Lithium Batteries

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The Design of a $LiFePO_4$/Carbon Nanocomposite With a Core–Shell Structure and Its Synthesis by an In Situ Polymerization Restriction Method**

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Nano-sized electrode materials for lithium-ion batteries have attracted much attention recently[1–4] because their reduced dimensions enable much higher power. However, the large electrolyte/electrode interface arising from their size leads to more undesired reactions, which result in poor cycling performance.[1,2] Moreover, some nano-sized cathode materials synthesized by low-temperature methods are poorly crystalline, which also reduces their electrochemical stability. The synthesis of highly crystalline nanomaterials completely coated with conductive carbon (or a carbon shell) would be an effective means of eliminating these problems. Such a synthesis is a significant challenge, however, as the highly crystalline structure and its subsequent coating with conductive carbon have to be achieved at high temperature, where larger crystallite sizes are almost inevitable.

Olivine ($LiFePO_4$) is considered to be one of the most promising cathode materials for the next generation of lithium batteries due to its low toxicity, low cost, and high safety.[5,6] However, its power performance is greatly limited by slow diffusion of lithium ions across the two-phase boundary and/or low conductivity.[7,8] Many efforts have been made over the past few years to improve the power performance of $LiFePO_4$ by using low-temperature routes to obtain tailored particles or carbon painting to improve the conductivity of the solid phase. However, these previous studies have always focused on the "nano-size" or the "coating with conductive carbon" separately, rather than considering both of them together. Various low-temperature methods (synthesis temperature below 600 °C), such as low-temperature ceramic routes[9–13] or hydrothermal syntheses,[14,15] have been developed to lower the particle size of $LiFePO_4$, although none of them have been able to ensure the conductivity of the carbon coating. Furthermore, some low-temperature routes are not able to produce the required highly crystalline olivine structure, thus reducing the electrochemical stability of $LiFePO_4$. The high surface area arising from the nano-size of the products also greatly increases the undesirable electrode/electrolyte reactions, which leads to a poor cycling performance[1,2] From a review of previous studies of nano-sized $LiFePO_4$ (less than 100 nm), we can see that a "perfect" cycle-life (> 200 cycles) at high charge/discharge depth (90 %) is almost unheard of.

Approaches based on the thermal decomposition of carbon-containing precursors have also been widely studied for the preparation of carbon-coated $LiFePO_4$ particles.[16–23] However, these methods generally involve a high-temperature treatment, during which an increase in crystallite size is inevitable, to ensure the conductivity of the resulting carbon materials. Accordingly, those approaches based on the thermal decomposition of carbon-containing precursors can only produce $LiFePO_4$ particles with a partial coating of carbon (Figure 1 a).[17] As shown in Figure 1 a, during the intercalation process, the electrons cannot reach all the positions where Li^+ ion intercalation takes place, thus resulting in polarization of the electrode. In view of the one-dimensional Li^+ ion mobility in the framework,[24] full coating with carbon, which ensures $LiFePO_4$ particles get electrons from all directions, could further alleviate this polarization phenomenon. According to our analysis of previous studies, the ideal structure for high-performance $LiFePO_4$ should contain nano-size particles completely coated with conductive carbon (Figure 1 b).

It should be noted that many previous studies involving the synthesis of nano-sized $LiFePO_4$ employ Fe^{2+} salts as precursors.[7a,9,11–13,21] However, these salts are much more expensive and unstable than Fe^{3+} salts, therefore the synthesis of a nano-sized $LiFePO_4$/carbon composite with a core–shell structure from Fe^{3+} salts would be of great interest.

Herein we report an in situ polymerization restriction method for the synthesis of a $LiFePO_4$/carbon composite formed from a highly crystalline $LiFePO_4$ core with a size of about 20–40 nm and a semi-graphitic carbon shell with a thickness of about 1–2 nm. As shown in Figure 1 c, our strategy includes one in situ polymerization reaction and two typical restriction processes. The first of these restriction processes involves the addition of Fe^{3+} ions to a solution containing PO_4^{3-} ions and aniline, where it acts as both a precipitator for PO_4^{3-} and oxidant for aniline. The reaction during this process can be summarized as Equations (1) and (2).

