

MICROEMULSION-MEDIATED HYDROTHERMAL SYNTHESIS OF LiFePO_4 CATHODE MATERIAL

Maja Jovic^a, Dragana Jugovic^a, Miodrag Mitric^b, Nikola Cvjeticanin^c, Sreco Skapin^d, Dragan Uskokovic^a

^aInstitute of Technical Sciences of the Serbian Academy of Sciences and Arts, Serbia

^bThe Vinca Institute, Condensed Matter Physics Laboratory, Serbia

^cFaculty of Physical Chemistry, University of Belgrade, Serbia

^d“Jozef Stefan” Institute, Ljubljana, Slovenia

ABSTRACT

LiFePO_4 is a material of great interest as cathode material for lithium ion batteries thanks to its good characteristics. LiFePO_4 has high 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. One of the advanced techniques for LiFePO_4 powder preparation is hydrothermal synthesis. In this work, LiFePO_4 powders were prepared by a new approach, a microemulsion-mediated hydrothermal method in which microemulsion medium was further treated by hydrothermal reaction. The main advantage of the proposed route is low reaction temperature and relatively short processing time. LiFePO_4 powders were prepared by microemulsion-mediated hydrothermal method in cyclohexane/Triton X-100/n-hexanol/water at 180°C. The product of hydrothermal synthesis was heat treated at 700°C in inert atmosphere to avoid oxidation of Fe^{2+} to Fe^{3+} .

EXPERIMENTAL

The microemulsion composed of 3ml Triton X-100, 20 ml cyclohexane and 2.5 ml n-hexanol was divided in two fractions. In the first fraction, water solutions of FeSO_4 , $(\text{NH}_4)_2\text{HPO}_4$ and citric acid were added. The second fraction of the microemulsion was mixed with LiOH water solution, and slowly added to the previous fraction with constant stirring. Molar ratio for $\text{Li}:\text{Fe}:\text{P}$ was 3:1:1. Resulting microemulsion was transferred to the Teflon lined stainless steel autoclave and purged with argon. Autoclave was heated at 180°C for 15 hours. After cooling down to the room temperature, the precipitate was collected by the suction filtration, washed several times with distilled water and dried at 60°C in air for 12 hours. Collected powder was mixed with oxalic acid and annealed at 700°C for 3 hours in argon gas flow. Oxalic acid decomposes to carbon while creating reductive atmosphere. After annealing powder was characterized by XRPD, FESEM and laser particle size analyzer. Electrochemical properties were evaluated by constant current charging/discharging. Cathode material was made from synthesized LiFePO_4 , carbon black as conducting agent and PVDF as binder. Lithium metal was used as counter electrode, and 1M LiClO_4 in PC as electrolyte.

RESULTS

Figure 1 presents the X-ray diffraction pattern of a typical sample, synthesized by microemulsion mediated hydrothermal process, followed by heat treatment in presence of oxalic acid in argon atmosphere at 700°C for 3 hours. All diffraction lines can be attributed to the orthorhombic olivine type phase LiFePO_4 (space group: Pnma). There is no obvious carbon diffraction peaks due to the small amount of amorphous carbon present. The amount of carbon was determined by heating the lithium iron phosphate in air. Figure 2 shows that LiFePO_4 gains 3.5% in weight, compared to the theoretical value of 5.1% for complete oxidation of Fe(II) to Fe(III) . The carbon coating level is 1.6%.

FESEM images of LiFePO_4/C powder are shown in figure 3. The agglomerates composed of many small particles are forming porous structure, which is desirable because it provides penetration of the electrolyte into the electrode material and reduces lithium diffusion length within the particles. Smaller particles are about 50-100 nm in diameter, while size of agglomerates is about 1-3 μm . Particle size distribution curve (Figure 4) shows that average particle size is 418 nm, due to agglomeration effect.

