POLYETHYLENE GLYCOL600-ASSISTED SOLVOTHERMAL SYNTHESIS OF NANO-LIFEPO$_4$/C CATHODE MATERIALS FOR LITHIUM-ION BATTERIES

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ABSTRACT

Abstract: Nano-sized LiFePO$_4$/C （ LFP/C ） composite cathode materials have been synthesized in a binary solvent of Polyethylene glycol600 （ PEG600 ） and water via solvothermal route at 180℃ for 10 h followed by annealing glucose surface coated LFP in 3% H_2/97% N_2 at 700℃ for 6 h. A mixture of PEG600/water has been utilized as the co-solvent and found to play an important role in the formation of the LEP/C particles. LiOH, $NH_4H_2PO_4$ and $FeSO_4$ were used as Fe, P and Li sources, respectively and mixing them with certain feeding sequence. Citric acid used as the oxidation inhibitor. Then the paper mainly focuses on preparing LFP/C by using the PEG600/H_2O mixtures in varying proportions. We briefly studied the effect of surfactant Na_2EDTA on the result of the experiment. The prepared samples were characterized by X-ray powder diffraction(XRD), scanning electron microscopy (SEM). The obtained results showed that PEG600 contributes to the formation of uniformly distributed and the block-like LFP/C particles with the average size of 200-500nm, and in the case of the volume ratio of PEG600 to water at 1:1, SEM observation showed that the LFP particles exhibited approximate definite shape and it was estimated that the size of the particles were between 200-300nm. Finally, the above results revealed that the crystallinity and the size of the particles depend on the nature of the mixed solvent used. The volume ratio to the mixture solvent of H_2O/PEG600 is the key factor for controlling the crystal growth of the particles.

1 INTRODUCTION

At present, lithium ion battery is perceived as one of the advanced energy storage and transformation system, so that it could be used hybrid or electric vehicles to increase the electric powered run time[1]. Lots of candidate cathode materials have been explored and researched to meet the requirement for the wider application[8]. Recently, lithium iron phosphate ($LiFePO_4$) with the olivine structure has become the focus of intensive research owing to their distinctive geometries, novel properties, and potential applications[12].Compared with the high cost and poor safety material, $LiFePO_4$ has advantages including large theoretical capacity,high operating voltage and long cycle life, low toxic, environmental compatibility, high safety and low cost[1,4]. LFP shows high theoretical capacity of 170 mAhg-1and charge discharge potential of 3.45Vversus [5]. However, olivine-type LFP

also has introduced other problems, that is, power performance is greatly limited by slow diffusion (~1.8×10 -14 cm2·s-1) of lithium ions across the two-phase boundary, the above drawbacks restrict its application in lithium ion power battery.

In order to alleviate flows above mentioned, the researchers developed a lot of modification methods, such as carbon coating, reducing the particle size and anion doping Etc[4]. Surface treatment of carbon improved the surface electronic conductivity of the lithium iron phosphate performance, and greatly improved the large current discharge performance[6]. But the carbon caused a decline in the volume specific capacity. Nanomaterials can bridged the diffusion distance of lithium ion in the solid phase, and improved the electricity rate of battery charged[4]. But it is not easy to loose when nanometer-sized particles is in contact with conductive material, what is be conducive to improving the cycle performance of battery[2]. Especially, fabrication of nano-sized $LiFePO_4$ has been considered as an effective way to improve its electrochemical performance, since the lithium ions diffusion will be facilitated if the grain size of cathode materials is greatly reduced[8]. Moreover,it was found that adding into the surfactant can make more refined uniform particle size. It is very important to synthesize the $LiFePO_4$ powders with well-defined shape and size controlling experimental conditions[1,9].

