^{2-} + 2e = H_2 + 2Cit^{3-} \tag{7}$$

$$Zn^{2+} + 2e = Zn \tag{8}$$

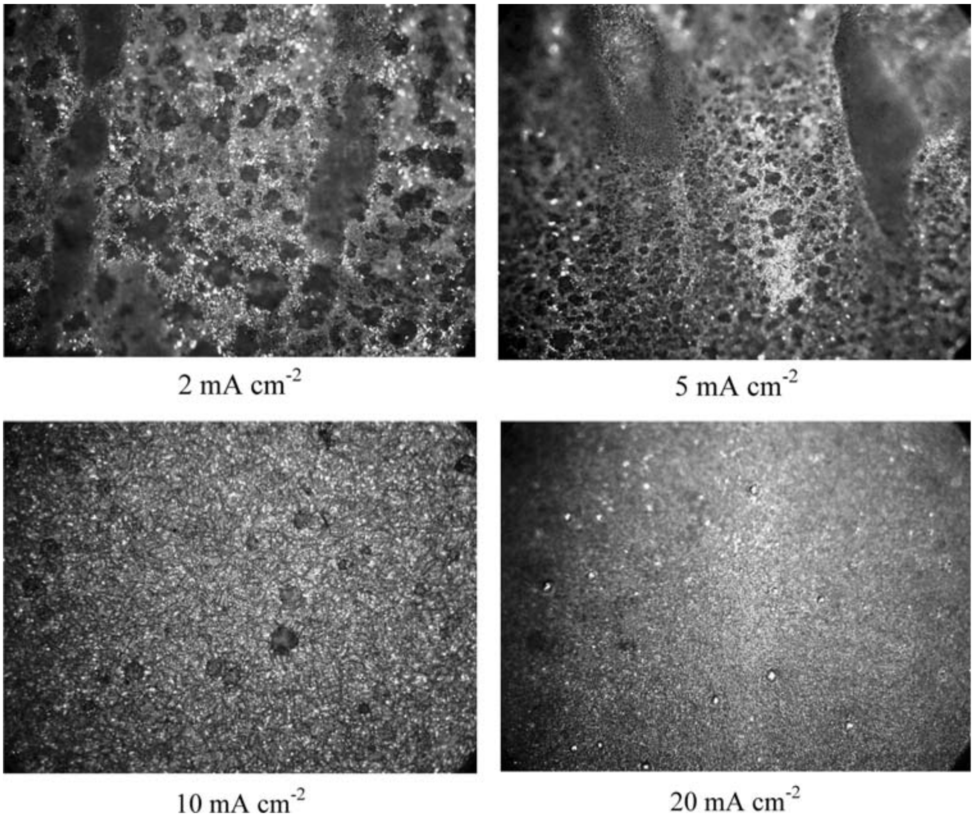
$$ZnCit_2{}^{4-} + 2e = Zn + 2Cit^{3-}. \tag{9}$$

Further increase of the current density (~5–15 mA cm^{-2}) leads to increases of the zinc deposition rate from more stable complex forms, such as

$$ZnHCit + 2e = Zn + HCit^{2-}, \tag{10}$$

or more probably,

Fig. 5 Micrographs of the zinc deposits for different current densities in citrate/chloride-contained electrolyte, magnification 100×


2 mA cm^{-2} 5 mA cm^{-2}
10 mA cm^{-2} 20 mA cm^{-2}

$$\mathrm{ZnCit^- + 2e = Zn + Cit^{3-}}. \qquad (11)$$

At the same time, the hydrogen evolution rate from protonated citrate species, which is now under the domination of limiting current, tends to much lower potentials, and practically does not affect the current efficiency. For the current density of 20 mA cm^{-2} and above, due to the negative potentials, the possibilities of hydrogen evolution from water molecule now exists, which influence further decrease of the zinc deposition current efficiency.

Considering the presented analysis, it could be suggested that some optimum zinc deposition current densities (battery charge) lie in the range of ~5–15 mA cm^{-2}. On the other hand, any anodic current density (battery discharge) in the range of 0.5 up to 30 mA cm^{-2} could be applied.

3.2 Polyaniline electrode

On the basis of determined "optimum composition of the electrolyte" for the zinc electrode, the electrochemical behavior of PANI electrode in the same electrolyte was investigated. Figure 6 shows galvanostatic curve of the aniline polymerization from the solution containing 1 M HCl and 0.25 M aniline monomer on graphite electrode at a current density of 2 mA cm^{-2} with a polymerization charge of 0.6 mA h cm^{-2}. Polymerization starts at the potential of ~0.6 V and proceeds in the potential range between 0.72 and 0.68 V.

After polymerization, electrode with 1 mA cm^{-2} was discharged, washed with bidistilled water, and transferred into the three-compartment electrochemical cell with chloride/citrate electrolyte. After transfer, the electrode

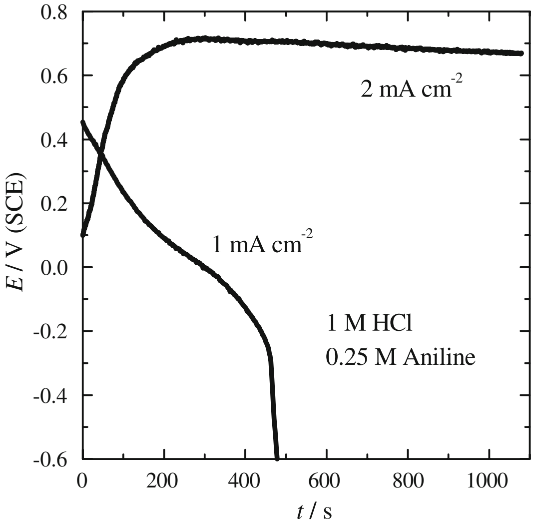


Fig. 6 Galvanostatic curves (2 mA cm^{-2}) for the aniline polymerization and discharge (1 mA cm^{-2}) in the solution containing 1 M HCl and 0.25 M aniline on graphite electrode

was conditioned at a potential of −0.6 V for 600 s to be completely discharged.

Figure 7 shows typical charge/discharge curves of PANI electrode for the different current densities. The potentials were limited to 0.35 V for charge and to –0.3 V for discharge. Charge of the discharged PANI electrode starts in the potential range between ∼−0.1 and ∼0.02 V depending on the applied current density. Potential increases practically linearly up to 0.35 V. Discharge of the electrode occurred in the potential range between ∼0.3 and ∼0.2 V with an average discharge potential of ∼0 V. For the potentials more negative than −0.2 V, diffusion limitations provoke the sharp decrease of the potentials.

Times of charge/discharge for different current densities determined from Fig. 7 are shown in Fig. 8. Calculated Columbic efficiency for the charge/discharge, shown in the inset of Fig. 8, was affected with the applied current density.

Assuming the limitations of anion diffusion through polymer film, it was possible to extrapolate the maximum electrode capacity by plotting the reciprocal square root values of the determined electrode capacity (shown in the inset of Fig. 9) with applied current densities. As it can be seen in Fig. 9, the determined maximum electrode capacity (q_0) of PANI electrode was ∼0.15 mA h cm^{-2}. On the other hand, some operating electrode capacity was in the range of 0.08–0.13 mA h cm^{-2} depending on the applied current density. All the investigated current densities (0.75–3 mA cm^{-2}) could be applied, but lower values will be favorable due to the higher capacity and Columbic efficiency.

Charge/discharge curves at a constant current density of 1 mA cm^{-2} versus the cycle number were shown in Fig. 10. The cycling potentials were limited to 0.35 V for charging and to −0.6 V for discharging. As it can be observed during the twenty cycles, the electrode capacity practically has a constant value without degradation. The same could be concluded from the cyclic voltammograms, shown in the inset of Fig. 10, since before the first and after twenty cycles, there were no changes in the shape of the voltammograms.

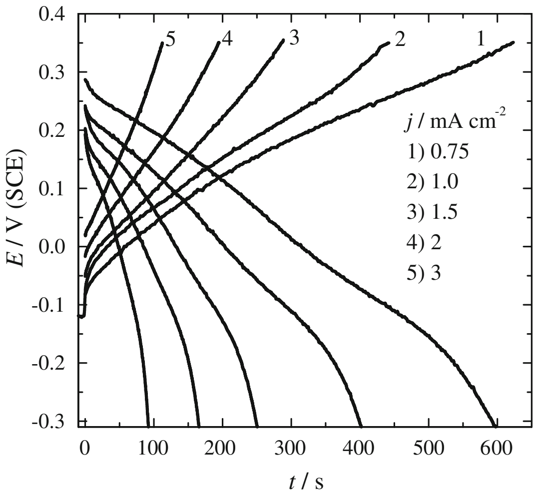


Fig. 7 Charge/discharge curve of the PANI electrode in citrate/chloride electrolyte for different current densities (marked in figure)

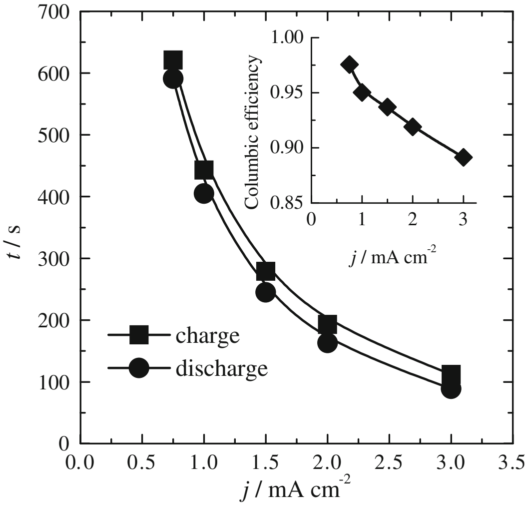


Fig. 8 Times of charge/discharge reaction determined for different current densities. Inset: dependence of columbic efficiency during charge/discharge on the applied current density

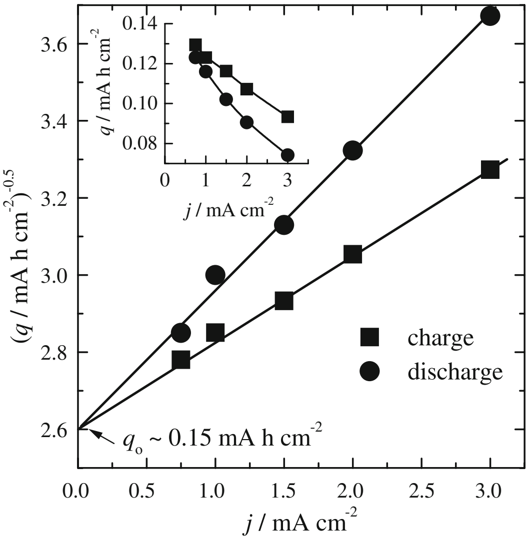


Fig. 9 Dependence of the reciprocal square root values of the electrode capacity (shown in the inset) on applied current densities

3.3 Possible characteristics of the real cell

Considering the above presented results for the zinc and PANI electrode in the optimum composition of the electrolyte, the possible electrochemical characteristics of

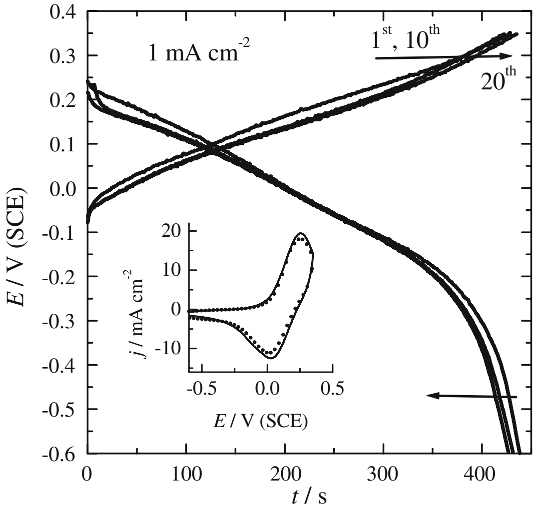


Fig. 10 Charge/discharge curve at a constant current density (1 mA cm^{-2}) versus cycle number in citrate/chloride electrolyte for the anodic potential limit of 0.35 V. Inset: cyclic voltammograms (v = 20 mV s^{-1}) of PANI electrode before first (—) and after twenty cycles (·····)

Zn|PANI secondary cell necessary for the cell optimization was discussed and simulated.

The Zn | 0.8 M Na-citrate, 0.3 M NH$_4$Cl, and 0.3 M ZnCl$_2$ | PANI electrochemical system will be mainly based on the following half-cell reactions:

$$[\mathrm{PANI}]_n + ny\mathrm{Cl}^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} \left[\mathrm{PANI}^{y+}(\mathrm{Cl}^-)_y\right]_n + nye \qquad (12)$$

(Positive electrode),

where y is doping degree, and

$$\mathrm{ZnCit}^- + 2\mathrm{e} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} \mathrm{Zn} + \mathrm{Cit}^{3-} \quad \text{(Negative electrode)}. \qquad (13)$$

The reactions during charge/discharge of the complete cell will be as follows:

$$2[\mathrm{PANI}]_n + 2ny\mathrm{Cl}^- + ny\mathrm{ZnCit}^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} 2\left[\mathrm{PANI}^{y+}(\mathrm{Cl}^-)_y\right]_n + ny\mathrm{Zn} + ny\mathrm{Cit}^{3-} \qquad (14)$$

The citrate anion was not considered as a doping anion for the PANI electrode during charge, because it was suggested that at less positive potentials, doping proceeds with chloride and at the more positive potentials (>0.35 V) with citrate anions, where faster degradation could occur [15].

It should be noted that the cell has to be formed in the discharged state.

For the given optimum composition of the electrolyte, the operating current densities will be in the range of ~0.75–3 mA cm^{-2} for the PANI electrode and 5–15 mA cm^{-2} for the zinc electrode. Due to the differences in the current densities, the area of PANI electrode should be at least five times higher than that for the zinc plate electrode. On that manner, Fig. 11 shows the simulation of charge/discharge curve with possible errors, for the complete Zn|PANI cell in chloride/citrate electrolyte for the current density of 1 mA cm^{-2} for PANI and 5 mA cm^{-2} for the zinc electrode. Data were extrapolated from Figs. 4 and 10, and simulation was done according to the procedure given in [20].

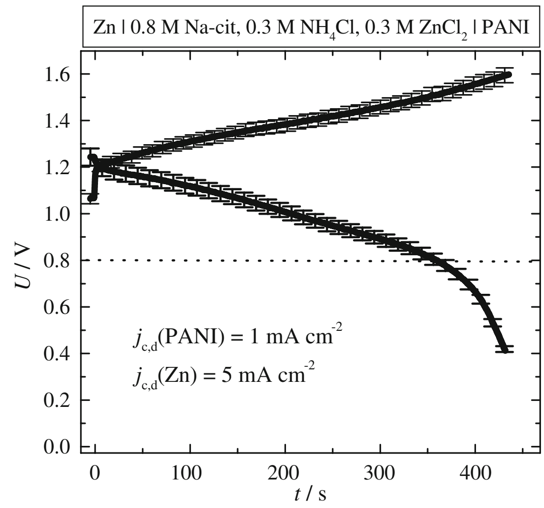


Fig. 11 Simulation of the possible charge/discharge characteristic of Zn|PANI cell in citrate/chloride-contained electrolyte

As it can be seen from Fig. 11, charge of the cell will occur in the voltage range between ~1.05 and ~1.62 V. After charge, the open circuit voltage will be ~1.25 V. Discharge will occur at the voltage range between 1.2 and ~0.4 V, with the most of the capacity (~85%) delivered above 0.8 V.

4 Conclusion

By investigating the polarization characteristic of the zinc deposition/dissolution reaction and corrosion rate from electrolytes containing 0.8 M sodium citrate, 0.3 M ammonium chloride, and different concentrations of zinc chloride (0.05–0.5 M), it was suggested that there will be some optimum electrolyte composition with ~0.3 M of zinc chloride.

Based on the determined deposition current efficiency and morphology of zinc deposits, it was suggested that some optimum deposition (charge) current density will be in the range of ~5–15 mA cm^{-2}.

In the optimum electrolyte, PANI electrode shows satisfactory characteristics for potential application as a positive electrode in the Zn|PANI secondary cell. Operating electrode capacity in the range of 0.8 to 0.13 mA h cm^{-2} depending on the applied current density (0.75–3 mA cm^{-2}) was determined. All the investigated current densities could be applied, but lower values will be favorable due to the higher electrode capacity and Columbic efficiency.

According to the differences in the electrodes optimum current densities, the area of the PANI electrode should be at least five times higher than that for the zinc electrode.

By the simulation of the charge/discharge characteristic of the real cell, it was suggested that charge will occur in the voltage range between ~1 and ~1.6 V. After charge, the open circuit voltage will be ~1.25 V, and discharge will occur in the voltage range between 1.2 and ~0.4 V, with the most of the capacity (~85%) delivered above 0.8 V.

Acknowledgment This study is financially supported by the Ministry of Science and Environmental Protection, Republic of Serbia, contract No. 142044.

References

1. Rüetschi P (1993) J Power Sourc 42:1
2. Beck F, Rüetschi P (2000) Electrochim Acta 45:2467
3. Novák P, Müller K, Santhanam KSV, Haas O (1997) Chem Rev 97:207
4. Kaya M, Kitani A, Sasaki K (1984) Denki Kagaku 52:847
5. Kitani A, Kaya M, Sasaki K (1986) J Elecrochem Soc 133:1069
6. Sima M, Visan T, Buda M (1995) J Power Sourc 56:133
7. Mirmohseni A, Solhjo R (2003) Eur Polym J 39:219
8. Kan J, Xue H, Mu S (1998) J Power Sourc 74:113
9. Shaolin Mu (2004) Synth Metals 143:269
10. Mengoli G, Musiani MM, Pletcher D, Valcher S (1987) J Appl Electrochem 17:515
11. Rahmanifar MS, Mousavi MF, Shamsipur M, Ghaemia M (2004) J Power Sourc 132:296
12. Rahmanifar MS, Mousavi MF, Shamsipur M, Heli H (2005) Synth Metals 155:480
13. Ghanbari K, Mousavi MF, Shamsipur M, Karami H (2007) J Power Sourc 170:513
14. Xinsheng W, Xin J, Dawei GU, Linjiang S (2006) Rare Metals 25:67
15. Jugović BZ, Trišović TLj, Stevanović JS, Maksimović MD, Grgur BN (2006) Electrochim Acta 51:6268
16. Jugović BZ, Trišović TLj, Stevanović JS, Maksimović MD, Grgur BN (2006) J Power Sourc 160:1447
17. Marinović V, Despić AR (1997) J Electroanal Chem 431:127
18. Stanković S, Grgur B, Krstajić N, Vojnović M (2003) J Electroanal Chem 549:37
19. Berthon G, May PM, Williams DR (1978) J Chem Soc Dalton Trans 1433
20. Grgur BN, Ristić V, Gvozdenović MM, Maksimović MD, Jugović BZ (2008) J Power Sourc 180(1):635

M 23

ALI RAMADAN ELKAIS[1]
MILICA M GVOZDENOVIĆ[1]
BRANIMIR Z. JUGOVIĆ[2]
TOMISLAV LJ. TRIŠOVIĆ[2]
MIODRAG M. MAKSIMOVIĆ[1]
BRANIMIR N. GRGUR[1]

[1]Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija
[2]Institut tehničkih nauka Srpske akademije nauka i umetnosti, Beograd, Srbija

NAUČNI RAD

UDK 678.652:620.1/.2:669

DOI: 10.2298/HEMIND100901069E

SINTEZA I KOROZIONO PONAŠANJE POLIANILINA NA MEKOM ČELIKU, BAKRU I ALUMINIJUMU IZ BENZOATNIH RASTVORA

U radu je ispitivana elektrohemijska sinteza polianilina (PANI) na mekom čeliku, aluminijumu i bakru iz rastvora natrijum-benzoata i monomera anilina. Ustanovljeno je da se tanki, dobro adherentni, filmovi polianilina mogu formirati na svim ispitivanim metalima pri anodnim gustinama struja od 0,5–1,5 mA cm^{-2}*. Ispitivano je koroziono ponašanje metala sa prevlakom polianilina u rastvoru 0,5 mol dm*$^{-3}$ *NaCl (3%). Ustanovljeno je da ove prevlake pružaju korozionu zaštitu svim ispitivanim metalima u datoj korozionoj sredini.*

Primena filmova elektroprovodnih polimera kao jednog od načina aktivne zaštite metala od korozije predstavlja novi vid zaštite baziran na potpunoj ili delimičnoj zameni katodnih reakcija korozije, redukcije kiseonika (u atmosferi odnosno kiselim, neutralnim i alkalnim rastvorima) ili vodoničnih jona (u kiseloj sredini) katodnom reakcijom redukcije (dedopovanja) elektroprovodnog polimera [1–3]:

$$\mathrm{M{-}[EP^{y+}\,(A^{m-})_{y}]_{\mathit{n}}} + ny\mathrm{e^{-}} \longrightarrow \mathrm{M{-}[EP]_{\mathit{n}}} + ny\mathrm{A^{m-}} \qquad (1)$$

gde je EP elektroprovodni polimer, A anjon (dopant), a y stepen dopovanja, uz odgovarajuću reakciju anodnog rastvaranja metala:

$$\mathrm{M} \longrightarrow \mathrm{M}^{m+} + m\mathrm{e}^{-} \qquad (2)$$

Za razliku od klasičnih premaza, kod prevlaka na bazi elektroprovodnih polimera tokom vremena dolazi do povećanja otpornosti filma (usled dedopovanja, odnosno otpuštanja anjona iz elektroprovodnog polimera) i povećanja stepena zaštite od korozije [2,3].

Osnovni problem pri elektrohemijskom dobijanju filmova elektroprovodnih polimera na metalima predstavlja visok potencijal elektropolimerizacije od približno 0,7 do i preko 1 V, što uslovljava intenzivno rastvaranje metala. Iz tog razloga, pri sintezi se moraju koristiti rastvori elektrolita koji pasiviraju metal, čime se umanjuje rastvaranje, ali pri tome formirani film ne sme imati izolatorska svojstva čime bi se sprečilo taloženje elektroprovodnog polimera. Jedan takav primer je oksalna kiselina u čijim rastvorima su dobijene zadovoljavajuće karakteristike filmova polipirola ali uz znatno rastvaranje čelika u početnom periodu taloženja (takozvani indukcioni period) [2–5]. Polianilin, sa druge strane, predstavlja izazovan materijal zbog znatno niže cene polazne sirovine (monomera anilin) od pirola. Camaleta je u seriji radova [6-8] ispitivao uslove taloženja polianilina na čeliku iz rastvora para-toluensulfonske kiseline, oksalne kiseline, kao i litijum-perhlorata. Iz svih rastvora dobijena je prevlaka, ali uz primetno rastvaranje čelika u početnom periodu polimerizacije.

U prethodnim radovima, ustanovljeno je da se tanke prevlake, od nekoliko μm polianilina mogu dobiti iz rasvora natrijum-benzoata na mekom čeliku, kao podsloja za kataforetsko nanošenje epoksidnih prevlaka [9]. Ovakva kombinacija je pokazala neuobičajeno poboljšanje korozionih karakteristika sistema u odnosu na klasične kataforetske prevlake u kiselim i neutralnim rastvorima [10,11].

Cilj ovoga rada je da se ispitaju uslovi elektropolimerizacije tankih filmova polianilina iz rastvora natrijum-benzoata i korozione karakteristike na čeliku, aluminijumu i bakru kao jednih od najznačajnijih konstrukcionih materijala.

EKSPERIMENTALNI DEO

Elektrohemijska sinteza polianilina ispitivana je u 0,5 M natrijum-benzoata (p.a. Merck) uz dodatak anilina (predhodno destilisanog u atmosferi argona) koncentracije 0,1 M. Svi eksperimenti su urađeni u trodelnoj staklenoj elektrohemijskoj ćeliji zapremine 150 cm^3 u prisustvu vazduha. Radne elektrode su bile od mekog čelika Č1212, aluminijuma i bakra (p.a. čistoće). Korišćene su elektrode dimenzija 1×1 cm sa ukupnom površinom od 2 cm^2. Kontra elektroda je bila mrežica od platine površine oko 5 cm^2, a referentna elektroda je bila zasićena kalomelova elektroda. Eksperimentalna debljina filma polianilina je procenjena merenjem mase uzoraka pre i posle elektropolimerizacije. Koroziono ponašanje metala sa prevlakom polianilina je ispitivano u 3%

Autor za prepisku: B.N. Grgur, Tehnološko-metalurški fakultet, Karnegijeva 4, 11120 Beograd, Srbija.
E-pošta: bngrgur@tmf.bg.ac.rs
Rad primljen: 1. septembar 2010.
Rad prihvaćen: 17. novembar 2010.

rastvoru (0,5 M) NaCl snimanjem polarizacionih krivih. Temperatura elektrolita u svim eksperimentima je bila sobna 22±3 °C

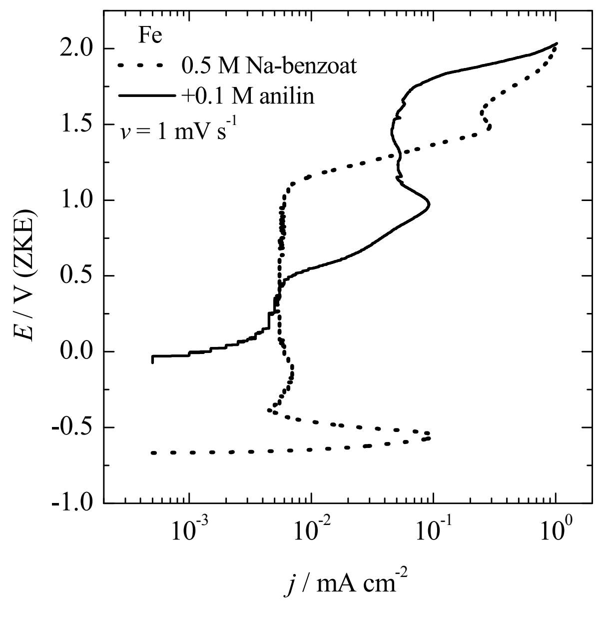
U svim eksperimentima je korišćen potenciostat/ /galvanostat PAR M273 u interaktivnoj vezi sa računarom.

REZULTATI I DISKUSIJA

Sinteza polianilina na mekom čeliku, aluminijumu i bakru

Sinteza polianilina na mekom čeliku

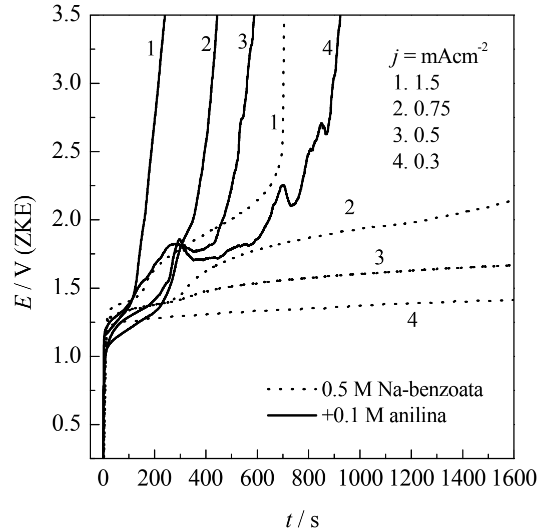
Na slici 1 prikazane su anodne polarizacione krive mekog čelika u rasvoru natrijum-benzoata i uz dodatak anilina počevši od korozionog potencijala do vidljivog izdvajanja kiseonika. Anodna polarizaciona kriva u rastvoru natrijum-benzoata ima tipičan izgled pasivacione krive za metale.



Slika 1. Anodne polarizacine krive za meki čelik u rastvoru 0,5 M natrijum-benzoata i uz dodatak 0,1 M anilina.
Figure 1. Anodic polarization curves for mild steel in 0.5 M sodium benzoate and with addition of 0.1 M aniline.

Početak pasivacije u 0,5 M rastvoru natrijum-benzoata odigrava se pri potencijalima od ~ –0,500 V (ZKE). Gustina struje početka pasivacije je iznosila 0,09 mA cm^{-2}, dok je srednja vrednost gustine struje pasivne oblasti iznosi oko 5 μA cm^{-2}. U prisustvu anilina korozioni potencijal se pomera ka pozitivnijim vrednostima za skoro 0,7 V. To bi moglo da ukaže da monomer anilina deluje kao inhibitor korozije u ispitivanom rastvoru. Elektropolimerizacija anilina se odigrava u oblasti potencijala od 0,4 do ~1,7 V.

Na slici 2 prikazane su galvanostatske krive rastvaranja mekog čelika i elektropolimerizacije anilina pri različitim gustinama struja taloženja.



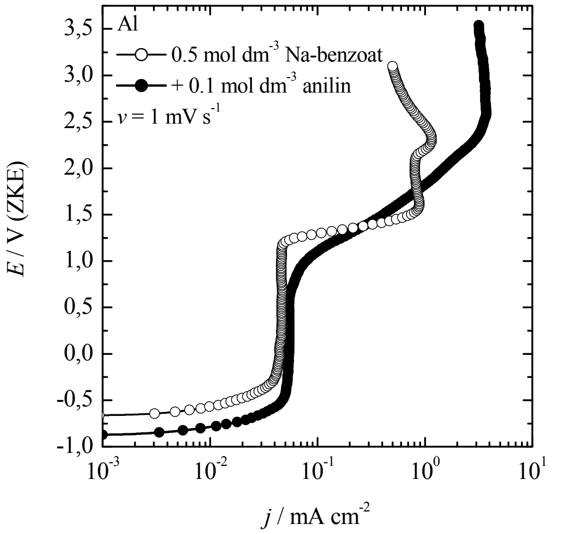
Slika 2. Galvanostatske krive mekog čelika u rastvoru 0,5 M natrijum-benzoata (tačkaste linije) i u rastvoru 0,5 M natrijum-benzoata i 0,1 M anilina (pune linije) pri različitim gustinama struja.
Figure 2. Galvanostatic curve of the mild steel in 0.5 M sodium benzoate (dotted line) and in 0.5 M sodium benzoate and 0.1 M aniline (full line) for different current densities.

Sa slike se može videti da ne postoji indukcioni period, odnosno da ne dolazi do rastvaranja gvožđa pre polimerizacije anilina. Za razliku od taloženja polipirola iz oksalatnih rastvora [1–3] gde ne dolazi do porasta potencijala tokom vremena, iz rastvora na bazi Na-benzoata i anilina potencijal formiranja polianilina je znatno viši i iznosi u početnom periodu oko 1,2 V. Nakon početnog perioda dolazi do blagog povećanja potencijala što je praćeno prekrivanjem slobodne površine mekog čelika prevlakom polianilina. Nakon što je celokupna površina prekrivena prevlakom polianilina, što je ustanovljeno vizualnim posmatranjem, dolazi do naglog porasta potencijala i do vidljivog izdvajanja kiseonika. Ovo je verovatno posledica male provodljivosti formiranog filma gvožđe-benzoat-polianilin i znatnog usporavanja dalje polimerizacije anilina na već formiranom filmu. Da bi se izbegla visoka preoksidacija filma svi uzorci predviđeni za koroziona ispitivanja su taloženi sa gustinom struje od 1,5 mA cm^{-2} do potencijala od 3 V.

Sinteza polianilina na aluminijumu

Na slici 3 prikazane su anodne polarizacione krive aluminijuma u 0,5 M natrijum-benzoata i uz dodatak 0,1 M anilina.

Korozioni potencijal bez anilina je iznosio –0,66 V, a pri dodatku anilina, za razliku od mekog čelika, negativirao se za ~200 mV (–0,87 V). U osnovnom rastvoru natrijum-benzoata nije primećena tipična pasivaciona kriva za metale. Pri potencijalima između – 0,3 do 1,3 V opažen je plato sa vrednošću gustine struje od oko 40 μA cm^{-2} koji se može pripisati formiranju poroznog hidratisanog filma aluminijum-oksida. Pri višim potencijalima od 1,3 V opažaju se još dva platoa sa gustinama struje od ~80 μA cm^{-2}, koji su verovatno posledica transformacija u hidratisanom oksidnom sloju. Pri dodatku monomera anilina, polimerizacija započinje pri potencijalu od oko 0,7 V, a polarizaciona kriva pokazuje karakteristike slične taloženju metala. Granična gustina struje difuzije iznosila je oko 4 mA cm^{-2}.



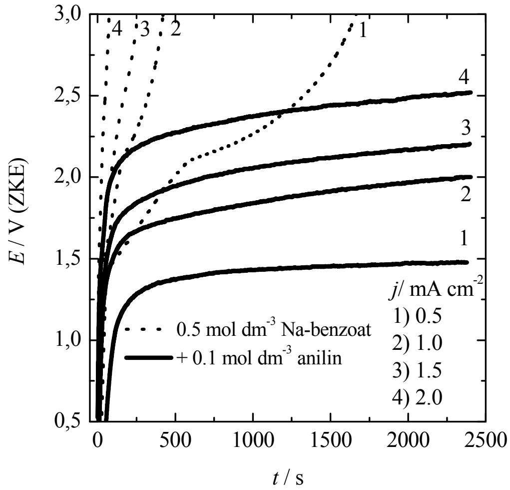
Slika 3. Anodne polarizacine krive aluminijuma u rastvoru 0,5 M natrijum-benzoata i uz dodatak 0,1 M anilina.
Figure 3. Anodic polarization curves of aluminum in 0.5 M sodium benzoate and with addition of 0.1 M aniline.

Na slici 4 prikazane su galvanostatske krive oksidacije aluminijuma u natrijum-benzoatu i uz dodatak anilina. Kao što se sa slike može videti u odsustvu anilina, visoki potencijali se veoma brzo dostižu pri bilo kojoj primenjenoj gustini struje. Krive su okarakterisane sa nekoliko prevojnih tačaka, koje verovatno odgovaraju transformaciji hidratisanih oksida i na višim potencijalima izdvajanju kiseonika. Dodatkom monomera anilina, galvanostatske krive polimerizacije ukazuju da dolazi do sinteze polianilina, ali konstantni nagib tokom produžene oksidacije takođe ukazuje da se verovatno simultano odigrava i oksidacija aluminijuma. Za dalja ispitivanja korišćeni su uzorci dobijeni pri gustinama struja od 1,5 mA cm^{-2}.

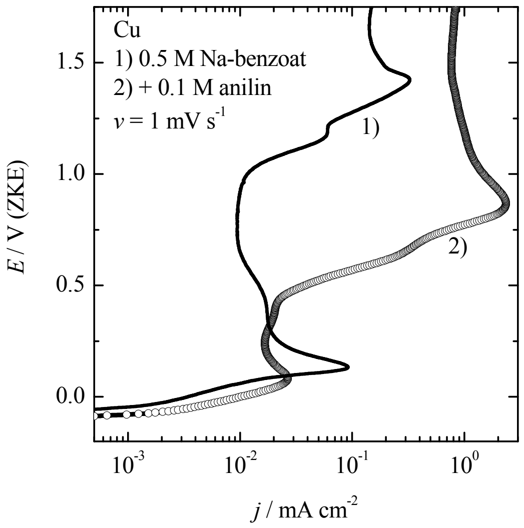
Sinteza polianilina na bakru

Na slici 5 prikazane su anodne polarizacione krive bakra u 0,5 M natrijum-benzoata i uz dodatak 0,1 M anilina.

Anodna polarizaciona kriva u rastvoru natrijum-benzoata ima tipičan izgled pasivacione krive za metale. Korozioni potencijal je iznosio –0,06 V, a početak pasivacije se odigrava pri potencijalima od ~0,14 V. Gustina struje početka pasivacije je iznosila 100 μA cm^{-2}, dok je srednja vrednost gustine struje pasivne oblasti iznosi oko 10 μA cm^{-2}. Pri potencijalima višim od 1 V uočava se transpasivna oblast, usled verovatne transformacije površinskog filma bakra i izdvajanja kiseonika. U prisustvu anilina korozioni potencijal se vrlo malo pomera ka negativnijim vrednostima. Elektropolimerizaciji anilina koja se odigrava u oblasti potencijala od 0,25 do 1,25 V, verovatno predhodi formiranje slabo rastvornog bakar-benzoata pri potencijalima nižim od 0,25 V.



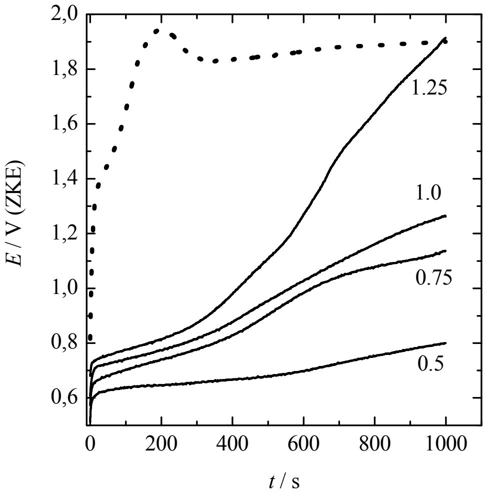
Slika 4. Galvanostatske krive aluminijuma u rastvoru 0,5 M natrijum-benzoata (tačkaste linije) i u rastvoru 0,5 M natrijum-benzoata i 0,1 M anilina (deblje linije) pri različitim gustinama struja.
Figure 4. Galvanostatic curve of the aluminium in 0.5 M sodium benzoate (doted line) and in 0.5 M sodium benzoate and 0.1 M aniline (thicker line) for different current densities.



Slika 5. Anodne polarizacine krive bakra u rastvoru 0,5 M natrijum-benzoata i uz dodatak 0,1 M anilina.
Figure 5. Anodic polarization curves of copper in 0.5 M sodium benzoate and with addition of 0.1 M aniline.

Na slici 6 prikazane su galvanostatske krive oksidacije bakra u natrijum-benzoatu i uz dodatak anilina.

Kao što se sa slike može videti, u odsustvu anilina visoki potencijal se veoma brzo dostiže i pri veoma niskoj gustini struje (0,5 mA cm^{-2}). Krive elektropolimerizacije anilina su okarakterisane sa nekoliko prevojnih tačaka, koje se verovatno mogu pripisati transformacijama različitih stanja polianilina. Za dalja ispitivanja korišćeni su uzorci dobijeni pri gustinama struja od 1,0 mA cm^{-2}, s obzirom da pri višim gustinama struje dolazi do znatnog porasta potencijala i izdvajanja kiseonika.



Slika 6. Galvanostatska kriva bakra u rastvoru 0,5 M natrijum-benzoata pri gustini struje od 0,5 mA cm^{-2} (tačkasta linija) i elektropolimerizacije anilina na bakru iz rastvora 0,5 M natrijum-benzoata i 0,1 M anilina pri različitim gustinama struja (mA cm^{-2}) označenim na slici.

Figure 6. Galvanostatic curve of the copper in 0.5 M sodium benzoate at current density of 0.5 mA cm^{-2} (dotted line) and in 0.5 M sodium benzoate and 0.1 M aniline for different current densities marked on the figure.

Karakteristike polianilinskog filma na ispitivanim metalima

Na svim metalima dobijene su prevlake polianilina crne boje Metodom savijanja je ustanovljeno da su prevlake adherentne pošto pri pucanju osnovnog metala nije došlo do odvajanja prevlake od osnovnog metala.

Na osnovu određenog priraštaja mase po jedinici površine tokom elektropolimerizacije i uz pretpostavku da je gustina polianilina dopovanog benzoatnim anjonima $\rho \approx 1,5$ g cm^{-3} [12] procenjene su debljine, δ, filmova polianilina. Teorijska debljina filma je izračunata korišćenjem jednačine [9]:

$$\delta = \frac{jt(M_{\rm m} + yM_{\rm A})}{(2+y)F\rho} \qquad (3)$$

gde je $M_{\rm m}$ molarna masa anilina (93,13 g mol^{-1}), $M_{\rm A}$ molarna masa benzoatnog anjona (121,12 g mol^{-1}), t vreme elektropolimerizacije, a y procenjeni stepen dopovanja benzoatnim anjonima. S obzirom na visoke potencijale elektropolimerizacije za proračun je predpostavljeno da se dobija perningranilin sa stepenom dopovanja od ~1 [12]. Rezultati procenjenih eksperimentalnih i teorijskih debljina filmova polianilina sumarno su prikazani u Tabeli 1.

Poređenjem ekesperimentalno dobijenih i teorijski procenjenih debljina filmova, koje odgovaraju masi polianilina, procenjeno je iskorišćenje struje elektropolimerizacije. Kod bakra i mekog čelika iskorišćenje struje $\eta_{(j)}$ tokom elektropolimerizacije je procenjeno na oko 80%, dok je kod aluminijuma procenjeno na ~70%.

Koroziono ponašanje

S obzirom da se tanke prevlake polianilina predviđaju za upotrebu kao podsloj za taloženje kataforetskih epoksidnih prevlaka, ispitivanja korozionog ponašanja su ograničena na relativno kratki vremenski period od 10 časova.

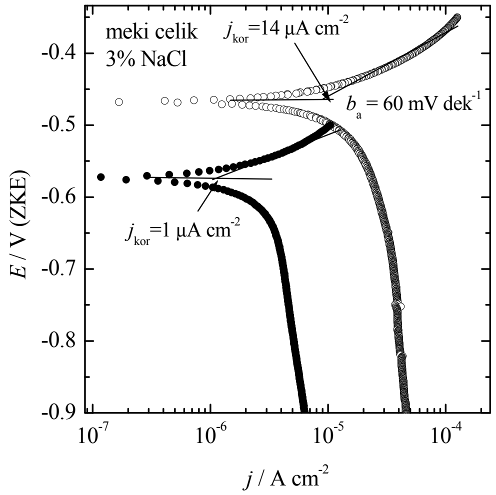
Na slikama 7–9 prikazane su uporedne polarizacione krive ispitivanih metala i metala sa prevlakom polianilina u 3% rastvoru natrijum-hlorida koji je sadržavao rastvoreni kiseonik iz vazduha. Kod svih čistih metala katodna reakcija je redukcija rastvorenog molekularnog kiseonika pod uslovima dominantne difuzione kontrole, dok je anodna reakcija aktivaciono kontrolisano rastvaranja metala. Iz preseka anodne Tafelove linije sa korozionim potencijalom određene su gustine struje korozije koje su sumarno date u tabeli 2. Na istim slikama (slike 7–9) date su i polarizacione krive ispitivanih metala sa prevlakom polianilina. Sa slika se može videti da su polarizacione krive metala sa prevlakom polianilina veoma slične polarizacvionim krivama za osnovne metale posebno u anodnom delu, ali sa znatno nižim gustinama struja. S obzirom na relativno niske vrednosti korozionog potencijala (redoks potencijal za polianilin iznosi oko 0,3 V) može se smatrati da se po-

Tabela 1. Priraštaj mase pri različitim gustinama struja elektropolimerizacije anilina, procenjena eksperimentalna i teorijska debljina filma i iskorišćenje struje elektroplimerizacije $\eta_{(j)}$

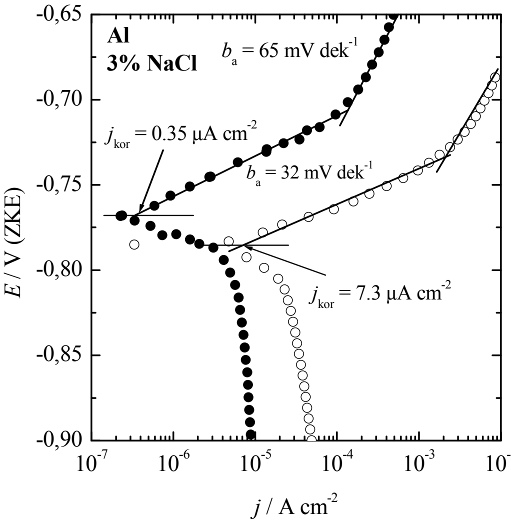
Table 1. Increase in mass at different current densities of the aniline electropolymerization, the estimated experimental and theoretical film thickness and current efficiency of the electropolymerization $\eta_{(j)}$

M-PANI	j / mA cm^{-2}	t / s	m / mg cm^{-2}	$\delta_{\rm (exp)}$ / μm	$\delta_{\rm (teor)}$ / μm	$\eta_{(j)}$ / %
MČ	1.50	215	0.20	0.13	0.16	81.2
Al	1.50	2400	1.8	12	17.7	70.6
Cu	1.00	1080	0.65	0.43	0.53	81.1

lianilin nalazi u delimično dedopovanom stanju, ali koji još uvek poseduje određenu provodljivost ($y > 0$).



Slika 7. Polarizaciona kriva za meki čelik (○) i meki čelik sa prevlakom polianilina (●) debljine 0,13 μm u 3% rastvoru NaCl.
Figure 7. Polarization curve of mild steel (○) and mild steel with polyaniline (0.13 μm) coatings (●) in 3% NaCl solution.



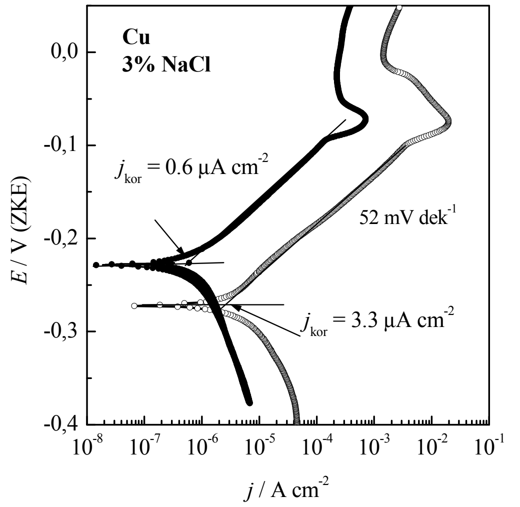
Slika 8. Polarizaciona kriva za aluminijum (○) i aluminijum sa prevlakom polianilina (●) debljine 12 μm u 3% rastvoru NaCl.
Figure 8. Polarization curve of aluminum (○) and aluminum with polyaniline (12 μm) coatings (●) in 3% NaCl solution.

Na osnovu izloženih rezultata i sličnosti polarizacionih krivih korozionih reakcija, može se zaključiti da se rastvaranje metala odigrava kroz pore filma polianilina, a redukcija korozionog agensa verovatno na samoj površini filma smanjene provodljivosti. To ukazuje da polianilin u zaštiti ispitivanih metala od korozije ima prevashodno barijerni zaštitni efekat, odnosno smanjenje izložene površine metala korozionom agensu.

Na osnovu određenih vrednosti gustina struje korozije moguće je izračunati stepen zaštitnog dejstva izraženih u procentima preko sledeće jednačine:

$$Z = \left(\frac{j_{kor}^{M} - j_{kor}^{M(PANI)}}{j_{kor}^{M}} \right) \times 100 \tag{4}$$

gde su j_{kor}^{M} i $j_{kor}^{M(PANI)}$ gustine struje korozije za metale i metale sa prevlakom polianilina.



Slika 9. Polarizaciona kriva za bakar (○) i bakar sa prevlakom polianilina (●) debljine 0,43 μm u 3% rastvoru NaCl.
Figure 9. Polarization curve of copper (○) and copper with polyaniline (0.43 μm) coatings (●) in 3% NaCl solution.

Stepen zaštitnog dejstva može poslužiti i za procenu poroznosti prevlaka polianilina prema jednačini:

$$\text{Poroznost} \approx 100 - Z \tag{5}$$

Sumarni rezultati određenih gustina korozije čistih metala, metala sa prevlakom polianilina, zaštitni efekat i procenjena poroznost su prikazani u Tabeli 2.

Zahvaljujući korozionoj stabilnosti filma poliani-

Tabela 2. Određene vrednosti gustina struje korozije ispitivanih metala bez i sa prevlakom polianilina, izračunati stepen zaštitnog dejstva i procenjena poroznost prevlake polianilina
Table 2. Determined corrosion current density of investigated metals without and with polyaniline coatings, calculated protection degree, and estimated porosity of polyaniline coatings

Metal	j_{kor} / μA cm^{-2}	d(PANI) / μm	j_{kor}(PANI) / μA cm^{-2}	Z / %	Poroznost, %
Fe	14	0,13	1,0	92,9	7,1
Al	7,3	12	0,35	95,2	4,8
Cu	3,3	0,43	0,6	82,0	18

lina koji ne pokazuje klasične mane epoksidnog premaza (bubrenje i degradacija tokom vremena) moguće je predpostaviti ranije uočenu dugotrajnost veoma tankih filmova polianilina u zaštiti metala od korozije [9–11]. U prvim trenucima nakon kontakta sa korozionim agensom, usled relativno niskog korozionog potencijala metala, dolazi do brzog dedopovonja površine filma polianilina. S druge strane, difuziono usporeno dedopovanje zaostalih količina anjona u dubini filma polianilina i smanjenjivanje provodljivosti, može objasniti ranije primećeni porast impedanse tokom vremena kao posledice usporavanja reakcije redukcije kiseonika na slabo provodnom filmu polianilina [9–11].

ZAKLJUČAK

Na osnovu rezultata može se zaključiti da se iz rastvora na bazi natrijum-benzoata i monomera anilina mogu dobiti dobro adherentni filmovi polianilina na svim ispitivanim metalima. Ispitivanjem korozionog ponašanja čistih metala i metala sa prevlakom polianilina u 3% rastvoru natrijum-hlorida, zaključeno je da do smanjenja brzine korozije metala dolazi uglavnom zbog barijernog efekta relativno poroznog filma. Kroz pore filma odigrava se anodna reakcija rastvaranja metala, a redukcija agensa korozije se verovatno odigrava na površini filma polianilina smanjene provodljivosti.

Zahvalnica

Autori se zahvaljuju Ministarstvu za nauku i tehnologiju Republike Srbije koje je finansiralo ovaj rad preko projekta H172046. Autor Ali Ramadan Elkais se zahvaljuje vladi Narodne Socijalističke Republike Libije koja mu je omogućila rad na doktorskim studijama.

LITERATURA

[1] F. Beck, R. Michaelis, F. Schloten, B.Zinger, Filmforming electropolymerization of pyrrole on iron in aqueous oxalic acid, Electrochim. Acta **39** (1994) 229–234.

[2] B.N. Grgur, N.V. Krstajić, M.V. Vojnović, Č. Lačnjevac, Lj. Gajić-Krstajić, The influence of polypyrrole films on the corrosion behavior of iron in acid sulfate solutions, Prog. Org. Coat. **33** (1998) 1–6.

[3] N.V. Krstajić, B.N. Grgur, S.M. Jovanović, M.V. Vojnović, Corrosion protection of mild steel by polypyrrole coatings in the acid sulfate solution, Electrochim. Acta **11** (1997) 1685–1691.

[4] S. Wencheng, J.O. Iroh, Electrodeposition mechanism of polypyrrole coatings on steel substrates from aqueous oxalate solutions, Electrochim. Acta **46** (2000) 1–8.

[5] F. Beck, Electrodeposition of polymer coatings, Electrochim. Acta **33** (1988) 839–850.

[6] J.L.Camalet, J.C. Lacroix, S. Aeiyach, P.C. Lacaze, Characterization of polyaniline films electrodeposited on mild steel in aqueous p-toluenesulfonic acid solution, J. Electroanal. Chem. **445** (1998) 117–124.

[7] J. L. Camalet, J.C. Lacroix, S. Aeiyach, K. Chane-Ching, P.C. Lacaze, Electrodeposition of protective polyaniline films on mild steel, J. Electroanal. Chem. **416** (1996) 179–182.

[8] J. L. Camalet, J.C. Lacroix, T. Dung Nguyen, S. Aeiyach, M.C. Pham, J. Petitjean, P.C. Lacaze, Aniline electropolymerization on platinum and mild steel from neutral aqueous media, J. Electroanal. Chem. **485** (2000) 13–20.

[9] M.M. Popović, B.N. Grgur, Electrochemical synthesis and corrosion behavior of thin polyaniline-benzoate film on mild steel, Synthetic Met. **143** (2004) 191–195.

[10] B.N. Grgur, M.M. Gvozdenović, V. Mišković-Stanković, Z. Kačarević-Popović, Corrosion behavior and thermal stability of electrodeposited PANI/epoxy coating system on mild steel in sodium chloride solution, Prog. Org. Coat. **56** (2006) 214–219.

[11] M.M. Popović, B.N. Grgur, V.B. Mišković–Stanković, Corrosion studies on electrochemically deposited PANI and PANI/epoxy coatings on mild steel in acid sulfate solution, Prog. Org. Coat. **52** (2005) 359–365.

[12] J. Stejskal, R.G. Gilbert, Polyaniline. Preparation of a conducting polymer (IUPAC Technical Report), Pure Appl. Chem. **74** (2002) 857–867.

SUMMARY

ELECTROCHEMICAL SYNTHESIS AND CORROSION BEHAVIOR OF THIN POLYANILINE FILM ON MILD STEEL, COPPER AND ALUMINUM

Ali Ramadan Elkais[1], Milica M. Gvozdenović[1], Branimir Z. Jugović[2], Tomislav Lj. Trišović[2],
Miodrag M. Maksimović[1], Branimir N. Grgur[1]

[1]Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia
[2]Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade, Serbia

(Scientific paper)

The electrochemical synthesis of polyaniline (PANI) on mild steel, aluminum and copper from the sodium benzoate solutions has been investigated. It has been shown that thin, highly adherent, polyaniline films on the investigated metals could be obtained by anodic oxidation with current densities in the range of 0.5 and 1.5 mA cm^{-2}. The corrosion behavior of mild steel, aluminum and copper with polyaniline coating in 0.5 mol dm^{-3} NaCl (pH 3) solutions, has been investigated by polarization technique. The corrosion current densities, porosity and protection efficiency was determined. It has been shown that polyaniline coating provided corrosion protection of all mentioned metals.

Ključne reči: Polianilin • Meki čelik • Bakar • Aluminijum • Korozija
Key words: Polyaniline • Mild steel • Copper • Aluminum • Corrosion

Развој титанских RuO_2/TiO_2 анода и уређаја за *in situ* производњу активног хлора

Мирослав Д. Спасојевић[1], Томислав Љ. Тришовић[1,2], Ленка Рибић-Зеленовић[1], Павле М. Спасојевић[3]

[1]*Универзитет у Крагујевцу, Агрономски факултет, Чачак, Србија*
[2]*Институт техничких наука САНУ, Београд, Србија*
[3]*Универзитет у Београду, Технолошко–металуршки факултет, Београд, Србија*

Извод

У раду је дат преглед развоја активних титанских анода за реакцију оксидације хлоридних јона у истраживачким лабораторијама у Србији. Приказани су и нови резултати истраживања ефекта температуре термичке обраде, састава и дебљине активне RuO_2/TiO_2 превлаке на титану на њена микроструктурна својства и одраз ових својстава на каталитичку активност, јонселективност и корозиону стабилност у процесу добијања активног хлора. Установљен је и ефекат кинетичких и оперативних параметара процеса електролизе разблажених раствора натријум-хлорида на искоришћење струје и енергије по активном хлору. На основу ових испитивања конструисана је ћелија за електролизу и утврђене су оптималне вредности технолошких параметара процеса производње активног хлора. Свеобухватна истраживања резултирала су конструкцијом различитих типова постројења за *in situ* производњу активног хлора.

Кључне речи: дезинфекција, активни хлор, анода.

Доступно на Интернету са адресе часописа: http://www.ache.org.rs/HI/

НАУЧНИ РАД

УДК 621.3.032.22:661.417/.418

Hem. Ind. **67** (2) 313–321 (2013)

doi: 10.2298/HEMIND120414076S

Микробиолошки неисправна вода за пиће и вода која се користи у процесу производње у погонима прехрамбене индустрије узрок је честих епидемија заразних болести. Зато је за добијање здравствено безбедних производа неопходна ефикасна дезинфекција воде, као и дезинфекција објеката и опреме. У свету се у многим земљама вода дезинфикује гасовитим хлором. Због потенцијалне опасности од избијања инцидената, у Европској Унији је забрањен транспорт и складиштење токсичног гасовитог хлора. Вишегодишња истраживања у лабораторијама факултета и института у Србији [1––31] резултирала су развојем домаћих уређаја за производњу дезинфекционог средства – активног хлора од нетоксичне сировине – воденог раствора натријум-хлорида. У овим уређајима се електролизом разблаженог, неутралног воденог раствора натријум-хлорида добија раствор хипохлорита и хипохлоритне киселине, снажног оксидационог средства које уништава микроорганизме. Овај технолошки поступак не загађује околину и нема штетних утицаја на здравље радника.

У процесу добијања активног хлора електролизом разблаженог раствора натријум-хлорида на аноди се анодном оксидацијом хлоридних јона издваја хлор:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (1)$$

Издвојени хлор дифундује кроз анодни дифузиони слој ка маси раствора и притом симултано хидролизује. Хидролиза је брза реакција тако да при pH вредностима раствора већим од 6,5 готово сав хлор хидролизује у анодном дифузионом слоју реакцијом:

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \qquad (2)$$

Успоставља се равнотежа дисоцијације хипохлоритне киселине:

$$HClO \rightleftarrows H^+ + ClO^- \qquad (3)$$

Настала хипохлоритна киселина и јони хипохлорита (активни хлор) из дифузионог слоја дифундују са једне стране ка аноди, где се оксидују до хлората:

$$6OCl^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + \frac{3}{2}O_2 + 6e^- \qquad (4)$$

а са друге стране у масу раствора, где подлежу хемијској конверзији до хлората:

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2Cl^- + 2H^+ \qquad (5)$$

Преписка: М.Д. Спасојевић, Агрономски факултет, Универзитет у Крагујевцу, Цара Душана 34, Чачак, Србија.
Е-пошта: ljiljana.spasojevic51@yahoo.com

Рад примљен: 14. април, 2012
Рад прихваћен: 2. јул, 2012

Дифузија и хидролиза хлора и дифузија активног хлора одређују концентрациони профил активног хлора у анодном дифузионом слоју. Овај профил одређује флукс активног хлора на анодној површини, а тиме и анодне губитке струје настале оксидацијом активног хлора [3–5,9–11,23]. Губици струје настају и анодном оксидацијом воде [3–5,9–11,23]:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{6}$$

У процесу добијања активног хлора температура електролита је релативно ниска (t < 30 °C) што успорава реакцију хемијске конверзије активног хлора до хлората [3–5,9–11,23]. При вредностима pH око 6,2 конверзија је најбржа, јер је у тој области однос концентрација хипохлоритне киселине и јона хипохлорита такав да обезбеђује максималну брзину хемијске конверзије активног хлора до хлората [11]. Зато се процес производње активног хлора изводи у алкалној средини. Међутим, у многим случајевима у пракси, јако алкални раствори активног хлора не могу да се користе. Део активног хлора се транспортује на катоду где се редукује до хлоридних јона што узрокује губитке активног хлора који се у литератури, ради лакшег обрачуна укупног искоришћења струје, означава као катодни губици [8–11,14––17]:

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \tag{7}$$

Пошто је концентрација натријум-хлорида у процесу добијања активног хлора обично мања од 30,0 g dm^{-3}, значајне анодне губитке струје узрокује и анодна оксидација воде.

