HYDROTHERMAL SYNTHESIS OF $LiFePO_4$ POWDERS AS CATHODE MATERIAL FOR Li-ION BATTERIES

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Introduction

Phospho-olivine $LiFePO_4$ has been intensively studied as lithium insertion cathode materials for next generation of Li-ion secondary batteries. $LiFePO_4$ has an interesting theoretical specific capacity, good cycle stability and technically attractive flat voltage versus current profile of 3.45 V versus Li^+/Li. A further advantage of this material, thanks to its stability, is improved safety of batteries at high temperatures. $LiFePO_4$ can be synthesized by various methods. Unlike traditional solid state reaction, hydrothermal synthesis is quick, easy to perform, low-cost and energy saving.

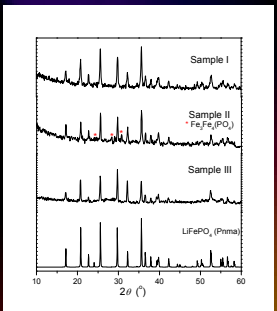

Figure 1 XRD of sample I (with citric acid), sample II (with PVA), sample III (with PVP) and standard $LiFePO_4$

Experimental

The starting materials for hydrothermal reaction were $LiOH \cdot H_2O$, $FeSO_4 \cdot 7H_2O$ and H_3PO_4 (85 wt% solution). Molar ratio for Li:Fe:P was 3:1:1. To prevent Fe^{2+} oxidation citric acid, polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP) was added. First of all, citric acid (sample I), PVA (sample II) or PVP (sample III) water solutions were prepared. $FeSO_4$ and H_3PO_4 water solutions were prepared and mixed together. The resulting solution was then added to the surfactant solution under constant stirring and only at the end, to avoid the formation of $Fe(OH)_2$ which can be easily oxidized to Fe^{3+}, LiOH water solution was added. pH value was adjusted to 8 by adding NH_3. The mixture was quickly transferred to stainless steel autoclave and heated at 180°C for 20 hours. After cooling down to room temperature, precipitates were collected by suction filtration, washed several times with distilled water and dried at 60°C in air for 12 hours. Powders were analyzed by XRPD, FESEM, laser particle size analyzer and galvanostatic charging/discharging.

Results and discussion

Figure 1 shows the XRPD patterns of the samples synthesized in the presence of the citric acid, PVA and PVP. The main diffraction peaks attribute to the orthorombic $LiFePO_4$ olivine-type phase. Some minor peaks in sample II are due to impurities, mainly to mixed phosphates $Fe_3Fe_4(PO_4)_6$.

SEM images and the particle size distributions are shown on Figure 2, 3 and 4. For sample I, prepared with citric acid, particles are highly agglomerated. Particle size analysis results show that average particle size (d_{50}) is 2.27 μm. For sample II, prepared with PVA, there are two shapes of particles: needle like and prismatic like particles. Size of prismatic like particles is about 2 μm while needle like particles are about 100 nanometers width, and 1 to few micrometers long. Particle size analysis results show two peaks that correspond to two different shapes of particles. Uniform rectangular-like particles are shown on figure 4 for sample III, prepared with PVP. Narrow peak at particle size distribution curve confirms particle uniformity. Average particle size (d_{50}) is 4.15 μm.

Electrochemical characteristics are investigated by galvanostatic charging/discharging with small constant current rate of C/10. Electrochemical performance of sample I is shown on Figure 5. Initial discharge capacity is about 32 mAh/g and after 50 cycles its value increases for 6%. Efficiency (discharge/charge capacity ratio) is very high, about 100%.