Generally, preparation methods is important to the particle size and distribution of the $LiFePO_4$. There are many synthesis methods of Lithium iron phosphate ($LiFePO_4$), such as high temperature solid state reaction method, sol-gel method, microwave radiation method,hydrothermal method and co-precipitation method. Among these methods, hydrothermal method obtain materials with regular morphology and good dispersion, and solvothermal methods have been widely researched based on hydrothermal method[6]. The different solvents have different influence on the shape, size and composition of nanocrystals[5,12]. Besides, the ratio of water and solvents also impacts on crystal structure.A methods synthesized $LiFePO_4$ using the water/polyethylene glycol 400(PEG400) mixture as co-solvent[10,12]. According it , Polyethylene glycol(PEG) plays an important role in directing the mode of crystal growth (self-assembly) in unique structures along specific directions[4,14]. It is likely that the diffusion along the surface might be affected by the Polyethylene glycol(PEG) as the viscosity affects the growth rate constants for the bulk diffusion controlled growth. The size of particle will become smaller,with the increase of solvent PEG viscosity. Considering PEG have higher viscosity than PEG400. Therefore, in this paper, we selected the PEG600 as the object of study. At the same time, we further investigated the influence of the volume ratio of PEG to water and adding the surfactant on synthesis.

In this work, co-solvent system of Polyethylene glycol600(PEG600) and water was applied to synthesis $LiFePO_4$/C particle via a simple solvothermal method with the different volume ratio. Meanwhile,we explored the effects of surfactant on the formation of $LiFePO_4$/C particles with specific morphology and size under solvothermal conditions. Glucose is used as carbon source to obtain $LiFePO_4$/C.

2 EXPERIMENTAL

In this paper, all chemicals were used as purchased without further purification.

2.1 Preparation of LiFePO4/C samples

The LFP powders were synthesized via a solvothermal reaction from the raw materials lithium hydroxide ($LiOH·H_2O$), ferrous sulfate ($FeSO_4·7H_2O$), ammonium dihydrogen phosphate($NH_4H_2PO_4$) and citric acid. The overall molar ratio of Li:Fe:P:citric acid was 3:1:1:1. Firstly, 0.03mol $LiOH·H_2O$ was completely dissolved in a desired amount co-solvent of deionized water and PEG600 stirred rapidly with a magnetic stirrer, maintaining stirring,slowly added 0.01mol $NH_4H_2PO_4$ into the $LiOH·H_2O$ solution. Then, 0.01mol citric acid and 0.01mol FeSO4·$7H_2O$ was added to the mixture under stirring.In order to prevent the conversion of $Fe^{2+}$to Fe^{3+}, citric acid was added as oxidation inhibitor. After stirring uniformly for 8h, the mixed solution was transferred into a teflon-lined stainless steel autoclave with volume of about 80mL. The reaction vessel was transferred to an oven with temperature of 180℃ and then maintained the temperature for 10 h to complete the

solvothermal synthesis reaction. After the mixture cooled to room temperature, the products were separated centrifugally and washed with deionized water and absolute ethanol for several times, and then dried in oven at 80℃for 12h. The obtained products were coated with carbon as follows:the synthesized precursor of LFP was mixed with glucose (7.5 wt%) by ball-milling. After drying, LFP/C carbonized at 700℃ for 6h under Ar atmosphere with a heating rate of 5℃ min−1. By changing the volume ratio of PEG600 and H_2O and adding the surfactant, we can synthesize a series of samples.The samples prepared with different volume ratio of PEG600 to water are list in Table 1.

Sample No.	V(PEG600):V(H2O)	The concentration of $Na_2EDTA/mol.L^{-1}$
LFP/C-1	**0:1**	**0**
LFP/C-2	**1:1**	**0**
LFP/C-3	**1:2**	**0**
LFP/C-4	**1:3**	**0**
LFP/C-5	**2:1**	**0**
LFP/C-6	**3:1**	**0**
LFP/C-7	**0:1**	**0.05**
LFP/C-8	**1:1**	**0.05**
LFP/C-9	**1:3**	**0.05**
LFP/C-10	**2:1**	**0.05**

Table 1: Samples prepared with different parameters.