ЕКСПЕРИМЕНТАЛНИ ДЕО

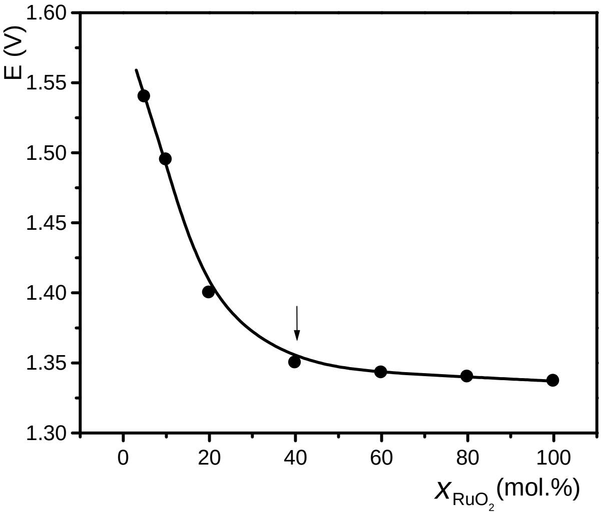
На подесно припремљеној титанској основи термичким поступком је формиран активни филм од оксида рутенијума и титана [3–5,8]. Глатке титанске плоче су, после пескирања и одмашћивања са засићеним раствором NaOH у етанолу, нагризане 20 min у кључалој 20 мас.% HCl. На овако припремљене плоче наношен је раствор $RuCl_3 \cdot 3H_2O$ и $TiCl_4$ у 2-пропанолу концентрације 20 g dm^{-3} рачунато на чисте метале. Састав раствора је варирао од 5,0 до 100 mol% Ru. Раствор је наношен више пута, све док се не постигне дебљина превлаке која одговара маси од 1,0 до 20 g m^{-2} чистих метала. После наношења сваког слоја раствора, плоче су сушене на 50 °C, а затим печене 10 min на испитиваној температури. Након последњег наношења раствора плоче су печене 60 min на испитиваној температури која је варирала од 300 до 800 °C. Кристална структура формиране превлаке испитана је рендгенском структурном анализом на Philips дифрактометру са графитним монохроматром и CuKα зрачењем.

Електрохемијска мерења вршена су у класичној електрохемијској ћелији запремине 1,0 dm^3 са посебним делом за референтну засићену каломелову електроду. Радне електроде биле су у облику плоча површине 4 cm^2, а помоћну електроду је чинила паралелно постављена титанска плоча. Сви потенцијали у тексту и на сликама дати су према стандардној водоничној електроди. Током електрохемијских мерења коришћено је стандардно електрично коло састављено од програмера са потенциостатом (RDE Potentiostat Pine instrument Co., Grove City, Pennsylvania), *X*–*Y* писача (Hewlett Packard 7035B) и дигиталног волтметра (Pro's Kit 03-9303C). Раствори су прављени од три пута дестилисане воде и Merck хемикалија. Анодно, катодно и укупно искоришћење струје одређивано је на основу састава гасне смеше која излази из електролизера [5]. Кумулативно искоришћење струје одређивано је на бази концентрације активног хлора у раствору. Концентрација активног хлора одређивана је потенциометријском титрацијом натријум-арсенатом(III) [5].

РЕЗУЛТАТИ И ДИСКУСИЈА

Испитиван је утицај природе анодног и катодног материјала, кинетичких и оперативних параметара на електродне пренапетости, пад напона у електролиту, катодно, анодно и укупно искоришћење струје и на потрошњу енергије по јединици производа-активног хлора. На основу добијених резултата утврђена је оптимална конструкција ћелије и оптималне вредности технолошких параметара процеса. Коначни исход истраживања на овом пројекту је конструкција нових постројења за производњу активног хлора [1–31].

У току реализације пројекта примењена је домаћа технологија израде активираних титанских анода за електролизу разблажених раствора хлорида у алкалној средини. Снимањем анодних поларизационих криви при електролизи разблажених раствора хлорида испитан је утицај садржаја RuO_2 у превлакама на њихову каталитичку активност. На основу тих поларизационих кривих одређена је зависност анодног потенцијала на густини струје до 1,0 kA m^{-2} од садржаја RuO_2 (слика 1). Превлаке са садржајем 40 mol% имају велику каталитичку активност. Са повећањем садржаја RuO_2 изнад 40 mol% каталитичка активност се значајније не мења. Међутим, повећање садржаја RuO_2 поспешује издвајање кисеоника анодном оксидацијом воде што смањује јонселективност превлака. Појачано издвајање кисеоника смањује и стабилност анода, јер издвојени кисеоник убрзава растварање RuO_2 и формирање слабопроводног међуслоја од нестехиометријских оксида титана. При садржајима RuO_2 мањим од 40 mol% потенцијал нагло расте са смањењем садржаја RuO_2 због повећања електричне отпорности превлаке и смањења броја активних центара за реакцију оксидације хлоридних јона.



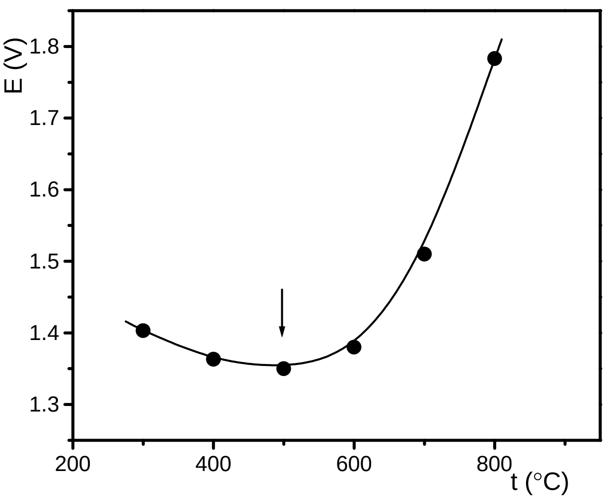
Слика 1. Зависност потенцијала RuO_2/TiO_2 анода од садржаја RuO_2 у превлакама (30 g dm^{-3} NaCl, pH 7,0 t = 25 °C, j = 1,0 kA m^{-2}).
Figure 1. RuO_2/TiO_2 anode potential as a function of RuO_2 content in the coating (30 g dm^{-3}, t = 25 °C, j = 1.0 kA m^{-2}, pH 7.0).

Анализа експерименталних резултата указује да најбоља електрохемијска својства поседује титанска анода са превлаком састава 40 и 60 mol% TiO_2 (слика 1).

Ове превлаке садрже минималне количине племенитог метала рутенијума који им обезбеђује велику каталитичку активност, добру јонселективност и добру корозиону стабилност при електролизи водених раствора натријум-хлорида [3–5,8].

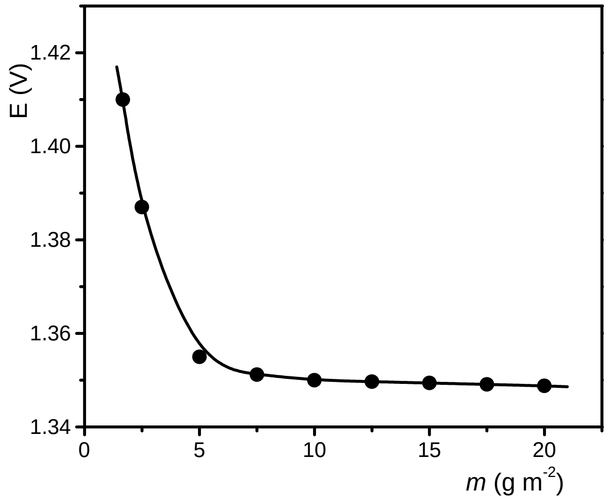
Рендгенском анализом испитан је утицај садржаја RuO_2 и температуре формирања на микроструктурна својства превлака. Све превлаке са рутенијумом формиране на температурама нижим од 600 °C садрже фазу метастабилног чврстог раствора RuO_2–TiO_2 са величином кристалног зрна око 10 nm, са великом минималном густином хаотично распоређених дислокација и великом средњом вредношћу микронапрезања. Превлаке са садржајем RuO_2 мањим од 10 mol% поред рутилне структуре чврстог раствора садрже и фазу анатаса TiO_2. Са порастом садржаја RuO_2 од 5 до 40 mol% у превлакама формираним на 500 °C повећава се просечна димензија кристалних зрна са 12 на 26 nm. При даљем повећању садржаја RuO_2 до 100 mol% величина кристалних зрна се значајније не повећава [3,4]. Превлаке формиране на температурама вишим од 700 °C садрже две фазе рутилне структуре: фазу чистог RuO_2 и фазу чистог TiO_2. Са порастом температуре формирања превлака од 500 на 700 °C расте средња димензија кристала са 26 на 75 nm. При формирању превлака на температурама нижим од 400 °C хлориди рутенијума и титана се не конвертују у целости у оксиде, па ове превлаке имају мању електричну проводљивост. Превлаке формиране на температурама вишим од 550 °C такође имају мању електричну проводљивост због формирања нестехиометријских оксида титана у међуслоју титан-активна превлака [3,4].

Најбоља електрохемијска својства поседују превлаке добијене термичким поступком – конверзијом хлорида рутенијума и титана растворених у 2-пропанолу у њихове оксиде, и то у уском температурном интервалу од 420 до 500 °C (слика 2). У том интервалу температура формира се метастабилни чврст раствор оксида рутенијума и титана високе компактности и добре адхезије. Рутилна структура чврстог раствора обезбеђује добра електрохемијска својства [3,4].



Слика 2. Зависност потенцијала 40 mol% RuO_2, 60 mol% TiO_2 аноде од температуре формирања превлака (30 g dm^{-3} NaCl, pH 7,0 t = 25 °C, j = 1,0 kA m^{-2}).
Figure 2. Potential of 40 mol% RuO_2, 60 mol% TiO_2 anode as a function of coating formation temperature (30 g dm^{-3} NaCl, t = 25 °C, j = 1.0 kA m^{-2}, pH 7.0).

На слици 3 приказан је утицај дебљине превлаке на њену каталитичку активност за реакцију оксидације хлоридних јона. Дебљина превлака изражена је преко масе нанетих метала рутенијума и титана по јединици површине титанске плоче, као што је уобичајено. Са порастом дебљине превлаке њена каталитичка активност изражена потенцијалом при густини струје од 1 kA m^{-2} споро расте у интервалу дебљина од 5 до 20 g m^{-2}. Повећање каталитичке активности је знатно мање изаражено од повећања реалне површине. Са повећањем дебљине превлака расте и дубина пора, па је отежан пренос хлоридних јона у њихову унутрашњост и пренос насталог хлора и активног хлора из пора у масу електролита. Превлаке дебљине од 10 до 15 g m^{-2} су компактне, док превлаке дебље од 15 g m^{-2} имају пукотине и њихов број расте са порастом дебљине. Зато ове превлаке брже коридирају и лакше се пасивирају. Код превлака тањих од 5 g m^{-2} са смањењем дебљине каталитичка активност нагло опада. Током термичког формирања танких превлака настају слабопроводни нестехиометријски оксиди титана. Ово узрокује брзу корозију и пасивацију танких превлака при електролизи разблажених хлоридних раствора [3,4]. Приказани резултати показују да најбоља електрохемијска својства имају превлаке дебљине од 10 до 15 g m^{-2} [3,4].



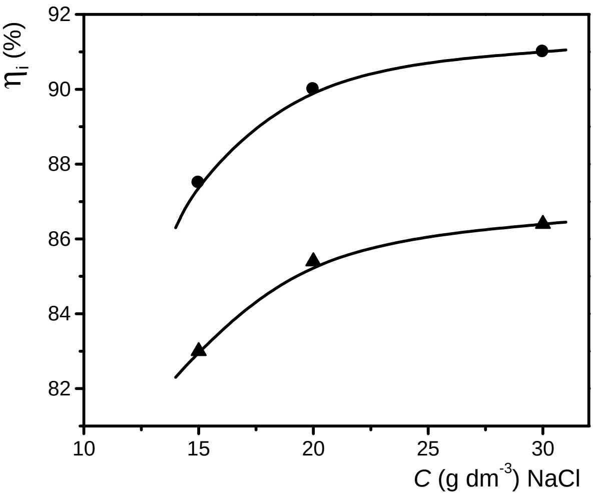
Слика 3. Зависност потенцијала 40 mol% RuO_2, 60 mol% TiO_2 аноде од дебљине превлаке (30 g dm^{-3} NaCl, pH 7,0, t = 25 °C, j = 1,0 kA m^{-2}).
Figure 3. Potential of 40 mol% RuO_2, 60 mol% TiO_2 anode as a function of coating thickness (30 g dm^{-3} NaCl, t = 25 °C, j = 1.0 kA m^{-2}, pH 7.0).

На основу поларизационих кривих симултаних реакција издвајања хлора и кисеоника оксидацијом хлоридних јона и воде при електролизи разблаженог раствора натријум-хлорида (од 20 до 30 g dm^{-3} NaCl) na 25 °C и pH 7,0, одређена је оптимална област потенцијала за производњу активног хлора од 1,35 до 1,39 V којој одговара густина струје од 1,0 kA m^{-2}.

При електролизи раствора састава 30 g dm^{-3} NaCl и 5 g dm^{-3} NaClO густином струје од 1,0 kA m^{-2} на t = 25 °C и при pH 7,0 постиже се високо анодно искоришћење струје од 86% [4,5,8] и добија раствор који се може користи као ефикасан раствор за дезинфекцију.

Оптималне густине струје при електролизи раствора са садржајем NaCl од 10 до 30 g dm^{-3} при 6,5 < pH < 7,5 на температури од 15 до 30 °C одговарају области потенциајала од 1,35 до 1,39 V. Ове густине струје обезбеђују велику производност електролизера са максималним искоришћењем струје уз велику каталитичку активност и малу корозију анода [4,5,8].

Са смањењем концентрације NaCl у раствору фаворизује се оксидација воде, па опада искоришћење струје и производност ћелије за електролизу, а расте утрошак енергије по количини произведеног активног хлора (слика 4).

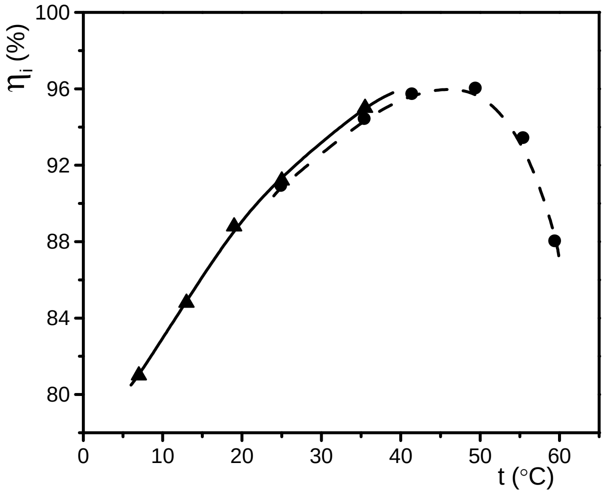


Слика 4. Зависност анодног искоришћења струје (η_i) од концентрација натријум-хлорида и активног хлора у раствору: ● – 1,0×10^{-2} и ▲ – 5×10^{-2} mol dm^{-3} NaClO (pH 7,0 t = 25 °C, j = 1,0 kA m^{-2}).
Figure 4. Anodic current efficiency (η_i) as a function of sodium chloride and active chlorine concentration in the solution: ● – 1.0×10^{-2} and ▲ – 5×10^{-2} mol dm^{-3} NaClO (t = 25 °C, j = 1.0 kA m^{-2}, pH 7.0).

Раствор активног хлора са великим садржајем NaCl, већим од 50 g dm^{-3} често је због великог салинитета, неподесан за коришћење у дезинфекционе сврхе. Анализирајући квалитет произведеног раствора, производност ћелије за електролизу, утрошак енергије по јединици количине активног хлора и трајност анодне превлаке, установљена је оптимална концентрација натријум-хлорида у раствору за електролизу од 25 до 35 g dm^{-3} [3–5,8,12,26].

Температура електролита утиче на вредност анодног потенцијала и на анодно искоришћење струје по активном хлору. Анодни потенцијал опада са повишењем температуре док искоришћење струје расте (слика 5).

Дијаграм приказан на слици 5 указује на то да повећање температуре раствора знатно више убрзава реакцију оксидације хлоридних јона него реакцију оксидације воде и дифузију активног хлора. Са повећањем температуре интензивира се конверзија активног хлора у хлорат, што узрокује губитке активног хлора [4,5,8,11,23]. Ако се ови губици израчунају и припишу анодним губицима, добија се да укупно анодно искоришћење струје расте са повећањем температуре до 50 °C, а при даљем расту температуре искоришћење струје опада (слика 5). Температурни интервал од 25 до 35 °C је оптималан интервал који обезбеђује максималну електрохемијску ефикасност електролизера за производњу активног хлора. Међутим, ако је захтевана температура раствора приметно већа од температуре околине, у систему мора да постоји посебан уређај за загревање раствора. Укључивши и овај параметар у анализу ефикасности производње активног хлора закључује се да је оптимални температурни интервал од 15 до 30 °C.



Слика 5. Зависност искоришћења струје од температуре: ▲ – анодно искоришћење; ● – обрачунато укупно анодно искоришћење (1,0×10^{-2} mol dm^{-3} NaClO, 30 g dm^{-3} NaCl, j = 1,0 kA m^{-2}, pH 7,0).

Figure 5. Temperature dependence of current efficiency: ▲ – anodic efficiency; ● – calculated total anodic efficiency (1.0×10^{-2} mol dm^{-2} NaClO, 30 g dm^{-3} NaCl, j = 1.0 kA m^{-2}, pH 7.0).

У електролитичком процесу добијања активног хлора електролизом разблажених раствора хлорида у алкалној средини, на катоди се одвија реакција издвајања водоника и дифузионо контролисана редукција активног хлора. Анализом вредности пренапетости издвајања водоника, корозионе стабилности и цене коштања катодног материјала и могућности формирања биполарних електрода установљено је да је титан најподеснији материјал за израду катода [6,7,9,10].

Важно је истаћи да катоде од титана током електролизе апсорбују атомски водоник који постепено разара металну кристалну решетку, што се уочава појавом црног праха на површини катода. При густинама струје мањим од 1,2 kA m^{-2} овај процес је релативно спор, па се и након 10 година рада у ћелијама за производњу активног хлора титанске катоде значајније не оштете.

Облик ћелије, димензије електрода и међуелектродно растојање утичу на искоришћење струје и енергије. Анализом времена задржавања елемената запремине електролита у ћелији установљен је њен оптималан облик [1,2,13–17,27,28]. Димензије електрода зависе од капацитета електролизера. Повећањем висине електрода повећава се нагомилавање мехурова катодно издвојеног водоника у горњим деловима ћелије што узрокује неравномерну расподелу густине струје по висини електродних површина. Брзина кретања електролита дуж електродних површина зависи од односа висине и ширине електроде. При односу 3:1 обезбеђује се брзина кретања електролита која спречава нагомилавање мехурова водоника у горњим деловима ћелије и која обезбеђује ефикасно одношење активног хлора у прихватни резервоар. Ћелија се поставља у раствор на одређеној дубини тако да се отвор за улаз раствора налази у доњем, а излаз производа електролизе у горњем делу ћелије. Током електролизе у ћелији се налази смеша раствора и гасовитог водоника, а у прихватном резервоару око ћелије од њеног улаза до излаза, налази се само раствор. Услед разлике специфичних маса садржаја у ћелији и раствора у прихватном резервоару одвија се рециркулација раствора чија је брзина пропорционалана висини ћелије („лифтинг ефекат“). Аноде могу бити у облику мреже и у облику плоче. Активна површина аноде облика мреже је 1,3 до 1,6 пута већа од геометријске површине анода у облику плоча.

Катодни губици струје узроковани редукцијом активног хлора се смањују повећањем односа анодне и катодне површине. Технички је најједноставније да мали електролизери са анодном површином до 0,04 m^2, имају електроде у облику плоча [9].

Анализа конструкције ћелије, димензија електрода, механичке чврстоће и електричне отпорности титана указује на то да дебљина електрода од 2,0 до 3,0 mm обезбеђује чврсту конструкцију ћелије и релативно мали пад напона у титанским плочама. Пад напона у електролиту зависи од међуелектродног растојања. Смањење међуелектродног растојања узрокује: а) смањење електричне отпорности раствора услед смањења дужине пута којим се преноси наелектрисање и б) повећање отпорности услед смањења ефективне површине раствора кроз коју се преноси наелектрисање због повећања концентрације гасних мехурова катодно издвојеног водоника. Установљено је да је оптималан размак 3,0 mm [1,2,13–17,27,28].

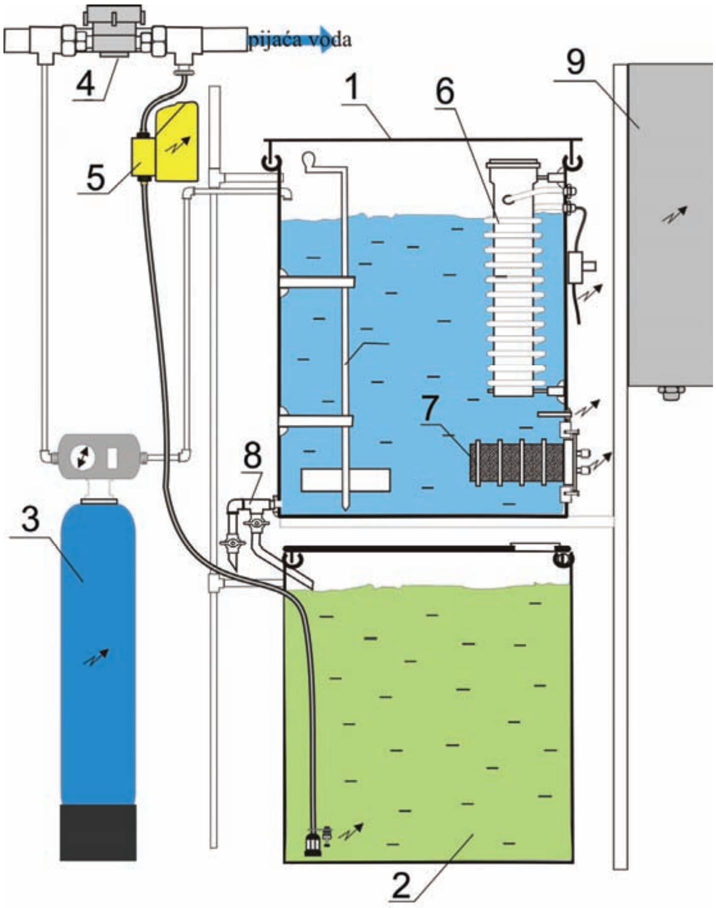
На основу приказаних истраживања и закључака [1–31] конструисани су нови типови шаржних рециркулационих и проточних постројења за производњу активног хлора са потпуном аутоматизацијом и даљинским управљањем. Капацитет и карактеристике постројења зависе од његове намене.

На слици 6 приказана је шема једног шаржног постројења произведеног у Србији. Уређај је конструисан на основу експерименталних резултата вишегодишњих испитивања изведених у лабораторијама неколико факултета и института у земљи.

Пре пуштања у рад овог уређаја, у реакциону посуду се дода одмерена количина натијум-хлорида и посуда напуни омекшаном водом. Уређај за омекшавање воде поред колоне садржи и аутоматизован систем за регенерацију јонизмењивачке масе. Током рада уређаја, у електролизеру настаје активни хлор који се струјањем раствора транспортује у реакциону посуду. На сваких седам минута електролизе аутоматски се укључи у рад измењивач топлоте. Кроз њега током троминутног рада протиче хладна вода и хлади раствор у реакционој посуди. Процес електролизе траје 30 часова. За ово време добија се 80 dm^3 раствора NaClO концентрације 1,0 g dm^{-3}. Након завршене електролизе отварањем вентила (8) раствор прелази у прихватни резервоар одакле се системом за дозирање убризгава у предвиђени простор.

На слици 7 приказана је шема једног типа рециркулационог постројења произведеног у Србији. Овај тип уређаја је намењен за производњу активног хлора за дезинфекцију базенских вода у којима се налази од 3 до 6 g dm^{-3} NaCl.

Центрифугалном пумпом се на једном крају базена усисава базенска вода и потискује кроз пешчани филтер и измењивач топлоте у електролизер. Пешчани филтер се користи за одстрањивање механичких нечистоћа из воде, а измењивач топлоте са аутоматском регулацијом за њено хлађење или загревање. У електролизеру се производи активни хлор и убацује у базен струјањем раствора. У базену, активни хлор оксидује присутне микроорганизме и редукује се до хлоридних јона. Воду са насталим хлоридним јонима центрифугална пумпа усисава и поново потискује у електролизер. На тај начин се понавља циклус оксидације хлоридних јона и редукције активног хлора. Производња потребне количине активног хлора за ефикасну дезин-



Слика 6. Шема шаржног уређаја за производњу активног хлора: 1 – реакциона посуда; 2 – прихватна посуда; 3 – колона за омекшавање воде; 4,5 – систем за дозирање; 6 – измењивач топлоте; 7 – електролизер; 8 – вентил; 9 – исправљач и мерно-регулациони систем.

Figure 6. A schematic of a batch-type device for active chlorine generation: 1 – reaction vessel; 2 – receptacle; 3 – water softening column; 4,5 – dosing system; 6 – heat exchanger; 7 – electrolyzer; 8 – valve; 9 – rectifier and measurement and regulation system.

фекцију базенске воде регулише се избором јачине струје и времена трајања електролизе. У најновијим типовима електролизера уграђене су електроде са „самопречишћавањем“. То су титанске електроде са активним каталитичким слојем чији се поларитет током електролизе мења. У случају константног напајања, поларитет електрода се мења у тренутку укључења уређаја у рад док се код чоперског и прекидачког напајања поларитет мења након одређеног времена у временском распону од нула до осам часова. Код ових електролизера свака електрода једно време ради као анода, а потом као катода. У катодном циклусу, издвојени водоник разара каменац на електроди [31].

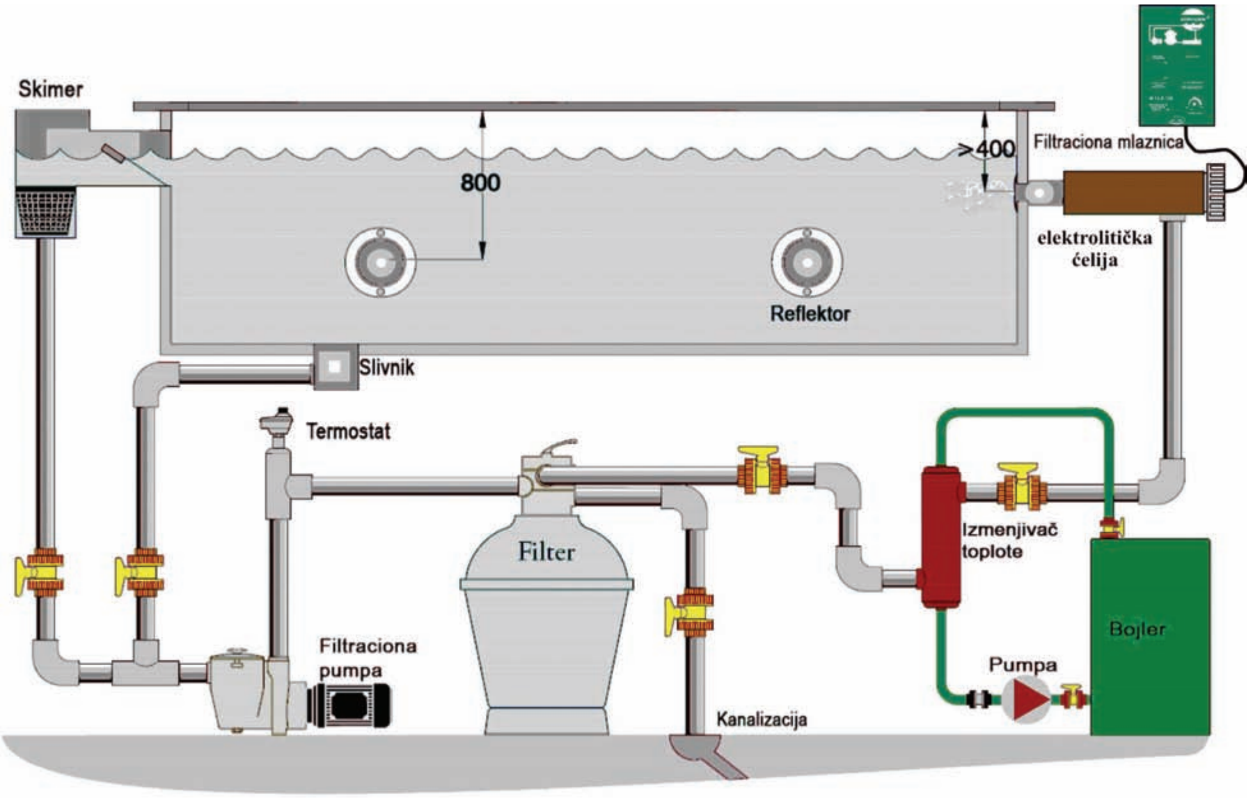
Раствори произведени у уређајима за производњу активног хлора могу да се користе за велике градске и мале сеоске системе водоснабдевања, за сеоске бунаре, за базене за купање, дезинфекцију опреме и објеката у прехрамбеној индустрији, за бељење текстила, у фармацеутској индустрији и у примарној пољопривредној производњи (за дезинфекцију семена и објеката у сточарској производњи), при преради отпадних вода, итд.

ЗАКЉУЧАК

На основу експериментално испитаног ефекта температуре термичке обраде, састава и дебљине активне RuO_2/TiO_2 превлаке на њену каталитичку активност, јонселективност и корозиону стабилност у процесу добијања активног хлора електролизом разблажених раствора натријум-хлорида одређене су оптималне вредности параметара термичког формирања чврстог раствора оксида рутенијума и титана. Најбоља електрохемијска својства имају нанокристакне превлаке чврстог раствора рутилне структуре, састава 40 mol% RuO_2, 60 mol% TiO_2, добијене на 500 °C. Превлаке су компактне и адхерентне, дебљине 10 до 15 $g\ m^{-2}$ са кристалима просечних димензија 26 nm. Установљен је и ефекат кинетичких и оперативних параметара електрохемијског процеса добијања активног хлора на искоришћење струје и енергије по активном хлору. На основу добијених резултата утврђене су оптималне вредности технолошких параметара процеса производње активног хлора. Свеобухватна истраживања резултирала су конструкцијом различитих типова постројења за производњу активног хлора.

ЗАХВАЛНИЦА

Аутори се захваљују Министарству просвете, науке и технолошког развоја Републике Србије на финансијској помоћи током израде овог рада (Пројекат број 172 057).



Слика 7. Шема рециркулационог уређаја за производњу активног хлора.
Figure 7. A schematic of a recirculating device for active chlorine generation.

ЛИТЕРАТУРА

[1] M. Jakšić, B. Nikolić, M. Spasojević, Die Grundlagem der optimalen Auslegung von Chloratzellen, Teil II, Chem. Technol. **27** (1975) 534–538.

[2] I. Roušar, V. Cezner, J. Nejepsova, M. Jakšić, M. Spasojević, B. Nikolić, Calculation of local current densities and terminal voltage for a monopolar sandwich electrolyser: application to chlorate cells, J. Appl. Electrochem. **7** (1977) 427–435.

[3] M.D. Spasojević, N.V. Krstajić, M.M. Jakšić, Optimization of on anodic electrocatalyst: RuO_2/TiO_2 on titanium, J. Res. Inst. Catalysis, Hokkaido Univ. **31** (1983) 77–94.

[4] N. Krstajić, M. Spasojević, M. Jakšić, A selective catalyst for titanium anodes: Development and optimization, I Catalyst structure, Activity and durability, J. Res. Inst. Catalysis, Hokkaido Univ. **32** (1984) 19–28.

[5] M. Spasojević, N. Krstajić, M. Jakšić, A selective catalyst for titanium anodes: Development and optimization, II Selectivity features, J. Res. Inst. Catalysis, Hokkaido Univ. **32** (1984) 29–36.

[6] N. Krstajić, M. Spasojević, R. Atanasoski, Lanthanum-molybdenum coating for hydrogen evolution on titanium, J. Appl. Electrochem. **14** (1984) 131–134.

[7] M. Spasojević, N. Krstajić, P. Despotov, R. Atanasoski, K. Popov, The evolution of hydrogen on cobalt-molybdenum coating: polarization characteristics, J. Appl. Electrochem. **14** (1984) 265–266.

[8] N.V. Krstajić, M.Spasojević, M. Jakšić, A selective catalyst for titanium anodes, J. Mol. Catalys. **38** (1986) 81––88.

[9] N. Krstajić, V. Nakić, M. Spasojević, Hypochlorite production. I. A model of the cathodic reactions, J. Appl. Electrochem. **17** (1987) 77–81.

[10] N. Krstajić, V. Nakić, M. Spasojević, Hypocholorite production II. Direct electrolysis in a cell divided by on anionic membrane, J. Appl. Electrochem. **21** (1991) 637––641.

[11] M. Spasojević, N. Krstajić, M. Jakšić, Electrocatalytic optimization of faradaic yields in the chlorate cell process, Surf. Technol. **21** (1984) 19–26.

[12] Lj. Gajić-Krstajić, T.Lj. Trišović, N.V. Krstajić, Spectrophotometric study of the anodic corrosion of Ti/RuO_2 Electrode in acid sulfate solution, Corr. Sci. **46** (2006) 65–74.

[13] M.M. Jakšić, B.Ž. Nikolić, Die Grundlagen der optimalen Auslegung von Chloratzellen, Teil I, Chem. Technol. **27** (1975) 158/.

[14] M.M. Jakšić, A.R. Despić, I.M. Čonka, B.Ž. Nikolić, Studies on Chlorate Cell Process, J. Electrochem. Soc. **116** (1969) 1316.

[15] M.M. Jakšić, A.R. Despić, I.M. Čonka, B.Ž. Nikolić, Studies on chlorate cell process, V. Theory and practice of a modified technology for electrolytic chlorate production, J. Electrochem. Soc. **117** (1970) 414.

[16] M.M. Jakšić, B.Ž. Nikolić, D.M. Karanović, C.R. Milovanović, Studies on chlorate cell process, J. Electrochem. Soc. **116** (1969) 394.

[17] M.M. Jakšić, Mass transfer and optimization of faradaic yields in chlorate cell process Electrochim. Acta **21** (1976) 1127–1136.

[18] V.V. Panić, V.M. Jovanović, S.I. Terzić, M.W. Barsonm. V.D. Jović, A.B. Dekanski, The properties of electroactive ruthenium oxide coatings supported by titanium-based ternary carbides, Surf. Coat. Technol. **202** (2007) 319.

[19] V. Panić, A. Dekanski, S. Milonjić, R. Atanasoski, B. Nikolić, The influence of the aging time of RuO_2 and TiO_2 sols on the electrochemical properties and behavior for the chlorine evolution reaction of activated titanium anodes obtained by the sol-gel procedure, Electrochim. Acta **46** (2000) 415–421.

[20] V. Panić, A. Dekanski, V.B. Mišković-Stanković, S. Milonjić, B. Nikolić, On the deactivation mechanism of RuO_2–TiO_2/Ti anodes prepared by the sol-gel procedure, J. Electrional. Chem. **579** (2005) 67–76.

[21] V.V. Panić, T.R. Vidaković, A.B. Dekanski, V.B. Mišković-Stanković, B.Ž. Nikolić, Capacitive properties of RuO_2-coated titanium electrodes prepared by the alkoxide ink procedure, J. Electroanal. Chem. **609** (2007) 120–128.

[22] V. Panić, A. Dekanski, G. Wang, M. Fedoroff, S. Milonjić, B. Nikolić, Morphology of RuO_2–TiO_2 coatings and TEM characterization of oxide sols used for their preparation, J. Coloid Interf. Sci. **263** (2003) 68–73.

[23] A.B. Đorđević, B.Ž. Nikolić, I.V. Kadija, A.R. Despić, M.M. Jakšić, Kinetics and mechanism of electrochemical oxidation of hypochlorite ions, Electrochim. Acta **18** (1973) 465–471.

[24] V.V. Panić, A. Dekanski, S.K. Milonjić, R.T. Atanasoski, B.Ž. Nikolić, RuO_2–TiO_2 coated titanium anodes obtained by the sol–gel procedure and their electrochemical behaviour in the chlorine evolution reaction, Coll. Surf., A **157** (199) 269–274.

[25] V.M. Jovanović, A. Dekanski, P. Despotov, B.Ž. Nikolić, R.T. Atanasoski, The roles of the ruthenium concentration profile, the stabilizing component and the substrate on the stability of oxide coatings, J. Electroanal. Chem. **339** (1992) 147–165.

[26] M.D. Spasojević, N.V. Krstajić, M.M. Jakšić, Structure properties and optimization of an anodic electrocatalyst: RuO_2–TiO_2 on titanium, J. Mol. Catalys. **40** (1987) 881–885.

[27] M. Spasojevic, M. Jaksic, N. Krstajic, R. Atanasoski, Advances in the chlorate cell process, B.C.D., Athens, 1980.

[28] N. Krstajic, M. Spasojevic, M.M. Jaksic, I. Rousar, V. Cezner, Design and optimization of voltage and faradaic yields in bipolar cells for sea water electrolysis. CHISA, Praha, 1981

[29] Lj.Gajić-Krstajić, N. Krstajić, N. Trišović, T. Trišović, Univerzalni šaržni uređaj za elektrohemijsku proizvodnju aktivnog hlora – hipohlorita, patent YU 659 MP, 2004.

[30] N. Trišović, Lj. Gajić-Krstajić, T. Trišović, Aparat za proizvodnju aktivnog hlora, patent YU 716 MP, 2005.

[31] T. Trišović, S. Gojković, M. Spasojević, B. Grgur, Modularni protočni elektrohemijski reaktor, P-2005/0349.

SUMMARY

DEVELOPMENT OF RuO_2/TiO_2 TITANIUM ANODES AND A DEVICE FOR *IN SITU* ACTIVE CHLORINE GENERATION

Miroslav D. Spasojević[1], Tomislav Lj. Trišović[1,2], Lenka Ribić-Zelenović[1], Pavle M. Spasojević[3]

[1]*University of Kragujevac, Faculty of Agronomy Čačak, Serbia*
[2]*Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade, Serbia*
[3]*University of Belgrade, Faculty of Technology and Metallurgy Belgrade, Serbia*

(Scientific paper)

Chlorine is used worldwide for water disinfection purposes. However, due to its toxicity the EU has imposed a set of standards that must be applied when transporting and storing chlorine. In Serbia, numerous studies have been conducted attempting to develop the technology for the generation of active chlorine disinfectant, but with a non-toxic aqueous solution of sodium chloride as the raw material. This study provides an overview of the titanium anodes activated by thermally obtained solid solution of ruthenium and titanium oxide development. It also presents new findings on the effect of the temperature of thermal treatment, the composition, the thickness of an active coating on its microstructural properties, and consequently on the catalytic activity, ion selectivity, and corrosion stability during active chlorine generation through the electrolysis of dilute sodium chloride solutions at room temperature. The study also evaluates the effect of the kinetic and operational parameters of the electrochemical process of active chlorine generation on both current and energy efficiencies. The results obtained were used to determine optimal values of technological parameters of the production process. This comprehensive research resulted in the construction of different types of remote-controlled and fully automated active chlorine generating plants.

Keywords: Disinfection • Active chlorine • Anode

M 33

Slovak Society of Chemical Engineering
Institute of Chemical and Environmental Engineering
Slovak University of Technology in Bratislava

PROCEEDINGS

37^{th} International Conference of Slovak Society of Chemical Engineering

Hotel Hutník
Tatranské Matliare, Slovakia
May 24 – 28, 2010

Editor: J. Markoš

ISBN 978-80-227-3290-1

Gvozdenovic, M., Trisovic, T., Stevanovic, J., Jugovic, B., Grgur, B.: Characteristics of polyaniline lead - dioxide power sources, Editor: Markoš, J., In *Proceedings of the 37th International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 871–875, 2010.

Characteristics of polyaniline lead - dioxide power sources

M. M. Gvozdenović, T. Lj.Trišović[*] , J. S. Stevanović[**], B. Z. Jugović[*], B. N. Grgur

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia
[*]*Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihalova 35, Belgrade, Serbia,*
[**]*CEH, Institute of Chemistry Technology and Metallurgy, Njegoševa 12, Belgrade, Serbia*

ABSTRACT:

Polyaniline (PANI) anode, electrochemically synthesized on graphite electrode from sulfuric acid solution, and electrochemically formed thin film lead dioxide cathode, were investigated for possible applications as electrode materials in PANI│H_2SO_4│PbO_2 aqueous based rechargeable power sources. The stimulation of charge/discharge characteristics of the cell, based on half cell reactions investigations, was evaluated. Charging of the cell would occur in the voltage range of 1.2 and 1.7 V, while discharge would occur in the range of 1.3 and 1 V.

Key words: polyaniline, lead dioxide, power sources

INTRODUCTION:

Electroconducting (ECP) polymers due to their specific properties such as: low specific weight compared to classical inorganic compounds, high energy and power density and ability of reversible exchange of ions, have gained much attention as possible electrode materials in electrochemical power sources. The determining factors of a battery system are recognized as “three E criteria” (energy, economics, environment), which are likely to be accomplished in systems based on ECP, metals and aqueous electrolytes[1]. Among numerous ECP, up to now only few of them has been investigated for possible use in electrochemical power sources. The most extensively investigated systems are based on polyaniline (PANI) combined to electronegative metals. In this work electrochemically synthesized PANI on graphite, as anodic material, and electrochemically synthesized lead dioxide as cathode were investigated for possible application in PANI│H_2SO_4│PbO_2 rechargeable power sources. In such system, the half reaction for charging of the cell can be given as:

$$[\mathrm{PANI}^{y+}(\mathrm{SO_4}^{2-})_y]_n + 2ny\mathrm{e} \rightarrow (\mathrm{PANI})_n + ny\mathrm{SO_4}^{2-} \quad (1)$$

$$\mathrm{PbSO_4} + 2\mathrm{H_2O} \rightarrow \mathrm{PbO_2} + \mathrm{SO_4}^{2-} + 4\mathrm{H}^+ + 2\mathrm{e} \quad (2)$$

Is important to note that in fully charged PANI│H_2SO_4│PbO_2 battery PANI is in its dedoped form.

EXPERIMENTAL: Polyaniline thin film electrode was formed by anodic polymerization from aqueous solution of 1.1 mol dm^{-3} H_2SO_4 and 0.2 mol dm^{-3}

aniline at constant current density of 2.5 mA cm^{-2} on graphite. Prior to use aniline (p.a. Aldrich) was distilled in argon. Cylindrically shaped graphite electrode was first mechanically polished with fine emery papers (2/0, 3/0 and 4/0) and than with polishing alumina (1μm Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.). After mechanical polishing, the traces of alumina were removed from the electrode surface in ethanol using ultrasonic bath. After polymerization, PANI electrode was dedoped with current density of 1.25 mA cm^{-2}, washed with bidistilled water and than investigated in 1.1 mol dm^{-3} H_2SO_4. The lead dioxide electrode was prepared from pure 99.95 % lead, according to established Planté formation procedure described by Peterson et al.[2].

All experiments were carried out in three compartment electrochemical cells. Saturated electrode served as reference, while platinum foil (S = 2 cm^2) was used as counter electrode. Electrochemical measurements were performed using GMRY PC3 potentiostat controlled by computer.

RESULTS AND DISCUSSION:

Characterization of PANI electrode

In Fig. 1. charge/discharge curves of PANI electrode for different current densities of: 0.50 – 1.25 mA cm^{-2} and anodic potential limit of 0.32 V in 1.1 mol dm^{-3} H_2SO_4 are shown. Anodic potential limit was chosen bearing in mind that at potentials higher than 0.35 V degradation of PANI is expected[3]. Charging of the electrode starts at potential of ~ 0.05V and discharging in the potential range between 0.3 and – 0.3 V. Charging capacity, as seen in insert of Fig. 1., is independent on current density, while discharging capacity decrease with increasing current density. For current densities below 1.25 mA cm^{-2}, columbic efficiency is higher than 100 %. This observation could be connected to possibilities of hydrogen evolution and protonization of emeraldine at negative potentials and low current densities. This additional charge is easily discharged at open circuit potentials and has no contribution in further charging

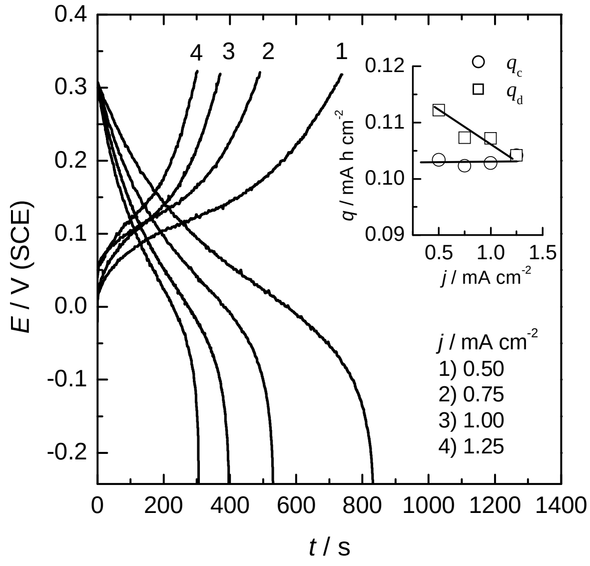


Fig.1. Charge/discharge curves of PANI electrode for different current densities in 1.1 mol dm^{-3} H_2SO_4. Insert: Charge/discharge capacity

Cycling characteristics of PANI electrode obtained with constant current density of 1.25 mA cm^{-2} during 15 cycles is given in Fig. 2. Since, the degradation of PANI possibly occurs above potentials of ~ 0.35 V, in order to investigate the influence of degradation, the cycling potential limits were extended to 0.45 V for charging and – 0.6 V for discharging[4].

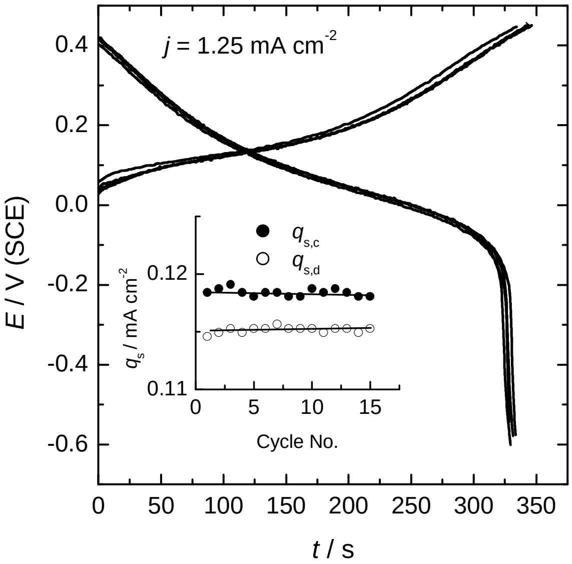


Fig. 2. Cycling characteristics of PANI electrode in 1.1 mol dm^{-3} H_2SO_4 at constant current density of 1.25 mA cm^{-2}. Insert: Dependence of the electrode capacity on cycle number

As it can bee seen from Fig. 2. charge/discharge curves are practicaly the same during fefteen cycles, with almost constant values of electrode charging and discharging capacity, with columbic efficiency of ~ 95 %. Based on obtained results, it could be concluded that in investigated potential range degradation of PANI didn’t occur, but it is expected to occur during prolonged cycliztion, so it is recommended that the optimal potential limit for charging of PANI electrode should be ~ 0.35 V[4].

Characterization of PbO_2 electrode

In order to investigate discharge characteristics of electrochemically formed PbO_2 electrode[2], the following procedure was applied. Electrode was always charged with current density of 2 mA cm^{-2} during 500 s, and than discharged with current densities between 1 and 4 mA cm^{-2} as seen in Fig. 3. Based on discharging times, the dependences of columbic efficiency and discharge capacity on applied current density were calculated and given in insert of Fig. 3. For lower current densities of 1.0 and 2.0 mA cm^{-2} columbic efficiency is ~ 85 %, while current efficiency and discharge capacity decrease for higher current densities, probably as a result of diffusion limitations. Thus, for further investigation discharge current of 2 mA cm^{-2} was used.

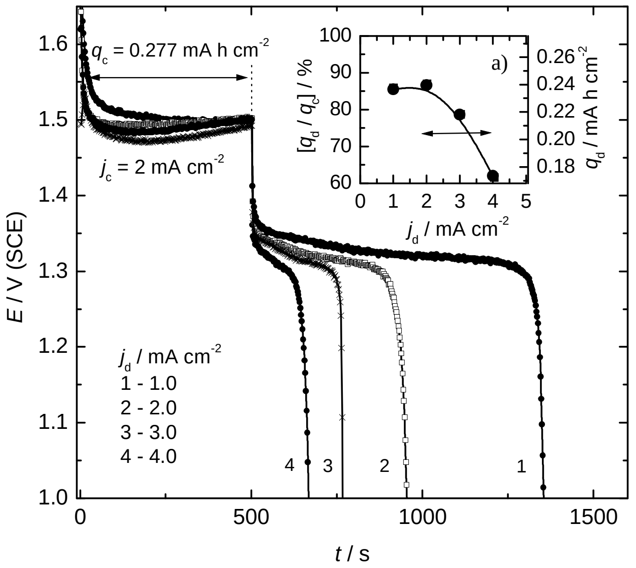


Fig. 3. Discharge characteristics of PbO_2 electrode in 1.1 mol dm^{-3} H_2SO_4 for different discharge current densities. Insert. Dependences of columbic efficiency and discharge capacity on discharge current density.

In order to investigate cyclic characteristic, PbO_2 electrode was submitted to fifteen charge/discharge cycles in 1.1 mol dm^{-3} H_2SO_4 with current density of 2.0 mA cm^{-2} and results are presented in Fig. 4.

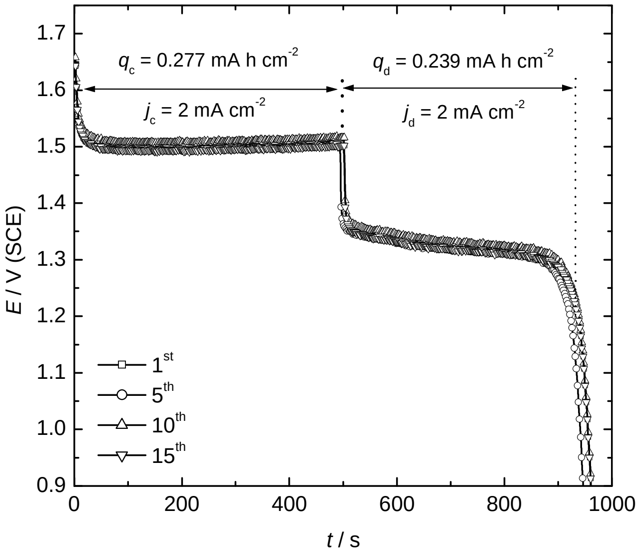


Fig. 4. Cycling characteristics of PbO_2 electrode in 1.1 mol dm^{-3} H_2SO_4 at constant current
density of 2.0 mA cm^{-2}

As it can been seen from Fig. 4., during fifteen cycles charge/discharge capacity has practically constant values, with constant columbic efficiency of ~ 85 %. These findings suggest that electrochemically formed PbO_2 electrode accomplishes demands for potential application in PANI│H_2SO_4│PbO_2 cell.

Possible characteristics of PANI /H_2SO_4 /PbO_2 power sources

Based on charge /discharge characteristics of PANI and PbO_2 electrodes (presented in Fig. 2. and Fig. 3.), simultation of the possible electrochemical characteristics of PANI│H_2SO_4│PbO_2 cell were done for anodic current density of 1 mA cm^{-2} (PANI electrode) and cathodic current density of 2 mA cm^{-2} (PbO_2 electrode), assuming that for low current densities voltage loss resulted from additional ohmic drops can be neglected, and that PANI electrode was formed on carbon support with low roughness factor of 2. Obtained results are presented in Fig. 5.

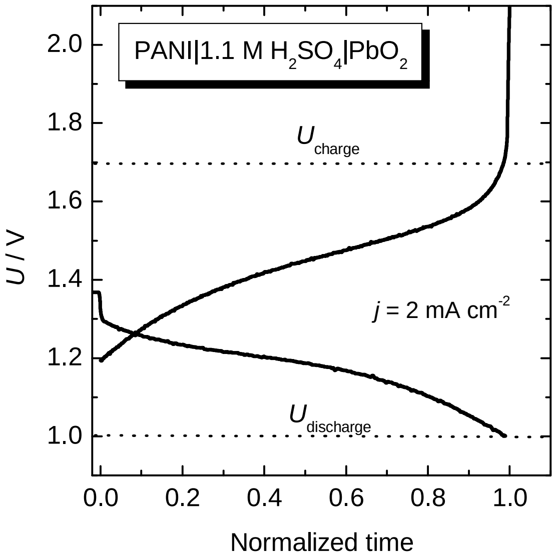


Fig. 5. Simulation of the possible electrochemical characteristics of
PANI│H_2SO_4│PbO_2 cell

As it can bee seen from Fig. 5. charging of the cell occurs in the voltage range between 1.2 and 2.1, but since there is no additional charge above 1.7 V, system should be charged only to that voltage. After charging open circuit voltage is ~ 1.35 V similar to metal hydride cells.

REFERENCES

1. P. Rüetschi, *J. Power Sources,* **42** (1993) 1
2. L. Peterson, B. Berghult, E. Ahlberg, *J. Power Sources,* **74** (1998) 68
3. N. Gospodinova, L. Terlemezyan, *Prog. Polym. Sci.*, **23** (1998) 1443
4. B. N. Grgur, V. Ristić, M. M. Gvozdenović, M. D. Maksimović, B. Z. Jugović *J. Power Sources,***180** (2008) 635

Acknowledgment: This work is financially supported by the Ministry of Science, Republic of Serbia, contract no. H 142044

Slovak Society of Chemical Engineering
Institute of Chemical and Environmental Engineering
Slovak University of Technology in Bratislava

PROCEEDINGS

37th International Conference of Slovak Society of Chemical Engineering

Hotel Hutník
Tatranské Matliare, Slovakia
May 24 – 28, 2010

Editor: J. Markoš

ISBN 978-80-227-3290-1

Jugovic, B., Trisovic, T., Stevanovic, J., Gvozdenovic, M., Grgur, B.: Improved electrolyte for zinc-polyaniline batteries, Editor: Markoš, J., In *Proceedings of the 37th International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 866–870, 2010.

Improved electrolyte for zinc-polyaniline batteries

B.Z. Jugović[1], T. Lj. Trišović[1], J. Stevanović[2], M. Gvozdenović[3], B.N. Grgur[3]
[1]*Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihailova 35, Belgrade*
[2]*Institute of Electrochemistry, ICTM, Njegoševa 12 Belgrade*
[3]*Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade*

Electrochemical behavior of zinc and polyaniline (PANI) electrode polymerized from 0.1 M HCl and 0.1 M aniline on graphite electrode, in 0.2 M $ZnCl_2$ and 0.50 M NH_4Cl (chloride electrolyte) and with addition of 0.33 M Na-citrate (chloride/citrate electrolyte) were investigated. In the chloride/citrate comparing with chloride containing electrolyte for the zinc electrode negative shift of the open circuit potential of 150 mV, decreases of exchange current density for more than order of magnitude and increase of cathodic Tafel slope, due to the zinc ions complexation, were observed. In citrate/chloride electrolyte zinc dendrite formation were completely suppressed. PANI electrodes show better discharge characteristic in chloride/citrate electrolyte with determined maximum discharge capacity of 164 mAh g^{-1}

Key words: polyaniline, citrate, batteries

1. Introduction

Up to now zinc-PANI batteries has not been commercialized from few main reasons. First reason is degradation process of PANI at potentials more positive than ~0.5 V [1, 2], and second is zinc passivation, which is possibly related to the formation of the solid phases $ZnCl_2 \cdot 3NH_4Cl$ and $ZnCl_2 \cdot 2NH_4Cl$ on the anode surface [3]. On the other hand, in chloride containing electrolytes Zn electrodes form dendrites during charge–discharge cycles [5]. It results in decreased coulombic efficiency of batteries and charge life. Main reason for that are sort circuit provoked by penetration of dendrites through separator to cathode or formation of the anodic slime.

It is well known that some organic anions can form complexes with the metal ions, that results much better quality of the metal deposits and suppress dendrite formation [7]. Probably, the best choice will be oxalic anions, due to the small ionic radius, good PANI doping-dedoping characteristics, etc [8]. Unfortunately, zinc oxalate is an insoluble salt.

In this paper we have investigated behavior of zinc and PANI electrodes in chloride containing electrolytes with addition of citrate anions, which at pH~5 that can form an soluble zinc citrate $[ZnCit]^-$ complex.

2. Experimental

Polyaniline was obtained from hydrochloric acid solution (0.1 M) with addition of 0.1 M aniline monomer (p.a. Merck, distilled in argon atmosphere), at constant current density of 1 mA cm^{-2} on graphite electrode. Electrolytes containing 0.5 M NH_4Cl, 0.20 M $ZnCl_2$ and with addition of 0.33 M Na-citrate were prepared from p.a. grade chemicals (Merck) and bidistiled water. For all experiments three compartment electrochemical cell, with platinum foil (S=2 cm^2) as a counter and saturated calomel electrode as a reference electrode at room temperature was used.

The working electrodes, graphite (S=0.64 cm^2) and zinc (S=2 cm^2), were mechanically polished with fine emery papers (2/0, 3/0 and 4/0, respectively) and then with polishing alumina of 1 μm (Banner Scientific Ltd.) on the polishing cloths (Buehler Ltd.). After mechanical polishing the traces of polishing alumina were removed from the electrode surface in an ultra-sonic bath during 5 min. The electrochemical measurements were carried using a PAR 273A potentiostat controlled by a computer through a GPBI PC2A interface.

