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B E L G R A D E

HYDROTHERMAL SYNTHESIS OF $LiFePO_4$ IN PRESENCE OF DIFFERENT ORGANIC ADDITIVES

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Abstract
In this work we have investigated possibility to obtain pure $LiFePO_4$ powder using different organic additives during hydrothermal synthesis at 180°C. Phase pure phospho olivine was obtained in presence of polyvinylpyrrolidone, while addition of polyvinyl alcohol leads to formation of $LiFePO_4$ with impurities. Impurity phase was successfully avoided by introducing citric acid into reaction vessel. Phase composition was determined by XRPD. Morphology was revealed by particle size analyzer and FESEM.

Introduction
Lithium iron phosphate has become one of the most promising cathode materials for use in lithium ion batteries, but its application still suffers from tough synthesis procedure resulting from instable nature of Fe(II). One of the advanced techniques for $LiFePO_4$ powder preparation is hydrothermal synthesis which is quick and simple process and has low energy consumption. Another advantage of hydrothermal synthesis is possibility of introducing different reductive compounds which can suppress Fe(II) oxidation. As reductive compounds ascorbic acid, citric acid, glucose, sucrose, hydrazine [1, 2] etc were used.

The aim of this work was to investigate the possibility of the hydrothermal synthesis of phase pure pospho- olivine in presence of polyvinylpyrrolidone and polyvinyl alcohol and their influence on particle morphologies.

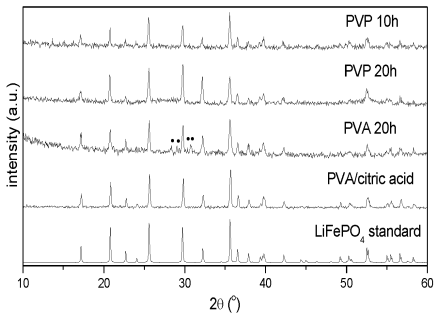

Fig. 1. XRD patern of $LiFePO_4$ powders synthesized with PVP after 10 and 20 hours, with PVA and PVA/citric acid

Experimental
$LiFePO_4$ was prepared by hydrothermal method starting from LiOH, $FeSO_4 \cdot 7H_2O$ and H_3PO_4 in molar ratio 3: 1: 1. First, a desired amount of organic compound i.e. PVP or PVA or PVA/citric acid was dissolved in distilled water. Then H_3PO_4, $FeSO_4$ and LiOH water solutions were added under constant stirring and transferred into the stainless steel autoclave. The precursor solution was purged with argon and heated at 180°C for 10-20 hours. The product was dried at 60°C in air overnight.

The XRPD patterns were recorded using $CuK_{\alpha 1,2}$ radiation in 2θ range 10-60° with the 0.05° step and 2 seconds exposition time. The surface morphology was observed using SUPRA 35 VP Carl Zeiss field-emission scanning electron microscope. Particle size distributions of the powders were measured by a particle size analyzer Mastersizer 2000 Malvern instruments.

Results and discussions

XRD patterns of the samples obtained after 10 and 20 hours of the hydrothermal treatment in the presence of PVP show well crystallized single $LiFePO_4$ phase, Fig 1. On the contrary, in the presence of PVA after 20 hours of the hydrothermal treatment there are some additional diffraction lines which can be mainly attributed to the mixed iron phosphates $Fe_2Fe_3(PO_4)_6$. Apparently PVA wasn't sufficient enough to provide reductive conditions that can prohibit the conversion of Fe^{2+} to Fe^{3+}. When citric acid was added to PVA precursor solution pure $LiFePO_4$ phase was obtained.

Cubic shape particles (0.5 to 4 μm) with sharp corners were obtained for samples prepared with PVP after 10 h (Fig.2a). By

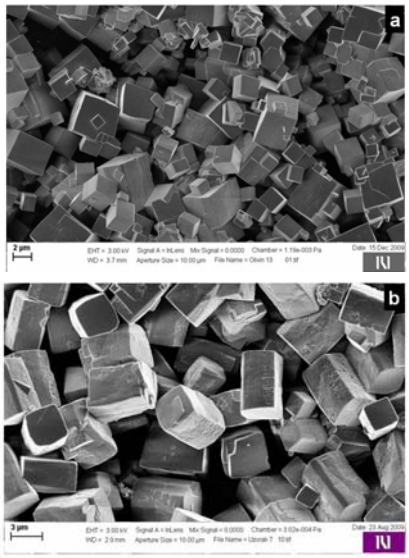

Fig. 2 FESEM images of the $LiFePO_4$ samples, synthesized with PVP after 10 (a) and 20 (b)