2.2 Characterization

The crystalline structure and phase purity of the LFP/C were characterized by an X-ray diffraction (XRD), which using Cu Kα radiation, operating at 40 KV and 40 mA in an angular range of 2θ = 10°–80° with an acquisition step of 0.02°and a scan rate of 0.2°per minute. Morphology and microstructure of the LiFePO4/C powders was characterized with scanning electron microscopy (SEM) with a JEOL JSM-7000F field emission scanning electron microscope operated at 15 kV and 10 mA.

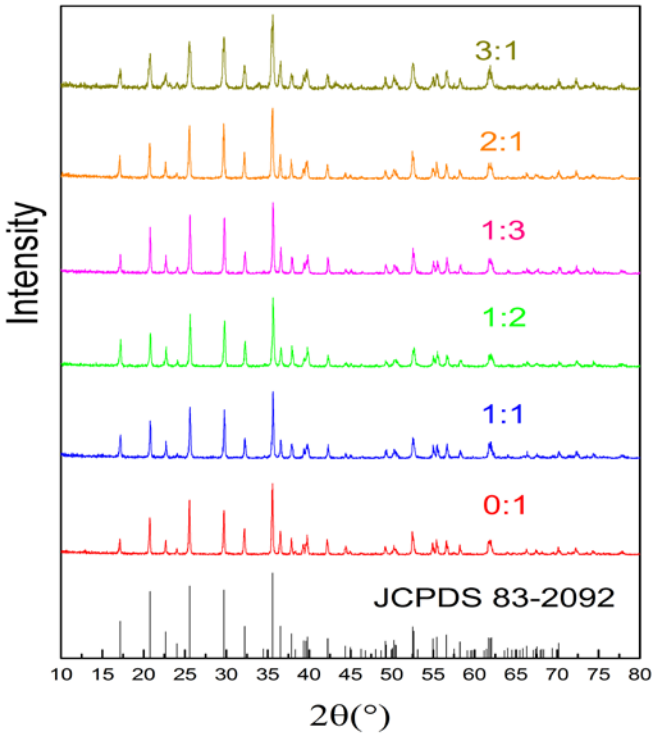


Fig1:XRD patterns of $LiFePO_4$/C powders solvothermal synthesized at180℃ for 10h with varying volume ratio and without surfactant.

3 RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of the LFP obtained from the precursor by solvothermal process. All intense peaks in both XRD patterns are indexed to an orthorhombic olivine type structure(JCPDS 83-2092). No secondary phases such as FeP, $FePO_4$ or Li_3PO_4 and diffraction peaks were found. Thereby,a nearly pure phase and well-crystallized product is obtained by a one-step microwave solvothermal synthesis. Moreover,the intensity of the peaks increases along with the increase of the PEG600 of the precursor. Also, the relative peak intensities only change slightly with volume ratio, so that there is apparently little change in morphology with increasing volume ratio.The particle size was estimated by Sherrer formula， indicating that LFP/C-2, LFP/C-3, LFP/C-4, LFP/C-5 and LFP/C-6 are with smaller size than LFP/C-1, which means the sizes of particles were limited by volume ratio of PEG600/H_2O, as well as the lattice constant. Carbon derived from glucose pyrolysis is likely to be amorphous and its presence has no detectable influence on the crystal structure of $LiFePO_4$.

In order to investigate the effect of different volume ratio of PEG600 and H_2O on the morphology of $LiFePO_4$/C composite, the samples were subjected to scanning electron microscopic (SEM) observation. Simply put,representative SEM images of particles obtained at constant condition are shown in Fig2. As exhibited in image, it is interesting to notice that nanosized $LiFePO_4$/C composites can be successfully obtained by using co-solvent. SEM images of samples, synthesized in solutions without PEG, are shown in Fig. 2A, which can be clearly seen that the sample that smooth rod-like nanocrystals with lengths of 2-5μm have a regular morphology and good crystalline state in the high-magnification . A few small debris with interface can also be seen in Fig2B. Figure 2B to 2E, illustrate that the PEG600 controlled the crystal growth and product morphologies, i.e. the size and morphologies of prepared $LiFePO_4$/C particles changed with the volume ratio of PEG600 and H_2O.The morphology of $LiFePO_4$/C powders were quite different from that of the samples