3. Results and discussion

On Fig. 1. comparison of zinc deposition-dissolution on graphite electrode from chloride and chloride/citrate containing electrolytes are shown. As it can be seen from chloride electrolyte, deposition processes starts at potentials around –1 V, thought one well defined peak, at –1.17 V, after at potentials more negative than –1.4 V proceed simultaneous zinc deposition and hydrogen evolution reactions. In anodic direction, zinc dissolution occurs at potentials more positive than –1 V through one pack and one shoulder. In citrate/chloride electrolyte deposition-dissolution reaction is shifted for ~0.15 V in negative direction and diffusion limited peak is two times smaller, than in chloride electrolytes. This behavior could be explained by zinc ions complexation and lowering of the free zinc ions activity, as well as diffusivity of zinc citrate complex comparing with chloride electrolyte.

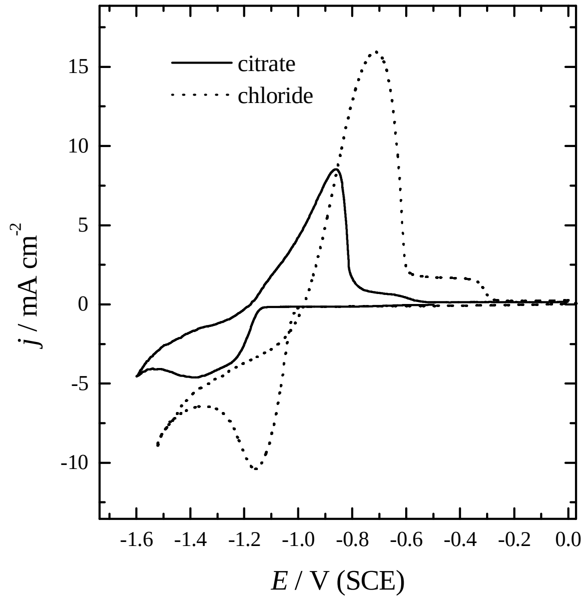
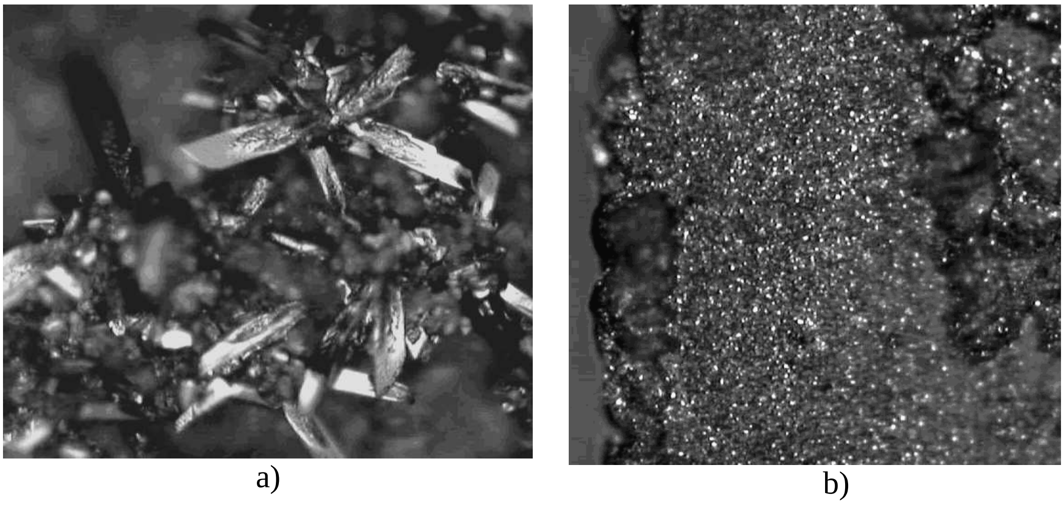


Fig. 1. Cyclic voltammograms of graphite electrode in 1) 0.50 M NH_4Cl + 0.20 M $ZnCl_2$ and 2) with addition of 0.33 M Na-citrate. Sweep rate 20 mV s^{-1}.

In Fig. 2 micrographs of zinc deposits obtained from chloride and chloride/citrate electrolytes at a constant current density of 3.5 mA cm^{-2} and with deposition charges of 10.5 mA h cm^{-2} are shown.



a) b)

Fig. 2. Micrographs of the zinc deposits from a) 0.20 M $ZnCl_2$ + 0.50 M NH_4Cl and b) with addition of 0.33 M Na-citrate.
Deposition current density 3.5 mA cm^{-2}, deposition time 3 h, magnification 200 x.

In chloride electrolyte, Fig. 2a, obtained deposits are practically completely dendritic, so potential risk of fast dendrite growth through separator, during the longer charging times, and formation of short circuits with cathode is permanently present. On the other hand in chloride/citrate electrolyte, Fig. 2b, deposit is smooth without irregularities even in the edges where local current density due to the current distribution phenomena is higher than at the central surface.

The overpotential and the current density in activation-controlled deposition inside the Tafel region are related by:

$$\eta = \frac{b_c}{2.3} \ln \frac{j}{j_0} \qquad (1)$$

Therefore, increasing b_c and decreasing j_0 leads to an increase in the deposition overpotential at the constant current density. It follows from all available data that the former effect is more pronounced resulting in deposits with a finer grain size with decreasing value of the exchange current density.

This analysis explain differences in deposit morphology for chloride and chloride/citrate electrolytes taking into account that Tafel slopes are –35 and –108 mV dec^{-1}, and exchange current densities are 0.38 and 0.027 mA cm^{-2}, respectively. Hence, in chloride electrolyte at 3.5 mA cm^{-2} deposition overpotential is only –30 V, while in chloride/citrate electrolyte is –220 mV.

Insert of Fig. 3. shows the galvanostatic curve for polymerization of aniline from solution containing 0.10 M HCl and 0.10 M aniline monomer on graphite electrode at current density of 1 mA cm^{-2} with polymerization charge of 0.3 mA h cm^{-2}. Polymerization starts at potential of 0.75 V and proceed in the potential range between 0.75 and 0.7 V. After polymerization, electrode was washed with bidistiled water and transferred in the three compartment electrochemical cell with chloride or chloride/citrate electrolyte. After transfer, electrode was conditioned at potential of –0.8 V for 600 s and cyclic voltammograms in the potential range between –0.8 and 0.4 V were taken as shown in Fig. 4. In anodic direction doping of the anions occur at potentials more positive than –0.2 V, with pronounced peak at 0.15 V. In cathodic direction dedoping of anions occur through one shoulder in the potential range of 0.4 to 0.05 V and one well defined peak with the maximum at –0.1 V. Dedoping of anions is finished at potentials of –0.4 V. Small differences in the shapes of cyclic voltammograms between chloride and chloride/citrate electrolytes, could indicate that only chloride anions are involved in doping/dedoping reaction.

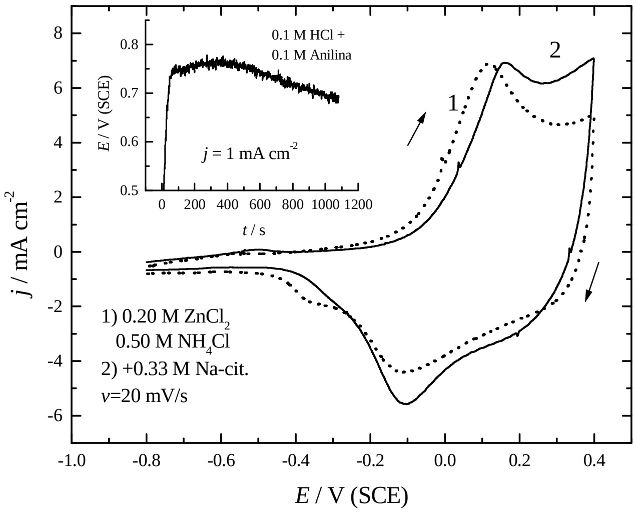


Fig. 3. Cyclic voltammograms of PANI electrode in 1) chloride and 2) chloride/citrate electrolyte (v=20 mV s^{-1}). Insert: galvanostatic curve for aniline polymerization from 0.1 M HCl and 0.1 M aniline at 1 mA cm^{-2} on graphite electrode.

Figure 4. shows charge-discharge curves in chloride and chloride/citrate electrolytes at current density of 0.25 mA cm^{-2}. Charging curves in both solutions are practically identical, but discharging curve in chloride/citrate solution have higher discharge potentials and longer discharge time. Up to now we do not have explanation for that kind of behavior.

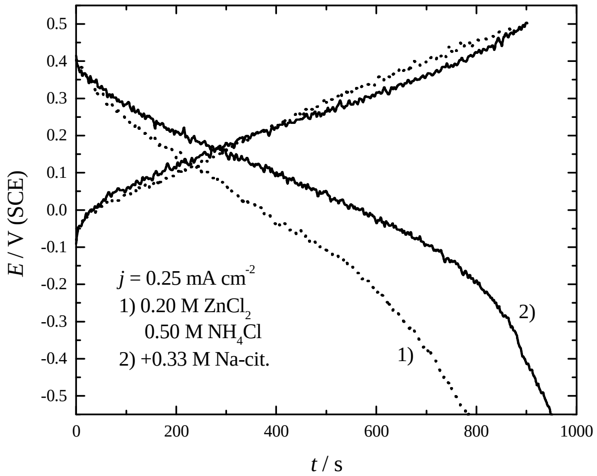


Fig.4. Charge-discharge curve for 1) chloride and 2) chloride/citrate electrolyte at current density of 0.25 mA cm^{-2}.

Charging/discharging characteristics of PANI film electrode are affected with applied current density, mainly because chloride anions diffusion limitation through PANI film. Charging/discharging reaction, assuming that only chloride anions are involved, can be given with following scheme [7]:

$$\text{PANI} + n\text{Cl} \xrightleftharpoons[\text{discharge}]{\text{charge}} \text{PANI(Cl)}_n + n\text{e} \qquad (3)$$

On Fig. 5 dependence of capacity during discharge processes for different discharging current densities are shown.

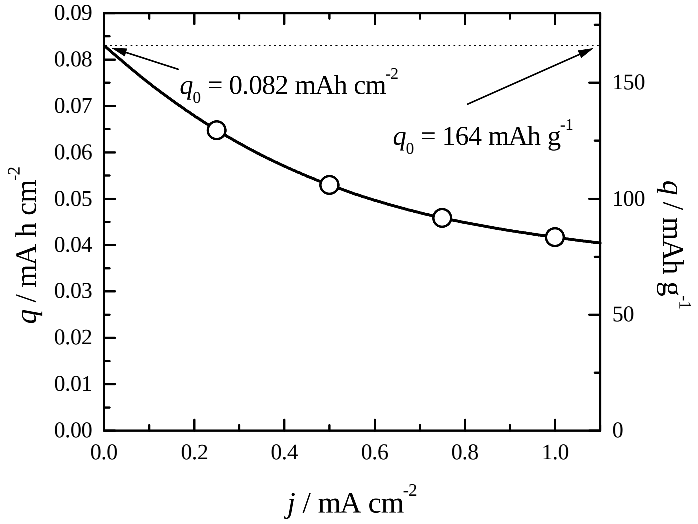


Fig. 5. Dependance of charge (left) and specific charge (right) at different discharge current density for PANI electrode in chloride/citrate electrolyte.

Discharge capacity increase with decreasing applied current density and for the limiting case when $j_d \rightarrow 0$, discharge capacity has a value of 0.082 mAh cm^{-2}.

Assuming the 100% current efficiency during the polymerization of aniline and using the equations [8]:

$$m = \frac{jt\left(M_m + yM_a\right)}{(2+y)F} \tag{4}$$

It could be calculated that mass of the PANI on graphite electrode was approximately 0.5 mg. Hence, for the limiting case with discharge capacity of 0.082 mAh cm^{-2} specific discharge capacity could be estimate on 165 mAh g^{-1}. In the range of investigated current densities of 0.25 to 1 mA cm^{-2}, specific discharge capacity was in the range of 130 to 85 mAh g^{-1}, respectively.

Acknowledgments

This work is supported by the Ministry of Science and Environmental protection, Republic of Serbia, contract No. 142044.

References

1. Arsov LD, Plieth W, Kossmehl G., J. Solid State Electrochem., 6(1998)355.
2. H. N. Dinh, J. Ding, S.J. Xia, V. I. Birss, J. Electroanal. Chem, 459(1998)45.
3. M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, M. Ghaemia, J. Pow. Sources, 132(2004)296.
4. J. Kan, H. Xue, S. Mu . J. Pow. Sources, 74(1998)113.
5. G. Mengoli, M.M. Musiani, D. Pletcher, S. Valcher, J. Appl. Electrochem., 17(1987)515.
6. E. Erdem, M. Saçak, M. Karakişla, Polymer International, 39(1996)153.
7. A. Mirmohseni, R. Solhjo, European Polymer Journal, 39(2003)219.
8. J. Kankare, in: D. Wise, G.E. Wnek, D.J. Trantolo, T.M. Cooper, J.D. Gresser (Eds.), Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications, Marcel Dekker, New York, 1998, Ch.6.

Slovak Society of Chemical Engineering
Institute of Chemical and Environmental Engineering
Slovak University of Technology in Bratislava

PROCEEDINGS

38$^{\mathrm{th}}$ International Conference of Slovak Society of Chemical Engineering

Hotel Hutník
Tatranské Matliare, Slovakia
May 23 – 27, 2011

Editor: J. Markoš

ISBN 978-80-227-3503-2

Jugovic, B., Gvozdenovic, M., Trisovic, T., Stevanovic, J., Grgur, B.: Electrochemical behavior of polyaniline in chloride/citrate electrolyte, Editor: Markoš, J., In *Proceedings of the 38th International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 963–967, 2011.

Electrochemical behavior of polyaniline in chloride/citrate electrolyte

B.Z. Jugović[1*], M.M. Gvozdenović[2], T.Lj. Trišović[1], J.S. Stevanović[3], B.N. Grgur[2]

[1]Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia,
[2]Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia
[3]ICTM, Institute of Electrochemistry, Njegoševa 12, 11000 Belgrade, Serbia

Abstract

Polyaniline electrode, was obtained by electrochemical polymerization at constant current density of 2.0 mA cm^{-2} from aqueous solution of 1.0 mol dm^{-3} HCl containing 0.25 mol dm^{-3} aniline. Electrochemical characterization of the polyaniline electrode in chloride and chloride/citrate electrolyte, for different anodic potential limits, was performed using cyclic voltammetry and galvanostatic measurements. It was observed that for anodic potential 0.32 V, higher electrode capacity in chloride/citrate was obtained. For anodic potential limit of 0.50 V, faster decrease of the electrode capacity in chloride/citrate electrolyte was also observed. It was suggested that influence of both chloride and citrate anions has to be taken into account.

Key words: polymers, electrochemical techniques, electrochemical properties

[*]Corresponding author. Tel./Fax:+381 11 3303695
E-mail address: branimir.jugovic@itn.sanu.ac.rs

1. Introduction

Due to their unique properties, such as: mechanical strength, electrical conductivity, corrosion stability, possibility of chemical and electrochemical synthesis, electroconducting polymers (ECP) were considered in wide area of practical application such as: microelectronics, optoelectronics, corrosion protection, sensors, electromagnetic shielding, and electrochemical power sources [1-8]

ECP could be synthesized by both chemical and electrochemical oxidative polymerization. However, electrochemical synthesis is favorable permitting the control of the reaction and polymerization without oxidizing agent together with doping by organic or inorganic ions in a single step.

Among large number of ECP, polyaniline (PANI) is the most investigated as cathode material in aqueous based electrochemical power sources [5-13]. Although systems consisted of PANI cathode combined to electronegative metal (mainly zinc) anode, are likely to accomplish most of the three E criteria: Energy (high energy content with respect to volume and weight), Economics (low manufacturing and maintenance costs, long service life), Environment (toxic free, safety, low energy consumption, easy to recycle) elaborated as the determining factors of an electrochemical power system success [14,15] they still have not been commercialized from several reasons.

2. Experimental

Electrochemical synthesis of PANI on graphite electrode (S = 0.64 cm^2) was performed at constant current density of 2 mA cm^{-2} from aqueous solution of 1.0 mol dm^{-3} HCl (p.a. Merck) and 0.25 mol dm^{-3} aniline. After polymerization, PANI electrode was discharged in the same solution with 1 mA cm^{-2} to the potential of – 0.6 V, than rinsed in bidestilled water, and transferred into electrochemical cell containing for further characterization. Prior to use aniline (p.a. Aldrich) was distilled in argon atmosphere. The working electrode, cylindrically shaped graphite inserted in Teflon holder was first mechanically polished with fine emery papers (2/0, 3/0 and 4/0, respectively), and than with polishing alumina (1μm, Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.), the traces of the polishing alumina were removed from the electrode surface in an ultrasonic bath during 5 min.

PANI electrode was characterized using cyclic voltammetry and galvanostatic cyclization measurements in chloride (0.5 mol dm^{-3} NH_4Cl and 0.2 mol dm^{-3} $ZnCl_2$) and chloride/citrate (0.5 mol dm^{-3} NH_4Cl and 0.2 mol dm^{-3} $ZnCl_2$ with addition of 0.3 mol dm^{-3} Na-citrate). All experiments were performed in standard three compartment electrochemical cell at ambient temperature (22 ^{0}C). Saturated calomel electrode was used as reference, while Pt wire served as counter electrode. The measurements were carried out using PAR 273A potentiostat/galvanostat interfaced to PC.

3. Results and discussion

Electrochemical polymerization of aniline on graphite electrode from 1.0 mol dm^{-3} and 0.25 mol dm^{-3} aniline at constant current density of 2.0 mA cm^{-2} during 1080 s is given in insert of Fig.1. After polymerization, PANI electrode was discharged with current density of 1 mA cm^{-2}, and transferred to another electrochemical cell for further investigation. Six successive cyclic voltammograms (v = 20 mV s^{-1}) of PANI electrode are shown in Fig.1. Voltamogramms are characterized by constant charge increase as a result of formation of insoluble PANI, while anodic and cathodic correspond to different oxidation forms of PANI.

As seen in insert Fig.1, PANI polymerization occurred at potentials around 0.7 V, meaning that polymerization undergoes through formation of perningraniline salt. Comparing the polymerization charge of 0.60 mAh cm^{-2} and discharge charge of ~ 0.14 mAh cm^{-2}, it could be concluded that only 23 % of the total mass was available for charge exchange, while rest of the charge refers to formation of inactive PANI oligomers and degradation products.

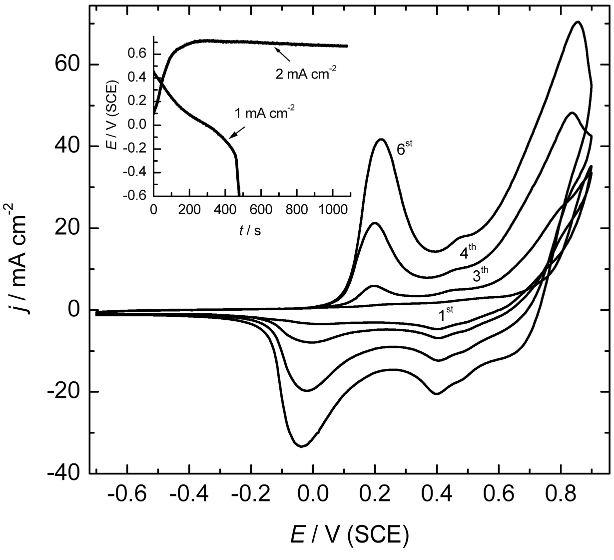


Fig. 1. Galvanostatic curve of electrochemical polymerization of aniline at graphite electrode in 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline, j = 2.0 mA cm^{-2}. Insert: Cyclic voltammogram of PANI electrode in 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline (v = 20 mV s^{-1}).

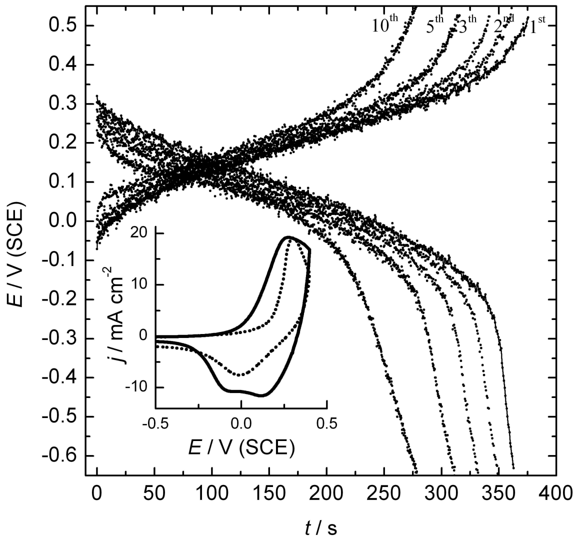


Fig.2. Charge/discharge curves of PANI electrode during ten cycles, j = 1 mA cm^{-2} in chloride/citrate electrolyte for anodic potential limit of 0.50 V. Insert: cyclic voltammograms:(—)-before and (…)-after ten cycles, v = 20 mV s^{-1}.

It was previously showed [10] that anodic potential limit had exhibited influence on charge/discharge characteristics of the PANI electrode, resulted in decrease of the electrode capacity during cyclization. Bearing in mind that addition of citrate anions had enhanced characteristics of negative zinc electrode [19], charge/discharge behavior of the PANI electrode were investigated in chloride/citrate electrolyte. In Fig. 2 and in Fig.3 charge/discharge curves of the PANI electrode in chloride/citrate electrode during ten cycles obtained by current density of 1 mA cm^{-2} and differnt anodic potential limits of 0.5 V and 0.32 V are given respectively . Inserts of Fig.2 and Fig.3 show cyclic voltammograms before and after ten cycles of the PANI electrode in chloride/citrate electrolyte.

As seen in Fig.2 and 3, anodic potential limit had grate influence on charge/discharge behaviour of the PANI electrode in chloride/citrate electrode. For anodic potential limit of 0.5 V (Fig.2) time for charging/discharging constantly decreased over time. As seen in insert of Fig.2, cyclic voltamograms taken before and after ten cycles showed capacity lost, suggesting that strong PANI degradation had occurred. For anodic potential limit of 0.32 V (Fig.3) charge/discharge curves of the PANI electrode in chloride/citrate electrolyte were the same over ten cycles, meaning that electrode capacity remained practically constant. This funding indicates that degradation of PANI had not occurred. As seen in insert of Fig.2, cyclic voltammograms of the PANI electrode before and after ten cycles remained the same, confirming again the fact that there was no PANI degradation during cyclization. It is interesting to mention that charge/discharge capacities of the PANI electrode were almost two times higher in chloride/citrate than in chloride electrolyte (given in dot lines on Fig.3).

The dependences of calculated charge and discharge capacities of the PANI electrode from Fig. 2 and 3 on cycle number is given in Fig.4.

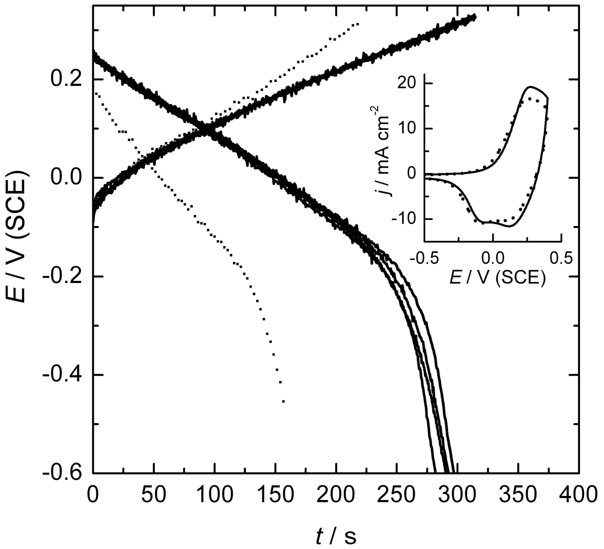


Fig.3. Charge/discharge curves of PANI electrode during ten cycles, j = 1 mA cm^{-2} in chloride/citrate-ful lines and chloride electrolyte-dot lines, for anodic potential limit of 0.32 V., dot lines-chloride. Insert: cyclic voltammograms:(—)-before and (…)-after ten cycles, v = 20 mV s^{-1}.

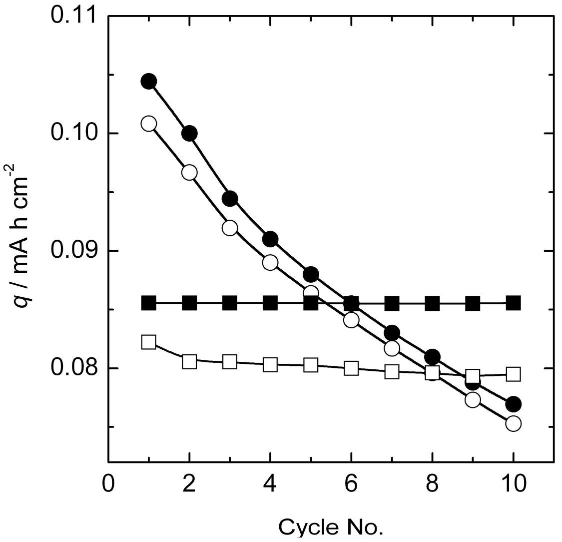


Fig.4. Dependences of PANI electrode capacities on cycle number in chloride/citrate electrolyte, for anodic potential limit of 0.5 V: (•)-charge, (○)-discharge and 0.32V (■)-charge, (□)-discharge. Insert: Columbic efficiency for anodic potential limit of: (•)-0.5 V and (■)-0.32 V.

As seen in Fig.5, for anodic potential limit of 0.50 V, permanent lost (around 25%) of capacity during ten cycles was observed even though the initial capacity was higher than for anodic potential of 0.50 V comparing to 0.32 V. On contrary, there was practically no capacity lost observed for the potential limit of 0.32 V. Since PANI was always polymerized under the same conditions, the decrease of the capacity for higher anodic potential limit of 0.5 V in chloride/citrate electrolyte could be connected to the presence of citrate anions. The effect of the doping anions, proposed by Yang et al. [16] could be attributed to the hydrophobic effect following the Hofmeister series [17]:

$$\mathrm{ClO_4^-}. > \mathrm{NO_3^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-} > \mathrm{F^-} > \mathrm{HPO_4^{2-}} > \mathrm{SO_4^{2-}}. > \mathrm{citrate^{3-}}$$

According to this, perchlorate ions are the most hydrophobic, citrate ions are the most hydrophilic, while chloride are in the middle. So, it was expected that chloride ions would form relatively stabile ion pars in oxidized PANI film, therefore PANI degradation could be limited to certain degree by dissociation of the ion par, resulting in slower degradation kinetics of PANI in chloride than in chloride citrate electrolyte.

In Fig.5 cyclic voltammograms of the PANI electrode in chloride, chloride/citrate and in pure citrate (0.3 mol dm^{-3} Na-citrate) are given.

As it can be seen in Fig.5, doping of PANI by anions in all electrolytes started at the same potential of about -0.15 V. Peak potential of emeraldine salt in chloride and chloride/citrate electrolytes occurred at almost same potential of ~ 0.25 V, while the peak potential in pure citrate electrolyte was shifted for more than 100 mV in positive direction. In chloride/citrate electrolyte doping preceded through broad peak, indicating that both chloride and citrate anions were involved in doping. It could be suggested that at lower potentials doping by chloride occurred, while at more positive potentials doping by citrate anions might have occurred. Comparing the values of the potentials in doping area for chloride and chloride/citrate electrolytes for the same value of current densities, it seams that doping reaction in chloride/citrate was shifted for about 30 mV in negative direction. This negative shift of the potential resulted in higher charge/discharge capacities obtained in chloride/citrate than in chloride electrolyte. On the other hand, in order to avoid fast PANI degradation and decrease in charge exchange ability, it is highly recommender that anodic potential limit during cyclization should not exceed ~ 0.35 V.

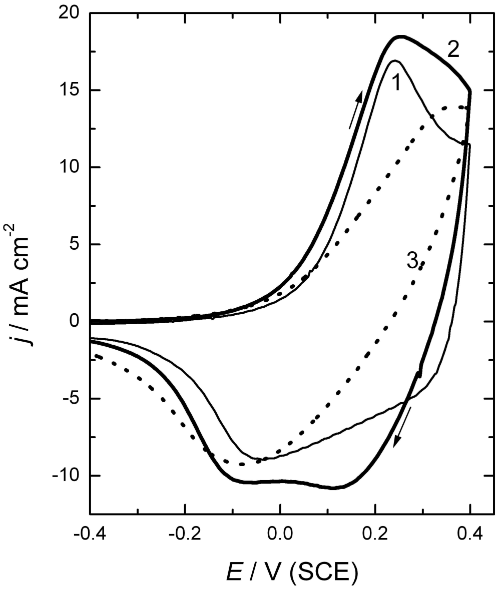


Fig.5. Cyclic voltammograms of PANI electrode in: chloride, 2-chloride/citrate and 3-citrate electrolyte, v = 20 mV s^{-1}.

4. Conclusion

Electrochemical synthesis of PANI on graphite from aqueous solution of hydrochloric acid containing aniline monomer was performed galvanostatically. The polymerization charge was 0.60 mAh cm^{-2} while discharge charge was ~ 0.14 mAh cm^{-2}, so it was concluded that only 23 % of the total polymer mass was available for charge exchange, while rest of the charge refers to formation of inactive PANI oligomers and degradation products. Based on electrochemical studies, it was concluded that in chloride/citrate electrolyte both citrate and chloride anions played role in doping. The faster decrease in charge/discharge capacity in chloride/citrate electrolyte compared to chloride for potential limit of 0.50 V was explained by hydrophilic effect of citrate ions, while higher charge/discharge capacities were explained by negative doping potential shift of about 30 mV. It was recommended that charging potential should not exceed 0.35 V.

Acknowledgment

This work is financially supported by the Ministry of Science, Republic of Serbia, No. 142044.

References

[1] A. Malinauskas, J. Malinauskienė, A. Ramanavičius, Nanotechnology 16 (2005) R51.

[2] D. E. Tallman, G. Sprinks, A. Dominis, G. G. Wallace, J. Solid State Electrochem. 6 (2002) 73.
[3] S. K.Shukla, M.A. Quraishi, R. Prakash, Corr. Sci. 50 (2008) 2867.
[4] B. Jugović, M. Gvozdenović, J. Stevanović, T. Trišović, B. Grgur, Mater. Chem. Phys. 114 (2009) 939.
[5] M. Sima, T. Visan, M. Buda, J. Power Sources 56 (1995)133.
[6] J. Kan, H. Xue, S. Mu, J. Power Sources 74 (1998) 113.
[7] B. Gupta, R. Prakash, Mat. Sci. Eng. 29 (2009) 1746.
[8] V. Singh, S. Mohan, G. Singh, P.C. Pandey, R. Prakash, Sens. Acutuarts. B: Chem. 132 (2008) 99.
[9] B. Z. Jugović, T. Lj. Trišović, J. Stevanović, M. Maksimović, B. N. Grgur, J. Power Sources 160 (2006) 1447.
[10] B. Z. Jugović, T. Lj. Trišović, J. Stevanović, M. Maksimović, B. N. Grgur, Electrochim. Acta 51 (2006) 6268.
[11] M. S. Rahmanifar, M. F. Mousavi, M. Shamsipur, H. Heli, Synth. Met. 155 (2005) 480.
[12] A. Mirmohseni, R. Solhjo, Europ. Polym. J. 39 (2003) 219.
[13] R. Mažeikiene, A. Malinauskas, Mater. Chem. Phys. 83 (2004) 184.
[14] P. Rüetschi, J. Power Sources 42 (1993) 1.
[15] F. Beck, P. Rüetschi, Electrochim. Acta 45 (2000) 2467.
[16] X. Yang, Q. Xie., S. Yao, Synth. Met., 143 (2004) 119.
[17] W. Kunz, J. Henle, B. W. Ninham, Curr. Opin. Coll. Interface Sci., 9 (2004) 19.

University of Belgrade
Technical Faculty in Bor and
Mining and Metallurgy Institute Bor

43rd International October Conference on Mining and Metallurgy

IOC 2011

PROCEEDINGS

Editors:
Desimir Marković
Dragana Živković
Svetlana Nestorović

October 12 - 15, 2011
Kladovo, Serbia

PROCEEDINGS,
43rd INTERNATIONAL OCTOBER CONFERNCE
on Mining and Metallurgy

Editors:
Prof. dr Desimir Marković
*University of Belgrade - **Technical Faculty in Bor***
Prof. dr Dragana Živković
*University of Belgrade - **Technical Faculty in Bor***
Prof. dr Svetlana Nestorović
*University of Belgrade - **Technical Faculty in Bor***

Technical Editors:
Ljubiša Balanović, PhD student
*University of Belgrade - **Technical Faculty in Bor***
Mr Ivana Marković
*University of Belgrade - **Technical Faculty in Bor***

Publisher: University of Belgrade - **Technical Faculty in Bor**
For the publisher: Dean Prof. dr Milan Antonijević
Circulation: 250 copies

Printed in Serbia by „Grafomed-trade“ Bor

ISBN 978-86-80987-87-3

Kladovo, Serbia, October 12-15, 2011

ELECTROCHEMICAL POLYMERIZATION OF PROTECTIVE POLYANILINE COATING ON COPPER

Milica Gvozdenović[1,*], Brnimir Jugović[2], Jasmina Stevanović[3], Tomislav Trišović[2], Brnimir Grgur[1]

[1]*Faculty of Technology and Metallurgy, University of Belgrade,*
Karnegijeva 4, 11120 Belgrade, Serbia

[2]*Insitute of Technical Science, Serbian Academy of Science and Arts,*
Knez Mihajlova 35, 11000 Belgrade, Serbia

[3]*Institute of Chemistry Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia*

[4]*Technical Faculty Čačak, University of Kragujevac, Svetog Save 65, 32000 Čačak, Serbia*

Abstract

Conditions for galvanostatic electrochemical polymerization of protective polyaniline (PANI) coating on copper were investigated. It was observed that uniform film of PANI on copper could be obtained with current density of 1.25 mA cm^{-2}, from aqueous solution containing 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline monomer. Corrosion behavior of PANI coated copper in 3.0 % sodium chloride solution was investigated using potentiodynamic and electrochemical impedance spectroscopy techniques. Thin (5 μm) PANI coating provided efficient protection (app. 96%), while unusual impedance behavior comparing to conventional organic coatings, was attributed to dedoping of benzoate anions from the coating.

Keywords: aniline, galvanostatic polymerization, copper, corrosion behavior

1. INTRODUCTION

Due to its high electrical and thermal conductivity and excellent formability, copper and its numerous alloys are widely used in industrial applications. Although copper exhibits good corrosion resistance, it corrodes in variety of aggressive environments. The corrosion protection strategy of copper and its alloys is usually based on usage of organic compounds (inhibitors) mainly benzotriazoles, animotriazole and derivates. Inhibitors provide good protection, however they are quite toxic. In last decade, electroconducting polymers (EPP), in first place polypyrrole (PPY) and polyaniline (PANI) were investigated in various practical fields, including environmental friendly corrosion protection. Although both chemical and electrochemical oxidative polymerization are usable in obtaining ECP, electrochemical synthesis is favorable permitting direct polymer film synthesis on metal surface without oxidizing agent. Generally, the basic problem in electrochemical polymerization of ECP on copper is occurrence of two competitive processes on anode: electrochemical synthesis and deposition of ECP and dissolution of copper on potentials necessary to oxidize the monomer. Therefore, it would be necessary to use electrolytes that can passivate copper and permit electrochemical polymerization. Although PANI, due to lower price of its monomer seams more challengeable, most of the studies were devoted to use of PPY [1-3], and only few to application of PANI and derivates in corrosion protection of copper and its alloys [4]. Since, it is evident that there is interest in application of PANI in corrosion protection of copper, the aim of this work was to consider conditions for electrochemical synthesis of protective PANI on copper from sodium benzoate electrolyte, which was proven to be efficient electrolyte for electrochemical synthesis of PANI on steel and aluminum [5,6].

2. EXPERIMENTAL

Potentiodynamic anodic polarization curves of copper electrode were recording at scan rate 0.5 mV s^{-1}, in 0.3 mol dm^{-3} sodium benzoate without and with addition of 0.2 mol dm^{-2} aniline. Electrochemical synthesis of polyaniline (PANI) film on copper was performed by electrochemical polymerization from aqueous solution of 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline. The polyemrization of aniline on copper sheet (S = 2.0 cm^2). was achieved under galvanostatic conditions using current density range between 0.50 and 1.25 mA cm^{-2}. Before all experiments, copper electrode was first mechanically abraded by fine emery papers and then by polishing alumina on polishing cloths, traces of the polishing alumina were removed from the electrode surface ultrasonically. Potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) were used for corrosion studies of copper electrode and PANI coated copper electrode in 3.0 % sodium chloride solution. In order to avoid the edge effects, the surface area of the copper and PANI coated copper electrode used in corrosion measurements was reduced to 1.0 cm^2. In all experiments standard three compartment electrochemical cell was used. Copper and PANI coated copper electrode served as working, standard calomel (SCE) as reference and platinum wire was used as counter electrode. EIS measurements were performed at open circuit potentials in the frequency range between 50 mHz and 100 kHz, while below 5 Hz the fast Fourier technique (FFT) was used. The EIS experiments were performed using PC controlled PAR263A potentiostat/galvanostat connected to PAR frequency response detector FRD100.

3. RESULTS AND DISSCUSION

3.1 Electrochemical polymerization

Optimal concentration of sodium benzoate for electrochemical polymerization of aniline on copper was estimated from previously recorded anodic polarization curves of copper electrode in different concentration of sodium benzoate. In order to monitor the course of anodic polymerization of aniline, anodic polarization curves of copper electrode in 0.3 mol dm^{-3} sodium benzoate with addition of 0.2 mol dm^{-3} aniline, were recorded and presented in Fig. 1.

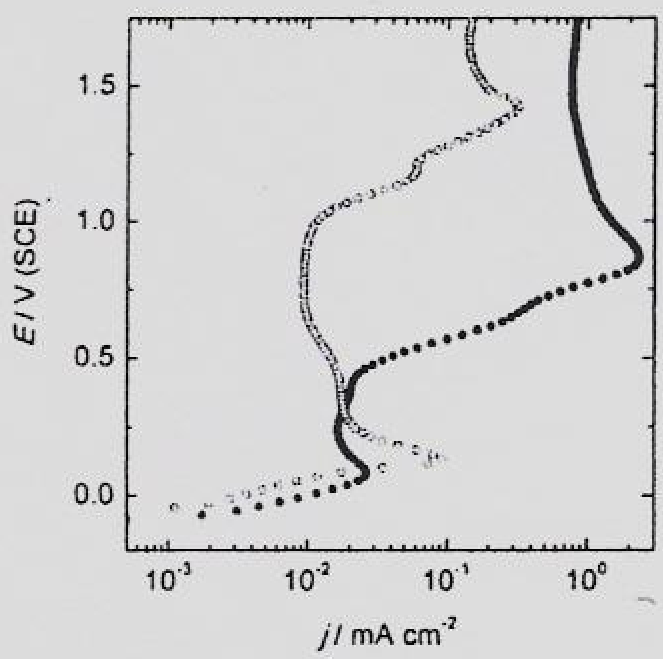


Figure 1. Potentiodynamic anodic polarization (v = 0.5 mV s^{-1}) curves of copper in: (○) - 0.3 mol dm^{-3} sodium benzoate and (●) - 0.3 mol dm^{-3} sodium benzoate and 0.20 mol dm^{-3} aniline

The presence of aniline shifted open circuit potential of copper for ~ 50 mV in the negative direction, connected to anodic inhibitory effect of absorbed aniline monomer. After short passivation of copper, in aniline containing electrolyte, polymerization started at potentials more positive than 0.4 V (SCE) and proceeded up to the potential of 2.5 V(SCE). The observed pick at ~ 0.7 V (SCE) could be connected to existence of polyaniline in the form of pernigraniline salt, at potentials more positive than ~ 2 V (SCE), slow oxygen reduction reaction was observed.

Chronopotentiometric (galvanostatic) curves of electrochemical polymerization of aniline on copper electrode from aqueous solution of 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline, using different current densities during 1000 s are given in Fig.2.

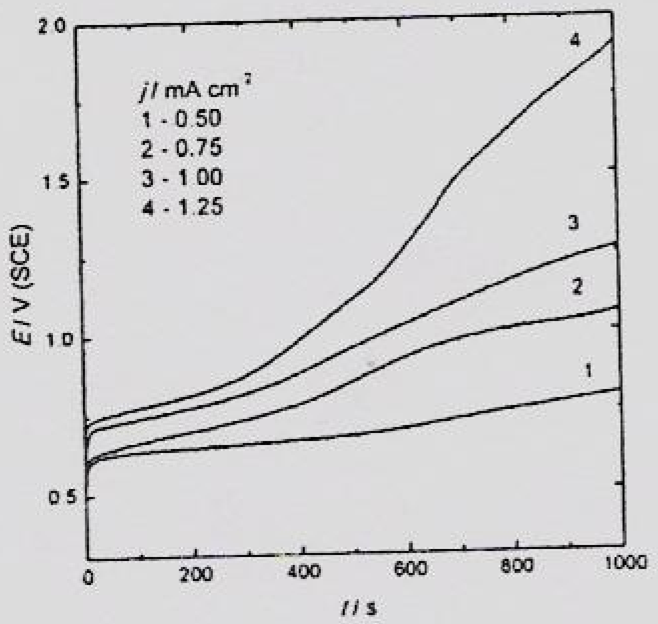


Figure 2. Galvanostatic polymerization of aniline on Cu electrode from 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline solutions using different current densities

Since, the completely uniform PANI films were obtained using higher current densities and in order to achieve lower extent of degradation, polymerization current density of 1.0 mA cm^{-2} was used in further experiments.

3.2 Corrosion studies

Potentiodymanic polarization curves (v = 0.5 mV s^{-1}) of copper and copper coated by electrochemically deposited PANI film, after 24 h of immersion in 3.0 % NaCl are given in Fig.3.

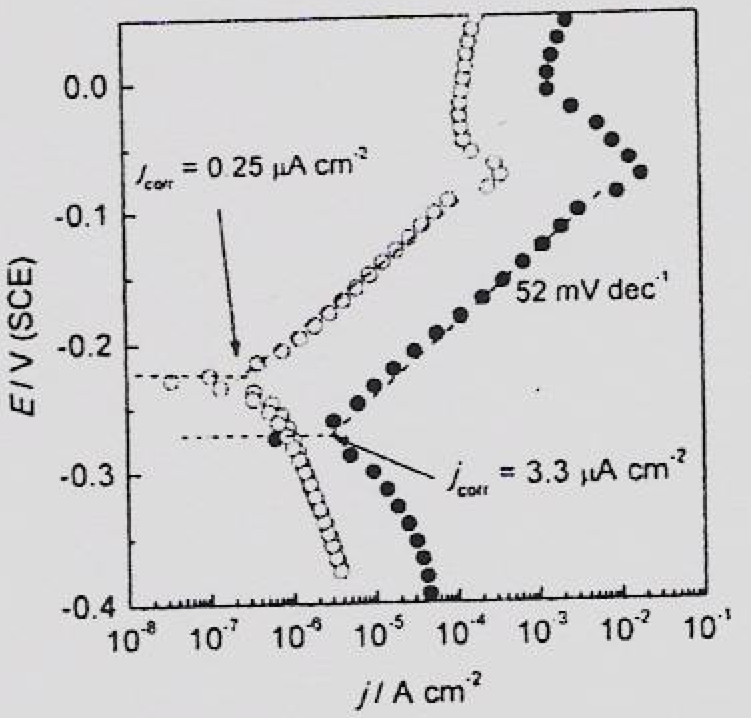


Figure 3. Potentiodynamic (v = 0.5 mV s^{-1}) polarization curves of: (●)- Cu and (○) – PANI coated Cu in 3.0 % NaCl

Anodic polarization curves of copper and PANI coated copper are both under activation control, characterized by the Tafel slope of ~ 54 mV dec^{-1}, connected to anodic dissolution of copper, while cathodic polarization curves are under mixed activacion-diffusion control of oxygen reduction. The corrosion potential of pure copper was, E_{corr} = -0.270 V (SCE), while corrosion potential of PANI coated copper was E_{corr} = - 0.225 V(SCE). Corrosion current densities were determined as intercept of anodic Tafel lines with corrosion potential. The protection efficiency of PANI was estimated to 96 %.

Complex plane spectra of PANI coated copper taken at different times of exposure in 3.0 % NaCl are given in Fig.4, while the time dependences of the corresponding open circuit (corrosion) potential, at which the impedance spectra were given in Insert.

The overall impedance of PANI coated copper, unusually to conventional organic coatings, firstly increased. The increase of the impedance might be a consequence of cathodic dedoping of benzoate anions from PANI film, according to:

$$(PANI^{y+}(C_6H_5COO^-)_y)_n + nye \rightarrow (PANI)_n + ny\, C_6H_5COO^-$$

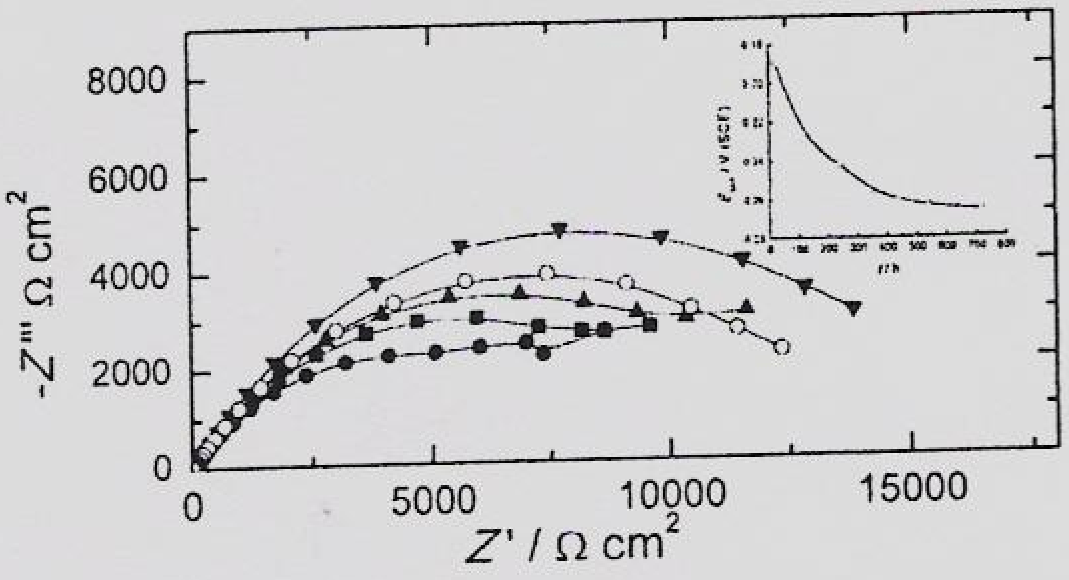


Figure 4. Complex plane impedance spectra of PANI coated Cu after:
(●) - 120 h, (■) – 240 h, (▲) – 360 h, (▼) – 540 h and (○) – 720h of exposure to 0.5 mol dm^{-3} NaCl.
Insert: Time dependences of corresponding open circuit potentials.

Dedoping lead the lost of the PANI film conductivity, reflected in the increase of the overall impedance. Since the shift of the open circuit potential to more negative values is characteristic of dedeoped state the observed decrease in corrosion potentials (Insert of Fig.4), also confirms the assumption of the dedoping process. After observed increase, the overall impedance of PANI started to decrease slowly, meaning that PANI started to act as conventional organic coating enabling barrier corrosion protection of the metal surface.

4. CONCLUSION

Electrochemical synthesis of PANI on copper was successfully performed from aqueous sodium benzoate solution containing aniline. PANI thin coating had provided high protection efficiency to copper. Based on potentiodynamic and EIS measurements, corrosion process of PANI coated copper in NaCl can be explained by the same processes of copper anodic dissolution and cathodic oxygen reduction occurring in parallel with slow cathodic dedoping of the benzoate anions from the PANI film, after dedoping, PANI coating started to act like conventional organic coating.

ACKNOWLEDGEMENTS

This work supported by the Ministry of Education and Science, Republic of Serbia, project TR 37001

REFERENCES

[1] Bazzaoui, M. Martins, J. Bazzaoui E, Martins L. and Machnikova E.: Sweet aqueous solution for electrochemical synthesis of polypyrrole part 1B: On copper and its alloys. Electrochim. Acta, 52(2007)3568-3581

[2] Redondo, M. and Breslin C.: Polypyrrole electrodeposited on copper from an aqueous phosphate solution: Corrosion protection properties. Corr. Sci. 49 (2007) 1765-1776

[3] Fenelon A. and Breslin C.: The electrochemical synthesis of polypyrrole at a copper electrode: corrosion protection properties. Electrochim. Acta, 47 (2002) 4467-4476

[4] Chaudhari S. and. Patil P.: Corrosion protective poly(o-ethoxyaniline) coatings on copper

[5] Popović, M. and Grgur, B.: Electrochemical synthesis and corrosion behavior of thin polyaniline-benzoate film on mild steel. Synth. Met. 143 (2004)191-195

[6] Gvozdenović M. and Grgur B. :Electrochemical polymerization and initial corrosion properties of polyaniline-benzoate film on aluminum, Prog. Org. Coat. 65 (2009) 401-404

University of Belgrade
Technical Faculty in Bor and
Mining and Metallurgy Institute Bor

43rd International October Conference on Mining and Metallurgy

IOC 2011

PROCEEDINGS

Editors:
Desimir Marković
Dragana Živković
Svetlana Nestorović

October 12 - 15, 2011
Kladovo, Serbia

PROCEEDINGS,
43rd INTERNATIONAL OCTOBER CONFERNCE
on Mining and Metallurgy

Editors:
Prof. dr Desimir Marković
University of Belgrade - ***Technical Faculty in Bor***
Prof. dr Dragana Živković
University of Belgrade - ***Technical Faculty in Bor***
Prof. dr Svetlana Nestorović
University of Belgrade - ***Technical Faculty in Bor***

Technical Editors:
Ljubiša Balanović, PhD student
University of Belgrade - ***Technical Faculty in Bor***
Mr Ivana Marković
University of Belgrade - ***Technical Faculty in Bor***

Publisher: University of Belgrade - **Technical Faculty in Bor**
For the publisher: Dean Prof. dr Milan Antonijević
Circulation: 250 copies

Printed in Serbia by „Grafomed-trade“ Bor

ISBN 978-86-80987-87-3

Kladovo, Serbia, October 12-15, 2011

ELECTROCHEMICAL WATER TREATMENT DEVICES

Tomislav Trišović, Branimir Jugović, Milica Gvozdenović, Jasmina Stevanović, Branimir Grgur

Abstract

Drinking water treatment plays an important role in maintaining public health. Chlorine is the most often disinfectant used for microbiological protection of water. Required residual chlorine concentration must be in treated water. The chlorine residual must be 0.5 mg/L at the entrance into the distribution system and 0.25 mg/l at consumers, according to the law. Any less and there is no guarantee that the water has adequate quality. The characterization of chlorinated by-products, particularly THMs (three-halo-methane's). The risks related to THMs formation force the community to look for alternative water sources, treatment methods or disinfectants. As an alternative disinfectant, ultraviolet germicidal irradiation (UV) commonly used in preoxidation. This study presents the results of combination UV and chlorine disinfection.

Key Words: water disinfection, water chlorination, UV disinfection

1. OVERVIEW OF THE EXISTING TECHNOLOGIES FOR WATER DISINFECTION IN THE WORLD

Four different technologies for water disinfection are used nowadays in the world:

- disinfection with gaseous or liquid chlorine;
- disinfection with ozone;
- disinfection with hypochlorite solution produced by the electrolysis of 3% solution of sodium chloride;
- disinfection with chlorine-dioxide (ClO_2).

The oldest and the most exploited one, which is known as conventional, is the disinfection with gaseous or liquid chlorine. During the last two decades ozonization has also been used, while only recently the other two technologies were used. The biggest producers of the equipment for the water treatment in the world (CAPITAL CONTROLS, WALLACE & TIERNAN, PROMINENT, TRAILIGAZ, etc.) mainly possess all mentioned technologies for water disinfection. The basic characteristics, i.e. the advantages and disadvantages of all technologies are given in Table 1.

The possible solution of the above given problem is removal of organic mater (formation of three-halo-methane's during the chlorinating) by strong and unstable oxidants in pre- treatment, and than application of oxidants with longer residual effect in main treatment. (1,2,3) Raw water firstly enters into device for magnetic treatment distorting the solvate shells of magnesium and calcium ions. After magnetic treatment, water enters photo- catalytical reactor in witch several meta stabile compounds are formed.

The ultraviolet (UV) oxidation process is designed to destroy dissolved organic contaminants (4,5) through an advanced chemical oxidation process using ultraviolet radiation and hydrogen peroxide. Hydrogen peroxide is added to the contaminated water, and the mixture is fed into the treatment system. The treatment system contains one or more oxidation chambers. Each chamber contains one high-intensity UV lamp,. mounted in a quartz tube. The contaminated water flows in the space between the chamber wall and the quartz tube in which each UV lamp is mounted. UV light catalyzes chemical oxidation of organic contaminants in water by its combined effect upon the organic substances and reaction with hydrogen peroxide. First, many organic contaminants that absorb UV light may undergo a change in their chemical structure or may become more reactive with chemical oxidants. Second and more importantly, UV light catalyzes the breakdown of hydrogen peroxide to produce hydroxyl radicals, which are powerful chemical oxidants. Hydroxyl radicals react with organic contaminants destroying them and producing harmless carbon dioxide, halides, and water byproducts. The process produces no hazardous by-products or air emissions. The hydrogen peroxide oxidation equipment includes circular wipers attached to the quartz tubes. These wipers periodically remove solids that may accumulate on the tubes; a feature designed to maintain treatment efficiency.

Table 1. Advantagees and disadvantagees of the existing technologies for water disinfection

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
Gaseous, or liquid chlorine	Very successful disinfection Relatively low cost of exploitation Medium investment expenses Removal of ammonia compounds from water	Risk of chlorine leaking during the transport and storage of gaseous chlorine (ecological catastrophe) Necessity of trained workers for hand ing Impossibility of storage of higher amount of gaseous chlorine Chlorinating plants must be located out of the towns Formation of three-halo-methane's during the chlorinating
Ozone	Very successful disinfection Production of ozone on the site of the ozonization Absence of three-halo-methane's in treated water Ecological technology	Very high investment expenses Very high cost of exploitation Necessity of trained workers for handling Short time of activity of ozone as a disinfectant (about 1h - it is usually combined with some other technology of disinfection, e.g. chlorinating)
Hypohlorite * (HIPOGEN®)	*Very successful disinfection* *Production of hypochlorite on the site of the chlorinating* *Ecological technology* *Removal of ammonia compounds from water* *Low cost of exploitation* *Medium investment expenses* *Possibility of storage of salt for a long time of exploitation* *(0.5 to 1 year)* *Unnecessity of trained workers for handling* *Completely automatized operation*	*Formation of three-halo-methane's during the chlorinating*

	Possibility of remote control	
chlorine-dioxide **ClO_2**	Very successful disinfection Production of ClO_2 on the site of the chlorinating There is no formation of three-halo-methane's	Very high investment expenses Very high cost of exploitation Necessity of import of the row materials for ClO_2 production Impossibility of storage of higher amount of row materials It does not remove ammonia compounds from water

Characteristics are mainly given for the system HIPOGEN®.

The chemical oxidation process in the hydrogen peroxide oxidation system is dependent upon a number of reaction conditions that can affect both performance and cost. The process variables that are related to the contaminated water condition are:

- Type and concentration of organic contaminant
- Total organic substances present
- Light transmittance of the water (turbidity or color)
- Type and concentration of dissolved inorganic substances (e.g., carbonates and iron)
- pH.

The process variables that are related to the treatment process design and operation are:

- UV and hydrogen peroxide dosage
- pH and temperature conditions
- Use of supplementary catalysts treatment mode (batch, recycle, or continuous).

After UV treatment and separation column, water is subjected to further treatment in two electrochemical reactors. One reactor serves for production of noble metal ions, while other produces ions of active chlorine (6).

Hipogen provides on site production of sodium hypochlorite, on demand from brine, which is safer to store than chlorine gas. Additionally when bulk salts in used the process requires no chemical handling. Up to 1kg capacity of equivalent chlorine per hour. Efficient operation giving 1kg of equivalent chlorine from as little as 2,5-3kg of salt (NaCl). Comprehensive alarm specification combined with a mimic control panel offering easy identification of system faults. Minimal maintanance requivements.

HIPOGEN presents a real alternative to gaseous chlorine, enabling completely safe disinfection with lower expenses. It can be used for drinking water disinfection, for waste textile and food industry waters treatments and also for swimming poll water disinfection.

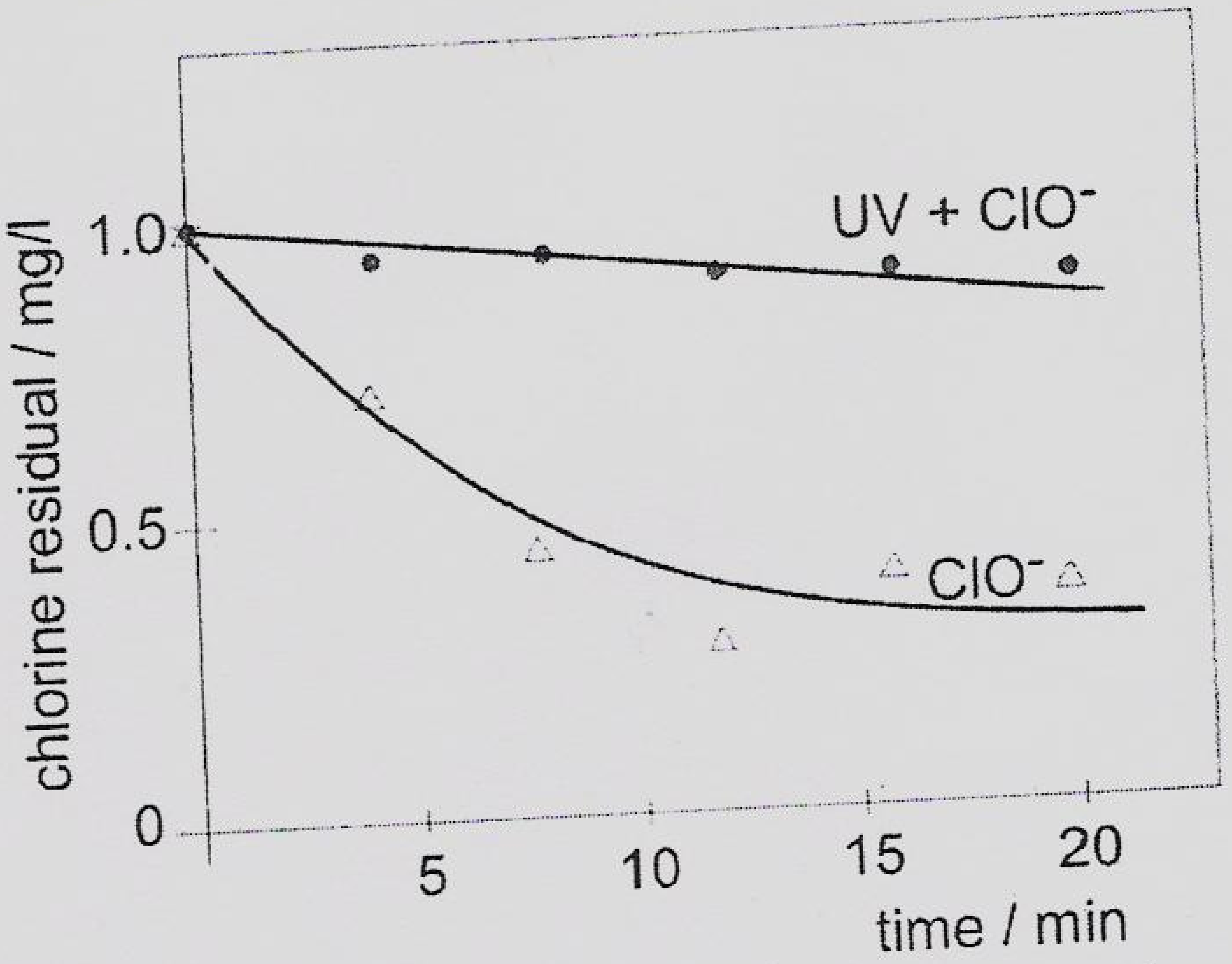


Figure 1. Experimental results for chlorine residual distribution in drinking water mains of "Obrenovic tim" Dobanovci a) UV irradiation (preoxidation) after that chlorination ClO^- b) only chlorination ClO^-

CONCLUSION

From the characteristics presented in this work it could be concluded that on site water chlorination combination with UV ray, has several advantages over the other technologies, with the most important one being ecological aspect of this technology.

