



## Solid state synthesis and characterization of LiFePO<sub>4</sub>/C as cathode material for Li-ion batteries

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**Abstract:** Lithium transition metal phosphates have been recognized as potential positive electrodes for use in large scale production of lithium ion batteries, specially due to high thermal and chemical stability. Amongst all positive electrode materials, such as Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, LiMnPO<sub>4</sub>, LiVPO<sub>4</sub>F, the olivine LiFePO<sub>4</sub> has the most promising characteristics. The LiFePO<sub>4</sub>/C composite was synthesized by solid state reaction using LiOH as source of lithium ion, stearic acid which acts as reductive agent and carbon source and FePO<sub>4</sub> precursor prepared from FeSO<sub>4</sub>·7H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The starting materials were mixed in stoichiometric ratio and heated at 700°C under N<sub>2</sub> flow to form the composite LiFePO<sub>4</sub>/C. Properties of synthesized material were analyzed by Raman spectroscopy, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Raman spectral analysis indicated some amorphous sp<sup>3</sup> bonded carbon, sp<sup>2</sup> graphite like phase and presence of carbides. Cyclic voltammograms confirmed good reversibility of intercalation and deintercalation of lithium ions from structure. Impedance response of the cells consisted of a depressed semicircle in the high frequency region, which is attributed to the charge-transfer process and sloping line in low frequency region which corresponds to the Warburg impedance.

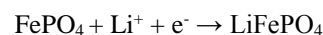
## INTRODUCTION

In the past few decades, over-consumption of fossil fuels led to serious environmental issues and depletion of their reserves. High demand for replacement of these sources of energy with renewable ones, has directed researchers toward lithium ion batteries. Outstanding performance of lithium ion batteries makes them attractive for wide range of applications, such as portable electronic devices, electric vehicles and hybrid electric vehicles.

Active material for positive electrode is one of the most important parts of the battery, which mostly determines its cost and performance. Many cathode materials have been subjects of studies over years and they include different classes of crystal structures: layered (LiCoO<sub>2</sub>), spinel (LiMn<sub>2</sub>O<sub>4</sub>) and olivine (LiFePO<sub>4</sub>) frameworks (Julien et al., 2014). However, iron-based compounds containing phosphate anion have been under intense research since 1997, when Goodenough and co-workers proposed LiFePO<sub>4</sub> as the most promising candidate for

cathode material in lithium ion battery (Padhi et al., 1997).

The discharge reaction for LiFePO<sub>4</sub> includes intercalation of lithium ion along with an equivalent number of electrons into the electrode material:



Olivine structured LiFePO<sub>4</sub> has significant advantages, such as high theoretical capacity (170 mAhg<sup>-1</sup>), low cost, nontoxicity, long cycle life and superior thermal and chemical stability. In the case of overoxidation (overcharge), phosphate group stabilizes the structure and material does not release oxygen (Kurzweil and Brandt 2009), which makes it safer than commercial, oxide based materials. Nevertheless, LiFePO<sub>4</sub> suffers from low electronic conductivity (<10<sup>-9</sup> Scm<sup>-1</sup>) and low diffusion coefficient of lithium ion, which is close to D = 10<sup>-14</sup> cm<sup>2</sup>s<sup>-1</sup> (Julien et al., 2014).

Coating  $\text{LiFePO}_4$  particles with carbon results in better electrochemical performance. This is usually achieved by adding carbon source during calcination in inert atmosphere. The presence of carbon may also limit particle growth, which ensures short lithium ion diffusion paths within positive electrode. Carbon source acts also as reducing agent and suppresses formation of  $\text{Fe}^{3+}$  impurities (Wang *et al.*, 2012). Recently, several studies have shown that doping with polyvalent metal ions can stabilize the crystal structure, improve electronic conductivity and reduce internal impedance of the cell, due to the enlarged lattice volume that provides more space for lithium ion transfer (Zhang *et al.*, 2011). In order to enhance electrochemical performance of  $\text{LiFePO}_4$ , optimization of synthetic procedure is necessary. Several preparative methods are commonly used, such as solid state reaction, sol-gel method, coprecipitation and hydrothermal processes (Koltypin *et al.*, 2007).

In this work,  $\text{LiFePO}_4/\text{C}$  cathode material was synthesized by solid-state reaction, after preparation of  $\text{FePO}_4$  precursor by inorganic synthesis procedure. Stearic acid was added as carbon source as well as reducing agent. In order to control particle size, stearic acid was added during calcination at high temperature in inert atmosphere.  $\text{LiFePO}_4/\text{C}$ -Li half cells were fabricated in an argon-filled glove box. Properties of synthesized material were analyzed using Raman spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy.

