

# STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF $\text{LiFePO}_4/\text{C}$ COMPOSITES OBTAINED THROUGH ULTRASOUND ASSISTED SYNTHESIS

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## ABSTRACT

Olivine structure  $\text{LiFePO}_4/\text{C}$  composite powders were prepared by combining sonochemical precipitation and calcination at three different temperatures. A polyvinyl alcohol solution was used as the source of an in situ formed carbon. The crystal structures of the powders were revealed by X-ray powder diffraction. Electrochemical properties of the powders calcined at different temperatures were discussed. It was shown that optimal electrochemical performance may be attained by using slightly reductive atmosphere and moderate temperature of 600 °C.

## INTRODUCTION

Lithium iron phosphate has become of great interest as storage cathode for rechargeable lithium batteries because of its high energy density, low raw materials cost, environmental friendliness and safety. At this time, the main obstacle for reaching the theoretical performances of  $\text{LiFePO}_4$  at ambient temperature is its very low electronic conductivity. Possible means to overcome this major problem are the synthesis of a  $\text{LiFePO}_4$ /electronic conductor composite compound to increase the extrinsic electronic conductivity, doping with supervalent cations, and the achievement of a small and homogeneous particle size distribution [1]. Here is presented novel synthesis route for obtaining composite powders made of olivine-type lithium iron phosphate and carbon combining sonochemical precipitation and calcination. Electrochemical properties of the powders calcined at different temperatures were discussed.

## XRD MEASUREMENTS

X-ray powder diffraction patterns (Figure 1) revealed the differences between powders obtained by varying the calcination temperature. In all cases, powders of phospho-olivines with or without impurities were obtained. It was shown that combining 500 or 600 °C with slightly reductive atmosphere resulted in single-phased olivine type  $\text{LiFePO}_4$  powders with no detectable Fe(III) impurities. On the other hand, the temperature increase (700 °C) caused the formation of another phase  $\text{Fe}_2\text{P}$  beside olivine type  $\text{LiFePO}_4$ . Apparently, reductive atmosphere together with the organic component in the precursor facilitate the reduction of phosphates into phosphides at 700 °C. There is no evidence for the formation of crystalline carbon, so internal carbon in all samples could be treated as a contribution to the background. The amount of an in situ formed carbon was determined by heating the powder in air, and the estimated value was 5wt%. The in situ formed carbon partly coated  $\text{LiFePO}_4$  particles as shown elsewhere [3].

## EXPERIMENTAL

The reaction mixture, consisting of 30 ml of 1wt% polyvinyl alcohol (PVA) aqueous solution, 25 ml of 0.2 M aqueous solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and appropriate amount of solid  $\text{Li}_3\text{PO}_4$ , was exposed to the ultrasound irradiation. The above mixture was sonicated for one hour by a Vibracell sonicator VCX 750 (Sonics & Materials Inc.) operating at 20 kHz, while reductive gas (75% Ar and 25%  $\text{H}_2$ ) was bubbled through it. The reaction product was centrifuged, washed with isopropanol, dried at 120 °C under vacuum and calcined at three temperatures 500, 600 and 700 °C, in a slightly reductive atmosphere (95% Ar and 5 %  $\text{H}_2$ ) for 1.5 hour. A PVA solution was used as a source of carbon which would enhance the electronic conductivity and suppress particle growth.



## ELECTROCHEMICAL MEASUREMENTS

Electrochemical performance of each sample, used as a cathode of a Li-ion battery, was examined by charge-discharge tests. The cyclings were done between 2.7 and 4.1 V and the current density was 59.7 mAh/g which corresponds nearly to C/3 rate. The discharge curves are shown in Figure 2. The best electrochemical performances showed the powder calcined at 600 °C, reaching 100 mAh/g at the end of the fiftieth cycle with excellent capacity retention, while the powder calcined at 700 °C showed slightly lower capacity, which is approximately proportional to the amount of pure  $\text{LiFePO}_4$  present in the samples. Powder calcined at 500 °C showed drastically different electrochemical behavior. Such different properties are probably consequences of lower crystallinity of the powder calcined at 500 °C, considering larger full width at half maximum observed in the XRD pattern of the specimen.

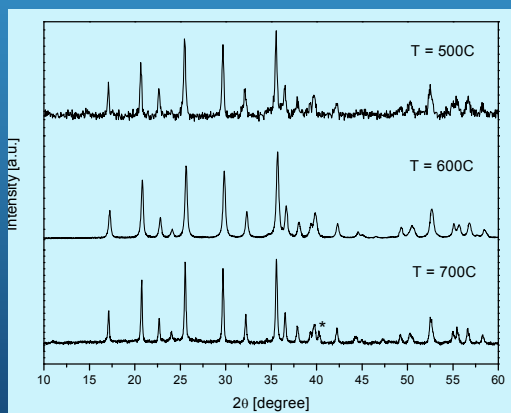


Figure 1. XRD patterns of composites  $\text{LiFePO}_4/\text{C}$  prepared by using sonochemical reaction with additional thermal treatment at 500, 600, and 700 °C, from the top to the bottom of the picture, respectively. Peak position of  $\text{Fe}_2\text{P}$  phase is marked with asterisk.

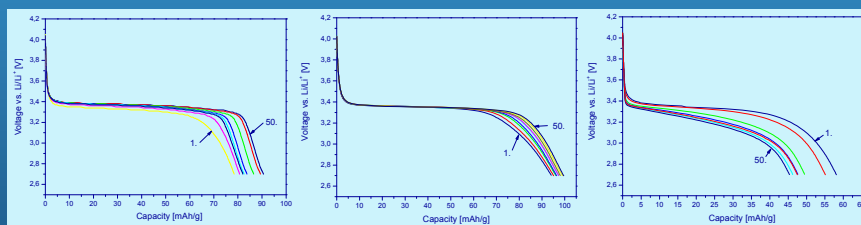


Figure 2. Discharge curves of  $\text{LiFePO}_4/\text{C}$  samples obtained by the use of sonochemical reaction with calcination at 500, 600, and 700 °C from the left to the right of the picture, respectively. Current density was C/3.

## CONCLUSION

Olivine structured  $\text{LiFePO}_4/\text{C}$  composites can be successfully synthesized by combining sonochemical precipitation and calcination. It was found that 600 °C is optimal temperature for obtaining powder of high purity with acceptable electrochemical performances. This method may also be suitable for selective doping with supervalent cations to increase the intrinsic electronic conductivity of  $\text{LiFePO}_4$  powder.

## REFERENCES:

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