REFERENCES

[1] Chang E.E., Chao S.H., Chian P.C. and Lee J.F. (1996) Effects of chlorination on THMs formation in raw water, *Toxicological and Environmental Chemistry*, **56**, 211-225.

[2] Nikolaou A.D., Kostopoulou M.N., Lekkas T.D. (1999) Organic By-Products of Drinking water Chlorination, *Global Nest: the Int. J.*, 1(3), 143-156.

[3] Sohn J., Amy G., Cho J., Lee Y. and Yoon Y. (2004) Disinfectant decay and disinfection byproducts formation model development: chlorination and ozonation by-products, *Water Research*, **38**, 2461-2478.

[4] Sohn J., Amy G., Cho J., Lee Y. and Yoon Y. (2004) Disinfectant decay and disinfection byproducts formation model development: chlorination and ozonation by-products, *Water Research*, **38**, 2461-2478.

[5] White D.M., Garland D.S., Narr J. and Woolard C.R. (2003) Natural organic matter and DBP formation potential in Alaskan water supplies, *Water Research*, **37**, 939-947.

[6] Islam M.R., Chaudry M.H., Clark R.M, (1997), Inverse modeling of chlorine concentration in pipe networks under dynamic condition, *Journal of Environmental Engineering*, **123**, 1033-1040.

Journal of Trends in the Development of Machinery
and Associated Technology
Vol. 16, No. 1, 2012, ISSN 2303-4009 (online), p.p. 219-222

MODIFICATION OF THE DYNAMICS CHARACTERISTICS USING A REANALYSIS PROCEDURES TECHNIQUE – NEW RESULTS

Nataša Trišović*, Taško Maneski***,**
Tomislav Trišović*, Ljubica Milović**

***Institute of Technical Sciences of SASA,**
Knez Mihailova 35/4, 11000 Belgrade, Serbia

****Faculty of Technology and Metallurgy, University of Belgrade,**
Karnegijeva 4, 11000 Belgrade, Serbia

*****Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, Belgrade, Serbia**

ABSTRACT

The present paper deals with the problem of dynamic improving characteristics for a sub-structure (bucket wheel excavator) of a complex mining structure. The procedure used in this paper is concerned with the analysis of the distribution of potential and kinetic energy in every element of structure, which gives prediction for which elements need reanalysis. Reanalysis technique can be done for the structure using finite element methods. Therefore, some information like material, size, and boundary conditions should be prepared before FE model is constructed. Because the optimum structure design has high natural frequency, the main aim of dynamic modification is to increase natural frequencies and to increase the difference between them.

Key words: Structural dynamic modification, reanalysis, FEM, eigenvalues, design variables

1. OVERVIEW OF THE EXISTING TECHNOLOGIES FOR WATER DISINFECTIONS

Dynamic analysis is more complex than static analysis, and the design requirements must include dynamic properties such as vibration level, resonance range, response properties, eigenvalues, dynamic stability and modal forms. To avoid dynamic problems, some modification will be done for structure in process of reanalysis. Reanalysis is a technique through which the dynamic response of the structure is improved. Finite element method is a powerful method to perform these processes using simple procedures. Modelling of complex structures using finite elements method is a helpful approach in solving problems in short time with reliable results.

The procedure of reanalysis depends on the concept of energy distribution through the structure. Study of the energy distribution leads to finding out the right place, which will be conducted by some modifications to improve the eigenvalues of the structure. Therefore, determination of distribution of kinetic and potential energies on the elements of whole structure is the main step in the reanalysis procedure. Complex structures need several steps during the analysis to reach the most accurate results. Starting with initial rough analysis of a structure which is followed by the precise analysis based on the sensitivity of each element of the structure. The improvement of dynamic characteristics, during the reanalysis steps, can be achieved by making some adjustment to the structure such as geometrical modifications, material properties and boundary conditions. The process of analysis is done using a computer program, based on the using of finite element methods and the implementation of structure energy distributions. The distributions of potential and kinetic energies of elements of the whole structure give a clear view to the problem, which help to make appropriate decision for structure modifications. The decision of the final modification can be made according to the structure dynamic behaviour during reanalysis steps and its obtained results. Several studies have been addressed to the subject of modal reanalysis and structure dynamic modifications [1-6]

2. THEORETICAL CONSIDERATION

For the system with no damping and no external force, the equation of motion in the matrix form is:

$$[M]\cdot\{\ddot{Q}(t)\}+[K]\cdot\{Q(t)\}=\{0\} \tag{1}$$

Then, the eigenvalues of the previous differential equation for r-th mode can be expressed as:

$$[K]\cdot\{Q_r\}-\lambda_r[M]\cdot\{Q_r\}=\{0\} \tag{2}$$

Where λ_r - is the r -th eigenvalue, and Q_r - is the r -th eigenvector for the structure.

Now, by multiplying the left side of equation (2) by transposed value of *r*-th eigenvector and divided by 2 one can get:

$$\frac{1}{2}\{Q_r\}^T[K]\{Q_r\}=\frac{1}{2}\lambda_i\{Q_r\}^T[M]\cdot\{Q_r\} \tag{3}$$

Equation (3) is the balance equation of potential and kinetic energy for a structure in main modes of oscillation. Furthermore, the potential energy of a structure on *r*-th main oscillation mode, having in mind the previous equation, can be rewritten as:

$$E_{p,r}=\frac{1}{2}\{Q_r\}^T[K]\{Q_r\}. \tag{4}$$

In the same way, the kinetic energy is:

$$E_{k,r}=\frac{1}{2}\lambda_r\{Q_r\}^T[M]\{Q_r\}, \tag{5}$$

For free vibration case the modified system can be describe by a modified equation (perturbation equation) as:

$$[K]'\{Q_r\}'=\lambda_i'[M]'\cdot\{Q_r\}' \tag{6}$$

After some manipulations and neglecting the higher order terms, the change of i-th eigenvalue under system modification can be expressed as:

$$\frac{\Delta\lambda_r}{\lambda_r'}=\frac{\frac{1}{2}\{Q_r\}'^T[\Delta K]\{Q_r\}'-\frac{1}{2}\lambda_r'\{Q_r\}'^T[\Delta M]\{Q_r\}'}{\frac{1}{2}\lambda_r'\{Q_r\}'^T[M]'\{Q_r\}'} \tag{7}$$

Where [Δ*K*] and [Δ*M*] are the corresponding changes in stiffness and mass matrices respectively, and Δλ and $\{\Delta Q_r\}$ are changes of eigenvalues and eigenvectors, respectively. The previous equation has an important definition to understand the procedures of reanalysis and to define the position of elements that require modifications to improve the dynamic behavior of the structure. Because the denominator has the same value, the numerator is the main interest of analysis. Consequently, the modification (increase/decrease structure rigidity or mass) which will be done for the structure depends on the sign value of numerator in equation (7). The main point of improving dynamic behavior of the structure is increasing its natural frequencies and maximizing the interval between adjacent natural frequencies. Hence, study of energy distribution will be done for each element in the structure to determine places of modification. The main point of improving dynamic behavior of a structure is increasing its natural frequencies and maximizing the interval between adjacent natural frequencies. This request, as previously mentioned, can be achieved by changing the design parameters of the structure. The procedure used in this paper is developed in PHD thesis [8] and concerned with distribution of potential and kinetic energy in all elements of structure. Calculations of main modes of oscillation were performed using KOMIPS software [7]. Structure has a good dynamic behavior when its first eigenvalue is high and the interval between adjacent eigenvalues is large.

2. DEMONSTRATION EXAMPLE

Crane bucket wheel excavator is a truss structure associated with one hand stationary hinge connection on the other lamella, which can be characterized as a elastic support. The dynamic behavior of the said excavator boom is interesting, because the natural frequencies and low stick close together and close to the frequency of coercive force digging. The figures 1 and 3 show the first and third main form of oscillation excavators and distribution of energy of the excavator boom, and on the basis of changes in the energy interval can be located segments for the modification of arrows. In this case it is technically feasible stiffening structure by adding new elements to the energy difference between the highest places.

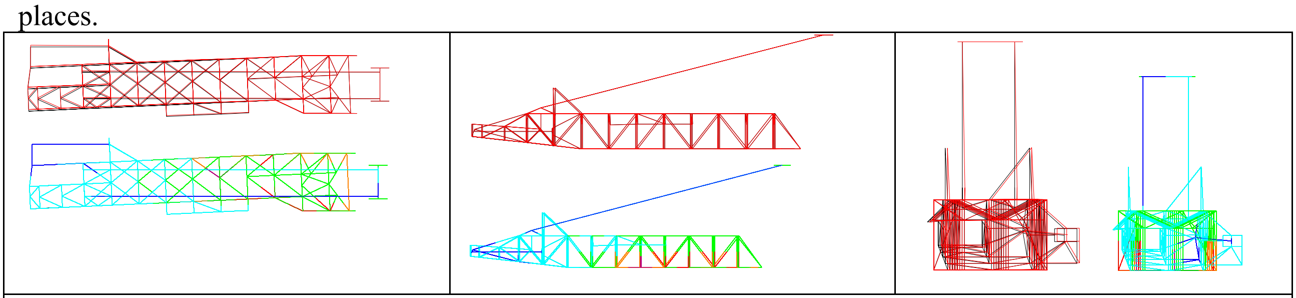


Figure 1. The first major form of oscillating boom bucket wheel excavator in the first frequency, f_{01} *= 1.6 Hz. Diagram of distribution differences of potential and kinetic energy* $(E_p - E_k)$ *[kNcm].*

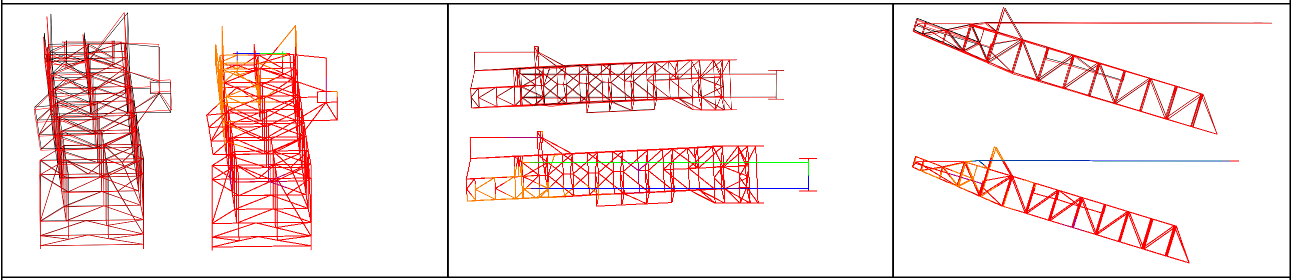


Figure 2. The third major form of oscillating boom bucket wheel excavator in the second position. The third frequency isf_{03} *=1.6 Hz. Diagram of distribution differences of potential and kinetic energy (Ep-Ek), boom bucket wheel excavators for the second position observed, III form of oscillation [kNcm].*

Two kinds of the models are used in analysis. First one is initial, unmodified model and second one is arbitrary, uniformly modified model. It is important to note that changes must be small. Distributions of the increment difference of potential and kinetic energy evaluated for the arbitrary, uniformly modified structure and unmodified.

3. CONCLUSIONS

Studying the dynamic behavior of structures can be predicted responses due to changes in its shape, size or design elements change materials. The main goal of dynamic optimization is to increase natural frequencies and to increase the difference between them. Especially, the lowest frequencies are the most interesting and those whose values are close to frequency excitation force in the system.

Consequently these are further characteristic areas:

I The elements with kinetics and potential energy, which values are negligible comparing to other elements.
II Elements with the kinetics energy greater than the potential energy.
III Elements with the potential energy greater than kinetics.
IV Elements with kinetics and potential energy, which values are not negligible comparing to other elements.

By observing diagrams of the distribution difference of the increment potential and kinetic energy on the modes shape of interest, modification can be suggested. The application of mentioned procedure of real structures shows its practical side.

4. ACKNOWLEDGMENT

This work has been performed within the projects TR172046, TR35011, TR35040 and ON74001 which are supported by the Ministry of Education and Science of the Republic of Serbia, whose financial help is gratefully acknowledged.

5. REFERENCES

[1] Tong, W.H., Jiang, J.S., and Liu, G.R., Solution Existence of the Optimization Problem of Truss Structure with Frequency Constraints, Int. Journal oj Solids and Structures, Vpol. 37., No. 30, 2000, pp. 4043-4060

[2] Wang, D., Zhang, W.H., and Jiang, J.S., Truss Optimization on Shape and Sizing with frequency Constraints, AIAA Journal, Vol. 42, No. 3, 2004, pp. 622-630.

[3] Nair, B.P., Keane, A.J., and Langley, R.S., Improved First-Order Approximation of Eigenvalues and Eigenvectors, AIAA Journal, Vol. 36, No. 9, September 1998, pp. 1722-1727.

[4] Tong, W.H., and Liu, G.R., An Optimization Procedure for Truss Structure with Discrete Design Variables and Dynamic Constraints, Computers and Structures, Vol. 79, No. 2, 2001, pp. 155-162

[5] Sergeyev, O., and Mroz., Z., Sensitivity Analysis and Optimal Design of 3D Frame Structures for Stress and Frequency Constraints, Computers and Structures, Vol. 75, No. 2, 2000. pp. 167-185

[6] Ki, I.K., Nonlinear Inverse Perturbation Method in Dynamic Redisgn, PhD, Thessis, Michigen University, USA, 1983.

[7] Maneski T., KOMIPS software, Monograph computer modeling and structures calculation, Faculty of Mechanical Engineering, University of Belgrade, 1998 [ISBN 86-7083-319-0].

[8] Trisovic, R., N., Modification of the Dynamics Characteristics in the Structural Dynamic Reanalysis, PhD, Thessis, University of Belgrade, Serbia, 2007

16th International Research/Expert Conference
”Trends in the Development of Machinery and Associated Technology”
TMT 2012, Dubai, UAE, 10-12 September 2012

UNIVERSAL MODULAR DEVICE FOR ELECTROCHEMICAL SYNTESIS OF THE DISINFICANT

Tomislav Trišović*, Branimir Jugović*, Milica Gvozdenović ,
Nataša Trišović*****

***Institute of Technical Sciences of SASA,
Knez Mihailova 35/4, 11000 Belgrade, Serbia**

****Faculty of Technology and Metallurgy, University of Belgrade,
Karnegijeva 4, 11000 Belgrade, Serbia**

*****Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije
16, Belgrade, Serbia**

ABSTRACT

For the water disinfections practically four different technologies (chlorine, ozone, hypochlorite, chlorine dioxide) are used nowadays in the world. The oldest and the most exploited one, so called conventional, is the disinfections with gaseous or liquid chlorine. The biggest producers of the equipment for the water treatment in the world mainly possess all mentioned technologies for water disinfections. It is easy to concluded that the technology of water disinfections with the hypochlorite solution produced by the electrolysis of 3% solution of sodium chloride on the site of water chlorination is not only the most convenient from the point of economical aspects, but also from the point of the ecological aspect.

Keywords: water disinfections, water chlorination, *in sity* water chlorination, hypochlorite production.

1. OVERVIEW OF THE EXISTING TECHNOLOGIES FOR WATER DISINFECTIONS

The four main chemical substances used for the water disinfection nowadays in the world are:

- disinfection with gaseous or liquid chlorine;
- disinfection with ozone;
- disinfection with hypochlorite solution produced by the electrolysis of 3% solution of sodium chloride;
- disinfection with chlorine-dioxide (ClO_2).

The oldest and the most exploited one, which is known as conventional, is the disinfection with gaseous or liquid chlorine. During the last two decades ozonization has also been used, while only recently the other two technologies were applied. The biggest producers of the equipment for the water treatment in the world (CAPITAL CONTROLS, WALLACE & TIERNAN, PROMINENT etc.) mainly possess all mentioned technologies for water disinfection.

2. UNIVERSAL MODULAR DEVICE FOR ELECTROCHEMICAL SYNTESIS OF THE DISINFICANT

System comprises: hypochlorite reactor (electrolyzer), reactor storage tank, hypochlorite storage tank, rectifier with control panel for automatic control of operation, hypochlorite dozing pump, electromagnetic valve, and ventilation system. This type of electrochemical generator is designed with upper, reaction, and lower, reception tanks, while between is modular electrolyzer, as shown on Figure 1. Above reception tanks two or more modular reactors in which dilute solutions of sodium chloride is converted in active chlorine by electrochemical reaction. Before electrolysis reaction tank is filed with water and specified quantity of sodium chloride. After starting, mixer prepares 3% NaCl solution in reaction tank followed by automatically connection of electrolyzer. After 60 h, electrolysis is finished, power supply is automatically switched off and active chlorine solution is ready for simply manual transfer in reaction tank and use by applying micro dozing pump. At the mean time, reception tank is again manually filed with water and specified quantity of sodium chloride. By this procedure, reception tank always contains some extra volume of active chlorine for unexpected situations.

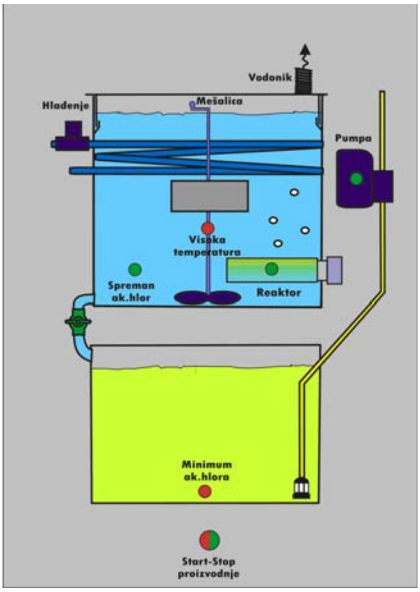


Figure 1. Schematic representation of the modular charge electrochemical generator for automatic production and dozing dezinfectans with self cleaning electrodes

Basic componets of MCEG

1. Modular electrolyser - reactor
2. Switch temperature
3. Reactor tank
4. Hypochlorite storage tank
5. Heat exchanger
6. Electomagnetic valve
7. Fan pipeline
8. Switch level
9. Dosing pump

Depending on the capacity of the devices a salt reactor tank can contain from 200 dm^3 to 1000 dm^3 of 3% NaCl. It should be refilled with the 3% NaCl every 15 – 60 days, depending on the capacity. Into the reactor tank which was previously filled with water from fountain, 6 to 30 kg crystals of common table salt-NaCl are added. By using the manual stirrer, salt is mixed until the complete dissolution of the salt. On the end of this operation, setting of the cover provides complete isolation of solution from the environment by the water valve. The only way to the solution to come into contact with air from atmosphere is through ventilating system. On the bottom of the reactor tank, 1 to 8 reactor modules depending on the capacity are placed. The temperature sensor is placed below the reaction modules. If the temperature go over the certain value, electromagnetic valve will active the function of the spiral heat exchanger in the reaction vessel. An electromagnetic valve closes after decreasing of the temperature, and consequently the process of cooling stops. These whole processing steps are necessary due to maintain the electrochemical reaction in optimal conditions which provides maximum efficiency. Gaseous hydrogen, produced on the cathode during the electrolysis, is vented out by the ventilation system. A temperature switch is also placed in the generator, switching off the system in the case of possible increase of the electrolyte temperature over the upper limit. The characteristics of the hypochlorite storage tank can contain from 200 dm^3 to 1000 dm^3 of 1,4% NaOCl. One switch are placed in the tank. When the hypochlorite level reaches the low-level switch, the brine pump and the rectifier are automatically being switched off and devices automatically being stopped (alarm low level hypohlorite). Depending on the system capacity, the characteristics of the rectifiers are:

Voltage - 2 - 20 V; current - 0 - 160 A.

The operation of the rectifier is automatically controlled from the control panel. These pumps were made of materials resistant to the very aggressive solutions such as NaCl and NaOCl solution.
Among the capacities given in this brochure, we can produce our system which can satisfy much higher needs for equivalent chlorine, up to 10 kg per day. Such system comprises all other elements except the reactor tank and hypochlorite storage tank, which are to big and must be placed separately.

Figure 2. Picture of the modular charge electrochemical generator for automatic production and dozing dezinfectans and with self cleaning electrodes

3. PRINCIPLE OF THE DEVICE FUNCTION

Into the reactor tank which was previously filled with water, crystals of NaCl are added. By using the manual stirrer, salt is mixed until the complete dissolution of the salt. On the end of this operation, setting of the cover through vessel provides complete isolation of solution from the environment by the water valve. Electrolysis process starts by pressing of the button START. Evolution of the chlorine on the anode undergoes to hydrolysis forming hypochlorite ions, until evolution of hydrogen occurs on the cathode and consequently throw the evolved gas into the atmosphere. Considering fact that part of electric energy is transform into the heat, spiral heating exchanger with water circulation is installed in the reaction tank. Circulation of the refrigerate fluid (water) is automatically provided by the measurements of the temperature during electrolysis. If the temperature go over the certain value, electromagnetic valve is opened until refrigerate fluid cooling the reaction solution to the certain stringer temperature, when is closed again. The device is turn off after 40 to 200 hours of constantly function, when the hypochlorite solution is ready to transfer by gravity into the hypochlorite tank. By using pump, the hypochlorite from the tank is dosing water in order to obtain disinfection. In addition, new bach is filled with reaction solution and parallel, new electrolysis-production of hypochlorite starts, too. After whole amount of the hypochlorite in the hypochlorite tank is consumed, alarm of low level of the present hypochlorite is turn on, which inform manipulator of the device about the situation and interrupt function of the pump. All stages in function of the device are connecting by internet and GSM net and are possible to send all the information about operating state of the device to the person in charge for the supervision or distance controller of the device.

The modular charge electrochemical generator is less expensive, trustful, drinking water disinfectant sources (based on the diluted hypo-chlorite solution) designed for the low population suburban areas.
The electrochemical generator consist the preparation-reaction tanks, with adjustable volume depending on the required quantities of disinfectants, and the electrolyser. The electrolyte is prepared in the reaction tanks, filling with water up to the marked volume and adding required mass of commercially available sodium chloride. After manual adding of the required mass of sodium

chloride, the electrolyte should be manually mixed with stirrer while whole sodium chloride was dissolved (les than five minutes), and electrolysis units should be start up, simply by pressing start-up button on external power supply. Depending on electrolyte volume, electrolysis can take 40 to 80 hours. During electrolysis, if the temperatures cross the certain value, the cooling of the electrolyte is automatically applied.

By applauing the automatic mode of the electrolysis (reverse curent at the certain times) the electrodes could be cleaned from carbonate deposites which is the main problem for the efficiency in such tupes of electrolysers.

After the electrolysis is complited, the dezinficient solytion is transfered in to the storage tank, and used due to the reqirements (using the dosing pump and active chlorine senzors).

REVERSE DSA (dimension stable electrodes) is predicted to work for anodic, as well as for cathodic reaction, so water softening is not necessary. Hence, by using this system, expensive ion exchange columns and their regeneration are avoided. This type of electrolysers is designed for water-works and water polls where constant control and measurements of active chlorine concentrations is necessary due to the regulations. This installation is in trail use.

Technological scheme of the device with signal and alarm positions is placed on the control board. Green light bulb is indication of work of the device respective component. Suitable element of the device is not in function if there is no green light on the board. Alarming situations (unsuitable temperature, low level of hypochlorite) are assigned with red light bulb. Function of the device is normal if there is no indication of red light. Red light beside sensor element indicates switching off of the device and it will show light to the length of the manual reset of the device.

By pumping the water with 0.3% of NaCl from water units through mechanical (sand) filters and electrolyser small amount of active chlorine is produced, which is used for continual disinfections of water in the rest of the water units. Power consumption is as small as 30 to 80 Wh.

4. CONCLUSION

This solution represents confidently technological answer which could be applied for synthesis of different organic and non-organic compounds. Innovation solves the problem of electrochemical synthesis obtainment with usage of modular reactor of simple construction which provides technical support during function of the device, as well.

The system can be applied for water disinfections, in disinfections of accessories in food and meat industry. The devices are attested and represent the loves price devices for in site disinfections, comparing with similar ones which can be found at the market.

5. ACKNOWLEDGMENT

This work has been performed within the projects TR172046, TR35011 and ON74001 which are supported by the Ministry of Education and Science of the Republic of Serbia, whose financial help is gratefully acknowledged.

6. REFERENCES

[1] Elkais Ali Ramadan, Gvozdenovic Milica M, Jugovic Branimir Z, Trisovic Tomislav Lj, Maksimovic Miodrag M, Grgur Branimir N.: Electrochemical Synthesis and Corrosion Behavior of Thin Polyaniline Film on Mild Steel, Copper and Aluminum, HEMIJSKA INDUSTRIJA, (2011), vol. 65 br. 1, str. 15-21

[2] Gvozdenovic Milica M, Jugovic Branimir Z, Trisovic Tomislav Lj, Stevanovic Jasmina S, Grgur Branimir N.: Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte, MATERIALS CHEMISTRY AND PHYSICS, (2011), vol. 125 br. 3, str. 601-605

Slovak Society of Chemical Engineering
Institute of Chemical and Environmental Engineering
Slovak University of Technology in Bratislava

PROCEEDINGS

39$^{\mathrm{th}}$ International Conference of Slovak Society of Chemical Engineering

Hotel Hutník
Tatranské Matliare, Slovakia
May 21–25, 2012

Editor: prof. J. Markoš

ISBN: 978-80-89475-04-9, EAN: 9788089475049

Gvozdenovic, M., Jugovic, B., Jambrec, D., Grgur, B., Trisovic, T., Stevanovic, J.: The influence of current density on charge/discharge characteristics of polyaniline electrode, Editor: Markoš, J., In *Proceedings of the 39th International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 1467–1471, 2012.

THE INFLUENCE OF CURRENT DENSITY ON CHARGE/DISCHARGE CHARACTERISTICS OF POLYANILINE ELECTRODE

Gvozdenovic, M.[a], Jugovic, B.[b], Jambrec, D.[c], Grgur, B.[a], Trisovic, T.[b], Stevanovic, J.[d]

[a] *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*
[b] *Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia*
[c] *Inovation center- Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*
[d] *IHTM-Institute of electrochemistry, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia*

ABSTRACT

Polyaniline (PANI) was electrochemically synthesized on graphite electrode galvanostaticaly from aqueous solution of 0.25 mol dm^{-3} aniline and 0.5 mol dm^{-3} p-toluenesulfonic acid. Charge capacity available for the exchange and the total theoretical weight of polyaniline polymerized on graphite electrode was determined. Characterization polianiline electrode was performed by cyclic voltametry in 0.5 mol dm^{-3} HCl. Based on the PANI electrodes behavior during the cyclization, was tested the possibility of practical application of polyaniline doped p-toluenesulfonic acid as the anode material of secondary electrochemical power sources.

INTRODUCTION

Conducting polymers (CP) is very interesting group of polymers due to their specific characteristic including electrical conductivity, mechanical strength, corrosion resistance and the possibility of their chemical and electrochemical synthesis. Therefore, the study of the synthesis, structure and properties of these materials in the world pays specail attention to the las twenty years. CP have found application in microelectronics, optoelectronics, the active protection of metals and alloys from corrosion and, lately as electrode materials for application in electrochemical energy sources [1].

Although the CP can be synthesized an the chemical and electrochemical oxidative polymerization, electrochemical synthesis is better because its performance is not the oxidizing agent is used directly in its conductive form [2]. CP can be electrochemically sythesized by different techniques: cyclic voltametry, potentioststic and galvanostatic technique. The most applicable is galvanostatic tehnique that allows control of polymerization in terms of thickness and morphology of the deposit.

The best known systems that are used in electrochemical energy sources usind electollytes based on aqueous solutions of the systems are composed of polymers based in polianiline (PANI) in combinatiob with electronegative metals (usually zinc) [3-10]. PANI is very interesting because of its unique charge transfer, an interesting behavior in aqueous solutions and features that no adverse impact on the environment. Although it appears that these systems can meet most of the 3-E criteria (Energetic, Economic and Enviromental): energy (high specific and volumetric capacity), economic (low cost of developing and maintaining a large number od cycles), the criteria of Environmental protection (intoxic, energy efficiency, ease of recycling) are the main factors of efficiency of electrochemical power sources [11-12], these systems have found practical application. The main reason is the appearance of degradation of polyaniline [13, 14].

The aim of this paper is to investigate the influence of the current density on charge/discharge characteristic of polianiline electrode.

EXPERIMENTAL

Polyaniline on graphite electrode was formed by anodic polymerization from aqueous solution of 0,5 mol dm^{-3} p- toluensulfonic acid and 0.25 mol dm^{-3} aniline at constant current density of 2.0 mA cm^{-2}. Prior to use aniline (p.a. Aldrich) was distilled in argon. The working electrode was first mechanically polished with fine emery papers (2/0, 3/0 and 4/0) and than with polishing alumina (1μm Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.). The traces of the polishing alumina were removed from the electrode surface ultrasonically during 10 min. After polymerization, PANI electrode was dedoped with current density of 1.0 mA cm^{-2}, washed with bidistilled water and than investigated in 0.5 mol dm^{-3} HCl. The characterization of *p* – TS doped polyaniline was firstly characterized by cyclic voltammetry using different scan rates. The efficiency of charge/discharge process was investigated using different discharge current densities in the range of 0.25 – 2.0 mA cm^{-2}. The experiments were carried out in three compartment electrochemical cells. Saturated electrode served as reference, while platinum foil was used as counter electrode. All electrochemical experiments were performed using GMRY PC3 potentiostat/galvanostat controlled by PC.

RESULTS AND DISCUSSION

Aniline electropolymerization on graphite electrode from 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline at constant current density of 2.0 mA cm^{-2} during 1080. Electrochemical polymerization of aniline occurs together with insertion of *p*-toluen sulfonic anion (doping) according to:

$$(\mathrm{PANI})_n + ny\,p\text{-}\mathrm{TS}^- \rightarrow [\mathrm{PANI}^{y+}(\,p\text{-}\mathrm{TS}^-)]_n + ny\mathrm{e}^- \qquad (1)$$

After synthesis, electrode was discharged (dedoped) in the same solution. From the ratio of the charge delivered during discharge and the charge used for the synthesis it could be concluded that 30% of the overall mass is available for the current exchange.

Fig. 1. shows cyclic voltammograms of polyaniline electrode obtained using different scan rates in the potential range between -0.6 and 0.6 V vs. SCE.

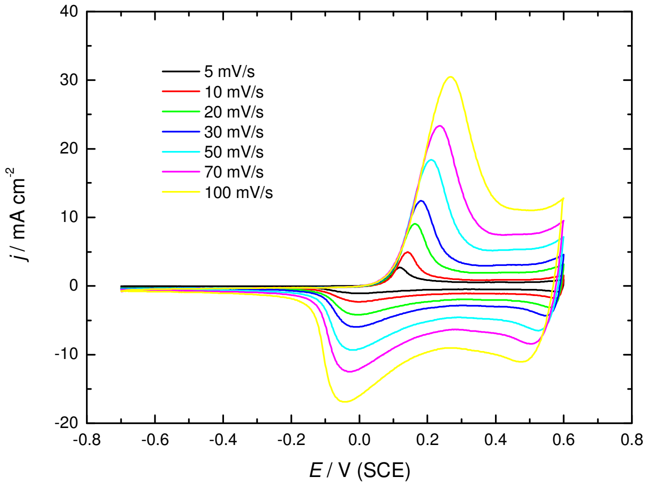


Fig. 1. Cyclic voltammograms of polyaniline electrode in 0.5 mol dm^{-3} HCl obtained by different scan rates (as marked in Fig.) in the potential range – 0.7 – 0.6 V.

From the data displayed at Fig. 1, dependences of peak current on squere rt. of scan rate is given on Fig. 2.

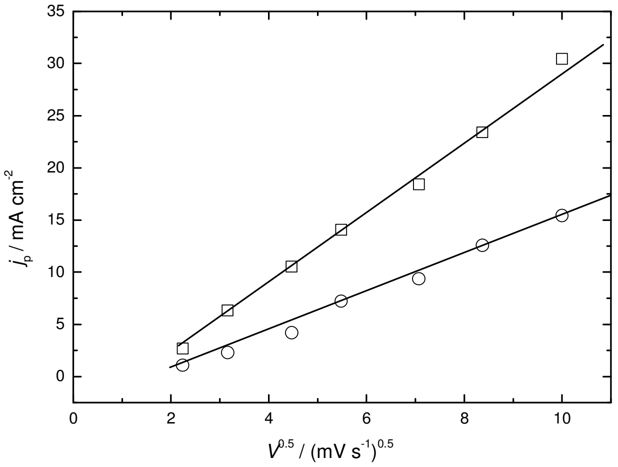


Fig. 2. Dependences of peak currents on square rt. of scan rate.

Linear dependences of current peak on sq. rt. of scan rate is linear indicating diffusion control of ions doping/dedoping process.

Polyaniline was subjected to charge / discharge by different current densities in the range of 0.25 to 2.0 mA cm^{-2}, charging process was performed until potential of 0.5 V was reached, while discharge was performed to potential of -0.4 V, and data are given in Table 1. and in Fig. 3.

Table 1. Charge and discharge time and capacities obtained by different current densities.

j = 0,25 mA cm^{-2}		
	Charge	discharge
t / s	1540	1520
Q / C cm^{-2}	0,385	0,380
j =0,5 mA cm^{-2}		
	charge	discharge
t / s	810	790
Q / C cm^{-2}	0,405	0,395
j =0,75 mA cm^{-2}		
	charge	discharge
t / s	590	550
Q / C cm^{-2}	0,442	0,412

j =1,0 mA cm^{-2}		
	Charge	discharge
t / s	370	350
Q / C cm^{-2}	0,370	0,350
j =1,5 mA cm^{-2}		
	charge	discharge
t / s	280	250
Q / C cm^{-2}	0,420	0,375
j =2,0 mA cm^{-2}		
	charge	discharge
t / s	190	170
Q / C cm^{-2}	0,380	0,340

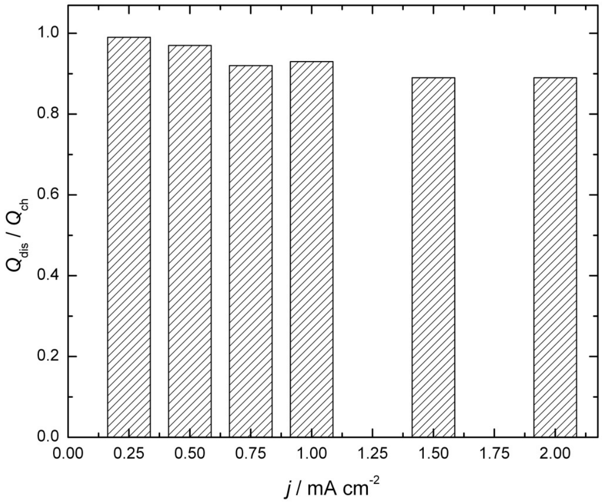


Fig 3. Calculated discharge/charge capacities ratio of polyaniline electrode in 0.5 mol dm^{-3} HCl, obtained by different current densities in the range of 0.5 – 2.00 mA cm^{-2}.

As it could bee seen from both Table1 and Fig. 3. Maximum efficiency of charge/discharge process expreced as ratio of discharge and charge capacities was achieved at low current densities of 0.25 (practically all the charge is delivered during discharge process, Q_{dis} / Q_{ch} ~ 100 %) after which the discharge/ charge ratio is lowered but remained constant with current densities in the range of 0.50 – 2.0 mA cm^{-2}. This investigation is still in progress but obtained results suggested that polyaniline doped by *p*-toluen sulfonic acid could be considered as interesting material for rechargeable power sources.

CONCLUSION

Polyaniline electrode was successfully obtained by galvanostatic deposition of polyaniline from aqueou *p*- toluen sulfonic acid electrolite containing aniline. Polyaniline electrode was investigated in by cyclic voltammetry galvanostatic charge/discharge. It was observed that polyaniline doped by *p*-toluen sulfonic anion could be considered as anodic material for electrochemical rechargeable power sources.

ACKNOWLEDGMENT

This work is financially supported by the Ministry of Science, Republic of Serbia, contract no. 172046.

REFERENCES

[1] Malinauskas A, Malinauskienė J, Ramanavičius A. *Conducting polzmer-based nanostructurized materials: electrohemical aspects.* Nanotechnologz 2005;16:R51-R62.
[2] Skotheim TA, editor. *Handbook of Conducting Polymers.* New York: Marrcel Dekker; 1986.
[3] Sima M, Visan T, Buda M. *A comparative study of yinc-polzaniline electrohemical cells having sulfate and chloride electrolytes.* Jurnal of Power Sources 1995;56:133-1 36.
[4] Kan J, Xue H, Mu S. *Effect of inhibitors on Zn-dendrite formation for zinc-polyaniline secondary baterry.* Jurnal of Power Sources 1998;74:113-116.
[5] Rahmanifar M S, Mousavi M F, Shamsipur M, Ghaemia M. *What is the limiting factor of the cycle-life of Zn-polyaniline rechargeable batteries.* Jurnal of Power Sources 2004;132:296-301.
[6] Karami H, Mousavi M F, Shamsipur M. *A new design for drz polyaniline rechargeable batteries.* Jurnal of Power Sources 2003;117:255-259.
[7] Jugović B Z, Trišović T Lj, Stevanović J, Maksimović M, Grgur B N. *Novel electrolyte for zinc-polzanilline baterries.* Jurnal of Power Sources 2006;160:1447-1450.
[8] Jugović B Z, Trišović T Lj, Stevanović J, Maksimović M, Grgur B N. *Comparative studies of chloride and chloride/citrate based electrolytes for zinc-polyaniline batteries.* Electrochimica Acta 2006;51:6268-6274.
[9] Rahmanifar M S, Mousavi M F, Shamsipur M, Heli H. *A study on open circuit voltage reduction as a main drawback of Zn-polyaniline rechargeable batteries.* Synthetic Metals 2005;155:480-484.
[10] Mirmohseni A, Solhjo R. *Preparation and characterization of aqueous polyaniline battery using a modified polyaniline electrode.* European Polymer Jurnal 2003;39:219-223.
[11] Rüetschi P. *Energy storage and the enviroment: the role of batterz technology. J. Power Sources. 1993;42:1-7.*
[12] Beck F, Rüetschi P. *Rechargeable batteries with aqueous electrolytes. Electrochemica acta.* 2000;45:2467-2482.
[13] Arsov Lj D, Plieth W, Koβmehl G. *Electrohemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline.* J. Sol. St. Electro. 1998;2:355-361.

Topola
RaDMI
2014
Serbia

14th International Conference
"Research and Development in Mechanical Industry"
RaDMI-2014
18-21 September 2014, Topola, Serbia

DISTILLATION PRODUCTS OF STANLEY PLUM OBTAINING

Svetomir Ž. Milojević[1], Boban S. Đurović[1], Miljojka D. Mijailović[2], Tomislav Lj. Trišović[2], Ivan V. Vuković[3], Vladimir P. Pavićević[4], Jasmina B. Nikolić[4]
[1] University of Priština, Faculty of Technical Sciences, Kosovska Mitrovica, SERBIA
[2] University of Kragujevac, Faculty of Agronomy, Čačak, SERBIA
[3] Veterinary Station, Ras–Vet d.o.o., Baljevac, SERBIA
[4] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, SERBIA

Summary: *The sort of plum used for distillation is Stanley picked in August 2013 in Gračac, Vrnjačka Banja, Serbia. 200 kg of ripe fruit was fermented with 40 dm^3 of potable water. Wine was removed from the obtained product, and the solid part was washed with water. The mixture of wine and water, 240 dm^3 was distilled to a soft brandy, where 36 dm^3 was obtained with 30 % of the ethanol. After that, this soft brandy was redistilled after 44 dm^3 of potable water was added. By this procedure, 20 dm^3 with 50 % of the ethanol was distillated, which means that the yield was 10 dm^3 of a brandy for 100 kg of plums.*

Keywords: *Stanley plum, fermentation, distillation, distillate, brandy.*

1. INTRODUCTION

Serbia is a country well known for a large number of autochthonous plum sorts, the most famous are "požegača" and "crvena ranka". However, due to the problems with dry weather and pollution, now the most common is the imported Stanley sort. It is a high quality industrial sort, very useful and important in food industry – dried fruits, marmelades and fruit juices, as well as a high quality brandy. Domestic productions of the plum brandy are also well known and popular [1]. Unfortunately, this popular domestic procedures are often flawed by the inadequate equipment and low hygienic conditions, resulting with a product of the low quality.

The development of new distilleries of higher capacity would raise the quality of local plum brandy, so they could be successful on both domestic and international market. Contribution of the "know–how" on obtaining of the high quality of plum fruit distillate, plum brandy, is presented in this study. The distillation process was followed by measuring of the ethanol concentration, and the aim was obtaining of a high quality distillate and the presentation of concentration profile of the ethanol in a fractions of distillate and in a residue.

2. STANLEY PLUM

Stanley is the USA plum sort, dating 1912. It becomes ripe in the second half of August and in September, and it is generally resistant to dry, hot weather and viruses. The attractive appearance, with large fruits of dark blue color adds to the quality and high yield adds to its popularity. According to standards, brandy is the alcoholic beverage with at least 25 %, and at most 80 % of the ethanol. It is produced by fermentation and then distillation of a substrate, fruit, vegetables or cereal [2, 3].

3. PLUM BRANDY PRODUCTION

The production of plum brandy starts with fruit picking, their fermentation, then distillation and leaving the distillate to rest for sometime in order to obtain a quality product. The fruit is picked when it reaches the technological ripeness, with the optimal concentration of sugar and fruit acids, which can be confirmed by chemical analysis and morphological appearance. The fermentation, anaerobic degradation of carbohydrates to the ethanol and the carbon–dioxide is catalyzed by selected sorts of yeasts. The mechanism of the carbohydrate conversion is a complex one [4, 5]. In dry years, like 2013, the high level of sugar, fruit acids, and microelements enables successful fermentation by the yeasts which exist on the fruit skin, and such method can be carried out in a domestic production. The next phase, distillation, is based on mixture separation based on a different boiling points. The parameter which describes the concentration of the certain component in the mixture is the rectification coefficient $K_{ir}= K_i/K_r$, where K_i and K_r are coefficient of vaporization of components i and r. For multicomponent alcoholic beverages, it is the relation between ethanol (r) and other components (i). Components with $K_{ir}>1$ have higher volatility than the ethanol, and those with $K_{ir}<1$ have lower volatility than the ethanol. As it is empirically determined, the latter fraction usually damages a flavor and quality of beverage and should be removed from distillate. As too many components influence on K_{ir}, it has no standard value. Knowing the boiling points of different components, the fractions can be successfully separated. The so–called soft brandy, obtained by first distillation, is then redistilled, which is the key to obtaining a high quality brandy with an attractive flavor as a product [6]. The freshly made brandy is then laid to rest in a glass bottles or wood barrels, mostly made of the oak. Leaving the brandy in wood barrels leads to the faster loss of volatile components, but also of methanol which is harmful and deteriorates the brandy quality. The oxidation and partial decomposition of some components leads to the formation of various tasteful secondary aromas, like vanillin, which can only raise the quality of the beverage. That is why more than 10 years old brandy, left in a wood barrel, is often of a supreme quality.

4. EXPERIMENTAL

The sort of plum used for distillation is Stanley picked in August 2013 in Gračac, Vrnjačka Banja, Serbia. 200 kg of ripe fruit was fermented with 40 dm^3 of drinking water. It was fermented for 24 days on 16−18 °C. The anaerobic conditions are obtained by adequate closing of the fermentation barrels. After the fermentation was complete, the wine was drained and the solid residue was washed with water added to the wine, resulting in 240 dm^3 of liquid mixture ready for distillation. The distillation process is divided in two steps – soft brandy production and redistillation. The distillation was carried out in a boiler 120 dm^3 heated by solid fuel, Figure 1.

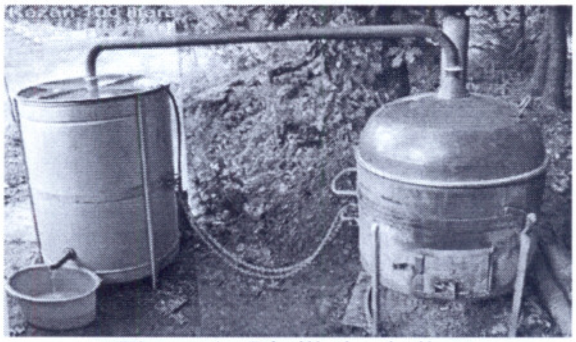


Figure 1: Distillation boiler

The boiler was filled with 120 dm^3 of distillation mixture and heated. First fraction, about 0.2 dm^3 was discarded. The process was continued with 9 fractions, each about 2 dm^3, which were tested by the standard for the concentration of ethanol by the n-Richter Tralkles T15 C device. After measurement, the fractions were mixed giving the distillate which concentration of the ethanol was measured again.

5. RESULTS AND DISSCUSION

The results of the measurement of ethanol concentration are given in Table 1. The phase diagram [7,8] was made based on the equilibrium data from which the concentration of ethanol in the boiler can be read from the concentrations in fractions, presented in Figure 2. Based on the data from Table 1, the concentration profile curves c = f(v) for the basic distillation were made, and they are presented on Figure 3 and the concentrations in different phases in Table 2.

Table 1: Equilibrium data for the ethanol–water system for basic distillation

Temperature, °C	Ethanol liquid, % v	Ethanol vapor, % v
100.062	0	0
97.216	3.170	33.878
95.099	6.204	45.669
93.260	9.111	53.042
91.677	11.898	58.141
89.173	17.141	64.704
87.353	21.987	68.715
86.005	26.477	71.423
83.827	36.385	75.585
82.496	44.759	78.165
81.555	51.931	80.094
80.836	58.142	81.684
80.268	63.572	83.073
79.813	68.361	84.338
79.446	72.616	85.523
79.152	76.421	86.659
78.918	79.844	87.770
78.734	82.940	88.873
78.592	85.753	89.985
78.485	88.321	91.126
78.406	90.674	92.319
78.345	92.839	93.596
78.292	94.836	94.999
78.227	96.685	96.568
78.192	97.387	97.244
78.148	98.069	97.942
78.092	98.731	98.646
78.059	99.055	98.994
78.023	99.374	99.335
77.985	99.689	99.665
77.961	100	100

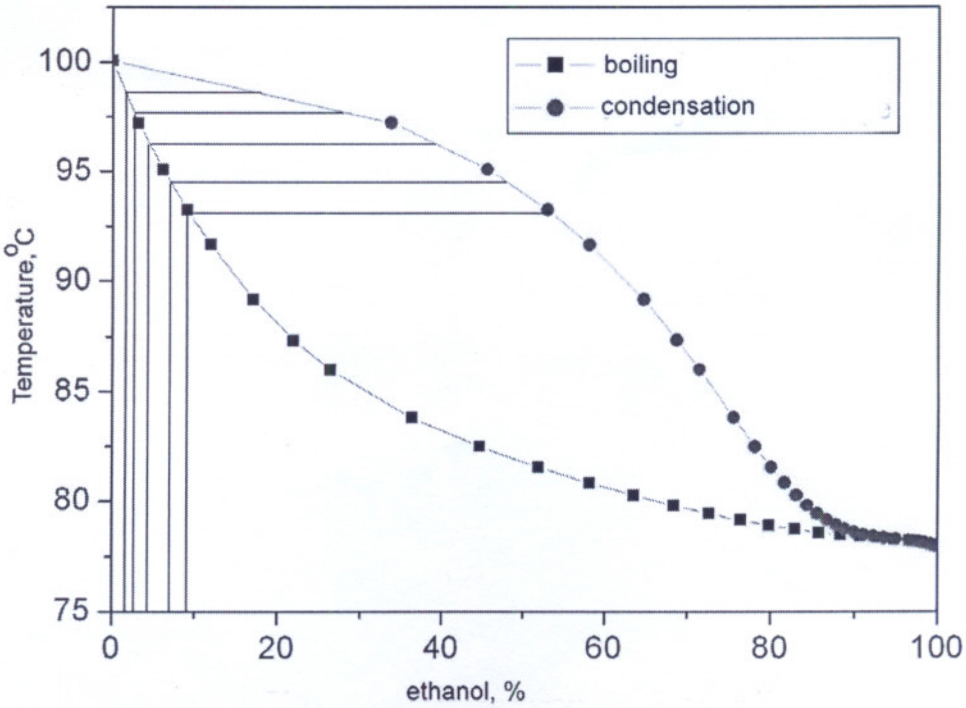


Figure 2: Phase diagram ethanol–water for the basic distillation

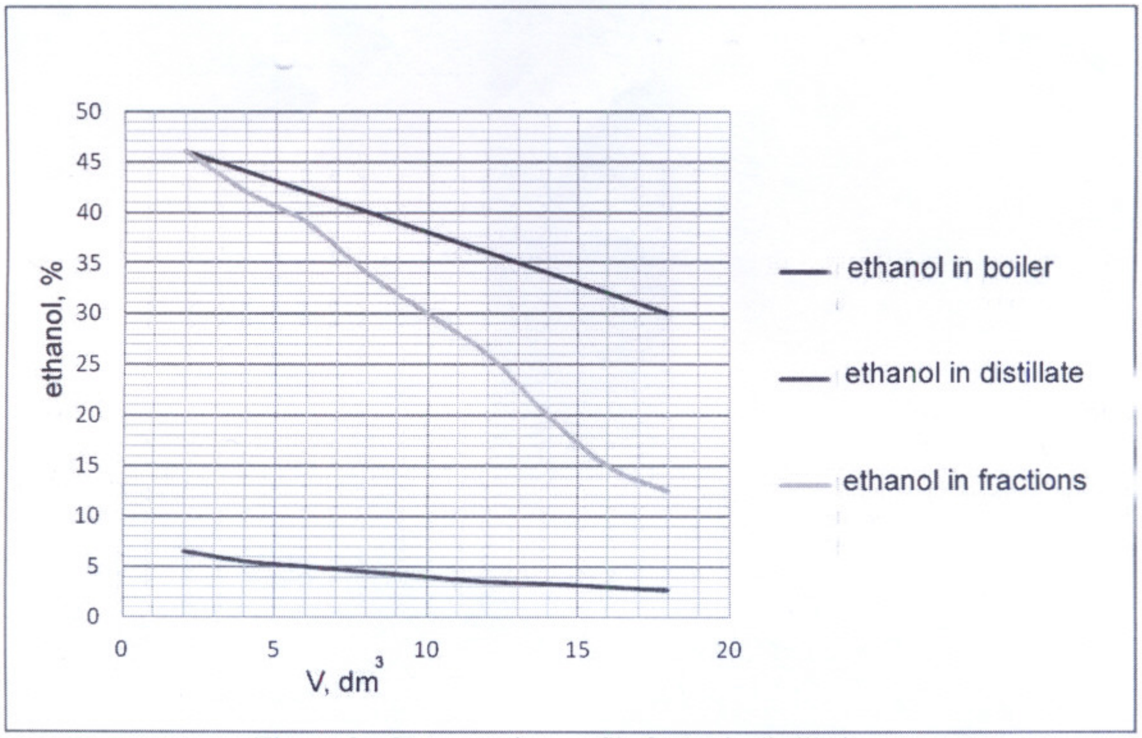


Figure 3: Concentration profile for basic distillation

The distillate obtained (so–called soft brandy) was 36 dm^3, it was dilluted with 44 dm^3 of potable water and then redistillated in the same boiler. The first fraction of 0.3 dm^3 was discarted, then 8 fractions were separated, about 5 dm^3, and the concentration of ethanol was measured. The fractions were successively mixed giving the distillate in which the concentration of ethanol was measured again. Based on the concentrations of the ethanol in fractions, the concentrations in boiler were read from the phase diagram for redistillation, Figure 4. The concentrations of ethanol in the boiler, fractions and distillate are given in Table 3. Based on Table 3, the corresponding concentration profile curves were made, c = f(v), Figure 5.

Table 2: Ethanol concentrations for basic distillation

V (dm^3)	Ethanol in boiler, %	Ethanol in fractions, % v	Ethanol in vapor, % v
2	6.50	46.00	46.00
4	5.50	42.00	44.00
6	5.00	39.00	42.00
8	4.50	34.00	40.00
10	4.00	30.00	38.00
12	3.50	26.00	36.00
14	3.30	20.00	34.00
16	3.00	15.00	32.00
18	2.70	12.50	30.00

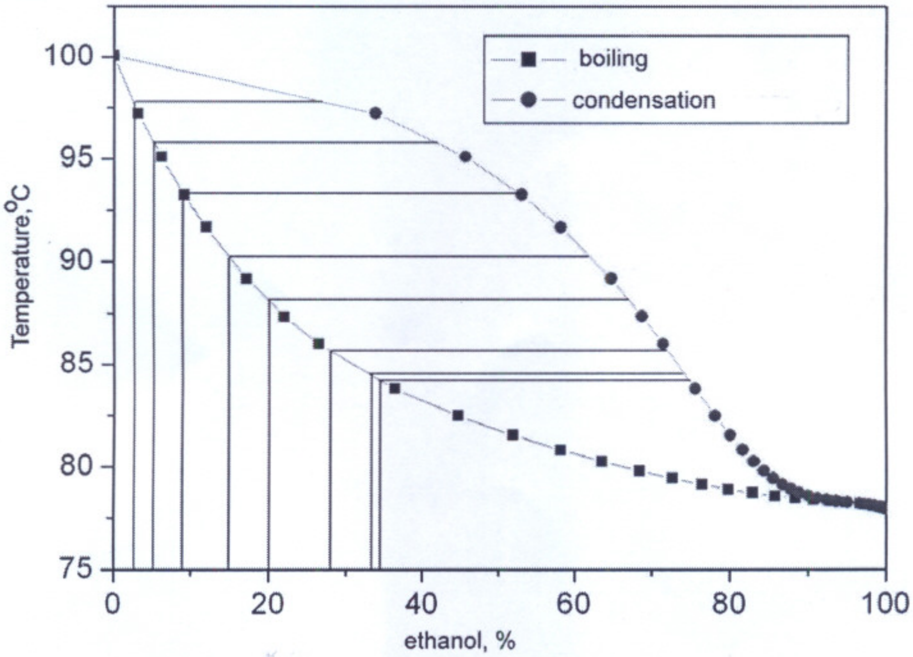


Figure 4: Phase diagram ethanol–water for the redistillation

Table 3: Ethanol concentrations for redistillation

V (dm^3)	Ethanol in boiler, %	Ethanol in fractions, % v	Ethanol in vapor, % v
5	13.50	60.00	60.00
10	11.00	55.00	57.50
15	9.50	48.00	54.33
20	7.50	37.00	50.00

The curves of concentration profile for ethanol in the distillate and in fractions point the decrease of the ethanol concentration during basic distillation and redistillation. The decrease of the ethanol concentration in the fractions is considerably sharper than in the distillate. The range of concentrations for basic distillation and redistillation is defined by the starting concentration of ethanol, which can be seen from the phase diagrams and concentration curves. Based on Table 3, the yield of 10 dm^3 of 50 % of the ethanol is determined for 100 kg of Stanley plum.

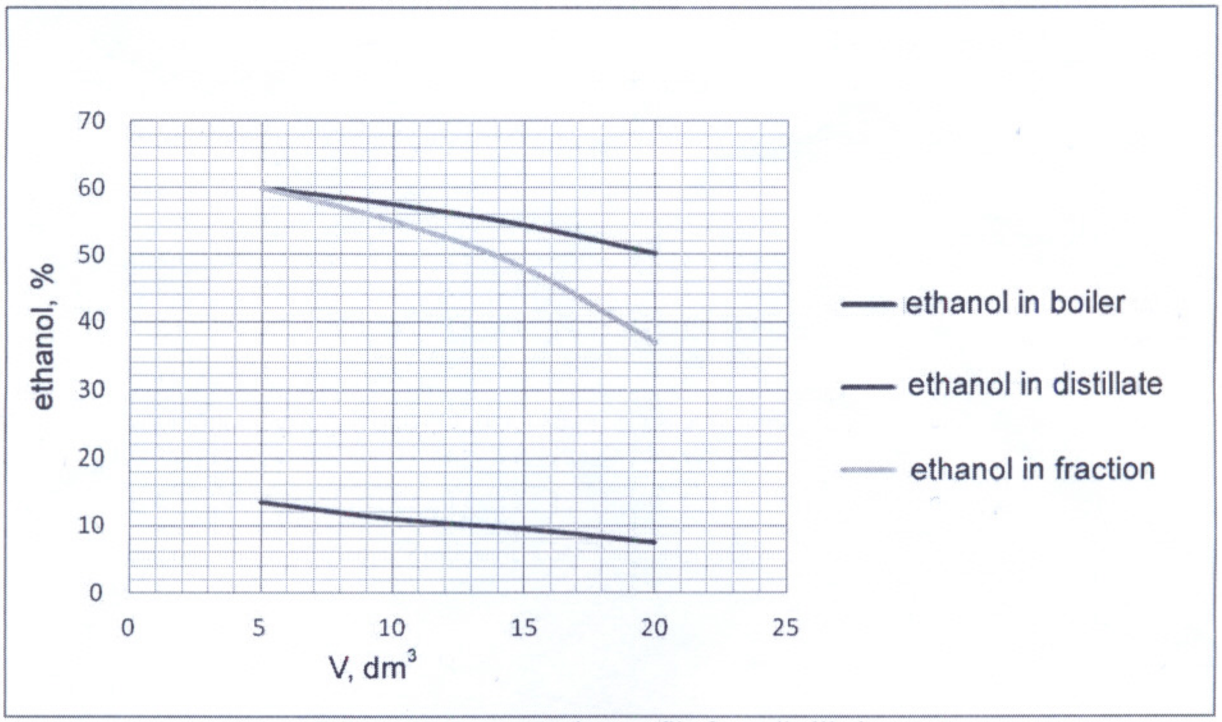


Figure 5: Concentration profile for redistillation

6. CONCLUSIONS

Using the equilibrium data of the water–ethanol binary system for a distillation, the concentration profile of the differential distillation can be determined. The concentration profile of the ethanol in fractions and in the distillate points the fact that the end of distillation can be more precisely determined from the fraction concentrations, as the change of that concentration is much faster at the end of a distillation process. The distillation products of a high purity and high ethanol concentration can be obtained in the classic boiler, so the production of a high quality plum brandy is possible in the domestic production.

