

# Ultrasound assisted synthesis of nanostructured LiFePO<sub>4</sub>/C composite

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**ABSTRACT** 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 LiFePO<sub>4</sub> at ambient temperature is its very low electronic conductivity. Several possible means to overcome this major problem were recently explored: the synthesis of a LiFePO<sub>4</sub>/electronic conductor composite compound, selective doping with supervalent cations to increase the intrinsic electronic conductivity, and the achievement of a small and homogeneous particle size distribution. Here we present synthesis conditions and properties of nanostructured LiFePO<sub>4</sub>/C composite. Olivine-type lithium iron phosphate partially carbon coated particles were obtained by ultrasound assisted synthesis. A polyvinyl alcohol solution was used as the source of an in situ formed carbon. The as-prepared powders were shortly heat-treated at various temperatures under slightly reductive atmosphere. X-ray powder diffraction confirmed the phase purity. X-ray powder diffraction data were used for the crystal structure refinements, based on Rietveld full profile method. All relevant structural and microstructural crystal parameters that could be significant for electrochemical intercalation/deintercalation processes were determined. Electrochemical characteristics were evaluated by using galvanostatic charge/discharge tests. Particle morphologies of the obtained powders were determined by both scanning and transmission electron microscopies.



## SYNTHESIS

The sonochemical reaction was carried out in a reaction vessel which was provided with two side openings for passing gas through the reaction mixture. The reaction mixture, consisting of 30 ml of 1wt% polyvinyl alcohol (PVA) aqueous solution, 25 ml of 0.2 M aqueous solution of FeSO<sub>4</sub>·7H<sub>2</sub>O, and appropriate amount of solid Li<sub>3</sub>PO<sub>4</sub>, 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% H<sub>2</sub>) was bubbled through it. The reaction product was centrifuged, washed with isopropanol, dried at 120 °C under vacuum, and calcined at 600 °C in a slightly reductive atmosphere (95% Ar and 5% H<sub>2</sub>) for 1.5 hours.

## XRD MEASUREMENTS

X-ray diffraction data were collected on a Philips PW 1050 diffractometer with Cu-Kα<sub>1,2</sub> radiation (Ni filter) at the room temperature. Measurements were done in 2θ range of 10-120° with scanning step width of 0.02° and 12 s time per step. Crystal structure refinement was based on the Rietveld full profile method using the Koalariet computing program. The refinement results show that sonochemical reaction gave sample that is well crystallized as single-phase phospho-olivine, without any impurities at detectable level. There is no evidence for the formation of crystalline carbon, so internal carbon 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 structure of the LiFePO<sub>4</sub> powder has been refined in the space group Pnma (D<sub>2h</sub><sup>16</sup>) in olivine type. The observed and calculated X-ray diffraction profiles are given in Figure 1, while the main results of the final Rietveld refinement are presented in Table 1. The cell parameters obtained from Rietveld refinement are a = 10.3149(6) Å, b = 5.9984(4) Å, c = 4.7010(3) Å, and volume V = 290.86(3) Å<sup>3</sup>, consistent with literature data obtained for the powder synthesized by solid state reaction. The Rietveld refinement also showed additional electron density on the lithium sites, indicating 3 at.% iron on the lithium site. Microstructural parameters data showed that sonochemical method is convenient for obtaining small particles of LiFePO<sub>4</sub>, which are suitable for ensuring a good connection with a conductive carbon.

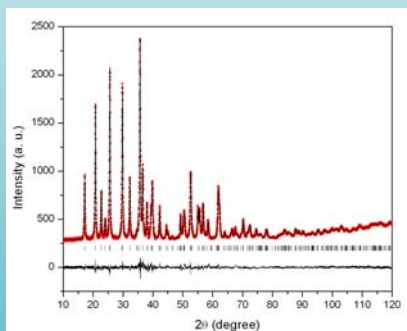


Fig. 1. The observed (red), calculated (black), and difference (bottom) X-ray diffraction data of LiFePO<sub>4</sub> taken at room temperature. Vertical markers below the diffraction patterns indicate positions of possible Bragg reflections.