synthesized at mixture of PEG600 and H_2O. The particle size of $LiFePO_4$/C samples estimated from SEM analysis is much smaller than that of the LFP/C-1 samples. The SEM micrographs of LiFePO4/C powers in Fig. 2C,D, which displays the block-like structures of all the samples on the whole(Fig.2C,D,E,F). The SEM put in evidence the strong grain-refining effect of PEG, which is directly related to its the amount of volume. It can be seen that the PEG plays an important role in controlling the morphologies of the resulting products.Each particle seems to be tightly agglomerated by a larger number of primary smaller particles.

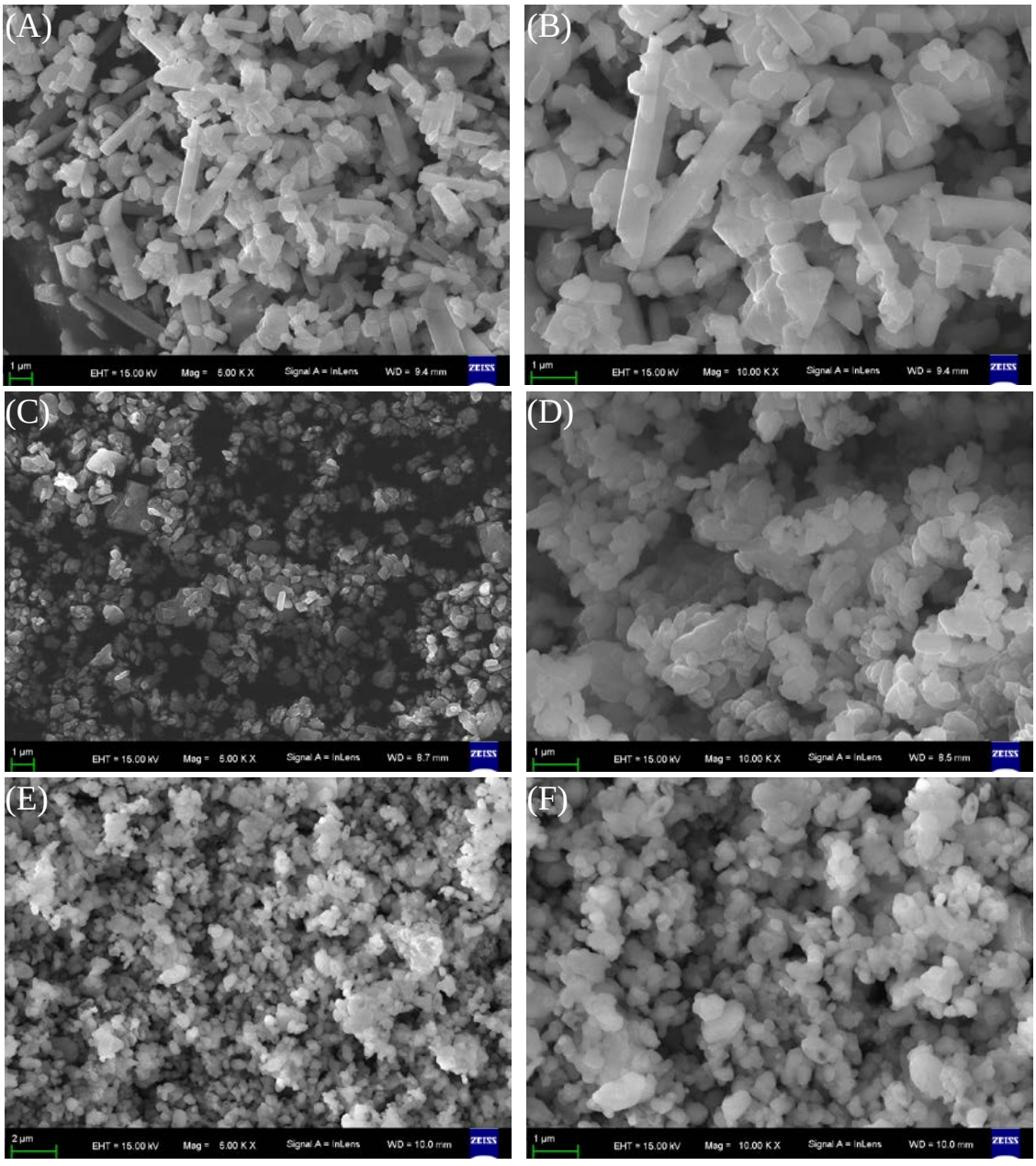


Fig2: SEM micrographs of LFP/C samples with different volume ratio of PEG600 and H_2O.(A, B) *V*(PEG600):*V*(H_2O)=0:1, (C, D) *V*(PEG600):*V*(H_2O)=1:1, (E, F)*V*(PEG600):*V*(H_2O)=3:1.

3.1 Effect of surfactant