ACKNOWLEDGMENTS

Authors are grateful to the Ministry of Education and Science of The Republic of Serbia for financial support (Project 172013).

REFERENCES

[1] T. Milošević, Šljiva – Tehnologija gajenja, Agronomski fakultet, Čačak, 2002., 49-59.
[2] N. Nikićević, V. Tešević, Jaka alkoholna pića – analitika i praksa, Poljoprivredni fakultet, Zemun, 2009., 38-40, 83-90, 133.
[3] N. Nikićević , Proizvodnja voćnih rakija vrhunskog kvaliteta, Poljoprivredni fakultet, Zemun, 2010.
[4] N. Nikićević, R. Paunović, Tehnologija jakih alkohilnih pića, Univerzitet u Beogradu, Poljoprivredni fakultet Beograd, 2013., 203.
[5] R. Lučić, Proizvodnja jakih alkoholnih pića, Nolit, Beograd, 1984.
[6] V. N. Stabnikov, Peregonka i rektifikacija etilovogo spirita, 2. izdanje, Pišćevaja promišljenost, Moskva, 1969., n 308, 281.
[7] A. Duduković, Destilacija I , *Hemijska industrija* 52 (5), Beograd, 1998., 212-219.
[8] A. Duduković, Destilacija II, *Hemijska industrija* 52 (7-8), Beograd, 1998., 317-326.

Slovak Society of Chemical Engineering
Institute of Chemical and Environmental Engineering
Slovak University of Technology in Bratislava

PROCEEDINGS

41st International Conference of Slovak Society of Chemical Engineering

Hotel Hutník
Tatranské Matliare, Slovakia
May 26–30, 2014

Editor: prof. Jozef Markoš

ISBN: 978-80-89475-13-1, EAN: 9788089475131

Gvozdenovic, M., Popovic, N., Stevanovic, J., Grgur, B., Trisovic, T., Jugovic, B.: Electrochemical determination of ascorbic acid using electrochemically deposited polyaniline, Editor: Markoš, J., In *Proceedings of the 41st International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 654–657, 2014.

Electrochemical determination of ascorbic acid using electrochemically deposited polyaniline

M.Gvozdenovic[1], N.Popovic[1], J. Stevanovic[2], B. Grgur[1], T. Trisovic[3], B. Jugovic[3,*]

[1]Faculty of Technology and Metallurgy, University of Belgrade,Karnegijeva 4, 11020 Belgrade, Serbia
[2]ICTM, Institute of Electrochemistry, Njegoseva 12, Belgrade,Serbia
[3]Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihailova 35, Belgrade, Serbia

Introduction

Electroconducting polymers are promising materials to be used in various fields including: batteries, capacitors, electronic devices, corrosion, biosensors and sensors[1,6]. Polyaniline is probably the most investigated electroconducting polymer, due to low cost monomer, conductivity, environmental stability. Polyaniline can be obtained by chemical or electrochemical oxidative polymerization of aniline. Electrochemical synthesis is performed in anodic process directly from acidic aqueous electrolyte containing aniline. Polyaniline can be used as electrode material for electrochemical determination of ascorbic acid based on electrocatalytic oxidation of ascorbic acid.

Experimental

Electrochemical oxidative polymerization of aniline at graphite electrode was carried out galvanostatically, from acidic aqueous solution of 1.0 mol dm^{-3} HCl (p.a. Merck) containing 0.20 mol dm^{-3} aniline (p.a. Fluka). In order to estimate the optimal conditions for electrochemical formation of polyaniline (PANI) modified graphite electrode, both cathodic and anodic chronoamperometric curves, obtained at different current densities were recorded.

Prior to polymerization aniline was distilled in argon atmosphere, while cylindrical graphite electrode, inserted into Teflon holder, was mechanically polished by fine emery papers (2/0, 3/0 and 4/0, respectively) and polishing alumina (1 μm, Banner Scientific Ltd.) on polishing cloths (Buhler Ltd.), the traces of the alumina were removed ultrasonically during 5 min.

Electrochemical characterization of PANI modified graphite electrode was performed by cyclic voltammetry (CV) in the potential range of -0.3 1.0 V (SCE) with different scan rates in buffered solution contining $10.0 \cdot 10^{-3}$ mol dm^{-3} L-ascorbic acid. Stock solution of L-ascorbic acid, (p.a. Merk) was prepared in phosphate buffer solution (PBS), 0.1M at pH 6.8.

The dependence of the current signal on ascorbic acid concentration was evolved from linear scanning voltammetry (LSV) results, recorded at scan rate of 20 mV s^{-1}. The solutions with different concentration of ascorbic acid were obtained by diluting of the stock solution with PBS

All experiments were carried out at ambient temperature (23 ± 1 ^{0}C) in three compartment electrochemical cell. Standard calomel electrode (SCE) served as reference electrode (all potentials in the text were referred to SCE), while Pt wire was used as counter electrode. The experiments were performed using SP-300 BioLogic Science Instruments, potentiostat/galvanostat connected to PC.

3. Results and discussion

3.1. Electrochemical synthesis of PANI on graphite electrode

Electrochemical synthesis of polyaniline was performed galvanostatically with different current densities between 0.5 to 3.0 mA cm^{-2}, during 600s. In order to estimate the amount of conductive form of polyaniline i.e. emeraldine salt, all electrodes were discharged with the same current density of 1.0 cmA $^{-2}$ (dedoped) in the same solution. The dependence of discharge and polymarization capacities ratio (which corresponds to amount of conductive form PANI, i.e. emeraldine salt) on polymerization current density is given in Fig. 1. The ratio decrease with increase of the polymerization current density, probably as a result of increase of the amount of formed nonconductive perningraniline and degradation products due to higher potentials. Since the best results were obtained when polymerization was performed with 1.0 mA cm^{-2}, this current density was used in further experiments.

In order to estimate the optimal time of polymerization, electrochemical polymerization of aniline was performed at current density of 1.0 mA cm^{-2} during 300, 600, 900, 1200 and 1500 s. After polymerization, the electrodes were discharged with the same current density and ratio of discharge and polymerization charge was evaluated and presented in Insert of Fig 1.

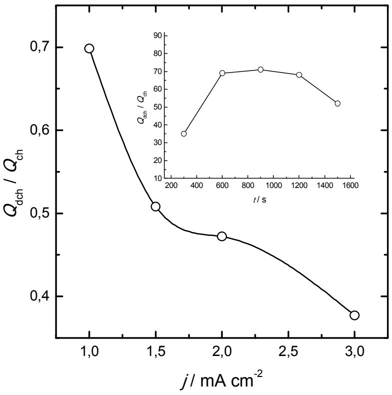


Fig.1. Dependence of discharge and polymerization capacities ratio on polymerization current density. Insert: Dependence of discharge and polymerization capacities ratio on polymerization time.

As it can be seen the discharge and polymerization capacities ratio are nearly the same for polymerization time of between 600 and 1200 s, while for higher polymerization time, decrease of this ratio is due to lost of the polymer film from electrode. Lower polymerization time, on the other hand, led to nonuniformly deposited film. In order to achieve greater available charge, PANI modified graphite electrode was deposited with current density of 1.0 mA cm^{-2} during 1200 s and used in further investigations.

3.2. Electrocatalytic oxidation of ascorbic acid on polyaniline electrode

CVs of electrochemical oxidation of ascorbic acid on both graphite and PANI modified electrode is given in Fig. 2.

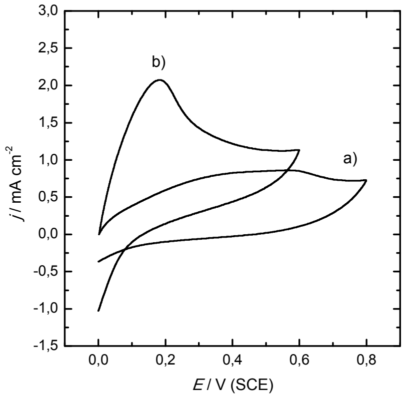


Fig. 2. Cyclic voltmmograms (v = 20 mV s^{-1}) in PBS (pH = 6.8) containing 10,0·10^{-3} mol dm^{-3} ascorbic acid on a) graphite and b) PANI modified graphite electrode

Electrochemical oxidation on graphite electrode is characterized by very broad response with not well defined current peak positioned at 0.5 V (SCE). On the other hand, electrochemical oxidation of ascorbic acid on PANI modified electrode proceeded with well defined anodic peak at potential of 0.18 V

(SCE). Electron transfer kinetics of ascorbic acid oxidation is highly dependent on surface properties of the electrode [6,9] therefore, both the increase of the peak current for ~ 2.5 times and shift of the oxidation potential for 0.32 V to less positive values, clearly indicates electrocatalytic oxidation of ascorbic acid on PANI modified electrode [14].
CVs of PANI modified electrode in PBS solution containing ascorbic acid, recorded with different scan rates are given in Fig. 2., while Insert of Fig.2. refers to dependence of the peak current density on square root of the scan rate.

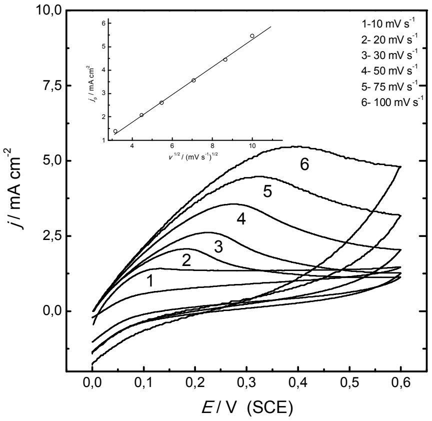


Fig.2. Cyclic voltmmograms of PANI modified electode in PBS (pH = 6.8) containing 10,0·10^{-3} mol dm^{-3} ascorbic acid obtained by different scan rates. Insert: Dependence of current peak density on square root of scan rate.

Position of the catalytic peak potentials shifts to more positive values for higher scan rates, while the values of the peak currents increase. Dependences of the peak current density on square root of the scan rate is linear indicating diffusion control of electrochemical oxidation of ascorbic acid on PANI modified electrode.

Response of PANI modified electrode in terms of current peak intensity on ascorbic acid concentration was obtained from anodic LSV curves and given in Fig.3. LSV curves were (Insert of Fig.3.) recorded in different concentration of ascorbic acid in PBS in the range of 0.5 – 50.0 at scan rate of 20 mV s^{-2} (for simplicity only several curves are given obtained at concentrations marked on Fig.3)

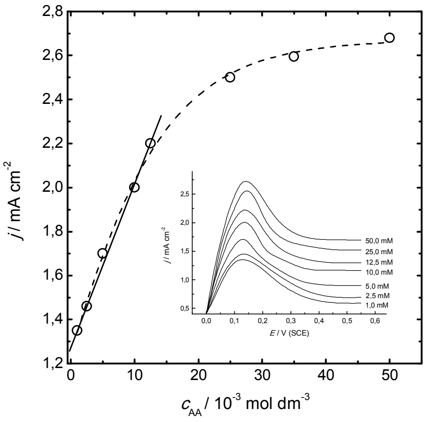


Fig. 3. Dependence of the current density peak on ascorbic acid concentration. Insert: LSV curves (v = 20 mV s^{-1}) for electrochemical oxidation of ascorbic acid in PBS (pH = 6.8) on PANI modified electrode obtained in different concentration of ascorbic acid in the range of 0.5 – 50.0 ·10^{-3} mol dm^{-3}

As it can be seen, the intensity of the oxidation peak current increased by increasing ascorbic acid concentration ranging from 0.5 to 50.0·10^{-3} mol dm^{-3}, with linearity in the range between 0.5 and 18.0 mol dm^{-3}.

3.3.1. Stability and real simple analysis

For estimation of the storage stability of PANI modified electrode, the electrode was refrigerated at 8^0C in PBS at pH 6.8, and LSV curves for ascorbic acid concentration of 10.0 ·10^{-3} mol dm^{-3} were recorded after 10, 15, 20 and 30 days and results, in terms of relative signal intensity, are given in Fig 4.

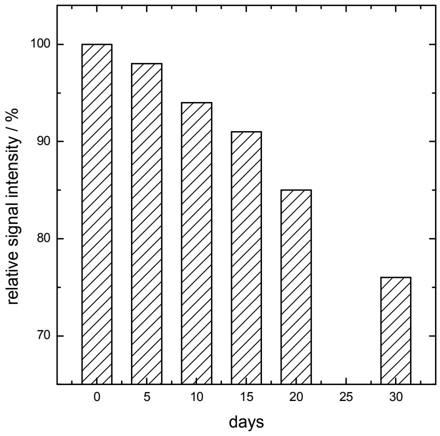


Fig. 4. Storage stability of PANI modified electrode.

As it can be seen, during first 5 days of storage PANI modified electrode lost about 2 % of the initial signal intensity, while after a month of storage electrode kept 75 % of signal. The decrease of the signal intensity during long term storage might be a consequence of the lost of PANI film conductivity and degradation at pH 6.8.

Acknowledgment: This work is supported by The Ministry of Education and Science, Republic of Serbia, under Contract No. 172046.

References:

1.Y. Cui, H. Chen, L. Hou, B. Zhang, B. Liu, G. Chen, D. Tang, Anal. Chim Acta 738 (2012) 76-84.
2. L. Zhang, X. Lin, Ana. Bioanal. Chem. 382 (2005) 1669-1677.
3. A. Mluinauskas, R. Garjontė, R. Mažeikienė, I. Jurevičiūtė, Talanta 64 (2004) 121-129.
4. R. Paulikante, M. E. Garcia, C. M. A. Brett, Anal. Bioanal. Chem. 381 (2005) 972-978.
5. L. Zhang, J. Lian, J. Electroanal. Chem. 611 (2007) 51-59.
6. J. Wang, Analytical Electrochemistry, third ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 2006.

Electrochemical characterization of polyaniline electrode for use in electrochemical power sources

M. Gvozdenović[1], B. Jugović[2], T. Trišović[2], J. Stevanović[3], B. Grgur[1]
[1]*Faculty of Tecnology and metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*
[2]*ITS-Serbian Academy of Science and Arts, Knez Mihailova 35,11000 Belgrade, Serbia*
[3]*ICTM-Institute of electrochemistry, Njegoševa 12, 11000 Belgrade, Serbia*
e-mail address: popovic@tmf.bg.ac.rs

Polyaniline (PANI) electrode was formed by electrochemical synthesis on graphite under galvanostatic condition at current density of 2.0 mA cm^{-2} from aqueous solution of 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline. Electrochemical characterization of the PANI electrode was performed in 0.5 mol dm^{-3} HCl using cyclic voltammetry and galvanostatic measurements. The overall charge capacity of the PANI electrode was estimated to be 0.154 mA h cm^{-2}, corresponding to 25 % of the theoretical mass of PANI available for the dopant exchange. It was observed that during initial cyclization at low pH, the extent of PANI degradation products was insignificant and practically had no influence on the charge/discharge characteristics of the PANI electrode.

Keywords: electrochemical synthesis, polyaniline, rechargeable power sources

Electrochemical characterization of electrochemically polymerized polyaniline in citrate containing electrolyte

Branimir Jugović[1], Milica Gvozdenović[2], Jasmina Stevanović[3], Tomislav Trišović[1], Branimir Grgur[2]
[1]ITS-Serbian Academy of Science and Arts, Knez Mihailova 35, Serbia
[2]Faculty of Tecnology and metallurgy, University of Belgrade, Karnegijeva 4, Serbia
[3]ICTM-Institute of electrochemistry, Njegoševa 12, Serbia
e-mail address: branimir.jugovic@itn.sanu.ac.rs

Polyaniline electrode, was obtained by electrochemical polymerization at constant current density of 2.0 mA cm^{-2} from aqueous solution of 1.0 mol dm^{-3} HCl containing 0.25 mol dm^{-3} aniline. Electrochemical characterization of the polyaniline electrode in chloride and chloride/citrate electrolyte, for different anodic potential limits, was performed using cyclic voltammetry and galvanostatic measurements. It was observed that for anodic potential 0.32 V, higher electrode capacity in chloride/citrate was obtained. For anodic potential limit of 0.50 V, faster decrease of the electrode capacity in chloride/citrate electrolyte was also observed. It was suggested that influence of both chloride and citrate anions has to be taken into account.

Key words: electrochemistry, polymers, power sources

M 53

ANNALS OF FACULTY ENGINEERING HUNEDOARA
– INTERNATIONAL JOURNAL OF ENGINEERING
Tome X (Year 2012) – FASCICULE 3 (ISSN 1584 – 2673)

[1.] M. M. GVOZDENOVIĆ, [2.] B. Z. JUGOVIĆ, [3.] T.LJ. TRIŠOVIĆ, [4.] J. S. STEVANOVIĆ,
[5.] M. V. PLAZINIĆ, [6.] B. N. GRGUR

ELECTROCHEMICAL CHARACTERISTICS OF POLYANILINE|LEAD-DIOXIDE POWER SOURCE

[1,5.] FACULTY OF TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE, KARNEGIJEVA 4, 11120 BELGRADE, SERBIA
[2,3.] INSTITUTE OF TECHNICAL SCIENCE, SERBIAN ACADEMY OF SCIENCE AND ARTS, KNEZ MIHAJLOVA 35, 11000 BELGRADE, SERBIA
[4.] CEH-INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE, NJEGOŠEVA 4, 11000 BELGRADE, SERBIA
[6.] TECHICAL FACULTY ČAČAK, UNIVERSITY KRAGUJEVAC, SVETOG SAVE 65, 32000 ČAČAK, SERBIA

ABSTRACT: *Polyaniline (PANI) anode, electrochemically formed on graphite from aniline containing sulfuric acid solution, and electrochemically formed thin film lead dioxide cathode, were investigated for possible applications as electrode materials in PANI /H_2SO_4 /PbO_2 aqueous based rechargeable power sources. The stimulation of charge/discharge characteristics of the cell, based on half cell reactions investigations, was evaluated. Charging of the cell would occur in the voltage range of 1.20 and 1.70 V, while discharge is expected in the voltage range of 1.35 and 1.00 V.*

KEYWORDS: *polyaniline, lead dioxide, electrochemical power sources*

INTRODUCTION

The determining factors of an electrochemical power sources success are often recognized as “three E” criteria: Energy (high energy content with respect to volume and weight), Economics (low manufacturing and maintenance costs, long service life), Environment (toxic free, safety, low energy consumption, easy to recycle) [1, 2].

Electrochemical power sources systems composed of electroconducting polymers (ECP), metals (Pb, Zn, Al, Mg) and aqueous electrolytes are likely to meet most of these demands. The unique properties of ECP such as: mechanical strength, electrical conductivity, high energy and power density compared to classical inorganic compounds, possibility of reversible exchange of ions etc., permitted them to be considered as possible electrode materials for electrochemical power sources [3].

ECP can be obtained using both chemical and electrochemical oxidative polymerization. However, electrochemical synthesis is favorable, permitting synthesis without oxidizing agent followed by doping with inorganic or organic ions in a single step [4].

Among numerous ECP only few have been investigated for possible application in electrochemical power sources. Since the price of aniline monomer is scientifically lower comparing to other monomers, power sources based on polyaniline (PANI) metals (mainly zinc) and aqueous electrolytes are the most investigated systems [5-10].

Even the characteristics of these systems are principally very good, this type of electrochemical power sources have not been commercialized. The main reason is connected to degradation of PANI [11,12].

Lead acid batteries (Pb | PbO_2) are the first discovered and although they have lot of problems in exploitation, up to now they are the most large-scale electrochemical power sources. The problems in exploitation are mainly connected to negative Pb electrode, such as: dendrite formation provoking short circuit breakdown of the battery, passivation of the Pb electrode due to formation of inactive $PbSO_4$, water loss due to hydrogen evolution, etc. The use of PANI instead of Pb as negative electrode could overcome some of the mentioned problems. On the other hand, due to much smaller mass of PANI electrode, the specific energy and specific power could be significantly increased comparing to classical Pb | PbO_2 systems. The advantage of such power sources could be better ecological acceptance as a result of much smaller lead content and lower sulfuric acid concentration. It is interesting to note that after earlier works reported by Sima et al. [7], there are no studies concerning the use of PANI in lead acid power sources. Hence, the aim of this work is to investigate electrochemically synthesized PANI on graphite, as anodic material, and electrochemically synthesized lead dioxide as cathode for possible use in PANI /H_2SO_4 /PbO_2 rechargeable power sources.

In such system, the half reaction for charging of the system can be given as:

$$[PANI^{y+}(SO_4^{2-})_y]_n + 2nye \underset{\text{DISCHARGING}}{\overset{\text{CHARGING}}{\rightleftarrows}} (PANI)_n + nySO_4^{2-} \tag{1}$$

$$PbSO_4 + 2H_2O \underset{\text{DISCHARGING}}{\overset{\text{CHARGING}}{\rightleftarrows}} PbO_2 + SO_4^{2-} + 4H^+ + 2e \qquad (2)$$

where y refers to doping degree (ratio between the number of charges in the polymer and the number of monomer units). Is important to note that in fully charged PANI /H_2SO_4 /PbO_2 rechargeable power source PANI is in its dedoped form.

EXPERIMENTAL

PANI electrode was formed by anodic polymerization from aqueous solution of 1.1 mol dm^{-3} H_2SO_4 and 0.2 mol dm^{-3} aniline at constant current density of 2.5 mA cm^{-2} on graphite (S = 0.64 cm^2). Prior to use, aniline (p.a. Aldrich) was distilled in argon atmosphere. Cylindrically shaped graphite electrode was first mechanically polished with fine emery papers (2/0, 3/0 and 4/0) and then with polishing alumina (1μm Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.). After mechanical polishing, the traces of the polishing alumina were removed from the electrode surface in ethanol using ultrasonic bath during 5 min. After polymerization, PANI electrode was dedoped with current density of 1.25 mA cm^{-2}, washed with distilled water and then investigated in 1.1 mol dm^{-3} H_2SO_4. The lead dioxide electrode (PbO_2) was prepared from pure 99.95 % lead, according to established Planté formation procedure described by Peterson et al [13,14].

All experiments were carried out in three compartment electrochemical cells at ambient temperature (22°C). Saturated electrode (SCE) served as reference, while platinum foil (S = 2 cm^2) was used as counter electrode. The measurements were carried out using PAR 273A potentiostat/galvanostat interfaced to PC.

RESULTS AND DISCUSSION. CHARACTERIZATION OF PANI ELECTRODE

In Fig. 1 charge/discharge (doping/dedoping) curves of the PANI electrode for different current densities of: 0.50 – 1.25 mA cm^{-2} and anodic potential limit of 0.32 V in 1.1 mol dm^{-3} H_2SO_4 are shown. Anodic potential limit was chosen bearing in mind that at potentials higher than 0.35 V degradation of PANI is expected [11,12].

Charging of the electrode started at potential of ~ 0.05V while discharging occurred in the potential range between 0.3 and – 0.3 V. Charging capacity, as seen in insert of Fig. 1., is independent on current density, while discharging capacity decreases with increasing current density. For current densities below 1.25 mA cm^{-2}, columbic efficiency is higher than 100 %. This observation could be connected to possibilities of hydrogen evolution and protonization of emeraldine form of PANI at negative potentials and low current densities [11,12]. This additional charge is easily discharged at open circuit potentials and has no contribution in further charging. Since the columbic efficiency of nearly 100 % was achieved with current density of 1.25 mA cm^{-2}, for further investigation of cyclic characteristic of the PANI electrode this charge/ discharge current was used.

Initial cycling characteristics of PANI electrode obtained with constant current density of 1.25 mA cm^{-2} during 15 cycles is given in Fig. 2. Since, the degradation of PANI is expected at the potentials above ~0.35 V, in order to investigate the influence of degradation, the cycling potential limit for charging of the electrode was extended to 0.45 V for charging and -0,6 V for discharging.

As it can bee seen from Fig. 2. charge/discharge curves remained practically the same during fifteen cycles, with almost constant values of the electrode charging and discharging capacity, with columbic efficiency of ~ 95 %. Based on obtained results, it could be concluded that in during initial cyclization in investigated potential range degradation of PANI could be neglected, but, based on

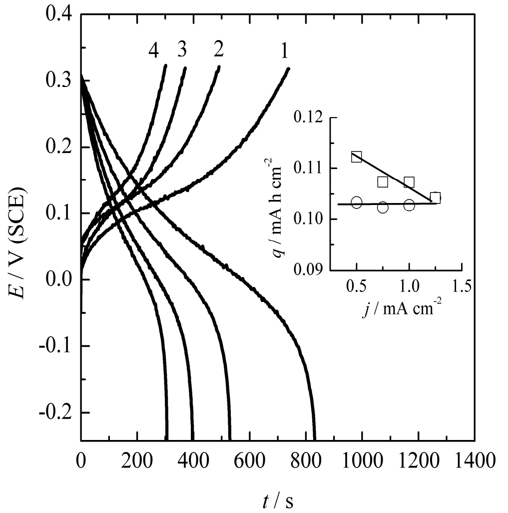


Fig. 1. Charge/discharge curves of PANI electrode in 1.1 mol dm^{-3} H_2SO_4, where the numbers in the figure refer to different current densities as: 1)-0.50, 2)-0.75, 3)-1.00 and 4)-1.25 mA cm^{-2}.
Insert: Dependences of: (○)-charge and (□)-discharge capacity on current density

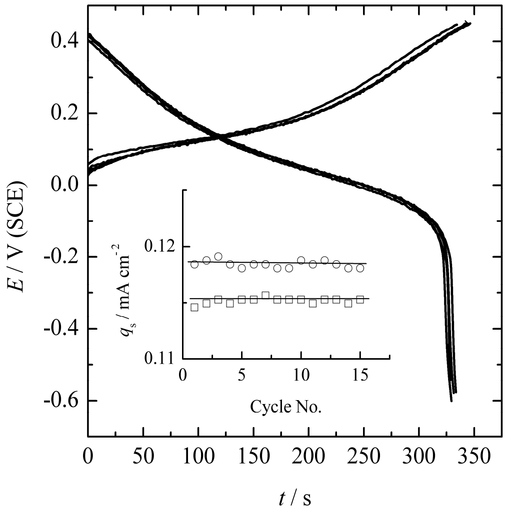


Fig. 2. Cycling characteristics of PANI electrode in 1.1 mol dm^{-3} H_2SO_4 at conctant current density of 1.25 mA cm^{-2}. Insert: Dependences of (○)-charge and (□)-discharge capacity on cycle number

literature data[11,12], it is possible to be expected to occur during prolonged cyclization, therefore it is recommended that the optimal potential limit for charging of PANI electrode should not exceed 0.35 V.

CHARACTERIZATION OF PbO_2 ELECTRODE

In order to investigate discharge characteristics of electrochemically formed PbO_2 electrode [11,12], the following procedure was applied. Electrode was always charged with current density of 2 mA cm^{-2} during 500 s, and then discharged with current densities between 1 and 4 mA cm^{-2} as seen in Fig. 3. Based on discharging times, the dependences of columbic efficiency and discharge capacity on applied current density were calculated and given in insert of Fig. 3.

For lower current densities of 1.0 and 2.0 mA cm^{-2} columbic efficiency is ~85 %, while current efficiency and discharge capacity decrease for higher current densities, probably as a result of diffusion limitations. Thus, for further investigation discharge current of 2 mA cm^{-2} was used.

In order to investigate initial cyclic characteristic, PbO_2 electrode was submitted to fifteen charge/discharge cycles in 1.1 mol dm^{-3} H_2SO_4 with current density of 2.0 mA cm^{-2} and results are presented in Fig. 4.

As it can been seen from Fig. 4, during fifteen cycles charge/discharge capacity has practically constant values, with constant columbic efficiency of ~85 %. These findings suggest that electrochemically formed PbO_2 electrode accomplishes demands for potential application in PANI /H_2SO_4 /PbO_2 electrochemical power sources.

SIMULATION OF PANI/H_2SO_4/PbO_2 POWER SOURCE CHARACTERISTICS

Based on charge /discharge characteristics of PANI and PbO_2 electrodes necessary data for estimation of the possible characteristics of PANI|PbO_2 power source are given in Fig.5.

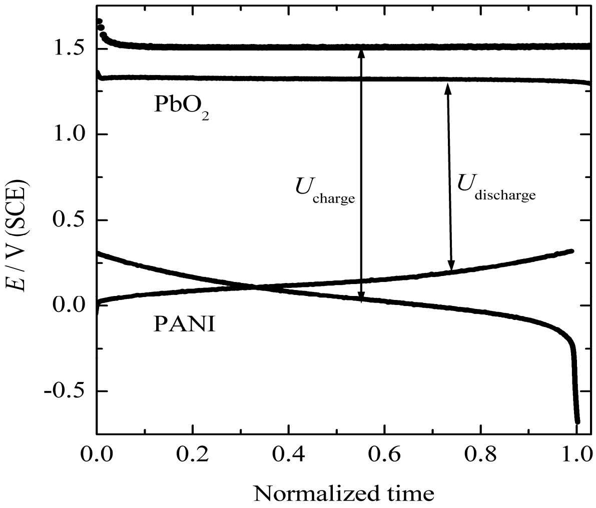


Fig. 5. Charge/discharge curves used for estimation of the possible characteristics of PANI|PbO_2 rechargeable power source

The possible voltage characteristics of PANI /H_2SO_4 /PbO_2 rechargeable power source system were done for anodic current density of 1 mA cm^{-2} (PANI electrode) and cathodic current density

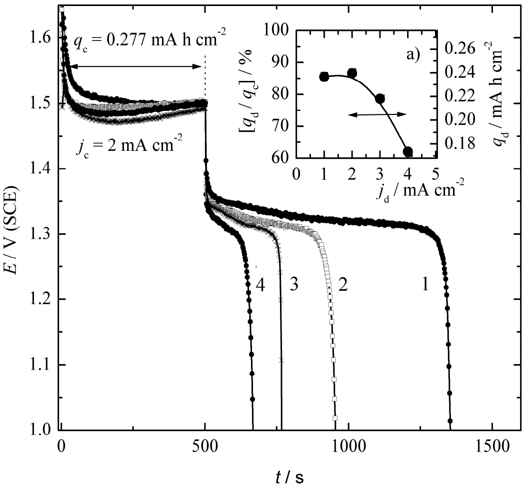


Fig.3. Discharge characteristics of PbO_2 electrode in 1.1 mol dm^{-3} H_2SO_4, where the numbers in the figure refer to different current densities as:1)-1.0, 2)-2.0, 3)-3.0 and 4)-4.0 mA cm^{-2}.
Insert: Dependences of columbic efficiency and discharge capacity on discharge current density.

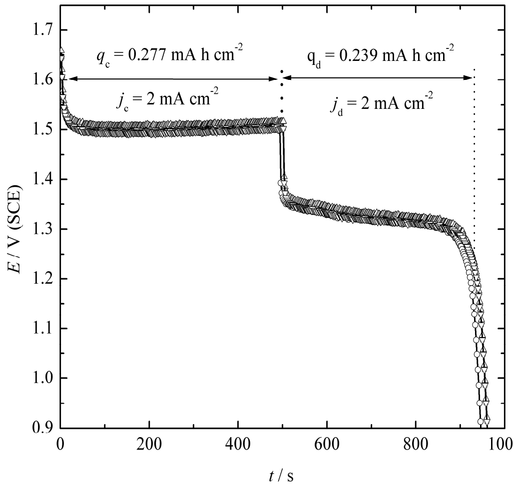


Fig.4. Cycling characteristics of PbO_2 electrode in 1.1 mol dm^{-3} H_2SO_4 at constant current density of 2.0 mA cm^{-2}

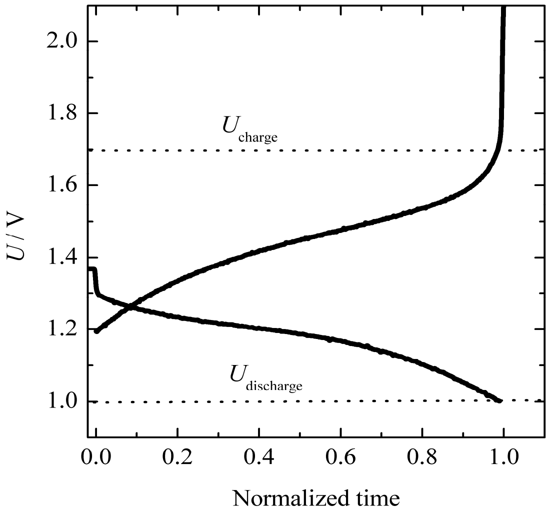


Fig.6. Possible voltage characteristics of PANI|PbO_2 rechargeable power source

of 2 mA cm^{-2} *(*PbO_2 *electrode), assuming that at low current densities voltage loss resulted from additional ohmic drops can be neglected, and that PANI electrode was formed on carbon support with low roughness factor of 2. Obtained results are presented in Fig. 6.*

As it can bee seen in Fig. 6 charging of PANI $/H_2SO_4$ $/PbO_2$ *system would occur in the voltage range between 1.2 and 2.1, but since there is no additional charge above 1.7 V, system should be charged only to that voltage, charging of the system above 2V could provoke hydrogen evolution reaction. After charging open circuit voltage is* $\sim$*1.35 V similar to metal hydride cells. Discharge of the system would occur in the voltage range between 1.35 and 1.0 V. For the discharge voltage below 1.0 V, corresponding to the PANI doping potentials of 0.32 V, the possibilities of PANI degradation are not excluded, so it is recommended that system should be discharge to 1.0 V.*

CONCLUSIONS

In the light of mentioned “three E” criteria, electrochemical rechargeable power sources based on PANI anode and lead dioxide cathode have some advantages comparing to classical $Pb|PbO_2$ *systems, such as: much lower lead content and electrolyte concentration, easier manufacturing demands, ecological acceptability, and possibility of avoiding some problems connected to Pb electrode. Disadvantages of this systems comparing to commercial* $Pb|PbO_2$ *are in the first place, connected to smaller discharge voltage and relatively small PANI electrode capacity. Therefore, further investigations of PANI synthesis on high surface are materials or powered PANI carbon composites are required in order to increase the specific active mass of the PANI anode. On the other hand, determination of the cycle life of PANI* $/PbO_2$ *rechargeable power sources in real conditions would be the most important parameter in further testing.*

Acknowledgment

This work is financially supported by the Ministry of Education, Science and technological development, Republic of Serbia, contract no. 172046.

REFERENCES

[1.] Rüetschi, R.: Energy storage and the environment: the role of battery technology, J. Power Sources 42, 1-7, 1993.

[2.] Beck, F., Rüetschi, P.: Rechargeable batteries with aqueous electrolytes, Electrochim. Acta 45, 2467-2482, 2000.

[3.] Malinauskas, A., Malinauskienė, J., Ramanavičius, A.: Conducting polymer-based nanostructurized materials: electrochemical aspects, Nanotechnology 16, R51-R62, 2005.

[4.] Skotheim, T. A.: Handbook of Conducting Polymers, vol.1, Marrcel Dekker, New York, 1986.

[5.] Karami, H., Mousavi, M. F., Shamsipur, M.: A new design for dry polyaniline rechargeble batteries, J. Power Sources 117, 255-259, 2003.

[6.] Mengoli, G., Musiani, M. M, Pletcher, D.; Valcher, S.: Studies on $Zn \mid ZnX_2 \mid$ polyaniline betteries I, X = Cl and Br, J. Appl. Electrochem. 17, 515-521, 1987.

[7.] Sima, M., Visan, T., Buda, M.: A comparative study of zinc-polyaniline electrochemical cells having sulfate and chloride electrolytes, J. Power Sources 56, 133-136, 1995.

[8.] Rahmanifar, M. S., Mousavi, M. F, Shamsipur, M., Ghaemia, M.: What is the limiting factor of the cycle-life of Zn-polyaniline batteries, J. Power Sources 132, 296-301, 2004.

[9.] Mirmohseni, A., Solhjo, R.: Preparation and characterization of aqueous polyaniline battery using modified polyaniline electrode, Eur. Polym. J. 39, 219-223, 2003.

[10.] Ghanbari, K., Mousavi, M. F., Shamsipur, M., Karami, H.: Synthesis of polyaniline/graphite composite as a cathode of Zn-polyaniline rechargeable battery, J. Power Sources 170, 513-519, 2007.

[11.] Arsov, Lj. D., Plieth, W., Koßmehl, G: Electrochemical and Raman spectroscopic study of polyaniline: influence of the potential on the degradation of polyaniline, J. Solid State Electrochem. 6, 355-361, 1998.

[12.] Gospodinova, N., Terlemezyan, L.: Conducting polymers prepared by oxidative polymerization: POLYANILINE, Prog. Polym. Sci. 23, 1443-1484, 1998.

[13.] Petersson, I., Berghult, B.; Ahlberg, E.: Thin lead dioxide electrodes for high current density applications in semi-bipolar batteries, J. Power Sources 74, 68-76, 1998.

[14.] Petersson, I., Ahlberg, E., Berghult, B.: Parameters influencing the ratio between electrochemically formed α- and β-PbO_2, J. Power Sources 76, 98-115, 1998.

ANNALS OF FACULTY ENGINEERING HUNEDOARA
– INTERNATIONAL JOURNAL OF ENGINEERING

FACULTY OF ENGINEERING HUNEDOARA,
5, REVOLUTIEI, 331128, HUNEDOARA, ROMANIA
http://annals.fih.upt.ro

M 63

UDRUŽENJE ZA TEHNOLOGIJU VODE I SANITARNO INŽENJERSTVO
ASSOCIATION FOR WATER TECHNOLOGY AND SANITARY ENGINEERING

UDRUŽENJE VODOVODA I KANALIZACIJE SRBIJE
WATERWORKS ASSOCIATION OF SERBIA

Pod pokroviteljstvom / Under the auspices

ПРИВРЕДНА КОМОРА СРБИЈЕ
CHAMBER OF COMMERCE AND INDUSTRY OF SERBIA

KVALITET VODE U SISTEMIMA VODOVODA I VODE U INDUSTRIJI

WATER QUALITY IN THE WATERWORK SYSTEMS AND INDUSTRY WATER

Beograd, 08-09. novembar 2012. godine

Izdavač
Udruženje za tehnologiju vode i sanitarno inženjerstvo
Sinđelićeva 21, 11000 Beograd

Za izdavača
Predsednik U.O. Udruženja za tehnologiju vode
i sanitarno inženjerstvo,
Predrag Bogdanović, dipl. ing.

Glavni urednik
Branislav Kujunddžić, dipl. ing.
Urednici:
Prof. dr Dragan Povrenović,
Dr Slavomir Popović, dipl. ing,
Tomislav Slavković, dipl. ing.,

Kompjuterska obrada
Jelena i *Zoran Dimić*

Tiraž 250

Štampa
PLANETA PRINT, Beograd

ISBN 978-86-882931-54-6

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

628.1/.3(082)

КВАЛИТЕТ воде у системима водовода и воде у индустрији (2012 ; Београд)
Kvalitet vode u sistemima vodovoda i vode u industriji, Beograd, 08-09. novembar 2012.
godine = Water Quality in the Waterwork Systems and Industry Water / [organizatori]
Udruženje za tehnologiju vode i sanitarno inženjerstvo [i] Udruženje vodovoda i
kanalizacije Srbije = [organizers]
Association for Water Technology and Sanitary Engineering [and] Waterworks Association of
Serbia ; [urednici Dragan Povrenović, Slavomir Popović, Tomislav Slavković]. -
Beograd : Udruženje za tehnologiju vode i sanitarno inženjerstvo, 2012 (Beograd :
Planeta print). - VI, 197 str. : ilustr. ; 24 cm

Tiraž 250. - Str. III: Predgovor / glavni urednik [Branislav Kujundžić]. - Napomene uz
tekst. - Bibliografija uz svaki rad.

ISBN 978-86-82931-54-6
1. Удружење за технологију воде и санитарно инжењерство (Београд)
a) Водовод - Зборници b) Снабдевање водом - Зборници c) Индустријска вода -
Зборници
COBISS.SR-ID 194445068

5. ZAKLJUČAK

U radu su predstavljeni bromati kao opasne supstance, jonska hromatografija kao način određivanja koncentracije bromata u vodi i metoda za određivanje bromata u vodi.

Takođe, prikazane su maksimalno dozvoljene koncentracija bromata prema Direktivama EU, Smjernicama SZO, preporukama US EPA i Pravilniku RS.

Bromati nastaju u procesu ozonizacije vode, oksidacijom bromida, složenim mehanizmom koji uključuje kombinaciju reakcija sa ozonom i OH radikalima. Potencijalni su kancerogeni, genotoksični i ne podliježu biodegradaciji na biološki aktivnim filterima.

Jonska hromatografija se pokazala kao uspješna metoda za određivanje bromata u vodi.

Analizirani su uzorci vode za piće i riječne vode. U svim analiziranim uzorcima koncentracija bromata je bila ispod granice detekcije. Koncentracije bromida su, takođe bile ispod granice detekcije.

LITERATURA

1. Dr Božo Dalmacija, Dr Jasmina Agbaba; Kontrola kvaliteta vode za piće, Novi Sad, 2006.
2. Dr Božo Dalmacija, Dr Jasmina Agbaba, Dr Mile Klašnja; Dezinfekcija vode, Novi Sad, 2005.
3. Dr Helwig Schafer, Dr Markus Laubli, Dr Roland Dorig, Jon Chromatography, Monograph
4. Prof.Dr Maximilian Kolb, Prof Dr Andreas Seubert, Dr Kai enning Viehweger; Practical Ion Chromatography
5. Veronika R. Meyer; Practical High-Performance Liquid Chromatography; Switzerland, Fourth Edition
6. WHO Guidelines for Drinking-water Quality; Bromate in Drinking-water, 2005.
7. Guidelines for Drinking-water Quality; Bromate, 2004.
8. Anthony J. Tarquin, Douglas D. Rittmann, Rodolfo M. Pino; Bromate Control during Ozonation of High-Bromide Drinking Water, 2002.
9. Pravilnik o higijenskoj ispravnosti vode za piće (Sl.list SRJ, br.42/98 i 44/99)
10. Council Directive 98/83/EC, 03.11.1998 on the quality of water intended for human consumption
11. EPA Method 300.0 determimation of inorganic anions by ion chromatography, 1998.

AUTOMATSKI UREDJAJI ZA ELEKTOHEMIJSKI TRETMAN VODA

T. Trišović[1], M. Spasojević[2], B.Grgur[3], M.Gvozdenović[3], L.Rafailović[4], B.Jugović[1]

Abstrakt

Osnovna mera u prevenciji oboljenja izazvanih higijenski neispravnom hranom i vodom je i dezinfekcija vode. Dezinfekcija vode je osnovni proces obrade vode, kojim se patogeni mikroorganizmi unuštavaju ili inaktiviraju. Najčešće korišćeno sredstvo za dezinfekciju je gasoviti hlor. Gasoviti hlor se u vodu dodaje pod pritiskom, gde se meša sa vodom, hidrolizuje stvarajući natrijum hipohlorit i hipohlorastu kiselinu koji su zapravo agensi dezinfekcije vode. S obzirom, da se manipulacija sa gasnim hlorom ostvaruje pod pritiskom, često dolazi do incidenata naročito u mašinskim halama odakle se hlor dozira u vodu.

Cilj ovog rada bio je razvoj uređaja za proizvodnju dezinfekcionog sredstva aktivnog hlora korišćenjem sirovina koje su potpuno bezopasne i nisu štetne za okolinu i zdravlje radnika. Uređaji koriste razblažen rastvor natrijum-hlorida (kuhinjske soli) i elektičnu energiju kao sirovinu, kako bi prozveli razblaženi rastvor aktivnog hlora – hipohlorita. Na ovaj način umesto skladištenja gasovitog hlora skladišti se bezopasna kuhinjaka so. Uređaji mogu biti različito konstruisani i različitih kapaciteta u zavisnosti od tipa vodovoda i količine vode koja se tretira. Pored tretmana pijaćih voda, mogu se koristiti i za tretman voda u bazenima za kupanje, preradu otpadnih voda, dezinfekciju opreme i objekata u prehrambenoj industriji, beljenje tekstila, kožnoj i farmaceutskoj industriji. Takođe, rastvor *in situ* proizvedenog aktivnog hlora je pH neutralan i može naći i široku primenu u primarnoj poljoprivrednoj proizvodnji.

U radu su data dva tehnička rešenja uređaja za elektohemijsku proizvodnju aktivnog hlora i to za male vodovodne sisteme sa oscilujućom potrošnjom (kapaciteta do 20 l/s) i za srednje vodovodne sisteme sa konstantnom ili oscilujućim protokom kroz cevovod (kapaciteta do 50 l/s). Ova istraživanja i projektovanje uređaja su rađena na osnovu analize i zahteva sa tržišta. Uređaji su potpuno automatizovani samostalni i jednostavni za rukovanje i održavanje.

Ključne reči: dezinfekcija, elektohlorinatori, aktivan hlor, elektohemijski tretman vode

1. UVOD

Komercijalna sredstva za dezinfekciju su: gasoviti hlor, natrijum hipohlorit, hlor-dioksid i ozon. Zbog duže sterilnosti vode, hlorna jedinjenja nemaju alternativu i svi drugi postupci čine pomoćne postupke koji mogu manje ili više da smanje korišćenje hlornih jedinjenja, ali ne i da ih potpuno supstituišu. Kod dezinfekcije vode za piće hlorom ili hlor dioksidom dolazi do hemijskih reakcija tzv. dvostrukog delovanja. Pozitivni efekat, zbog kojeg se dezinfekcija izvodi, je uništavanje mikroorganizama, posebno patogenih, što dovodi i održava kvalitet vode unutar zakonodavnih normi. Negativni efekti se iskazuju u stvaranju dezinfekcionih nusprodukata od kojih neki mogu imati izražena karcinogena, mutagena ili toksična delovanja na živa bića.

Dezinfekcija sa hlornim jedinjenjima mora da bude izvedena na odgovarajući način što podrazumeva:

1. vodu veoma male mutnoće
2. što niži pH
3. nisku koncentraciju azota posebno amonijačnog azota

---

1) Institute tehničkih nauka Srpske akademije nauka i umetnosti, Knez Mihajlova 35/4, 11000 Beograd, Srbija

2) Agronomski fakultet, Univerzitet u Kragujevcu, Cara Dušana 34, 32000, Čačak

3) Tehnološko-metaluruški fakultet, Univerzitet u Beogradu, Karnegijeva 4, 11000 Beograd, Srbija

4) Center of Electrochemical Surface Technology CEST, Vitor Kaplan Strasse 2, 2700 Wr.Neustadt, Austria

4. ograničen sadržaj prirodnih organskih materija
5. obezbeđeno dovoljno dugo vreme kontakta

Uspešnost dezinfekcije pijaće vode daje tek mikrobiološka i hemijska analiza obrađene vode. Na ovaj način se konstatuje stanje ulazne vode i vode posle dezinfekcije kako u pogledu prisustva mikroorganizama tako i u pogledu nus-produkata dezinfekcije. Pravilnicima je definisana maksimalna koncentracija dezinficijensa koja se sme dodavati vodi koju tretiramo da bi se sprečilo nastajanje sporednih proizvoda.

Svako sredstvo za dezinfekciju ima svoje korisničke limite koji se mogu grupno nazvati: zdravstveni, tehnološki, sigurnosni i finansijski. Tako i najčešće korišteni dezinficijensi hlor i hlor dioksid uz svoje pozitivno delovanje imaju i velik broj nepoželjnih svojstava. Ti problemi su doveli do postupka kojim se pokušalo dobiti novo sredstvo za dezinfekciju tzv. elektrohemijski hipohlorit. Objedinio je najbolje karakteristike hlora i hlordioksida, a to su: delotvornost, proizvodnja na mestu korištenja (*in situ*), sigurnosne mere rada i niska cena proizvodnje.

Postupak dezinfekcije pomoću hipohlorita proizvedenog elektrolizom 3% rastvora NaCl na mestu upotrebe je pogodniji od ostalih postupaka dezinfekcije vode, ne samo sa aspekta ekonomske isplativosti, već i sa ekološkog aspekta. Uređaji koji proizvode aktivan hlor procesom elektolize su razvijeni poslednjih dvadeset godina posebno kad je Evropska Zajednica predvidela zabranu transporta gasovitog i tečnog hlora od 1998. godine, tako da će sadašnji konvencionalni postupak upotrebe hlora morati da se ukine. Elektroliza ne zahteva posebne mere zaštite, a delotvornost nastalog hipohlorita je jednaka ili bolja od učinka gasovitog hlora. Prema kalkulacijama, proizvod je jeftiniji od gasovitog hlora. Može se koristiti u javnim i privatnim vodovodima, bazenima za rekreaciju i za industrijske potrebe.

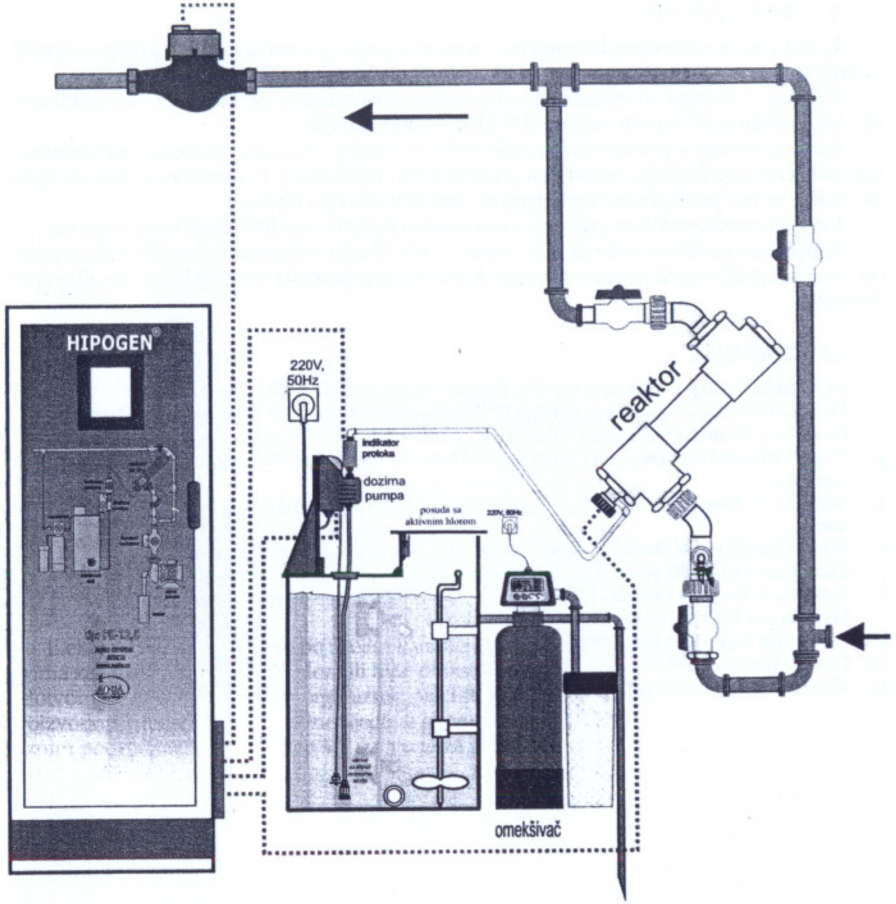
Proizvodnja na mestu korištenja, tj. na izvorištima, u tehnološkim procesima i sl. predstavlja najjeftiniju, pouzdanu i sigurnu alternativu postojećim sredstvima za dezinfekciju.

2. REZULTATI I DUSKUSIJA

Elektrohemijski reaktor se projektuje na osnovu analize anodnog i katodnog materijala, kinetičkih i operativnih parametara, elektrodne prenapetosti, pada napona u elektrolitu, katodno, anodno i ukupno iskorišćenje struje, i potrošnje energije po jedinici proizvoda aktivnog hlora. Na osnovu dobijenih rezultata utvrđena je optimalna konstrukcija ćelije i optimalne vrenosti tehnoloških parametara procesa. Ustanovljeno je iz eksperimentalno dobijenih rezultata da najbolja elektohemijska svojstva poseduje titanska anoda sa prevlakom rutenijum i titan oksida. Pri elektolizi rastvora sastava 30 g/l NaCl i 5 g/l NaOCl na t=25°C i pH=7,0, na gustini struje od 1000 A m^{-2} postiže se visoko anodno iskorišćenje struje od 85%.

Rastvor aktivnog hlora dobijen pod ovim uslovima[1-3] uspešno koristi kao efikasan rastvor za dezinfekciju. Analizirajući kvalitet proizvedenog rastvora, ustanovljena je optimalna koncentracija natrijum hlorida od 25 do 35g/l. Temperaturni interval od 25 do 35 °C obezbeđuje maksimalnu elektohemijsku efikasnost elektolizera za proizvodnju aktivnog hlora. Katodni gubici struje se smanjuju sa povećanjem odnosa anodne i katodne površine. Analiza dizajna ćelije, dimenzije elektoda, mehaničke čvrstoće i elektične otpornosti nosača ukazuje da debljina kolektora treba da bude od 2 do 3 mm. Ustanovljen je i optimalni razmak između elektoda od 3 mm.

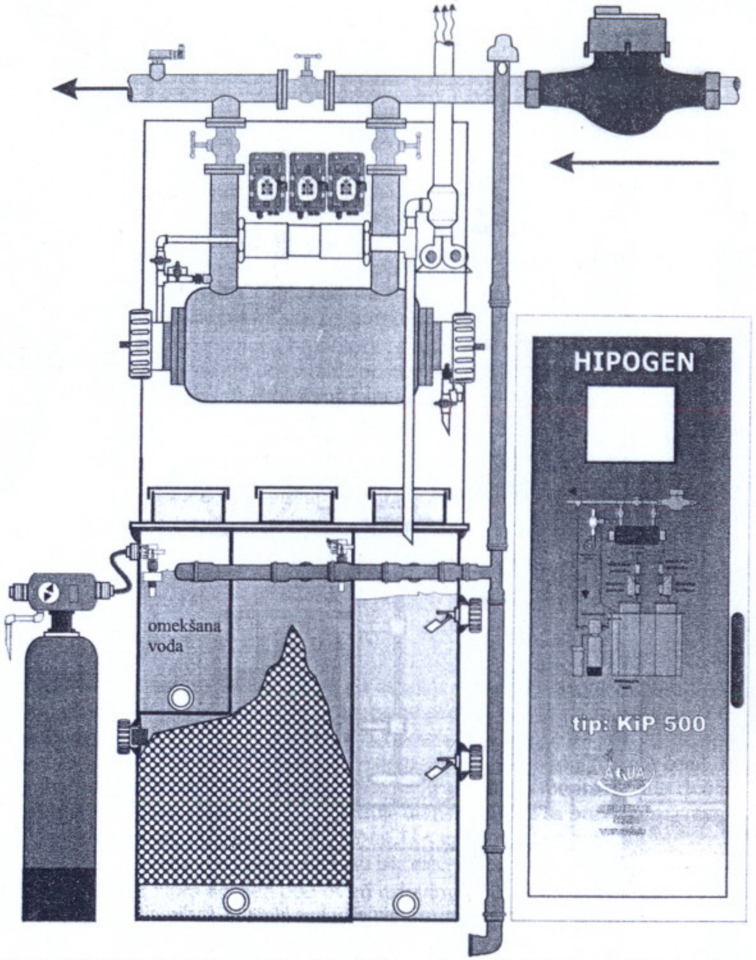
Uređaj za proizvodnju aktivnog hlora sa koaksijalnim reaktorom[4] (Slika 1.) se sastoji od elektro-bloka, rezervoara sa natrijum hloridom i hidruličkog sklopa. Hidrulički sklop se sastoji od dozirnih pumpi, ulaznog ventila, senzora protoka, koaksijalnog reaktora. Iz rezervoara (3% ili 30% NaCl) se rastvor natrijum hlorida pomoću dozirnih pumpi transportuje cevovodom (meša sa čistom vodom) i ubrizgava u koaksijalni reaktor preko nepovratnog ventila. Ulaskom u reaktor hloridi se elektrohemijski konvertuju u aktivan hlor na anodi dok se na katodi izdvaja vodonik. Svi produkti reakcije se preko nepovratnog ventila koji je na vrhu kućišta reaktora ubrizgavaju u vodu koju dezinfikujemo, a koja je istovremeno i rashladni fluid i izolacioni medij od eventualnog curenja aktivnog hlora u okolinu. Na ovaj način postižemo da se hloridni rastvor odnosno rastvor aktivnog hlora u kućištu reaktora održava na temperaturi (temperatura je obično između 15 i 30 °C) na kojoj neće doći do termohemijske reakcije pretvaranja hipohlorita u hlorat, što su idealni uslovi za elektrohemijsku sintezu aktivnog hlora.



Slika 1. *Blok shema uređaja za proizvodnju aktivnog hlora sa koaksijalnim reaktorom*

Zahvaljujući ovim konstrukcijama temperaturski režim rada reaktora je takav da se ne dostiže kritična temperatura izlaznog elektrolita preko 30 °C pa stoga termoregulator i izmenjivač toplote nije potreban. Nivo automatke je dosta pojednostavljen i svodi se na dva senzora i to za protok i nivoa. Uređaj može uključivati ili senzor protoka ili merač protoka ili elektoda koja meri koncentraciju hlora u vodi. Uredjaj za elektrohemijsku proizvodnju i doziranje aktivnog hlora sa koaksijalnim reaktorom se može primeniti za tretman vode sa protocima do 10 litara u sekundi.