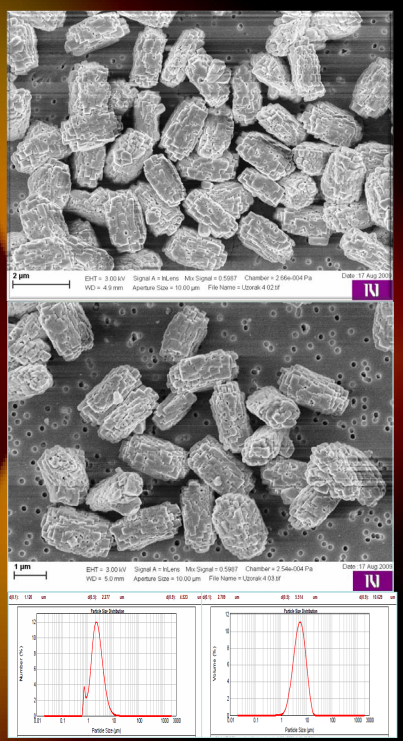

Figure 2 SEM image and size distribution curves of sample I (with citric acid)

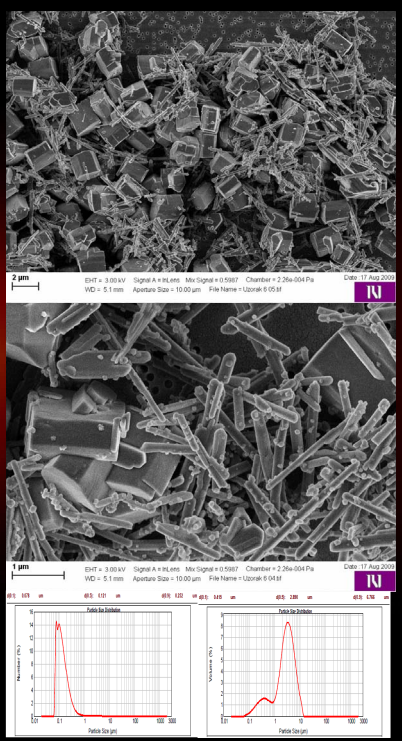

Figure 3 SEM image and size distribution curves of sample II (with PVA)

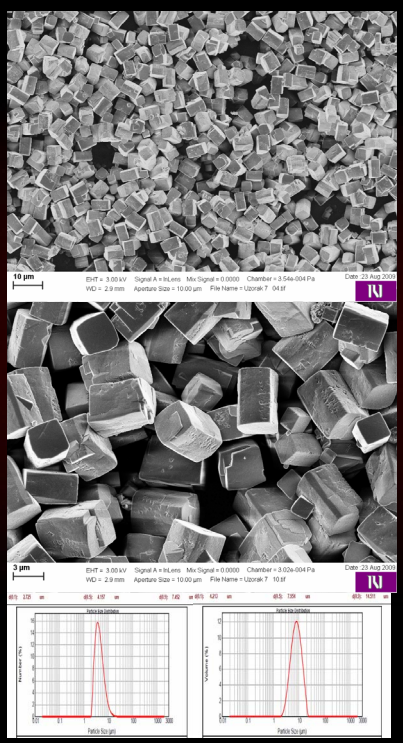

Figure 4 SEM image and size distribution curves of sample III (with PVP)

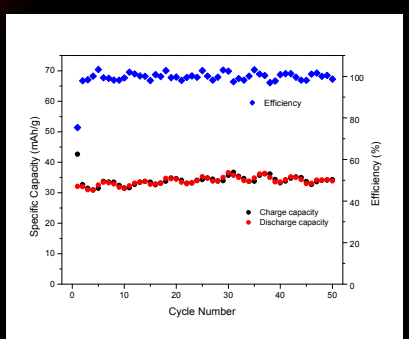

Figure 5 Cyclic performance and efficiency (discharge/charge capacity ratio) of sample I (prepared with citric acid)

Conclusions

Phospho-olivine $LiFePO_4$ was successfully synthesized hydrothermally. XRPD results show that pure $LiFePO_4$ was produced when citric acid or PVP was added to precursor solution, while addition of PVA leads to formation of $LiFePO_4$ with small amount of impurities in form of mixed iron phosphates. Different organic compounds which were added to precursor solution had significant influence on powder morphologies. Particle size analysis results had confirmed SEM results. Electrochemical measurements show that sample I has low capacity, but it is stable and shows slight increase after prolonged cycling. This could be explained with ordering structure during lithium intercalation and deintercalation process.