The XRD patterns of $LiFePO_4$ powders solvothermal synthesized at 180℃ for 10h with Na_2EDTA via different volume ratio of PEG600 to water are shown in Fig3. All the samples can be indexed to single-phase orthorhombic $LiFePO_4$/C with the space group of Pnma (JCPDS 83-2092). And no

characteristic peaks related to the impurity phases were observed, which indicates the addition of Na_2EDTA has no effect on the phase of $LiFePO_4/C$ and does not generate impurities.

The SEM images of the products obtained from a volume ratio of PEG600 and H_2O with Na_2EDTA are given in Fig 4. Visually, the particle size of $LiFePO_4/C$ with surfactant is become more uniform and dispersed, compared to the sample without surfactant , the particles seem more homogeneous in size with less signs of coalescence between the grains to in Fig 4D, which demonstrating that the size of $LiFePO_4/C$ nanoparticles can be effectively controlled by using surfactant.This effect of refining and homogenizing the size of the grains induced by the presence of the surfactant has been already reported.

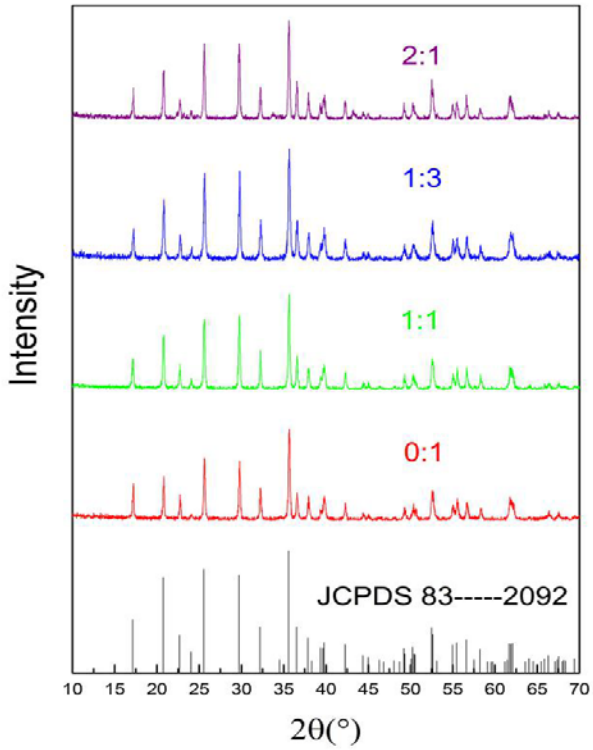
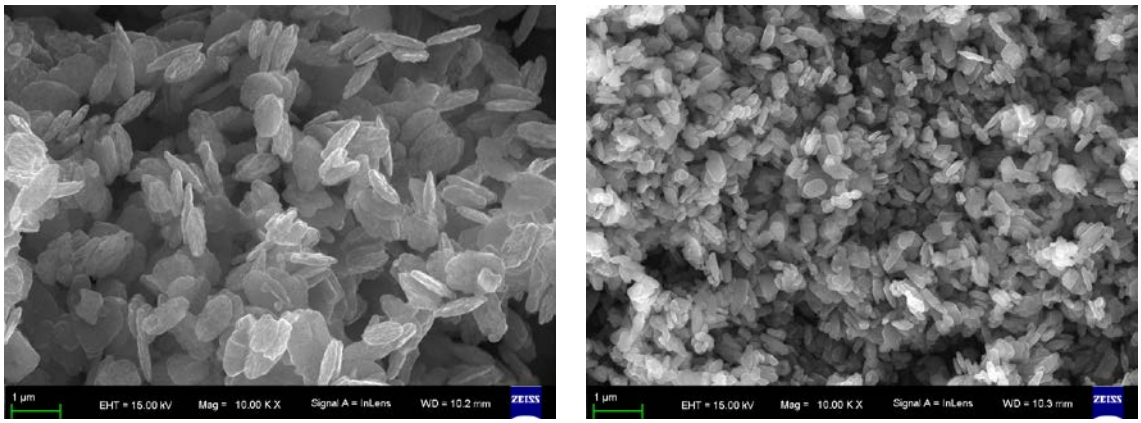