Table 1. The final results of the structural refinement for LiFePO<sub>4</sub> sample.

s.g. Pnma	LiFePO <sub>4</sub> /C
Lattice parameters [Å]	a = 10.3149(6) b = 5.9984(4) c = 4.7010(3)
Primitive cell volume [Å <sup>3</sup> ]	V = 290.86
Mean crystallite size [nm]	70(5)
Microstrain [%]	0.23(2)
Li site occ. by Fe [%]	3
R factors [%]	R <sub>wp</sub> 3.2 R <sub>B</sub> 2.3

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## SCANNING AND TRANSMISSION ELECTRON MICROSCOPIES

Figure 2a shows particle morphology of the sample revealed by scanning electron microscopy. The particles are irregular in shape and agglomerated, with mean size 200-300 nm. By comparing these results with the mean crystallite size of 70 nm obtained from XRPD analysis (Table 1) it can be concluded that polycrystalline particles are composed of large number of crystallites. More detailed analysis of particle microstructure was accomplished using TEM images. Due to pronounced particle agglomeration, grain boundaries are not quite clear, and within a relatively broad grain size distribution, average grain size was estimated to be about 30 – 40 nm. On the thin particle edges (Figure 2b) carbon film with a typical thickness of several nanometers can be observed. We believe that this carbon layer is responsible for improved electrical conductivity.

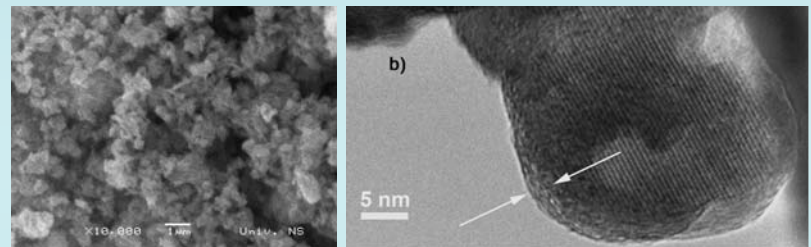


Fig. 2a SEM micrograph of composite LiFePO<sub>4</sub>/C powder. Fig. 2b TEM image of LiFePO<sub>4</sub>/C powder. Arrows point out 2-3 nm thick layer of amorphous carbon.

## CHARGE / DISCHARGE TESTS

Electrochemical performance of the 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 mA/g, which correspond nearly to C/3. It is interesting to notice that discharge capacity increases during cycling, starting from the value of 94.1 mAh/g for the first cycle and reaching 99.5 mAh/g at the end of the fiftieth cycle (inset of Fig.3). During structural refinement, it was shown that part of lithium sites (3%) are occupied by iron ions. Iron ion positioned on lithium site could block the whole channel and prevents lithium motion, leaving isles of LiFePO<sub>4</sub> domains in the FePO<sub>4</sub> surround, and causing smaller specific capacity as a result. Capacity increase observed during cycling suggests structural relaxation most likely through ordering of the iron ions. This may be the explanation for the decrease in microstrain observed in cycled material.

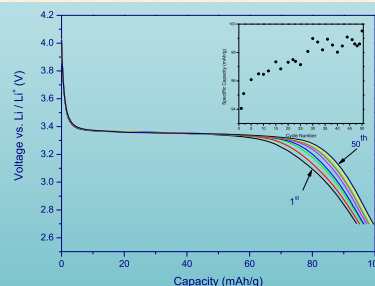


Fig. 3 Cycle performance for LiFePO<sub>4</sub>/C at C/3 rate. The inset shows capacity vs. cycle number.

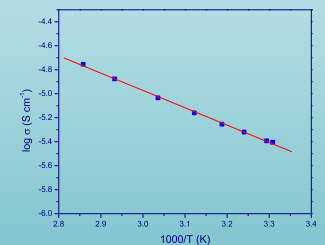


Fig. 4 Arrhenius plot of electrical conductivity for synthesized sample.

## CONDUCTIVITY MEASUREMENTS

The measured a.c. conductivity data were arranged in a standard Arrhenius plot  $\sigma = \sigma_0 \exp(-E_a/kBT)$  (Figure 4), where  $E_a$  is the activation energy. These results show an usual increase of the conductivity with increasing temperature. The observed room temperature value was within the order of magnitude of 10<sup>-6</sup> S cm<sup>-1</sup>, which is notably higher than 10<sup>-9</sup> S cm<sup>-1</sup> characteristic of the carbon-free LiFePO<sub>4</sub> sample. Furthermore, plot of log(σ) vs. 1/T was found to be linear in the temperature range considered.

## CONCLUSION

We have shown that olivine nano-structured LiFePO<sub>4</sub>/C composite can be successfully synthesized combining sonochemical precipitation and calcination. The main advantage of this method is the formation of an in situ C-coated LiFePO<sub>4</sub> nanostructured powder of high purity, which provides homogeneous material with improved electrical conductivity. This method may also be suitable for selective doping with supervalent cations to increase the intrinsic electronic conductivity of LiFePO<sub>4</sub> powder.