Effect of reaction time on the $FePO_4$ synthesized for the $LiFePO_4$/C cathode material of lithium ion batteries

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Keywords: $FePO_4$, calcination time, cathode materials, lithium ion batteries

Abstract. Phase-pure, monoclinic, and nanostructured $FePO_4$ composites have been synthesized by a hydrothermal method at different waterbath reaction time and characterized by XRD, SEM. The results showed that calcination time have great influence on the $FePO_4$ composite. When the waterbath reaction time was 7 days, the $LiFePO_4$/C composite showed high coulombic efficiency and excellent cyclabilities.

Introduction

Rechargeable lithium-ion batteries are now considered as the next generation of power sources for applications in electric vehicles, hybrid electric vehicles, and plug-in hybrid electric vehicles[1-3]. Olivine phase $LiFePO_4$, with a theoretical capacity of 170 mA h g^{-1} and a flat voltage plateau at 3.4 V (*vs.* Li^+/Li), has been considered as a promising electrode material for these rechargeable lithium-ion batteries[5-8]. Although $LiFePO_4$ possesses many advantages, it has suffered from poor electronic conductivity and Li-ion diffusion coefficient. Among these approaches, coating with carbonaceous conductors on the surface of nanoparticles has been proved to be an effective way to improve the electronic conductivity of $LiFePO_4$ particles[9-10] .

In this paper, we synthesized nanscale $FePO_4 \cdot 2H_2O$ using a hydrothermal method and are lithiated to $LiFePO_4$/C with the same structures by a simple rheological phase method. The waterbath reaction time and the electrochemical performances as the cathode materials for lithium ion batteries was studied. It was found that 7 days was the best waterbath reaction time for $LiFePO_4$/C when it was synthesized by rheological phase reaction method. The as-synthesized $LiFePO_4$/C composite showed very high coulombic efficiency and excellent cyclabilities.

Experimental

The $FePO_4 \cdot 2H_2O$ were synthesized using the same formulas as literature [4]. $FeCl_3$ was dissolved in water to give a 0.50mol/L Fe^{3+} precursor. In a typical synthesis, The CTAB surfactant was added to distilled water and stirred for 30 min. Then, $FeCl_3$ was added and stirred. After that, H_3PO_4 was dropped to the solution and stirred. Then the solution was aged for different reaction time in waterbath and dried at 100℃ for 4h.

A simple rheological phase method was employed to synthesize $LiFePO_4$/C composite as reported[11]. The $FePO_4 \cdot 2H_2O$ nanoplates, $LiOH \cdot H_2O$, PEG and appropriate amount of water were mixed, then ground for several to get a rheological phase. After several time, the rheological body was calcined at 650℃ in a tube furnace for 10 h under argon flow. After cooling to room temperature, the $LiFePO_4$/C composite was obtained.

The phase purity of the products was examined by powder X-Ray Diffraction on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.54056 Å). The crystal size and morphology of the products were examined with a scanning electron microscope(SEM, QUANTA 200, Holland).

Electrochemical measurements were carried out using two-electrode cells with lithium metal as the counter electrode. The working electrode was fabricated by compressing a mixture of the $LiFePO_4$/C composite/acetylene black/polyvinylidene fluoride (PVdF) with a weight ratio 65/30/5. The weight of active materials varied between 2.0 and 3.0 mg. The electrolyte was a 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) and the separator was Celgard 2500. The cell was assembled in a glove box filled with high purity argon gas. The galvanostatic charge/discharge experiment was performed between 2.0 and 4.4 V at 1C current density with each experiment repeated at least 5 times. The experiments produced reproducible results.

Results and discussion

The X-ray diffraction (XRD) results for the $FePO_4$ are presented in Figure 1. The diffraction peaks are in good agreement with the standard values for $FePO_4$ (JCPDS 33-0667), which shows the high-purity of the as-synthesized samples. the waterbath reaction time was 3 days, a small amount of the diffraction peaks of monoclinic pattern of $FePO_4$, and the characteristic peaks of monoclinic relative intensity relatively low strength. When the waterbath reaction time was 5 days, the characteristic peaks of $FePO_4$ monoclinic relative intensity increased significantly. When the waterbath reaction time was 7 days, the sample phase pure monoclinic of $FePO_4$.

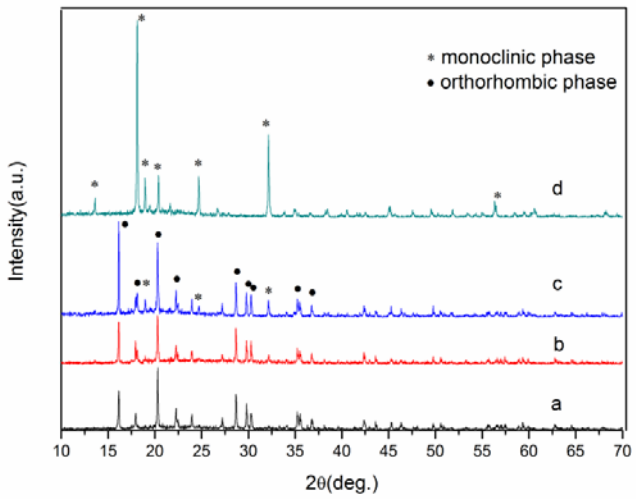

Fig.1. The XRD curve of the $FePO_4$ of the different waterbath reaction time
(a) 24h, (b) 3 days, (C) 5 days, (d) 7 days

