ABSTRACT

LiFePO₄ is a material of great interest as cathode material for lithium ion batteries thanks to its good characteristics. LiFePO₄ 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 LiFePO₄ powder preparation is hydrothermal synthesis. In this work, LiFePO₄ 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. LiFePO₄ powders were prepared by microemulsion-mediated hydrothermal method in cyclohexane/Triton X-100/hexanol/water at 180°C. The product of hydrothermal synthesis was heat treated at 700°C in inert atmosphere to avoid oxidation of Fe²⁺ to Fe³⁺.

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 LiFePO₄ (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 LiFePO₄ 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 LiFePO₄/C powder are shown in figure 3. The agglomerates composed of 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 LiFePO₄/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 LiFePO₄. The cyclic performance of LiFePO₄/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.

CONCLUSIONS

Cathode material LiFePO₄ was successfully synthesized by microemulsion mediated hydrothermal method. The obtained product is pure and well crystallized LiFePO₄ 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.