## EXPERIMENTAL

### Synthesis of precursor ( $\text{FePO}_4$ )

$\text{FePO}_4$  precursor was prepared using low cost  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$  (Merck) and  $\text{NH}_4\text{H}_2\text{PO}_4$  (Merck) as raw materials. Aqueous solutions of  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  were mixed together in stoichiometric amounts, and pH value was adjusted to 9 by adding  $\text{NH}_3 \times \text{H}_2\text{O}$ . In order to obtain  $\text{Fe}_3(\text{PO}_4)_2 \times 8\text{H}_2\text{O}$  precipitate, mixture was stirred for 30 minutes at room temperature. The precipitate was dissolved in  $\text{H}_3\text{PO}_4$  (Merck, p.a.) and  $\text{H}_2\text{O}_2$  (Sigma-Aldrich, p.a.) is added as oxidizing agent, as well as  $\text{NH}_3 \times \text{H}_2\text{O}$  for adjustment of pH value to 9. The mixture was stirred for 6 hours at  $90^\circ\text{C}$  and bright yellow precipitate of  $\text{FePO}_4 \times 2\text{H}_2\text{O}$  is obtained. Afterwards,  $\text{FePO}_4 \times 2\text{H}_2\text{O}$  was dried at  $120^\circ\text{C}$  for 5 hours, followed by drying at  $500^\circ\text{C}$  for 6 hours and final precursor  $\text{FePO}_4$  was formed.

### Preparation of $\text{LiFePO}_4/\text{C}$

Composite material was prepared by solid state reaction. Stearic acid was dissolved in isopropanol (Carlo Erba) to form transparent solution and added to  $\text{LiOH}$  (Sigma-Aldrich) powder. The mixture was stirred and homogenised in mortar. The precursor,  $\text{FePO}_4$ , was added to previous mixture along with 100 mL of isopropanol. The molar ratio of  $\text{FePO}_4$  and  $\text{LiOH}$  was 1:1, but excessive amount of  $\text{LiOH}$  was added to compensate the loss of Li during calcination. Isopropanol was removed from mixture by heating it up to  $50^\circ\text{C}$  for 72 hours, under continuous stirring at moderate speed. The obtained paste was dried at  $70^\circ\text{C}$  for 6 hours. Carbon coating of  $\text{LiFePO}_4$  material was carried out in the tube furnace at  $700^\circ\text{C}$

under nitrogen flow for 6 hours. The obtained composite,  $\text{LiFePO}_4/\text{C}$  was cooled down to room temperature, under inert atmosphere.

### Electrochemical measurements

Electrochemical characterization was conducted using PAR263A potentiostat/galvanostat, connected to PowerCV software. All electrochemical measurements were carried out at room temperature.

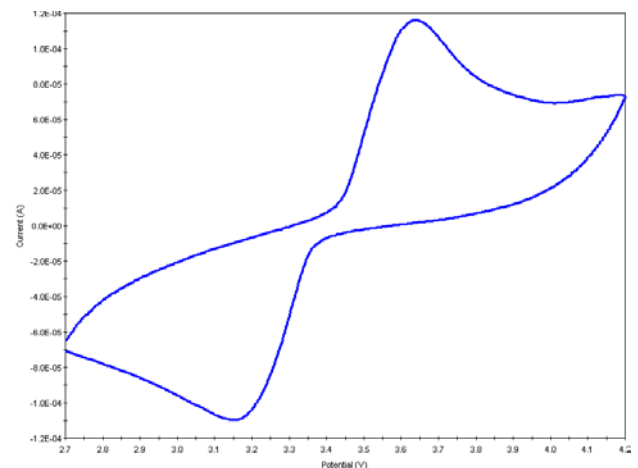
The working electrode was prepared by mixing the active material with graphite and poly(vinylidene fluoride) in a weight ratio of 80:10:10 dissolved in an appropriate amount of dimethylformamide (DMF) to make slurry, using ultrasound treatment. The slurry was coated on aluminum foil current collector using automatic film-coating equipment, with controlled thickness of  $300 \mu\text{m}$  and dried at  $180^\circ\text{C}$  for 3 hours. Afterwards, the electrode was cut into round samples of required size.

Metallic lithium foil was used as reference and counter electrode. The electrolyte was composed of  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$  in a 1:1 solvent mixture of propylene carbonate (PC) and dimethyl carbonate (DMC). Commercial three-electrode Gamry cell was assembled in an argon-filled dry glove box, followed by electrochemical testing outside the glove box.

Cyclic voltammetry was measured at scan rates of  $0.1$  and  $1 \text{ mVs}^{-1}$  between  $2.7$  and  $4.2 \text{ V}$ . Electrochemical impedance spectroscopy was performed by applying a  $10 \text{ mV}$  amplitude signal in the frequency range of  $10^5$ - $10^2 \text{ Hz}$ .