Constant current charge and discharge cycling was performed to obtain electrochemical properties of synthesized material. The cell was cycled at 0.1 C rate between 2.7 and 4.1 V versus Li/Li^+ . The discharge curves of LiFePO_4/C powder are presented in figure 5. The discharge plateaus appear at 3.4 V versus Li/Li^+ after initial charging and this electrochemical property corresponds to the simple lithium deintercalation-intercalation process in pure olivine LiFePO_4 . The cyclic performance of LiFePO_4/C cathode is shown in figure 6. The initial discharge capacity is about 105 mAhg^{-1} . After 15 cycles the discharge capacity is slightly increased and it is about 115 mAhg^{-1} .

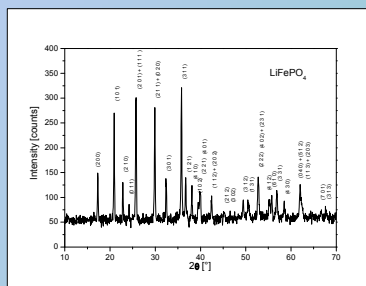


Figure 1 XRD of LiFePO_4/C powder

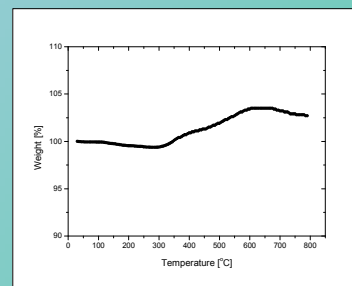


Figure 2 TGA curve of LiFePO_4/C powder

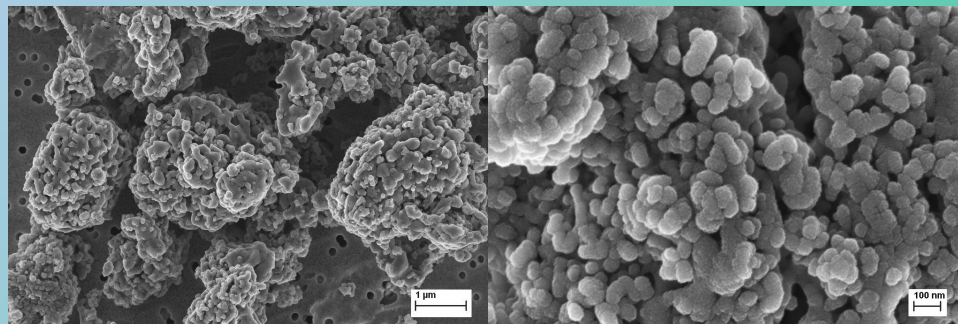


Figure 3 FESEM images of LiFePO_4/C powder

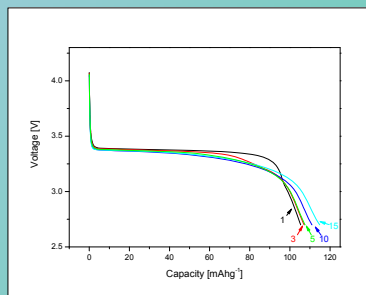


Figure 5 Discharge curves of LiFePO_4/C cathode

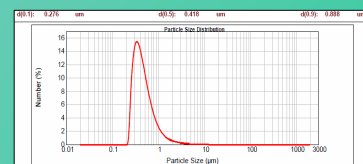


Figure 4 Particle size distribution of LiFePO_4/C powder

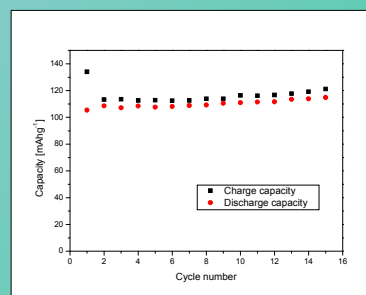


Figure 6 Cycling performance of LiFePO_4/C cathode

CONCLUSIONS

Cathode material LiFePO_4 was successfully synthesized by microemulsion mediated hydrothermal method. The obtained product is pure and well crystallized LiFePO_4 olivine phase. Particles morphology revealed from FESEM images shows agglomerates composed of nanoparticles. Electrochemical measurements show good cycling performance. The initial discharge capacity of about 105 mAhg^{-1} is smaller than theoretical probably because of agglomerates which increase lithium diffusion length. After 15 cycles discharge capacity was increased to 115 mAhg^{-1} . This could be explained with ordering structure during lithium intercalation and deintercalation process.