Uređaj za proizvodnju aktivnog hlora sa koaksijalno-protočnim reaktorom[5,6] u zavisnosti od potrebe može raditi na dva načina i to: 1. Kao uređaj sa koaksijalnim reaktorom i bez lagerovanja aktivnog hlora 2. Kao uređaj sa protočnim reaktorom i sa lagerovanjem aktivnog hlora. Oba načina rada zahtevaju autonomni sistem za dobijanje omekšane vode 2 koji ima zadatak da vodu koja napaja uređaj potpuno oslobodi jona kalcijuma i magnezijuma (da ukloni tvrdoću). U pomoćnom rezervoaru se nalazi usisna korpa dozirnih pumpi koje doziraju koncentovan rastvor natrijum hlorida i omekšanu vodu. Ove pumpe su proporcionalne i mogu imati, ili konstantan protok, ili protok proporcionalan promeni protoka vode koji meri vodomer.



Slika 2. *Blok shema uređaja za proizvodnju aktivnog hlora sa koaksijalno-protočnim reaktorom*

Ako je potrebno da uređaj radi kao uređaj sa koaksijalnim reaktorom, princip rada je indentičan onom datom na slici 2 što znači manje komponenata na samom uređaju, pa je samim tim uređaj i jeftiniji. Ako je potrebno da uređaj radi kao uređaj sa protočnim reaktorom i lagerovanjem aktivnog hlora princip reada je sledeći. Dve dozirne pumpe, jedna za omekšanu vodu, a druga za koncentrovani rastvor natrijum hlorida, potiskuju vodu/rastvor kuhinjske soli u koaksijalni elektolizer, gde se oksidišu hloridni joni i redukuju joni vode stvarajući natrijum hipohlorit na anodi i gasoviti vodonik na katodi. Ova smeša tečnosti i gasa iz elektolizera ulazi u separator, gde se u uslovima podpritiska, oslobađa vodonik iz vodenog rasvora natrijum hipohlorita i potiskuje u atmosferu. Čist 1% rasvor natrijum hipohlorita se gravitaciono odlaže u prihvatnu posudu za hipohlorit. Sve posude za vodu i rasvore (soli i hipohlorita) su smestene u zbirni rezervoar koji čini kompaktnu celinu kaku za instalaciju i transport i bilo kavu drugu manipulaciju. Iz posude za hipohlorit se, pomoću automatskog dozirnog sistema, koji je upravljan direktnim ili indirektnim merenjem koncentracije rezidualnog hlora u vodi rastvor aktivnog hlora dozira u vodu.

U toku trajanja elektolize pneumatski prostor koji obuhvata elektolizer i posuda za prihvat aktivnog hlora, a koji je iznad vodene linije, se održava na podpritisku u odnosu na atmosferski pritisak. Održavanje podpritiska ima dve prednostosti i to prvo što omogućuje kakše izdvajanje mehurova vodonika iz vodenog rastvora aktivnog hlora, a drugo štp ne postoji mogućnost curenja vodonika u prostoriju u kojoj se uređaj nalazi. Izbacivanje vodonika stvaranjem podpritiska daleko je pouzdanije rešenje od produvavanja ventilatorima sa nadpritiskom,zbog mogućeg curenja vodonika u prostoriju u kojoj je istaliran uređaj. Uredjaj za elektrohemijsku proizvodnju i doziranje aktivnog hlora sa koaksijalno – protočnim reaktorom se može primeniti za kapacitete između 10 i 100 litara u sekundi protoka vode. Reaktorski moduli se mogu paralelno ili redno povezivati.

Osnovne prednosti su koriščenja uređaja za *in situ* dobijanje aktivnog hlora su:

- Siguran u radu za ljude u proizvodnji i za okolinu
- Smanjeni troškovi proizvodnje
- Sirovine za proizvodnju su: so (NaCl), voda i električna energija
- Moguća nadogradnja uređaja prema potrebi korisnika
- Jednostavno održavanje
- Garancija na elektrode 7 godina
- Zadovoljava sve uslove zdravstvenog i sigurnosnog zakonodavstva
- Poboljšava kvalitet vode
- Smanjeni broj dezinfekcijskih nusprodukata
- Garancija za funkcijonalnost
- Proizvodnja elrktrohemijskog hipohlorita prema potrebama korisnika
- Rad uređaja ne zavisi od nabavke specijalnih hemikalija

3. ZAKLJUČAK

Elektrohemijski hipohlorit, po svojim karakteristikama, može biti efikasna alternativa sredstvima za dezinfekciju na bazi hlora ili hlor-dioksida. Mogućnost proizvodnje „na licu mesta„ delotvornost na patogene mikroorganizme, niski stepen sigurnosnih mera i niska cena troškova proizvodnje predstavljaju osnovne njegove glavne prednosti. Ova tehnologija je proverena u raznim područjima primene kao što su: vode za piće, bazeni za rekreaciju, prerada otpadnih voda, uređaji za hlađenje i slično.

LITERATURA

1. P.M. Robertson and W.Gnehm, J. Appl. Electrochem, 13, 307-315 (1983).
2. N.Krstajić, T.Trišović, V.Jović, N. Trišović, I međunarodni naučno-razvojni simpozijum Stvaralaštvo kao osnov privrednog razvoja, Knjiga radova, 8.53, (1996)
3. V.D.Jović, N.V.Krstajić, Lj. Gajić-Krstajić, B.M.Jović, T.Tišović, Technologica Acta 1 (2) 169 – 172 (2005).
4. Trišović, M. Gvozdenović, L. Rafailović, B. Jugović, B.Grgur, prijavljen patent, P-2011/0529 (2011)
5. T. Trišović, N. Trišović, P-2011/0518, prijavljen patent, (2011).
6. T. Trišović, L. Rafailović, M. Gvozdenović, B. Jugović, J. Stevanović, prijavljen patent, P- 2011/0528, (2011).

Прилог 10а. Техничка решења

Универзитет у Крагујевцу		**University of Kragujevac**
Агрономски факултет		**Faculty of Agronomy**
Чачак		**Čačak**
Университет в Крагуевце		**Université de Kragujevac**
Агрономический факулътет		**Faculte des sciences agronomiques**
Чачак		**Čačak**

32 000 Čačak, Cara Dušana 34, P.O. Box 95, Serbia
Tel.: +381 32 303400 (or 303410); Tel/fax: +381 32 303401 Žiro račun: 840-948666-13
Web: www.afc.kg.ac.rs E-mail: afdekanat@tfc.kg.ac.rs

Број: 1282/21-VIII
Ч а ч а к, 05.07.2010.год.

Наставно - научно веће Агрономског факултета у Чачку на седници одржаној 05. 07. 2010. год. разматрало је позитивна мишљења два рецензента за прихватање техничких решења , па је на основу члана 59. Закона о научноистраживачкој делатности (Сл. Гласник РС бр. 110/05),Правилника о поступку и начину вредновања, квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС бр. 38/2008)-Прилог 2. и чл.199. Статута Факултета (број 1635/2 од 28.09.2006.г., 1980/2-VII од 19.09.2008.г .и 818/2-IV од 04.05.2010.г.), донело је

ОДЛУКУ

Прихвата се и верификује научно истраживачки резултат на пројекту Министарства за науку и технолошки развој RS - PTP-2108B - *Електрохемијски генератори средстава за дезинфекцију (активног хлора, јонског сребра и бакра) са шаржним рециркулационим типом реактора* и IP8025 - *Електрохемијско постројење за производњу средстава за дезинфекцију са модуларним реактором и реверсним електродама*: **"Електохемијски уређај за дезинфекцију воде са рециркулационим типом реактора и реверсним електродама"**, аутора: Мирослава Спасојевић, Снежане Танасковић, Милице Гвозденовић, Томислава Тришовић у оквиру категорије *Нови производ или технологија уведени у производњу* (М81).

ОБРАЗЛОЖЕЊЕ

На основу презентованог и образложеног, горе наведеног оствареног резултата научноистраживачког рада и писаног позитивног мишљења два рецензента- др Раде Стевановић и др Ђорђе Јанаћковић, Наставно-научног већа се једногласно изјаснило за усвајање и верификацију резултата у новеденој категорији.

Достављено:

Ауторима
Руководиоцу пројекта
Архиви

Председник
Наставно-научног већа

проф. др Мирослав Спасојевић

Универзитет у Крагујевцу	**University of Kragujevac**
Агрономски факултет	**Faculty of Agronomy**
Чачак	**Čačak**
Университет в Крагуевце	**Université de Kragujevac**
Агрономический факулътет	**Faculte des sciences agronomiques**
Чачак	**Čačak**

32 000 Čačak, Cara Dušana 34, P.O. Box 95, Serbia
Tel.: +381 32 303400 (or 303410); Tel/fax: +381 32 303401 Žiro račun: 840-948666-13
Web: www.afc.kg.ac.rs E-mail: afdekanat@tfc.kg.ac.rs

Број: 1282/20-VIII
Ч а ч а к, 05.07.2010.год.

Наставно - научно веће Агрономског факултета у Чачку на седници одржаној 05. 07. 2010. год. разматрало је позитивна мишљења два рецензента за прихватање техничких решења , па је на основу члана 59. Закона о научноистраживачкој делатности (Сл. Гласник РС бр. 110/05),Правилника о поступку и начину вредновања, квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС бр. 38/2008)-Прилог 2. и чл.199. Статута Факултета (број 1635/2 од 28.09.2006.г., 1980/2-VII од 19.09.2008.г .и 818/2-IV од 04.05.2010.г.), донело је

ОДЛУКУ

Прихвата се и верификује научно истраживачки резултат на пројекту Министарства за науку и технолошки развој RS - PTP-2108B - *Електрохемијски генератори средстава за дезинфекцију (активног хлора, јонског сребра и бакра) са шаржним рециркулационим типом реактора* и IP8025 - *Електрохемијско постројење за производњу средстава за дезинфекцију са модуларним реактором и реверсним електродама*: "**Електохемијски уређај за дезинфекцију воде са рециркулационим типом реактора и стандардним електодама**", аутора: Мирослава Спасојевић, Јасмине Стевановић, Лидије Рафаиловић, Томислава Тришовић у оквиру категорије *Нови производ или технологија уведени у производњу* (M81).

ОБРАЗЛОЖЕЊЕ

На основу презентованог и образложеног, горе наведеног оствареног резултата научноистраживачког рада и писаног позитивног мишљења два рецензента-експерта, чланови Наставно-научног већа су се једногласно изјаснили за усвајање и верификацију резултата у наведеној категорији.

Достављено:

Ауторима
Руководиоцу пројекта
Архиви

Председник
Наставно-научног већа

проф. др Мирослав Спасојевић

Универзитет у Крагујевцу		**University of Kragujevac**
Агрономски факултет		**Faculty of Agronomy**
Чачак		**Čačak**
Университет в Крагуевце		**Université de Kragujevac**
Агрономический факулътет		**Faculte des sciences agronomiques**
Чачак		**Čačak**

32 000 Čačak, Cara Dušana 34, P.O. Box 95, Serbia
Tel.: +381 32 303400 (or 303410); Tel/fax: +381 32 303401 Žiro račun: 840-948666-13
Web: www.afc.kg.ac.rs E-mail: afdekanat@tfc.kg.ac.rs

Број: 1282/19-VIII
Ч а ч а к, 05.07.2010.год.

Наставно - научно веће Агрономског факултета у Чачку на седници одржаној 05. 07. 2010. год. разматрало је позитивна мишљења два рецензента за прихватање техничких решења , па је на основу члана 59. Закона о научноистраживачкој делатности (Сл. Гласник РС бр. 110/05),Правилника о поступку и начину вредновања, квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС бр. 38/2008)-Прилог 2. и чл.199. Статута Факултета (број 1635/2 од 28.09.2006.г., 1980/2-VII од 19.09.2008.г .и 818/2-IV од 04.05.2010.г.), донело је

ОДЛУКУ

Прихвата се и верификује научно истраживачки резултат на пројекту Министарства за науку и технолошки развој RS - IP8025 - *Електрохемијско постројење за производњу средстава за дезинфекцију са модуларним реактором и реверсним електродама* и 45-01-000-65/2008-01/88 - *Аутоматски уређај за физичко-хемијски третман вода са комбинованим модуларним генераторима*: **"Електохемијски уређај за производњу дезинфиуцијенса са коаксијалним плаг реактором"**, аутора: Томислава Тришовић, Бранимира Гргур, Снежане Тансковић, Наташе Тришовић, Јасмине Стевановић, у оквиру категорије *Нови производ или технологија уведени у производњу* (М81).

ОБРАЗЛОЖЕЊЕ

На основу презентованог и образложеног, горе наведеног оствареног резултата научноистраживачког рада и писаног позитивног мишљења два рецензента- др Раде Стевановић и др Ђорђе Јанаћковић, Наставно-научног већа се једногласно изјаснило за усвајање и верификацију резултата у новеденој категорији.

Достављено:

Ауторима
Руководиоцу пројекта
Архиви

Председник
Наставно-научног већа

проф. др Мирослав Спасојевић

Универзитет у Крагујевцу		**University of Kragujevac**
Агрономски факултет		**Faculty of Agronomy**
Чачак		**Čačak**
Университет в Крагуевце		**Université de Kragujevac**
Агрономический факулътет		**Faculte des sciences agronomiques**
Чачак		**Čačak**

32 000 Čačak, Cara Dušana 34, P.O. Box 95, Serbia
Tel.: +381 32 303400 (or 303410); Tel/fax: +381 32 303401 Žiro račun: 840-948666-13
Web: www.afc.kg.ac.rs E-mail: afdekanat@tfc.kg.ac.rs

Број: 1282/18-VIII
Чачак, 05.07.2010.год.

Наставно - научно веће Агрономског факултета у Чачку на седници одржаној 05. 07. 2010. год. разматрало је позитивна мишљења два рецензента за прихватање техничких решења , па је на основу члана 59. Закона о научноистраживачкој делатности (Сл. Гласник РС бр. 110/05),Правилника о поступку и начину вредновања, квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС бр. 38/2008)-Прилог 2. и чл.199. Статута Факултета (број 1635/2 од 28.09.2006.г., 1980/2-VII од 19.09.2008.г .и 818/2-IV од 04.05.2010.г.), донело је

ОДЛУКУ

Прихвата се и верификује научно истраживачки резултат на пројекту Министарства за науку и технолошки развој RS - PTP-2108B - *Електрохемијски генератори средстава за дезинфекцију (активног хлора, јонског сребра и бакра) са шаржним рециркулационим типом реактора*: "**Електохемијски генератори средстава за дезинфекцију са шаржним типом реактора**", аутора: Томислав Тришовић, Лидија Рафаиловић, Милица Гвозденовић, Наташа Тришовић, Бранимир Југовић у оквиру категорије *Нови производ или технологија уведени у производњу* (М81).

ОБРАЗЛОЖЕЊЕ

На основу презентованог и образложеног, горе наведеног оствареног резултата научноистраживачког рада и писаног позитивног мишљења два рецензента- др Раде Стевановић и др Ђорђе Јанаћковић, Наставно-научног већа се једногласно изјаснило за усвајање и верификацију резултата у новеденој категорији.

Достављено:

Ауторима
Руководиоцу пројекта
Архиви

Председник
Наставно-научног већа

проф. др Мирослав Спасојевић

Универзитет у Крагујевцу	University of Kragujevac
Агрономски факултет	Faculty of Agronomy
Чачак	Čačak
Университет в Крагуевце	Université de Kragujevac
Агрономический факулътет	Faculte des sciences agronomiques
Чачак	Čačak

32 000 Čačak, Cara Dušana 34, P.O. Box 95, Serbia
Tel.: +381 32 303400 (or 303410); Tel/fax: +381 32 303401 Žiro račun: 840-948666-13
Web: www.afc.kg.ac.rs E-mail: afdekanat@tfc.kg.ac.rs

Број: 1282/7-VIII
Чачак, 05.07.2010.

Наставно - научно веће Агрономског факултета у Чачку на седници одржаној 05. 07. 2010. год. разматрало је позитивна мишљења два рецензента за прихватање техничких решења , па је на основу члана 59. Закона о научноистраживачкој делатности (Сл. Гласник РС бр. 110/05),Правилника о поступку и начину вредновања, квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС бр. 38/2008)-Прилог 2. и чл.199. Статута Факултета (број 1635/2 од 28.09.2006.г., 1980/2-VII од 19.09.2008.г .и 818/2-IV од 04.05.2010.г.), донело је

ОДЛУКУ

Прихвата се и верификује научно истраживачки резултат на пројекту Министарства за науку и технолошки развој РС - МТНС I.5.0757 - *Електрохемијски поступак дезинфекције воде за пиће*: "**Индустријско постројење за електрохемијску дезинфекцију воде**", аутора: Томислава Тришовић, Недељка Крстајић, Владимира Јовић, Бранимира Гргура у оквиру категорије *Нови производ или технологија уведени у производњу* (М81).

ОБРАЗЛОЖЕЊЕ

На основу презентованог и образложеног, горе наведеног оствареног резултата научноистраживачког рада и писаног позитивног мишљења два рецензента- др Раде Стевановић и др Ђорђе Јанаћковић, Наставно-научног већа се једногласно изјаснило за усвајање и верификацију резултата у новеденој категорији.

Достављено:

Ауторима
Руководиоцу пројекта
Архиви

Председник
Наставно-научног већа

проф. др Мирослав Спасојевић

Универзитет у Крагујевцу		**University of Kragujevac**
Агрономски факултет		**Faculty of Agronomy**
Чачак		**Čačak**
Университет в Крагуевце		**Université de Kragujevac**
Агрономический факулътет		**Faculte des sciences agronomiques**
Чачак		**Čačak**

32 000 Čačak, Cara Dušana 34, P.O. Box 95, Serbia
Tel.: +381 32 303400 (or 303410); Tel/fax: +381 32 303401 Žiro račun: 840-948666-13
Web: www.afc.kg.ac.rs E-mail: afdekanat@tfc.kg.ac.rs

Број: 1282/22-VIII
Чачак, 05.07.2010.год.

Наставно - научно веће Агрономског факултета у Чачку на седници одржаној 05. 07. 2010. год. разматрало је позитивна мишљења два рецензента за прихватање техничких решења , па је на основу члана 59. Закона о научноистраживачкој делатности (Сл. Гласник РС бр. 110/05),Правилника о поступку и начину вредновања, квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС бр. 38/2008)-Прилог 2. и чл.199. Статута Факултета (број 1635/2 од 28.09.2006.г., 1980/2-VII од 19.09.2008.г .и 818/2-IV од 04.05.2010.г.), донело је

ОДЛУКУ

Прихвата се и верификује научно истраживачки резултат на пројекту Министарства за науку и технолошки развој RS - PTP- IP8025 - Електрохемијско постројење за производњу средстава за дезинфекцију са модуларним реактором и реверсним електродама, Иновациони пројекат и 45-01-000-65/2008-01/88 - Аутоматски уређај за физичко-хемијски третман вода са комбинованим модуларним генераторима: **"Уређај за уклањање високих концентрација амонијака, гвожђа и мангана из пијаће воде",** аутора: Томислава Тришовић, Јасмине Стевановић, Бранимира Југовић, Наташе Тришовић у оквиру категорије *Нови производ или технологија уведени у производњу* (М81).

ОБРАЗЛОЖЕЊЕ

На основу презентованог и образложеног, горе наведеног оствареног резултата научноистраживачког рада и писаног позитивног мишљења два рецензента- др Раде Стевановић и др Ђорђе Јанаћковић, Наставно-научног већа се једногласно изјаснило за усвајање и верификацију резултата у новеденој категорији.

Достављено:

Ауторима
Руководиоцу пројекта
Архиви

Председник
Наставно-научног већа

проф. др Мирослав Спасојевић

Прилог 10б. Текст техничких решења

GRUPA M80: TEHNIČKA REŠENJA

Kategorija: „Novi proizvod ili tehnologija“
Rezultat M82: Novi proizvod ili tehnologija uvedeni u proizvodnju

1. **ustanova/Autori rešenja: Institut tehničkih nauka SANU, K.Mihajlova 35/4, 11000, Beograd, Tehnološko – metaluruški fakultet, Beograd; Institut za multidisciplinarne studije, Beograd**
   Autori: Tomislav Trišović, Nedeljko Krstajić, Vladimir Jović, Branimir Grgur

2. **Naziv i evidencioni broj projekta sa brojem aktivnosti, u kome je ostvaren rezultat iz kategorije M80: Projekat** Inovacioni
   "Elektrohemijski postupak dezinfekcije vode za piće", MTNS I.5.0757, 1996-97.

3. **Naziv tehničkog rešenja**

   Industrijsko postrojenje za elektrohemijsku dezinfekciju vode

4. **Oblast na koju se tehničko rešenje odnosi:**

   Tehničko-tehnološke i biotehničke nauke

5. **Problem koji se tehničkim rešenjem rešava**

U svetu a i kod nas oko 80% velikih vodovoda (kapciteti iznad 20 litara proizvedene vode u sekundi) dezinfekciju ostvaruje sa gasovitim hlorom. Razvijene zemlje zakonskom regulativom pokušavaju da redukuju korišćenje gasovitog hlora sa drugim tehnološkim rešenjima prvenstveno korišćenjem vodenog rastvora natrijum hipohlorita, hlor dioksida, ozona UV zračenja. Postoje dva razloga zbog kojih se potiskuje stara tehnologija gasnog hlorisanja vode. Prvi razlog je opasnost vezana za sadašnju tehnologiju po kojoj se proizvodi hlor. To je tzv. živina tehnologija koja je kod nas isključivo prisutna. Hlor i hipohlorit koji proizvode naše fabrike, a i mnoge fabrike u svetu, se dobija u reaktorima gde je živa kao katoda u direktnom kontaktu sa gasovitim hlorom. Zapravo u elektrohemijskim reaktorima odnosno elektrolizerima pare žive i gasovitog hlora odlaze u rezervoare za hlor. Takav hlor sa primesama žive (90 do 228g žive se nalazi po toni hlora) se trenutno kod nas široko upotrebljava za gasovito hlorisanje pijaće vode. **Druga,** još veća opasnost, su incidentne situacije pri transportu, skladištenju i manipulaciji sa hlorom. Naime, ekspertski timovi u EU su ispitivali i dokazali sve opasnosti koje su prisutne pri gasovitom hlorisanju i opasnostima pri manipulaciji hlorom tako da je EU zabranila korišćenje uređaja za gasovito hlorisanje i transport hlora na teritoriji unije od 1998 godine.

Među prvima u svetu smo osvojili ovo tehničko rešenje za in situ proizvodnju “aktivnog hlora” na mestu njegove upotrebe koje se i danas plasira na našem tržištu. Rešenje potpuno zamenjuje dosadašnji način hlorisanja pijaće vode sa gasnim hlorom u velikim vodovodima. Uređaj je projektovan kao minijaturna fabrika koja kao ulaznu sirovinu koristi slanu vodu (može i morska voda) i električnu struju da bi stvorio proizvod - razblaženi vodeni rastvor “aktivnog hlora” (tečno jedinjenje hlora koje nije u grupi opasnih materija). Dobijeni rastvor se pomoću dozirnog sistema dodaje u pijaću vodu u odgovarajućoj -maloj količini dovoljnoj da potpuno izvrši njenu dezinfekciju. Uređaji su potpuno automatizovani i imaju daljinski nadzor i upravljanje. Ovi uređaji uspešno zamenjuju uređaje za gasno hlorisanje koje predstavlja potencijalan izvor ekološkog zagađenja. Takođe ova postrojenja i u početnoj investiciji i eksploataciji najjeftinije rešenje dezinfekcije pijaće vode.

6. Stanje rešenosti tog problema u svetu

Danas se u svetu koriste sledeći postupci za dezinfekciju vode u velikim fabrikama za proizvodnju pijaće vode:

- dezinfekcija pomoću tečnog ili gasovitog hlora;
- dezinfekcija pomoću ozona;
- dezinfekcija pomoću hipohlorita proizvedenog elektrolizom 3% rastvora NaCl;
- dezinfekcija pomoću hlor-dioksida (ClO_2).

Najstariji i najšire primenjen, može se reći konvencionalan, je postupak dezinfekcije pomoću gasovitog ili tečnog hlora. U novije vreme često se koristi i postupak ozonizacije, a nedavno je otpočela primena i preostala dva postupka. Najveći proizvođači opreme za vodo-snabdevanje u svetu (CAPITAL CONTROLS, WALLACE & TIERNAN, PROMINENT, TRAILIGAZ idr.) uglavnom poseduju sve pomenute tehnologije (postupke) za dezinfekciju vode. Osnovne karakteristike, odn. prednosti i nedostatci ovih postupaka prikazani su u Tabeli 1.1.

Tabela 1.1: Prednosti i nedostatci postupaka za dezinfekciju vode koji se danas koriste u svetu.

POSTUPAK	PREDNOSTI	NEDOSTATCI
Gasoviti, tečni hlor	Veoma uspešna dezinfekcija Relativno mali troškovi eksploata-cije Umereni investicioni troškovi Otklanjanje amonijačnih jedinjenja	Opasnost od curenja hlora pri transportu i skladištenju (ekološka katastrofa) Neophodnost obučene radne snage za rukovanje Nemogućnost skladištenja veće količine hlora Lociranje postrojenja van gradova Stvaranje trihalometana
Ozon	Veoma uspešna dezinfekcija Proizvodnja ozona na mestu upotrebe Ne stvara trihalometane Ekološki postupak	Veliki investicioni troškovi Neophodnost obučene radne snage za rukovanje Kratko vreme delovanja ozona kao dezinfektanta (oko 1 h)
Hipohlorit [*] ***(HLOROGEN®)***	***Veoma uspešna dezinfekcija*** ***Proizvodnja NaClO na mestu upotrebe*** ***Mali troškovi eksploatacije*** ***Mogućnost skladištenja sirovine za duži period eksploatacije*** ***Nepotrebna obučena radna snaga*** ***Potpuno automatizovan rad*** ***Mogućnost daljinske kontrole i upravljanja procesom*** ***Nesmetana dezinfekcija vode i u vanrednim prilikama*** ***Otklanjanje amonijačnih jedinjenja*** ***Ekološki postupak***	***Stvaranje trihalometana***
hlor-dioksid ClO_2	Veoma uspešna dezinfekcija Proizvodnja ClO_2 na mestu upotrebe Naročito pogodan za dezinfekciju vode iz akumulacionih sistema Nema stvaranja trihalometana	Veliki investicioni troškovi Neophodnost uvoza sirovine za proizvodnju ClO_2 (hlorasta kiselina) Nemogućnost skladištenja veće količine sirovine za proizvodnju, veoma eksplozivan Ne otklanja amonijačna jedinjenja

[*] ***Karakteristike se u najvećoj meri odnose na domaće postrojenje HLOROGEN®.***

Iz Tabele 1.1 može se zaključiti da je postupak dezinfekcije pomoću hipohlorita proizvedenog elektrolizom 3% rastvora NaCl na mastu upotrebe pogodniji od ostalih postupaka dezinfekcije vode, ne samo sa aspekta ekonomske isplativosti, već i sa ekološkog aspekta. Ovde treba naglasiti da je Evropska Zajednica predvidela zabranu transporta gasovitog i tečnog hlora od 1998. godine, tako da će sadašnji konvencionalni postupak upotrebe hlora morati da se ukine.

Osnovne prednosti primene navedenog postupka u odnosu na konvencionalni postupak gasovitim hlorom su sledeće:

1. Izbegnuta potencijalna opasnost kod transporta i skladištenja gasovitog hlora,
2. Nesmetana dezinfekcija vode u vanrednim prilikama (ratovi, zemljotresi, poplave...)
3. Potpuna automatizacija procesa.
4. Mogućnost primene i u malim prigradskim i u velikim gradskim vodovodima.
5. Mogućnost daljinske kontrole i upravljanja procesom.
6. Znatno niži eksploatacioni troškovi.
7. Ne zahteva prisustvo specijalizovanog osoblja, što omogućava primenu i u seoskim vodovodima.

7. Za koga je rešenje rađeno:

Rešenje je rađeno za industrijsko tržiste i „Fabriku vagona“ Kraljevo kao izvođaća radova i montaže takvih postrojenja

8. Godina kada je rešenje urađeno i ko ga je prihvatio/primenjuje:

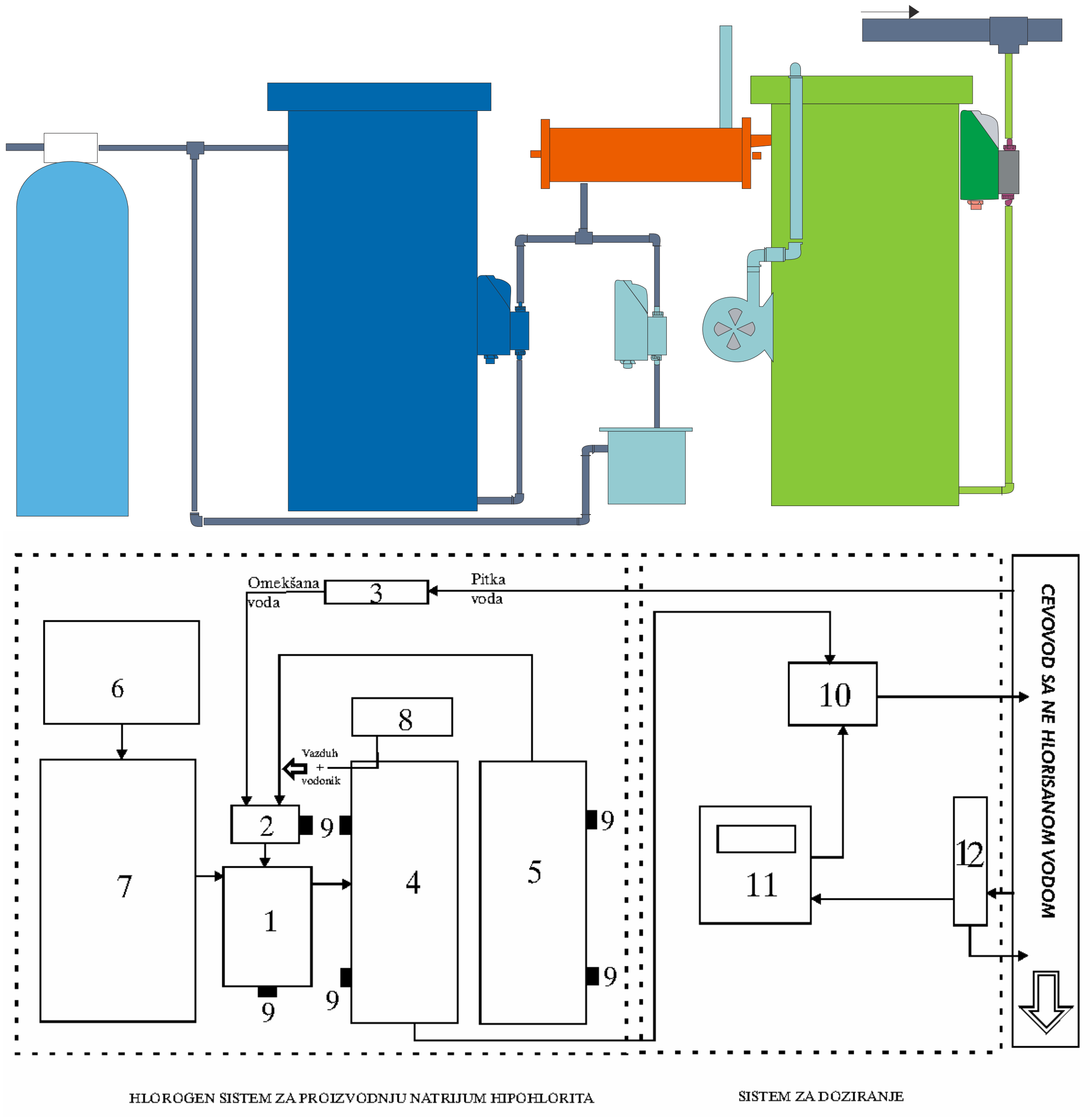
1997 god. pp „Sigma“ Kula

9. Kako su rezultati verifikovani (od strane kog tela):

Institut zaštite na radu u Nišu na osnovu podnete dokumentacije

10. Objašnjenje suštine tehničkog rešenja i detaljan opis sa karakteristikama

Kratki opis (uz pomoc blok šeme) bazicnog funkcionisanja «Hlorogen» uređaja:



Slika 1. Shema postrojenja „Elektrohemijski postupak dezinfekcije vode za piće“

Iz cevovoda (Slika 1) se transportuje voda u omekšivač (3) gde se uklanjaju joni kalcijuma i magnezijuma i dobija se omekšana voda. Omekšana voda se dozirnom pompom dovodi do mešača (2) gde se meša sa koncentrovanim rastvorom natrijum hlorida (dozirnom pumpom doprema se iz rezervoara (5) gde je koncentrovani rastvor natrijum hlorida), pravi razblažen rastvor koji se ulazi u elektrolizer (9). U elektrolizeru koji se napaja jednosmernom strujom iz energetskog dela «Hlorogena» (7) dolazi do elektrohemijske reakcije gde se hloridni anjoni konvertuju u hipohlorit koji se potom lageruje u rezervoar (4). U toku reakcije sinteze hipohlorita nastaje vodonik koji se ventilacionim sistemom (8) odvodi u atmosferu. Uz pomoc automatike (6) se ostvaruje optimalna proizvodnja hipohlorita i ostvaruje monitoring nad kompletnim radom postrojenja. Dobijeni rastvor hipohlorita se ubrizgava u cevovod uz pomoć membranskih pumpi (10) čija dinamika rada je komandovana sa amperometrijskom elektodom (12) i transmiterom - analizator (11). Analizator (11) dobija informaciju o koncentraciji hlora od amperometrijske elektode (12) i preko pumpi održava njegovu zadatu koncentraciju u pijaćoj vodi. Na ovaj način je obezbedena kontinualna proizvodnja hipohlorita sa automatskom kontrolom procesa a takode i automatsko doziranje i merenje rezidualnog hlora.

Kompletan rad postrojenja se pratiti preko računara. Procesorska jedinica upravlja i kontroliše kompletan tehnološki proces uz internu komunikaciju sa ostalim regulacionim jedinicama i PC-jem, sa slovnom i brojčanom displej indikacijom radnih stanja, merenih vrednosti kao i aktivnih alarmnih stanja. Komunikacijom sa PC-jem ostvaruje zatvoreni sistem kontrole tehnološkog procesa. Sa operaterom postoji i komunikacija pomoću GPRS-a i GSM gde se sva alarmna stanja šalju operateru i proizvodjaču onog trenutka kada se dogode.

Slika 2. Postojenje koje je nastalo kao rezultat inovacionog projekta „Elektrohemijski postupak dezinfekcije vode za piće“

11. **Kako je rešenje realizovano i gde se primenjuje / mogućnosti primene tehničkog rešenja, tj na koji način se koristi:**

Rešenje primenjeno u sledećim fabrikama za proizvodnju pijaće vode:

1. **IM "CARNEX" Vrbas 1997 god. Postrojenje kapaciteta 250 g/h**
2. **KP „VODOVOD" Bezdan 1997 god. Postrojenje kapaciteta 500 g/h**
3. **JP „KOMUNALAC" Kula 1998 god. Postrojenje kapaciteta 250 g/h**
4. **JP „KOMUNALAC" Kula 2006 god. Postrojenje kapaciteta 250 g/h**
5. **SPC „VOJVODINA" Novi Sad 2001 god. Postrojenje kapaciteta 1000 g/h**
6. **JKP „Beočin" Beočin 2002 god. Postrojenje kapaciteta 1000 g/h**
7. **JKP „STANDARD" Žabalj 2003 god. Postrojenje kapaciteta 125 g/h**
8. **JKP „STANDARD" Žabalj 2003 god. Postrojenje kapaciteta 1000 g/h**
9. **JKP „STANDARD" Žabalj 2004 god. Postrojenje kapaciteta 1000 g/h**
10. **JKP „VODOVOD" Ćuprija 2004 god. Postrojenje kapaciteta 250 g/h**
11. **JKP „USLUGA" Odžaci 2003 god. Postrojenje kapaciteta 1000 g/h**
12. **JKP „USLUGA" Odžaci 2003 god. Postrojenje kapaciteta 1000 g/h**
13. **JKP „USLUGA" Odžaci 2004 god. Postrojenje kapaciteta 1000 g/h**
14. **JKP „Beogradski vodovod" CS Lipovica Postrojenje kapaciteta 1000 g/h**
15. **JKP „Vodovod" Smederevo 2006 Postrojenje kapaciteta 1000 g/h**
16. **JKP „VODOVOD" Prokuplje 2007 Postrojenje kapaciteta 1000 g/h**
17. **JKP „VODOVOD" Vlasotinci 2007 Postrojenje kapaciteta 1000 g/h**

GRUPA M80: TEHNIČKA REŠENJA

Kategorija: „Novi proizvod ili tehnologija“
Rezultat M82: Novi proizvod ili tehnologija uvedeni u proizvodnju ustanova/Autori rešenja:

Institut tehničkih nauka SANU, K.Mihajlova 35/4, 11000 Beograd;
Tehnološko – metaluruški fakultet, Karnegijeva 4, 11000 Beograd;
Institut za multidisciplinarne studije, Beograd , Physics of Nanostructured Materials, Faculty of Physics, University of Vienna
Mašinski fakultet, Beograd, Kraljice Marije

1. **Autori:** Tomislav Trišović, Lidija Rafailović, Milica Gvozdenović, Trišović Nataša, Branimir Jugović

2. **Naziv i evidencioni broj projekta sa brojem aktivnosti, u kome je ostvaren rezultat iz kategorije M80:**

„Elektrohemijski generatori sredstava za dezinfekciju (aktivnog hlora, jonskog srebra i bakra) sa šaržnim recirkulacionim tipom reaktora“**,** Inovacioni projekat, MNTRS, **PTP-2108B, 2005-2006.** rukovodilac T. Trišović

3. **Naziv tehničkog rešenja**

   Elektohemijski generatori sredstava za dezinfekciju sa šaržnim tipom reaktora

4. **Oblast na koju se tehničko rešenje odnosi:**

   Tehničko-tehnološke i biotehničke nauke

5. **Problem koji se tehničkim rešenjem rešava**

   Veliki problem predstavlja dezinfekcija tehnoloških i sanitarnih voda, kao i opšta dezinfekcija radnih površina i opreme, tretman otpadnih industrijskih voda u pogonima prehrambene industrije i dezinfekcija pijaćih voda u prigradskim i seoskim vodovodima i malim vodnim zajednicama. Ogroman problem predstavlja kupovina i transport dezinficijenasa posebno u ruralnim sredinama koje su daleko od gradskih sredina. Usluge transporta, skladištenja i rukovanja opasnim hemiklaijama često su skuplji od njihove jedinične cene. Takođe ovi korisnici imaju veoma velike oscilacije u potrošnji sredstava za dezinfekciju u toku dana čak i za red veličine od nekih jutarnjih do popodnevnih časova. Ovi uređaji su prilagođeni da se mogu primeniti gde su veoma velike oscilacije u potrošnji sanitarne i tehnološke vode kao i potrebe za dezinfekcijom otpadnih voda i dezinfekcijom radnih površina. Korišćenjem ovih jednostavnih i jeftinih uređaja predstavljene ovim tehničkim rešenjem ovi problemi su rešeni jer oni sintetizuju sredstva za dezinfekciju polazeći od bezopasnih hemikalija kao što je kuhinjska so, metalno srebro i bakar i česmenska voda. Nabavka i transport ovih materijala je potpuno bezopasna i oni su veoma stabilni tokom više godina lagerovanja.

6. Stanje rešenosti tog problema u svetu

U svetu takođe nema adekvatnog a jeftinog rešenja za dezinfekciju voda u ruralnim sredinama, vojnim objektima, turističkim centrima. Javnosti su poznati podaci da u Srbiji postoji nekoliko hiljada registrovanih i još na desetine hiljada neregistrovanih vodovoda (prvenstveno seoski vodovodi) koji nemaju nikakav tretman pijaće vode. Od registrovanih 4500 vodovoda u Srbiji kapaciteta od 12 do 15 litara u sekundi samo 2% ostvaruje dezinfekciju pijaće vode a kontrola kvaliteta vode se ostvaruje na samo 3% ovih vodovoda. Iako se Srbiji troši za hlorisanje vode oko 100 tona mesečno hlora i tečnih jedinjenja hlora seoski i prigradski vodovodi nemaju tehničkih mogućnosti da rade dezinfekciju zbog teškoća pri upravljanju i održavanju postrojenja za hlorisanje. Jedini način da ti vodovodi obezbede dezinfekciju pijaće vode je instalacija ovakvih uređaja čiji je rad potpuno automatski i ne zahteva nadzor čoveka.. Danas njihov plasman treba prvenstveno usmeriti prema vodovodima koji nemaju nikakvu obradu pijaće vode da bi se na vreme sprečile posledice upotrebe bakteriološki neispravne vode. Broj malih vodovoda je u porastu kao i broj individualnih bunara kod fizičkih i pravnih subjekata koji imaju tehničkih mogućnosti da crpe vodu sa svojih placeva. Ovaj trend povećanja bunara za sanitarnu I tehnološku vodu je prvenstveno zbog povećanja potrošnje vode i poskupljenja gradske vode.

U svetu i kod nas postoje rešenje za dezinfekciju voda na malim izvorištima i to sa hlor dioksidom i koncentrovanim aktivnim hlorom ali je cena takvih uređaja za naše siromašno tržište neprihvatljiva. Naše rešenje koje je verifikovano na tržištu je isplativo za najviše dve godine ako se uzmu svi troškovi neophodni da se process dezinfekcije ostvari sa drugim dezinficijensima.

Slika 3. Elektrohemijski generatori sredstava za dezinfekciju sa šaržnim tipom reaktora

7. Za koga je rešenje rađeno:

Rešenje je rađeno za potrošačko tržište odnosno „Nobel corporation“ Beograd, Upotreba: dezinfekcija vode, dezinfekcija i pranje filtera i membrana koji se koriste u aparatima za dobijanje ultračiste vode, dezinfekcija radnih površina, dezinfekcija otpadne vode u pogonima prehrambene industrije.

Proizvodi AQUA CRYSTAL DOO Beograd

8. Godina kada je rešenje urađeno i ko ga je prihvatio/primenjuje:

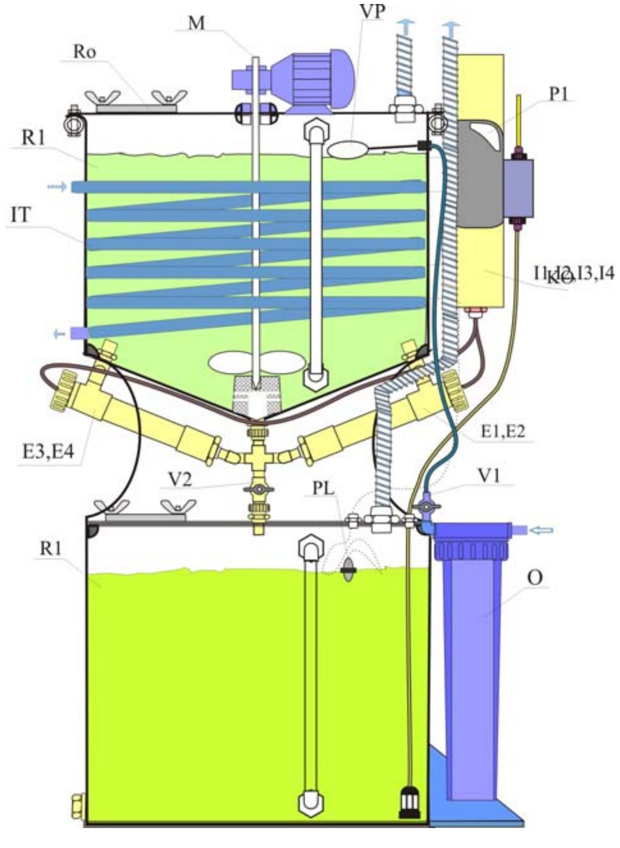
2006 gpd. „Nobel corporation“ 2008, „Obrenović tim“ 2010 god.

9. Kako su rezultati verifikovani (od strane kog tela):

„Kvalitet“ Nišu na osnovu podnete dokumentacije

10. Objašnjenje suštine tehničkog rešenja i detaljan opis sa karakteristikama

Uređaj se sastoji (Slika 4) od dve posude koje su postavljene jedna iznad druge. U gornjoj reakcionoj posudi (R1) se nalazi mešalica (M) (ručna ili na elekto pogon) izmenjivač toplote (IT) i reaktori – elektolizeri (E1,E2,E3,E4) (mogu biti van ili unutar posude). U reakcionoj posudi se takođe nalazi termo sonda koja pomoću termoregulatora uključuje ili isključuje elektomagnetni ventil (ili rashladni uređaj) koji održava temperaturu reakcionog rastvora u optimalnim granicama. U Prihvatnoj posudi (R2) se lageruje proizvedeno sredstvo za dezinfekciju koje se pomoću dozirne pumpe (P1) dozira u medijum koji treba dezinfikovati. Rad dozirne pumpe je on/off ili je spregnuta sa indikatorom protoka tako da radi samo kad postoji tok fluida u cevi. U slučajevima promenljivog protoka kad protok kroz cev osciluje od napr 1 do 20 litara u sekundi (slučaj u prehrambenoj industriji), dozirna pumpa (P1) mora biti spregnuta sa meračem protoka tzv inpulsni vodomer koji na osnovu protoka komanduje sa dinamikom rada dozirne pumpe (P1). Dok je potrošnja sredstva za dezinfekciju iz rezervoara (R2) veoma neujednačena u rezervoaru (R1) se on proizvodi po uslovima kolika je njegova prosečna potrošnja u toku dana. Na ovaj nači je praktično uštеđeno u dimenzionisanju reaktora, izmenjivača toplote, napajanja i automatike a praktično potpuno pokrivena vršna opterećenja u potrošnji dezinficijensa.



Slika 4. Shema elektrohemijskog generatora sredstava za dezinfekciju sa šaržnim tipom reaktora

Kada se potroši sredstvo za dezinfekciju iz rezervoara (R2) i plovak (PL) padne na dno prihvatne posude (R1) tada prestaje rad dozirne pumpe (P1) i uključuje se alarmno stanje (eventuaslno salje SMS poruka korisniku) koje upozorava korisnika da je potrebno iz reakcionog rezervoara (R1) napuniti sredstvom za dezinfekciju (čija je sinteza već završena) prihvatni rezervoar (R2). Ovo se ostvaruje što se otvori ručni ventil (V2). Čim se plovak (PL) odvoji od dna prihvatne posude (R2) počinje automatizovano doziranje sredstva za dezinfekciju. Kada se potpuno isprazni reakcioni rezervoar (R1) prvo se zatvara ventil (V2) pa se puni omekšanom vodom koja se omekšava prolaskom kroz kolone (O) a potom dodaje kuhinjska so ako se radi o sintezi aktivnog hlora ili se ništa ne dodaje ako je sinteza koloidnog srebra naprimer. Kada je to ostvareno pritiska se dugme Start kada počinje nov proces elektohemijske sinteze dezinficijensa u periodu od 20 do 160 časova u zavisnosti od kapaciteta i vrste dezinficijensa. Ciklus rada automatike na uređaju je sledeći. Pritiskom na dugme start prvo se uključuje mešalica (M) koja deset minuta meša rastvor tako da u tom periodu dođe do potpunog rastvaranja soli koja je dodata u reakcionu posudu (R1). Po isteku tog vremenskog perioda isključuje se rad mešalice a uključuje se rad četiri napajanja koja napajanju jednosmernim naponom reaktorske module (E1,E2,E3,E4). Uključenje reaktorskih modula je pokazano na komandnoj tabli pomoću signalnih sijalica (svetle četiri zelene signalne sijalice). U toku procesa elektohemijske sinteze dolazi do izdvajanja vodonika i delimično kiseonika koji se ventilacionim vodom odstranjuju u atmosferu. Kontrola jačine struje pri elektohemijskoj sintezi je ostvarena novim tipom prekidačkog izvora struje tako da strujni kontroler održava optimalne uslove sinteze bez obzira na varijacije napona u mreži. Drugi vazan parametar je temperatura reakcionog rastvora koja se održava pomoću termoregulatora. Programabilni logički kontroler (PLC) je tako programiran da upušta u izmenjivač toplote rashladnu vodu tako da temperature ne pređe vrednost od 35 stepeni celzjusa. Ukoliko se to dogodi uređaj se privremeno isključuje i čeka da temperatura rastvora padne na 20 stepeni celzjusa kada se ponovo uključuje sve dok se ne dostigne vremenski uslov rada uređaja od 20 do 160 časova. Kada je vreme sinteze isteklo rad reaktora – elektolizera prestaje a pomoću GSM komunikatora se upućuje obaveštajna poruka operateru „sinteza je uspešno završena – dezinficijens je spreman“.

Operater tako upoznat da postoji rezerva sredstava za dezinfekciju i on čeka alarmno stanje (da je prihvatni rezervoar prazan) koje će dobiti GSM porukom „sredstvo za dezinfekciju je potrošeno šaržirajte prihvatni rezervoar (R2). U tom slučaju odlazi do uređaja i ponavlj gore objašnjene operacije.

11. Kako je rešenje realizovano i gde se primenjuje / mogućnosti primene tehničkog rešenja, tj na koji način se koristi:

Rešenje komercijalizovala pp Aqua crystal i primenjeno je u sledećim fabrikama:

1. Fabrika za preradu mesa „Obrenović tim“ Dobanovci instalirano 2010.
2. Nobel coropration Beograd instaliran 2008,
3. Polimark Beograd 2008

GRUPA M80: TEHNIČKA REŠENJA

Kategorija: „Novi proizvod ili tehnologija“
Rezultat M82: Novi proizvod ili tehnologija uvedena u proizvodnju

1. **Ustanova/Autori rešenja:**
   Institut tehničkih nauka SANU, K.Mihajlova 35/4, 11000, Beograd
   Agronomski fakultet – Čačak, Cara Lazara 4, 32 000 Čačak
   Mašinski fakultet, Beograd, Kraljice Marije
   Institut za hemiju tehnologiju i metalurgiju, Beograd, Njegoševa 4, 11000 Beograd

Autori: Tomislav Trišović, Branimir Grgur, Snežana Tansković, Nataša Trišović, Jasmina Stevanović

2. **Naziv i evidencioni broj projekta sa brojem aktivnosti, u kome je ostvaren rezultat iz kategorije M80:**

   Elektrohemijsko postrojenje za proizvodnju sredstava za dezinfekciju sa modularnim reaktorom i reversnim elektrodama, Inovacioni projekat, MNTRS, IP8025, 2006-2007. rukovodilac T. Trišović

   Automatski uređaj za fizičko-hemijski tretman voda sa kombinovanim modularnim generatorima, Inovacioni projekat, MNTRS, **45-01-000-65/2008-01/88,** rukovodilac T. Trišović

3. **Naziv tehničkog rešenja**

Elektohemijski uređaj za proizvodnju dezinfiucijensa sa koaksijalnim plag reaktorom

4. **Oblast na koju se tehničko rešenje odnosi:**

   Tehničko-tehnološke i biotehničke nauke

5. **Problem koji se tehničkim rešenjem rešava**

Procesi dodatne dezinfekcije i dohlorisanja u velikim vodovodnim sistemima, dezinfekcija tehnoloških, opadnih i sanitarnih voda koje se transportuju cevovodom u manjim industrijama, dezinfekcija pijaćih voda u seoskim i prigradskim vodovodima i manjim vodnim zajednicam. Stanice za gasno hlorisanje i sistemi za doziranje hlor-dioksida i hipohlorita nisu primenjivo rešenje dohlorisanje u u pojedinim „džepovima" gradskih vodovoda posebno što moraju biti locirani u podrumima zgrada gde postoje veliki rizici od incidentnih situacija tj eventualnog izlivanja ili curenja opasnih hemikalija. Upotreba dozirnih sistema sa hipohloritom ili hlor-dioksidom podrazumeva njihovo lagerovanje u posude i rezervoare koji su izloženi uticaju atmosferske temperature i eventualno sunčevog zračenja. Lagerovanje u takvim uslovima izaziva termohemijsku reakciju u kojoj se od natrijum hipohlorita stvara hlorat koji ima tri puta manji učinak u procesu dezinfekcije vode. Ovaj problem je posebno izražen u vrelim letnjim mesecima kada temperatura vazduha prelazi preko 30 stepeni Celzjusa. Da bi sprečili degradaciju natrijum hipohlorita mora da se obezbede klimatizovani skladišni prostori i posude od materijala koji ne propušta UV zračenje. Pored zagađenja vode hloratom, manje dezinfekcione moći natrijum hipohlorita, skladištenje dodatno poskupljuje korišćenje ovog sredstva za dezinfekciju. Lagerovanje opasnih hemikalija se ostvaruje tamo gde nismo u mogućnosti da ih proizvedemo na mestu njihove primene.

Primenom elektohemijskog uređaja za proizvodnju dezinfiucijensa sa koaksijalnim plag reaktorom otklonjeni su gore izneti problemi jer se proizvodi „aktivan hlor" u trenutku potrebe za njim ali bez njegovog lagerovanja kako bi se na obezbedila potpuna zaštita stanovnika od opasnih hemikalija u urbanim naseljima, sprečila degradacija lagerovanih hemikalija i zaštitili operateri prilikom manipulacija sa istim.

6. Stanje rešenosti tog problema u svetu

U svetu se ovaj problem rešava samo sa sistemima za doyiranje tako da postoji stalan problem šaržiranja takvih uređaja koje mora da obavlja stručno lice koje je obučeno da radi sa opasnim hemikalijama.

7. Za koga je rešenje rađeno:

Rešenje je rađeno za potrošačko tržište
Proizvodi AQUA CRYSTAL DOO Beograd

8. Godina kada je rešenje urađeno i ko ga je prihvatio/primenjuje:

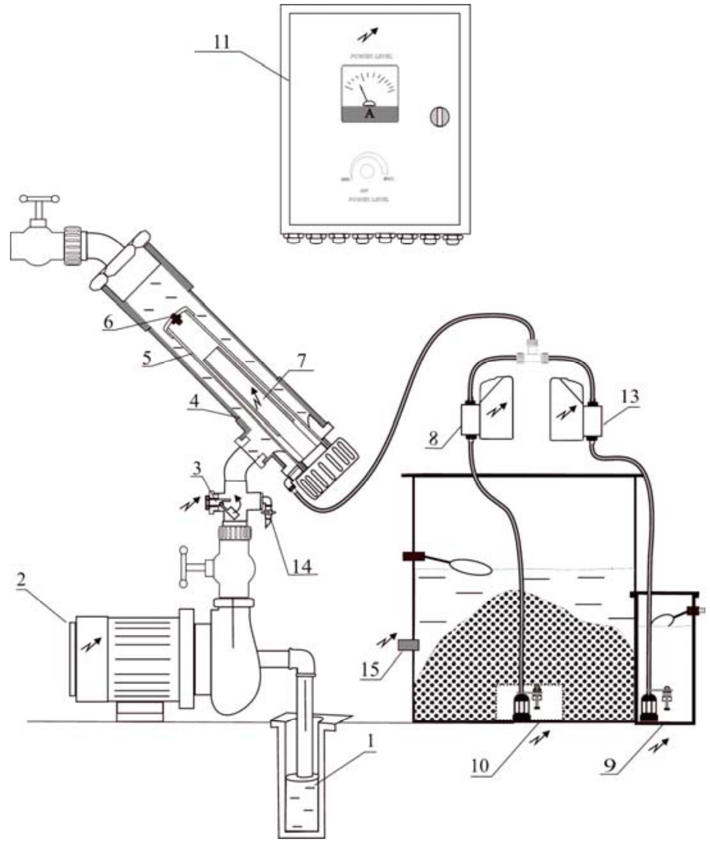
Rešenje je urađeno 2008
Distribuita Elektođurović - Čačak
Proizvodi AQUA CRYSTAL DOO Beograd

9. Kako su rezultati verifikovani (od strane kog tela):

„Kvalitet“ Nišu na osnovu podnete dokumentacije

10. Objašnjenje suštine tehničkog rešenja i detaljan opis sa karakteristikama

Da bi se rešili gore uočeni nedostaci na postojećim rešenjima projektovali smo uređaj za proizvodnju aktivnog hlora sa koaksijalnim tipom reaktora koji proizvodi samo onoliko natrijum hipohlorita koliko se potroši u procesu dezinfekcije vode (nema lagerovanja natrijum hipohlorita). Prilikom elektrohemijske sinteze aktivnog hlora moguće je zagrevanje elektrolita preko 35^0C posebno u letnjim mesecima pa je neophodno u sam reaktor instalirati i izmenjivač toplote.



Slika 5. Shema elektohemijskog uređaja za proizvodnju dezinfiucijensa sa koaksijalnim plag reaktorom

U novom rešenju sa koaksijalnim tipom reaktora voda koja se hloriše opstrujava oko kućišta reaktora i praktično rastvor koji se elektolizira u reaktoru je blizak temperaturi vodovodske vode. Na ovaj način izlazni rastvor natrijum hipohlorita na izlasku iz rakatora je ispod 30^0C, jer je temperatura vodovodske vode obično u granicama između 10 i 20 ^{0}C. Praktično voda koju hlorišemo je istovremeno i rashladna voda. Temperatura na izlasku iz reaktora manja je od 28^0C što i predstavlja dozvoljenu temperaturu pri kojoj je minimalna termohemijska reakcija degradacije hipohlorita u hlorat. Na ovaj način umesto termoregulatora i izmenjivača toplote neophodan je samo senzor protoka vode kroz anularni prostor koaksijalnog reaktora što predstavlja znatno pojednostavljenje i znatnu uštedu materijala i automatskog upravljanja procesom.

Da bi se obezbedilo pravilan rad uređaja postavljena su samo dva senzora i to za protok vode (3) koju tretiramo (indikacija ispravnosti rada crpne pumpe) i minimum hloridnog rastvora da bi se sprečio rad na prazno dozirne membranske pumpe (9) i (10). Uslov za uključenje elektolizera (7) je da postoji protok kroz cevovod i da rastvor kuhinjske soli u rezervoaru hlorida je veći od minimalnog. Rešenje sa koaksijalnim reaktorom kog rashlađuje voda koja se hloriše omogućuju da se ne koristi senzor temperature, termoregulator i ogdovarajuća automatika koja to prati. Takođe ovo rešenje isključuje i separaciju vodonika i odgovarajuće ventilacione odvode ka atmosferi jer se svi proizvodi reakcije ubrizgavaju u sirovu vodu zajedno sa aktivnim hlorom.