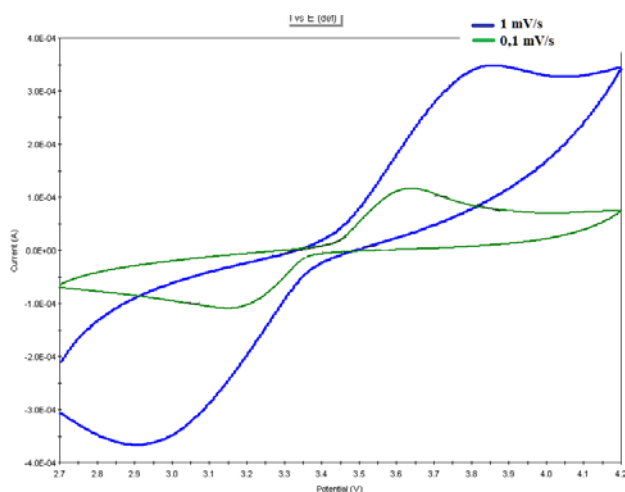
## RESULTS AND DISCUSSION

Figure 1 shows a cyclic voltammogram of  $\text{LiFePO}_4/\text{C}$  measured at room temperature, at scan rate of  $0.1 \text{ mVs}^{-1}$ . As shown in figure 1, oxidation and reduction peaks appear at  $3.64$  and  $3.15 \text{ V}$  vs.  $\text{Li}/\text{Li}^+$ . These redox reaction peaks correspond to the insertion (discharge reaction) and extraction (charge reaction) of lithium ion from  $\text{LiFePO}_4$ . The ratio between anodic and cathodic peak currents is close to 1, implying good reversibility of lithium intercalation into and deintercalation from  $\text{LiFePO}_4/\text{C}$ .



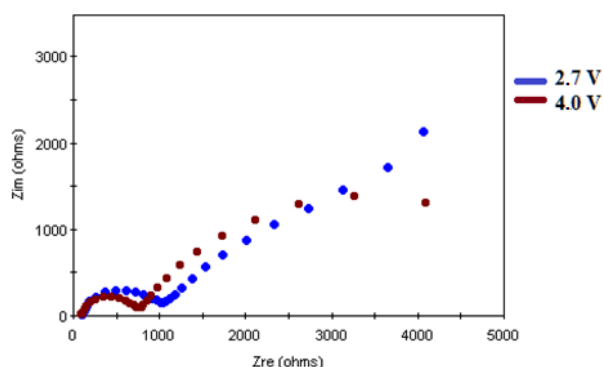
**Figure 1.** Cyclic voltammogram for  $\text{LiFePO}_4/\text{C}$  at scan rate of  $0.1 \text{ mVs}^{-1}$

Figure 2 shows the effect of the potential scanning rate on the cyclic voltammograms, measured at 0.1 and 1 mVs<sup>-1</sup>. The shapes of anodic and cathodic peaks were almost symmetrical in both cases. The anodic peak shifts to higher potential and the cathodic peak shifts to lower potential, which indicates increased kinetic polarization and increased internal resistance.



**Figure 2.** Cyclic voltammogram for LiFePO<sub>4</sub>/C at scan rates of 0.1 mVs<sup>-1</sup> and 1 mVs<sup>-1</sup>

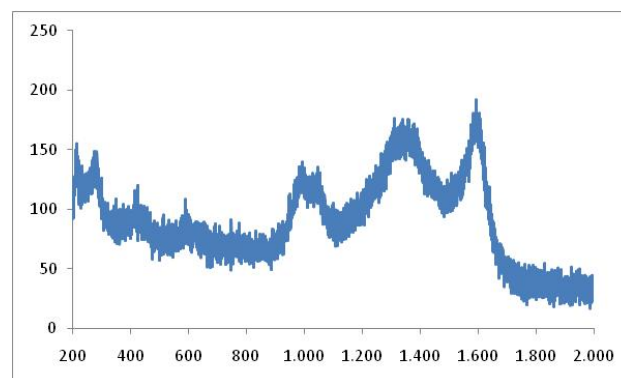
Figure 3 shows Nyquist diagram obtained by electrochemical impedance spectroscopy, at 2.7 and 4.0 V. Both spectra have a depressed semicircle in high frequency region which corresponds to the charge transfer resistance ( $R_{CT}$ ) and an inclined line in low frequency region which represents Warburg impedance or lithium ion diffusion resistance. As seen from the spectrum, the high frequency impedance of LiFePO<sub>4</sub>/C electrode is lower as Li deintercalation proceeds. At potential of 4.0 V high frequency impedance is about 663  $\Omega$ , whilst high frequency impedance at 2.7 V is about 905  $\Omega$ .