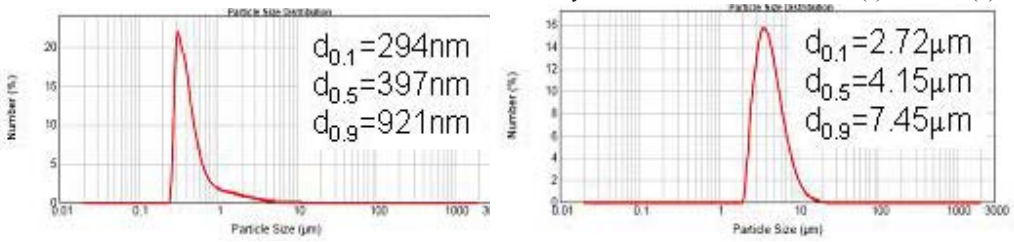

Fig.3. Particle size distributions of the $LiFePO_4$ samples, synthesized using PVP after 10 and 20 hours

prolonging hydrothermal treatment to 20 h more uniform prismatic particles with much smoother corners were obtained (Fig 2b). Prismatic particles are about 6μm long with diameter of about 2μm. The relative span, defined as $(d_{0.9}-d_{0.1})\backslash d_{0.5}$, is about 1.6 and 1.1 for PVP10h and PVP20h respectively, which suggest that prolonged hydrothermal treatment leads to more uniform particle size distribution inducing particle growth. The growing of bigger particles was most probable enabled by dissolution of smaller particles which resulted in increased and uniform particle size.

Sample prepared with PVA after 20 hours shows two different morphologies (Fig. 4a).This is in compliance with the XRD result where two phase powder was observed. Particle size distribution curve (Fig 5a) shows two peaks that correspond to two different morphologies.

Diamond- like particles (Fig 4b) typical for $LiFePO_4$ [1] were obtained when both citric acid and PVA were added to the precursor solution. Size of these particles is about 4- 7μm on a side and about 1-4μm thick. The average particle size (Fig 5b) is 4.374μm and the relative span is 0.8. Lower value of the relative span confirms particle size uniformity which is clearly seen from FESEM image. Comparing this with XRD results it can be concluded that needle like particles (Fig 4a) originate from impurity phase which was successfully avoided by introducing citric acid in the reaction vessel.

Conclusions

Well crystallized $LiFePO_4$ particles were successfully synthesized via hydrothermal reaction operated at 180°C in the presence of PVP and PVA/citric acid. PVA wasn't sufficient enough to provide reductive conditions, so it was necessary to introduce citric acid into reaction vessel to obtain pure $LiFePO_4$ phase. Organic compounds which were added to precursor solution have significant influence on particles morphologies. Powders prepared with PVP have cubic shape particles, while powders prepared with PVA and citric acid show diamod- like particles.

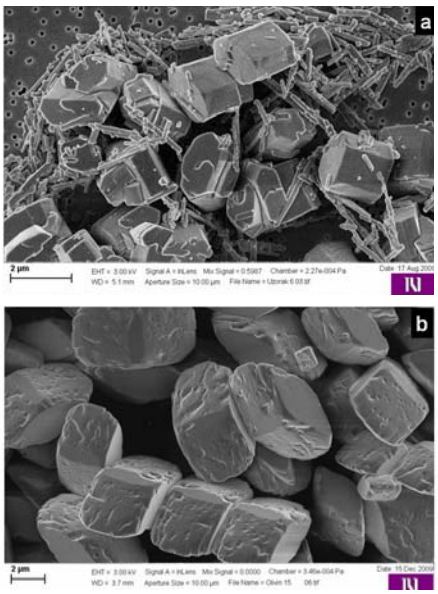

Fig. 4 FESEM images of the $LiFePO_4$ samples, synthesized with PVA (a) and PVA/citric acid (b)

Acknowledgement

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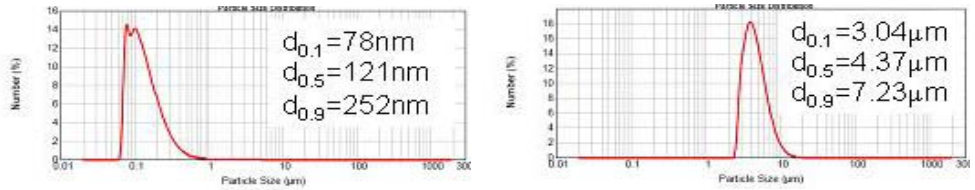

Fig.5 Particle size distributions of the $LiFePO_4$ samples using PVA and PVA/citric acid after 20 hours.

Literature

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