Kada se uređaj uključi dozirna pumpa usisava razblazeni rastvor hlorida (Slika 6) ili postoje dve dozirne pumpe (8) i (13) od kojih jedna usisava čistu vodu a druga koncentrovani rastvor kuhinjske soli i neposredno pred ulaz u reaktor se ta dva toka mešaju praveći razblažen rastvor hlorida. U cevnom reaktoru (5) se elektohemijskim putem hloridi konvertuju u hipohlorit i izlaskom iz cevnog reaktora i prolaskom kroz nepovratni ventil (6) ulaze u vodu koju tretiramo. Na osnovu protoka vode i pritiska u cevovodu podešava se protok dozirne pumpe i jačina struje u reaktoru. Uređaj se može instalirati na potisni ili usisni vod pumpe (2) koja crpi vodu (Slika 6) ili se može instalirati bilo gde na cevovodu stim što u tom slučaju umesto senzora protoka (3) potrebno je postaviti merač protoka koji će davati signal reaktoru kad da se uključi i kojim intenzitetom će raditi.

Slika 6. Elektohemijski uređaj za proizvodnju dezinfiucijensa sa koaksijalnim plag reaktorom

Jednostavno rešenje i modualran sistem reaktora, jednostavan i brz servis omogućuju pouzdan rad ovakvog sistema.

11. Kako je rešenje realizovano i gde se primenjuje / mogućnosti primene tehničkog rešenja, tj na koji način se koristi:

Rešenje primenjeno u sledećim fabrikama za proizvodnju pijaće vode:

Prodat Manastiru Rakovica – Beograd gde i danas uspešno radi.

GRUPA M80: TEHNIČKA REŠENJA

Kategorija: „Novi proizvod ili tehnologija“
Rezultat M82: Novi proizvod ili tehnologija uvedena u proizvodnju

1. **ustanova/Autori rešenja:**
   Institut tehničkih nauka SANU, K.Mihajlova 35/4, 11000, Beograd
   Agronomski fakultet – Čačak, Cara Lazara 4, 32 000 Čačak
   Physics of Nanostructured Materials, Faculty of Physics, University of Vienna

   Autori: Miroslav Spasojević, Jasmina Stevanović, Lidija Rafailović, Tomislav Trišović

2. **Naziv i evidencioni broj projekta sa brojem aktivnosti, u kome je ostvaren rezultat iz kategorije M80:**
   Elektrohemijski generatori sredstava za dezinfekciju (aktivnog hlora, jonskog srebra i bakra) sa šaržnim recirkulacionim tipom reaktora**,** Inovacioni projekat, MNTRS, **PTP-2108B, 2005-2006.** rukovodilac T. Trišović

   Elektrohemijsko postrojenje za proizvodnju sredstava za dezinfekciju sa modularnim reaktorom i reversnim elektrodama, Inovacioni projekat, MNTRS, IP8025, 2006-2007. rukovodilac T. Trišović

3. **Naziv tehničkog rešenja**

   Elektohemijski uređaj za dezinfekciju vode sa recirkulacionim tipom reaktora i standardnim elektodama

4. **Oblast na koju se tehničko rešenje odnosi:**

   Tehničko-tehnološke i biotehničke nauke

5. **Problem koji se tehničkim rešenjem rešava**
   Dezinfekcija vode u bazenima za kupanje.

PREDNOSTI KORIŠĆENJA SLANE VODE U BAZENIMA ZA KUPANJE:

- Nema više pogrešnih doziranja hlorom! Programski vođena dezinfekcija u najvećoj mjeri pojednostavljuje podešavanje ispravnog doziranja.
- Nema nikakvog rukovanja otrovnim hemikalijama! hlorni proizvodi su otrovni i posebno opasni za decu. Dezinfekcija solju ne traži nikakve hlorne proizvode, tako da ne otpada samo kupovina, već i transport i rukovanje opasnim supstancama.

- Za vreme kupanja nema više crvenih očiju! Radi jednostavnog podešavanja i ispravnog doziranja je voda u "ravnoteži" in ne nadražuje sluznicu. Upotrebljivost vode je duža.
- Koža se za vreme kupanja ne isušuje! Niska količina soli vodu čini mekanom i koža je izuzetno dobro podnosi. Primjereno za osobe koje pate od alergija!
- Voda ne miriše na hlor! Uz prirodni dezinfekcijski krug: so - hlor - so nestaje neugodan miris po hloru.
- Sistem deluje pH - neutralno! Sistem deluje gotovo pH-neutralno. Time ne otpadaju samo česte regulacije već i troškovi za regulatore. Ipak, preporučujemo postavljanje još i automatskog sistema za održavanje ispravne vrednosti pH vode.
- Sistem nije štetan po okolinu! Otpada kupovina, transport, skladištenje i rukovanje opasnim hemikalijama (hlor). So je prirodna i u prirodi je imamo gotovo u neograničenim količinama. Dakle, postupak ne samo što nije štetan po okolinu, već je i isplativ. Osim navedenog, so vodi daje izvanredne karakteristike koje pozitivno deluju na našu kožu.

Dezinfekcija solju pomoću uređaja "HIPOGEN"

Sadržaj soli od 0,3 % je potpuno zadovoljavajući da bi uređaj za elektrolizu proizveo hipohlorastu kiselinu HOCl koja ima sposobnost dezinfekcije, to jest da uništava sve alge, klice i bakterije. Kod ove reakcije se ponovno stvara so. Na taj način imate pomoću Hipogena potpuno prirodnu dezinfekciju bazenske vode. Potrebna količina soli u vodi je vrlo niska (0,3 %). Morska voda na primer sadrži 3,5 % soli.

6. Stanje rešenosti tog problema u svetu

U svetu takođe postoje slični uređaji stim što su znatno skuplji tako da je naša prednost upravo u tome niska cena, kratki rokovi isporuke, dobra logistika i brz i efikasan servis od 0 do 24h.

7. Za koga je rešenje rađeno:

Rešenje je rađeno za tržiste potrošačko tržište, „Beta bazeni“, „Aqua stars“, „GMC“, „Aquapur“, „Alfa bazeni“...

Proizvodi AQUA CRYSTAL DOO Beograd

8. Godina kada je rešenje urađeno i ko ga je prihvatio/primenjuje:

Rešenje je urađeno 2006
Distribuita: Beta bazeni“, „Aqua stars“, „GMC“, „Aquapur“, „Alfa bazeni“...
Proizvodi AQUA CRYSTAL DOO Beograd

9. Kako su rezultati verifikovani (od strane kog tela):

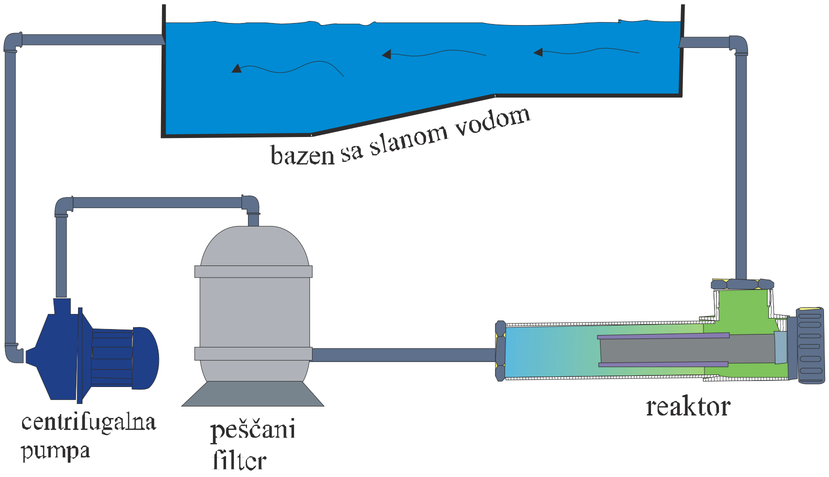
„Kvalitet“ Nišu na osnovu podnete dokumentacije

10. Objašnjenje suštine tehničkog rešenja i detaljan opis sa karakteristikama

Slika 7. Fotografija uređaja za proizvodnju za dezinfekciju vode u bazenima za kupanje sa recirkulacionim tipom reaktora i standardnim elektodama

Aparat proizvodi aktivan hlor vodeni rastvor polazeći od 0,3% do 0,6% rastvora kuhinjske soli. Rastvor za elektolizu je bazenska voda sa 0,3 do 0,5% kuhinjske soli koja uz pomoć pumpe struji kroz reaktor gde se elektohemijski dobija aktivni hlor (Slika 8). Centrifugalna pumpa, sa jednog kraja bazena usisava vodu i potiskuje je kroz peščani filter gde se odstranjuju mehaničke nečistoce. Po izlasku iz peščanog filtera voda ulazi u reaktor gde se na elektodama hloridni joni konvertuju elektohemijskom reakcijom u aktivni hlor. Pri elektrolizi razblaženog rastvora kuhinjske soli na anodi se odvija reakcija izdvajanja metastabilna jedinjenja na bazi kiseonika i hlora, dok se na katodi izdvaja gasoviti vodonik. Hlor, koji nastaje na anodi odmah hidrolizuje dajući uglavnom hipohloritni anjon (ClO^{-}) i u znatno manjoj meri hipohlorastu kiselinu (HClO). Ova dva produkta su u literaturi poznati i kao aktivni hlor. Aktivni hlor i hidroksiradikali kao i jonsko srebro, bakr i cink imaju algicidna i baktericidna svostva. Koncentraciju sredstava za dezinfekciju podešavamo regulacijom struje i vremena rada generatora. Po izlaku iz reaktora voda obogaćena dezinficijensima ulazi u bazen. Aktivni hlor u bazenu oksiduje bakterije, viruse i druga organska jedinjenja a sam se redukuje do hloridnog anjona. Na drugom kraju bazena pumpa usisava vodu zajedno sa hloridnim jonima koji su odradili proces dezinfekcije, potiskuje vodu kroz peščani filter i ulazi u reaktor gde se ponovo u elektrohemijskoj reakciji dobija aktivni hlor. Na ovaj način imamo stalno kruženje odnosno nastajanje i razgradnju aktivnog hlora odnosno oksidaciju i redukciju hloridnog jona pa se zbog toga ovaj tip uređaja naziva uređaj za proizvodnju aktivnog hlora sa recirkulacijom elektrolita. Uslov uključenja uređaja za proizvodnju aktivnog hlora je uključenje centrifugalne pumpe. Aparat sa standardnim elektrodama ima elektrode koje se mogu polarisati samo anodno ili samo katodno. Elektrode za katonu polarizaciju su na bazi hastel legure dok su elektrode za anodnu polarizaciju na bazi titan oksida I rutenijum oksida. Samo napajanje ih snabdeva konstantnom strujom ne menjajući polaritet u toku svog rada.

Čišćenje standardnih elektroda se vrši po potrebi kada se nahvata kamenac po reakcionim pločama najčešće jedanput nedeljno i predstavlja obavezu korisnika ili servisera da se strogo pridryava procedure date u uputstvu za korisnike ovih uređaja.



Slika 8. Shema instalacije uređaja za proizvodnju za dezinfekciju vode u bazenima za kupanje sa recirkulacionim tipom reaktora i standardnim elektodama

11.Kako je rešenje realizovano i gde se primenjuje / mogućnosti primene tehničkog rešenja, tj na koji način se koristi:

Rešenje se primenjuje na privatnim i javnim bazenima za kupanje na sledećim lokacijama:

1.	**Ađžemović Srđan**	**Bgd**	**SRB**	**2003**
2.	**Asanin**	**Kotor**	**Crna Gora**	**2001**
3.	**Anđelković Zorica**	**Jainci**	**Srbija**	**2002**
4.	**Bađžević**	**Beograd**		**2003**
5.	**„Dibek“ Milan Beko**	**Beograd**	**Srbija**	**2005**
6.	**COM TRADE Jevrosimović**	**Bdg**	**SRB**	**2006**
7.	**Božinovski Goca**	**Bgd**	**SRB**	**2005**
8.	**SPC „RC“ 3uređaja**	**Bgd**	**SRB**	**2007**
9.	**„Voda vrnjci“ Gobeljić**	**Bgd**	**SRB**	**2006**
10.	**„Telenor“ Eric Stein**	**Bgd**	**SRB**	**2008**
11.	**„Heineken“ pivara**	**Bgd**	**SRB**	**2009**
12.	**Miljan Miljanić**	**Bgd**	**SRB**	**2006**
13.	**Karić Sreten**	**Bgd**	**SRB**	**2004**
14.	**„Termoprodukt“ gen dir**	**Bgd**	**SRB**	**2006**
15.	**Bašanović**	**Bgd**	**SRB**	**2007**
16.	**Dušan Ivković – Duda**	**Bgd**	**SRB**	**2006**
17.	**„Impamil“ Bućan Nikola**	**Bgd**	**SRB**	**2008**
18.	**Danilović Predrag**	**Bgd**	**SRB**	**2007**
19.	**„Diplomatski klub“**	**Bgd**	**SRB**	**2008**
20.	**„Pirotehnika“ Đukanović**	**Bgd**	**SRB**	**2006**
21.	**D. Milovanović**	**Požerevac**	**SRB**	**2008**
22.	**Popović Saša**	**Bgd**	**SRB**	**2007**
23.	**Pichler Rainmund**	**Bgd**	**SRB**	**2008**
24.	**„OMV“ Rajević**	**Bgd**	**SRB**	**2007**
25.	**Rade Đukić**	**Bgd**	**SRB**	**2006**

26. Sekulovski Risto	**Bgd**	**MAKD**	**2007**
27. Škorić Boro	**Loznica**	**SRB**	**2008**
28. „Slobo“	**Doboj**	**BIH**	**2007**
29. „Navip“ Goran	**Beograd**	**SRB**	**2009**
30. Milan Brakoč	**N.Sad**	**SRB**	**2010**
31. „Omega“ Miša	**Beograd**	**SRB**	**2008**
32. „Tenis klub“ Košutić	**Beograd**	**SRB**	**2006**
33. Krstajić Milovan	**Bgd**	**SRB**	**2007**
34. Kocić Aca	**Bgd**	**SRB**	**2009**
35. Limun Branka	**Bgd**	**SRB**	**2008**
36. Mrđa Zoran	**Bgd**	**SRB**	**2007**
37. Miloš Vujanić	**M.Ivanča**	**SRB**	**2010**
38. Sity Oaza Welness kajak klub Crvena Zvezda	**Bgd**	**SRB**	**2010**
39. Hotel „Residence“	**Pržno**	**CG**	**2008**
40. Dragan Marković	**Kruševac**	**SRB**	**2009**
41. Vladimir Atanacković	**Bgd**	**SRB**	**2009**
42. Zoran Bašanović	**Bgd**	**SRB**	**2008**
43. Pralica Zoran	**Bgd**	**SRB**	**2008**
44. Klub „S’’,	**Jakovo**	**SRB**	**2006**
45. Vila “Rose”	**Budva**	**Crna Gora**	**2009**
46. Orinoco srl	**Bukurest**	**Rumunija**	**2009**
47. Komanija Agimi	**Bujanovac**	**SRB**	**2007**

Servisirano oko 130 stranih elektolizera – reaktora.

GRUPA M80: TEHNIČKA REŠENJA

Kategorija: „Novi proizvod ili tehnologija“
Rezultat M82: Novi proizvod ili tehnologija uvedena u proizvodnju

1. **Ustanova/Autori rešenja:**

Institut tehničkih nauka SANU, K.Mihajlova 35/4, 11000, Beograd
Agronomski fakultet – Čačak, Cara Dušana 34, 32 000 Čačak
Tehnološko – metaluruški fakultet, Karnegijeva 4, 11000 Beograd;

Autori: Miroslav Spasojević, Snežana Tanasković, Milica Gvozdenović, Tomislav Trišović

2. **Naziv i evidencioni broj projekta sa brojem aktivnosti, u kome je ostvaren rezultat iz kategorije M80:**

Elektrohemijski generatori sredstava za dezinfekciju (aktivnog hlora, jonskog srebra i bakra) sa šaržnim recirkulacionim tipom reaktora**,** Inovacioni projekat, MNTRS, **PTP-2108B, 2005-2006.** rukovodilac T. Trišović

Elektrohemijsko postrojenje za proizvodnju sredstava za dezinfekciju sa modularnim reaktorom i reversnim elektrodama, Inovacioni projekat, MNTRS, IP8025, 2006-2007. rukovodilac T. Trišović

3. **Naziv tehničkog rešenja**

Elektohemijski uređaj za dezinfekciju vode sa recirkulacionim tipom reaktora i reversnim elektodama

4. **Oblast na koju se tehničko rešenje odnosi:**

Tehničko-tehnološke i biotehničke nauke

5. **Problem koji se tehničkim rešenjem rešava**

Dezinfekcija vode u bazenima za kupanje.

PREDNOSTI KORIŠĆENJA SLANE VODE U BAZENIMA ZA KUPANJE:

12. Nema više pogrešnih doziranja hlorom! Programski vođena dezinfekcija u najvećoj mjeri pojednostavljuje podešavanje ispravnog doziranja.

13. Nema nikakvog rukovanja otrovnim hemikalijama! hlorni proizvodi su otrovni i posebno opasni za decu. Dezinfekcija solju ne traži nikakve hlorne proizvode, tako da ne otpada samo kupovina, već i transport i rukovanje opasnim supstancama.
14. Za vreme kupanja nema više crvenih očiju! Radi jednostavnog podešavanja i ispravnog doziranja je voda u "ravnoteži" in ne nadražuje sluznicu. Upotrebljivost vode je duža.
15. Koža se za vreme kupanja ne isušuje! Niska količina soli vodu čini mekanom i koža je izuzetno dobro podnosi. Primjereno za osobe koje pate od alergija!
16. Voda ne miriše na hlor! Uz prirodni dezinfekcijski krug: so - hlor - so nestaje neugodan miris po hloru.
17. Sistem deluje pH - neutralno! Sistem deluje gotovo pH-neutralno. Time ne otpadaju samo česte regulacije već i troškovi za regulatore. Ipak, preporučujemo postavljanje još i automatskog sistema za održavanje ispravne vrednosti pH vode.
18. Sistem nije štetan po okolinu! Otpada kupovina, transport, skladištenje i rukovanje opasnim hemikalijama (hlor). So je prirodna i u prirodi je imamo gotovo u neograničenim količinama. Dakle, postupak ne samo što nije štetan po okolinu, već je i isplativ. Osim navedenog, so vodi daje izvanredne karakteristike koje pozitivno deluju na našu kožu.

Dezinfekcija solju pomoću uređaja "HIPOGEN"

Sadržaj soli od 0,3 % je potpuno zadovoljavajući da bi uređaj za elektrolizu proizveo hipohlorastu kiselinu HOCl koja ima sposobnost dezinfekcije, to jest da uništava sve alge, klice i bakterije. Kod ove reakcije se ponovno stvara so. Na taj način imate pomoću Hipogena potpuno prirodnu dezinfekciju bazenske vode. Potrebna količina soli u vodi je vrlo niska (0,3 %). Morska voda na primer sadrži 3,5 % soli.

6. Stanje rešenosti tog problema u svetu

U svetu takođe postoje slični uređaji stim sto su znatno skuplji tako da je naša prednost upravo u tome niska cena, kratki rokovi isporuke, dobra logistika i brz i efikasan servis od 0 do 24h.

7. Za koga je rešenje rađeno:

Rešenje je rađeno za tržiste potrošačko tržište, „Beta bazeni“, „Aqua stars“, „GMC“, „Aquapur“, „Alfa bazeni“...
Proizvodi AQUA CRYSTAL DOO Beograd

8. Godina kada je rešenje urađeno i ko ga je prihvatio/primenjuje:

Rešenje je urađeno 2006
Distribuita: Beta bazeni“, „Aqua stars“, „GMC“, „Aquapur“, „Alfa bazeni“...
Proizvodi AQUA CRYSTAL DOO Beograd

9. Kako su rezultati verifikovani (od strane kog tela):

„Kvalitet“ Nišu na osnovu podnete dokumentacije

10. Objašnjenje suštine tehničkog rešenja i detaljan opis sa karakteristikama

Aparat sa samočišćućim elektodama tzv. „SELF CLEAN” predstavljaju daleko konfornije rešenje prvenstveno sa aspekta održavanja. Čišćenje elektroda kod uredjaja tipa „SELF CLEAN” jednom u 3 nedelje što predstavlja daleko konfornije rešenje od aparata koji koriste standardne elektode. Ukoliko se u bazenu nalazi slabo tvrda voda ili omekšana voda čišćenje elektoda se obavlja jednom u šest meseci. Aparat u toku svog rada menja polaritet elektroda tj elektroda koja je bila na minus polu se prebacuje na plus pol i elektroda koja je bila na plus polu prebacuje se na minus pol izvora struje. Suprotnom polarizacijom elektrolizer pored proizvodnje dezinficijensa istovremeno razara stvoreni kamenac u ciklusu kad je elektroda radila kao katoda dok se na elektodi koja je u prvom ciklusu proizvodila hlor sada izdvaja vodonik. Promena polariteta je moguća ako su elektokatalizatori na površini elekoda selektivni na oksidaciju hloridnih anjona i ako dobro podnose anodnu i katodnu polarizaciju a da ne menjasju svojstva na duži vremenski rok. Elektokatalizatori koji imaju takve karakteristike su na bazi oksida titana iridijuma i platine.

Sama automatika na uređaju je definisana tako da se polaritet menja sa ukljucenjem uređaja u slučaju korišćenja linearnih napajanja ili se može menjati u rasponu od 0 do 8 sati u slučaju korišćenja čoperskih i prekidačkih napajanja. Napajanje na uređaju se prvo isključi promeni polaritet i ponovo uključi.

Aparat proizvodi aktivan hlor vodeni rastvor polazeći od 0,3% do 0,6% rastvora kuhinjske soli. Rastvor za elektolizu je bazenska voda sa 0,3 do 0,5% kuhinjske soli koja uz pomoć pumpe struji kroz reaktor gde se elektohemijski dobija aktivni hlor (Slika 1). Centrifugalna pumpa, sa jednog kraja bazena usisava vodu i potiskuje je kroz peščani filter gde se odstranjuju mehaničke nečistoce. Po izlasku iz peščanog filtera voda ulazi u reaktor gde se na elektodama hloridni joni konvertuju elektohemijskom reakcijom u aktivni hlor. Pri elektrolizi razblaženog rastvora kuhinjske soli na anodi se odvija reakcija izdvajanja metastabilna jedinjenja na bazi kiseonika i hlora, dok se na katodi izdvaja gasoviti vodonik. Hlor, koji nastaje na anodi odmah hidrolizuje dajući uglavnom hipohloritni anjon (ClO^-) i u znatno manjoj meri hipohlorastu kiselinu ($HClO$). Ova dva produkta su u literaturi poznati i kao aktivni hlor. Aktivni hlor i hidroksiradikali kao i jonsko srebro, bakr i cink imaju algicidna i baktericidna svostva. Koncentraciju sredstava za dezinfekciju podešavamo regulacijom struje i vremena rada generatora. Po izlaku iz reaktora voda obogaćena dezinficijensima ulazi u bazen. Aktivni hlor u bazenu oksiduje bakterije, viruse i druga organska jedinjenja a sam se redukuje do hloridnog anjona. Na drugom kraju bazena pumpa usisava vodu zajedno sa hloridnim jonima koji su odradili proces dezinfekcije, potiskuje vodu kroz peščani filter i ulazi u reaktor gde se ponovo u elektrohemijskoj reakciji dobija aktivni hlor. Na ovaj način imamo stalno kruženje odnosno nastajanje i razgradnju aktivnog hlora odnosno oksidaciju i redukciju hloridnog jona pa se zbog toga ovaj tip uređaja naziva uređaj za proizvodnju aktivnog hlora sa recirkulacijom elektrolita. Uslov uključenja uređaja za proizvodnju aktivnog hlora je uključenje centrifugalne pumpe.

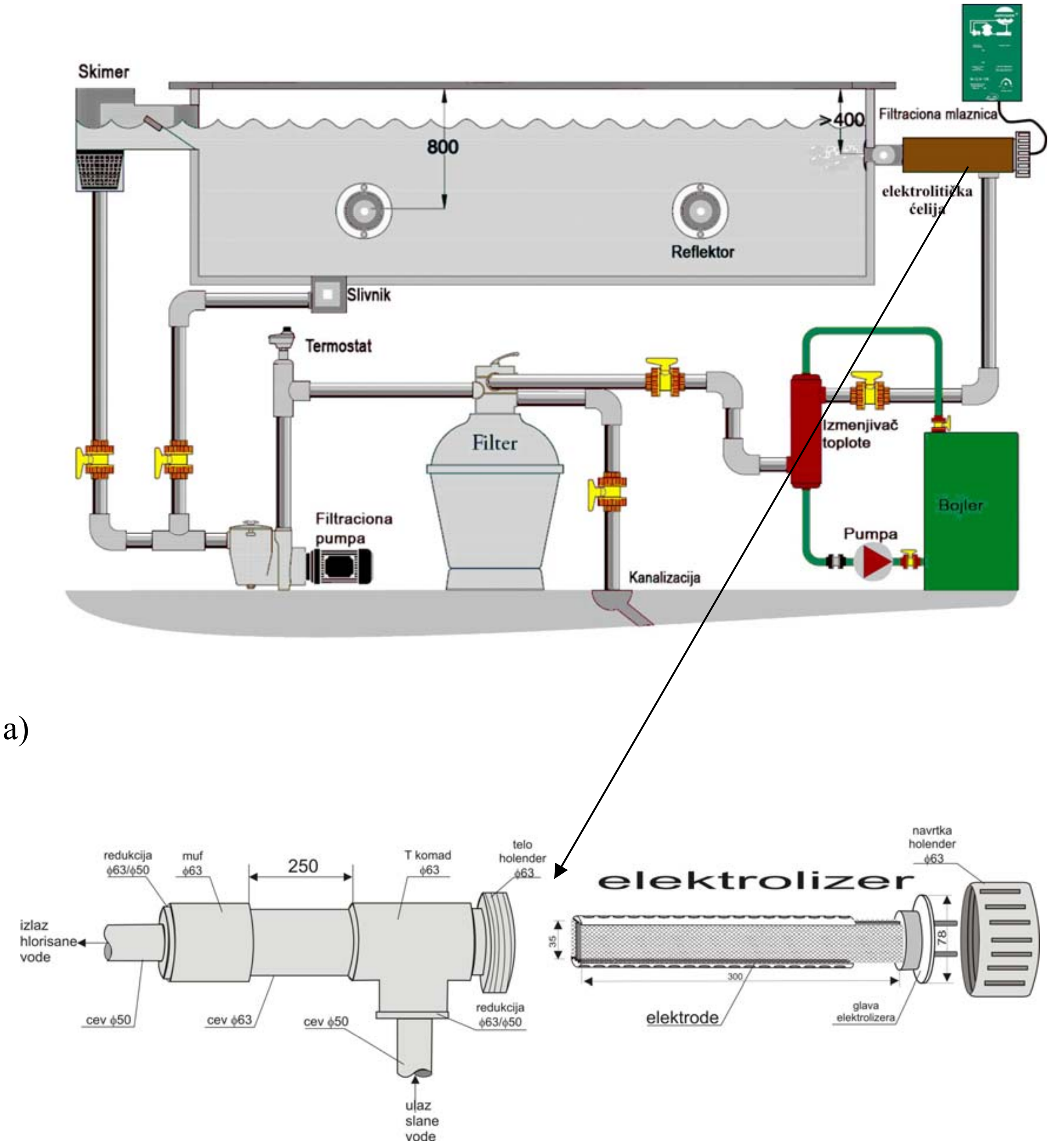
Uređaj se sastoji iz upravljačkog dijela na kojem se nalazi (Slika 3):

- Indikacija rada elektolizera (zelena sijalica svetli kada radi);
- automatski osigurač za zaštitu elektoda od preopterećenja;
- analogni ampermetar pokazuje intezitet proizvodnje aktivnog hlora;
- dugme za podešavanje intenziteta proizvodnje aktivnog hlora;

HIPOGEN UREĐAJ SA TEHNIČKIM KARAKTERISTIKAMA

TIP	KAPACITET (g h^{-1}) akt.hlora	ZAPREMINA BAZENA m^3	UKUPNA SNAGA W	BROJ REAKTORA V
HIPOGEN PS	12,5	50-100	100	1
HIPOGEN PR	12,5	50-100	100	1

Slika 9. Shema instalacije uređaja za proizvodnju za dezinfekciju vode u bazenima za kupanje sa recirkulacionim tipom reaktora i standardnim elektodama



b)

Slika 10. Shema instalacije uređaja za proizvodnju za dezinfekciju vode u bazenima za kupanje sa recirkulacionim tipom reaktora i reversnim elektodama (a) i shema instalacije elektolizera (b)

4. Tehnički podaci

- *Ulazni elektrolit:* ~3-6 g lit^{-1} NaCl;
- *Izlazni elektrolit:* 0,05 – 0,1% NaClO;
- ***Stepen konverzije:*** ***3,5 kg NaCl / 1 kg NaClO;***

- *Radna temperatura:* *10 - 38 ^{o} C;*
- *Radna gustina struje:* *30-100 mA cm^{-2};*
- *Radni napon:* *3.5 - 10 V.*
- *Kapacitet* *12,5g ak.hlora/h*
- *Snaga* *190W*
- *Maksimalan pritisak* *0,1bar*

11.Kako je rešenje realizovano i gde se primenjuje / mogućnosti primene tehničkog rešenja, tj na koji način se koristi:

Rešenje se primenjuje na privatnim i javnim bazenima za kupanje na sledećim lokacijama:

1. „ERC comerc“ Pavlović	**Bgd**	**SRB**	**2008**
2. „Schengen boss“ Popović	**Bgd**	**SRB**	**2009**
3. Sparavalo Vlado	**Bgd**	**SRB**	**2008**
4. Stanišić Vlada	**Bgd**	**SRB**	**2009**
5. Stojkov Branko	**Bgd**	**SRB**	**2010**
6. Marković Toma	**Bgd**	**SRB**	**2009**
7. Mišković Vlada	**Bgd**	**SRB**	**2009**
8. Ćurčić Miša	**Bgd**	**SRB**	**2008**
9. Tomić Boriša	**Bgd**	**SRB**	**2009**
10. „Royal color“ Voja	**Bgd**	**SRB**	**2002**
11. Vučko Vranić	**Bgd**	**SRB**	**2004**
12. Vujović Svetlana	**Bgd**	**SRB**	**2003**
13. „USAID“ Ekmeđžić	**Bgd**	**SRB**	**2004**
14. USAID	**Podgorica**	**CG**	**2005**
15. Ambasada Maroka	**Bgd**	**SRB**	**2005**
16. Belgeš Predrag	**Bgd**	**SRB**	**2002**
17. Kuveljić Bora	**Čačak**	**SRB**	**2010**
18. Srećko Grbavćić	**Pula**	**Hrvatska**	**2010**
19. Kuveljić Bora	**Čačak**	**SRB**	**2010**
20. Srećko Grbavčić	**Pula**	**Hrvatska**	**2010**

Servisirano oko 80 stranih elektolizera – reaktora.

GRUPA M80: TEHNIČKA REŠENJA

Kategorija: „Novi proizvod ili tehnologija“
Rezultat M82: Novi proizvod ili tehnologija uvedena u proizvodnju

16. Ustanova/Autori rešenja:

Institut tehničkih nauka SANU, K.Mihajlova 35/4, 11000, Beograd
Institut za hemiju tehnologiju i metalurgiju, Beograd, Njegoševa 4, 11000 Beograd
Mašinski fakultet, Beograd, Kraljice Marije 16, 11000 Beograd

Autori: Tomislav Trišović, Jasmina Stevanović, Branimir Jugović, Nataša Trišović,

17. Naziv i evidencioni broj projekta sa brojem aktivnosti, u kome je ostvaren rezultat iz kategorije M80:

Elektrohemijsko postrojenje za proizvodnju sredstava za dezinfekciju sa modularnim reaktorom i reversnim elektrodama, Inovacioni projekat, MNTRS, IP8025, 2006-2007. rukovodilac T. Trišović

Automatski uređaj za fizičko-hemijski tretman voda sa kombinovanim modularnim generatorima, Inovacioni projekat, MNTRS, **45-01-000-65/2008-01/88,** rukovodilac T. Trišović

18. Naziv tehničkog rešenja

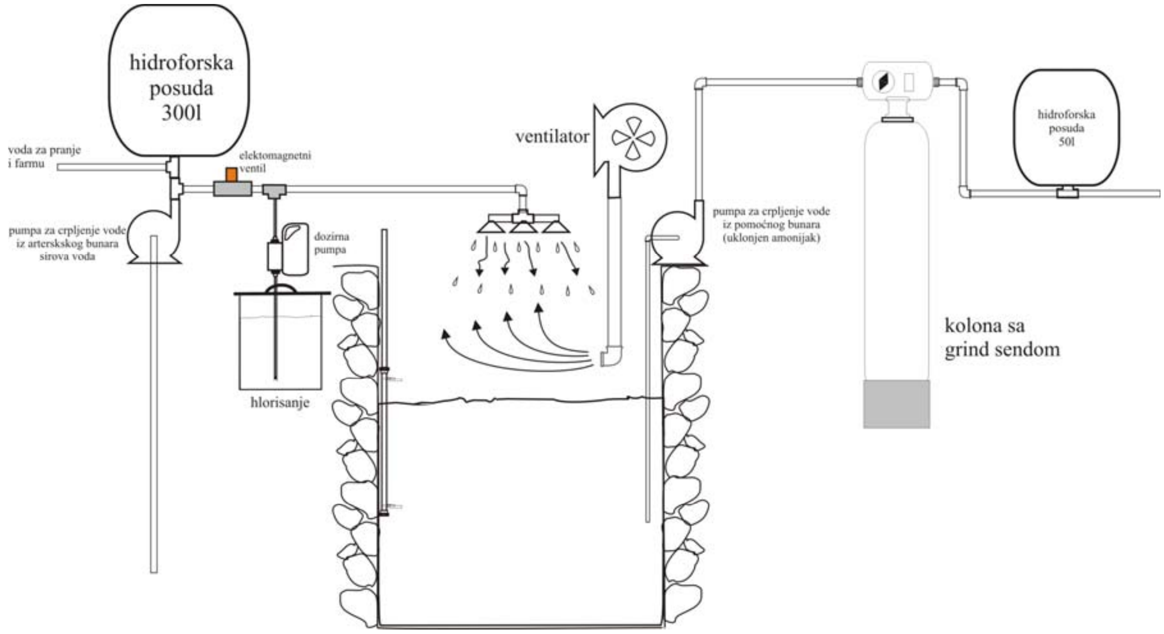
Uređaj za uklanjanje visokih koncentracija amonijaka, gvožđa i mangana iz pijaće vode

19. Oblast na koju se tehničko rešenje odnosi:

Tehničko-tehnološke i biotehničke nauke

20. Problem koji se tehničkim rešenjem rešava

Uklanjanje amonijaka, gvožđa i mangana u individualnim i malim vodovodima koristeći postojeću infrastrukturu uz minimalna ulaganja u novu opremu.



Slika 11. Shema uređaja za uklanjanje većih koncentracija amonijaka, gvožđa i mangana iz pijaće vode

21. Stanje rešenosti tog problema u svetu

U svetu se ovaj uklanjanje amonijaka rešava na nekoliko načina. Ekološki najprihvatljiviji postupak je biološkim putem pomoću bakterija koje amonijak prevode prvo u nitrir pa potom u nitrat. Drugi postupak predstavlja hiperhlorisanjem preko prevojne tačke kada amonijak prevodimo u mono di i tri hlor amine čija je koncentracija u pijaćoj vodi dozvoljena u većim koncentracijama nego li amonijaka. Treći način je metoda sorpcije tj prolaskom sirove vode kroz kolonu u kojoj se nalazi adekvatni sorbent za amonijak kao što je zeolit ili se radi o nekoj vrasti katalitičke oksidacije na mangan oksidu. Sva ova izložena rešenja su skupa i ne prihvatljiva za male i individualne vodovode malih pogona ili poljoprivrednih gazdinstava.

22. Za koga je rešenje rađeno:

Rešenje je rađeno za potrošačko tržište
Proizvodi AQUA CRYSTAL DOO i Hidrosanitas doo Beograd

23. Godina kada je rešenje urađeno i ko ga je prihvatio/primenjuje:

Rešenje je urađeno 2010 god
Izvođač radova Hidrosanitas doo Beograd

24. Kako su rezultati verifikovani (od strane kog tela):

„Gradski zavod za javno zdravlje“ Šabac na osnovu podnete dokumentacije i hemijske analize ulazne i vode posle tretmana

25. Objašnjenje suštine tehničkog rešenja i detaljan opis sa karakteristikama

Pijaće vode su najčešće sa povećanom koncentracijom amonijaka, mangana i gvožđa i to po nekoliko puta iznad maksimalno dozvoljene koja je propisana pravilnikom o ispravnosti pijaćih voda. S obzirom da je potrošnja vode sve veća kako u gradskim tako i seoskim sredinama svi oni koji imaju tehničkih mogućnosti pokušavaju da prave bunare koji crpe vodu sa donjih horizonata. Takva voda često nije hemijski ispravna i uglavnom sa većim koncentracijama amonijaka gvožđa i mangana. Nasš tim je razvio originalnu metodu koja iskorišćava sve postojeće infrastrukturne objekte koji se koriste u invidualnim i malim vodovodima. Obično u skoro svim domaćinstvima i proizvodnim pogonima koji imaju sopstveni vodovod postoje stari bunari koji su zidani kamenom ili su oplašteni betonskim kacama i dubina su od par metara do pedesetak metara. Iz tih bunara voda se crpi ili ručno pomoću vitla ili poloću potapajuće pumpe i hidroforskog sistema a uglavnom postoji i jedno i drugo rešenje. S obzirom na malu izdašnost ovih bunara danas se u njihovoj blizini izrađuju bunari koji crpe vodu sa znatno većih dubina i obično su oni znatno veće izdašnosti. Međutim takvi bunari često nemaju hemijski ispravnu vodu pa se mora pristupiti operacijama koje ce je dovesti u stanje propisano standardima. Naše rešenje koje se odnosi na uklanjanje gvožđa, mangana i amonijaka se sastoji od sledećih komponenata (Slika 11).

Crpna pumpa koja crpi vodu iz arteškog bunara i komprimuje u hidroforsku posudu koja na sebi ima presostat koji isključuje rad crpne pumpe kada se dostigne odgovarajući pritisak u hidroforskoj posudi. Iz hidroforske posude se napajaju sistemi za zalivanje, pojenje stoke i pranja mašina i opreme. Drugi izvod iz hidroforske posude preko elektomagnetnog ventila je spojen sa starim bunarom. Posle elektomagnetnog ventila se nalazi injekcioni ventil za doziranje aktivnog hlora koji dozira dozirna pumpa u slučaju otvorenog elektomagnetnog ventila. Uslov da se otvori elektomagnetni ventil je da se dostigne donji nivo vode u starom bunaru. Voda prolazi kroz elektomagnetni ventil pa se hlorise aktivnim hlorom a na samom ulazu u bunar raspršuje u sprej diznama. Sa dna bunara tj gornje kote nivoa vode se istovremeno uduvava svež vazduh. U ovom procecu u vazdušnoj zoni starog bunara dolazi do intenzivne oksidacije, aeracije i degazacije gde je veliki deo amonijaka oslobodi kao gas a takođe se i veliki deo gvožđa i mangana oksidiše. Kada nivo vode dostigne gornju višu kotu u bunaru ovaj se proces zaustavlja i voda odležava u bunaru gde joj je potrebno kontaktno vreme u reakciji sa aktivnim hlorom. Kada mala hidrorska pumpa povuče vodu iz starog bunara ona prvo vodu transportuje kroz kolonu sa grind sendom gde katalitički oksiduju i sorbuju joni gvožđa i mangana tako da voda izlaskom iz kolone je potpuno hemijski i bakteriološki ispravna.

26. Kako je rešenje realizovano i gde se primenjuje / mogućnosti primene tehničkog rešenja, tj na koji način se koristi:

Rešenje je primenjeno na sledećim lokacijama za proizvodnju pijaće vode:

1. EURO LINE – JAZOVNIK, ŠABAC primenjeno 2010 god.

2. POLJOPRIVREDNO GAZDINSTVO RANKOVIĆ – JAZOVNIK, ŠABAC primenjeno 2010 god.

Прилог 11. Извештај о цитираности

ИЗВЕШТАЈ О ЦИТИРАНОСТ РАДОВА ДР ТОМИСЛАВА ТРИШОВИЋА

Према базама података *Web ofScience Core Collection* и *Scopus*, 7. октобра 2014. године

Радови др Томислава Тришовића цитирани су укупно 167 пута (151 хетероцитат и 16 аутоцитата)

The morphology of different metals electrodeposited onto polyaniline films
By: Jovic, VD; Trisovic, T; Jovic, BM; et al.
JOURNAL OF ELECTROANALYTICAL CHEMISTRY Volume: 408 Issue: 1-2 Pages: 149-155
Published: MAY 30 1996

Хетероцитати:

1. Electrodeposition of nickel, cobalt, and iron on polypyrrole films
   By: Wysocka-Zolopa, Monika; Gradzka, Emilia; Szymanski, Krzysztof; et al.
   THIN SOLID FILMS Volume: 548 Pages: 44-51 Published: DEC 2 2013

2. Electrochemical Preparation of Nanoparticle Deposits: Application to Membranes and Catalysis
   Arias-Pardilla, J., Berenguer-Murcia, A., Cazorla-Amorós, D., Morallón, E.
   in *Membranes for Membrane Reactors: Preparation, Optimization and Selection*, pp. 395-407, Wiley 2011, Print ISBN: 9780470746523, Online ISBN: 9780470977569 (poglavlje u knjizi)

3. Metallic-Based Nanocomposites of Conductive Polymers.
   Tsakova, V." In *Nanostructured Conductive Polymers*, 289–340, Wiley 2010. Print ISBN: 9780470745854, Online ISBN: 9780470661338

4. Electrocatalytic oxidation of methanol on Cu modified polyaniline electrode in alkaline medium
   By: Nagashree, K. L.; Ahmed, M. F.
   JOURNAL OF APPLIED ELECTROCHEMISTRY Volume: 39 Issue: 3 Pages: 403-410 Published: MAR 2009

5. Electrosynthesis and Catalytic Activity of Polymer-Nickel Particles Composite Electrode Materials
   By: Melki, Tahar; Zouaoui, Ahmed; Bendemagh, Barkahoum; et al.
   JOURNAL OF THE BRAZILIAN CHEMICAL SOCIETY Volume: 20 Issue: 8 Pages: 1523-1534

6. How to affect number, size, and location of metal particles deposited in conducting polymer layers
   By: Tsakova, V.
   JOURNAL OF SOLID STATE ELECTROCHEMISTRY Volume: 12 Issue: 11 Pages: 1421-1434 Published: NOV 2008

7. Functionalised hybrid materials of conducting polymers with individual wool fibers
   By: Kelly, Fern M.; Johnston, James H.; Borrmann, Thomas; et al.
   JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY Volume: 8 Issue: 4 Pages: 1965-1972 Published: APR 2008

8. Laterally Controlled Template Electrodeposition of Polyaniline
   By: Sehayek, Tali; Meisel, Dan; Vaskevich, Alexander; et al.
   ISRAEL JOURNAL OF CHEMISTRY Volume: 48 Issue: 3-4 Pages: 359-366 Published: 2008

9. Electrochemical and morphologic studies of nickel incorporation on graphite electrodes modified with polytyramine
   By: de Castro, Cladio M.; Vieira, Sabrina N.; Goncalves, Rafael A.; et al.
   Conference: 5th Meeting of the Brazilian-Society-for-Materials-Research Location: Florianopolis, BRAZIL Date: OCT 08-12, 2006

JOURNAL OF MATERIALS SCIENCE Volume: 43   Issue: 2   Pages: 475-482
Published: JAN 2008

10. Functionalised hybrid materials of conducting polymers with individual fibres of cellulose
    By: Kelly, Fern M.; Johnston, James H.; Borrmann, Thomas; et al.
    EUROPEAN JOURNAL OF INORGANIC CHEMISTRY Issue: 35   Pages: 5571-5577
    Published: DEC 2007

11. Electrochemical fabrication of two-dimensional palladium nanostructures as substrates for surface enhanced Raman scattering
    By: Li, Yin; Lu, Gewu; Wu, Xufeng; et al.
    JOURNAL OF PHYSICAL CHEMISTRY B Volume: 110   Issue: 48   Pages: 24585-24592
    Published: DEC 7 2006

12. Electroless silver deposition on polypyrrole and poly(3,4-ethylenedioxythiophene): The reaction/diffusion balance
    By: Ocypa, M.; Ptasinska, M.; Michalska, A.; et al.
    JOURNAL OF ELECTROANALYTICAL CHEMISTRY Volume: 596   Issue: 2   Pages: 157-168
    Published: NOV 1 2006

13. Study of electrocatalytic properties of platinum-loaded poly-ortho-aminophenol film towards methanol oxidation and hydrogen evolution
    By: Panah, NB; Mahjani, MG; Jafarian, M; et al.
    INDIAN JOURNAL OF CHEMISTRY SECTION A-INORGANIC BIO-INORGANIC PHYSICAL THEORETICAL & ANALYTICAL CHEMISTRY Volume: 44   Issue: 10   Pages: 2015-2023
    Published: OCT 2005

14. Polyaniline fibres as electrodes. Electrochemical characterisation in acid solutions
    By: Pauliukaite, R; Brett, CMA; Monkman, AP
    ELECTROCHIMICA ACTA Volume: 50   Issue: 1   Pages: 159-167   Published: NOV 15 2004

15. Electronic, structural, and magnetic properties of cobalt aggregates embedded in polypyrrole
    By: Watanabe, N; Morais, J; Accione, SBB; et al.
    JOURNAL OF PHYSICAL CHEMISTRY B Volume: 108   Issue: 13   Pages: 4013-4017
    Published: APR 1 2004

16. The preparation of polypyrrole coated brass and copper electrodes for electrocatalysis
    By: Tuken, T; Arslan, G; Yazici, B; et al.
    PROGRESS IN ORGANIC COATINGS Volume: 49   Issue: 2   Pages: 153-159
    Published: MAR 2004

17. Structure and properties of C-60-Pd films formed by electroreduction of C-60 and palladium(II) acetate trimer: evidence for the presence of palladium nanoparticles
    By: Winkler, K; Noworyta, K; de Bettencourt-Dias, A; et al.
    JOURNAL OF MATERIALS CHEMISTRY Volume: 13   Issue: 3   Pages: 518-525
    Published: 2003

18. Preparation of Au/PAni/GC electrode and their electrocatalytic activity for the oxidation of formaldehyde
    By: Yang, HZ; Deng, YQ
    ACTA CHIMICA SINICA Volume: 60   Issue: 4   Pages: 569-573   Published: APR 2002

19. Electrochemical and quartz crystal microbalance studies of lead(II) deposition and stripping in the presence of copper on a gold electrode modified with 2,2 '-bipyridyl in polyaniline
    By: Wagner, K; Strojek, JW; Koziel, K
    ANALYTICA CHIMICA ACTA Volume: 455   Issue: 1   Pages: 69-81   Article Number: PII S0003-

2670(01)01576-8
Published: MAR 18 2002

20. Mechanism of underpotential deposition of metal on conducting polymers
By: Liu, YC; Yang, KH; Ger, MD
SYNTHETIC METALS Volume: 126 Issue: 2-3 Pages: 337-345 Article Number: PII S0379-6779(01)00581-1
Published: FEB 14 2002

21. Studies of processes during ASV determination of lead in the presence of copper on a solid electrode modified with 2,2 '-bypyridyl in polyaniline
By: Wagner, K; Strojek, JW; Koziel, K
CHEMIA ANALITYCZNA Volume: 47 Issue: 3 Pages: 385-397 Published: 2002

22. A polyaniline-modified electrode-based FIA system for sub-ppb-level chromium(VI) analysis
By: Yang, YJ; Huang, HJ
ANALYTICAL CHEMISTRY Volume: 73 Issue: 6 Pages: 1377-1381
Published: MAR 15 2001

23. Sulfonated polyaniline coated mercury film electrodes for voltammetric analysis of metals in water
Fungaro, D.A.
2001 Sensors 1 (6), pp. 206-214

24. Polypyrrole incorporating electroless nickel
By: Abrantes, LM; Correia, JP
Conference: 3rd Electrocatalysis Meeting (ECS 99) Location: PORTOROZ, SLOVENIA Date: 1999
ELECTROCHIMICA ACTA Volume: 45 Issue: 25-26 Pages: 4179-4185 Published: 2000

25. Synthesis and characterization of a composite of polyaniline and carbon black
By: Del Rio, R; Zagal, JH; Andrade, GD; et al.
JOURNAL OF APPLIED ELECTROCHEMISTRY Volume: 29 Issue: 6 Pages: 759-764
Published: JUN 1999

26. Interaction of copper(I)-polypyrrole complexes prepared by depositing-dissolving copper onto and from polypyrroles
By: Liu, YC; Hwang, BJ
THIN SOLID FILMS Volume: 339 Issue: 1-2 Pages: 233-239
Published: FEB 8 1999

27. Effect of temperature on the electrooxidation of some organic molecules on Pt doped conducting polymer coated electrodes
By: Becerik, I; Ficicioglu, F; Kadirgan, F
TURKISH JOURNAL OF CHEMISTRY Volume: 23 Issue: 4 Pages: 353-359 Published: 1999

28. Poly(3-methylthiophene) incorporating electrolessly deposited Ni-P particles
By: Abrantes, LM; Correia, JP
SURFACE & COATINGS TECHNOLOGY Volume: 107 Issue: 2-3 Pages: 142-148
Published: SEP 10 1998

29. A spectroelectrochemical study on polaron transformations in polyaniline in sulphuric and p-toluenesulphonic acids
By: Abd El-Rahman, HA
POLYMER INTERNATIONAL Volume: 44 Issue: 4 Pages: 481-489
Published: DEC 1997

30. Electrooxidation of methanol on platinum doped polyaniline electrodes: deposition potential and temperature effect
By: Ficicioglu, F; Kadirgan, F
JOURNAL OF ELECTROANALYTICAL CHEMISTRY Volume: 430 Issue: 1-2 Pages: 179-182
Published: JUN 30 1997

Аутоцитати:

31. Investigation of the polyaniline film porosity by the electrodeposition of cadmium on the film
By: Jovic, VD; Jovic, BM; Stojilkovic, ER; et al.
JOURNAL OF THE SERBIAN CHEMICAL SOCIETY Volume: 64 Issue: 4 Pages: 265-273
Published: 1999

Spectrophotometric study of the anodic corrosion of Ti/RuO2 electrode in acid sulfate solution
By: Gajic-Krstajic, LM; Trisovic, TL; Krstajic, NV
CORROSION SCIENCE Volume: 46 Issue: 1 Pages: 65-74 Published: JAN 2004

Хетероцитати:

1. High-performance Ti/Sb-SnO2/Pb3O4 electrodes for chlorine evolution: Preparation and characteristics
By: Shao, Dan; Yan, Wei; Cao, Lu; et al.
JOURNAL OF HAZARDOUS MATERIALS Volume: 267 Pages: 238-244
Published: FEB 28 2014

2. The effect of layer number on the nanostructural Ternary Mixed Oxide containing Ti, Ru and Ir on titanium
By: Goudarzi, Mona; Ghorbani, Mohammad
Edited by: Parsa, MH
Conference: 4th International Conference on Ultrafine Grained and Nano-Structured Materials (UFGNSM 2013) Location: Tehran, IRAN Date: NOV 05-06, 2013
ULTRAFINE GRAINED AND NANO-STRUCTURED MATERIALS IV Book Series: Advanced Materials Research Volume: 829 Pages: 638-642 Published: 2014

3. Synthesis and Characterization of Pt Catalysts on SnO2 Based Supports for Oxygen Reduction Reaction
By: Elezovic, N. R.; Babic, B. M.; Radmilovic, V. R.; et al.
JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 160 Issue: 10 Pages: F1151-F1158
Published: 2013

4. Influence of electrolyte composition on deactivation mechanism of a Ti/Ru0.25Ir0.25Ti0.5O2 electrode
By: Hoseinieh, S. M.; Ashrafizadeh, F.
IONICS Volume: 19 Issue: 1 Pages: 113-125 Published: JAN 2013

5. Intrinsic Potential-Dependent Performances of a Sol-Gel-Prepared Electrocatalytic IrO2-TiO2 Coating of Dimensionally Stable Anodes
By: Nikolic, Branislav Z.; Panic, Vladimir V.; Dekanski, Aleksandar B.
ELECTROCATALYSIS Volume: 3 Issue: 3-4 Pages: 360-368 Published: DEC 2012

6. Utilization of the catalyst layer of dimensionally stable anodes-Interplay of morphology and active surface area
By: Zeradjanin, Aleksandar R.; La Mantia, Fabio; Masa, Justus; et al.
ELECTROCHIMICA ACTA Volume: 82 Special Issue: SI Pages: 408-414 Published: NOV 1 2012

7. Role of Water in the Chlorine Evolution Reaction at RuO2-Based Electrodes-Understanding Electrocatalysis as a Resonance Phenomenon

By: Zeradjanin, Aleksandar R.; Menzel, Nadine; Strasser, Peter; et al.
CHEMSUSCHEM Volume: 5 Issue: 10 Pages: 1897-1904 Published: 2012

8. Ti/RuO2-Sb2O5-SnO2 electrodes for chlorine evolution from seawater
   By: Chen, Shenying; Zheng, Yinghan; Wang, Siwen; et al.
   CHEMICAL ENGINEERING JOURNAL Volume: 172 Issue: 1 Pages: 47-51 Published: AUG 1 2011

9. Electrooxidation of Phenol on a Ti/RuO(2)Anode: Effect of Some Electrolysis Parameters
   By: dos Santos, Iranildes D.; Afonso, Julio C.; Dutra, Achilles J. B.
   JOURNAL OF THE BRAZILIAN CHEMICAL SOCIETY Volume: 22 Issue: 5 Pages: 875-883 Published: MAY 2011

10. Differences in the electrochemical behavior of ruthenium and iridium oxide in electrocatalytic coatings of activated titanium anodes prepared by the sol-gel procedure
    By: Panic, Vladimir V.; Dekanski, Aleksandar B.; Miskovic-Stankovic, Vesna B.; et al.
    JOURNAL OF THE SERBIAN CHEMICAL SOCIETY Volume: 75 Issue: 10 Pages: 1413-1420 Published: 2010

11. The effect of the addition of colloidal iridium oxide into sol-gel obtained titanium and ruthenium oxide coatings on titanium on their electrochemical properties
    By: Panic, Vladimir V.; Dekanski, Aleksandar B.; Mitric, Miodrag; et al.
    PHYSICAL CHEMISTRY CHEMICAL PHYSICS Volume: 12 Issue: 27 Pages: 7521-7528 Published: 2010

12. Increasing the service lifetime of coated titanium anodes
    Hoseinieh, S.M., Maddahi, M.H., Ashrafizadeh, F.
    in Society of Petroleum Engineers - 5th SPE International Conference on Oilfield Corrosion 2010, pp. 58-66, **ISBN:** 978-161738668-8

13. Electrochemical characterization of ruthenium oxide on carbon paste electrodes in acid system
    Martinez-Alvarez, O., Miranda-Hernandez, M.
    2009 Carbon - Science and Technology 2 (3), pp. 125-130

14. Layer-by-layer assembly of Ru3+ and Si8O208- into electrochemically active silicate films
    By: Rassaei, Liza; Sillanpaa, Mika; Milsom, Elizabeth V.; et al.
    JOURNAL OF SOLID STATE ELECTROCHEMISTRY Volume: 12 Issue: 6 Pages: 747-755 Published: JUN 2008

15. Electrocatalytic properties and stability of titanium anodes activated by the inorganic sol-gel procedure
    By: Panic, Vladimir V.; Nikolic, Branislav Z.
    JOURNAL OF THE SERBIAN CHEMICAL SOCIETY Volume: 73 Issue: 11 Pages: 1083-1112 Published: 2008

16. The properties of electroactive ruthenium oxide coatings supported by titanium-based ternary carbides
    By: Panic, V. V.; Jovanovic, V. M.; Terzic, S. I.; et al.
    SURFACE & COATINGS TECHNOLOGY Volume: 202 Issue: 2 Pages: 319-324 Published: NOV 25 2007

17. Sol-gel prepared active ternary oxide coating on titanium in cathodic protection
    By: Panic, Vladimir V.; Nikolic, Branislav Z.
    JOURNAL OF THE SERBIAN CHEMICAL SOCIETY Volume: 72 Issue: 12 Pages: 1393-1402 Published: 2007

18. A nanogravimmetric investigation of the charging processes on ruthenium oxide thin films and their effect on methanol oxidation
    By: Santos, M. C.; Cogo, L.; Tanimoto, S. T.; et al.
    APPLIED SURFACE SCIENCE Volume: 253 Issue: 4 Pages: 1817-1822 Published: DEC 15 2006

19. Electrocatalytic activity of sol-gel-prepared RuO2/Ti anode in chlorine and oxygen evolution reactions
    By: Panic, V. V.; Dekanski, A. B.; Milonjic, S. K.; et al.
    Conference: 8th International Frumkin Symposium on Kinetics of Electrode Processes Location: Moscow, RUSSIA Date: OCT 18-22, 2005
    RUSSIAN JOURNAL OF ELECTROCHEMISTRY Volume: 42 Issue: 10 Pages: 1055-1060

20. Effect of solvent on the preparation and characterization of DSA((R))-type anodes containing RuO2-TiO2-SnO2
    By: Coteiro, Roberta D.; Teruel, Fernando S.; Ribeiro, Josimar; et al.
    JOURNAL OF THE BRAZILIAN CHEMICAL SOCIETY Volume: 17 Issue: 4 Pages: 771-779 Published: JUL-AUG 2006

21. Activity and stability of RuO2-coated titanium anodes prepared via the alkoxide route
    By: Panic, Vladimir; Dekanski, Aleksandar; Milonjic, Slobodan; et al.
    JOURNAL OF THE SERBIAN CHEMICAL SOCIETY Volume: 71 Issue: 11 Pages: 1173-1186 Published: 2006

Аутоцитати:

22. DEVELOPMENT OF RuO2/TiO2 TITANIUM ANODES AND A DEVICE FOR IN SITU ACTIVE CHLORINE GENERATION
    By: Spasojevic, Miroslav D.; Trisovic, Tomislav Lj; Ribic-Zelenovic, Lenka; et al.
    HEMIJSKA INDUSTRIJA Volume: 67 Issue: 2 Pages: 313-321 Published: MAR-APR 2013

Characterization of electrochemically synthesized PANI on graphite electrode for potential use in electrochemical power sources
By: Jugovic, B.; Gvozdenovic, M.; Stevanovic, J.; et al.
MATERIALS CHEMISTRY AND PHYSICS Volume: 114 Issue: 2-3 Pages: 939-942 Published: APR 15 2009

Хетероцитати:

1. Effect of Graphene Oxide as a Dopant on the Electrochemical Performance of Graphene Oxide/Polyaniline Composite
   By: Hu, Fang; Li, Wenhai; Zhang, Ji; et al.
   JOURNAL OF MATERIALS SCIENCE & TECHNOLOGY Volume: 30 Issue: 4 Pages: 321-327 Published: APR 2014

2. Mesoporous Polyaniline Films for High Performance Supercapacitors
   By: Khdary, Nezar H.; Abdesalam, Mamduoh E.; EL Enany, Gaber
   JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 161 Issue: 9 Pages: G63-G68 Published: 2014

3. On the role of aniline oligomers on the corrosion protection of mild steel
   By: Grgur, Branimir N.
   SYNTHETIC METALS Volume: 187 Pages: 57-60 Published: JAN 2014

4. Preparation and characterization of the new conducting composites obtained from 2-methylaniline and aniline with activated carbon by in situ intercalative oxidative polymerization
   By: Chouli, Faiza; Zehhaf, Abdelhafid; Benyoucef, Abdelghani
   MACROMOLECULAR RESEARCH Volume: 22 Issue: 1 Pages: 26-31 Published: JAN 2014

5. Development of a reagentless electrochemiluminescent electrode for flow injection analysis using copolymerised luminol/aniline on nano-TiO2 functionalised indium-tin oxide glass
   By: Liu, Chao; Wei, Xiuhua; Tu, Yifeng
   TALANTA Volume: 111 Pages: 156-162 Published: JUL 15 2013

6. Electrochemical oxidation of aniline on the surface of an amorphous metal alloy Al87Ni8Y5
   By: Yatsyshyn, M. M.; Boichyshyn, L. M.; Demchyna, I. I.; et al.
   RUSSIAN JOURNAL OF ELECTROCHEMISTRY Volume: 48 Issue: 5 Pages: 502-508 Published: MAY 2012

7. The hydrogen evolution reaction on nickel-polyaniline composite electrodes
   By: Dalla Corte, Daniel A.; Torres, Camila; Correa, Patricia dos Santos; et al.
   INTERNATIONAL JOURNAL OF HYDROGEN ENERGY Volume: 37 Issue: 4 Pages: 3025-3032 Published: FEB 2012

8. Preparation and Electrochemical Characterization of Polyaniline/Activated Carbon Composites as an Electrode Material for Supercapacitors
   By: Oh, Misoon; Kim, Seok
   JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY Volume: 12 Issue: 1 Pages: 519-524 Published: JAN 2012

9. Effect of dodecyl benzene sulfonic acid on the preparation of polyaniline/activated carbon composites by in situ emulsion polymerization
   By: Oh, Misoon; Kim, Seok
   ELECTROCHIMICA ACTA Volume: 59 Pages: 196-201 Published: JAN 1 2012

10. Synthesis, Characterization and Electrochemical Behavior of p-NiO/n-TiO2/Polyaniline Composites
    By: Cui Kun; Ding Guang-zhu; Chen Shi-fu; et al.
    CHEMICAL RESEARCH IN CHINESE UNIVERSITIES Volume: 27 Issue: 5 Pages: 870-874

11. Electrochemically synthesized polyaniline as support for lipase immobilization
    By: Bezbradica, Dejan; Jugovic, Branimir; Gvozdenovic, Milica; et al.
    JOURNAL OF MOLECULAR CATALYSIS B-ENZYMATIC Volume: 70 Issue: 1-2 Pages: 55-60 Published: JUN 2011

12. Electrochemical determination of glucose using polyaniline electrode modified by glucose oxidase
    By: Gvozdenovic, M. M.; Jugovic, B. Z.; Bezbradica, D. I.; et al.
    FOOD CHEMISTRY Volume: 124 Issue: 1 Pages: 396-400 Published: JAN 1 2011

13. Synthesis of high conductivity Polyaniline/Ag/graphite nanosheet composites via ultrasonic technique
    By: Wu, Xinming; Qi, Shuhua; He, Jie; et al.
    JOURNAL OF POLYMER RESEARCH Volume: 17 Issue: 5 Pages: 751-757 Published: SEP 2010

14. Synthesis and characterization of polyaniline/activated carbon composites and preparation of conductive films
    By: Zengin, Huseyin; Kalayci, Guellue
    MATERIALS CHEMISTRY AND PHYSICS Volume: 120 Issue: 1 Pages: 46-53 Published: MAR 15 2010

15. Electrochemical Synthesis of Polyaniline Nanobelts with Predominant Electrochemical Performances
    By: Li, Gao-Ren; Feng, Zhan-Ping; Zhong, Jin-Hui; et al.
    MACROMOLECULES Volume: 43 Issue: 5 Pages: 2178-2183 Published: MAR 9 2010

16. Electrodeposition of polyaniline nanowires and their electrochemical properties
    Nie, J.-T., M. Guo, M. Zhang, and P. Diao
    Beijing Keji Daxue Xuebao/Journal of University of Science and Technology Beijing 32, no. 4 (2010): 494–98.

