Facile synthesis of nanostructured LiFePO_4/C cathode material for lithium-ion batteries

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Nanostructured LiFePO_4/C cathode material was prepared by $\text{FePO}_4 \cdot 2\text{H}_2\text{O}/\text{C}$ precursor by *in situ* restriction reaction. The synthesized LiFePO_4/C cathode material presents a narrow distribution of nano-sized particles and exhibits an excellent electrochemical property with various rates. The facile synthesis route for the preparation of nano-sized LiFePO_4 material has the particular advantage of simple synthesis process and low synthesis cost.

lithium-ion batteries, cathode, lithium iron phosphate

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In the face of global warming and climate change, all the country should reduce the emission of carbon dioxide which is the main component of greenhouse gases. Since the automobile is one of the main emissions of carbon dioxide, it is a hot research topic to develop the plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs). Lithium-ion batteries exhibiting high energy and high power density have fast become the attractive power source for many portable electronic devices, as well as PHEVs and EVs [1,2]. However, the development and application of lithium-ion batteries are mainly limited by the cathodes [3]. Olivine structured LiFePO_4 is believed to be a promising cathode material for the next generation of lithium-ion batteries used in electric vehicles because of no toxicity, good thermal stability and high reversibility [1–5]. However, LiFePO_4 has a low electronic conductivity and a low lithium diffusivity which prevent its large-scale application in EVs and PHEVs. To overcome the problems, many effective approaches have been introduced, including doping cation into the olivine structure [4], coating conductive materials on the particles [5], minimizing the particle size with different synthesis

methods [6].

Minimizing the particle size of the cathode is a common route to improve the electronic conductivity of LiFePO_4 . Minimizing the particle size could be achieved by different synthesis methods, involving the sol-gel process [7], hydrothermal synthesis [8], microwave synthesis [9], the solvothermal method [10] and emulsion drying synthesis [11]. However, the synthesis procedure has become more complicated, which is difficult to achieve industrialization.

This paper introduces an *in situ* restriction method for the synthesis of nano- FePO_4/C to prepare nanostructure LiFePO_4/C . Our strategy includes *in situ* restriction reaction and secondary coating restriction process shown in Figure 1.

Figure 1 Schematic illustration for the preparation process of the FePO_4/C composite precursor.

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The restriction process involves the addition of PO_4^{3-} ions to a solution containing Fe^{3+} and functionalization of acetylene black that has many anionic groups such as $-\text{OH}$ and $-\text{COOH}$, which would adsorb each other because of the electrostatic attraction between positive and negative charge. Therefore, the modified acetylene black has played a role in the grain growth restriction of FePO_4 precursor during the precipitation process. Moreover, nano- FePO_4/C material was prepared by the method involving separate nucleation and aging steps (SNAS), in which rapid mixing and nucleation in a colloid mill is followed by a separate aging process. The major advantages of this method for preparation of precursor are summarized as follows: (1) simple synthesis process, (2) small crystallite size and (3) a very narrow distribution of crystallites.

The SNAS process involves the mixing of PO_4^{3-} ions to a solution containing Fe^{3+} ions and modified acetylene black. Functionalization of acetylene black was prepared by the KMnO_4 oxidation technique in H_2SO_4 medium solution. The resulting slurry is removed from the colloid mill and aged at 30°C for 2 h. The precipitate is filtered and dried at 100°C for 12 h. The mixture of nano- FePO_4/C , LiOH and sugar after mixing and milling for 1 h, was heated at 450°C for 4 h under nitrogen and then remilled for about 1 h, and finally calcined at 660°C for 5 h in nitrogen atmosphere to obtain LiFePO_4/C composite. In this process, the sugar would further restrict the grain growth and form a thin coating layer on the surface of particles. The structures of the products were analyzed by powder X-ray diffraction (XRD), using a Shimadzu XRD-6000 diffractometer operated at 40 kV and 30 mA from 10° to 70° at the wavelength of $\text{Cu K}\alpha$ radiation ($\lambda=0.15406\text{ nm}$). The particle morphologies of the products were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S4700). The chemical composition on the surface of the material was determined by energy dispersive X-ray spectrometry (EDS, EDAX Genesis 60). Transmission electronic microscopy (TEM) was carried out on a JEM-2100 instrument for investigating the microstructure of the samples. The electrochemical performance of Li batteries was recorded by a LADN CT2001A battery tester with $\text{Li}/\text{LiFePO}_4/\text{C}$ button cell including a lithium metal foil as counter electrode. The cyclic voltammetry (CV) was performed with a PAR 263A potentiostat/galvanostat (EG&G Instruments) controlled by a computer between 2.5 and 4.2 V at a scan rate of 0.1 mV s^{-1} .