Figure 2 shows the scanning electron microscope (SEM) image of the as-synthesized $FePO_4$. The measurement is in agreement with the crystallite size deduced from XRD analysis.The waterbath reaction time is 24h, is the product of micron sized particles by particle size of acomposition, have obvious agglomeration between the particles. When thewaterbath reaction time increased by 3 days, from the figure we can see that the product has a large sheet of the form, but this sheet is not stable, and the thickness is about 40nm. At the same time, there are also transformed into irregular shaped particles.When the waterbath reaction time is 5 days, irregular particles in the product almost completely evolved into thin slices; the waterbath reaction time is 7 days, the formation of uniform thickness, regular structure, good dispersion of nano film, film thickness is about 100nm.

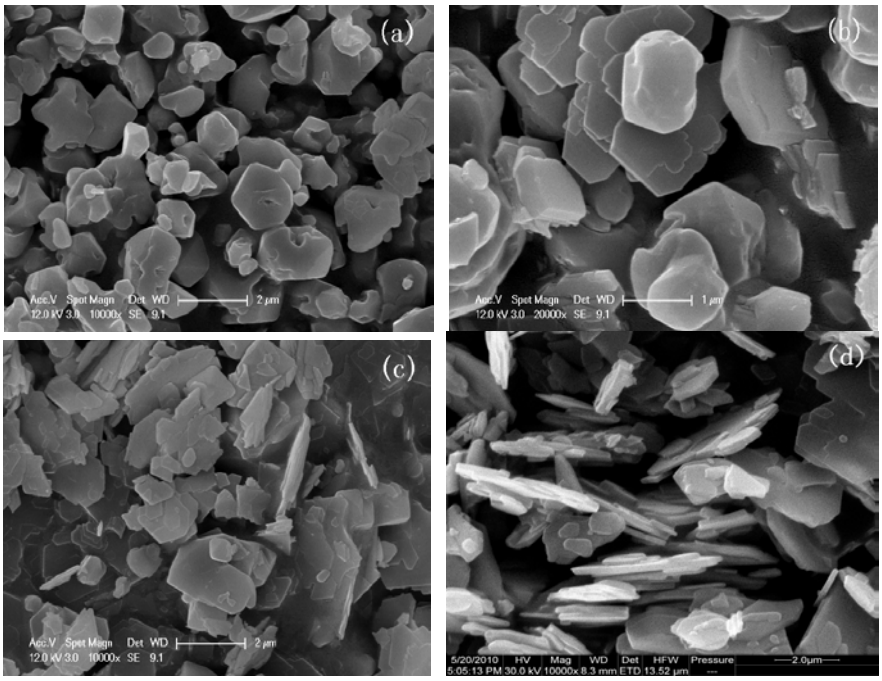

Fig.2. The SEM curve of the $FePO_4$ of the different waterbath reaction time .
(a) 24h, (b) 3 days, (C) 5 days, (d) 7 days

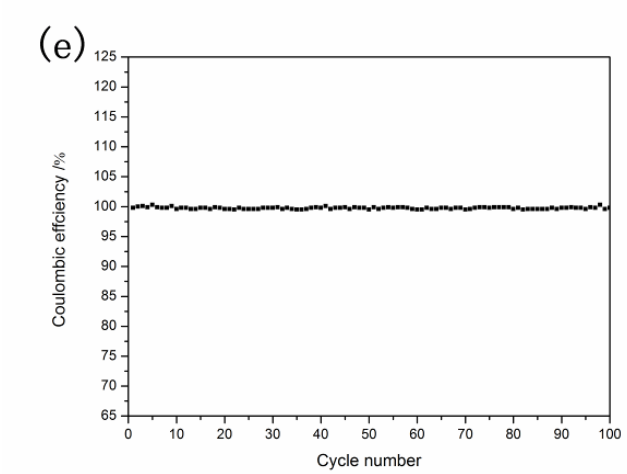

Fig.3. The coulombic efficiency curve of the $LiFePO_4$/C

Figure 3 is a product of $LiFePO_4$/C in the ratio of 100 laps under 5C coulombic efficiency map using $FePO_4$ as precursor which the waterbath reaction time was 7 days. From the figure we can clearly see, in the ratio of 5C under 100 cycles, the material of Kulun efficiency almostas high as 100%, indicating that this material has good electrochemical performance

Conclusions

In summary, nanscale $FePO_4 \cdot 2H_2O$ are synthesized using a hydrothermal method and lithiated to $LiFePO_4$/C by a simple rheological phase method. The waterbath reaction time of $FePO_4$ is 7 days, the formation of uniform thickness, regular structure, good dispersion of nano film, film thickness is about 100nm. As a result, increasing waterbath reaction time can improve the crystallinity of product, nanosheet thickness is small and stable, has been making lithium after the product of smaller particle size, better electrochemical performance. The nanoscale $LiFePO_4$/C show a better coulombic efficiency and excellent electrochemical performance.

Acknowledgement

This study was supported by the Youth Foundation of Wuhan Donghu University and the Natural Science Foundation of HuBei Province of China (Grant No. 2014CKC526), Hubei Provincial Department of education outstanding young scientific and technological innovation team project (T201428).

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