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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 phospho- olivine in presence of polyvinylpyrrolidone and polyvinyl alcohol and their influence on particle morphologies.

Experimental

LiFePO_4 was prepared by hydrothermal method starting from LiOH , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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.

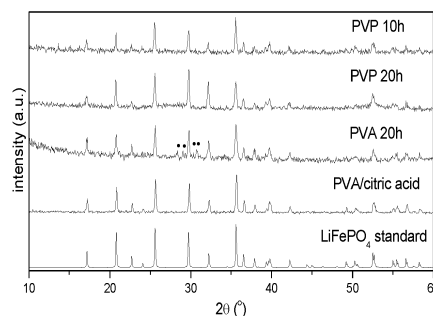


Fig. 1. XRD pattern of LiFePO_4 powders synthesized with PVP after 10 and 20 hours, with PVA and PVA/citric acid

The XRPD patterns were recorded using $\text{CuK}_{\alpha 1,2}$ radiation in 2θ range $10\text{--}60^\circ$ 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 $\text{Fe}_2\text{Fe}_3(\text{PO}_4)_6$. 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

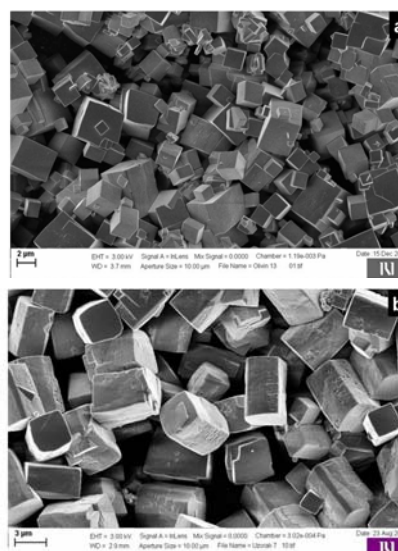


Fig. 2 FESEM images of the LiFePO_4 samples, synthesized with PVP after 10 (a) and 20 (b)

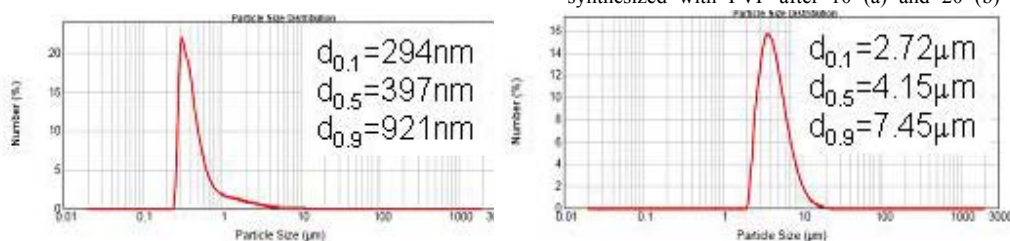


Fig.3. Particle size distributions of the LiFePO_4 samples, synthesized using PVP after 10 and 20 hours

prolonging hydrothermal treatment to 20 h more uniform prismatic particles with much smoother corners were obtained (Fig 2b). Prismatic particles are about $6\mu\text{m}$ long with diameter of about $2\mu\text{m}$. The relative span, defined as $(d_{0.9}-d_{0.1})/d_{0.5}$, 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- 7 μm on a side and about 1-4 μm thick. The average particle size (Fig 5b) is 4.374 μm 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 diamond- like particles.

Acknowledgement

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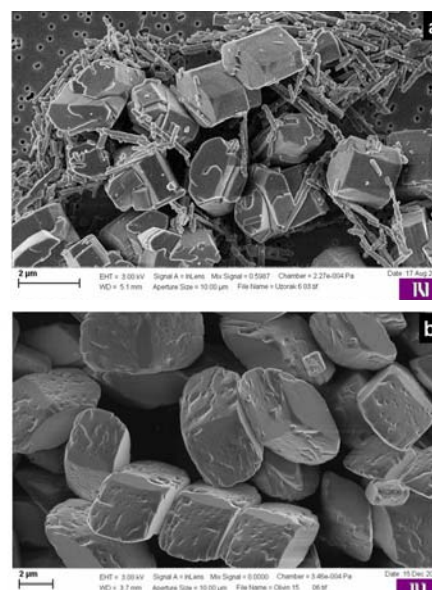


Fig. 4 FESEM images of the LiFePO_4 samples, synthesized with PVA (a) and PVA/citric acid (b)

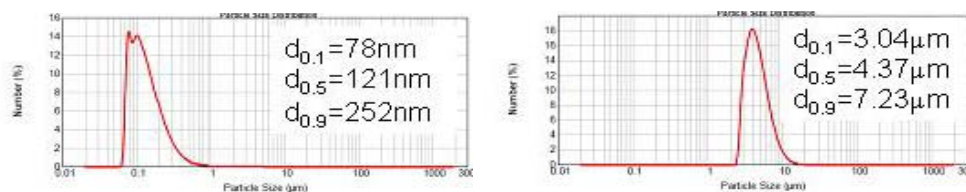


Fig.5 Particle size distributions of the LiFePO_4 samples using PVA and PVA/citric acid after 20 hours.

Literature

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- [2] J. Ni, M. Morishita, Y. Kawabe, M. Watada, N. Takeichi, T. Sakai, *Journal of Power Sources*, 2010, **195**, 2877-2882