Fig3: XRD patterns of $LiFePO_4/C$ powders solvothermal synthesized at180℃ for 10h with varying volume ratio and with Na_2EDTA.



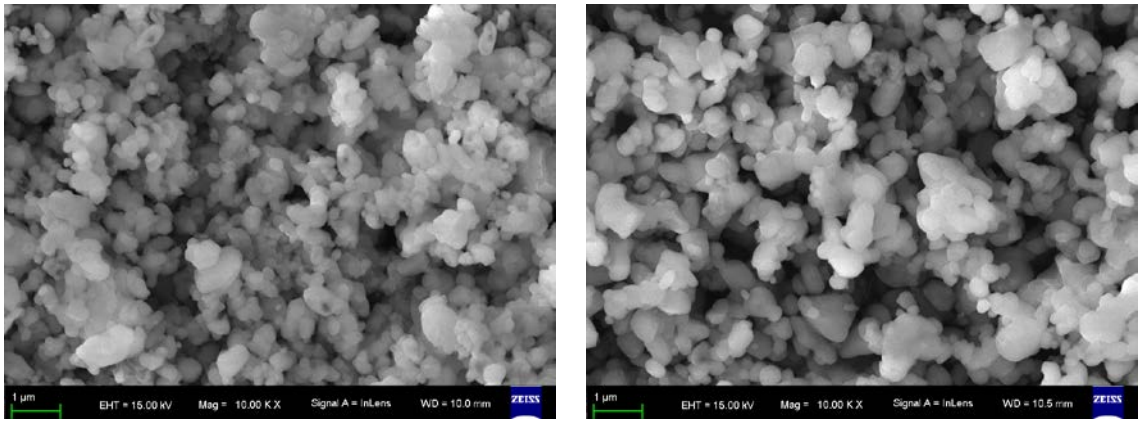


FIG 1: SEM micrographs of LFP/C samples with different volume ratio of PEG600 and H_2O and with Na_2EDTA.(A) *V*(PEG600):*V*(H_2O)=0:1,
(B) *V*(PEG600):*V*(H_2O)=1:1,(C) *V*(PEG600):*V*(H_2O)=1:3,(D) *V*(PEG600):*V*(H_2O)=2:1.

4 CONCLUSIONS

In summary, we have adopted a solvothermal route to synthesize LFP/C nanoparticles, with adjusting the volume ratio of PEG600 to H_2O by using glucose as carbon source.Solvent played a crucial role in controlling the size and morphology of $LiFePO_4$/C nanostructure. The formation of small and uniformly sized particles are results of increasing nucleation and inhibition rates of crystal growth process induced by PEG as a co-solvent. Results of this work shows that the proper choice of solvent contributes to the lower electronic and ionic resistance at the boundary of the crystallites and favors its electrochemical properties.

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