**Figure 3.** Nyquist diagram at 2.7 V and 4.0 V

Two intense broad bands in Raman spectrum at 1395 and 1590 cm<sup>-1</sup> can be assigned to the D and G bands of carbon in the LiFePO<sub>4</sub>/C composite, respectively. Raman modes in the range of 900 to 1150 cm<sup>-1</sup> are due to the stretching mode of PO<sub>4</sub><sup>3-</sup> unit and involve symmetric and asymmetric of P-O bonds. Raman modes observed around 200 cm<sup>-1</sup> indicate presence of iron carbide, Fe<sub>3</sub>C (Kumar et al., 2009). Iron carbide was formed during

calcination at high temperatures, and affects the performance of cathode.



**Figure 4.** Raman spectrum

CV peaks are significantly broader than ideal intercalation/deintercalation peaks, which suggests existence of some difficulties in charge transport. Broadened peaks are present due to the low kinetics mechanism of lithium extraction and insertion in LiFePO<sub>4</sub> crystal structure. Possible cause can be presence of some impurities, particularly iron carbide (Koltypin et al., 2007). Hysteresis in CV peaks increased as scan rate increased, which might be due to an increase in the internal impedance of cell during charge/discharge cycling (Jin et al., 2008).

As seen from figure 3, high frequency response of impedance spectroscopy is higher than expected for LiFePO<sub>4</sub>/C. Possible explanation is weak distribution of carbon on the surface of LiFePO<sub>4</sub> particles. Another reason might be the quality of graphite used for preparation of slurry, with particles size of less than 20  $\mu$ m. Depressed semicircles observed in high frequency region are not complete, which is a strong indication for the slow kinetics of electrode, due to impeded charge transfer (Koltypin et al., 2007). Another explanation for high impedance could be due to the LiPF<sub>6</sub> electrolyte used during electrochemical measurements. Trace HF, which is always present in LiPF<sub>6</sub>, can lead to formation of surface LiF films. These films are resistive to Li-ion migration and their presence probably increases the charge transfer resistance of positive electrode (Koltypin et al., 2007).

## CONCLUSION

LiFePO<sub>4</sub>/C particles have been successfully synthesized by solid state reaction, using FePO<sub>4</sub> precursor prepared by inorganic synthesis. Stearic acid was used as carbon source, and Raman spectrum showed presence of amorphous and graphitic carbon. Calcination at temperature around 700°C led to formation of iron carbide, which significantly deteriorates electrochemical performance. The ratio of anodic and cathodic currents, which is close to 1, indicated good reversibility of lithiation and delithiation processes. Electrochemical measurements indicated slow lithium ion diffusion, which can be observed from broadened CV peaks and incomplete high frequency semicircles.

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## Summary/Sažetak

Zahvaljujući visokoj termičkoj i hemijskoj stabilnosti, katodni materijali na bazi fosfata prepoznati su kao potencijalne pozitivne elektrode za masovnu proizvodnju Li-jonskih baterija. Od svih katodnih materijala na bazi fosfata, kao što su Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, LiMnPO<sub>4</sub>, LiVPO<sub>4</sub>F, olivinski LiFePO<sub>4</sub> pokazuje obećavajuće performanse. Kompozit LiFePO<sub>4</sub>/C sintetiziran je pomoću reakcije u čvrstoj fazi. Kao polazni spojevi korišteni su LiOH kao izvor litijumovog jona, stearinska kiselina koja se koristi kao reducirajući agens i izvor ugljika, te FePO<sub>4</sub> prekursor pripremljen iz FeSO<sub>4</sub>×7H<sub>2</sub>O i NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. Reaktanti su pomiješani u stehiometrijskom odnosu i zagrijani na 700°C u atmosferi azota, pri čemu se dobije LiFePO<sub>4</sub>/C. Karakteristike sintetiziranog materijala analizirane su Raman spektroskopijom, cikličnom voltametrijom i elektrohemijom impedansnom spektroskopijom. Raman spektar pokazao je prisustvo amorfnog sp<sup>3</sup> vezanog ugljika, sp<sup>2</sup> vezanog grafita i karbida. Cikličnom voltametrijom potvrđena je dobra reverzibilnost procesa interkalacije i deinterkalacije litijumovog jona iz strukture. Impedansni spektar sastoji se od polukruga u visoko-frekventnom području, što se pripisuje procesima prenosa naboja, te pravolinijski tok pod približno 45° u odnosu na realnu osu što odgovara difuziono kontroliranim procesima, odnosno Warburgovoj impedansi.