Аутоцитати:

17. Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte
    By: Gvozdenovic, M. M.; Jugovic, B. Z.; Trisovic, T. Lj.; et al.
    MATERIALS CHEMISTRY AND PHYSICS Volume: 125 Issue: 3 Pages: 601-605 Published: FEB 15 2011

Microstructure and mechanical properties of disperse Ni-Co alloys electrodeposited on Cu substrates

By: Rafailovic, L. D.; Karnthaler, H. P.; Trisovic, T.; et al.

MATERIALS CHEMISTRY AND PHYSICS Volume: 120 Issue: 2-3 Pages: 409-416 Published: APR 15 2010

Хетероцитати:

1. Effect of Electrodeposition Current Density on the Microstructure and Magnetic Properties of Nickel-cobalt-molybdenum Alloy Powders
   By: Pesic, O.; Spasojevic, M.; Jordovic, B.; et al.
   SCIENCE OF SINTERING Volume: 46 Issue: 1 Pages: 117-127 Published: JAN-APR 2014

2. Electrodeposited Ni and Ni-Co alloys using cysteine and conventional ultrasound waves
   By: El-Feky, Hesham; Negem, Mosaad; Roy, Sudipta; et al.
   SCIENCE CHINA-CHEMISTRY Volume: 56 Issue: 10 Pages: 1446-1454 Published: OCT 2013

3. Preparation of Co-Ni alloy coatings by ultrasound electrodeposition
   Sheng, M., Zhong, Q., Lv, C., Wan, K.
   2013 Cailiao Yanjiu Xuebao/Chinese Journal of Materials Research
   27 (3), pp. 267-272

4. Investigation of microstructural, mechanical and thermal properties of rapidly solidified Ni-7 wt% Si alloy
   By: Karakose, Ercan; Keskin, Mustafa
   MATERIALS SCIENCE AND ENGINEERING A-STRUCTURAL MATERIALS PROPERTIES MICROSTRUCTURE AND PROCESSING Volume: 553 Pages: 181-191 Published: SEP 15 2012

5. Microstructure evolution and mechanical properties of intermetallic Ni-xSi (x=5, 10, 15, 20) alloys
   By: Karakose, Ercan; Keskin, Mustafa
   JOURNAL OF ALLOYS AND COMPOUNDS Volume: 528 Pages: 63-69 Published: JUL 5 2012

6. Co-Ni alloy electrodeposition under different conditions of pH, current and composition
   By: Vazquez-Arenas, Jorge; Altamirano-Garcia, Liliana; Treeratanaphitak, Tanyakarn; et al.
   ELECTROCHIMICA ACTA Volume: 65 Pages: 234-243 Published: MAR 30 2012

7. Vertically Cobalt Nanoplate Arrays Based on One-Step Electrochemical Growth and Their Magnetic Properties
   By: Xu, Lixia; Zhang, Shichao; Liu, Wenbo; et al.
   JOURNAL OF PHYSICAL CHEMISTRY C Volume: 116 Issue: 4 Pages: 2801-2806 Published: FEB 2 2012

8. Preparation of CoNi high surface area porous foams by substrate controlled electrodeposition
By: Rafailovic, Lidija D.; Gammer, Christoph; Rentenberger, Christian; et al.
PHYSICAL CHEMISTRY CHEMICAL PHYSICS Volume: 14 Issue: 2 Pages: 972-980 Published: 2012

9. Effects of the anion in glycine-containing electrolytes on the mechanical properties of electrodeposited Co-Ni films
By: Pellicer, E.; Pane, S.; Sivaraman, K. M.; et al.
MATERIALS CHEMISTRY AND PHYSICS Volume: 130 Issue: 3 Pages: 1380-1386 Published: NOV 1 2011

10. The Phase Structure and Morphology of Electrodeposited Nickel-Cobalt Alloy Powders
By: Spasojevic, M.; Ribic-Zelenovic, L.; Maricic, A.
SCIENCE OF SINTERING Volume: 43 Issue: 3 Pages: 313-326 Published: SEP-DEC 2011

11. Recent applications of SEM and AFM for assessing topography of metal and related coatings - a review
By: Smith, J. R.; Larson, C.; Campbell, S. A.
TRANSACTIONS OF THE INSTITUTE OF METAL FINISHING Volume: 89 Issue: 1 Pages: 18-27 Published: JAN 2011

12. The kinetics of Ni-Co/SiC composite coatings electrodeposition
By: Bahadormanesh, B.; Dolati, A.
JOURNAL OF ALLOYS AND COMPOUNDS Volume: 504 Issue: 2 Pages: 514-518 Published: AUG 20 2010

Аутоцитати:

13. Enhanced oxygen evolution and reduction reactions of porous ternary NiCoFe foam electrodes prepared by dynamic hydrogen template deposition
By: Rafailovic, Lidija D.; Gammer, Christoph; Rentenberger, Christian; et al.
NANO ENERGY Volume: 2 Issue: 4 Pages: 523-529 Published: JUL 2013

14. Study of the Dendritic Growth of Ni-Co Alloys Electrodeposited on Cu Substrates
By: Rafailovic, L. D.; Minic, D. M.; Karnthaler, H. P.; et al.
JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 157 Issue: 5 Pages: D295-D301 Published: 2010

Comparative studies of chloride and chloride/citrate based electrolytes for zinc-polyaniline batteries
By: Jugovic, B. Z.; Trisovic, T. Lj.; Stevanovic, J. S.; et al.
ELECTROCHIMICA ACTA Volume: 51 Issue: 28 Pages: 6268-6274 Published: SEP 15 2006

Heterocitati

1. Studies on new type current collectors for polyaniline batteries
Ding, Y., Kan, S., Gu, J., Kan, J.
2014 International Journal of Electrochemical Science 9 (11), pp. 6281-6293

2. High cycling stability of zinc-anode/conducting polymer rechargeable battery with non-aqueous electrolyte
By: Guerfi, A.; Trottier, J.; Boyano, I.; et al.
JOURNAL OF POWER SOURCES Volume: 248 Pages: 1099-1104 Published: FEB 15 2014

3. A single flow zinc//polyaniline suspension rechargeable battery
By: Zhao, Yongfu; Si, Shihui; Liao, Cui
JOURNAL OF POWER SOURCES Volume: 241 Pages: 449-453 Published: NOV 1 2013

4. Study of cylindrical Zn/PANI secondary batteries with the electrolyte containing alkylimidazolium ionic liquid
   By: Ma, Zhaoling; Kan, Jinqing
   SYNTHETIC METALS Volume: 174 Pages: 58-62 Published: JUN 15 2013

5. Zinc deposition and dissolution in methanesulfonic acid onto a carbon composite electrode as the negative electrode reactions in a hybrid redox flow battery
   By: Leung, P. K.; Ponce-de-Leon, C.; Low, C. T. J.; et al.
   ELECTROCHIMICA ACTA Volume: 56 Issue: 18 Pages: 6536-6546 Published: JUL 15 2011

6. Arsenic, heavy metals and SO2 derived in a mining-metallurgical production process
   Serbula, S.M., Stevanovic, J., Trujic, V.
   in *Hazardous Materials: Types, Risks and Control*, pp. 187-223, Nova Science Publishers, Inc. 2011, **ISBN:** 978-161324425-8

7. Synthesis, infrared stealth and corrosion resistance of organically modified silicate-polyaniline/carbon black hybrid coatings
   By: Wu, K. H.; Chang, Y. C.; Yang, C. C.; et al.
   EUROPEAN POLYMER JOURNAL Volume: 45 Issue: 10 Pages: 2821-2829 Published: OCT 2009

8. Polypyrrole as possible electrode materials for the aqueous-based rechargeable zinc batteries
   By: Grgur, B. N.; Gvozdenovic, M. M.; Stevanovic, J.; et al.
   ELECTROCHIMICA ACTA Volume: 53 Issue: 14 Pages: 4627-4632 Published: MAY 30 2008

9. Polyaniline as possible anode materials for the lead acid batteries
   By: Grgur, B. N.; Ristic, V.; Gvozdenovic, M. M.; et al.
   JOURNAL OF POWER SOURCES Volume: 180 Issue: 1 Pages: 635-640 Published: MAY 15 2008

10. Effect of carbon black content on electrical and microwave absorbing properties of polyaniline/carbon black nanocomposites
    By: Wu, K. H.; Ting, T. H.; Wang, G. P.; et al.
    POLYMER DEGRADATION AND STABILITY Volume: 93 Issue: 2 Pages: 483-488 Published: FEB 2008

Аутоцитати:

11. Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte
    By: Gvozdenovic, M. M.; Jugovic, B. Z.; Trisovic, T. Lj.; et al.
    MATERIALS CHEMISTRY AND PHYSICS Volume: 125 Issue: 3 Pages: 601-605 Published: FEB 15 2011

12. Citrate-based zinc-polyaniline secondary cell: part I: optimization of the citrate/chloride electrolyte
    By: Jugovic, B. Z.; Trisovic, T. Lj.; Stevanovic, J. S.; et al.
    JOURNAL OF APPLIED ELECTROCHEMISTRY Volume: 39 Issue: 12 Pages: 2521-2528 Published: DEC 2009

13. Corrosion behavior of magnesium, aluminum and zinc as anodic materials in chloride based electrolytes for use in primary and secondary electrochemical power sources
    By: Jugovic, B.; Gvozdenovic, M.; Stevanovic, J.; et al.
    MATERIALS & DESIGN Volume: 30 Issue: 8 Pages: 3291-3294 Published: SEP 2009

14. Characterization of electrochemically synthesized PANI on graphite electrode for potential use in electrochemical power sources

By: Jugovic, B.; Gvozdenovic, M.; Stevanovic, J.; et al.
MATERIALS CHEMISTRY AND PHYSICS Volume: 114 Issue: 2-3 Pages: 939-942 Published: APR 15 2009

Novel electrolyte for zinc-polyaniline batteries
By: Jugovic, B. Z.; Trisovic, T. Lj.; Stevanovic, J.; et al.
JOURNAL OF POWER SOURCES Volume: 160 Issue: 2 Special Issue: SI Pages: 1447-1450 Published: OCT 6 2006

Heterocitati

1. A single flow zinc//polyaniline suspension rechargeable battery
   By: Zhao, Yongfu; Si, Shihui; Liao, Cui
   JOURNAL OF POWER SOURCES Volume: 241 Pages: 449-453 Published: NOV 1 2013

2. Performance study of magnesium-polyaniline rechargeable battery in 1-ethyl-3-methylimidazolium ethyl sulfate electrolyte
   By: Ju, Qingqing; Shi, Yao; Kan, Jinqing
   SYNTHETIC METALS Volume: 178 Pages: 27-33 Published: AUG 15 2013

3. Studies on the influence factors of the cyclic life for Zn-PANi secondary batteries
   Han, J.-J., Cheng, J.-N., Geng, L.
   2012 Harbin Gongye Daxue Xuebao/Journal of Harbin Institute of Technology Volume 44, Issue 6, June 2012, pp. 105-109

4. Studies on synthesis of polyaniline/carbon composite and its electrochemical performance
   Han, J.-J., Geng, L., Cheng, J.-N., Zhu, C.
   2012 Cailiao Kexue yu Gongyi/Material Science and Technology Volume 20, Issue 1, February 2012, Pages 83-87

5. Arsenic, heavy metals and SO2 derived in a mining-metallurgical production process
   Serbula, S.M., Stevanovic, J., Trujic, V.
   in *Hazardous Materials: Types, Risks and Control*, pp. 187-223, Nova Science Publishers, Inc. 2011, **ISBN:** 978-161324425-8

6. Zinc-poly(aniline) rechargeable battery assembled-with aqueous electrolyte
   By: Dalui, Bharat Chandra; Basumallick, I. N.; Ghosh, Susanta
   INDIAN JOURNAL OF CHEMICAL TECHNOLOGY Volume: 15 Issue: 6 Pages: 576-580 Published: NOV 2008

7. Polypyrrole as possible electrode materials for the aqueous-based rechargeable zinc batteries
   By: Grgur, B. N.; Gvozdenovic, M. M.; Stevanovic, J.; et al.
   ELECTROCHIMICA ACTA Volume: 53 Issue: 14 Pages: 4627-4632 Published: MAY 30 2008

8. Polyaniline as possible anode materials for the lead acid batteries
   By: Grgur, B. N.; Ristic, V.; Gvozdenovic, M. M.; et al.
   JOURNAL OF POWER SOURCES Volume: 180 Issue: 1 Pages: 635-640 Published: MAY 15 2008

Аутоцитати:

9. Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte
   By: Gvozdenovic, M. M.; Jugovic, B. Z.; Trisovic, T. Lj.; et al.
   MATERIALS CHEMISTRY AND PHYSICS Volume: 125 Issue: 3 Pages: 601-605 Published: FEB 15 2011

10. Citrate-based zinc-polyaniline secondary cell: part I: optimization of the citrate/chloride electrolyte
By: Jugovic, B. Z.; Trisovic, T. Lj.; Stevanovic, J. S.; et al.
JOURNAL OF APPLIED ELECTROCHEMISTRY Volume: 39 Issue: 12 Pages: 2521-2528 Published: DEC 2009

11. Corrosion behavior of magnesium, aluminum and zinc as anodic materials in chloride based electrolytes for use in primary and secondary electrochemical power sources
By: Jugovic, B.; Gvozdenovic, M.; Stevanovic, J.; et al.
MATERIALS & DESIGN Volume: 30 Issue: 8 Pages: 3291-3294 Published: SEP 2009

12. Characterization of electrochemically synthesized PANI on graphite electrode for potential use in electrochemical power sources
By: Jugovic, B.; Gvozdenovic, M.; Stevanovic, J.; et al.
MATERIALS CHEMISTRY AND PHYSICS Volume: 114 Issue: 2-3 Pages: 939-942 Published: APR 15 2009

Electrochemical oxidation of iodide in aqueous solution
By: Grgur, B. N.; Gvozdenovic, M. M.; Stevanovic, J. S.; et al.
CHEMICAL ENGINEERING JOURNAL Volume: 124 Issue: 1-3 Pages: 47-54 Published: NOV 1 2006

1. Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: Effect of electrode materials
By: Oturan, Nihal; Wu, Jie; Zhang, Hui; et al.
APPLIED CATALYSIS B-ENVIRONMENTAL Volume: 140 Pages: 92-97 Published: AUG-SEP 2013

2. A Kinetic Study on Electrooxidation of Propyl-Thiouracil: An Anti-Hyperthyroid Drug by Potassium Iodide
By: Jalali, Fahimeh; Riahi, Sajjad; Nematollahi, Davood
JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 160 Issue: 10 Pages: H710-H714 Published: 2013

3. Energy-saving synthesis of potassium iodate via electrolysis of potassium iodine and O-2 in a membraneless cell
By: Tang, Yang; Li, Yunjin; Yu, Zhanglong; et al.
GREEN CHEMISTRY Volume: 14 Issue: 2 Pages: 334-337 Published: 2012

4. Electrochemical Modulation of the Thickness of Polypyrrole Films by Using Different Anionic Dopants
By: Paramo-Garcia, U.; Ibanez, J. G.; Batina, N.
INTERNATIONAL JOURNAL OF ELECTROCHEMICAL SCIENCE Volume: 6 Issue: 11 Pages: 5172-5188 Published: NOV 2011

5. Arsenic, heavy metals and SO2 derived in a mining-metallurgical production process
Serbula, S.M., Stevanovic, J., Trujic, V.
in *Hazardous Materials: Types, Risks and Control*, pp. 187-223, Nova Science Publishers, Inc. 2011, **ISBN:** 978-161324425-8

6. Electrolytic cell for hydrogen and sulfuric acid production
Petrov, K., Nikolov, I., Nikolova, V., (...), Uzun, D., Vitanov, T.
2011 Bulgarian Chemical Communications 43 (1), pp. 105-110

7. Electrochemical Oxidation Behavior of Iodide on Platinum Electrode in Acid Solution
By: Gao Yun-Fang; Yu Li-Li; Lu Qing-Qing; et al.
ACTA PHYSICO-CHIMICA SINICA Volume: 25 Issue: 7 Pages: 1421-1426 Published: JUL 2009

8. Green chemistry: Pretreatment of seawater by a one-step electrochemical method
   By: Yi, Shouzhi; Ma, Yingying; Wang, Xiaocong; et al.
   DESALINATION Volume: 239 Issue: 1-3 Pages: 247-256 Published: APR 2009

9. Electrochemical oxidation behavior of iodide on platinum electrode in acid solution
   Gao, Y.-F., Yu, L.-L., Lu, Q-.Q., Ma, C.-A.
   2009 Wuli Huaxue Xuebao/ Acta Physico - Chimica Sinica Volume 25, Issue 7, 2009, Pages 1421-1426

10. Nitrite oxidation on RuO2 electrodes
   By: Amadelli, R.; De Battisti, A.; Doubova, L.; et al.
   RUSSIAN JOURNAL OF ELECTROCHEMISTRY Volume: 44 Issue: 1 Pages: 131-137 Published: JAN 2008

Study of the Dendritic Growth of Ni-Co Alloys Electrodeposited on Cu Substrates
By: Rafailovic, L. D.; Minic, D. M.; Karnthaler, H. P.; et al.
JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 157 Issue: 5 Pages: D295-D301 Published: 2010

Heterocitati

1. Ruthenium Electrodeposition from Aqueous Solution at High Cathodic Overpotential
   By: Oppedisano, Daniel K.; Jones, Lathe A.; Junk, Tabea; et al.
   JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 161 Issue: 10 Pages: D489-D494 Published: 2014

2. Enhanced oxygen evolution and reduction reactions of porous ternary NiCoFe foam electrodes prepared by dynamic hydrogen template deposition
   By: Rafailovic, Lidija D.; Gammer, Christoph; Rentenberger, Christian; et al.
   NANO ENERGY Volume: 2 Issue: 4 Pages: 523-529 Published: JUL 2013

3. Cobalt-Nickel-Iron Nanoparticles Coated on Stainless Steel Substrate
   By: Resali, Nor Azrina; Hyie, Koay Mei; Berhan, M. N.; et al.
   Edited by: Hassan, MB
   Conference: Malaysian International Tribology Conference (MITC) Location: Kota Kinabalu, MALAYSIA Date: NOV 18-20, 2013
   INTERNATIONAL TRIBOLOGY CONFERENCE MALAYSIA 2013 Book Series: Procedia Engineering Volume: 68 Pages: 30-36 Published: 2013

4. Synthesis and characterization of electrodeposited hierarchical nanodendritic NiCoFe alloy powders
   By: Rafailovic, L. D.; Gammer, C.; Kleber, C.; et al.
   JOURNAL OF ALLOYS AND COMPOUNDS Volume: 543 Pages: 167-171 Published: DEC 5 2012

5. Fabrication of Three-Dimensional Dendritic Ni-Co Films By Electrodeposition on Stainless Steel Substrates
   By: Silva, R. P.; Eugenio, S.; Silva, T. M.; et al.
   JOURNAL OF PHYSICAL CHEMISTRY C Volume: 116 Issue: 42 Pages: 22425-22431 Published: OCT 25 2012

6. The chemistry and structure of nickel-tungsten coatings obtained by pulse galvanostatic electrodeposition
   By: Arganaraz, M. P. Quiroga; Ribotta, S. B.; Folquer, M. E.; et al.
   ELECTROCHIMICA ACTA Volume: 72 Pages: 87-93 Published: JUN 30 2012

7. Preparation of CoNi high surface area porous foams by substrate controlled electrodeposition
   By: Rafailovic, Lidija D.; Gammer, Christoph; Rentenberger, Christian; et al.
   PHYSICAL CHEMISTRY CHEMICAL PHYSICS Volume: 14 Issue: 2 Pages: 972-980 Published: 2012

8. Catalyst layers for proton exchange membrane fuel cells prepared by electrospray deposition on Nation membrane
   By: Chaparro, A. M.; Ferreira-Aparicio, P.; Folgado, M. A.; et al.
   JOURNAL OF POWER SOURCES Volume: 196 Issue: 9 Special Issue: SI Pages: 4200-4208 Published: MAY 1 2011

Аутоцитати:

9. Enhanced oxygen evolution and reduction reactions of porous ternary NiCoFe foam electrodes prepared by dynamic hydrogen template deposition
   By: Rafailovic, Lidija D.; Gammer, Christoph; Rentenberger, Christian; et al.
   NANO ENERGY Volume: 2 Issue: 4 Pages: 523-529 Published: JUL 2013

Electrochemical synthesis and corrosion behavior of polyaniline-benzoate coating on copper
By: Gvozdenovic, Milica M.; Jugovic, Branimir Z.; Stevanovic, Jasmina S.; et al.
SYNTHETIC METALS Volume: 161 Issue: 13-14 Pages: 1313-1318 Published: JUL 2011

Heterocitati

1. Anticorrosive properties with catalytic behaviour of primer PANI film and top PPy coating synthesised in presence of novel norephedrine based amino alcohol compound
   By: Ozyilmaz, A. T.; Aydin, A. E.; Akdag, A.
   TRANSACTIONS OF THE INSTITUTE OF METAL FINISHING Volume: 92 Issue: 1 Pages: 34-40 Published: JAN 2014

2. Anticorrosion property of polyaniline doped twice with functional acid
   Yang, X., Yang, X., Ma, X.
   2014 Huagong Xuebao/CIESC Journal 65 (9), pp. 3738-3743

3. A ferrocene functionalized polymer: Poly [N-(ferrocenylmethyl)-o-phenylenediamine]. Electrochemical production and spectroelectroelectrochemical investigation in acetonitrile medium
   By: Gulce, Handan; Yetkin, Ahmet; Akgul, Eda; et al.
   THIN SOLID FILMS Volume: 545 Pages: 81-88 Published: OCT 31 2013

4. Galvanostatic polymerisation of aniline on steel: Improving the coating performance in chloride-containing environment
   By: Kazum, O.; Kannan, M. Bobby
   SYNTHETIC METALS Volume: 180 Pages: 54-58 Published: SEP 15 2013

5. Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications
   By: Ciric-Marjanovic, Gordana
   SYNTHETIC METALS Volume: 177 Pages: 1-47 Published: AUG 1 2013

6. The influence of thin benzoate-doped polyaniline coatings on corrosion protection of mild steel in different environments
   By: Elkais, Ali R.; Gvozdenovic, Milica M.; Jugovic, Branimir Z.; et al.
   PROGRESS IN ORGANIC COATINGS Volume: 76 Issue: 4 Pages: 670-676 Published: APR 2013

7. Influence of electrochemically prepared poly(pyrrole-co-N-methyl pyrrole) and poly(pyrrole)/poly(N-methyl pyrrole) composites on corrosion behavior of copper in acidic

medium
By: Cakmakci, Irem; Duran, Berrin; Bereket, Gozen
PROGRESS IN ORGANIC COATINGS Volume: 76 Issue: 1 Pages: 70-77 Published: JAN 2013

8. Polyester based-siloxane modified waterborne anticorrosive hydrophobic coating on copper
   By: Verma, Garima; Dhoke, S. K.; Khanna, A. S.
   SURFACE & COATINGS TECHNOLOGY Volume: 212 Pages: 101-108 Published: NOV 2012

Electrochemical characteristics of rechargeable polyaniline/lead dioxide cell
By: Grgur, Branimir N.; Zeradjanin, Aleksandar; Gvozdenovic, Milica M.; et al.
JOURNAL OF POWER SOURCES Volume: 217 Pages: 193-198 Published: NOV 1 2012

Heterocitati

1. Composites of polyaniline and lead dioxide: preparation, characterization, and catalytic activity
   By: El-Sharkawy, Rehab G.
   JOURNAL OF THE IRANIAN CHEMICAL SOCIETY Volume: 11 Issue: 4 Pages: 1027-1037 Published: AUG 2014

2. Bioinspired Synthesis of Novel Teeth-Like Hierarchical Architecture Polyaniline/Lead Tungstate Nanocomposites with Photoluminescence Property
   By: Cheng, Cheng; Shu, Hongyan; Wang, Yunlong; et al.
   POLYMER COMPOSITES Volume: 35 Issue: 3 Pages: 516-522 Published: MAR 2014

3. Electrochemical Behavior of Polyaniline Microparticle Suspension as Flowing Anode for Rechargeable Lead Dioxide Flow Battery
   By: Zhao, Yongfu; Si, Shihui; Wang, Lu; et al.
   JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 161 Issue: 3 Pages: A330-A335 Published: 2014

4. A single flow zinc//polyaniline suspension rechargeable battery
   By: Zhao, Yongfu; Si, Shihui; Liao, Cui
   JOURNAL OF POWER SOURCES Volume: 241 Pages: 449-453 Published: NOV 1 2013

5. Performance study of magnesium-polyaniline rechargeable battery in 1-ethyl-3-methylimidazolium ethyl sulfate electrolyte
   By: Ju, Qingqing; Shi, Yao; Kan, Jinqing
   SYNTHETIC METALS Volume: 178 Pages: 27-33 Published: AUG 15 2013

6. Study of cylindrical Zn/PANI secondary batteries with the electrolyte containing alkylimidazolium ionic liquid
   By: Ma, Zhaoling; Kan, Jinqing
   SYNTHETIC METALS Volume: 174 Pages: 58-62 Published: JUN 15 2013

On the kinetics of the hydrogen evolution reaction on zinc in sulfate solutions
By: Trisovic, T; Gajic-Krstajic, LJ; Krstajic, N; et al.
JOURNAL OF THE SERBIAN CHEMICAL SOCIETY Volume: 66 Issue: 11-12 Pages: 811-823 Published: 2001

Heterocitati

1. Kinetics of Polarization Mechanisms
   By: Roh, Heui-Seol
   JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 160 Issue: 9 Pages: H519-H528 Published: 2013

2. Statistical Thermodynamic Theory for Non-Equilibrium, Quasi-Equilibrium, and Equilibrium Electrochemical Reactions

By: Roh, Heui-Seol
JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 160 Issue: 8 Pages: H420-H429 Published: 2013

3. Mathematical Modeling of the Hydrogen Evolution Reaction on Pt/C Electrodes Considering Diffusion Effects
   By: Ortega Chavez, L.; Herrera-Peraza, E.; Verde-Gomez, Y.
   Conference: 10th International Congress of the Mexican-Hydrogen-Society Location: Toluca, MEXICO Date: SEP 27-OCT 01, 2010
   JOURNAL OF NEW MATERIALS FOR ELECTROCHEMICAL SYSTEMS Volume: 13 Issue: 3 Special Issue: SI Pages: 283-287 Published: JUL 2010

4. Electrochemistry of zinc anode Z1 AS 2239-2003
   Flitt, H., Schweinsberg, P.
   in 48th Annual Conference of the Australasian Corrosion Association 2008: Corrosion and Prevention 2008, pp. 352-359, 2008. **ISBN:** 978-162276244-6

5. Singular points of electrochemical impedance function
   By: Garcia-Jareno, JJ; Gimenez-Romero, D; Vicente, F
   Conference: 1st International Meeting on Applied Physics (APHYS-2003) Location: Badajoz, SPAIN Date: OCT 15-18, 2003
   APPLIED SURFACE SCIENCE Volume: 238 Issue: 1-4 Pages: 449-456 Published: NOV 15 2004

Аутоцитати:

6. Electrolytic hydrogenation of glucose on amalgamated zinc in sulphate solutions
   By: Trisovic, T; Gajic-Krstajic, L; Krstajic, N
   Edited by: Uskokovic, DP; Milonjic, SK; Rakovic, DI
   Conference: 5th Conference of the Yugoslav-Materials-Research-Society (Yu-MRS 2003) Location: Herceg Novi, YUGOSLAVIA Date: SEP 15-19, 2003
   PROGRESS IN ADVANCED MATERIALS AND PROCESSES Book Series: MATERIALS SCIENCE FORUM Volume: 453-454 Pages: 145-150 Published: 2004

A kinetic study of D-glucose oxidation by bromine in aqueous solutions
By: Grgur, Branimir N.; Zugic, Dragana L.; Gvozdenovic, Milica M.; et al.
CARBOHYDRATE RESEARCH Volume: 341 Issue: 11 Pages: 1779-1787 Published: AUG 14 2006

Heterocitati

1. MECHANISTIC INVESTIGATION OF OXIDATION OF GLUCOSE AND FRUCTOSE BY N-CHLORONICOTINAMIDE (NCN)
   By: Pushpalatha, L.
   OXIDATION COMMUNICATIONS Volume: 37 Issue: 1 Pages: 121-128 Published: 2014

2. Kinetics and Mechanism of Oxidation of Reducing Sugars: A Review
   By: Singh, J. V.; Awasthi, Anupam; Dipti; et al.
   ASIAN JOURNAL OF CHEMISTRY Volume: 25 Issue: 2 Pages: 595-611 Published: FEB 2013

3. KINETICS AND MECHANISM OF OXIDATION OF GLUCOSE AND FRUCTOSE BY N-BROMONICOTINAMIDE (NBN)
   By: Pushpalatha, L.
   OXIDATION COMMUNICATIONS Volume: 36 Issue: 4 Pages: 901-913 Published: 2013

4. Structure and Kinetics of Hydrogen Bonds in Aqueous Glucose Solutions
   By: Chen Cong; Li Wei-Zhong; Song Yong-Chen; et al.
   ACTA PHYSICO-CHIMICA SINICA Volume: 27 Issue: 6 Pages: 1372-1378 Published: JUN 2011

5. Kinetics and mechanism of oxidation of galctose and mannose by N-Bromonicotinamide (NBN)
   By: Pushpalatha, L.
   AFINIDAD Volume: 68 Issue: 551 Pages: 57-63 Published: JAN-FEB 2011

Corrosion behavior of magnesium, aluminum and zinc as anodic materials in chloride based electrolytes for use in primary and secondary electrochemical power sources
By: Jugovic, B.; Gvozdenovic, M.; Stevanovic, J.; et al.
MATERIALS & DESIGN Volume: 30 Issue: 8 Pages: 3291-3294 Published: SEP 2009

Heterocitati

1. Electrochemical and structural characterization of AZ63 alloy surface film in MgSO4 solution
   By: Chen, Lin; Chen, Changguo; Wang, Ningning; et al.
   JOURNAL OF APPLIED ELECTROCHEMISTRY Volume: 44 Issue: 7 Pages: 773-779 Published: JUL 2014

2. Effect of chloride ion level on the corrosion performance of MAO modified AZ31 alloy in NaCl solutions
   By: Gu, Yanhong; Cai, Xiaojun; Guo, Yuanjun; et al.
   MATERIALS & DESIGN Volume: 43 Pages: 542-548 Published: JAN 2013

Аутоцитати:

3. Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte
   By: Gvozdenovic, M. M.; Jugovic, B. Z.; Trisovic, T. Lj.; et al.
   MATERIALS CHEMISTRY AND PHYSICS Volume: 125 Issue: 3 Pages: 601-605 Published: FEB 15 2011

Transition layer thickness in microlaminar deposits
Despić, A.R., Trišović, T.LJ.
Journal of Applied Electrochemistry
1993, 23 (6), pp. 662-668

1. Electrodeposition of Ru/Co compositionally modulated multilayers
   By: Juzikis, P; Gudaviciute, L; Messmer, A; et al.
   JOURNAL OF APPLIED ELECTROCHEMISTRY Volume: 27 Issue: 8 Pages: 991-994 Published: AUG 1997

2. Electrodeposition of alloys with composition modulated over their thickness: A review
   By: Gamburg, YD
   RUSSIAN JOURNAL OF ELECTROCHEMISTRY Volume: 37 Issue: 6 Pages: 585-590 Published: JUN 2001

3. Intermediate layers in electrodeposited CMA coatings
   By: Despic, AR; Jovic, VD; Tosic, N
   Conference: EU Conference on Compositionally Modulated Alloy Coatings Location: ATHENS, GREECE Date: MAY 28-29, 1997
   SURFACE & COATINGS TECHNOLOGY Volume: 105 Issue: 3 Pages: 206-212 Published: JUN 25 1998

Electrochemical polymerization of aniline
Milica M. Gvozdenović, **Branimir Z. Jugović**, Jasmina S. Stevanović, Tomislav Lj. Trišović, Branimir N. Grgur,
in Electropolymerization (Ewa Schab-Balcerzak, Eds.), INTECH, (2011), Chap. 4. pp. 77–96, ISBN 978–953–307–693–5.

Heterocitati

1. Electrochromic artificial muscles based on nanoporous metal-polymer composites
   By: Detsi, E.; Onck, P. R.; De Hosson, J. T. M.
   APPLIED PHYSICS LETTERS Volume: 103 Issue: 19 Article Number: 193101 Published: NOV 4 2013
2. Printing polyaniline for sensor applications
   By: Crowley, Karl; Smyth, Malcolm R.; Killard, Anthony J.; et al.
   CHEMICAL PAPERS Volume: 67 Issue: 8 Pages: 771-780 Published: AUG 2013
3. Coatings based on conducting polymers and functionalized carbon nanotubes obtained by electropolymerization
   By: Branzoi, Florina; Branzoi, Viorel; Musina, Ancuta
   PROGRESS IN ORGANIC COATINGS Volume: 76 Issue: 4 Pages: 632-638 Published: APR 2013

Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte

By: Gvozdenovic, M. M.; Jugovic, B. Z.; Trisovic, T. Lj.; et al.

MATERIALS CHEMISTRY AND PHYSICS Volume: 125 Issue: 3 Pages: 601-605 Published: FEB 15 2011

1. Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications
   By: Ciric-Marjanovic, Gordana
   SYNTHETIC METALS Volume: 177 Pages: 1-47 Published: AUG 1 2013

2. Capacitance Fading Induced by Degradation of Polyaniline: Cyclic Voltammetry and SEM Study
   By: Zhang, Hairui; Li, Hanlu; Wang, Jixiao
   Edited by: Cui, CX; Li, YL; Yuan, ZH
   Conference: 2nd International Conference on Advanced Engineering Materials and Technology (AEMT) Location: Zhuhai, PEOPLES R CHINA Date: JUL 06-08, 2012
   ADVANCED ENGINEERING MATERIALS II, PTS 1-3 Book Series: Advanced Materials Research Volume: 535-537 Pages: 1205-1209 Published: 2012

DEVELOPMENT OF RuO2/TiO2 TITANIUM ANODES AND A DEVICE FOR IN SITU ACTIVE CHLORINE GENERATION

By: Spasojevic, Miroslav D.; Trisovic, Tomislav Lj; Ribic-Zelenovic, Lenka; et al.

HEMIJSKA INDUSTRIJA Volume: 67 Issue: 2 Pages: 313-321 Published: MAR-APR 2013

1. Current efficiency in the chlorate cell process
   By: Spasojevic, Miroslav D.; Ribic-Zelenovic, Lenka J.; Spasojevic, Pavle M.; et al.
   JOURNAL OF THE SERBIAN CHEMICAL SOCIETY Volume: 79 Issue: 6 Pages: 677-688 Published: 2014

ELECTROCHEMICAL SYNTHESIS AND CORROSION BEHAVIOR OF THIN POLYANILINE FILM ON MILD STEEL, COPPER AND ALUMINUM

By: Elkais, Ali Ramadan; Gvozdenovic, Milica M.; Jugovic, Branimir Z.; et al.

HEMIJSKA INDUSTRIJA Volume: 65 Issue: 1 Pages: 15-21 Published: JAN-FEB 2011

1. THE STUDY OF Zn-Co ALLOY COATINGS ELECTROCHEMICALLY DEPOSITED BY PULSE CURRENT
   By: Bajat, Jelena B.; Maksimovic, Miodrag D.; Tomic, Milorad V.; et al.
   HEMIJSKA INDUSTRIJA Volume: 66 Issue: 5 Pages: 749-757 Published: SEP-OCT 2012

Прилог 12. Сарадња с привредом

PROJEKTANT:

INSTITUT TEHNIČKIH NAUKA
SRPSKA AKADEMIJA NAUKA I UMETNOSTI

INVESTITOR:

JAVNO PREDUZEĆE ZA KOMUNALNU PRIVREDU
"LAZAREVAC"

Јавно предузеће за комуналну привреду
„ЛАЗАРЕВАЦ"
Број 081-4042
Датум 29. 05 2012
ЛАЗАРЕВАЦ

Институт техничких наука С А Н У
Бр. 190/1
18.V 2012 год.
Кнез Михајлова35/IV, Београд, ПФ 377
Тел; 2636-994, 2185-437, Фах: 2185-263

GLAVNI TEHNOLOŠKI PROJEKAT

Hlorisanje vode za piće hipohloritom dobijenim elektrolizom vodenog rastvora natrijum-hlorida in situ u vodovodu "Peštan" u Lazarevcu

Beograd, 2012.

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ
Кнез Михаилова 35/IV, П.Ф. 377, 11000 Београд, Србија
Тел.: 011 21 85 437, 26 36 994; Факс: 21 85 263, мејл: its@itn.sanu.ac.rs, http://www.itn.sanu.ac.rs
Текући рачун: 840-1613660-30, 840-1613666-12, ПИБ: 100039438, матични бр. 07011016

FIZIBILITI STUDIJA ZA PROIZVODNJU NATIJUM HIPOHLORITA IZ GASOVITOG HLORA

NARUČIOC: BIN COMERC Beograd,
Zemunska 245v
11277 Ugrinovci, Beograd
telefon/fax: 011/ 3774655, 3774683
mail: office@bincommerce.rs

STUDIJU IZRADILI:

____

Dr Tomislav Trišović, viši naučni saradnik, ITN-SANU, Beograd

____

Dr Branimir Grgur, red. prof. Tehnološko metalurškog fakulteta, Beograd

____

Dr Milica Gvozdenović, docent Tehnološko metalurškog fakulteta, Beograd

____

Dr Branimir Jugović, viši naučni saradnik, ITN-SANU, Beograd

Институт техничких наука С А Н У
Бр. 348/1
23.09 20 13 год.
Кнез Михајлова35/IV, Београд, ПФ 377
Тел; 2636-994, 2185-437, Фах: 2185-263

УГОВОР

Закључен дана 23. септембра 2013. године у Београду.

УГОВОРНЕ СТРАНЕ

Bin commerce са седиштем у Београду, Устаничка 218, са основним подацима: матични број 17175025, ПИБ: 100023226, кога заступа директор Бојан Маравић (у даљем тексту: Наручилац),

и

Институт техничких наука САНУ, са седиштем у Београду, Кнез Михаилова 35/IV, са основним подацима: матични број 07011016, ПИБ 100039438, кога заступа директор Академик проф. др Зоран Ђурић (у даљем тексту: Извођач)

ПРЕДМЕТ УГОВОРА: Израда студије изводљивости за производњу натријум хипохлорита.

Члан 1.

Уговорне стране су сагласне да Извођач за рачун Наручиоца уради студију изводљивости за производњу натријум хипохлорита у обиму од 35 до 45 страна.

Члан 2.

Извођач је обавезан да уговорени посао уради у року од 35 радних дана од тренутка потписивања овог уговора.

Члан 3.

Уговарачи су сагласни да Наручилац плати Извођачу укупну цену урађеног решења у износу од :

- 136.800,00 динара без урачунатог ПДВ-а,
- порез на додатну вредност 27.360,00 динара,
- тако да је укупна уговорна цена 164.160,00 динара са ПДВ-ом.

Наведена уговорна цена је и фиксна са урачунатим ПДВ-ом по стопи од 20 %.

Члан 4.

Уплату уговореног износа Наручилац је дужан да плати Извођачу авансно.

Исплату уговорених износа Наручилац ће извршити уплатом на текући рачун Извођача на бр. 840-1613666-12 код Управе за јавна плаћања Филијала Стари Град.

Члан 5.

У свему осталом што није предвиђено овим уговором важе одредбе Закона о облигационим односима.

Члан 6.

Уговорне стране се споразумевају да све спорове настале из реализације овог уговора решавају споразумно.

Члан 7.

Овај уговор је сачињен у 4 (четири) истоветна примерка, од којих су по 2 (два) за сваку уговорну страну.

Руководилац пројекта
Др Томислав Тришовић

За Извођача
Директор
Академик Зоран Ђурић

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ
основан 1947.г

____
печат и потпис

За Наручиоца
Директор
Бојан Маравић

____
печат и потпис

BASATA d.o.o.
Beograd, Dobračina 59b
Tel/fax: 011/263 43 78, 263 49 34,
292 87 35, 292 87 38;
Mob: 063/33 95 29, 064 13 888 15
e-mail: basatabazeni@eunet.rs
website: www.basata.co.rs

IZJAVA

Ovim potvrdjujemo da Tomislav Trisovic, sa nama saradjuje na problematici tretmana

Vode u bazenima za kupanje.

Beograd,10.10.2014.

BASATA DOO

Direktor, Kolakovic Tatjana

• **Hidrosanitas** • d.o.o.
PREDUZEĆE ZA TRETMAN VODA
BEOGRAD, Bulevar despota Stefana 68 b, Tel/Fax 011/2765-777, 2764-161
PIB: SR 100122128 Tekući račun: 220-2208-64

Tomislav Lj. Trišović

Beograd
Mirijevski Venac 6/22

Beograd, 09.10.2014. godine

Na zahtev Tomislava Lj. Trišovića, višeg naučnog savetnika u Institutu tehničkih nauka Srpske akademije nauka, Preduzeće za tretman voda "Hidrosanitas" d.o.o., sa sedištem u Beogradu, Bulevar despota Stefana 68-b, izdaje sledeću:

POTVRDU

Kojom se potvrđuje da Tomislav Lj. Trišović učestvuje kao konsultant i saradnik na izradi projektno tehničke dokumentacije postrojenja za pripremu vode za piće, postrojenja za tretman otpadnih voda i nadzoru na izvođenju radova.

Direktor,
Miljković Milorad

"ХИДРОСАНИТАС" Д.О.О.

AQUAPUR
PROGRAM ČISTE VODE

d.o.o.KOSJERIĆ 31260 Kosjerić,Nikole Tesle 14
031/783-103, 064/6467-593 , 062/8799-360
mat.br. 20395958, PIB 105489094,t.rač. 205-128723-76
www.aquapur.rs aquapur@aquapur.rs

Kosjerić
09.10.2014

IZJAVA O SARADNJI

Izjavljujemo da već duže vreme poslovno saradjujemo sa firmom AQUA CRYSTAL doo iz Beograda i od njih kupujemo uredjaje za elektrohlorinaciju HIPOGEN tip SC. Uredjaji se instaliraju na bazenima za kupanje, koje mi proitzvodimo i ugradjujemo, u cilju dezinfekcije bazenske vode. Veoma smo zadovoljni kvalitetom i učinkom uredjaja, a posebno ističemo dobro rešenje za bilo kakav servis.

Takodje sa G-dinom Tomislavom Trisovicem saradjujemo na projektovanju, iznalaženju tehnoloških rešenja, konstrukciji za našu proizvodnju i izvodjenju postrojenja za preradu otpadnih voda. (www.aquapur.rs)

Direktor

MgA Vidan Vranešević

AQUAPUR
D.O.O.
KOSJERIĆ

AQUA
LINES

PREDMET: Potvrda o saradnji

Privredno društvo AQUA LINES d.o.o. Beograd, Krunska 54, ogranak Kosjerić, Nikole Tesle 10 nabavlja od firme Aqua crystal doo uređaje za elektohlorinaciju HIPOGEN tip SC. Uređaji se instaliraju na bazenima za kupanje u cilju dezinfekcije vode. Takođe sa Tomislavom Trišovićem sarađujemo na projektovanju i izvođenju postrojenja za preradu otpadnih voda i izrade uređaja za proizvodnju aktivnog hlora velikih kapaciteta.

AQUA LINES d.o.o.
Dušan Radosavljević
direktor

AQUA LINES D.O.O.

KRUNSKA 54
11000 BEOGRAD
SRBIJA

TEK.RAČ. 205 - 205320 - 78
PIB SR 108433631
MAT.BR. 20998580
aqualines.nenad@gmail.com
www.aqualines.net

TEL/FAX: 031 784 120
MOB: 060 640 83 89
063 815 24 89

BETA GROUP
princip slane vode
ZASTUPNIK ZA : WINNMAR INDUSTRIES & BETA POOLS S.A.
PIB:**100219682**
Sanje Zivanovic 25, Beograd
tel/Fax : 011/ 8062404
mob. tel : 062/ 278987
www.betabazeni.co.rs

Beograd,10.10.2014.god.

From:Beta group

Subject:POTVRDA

Preduzece Beta group d.o.o., Beograd u saradnji sa Tomislavom Trisovicem proizvodi elektode i elektohlorinatore tipa S koje se koriste kod tretmana vode u bazenima za kupanje sa slanom vodom.
Uredjaji se instaliraju na bazenima za kupanje u cilju dezinfekcije vode.

Za Beta group

"BETA GROUP"
d.o.o.
BEOGRAD

Прилог 13. Предавање по позиву

CHAMBER OF
COMMERCE AND
INDUSTRY OF SERBIA
1857

01-5/7

SOUTH EAST EUROPE
Transnational Cooperation Programme

NO-BLE Ideas

Programme co-funded by the
EUROPEAN UNION

Belgrade, 3 February 2014

Dear Sir/Madam,

It is our pleasure to invite you to the scientific and technical conference, within the framework of implementation of the project Network of Young Innovators in the Agro-Food Sector (NO-BLE Ideas Network), "Using Knowledge to enhance the Agro-Food Sector in Serbia", which will be held on 28 February 2014 at the Chamber of Commerce and Industry of Serbia, Terazije 23, Large Hall, 2nd floor, at 11:00AM.

The Chamber of Commerce and Industry of Serbia is a partner on the IPA Project Network of Young Innovators in the Agro-Food Sector-NOBLE Ideas, implemented with 13 partners from 7 countries through the South East Europe Transnational Cooperation Program.

The aim of the Project is to improve cooperation between the scientific and the business sectors through development and promotion of innovative ideas in the agro-food sector in order to transfer knowledge and technologies and link science and economy, improve competitiveness of enterprises and comply with the EU legal regulations in the field of agriculture. Visibility of new innovative ideas is guaranteed by international presentations and the transnational competition, which provide an opportunity for young researchers-innovators to present their projects to companies and interested investors, who will support the most valuable ideas by financing pilot projects.

Eminent academics and scientists from university schools and institutes and successful innovation firms have been invited to the Conference, who will present the results of researches and support to implementation of innovation in economy.

We believe that the subject of the Conference will excite your attention and that you will be interested in participating in the Conference and the NOBLE Ideas project.

With regards,

Željko Sertić

President
Chamber of Commerce and Industry of Serbia

Young InNOvators Network for SustainaBLE Ideas in the Agro-Food Sector, NO-BLE Ideas
South East Europe Transnational Cooperation Programme, 4th Call, Ref. No. SEE/D/0335/1.3/X

Conference

Using Knowledge to enhance the Agro-Food Sector

28 February 2014
Chamber of Commerce and Industry of Serbia, Large Hall, 2nd floor, Terazije 23, Belgrade

AGENDA

11:00 – 11:30	**PARTICIPANT REGISTRATION**
11:30 – 12:00	**WELCOME ADDRESS AND KEYNOTE SPEECH** **Željko Sertić**, President of the Chamber of Commerce and Industry of Serbia **Dragan Glamočić**, Minister of Agriculture, Forestry and Water Management **Representative** of the Ministry of Education, Science and Technological Development
12:00 – 12:15	**Young InNOvators Network for SustainaBLE Ideas in the Agro-Food Sector, NO-BLE Ideas, IPA Project** **Danica Mićanović, PhD**, Country Project Manager, CCIS
12:15 – 12:30	**The role of research and new developments in vegetable crops** **Bogoljub Zečević, PhD**, Director of Institute for Vegetable Crops, Smederevska Palanka
12:30 – 12:45	**Contribution of knowledge to improvements in fruit-growing in Serbia** **Svetlana Paunović, PhD**, Director of Fruit-Growing Institute in Čačak
12:45 – 13:00	**Beet juice as a product of a new technological process and entry in the EU market** **Nataša Milanović**, CEO of BIOSIL D.O.O.
13:00 – 13:30	**COFFEE BREAK**
13:30 – 13:45	**Using NS small grain seeds to increase the competitiveness of crop-raising in Serbia** **Prof. Novo Pržulj, PhD,** Head of Small Grains Department at the Institute of Field and Vegetable Crops Novi Sad
13:45 – 14:00	**Water as the source of life – Extraction and purification of ground water** **Prof. Tomislav Trišović, PhD,** CEO of AQUA CRYSTAL D.O.O.
14:00 – 14:30	**Innovative projects by NO-BLE members:** • **Aleksandra Ivetić, MSc**, Use of dry ice in ensilage of fodder • **Marko Kostić**, Use of BioSticks in the nutrition of home-grown plants • **Ivan Karman**, Expert Agriculture Network
14:30 – 14:45	**Education and knowledge** **Prof. Miladin Kostić, PhD**, Dean of State University of Novi Pazar
14:45 – 15:00	**HORIZON 2020** **Prof. Viktor Nedović, PhD**, Head of HORIZON 2020 Working Party, University of Belgrade
15:00	**COCKTAIL**

Прилог 14. Чланство у уређивачким одборима

EMIT

economics management information technology

Volume 3/ Number 1 / 2014 ISSN 2217-9011 e-ISSN 2334-6531

ČITAONICA EVROPA
Civic Library Europe

www.emit.kcbor.net

ISSN 2217-9011
9772217901005

EDITOR IN CHIEF

- **Editor** - Ph.D. Radmilo Nikolić (Technical Faculty in Bor, University of Belgrade, Serbia)
- **Co-Editor** -Ph.D. Snežana Urošević (Technical Faculty in Bor, University of Belgrade, Serbia)
- **Tehnical Editor** -Zvonko Damnjanović (Technical Faculty in Bor, University of Belgrade, Serbia)
- **Secretary** - Aleksandra Fedajev (Technical Faculty in Bor, University of Belgrade, Serbia)
- **Lector** - Bojana Pejčić (City of Nis, City Administration, Local Economic Development Office, Serbia)

Editorial board

- Ph.D. Vitomir Milić (Technical Faculty in Bor, University of Belgrade, Serbia)
- Ph.D. Dragan Mihajlović (Faculty of Management Zaječar, Megatrend University, Belgrade, Serbia)
- Ph.D. Drago Cvijanović (Institute of Agricultural Economics Belgrade, Serbia)
- Ph.D. Ivana Mladenović-Ranisavljević (Faculty of Technology, Leskovac, University of Niš, Serbia)
- Ph.D. Vidoje Stefanović (Faculty of Science and Mathematics - University of Niš, Serbia)
- Ph.D. Gordana Kokeza (Faculty of Technology and Metallurgy, Belgrade, University of Belgrade, Serbia)
- Ph.D. Jasmina Stevanović (Institute of Chemistry Technology and Metallurgy IHTM, Belgrade,Serbia)
- Ph.D. Dragan Đorđević (Faculty of Technology, Leskovac, University of Niš, Serbia)
- Ph.D. Milan Stamatović (Faculty of Management, Metropolitan University, Belgrade,Serbia)
- Ph.D. Goran Demboski (Faculty of Technology and Metallurgy, "St. Cyril and Methodius" University, Skopje, (FYROM)
- Ph.D. Miloš Sorak (Faculty of Technology Banja Luka, University of Banja Luka, Bosnia and Herzegovina)
- Ph.D. Miomir Pavlović (Faculty of Technology Zvornik, University of Eastern Sarajevo, Bosnia and Herzegovina)
- Ph.D. Vasyl H. Gerasymchuk (National Technical University of Ukraine “Kiev Polytechnic Institute”, International Economy Department, Kiev, Ukraine)
- Ph.D. Zlatina Kazlacheva (Faculty of Technics and Technologies, Yambol, Trakia University, Bulgaria)
- Ph.D. Bruno Završnik (Faculty of Economics and Business, Maribor, University of Maribor, Slovenia)
- Ph.D. Liliana Indrie (Faculty of Energy Engineering and Industrial Management, University of Oradea, Oradea, Romania)
- Ph.D. Zoran Stojković (Faculty of Management Zaječar, Megatrend University, Belgrade, Serbia)
- Ph.D. Dejan Riznić (Technical Faculty in Bor, University of Belgrade, Serbia)
- Ph.D. Tomislav Trišović (ISANU, Belgrade, Serbia)
- Ph.D. Aleksandar Grujić (Institute of Chemistry Technology and Metallurgy, IHTM, Belgrade, Serbia)
- Ph.D. Andon Kostadinović (High School for Transportation Management, Niš, Serbia)
- Ph.D. Miroslav Ignjatović (Institute of Mining and Metallurgy Bor, Serbia)

Прилог 15. Рецензија

Грешни Милоје

РАЗГОВОР
СА АКАДЕМИКОМ ЈОВАНОМ ДЕРЕТИЋЕМ
О СТАЊУ У СРБСКОЈ ПРАВОСЛАВНОЈ ЦРКВИ

РЕВНИТЕЉ
Ниш, 2014.

Грешни Милоје
РАЗГОВОР СА АКАДЕМИКОМ ЈОВАНОМ ДЕРЕТИЋЕМ
О СТАЊУ У СРПСКОЈ ПРАВОСЛАВНОЈ ЦРКВИ

Рецензент
Проф. др Томислав Тришовић

Библиотека
Братољубље

Сниматељ и монтажер
Дејан Васић
Ројал продукција
Косовска Митровица
децембар, 2013.

Транскрипт сачиниле
Наташа Лепосавић
и Весна Јовановић

Коректор
Љубица Наранчић

Фотографије
Дејан Васић

Припрема и штампа
Драслар партнер, Београд

Издавач
РЕВНИТЕЉ Ниш

Тираж
1.000 примерака

Разговор се може видети на следећем линку:
http://www.youtube.com/watch?v=xzaqzKPRLL8
или
уписивањем на youtube у простор за претрагу речи:
Грешни Милоје и академик Јован Деретић