The XRD patterns of the precursor of FePO_4/C and LiFePO_4/C are shown in Figure 2. The XRD patterns of FePO_4/C precursor prepared by SNAS method have no crystalline peaks detected in Figure 2(a). This indicates that the precursor is amorphous. The amorphous precursor is responsible for favoring well-mixing of lithium source material and precursor, which can help cathode materials obtain phase-pure oxides and uniform particles. The diffraction peaks of the LiFePO_4 are in full accord with the ordered LiFePO_4 olivine structure indexed by orthorhombic $Pnmb$.

Figure 2 The XRD patterns of the precursor of FePO_4/C (a) and LiFePO_4/C (b).

Impurity phases such as Fe_2O_3 , Li_3PO_4 and others, which often appear in the LiFePO_4 product synthesized by traditional routes, were not detected.

FE-SEM image of the LiFePO_4 material is shown in Figure 3, which has a well-dispersed structure, although a few agglomerations exist. The typical size of these LiFePO_4 particles is about 70 nm. This may mainly be attributed to the restriction reaction of the precursor FePO_4/C and the SNAS method. On the one hand, functionalization of acetylene black would effectively *in situ* restrict the growth of crystallites and impede the agglomeration of the LiFePO_4 . The result can also be confirmed by the TEM images in Figure 3(b), and the TEM images can clearly show that the LiFePO_4 crystallites have been embedded in the carbon conductive network. Such carbon conductive network is known to enhance the electronic conductivity of LiFePO_4 by connecting, wrapping, and existing in the interfaces between the LiFePO_4 particles. On the other hand, the key features of the SNAS method are suitable for production of nano-materials, which are a very rapid mixing and nucleation process in a colloid mill followed by a separate aging process. The mixing takes place in a very short time in the liquid thin film between the rotor and stator leading to nuclei which have an equal length of time to grow prior to aging, resulting in a narrow range of particle diameter. Subsequent aging allows the nuclei to grow together at approximately the same rate, giving a material containing particles with a narrow size distribution [12]. Uniform small particles can favor precursor and LiOH well-mixing easily. It is also helpful to get the narrow particle size distribution of the cathode material in the calcination process. The LiFePO_4 with nanosized particles can reduce the ion diffusion pathway and therefore has a great influence on the electrochemical Li^+ and de-intercalation processes leading to excellent electrochemical performance. In addition, the composition of the synthesized material has been studied by EDS analyses. The inset in Figure 3(a) is the result of EDS analyses, in which the sample contains iron, carbon, oxygen and phosphorus, and no other heavy metal element such as Mn has been detected.

Figure 3 FE-SEM (a) and TEM (b) micrograph of synthesized LiFePO_4/C material. The inset in (a) is the corresponding EDS analyses of the LiFePO_4/C material.

Figure 4 (Color online) The initial charge-discharge curves at rate of 0.2 C (a), cycle performance at various rates (b) and cyclic voltammograms at a scan rate of 0.1 mV s^{-1} (c) for synthesized LiFePO_4 .

The initial charge-discharge curves at rate of 0.2 C for synthesized LiFePO_4 are shown in Figure 4(a). The initial discharge specific capacity and coulomb efficiency of synthesized LiFePO_4 at 0.2 C are 160.2 mAh g^{-1} and 95.9%, respectively, as shown in Figure 4(a). The synthesized LiFePO_4 has a good cycling performance and high coulomb efficiency. Rate capability is an important and desirable feature in secondary battery applications. Figure 4(b) shows the rate capability and cyclability of the LiFePO_4 material between 2.5 and 4.2 V at various C-rates. The synthesized LiFePO_4 delivered a high specific capacity of 160.2, 152.2 and 139.1 mAh g^{-1} , respectively. After 30 cycles, the discharge specific capacity of the LiFePO_4 was 164.5, 150 and 139.3 mAh g^{-1} at rates of 0.2, 1.0 and 3.0 C, respectively. Therefore, the synthesized LiFePO_4 has high discharge specific capacity, good rate property and excellent cycling performance. Figure 4(c) shows cyclic voltammograms of the LiFePO_4 electrode, which reveals the single-electron reaction mechanism. After “activation” by the first cycle reaction, the current peaks of the following cycles become narrower and larger. The peak profiles are symmetric, in which the good overlap of the 2nd and 20th cycles indicates good stability of the electrode. This result is consistent with the cycling performance in Figure 4(b).

In summary, a simple and low-cost synthesis approach is used to prepare phase-pure LiFePO_4 powder, with a narrow nanosize particle distribution, which has an excellent electrochemical performance. This method could be easily scaled up for industrial production, and potentially be employed to synthesize other cathode materials or anode materials to produce series of high performance electrode materials for lithium-ion battery applications.

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