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \downarrow \tag{1}$$

$$n(\text{Aniline}) \xrightarrow{Fe^{3+}} \text{Polyaniline} \downarrow \tag{2}$$

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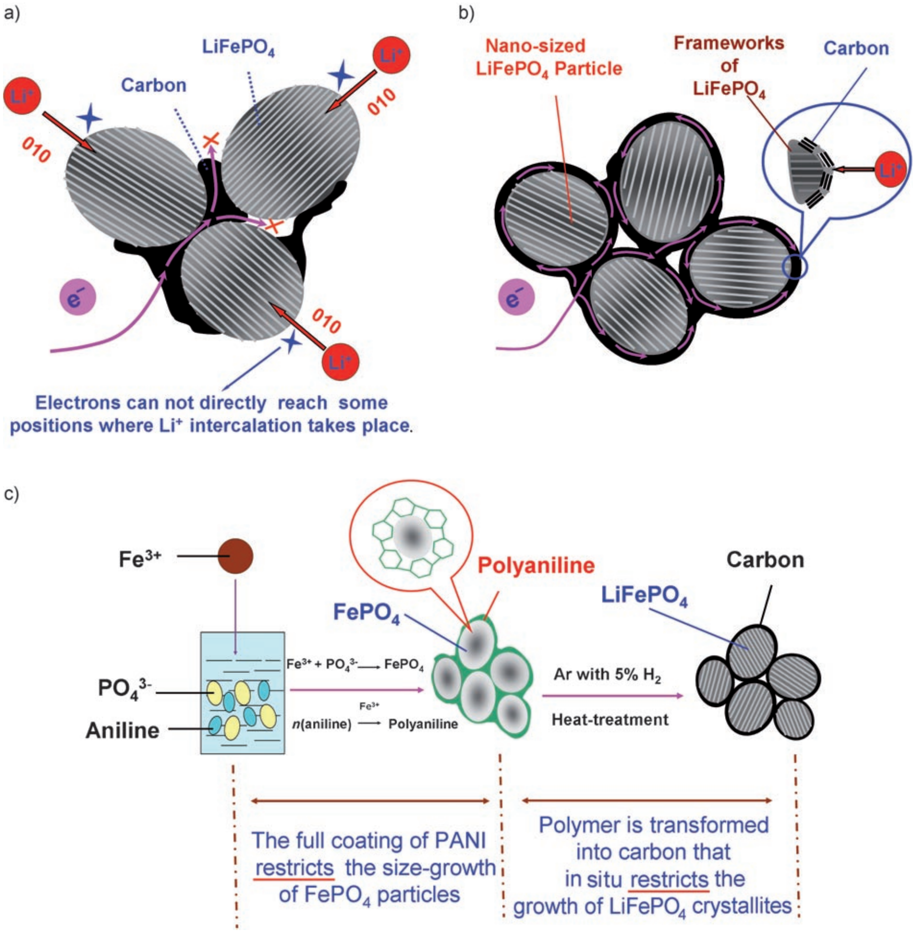

Figure 1. a) Electron-transfer pathway for $LiFePO_4$ particles partially coated with carbon. b) Designed ideal structure for $LiFePO_4$ particles with typical nano-size and a complete carbon coating. c) Preparation process for the $LiFePO_4$/carbon composite including an in situ polymerization reaction and two typical restriction processes.

It should be noted that the reaction in Equation (1) is faster than reaction in Equation (2). When Fe^{3+} was added to the solution containing PO_4^{3-} and aniline, a white precipitate of $FePO_4$ was formed. The Fe^{3+} ions on the outer surface of this precipitate then led to the oxidization polymerization of aniline.[25] Accordingly, Equation (2) should be re-written as Equation (3).

$$(FePO_4)_{surface}Fe^{3+} + n(\text{Aniline}) \rightarrow (FePO_4)_{core}(\text{Polyaniline})_{shell} \qquad (3)$$

As shown in Equation (3), aniline is polymerized in situ on the outer surface of the newly generated $FePO_4$ precipitate to form a green polyaniline (PANI) shell that can effectively restrict the growth of the $FePO_4$ particles (a very small account of surface Fe^{3+} ions are reduced to Fe^{2+} during this process). Subsequent heat treatment at 700 °C under argon containing 5 % H_2 in the presence of a lithium salt and some sugar led to the transformation of this $FePO_4$/PANI composite into a $LiFePO_4$/carbon composite. During this process the polymer shell is transformed into a carbon shell that restricts the in situ crystallite growth of $LiFePO_4$.

The FTIR spectrum of the $FePO_4$/PANI composite is shown in Figure 2 a. The characteristic peak at 1450 cm^{-1} corresponds to a benzene ring,[26] and the peak attributed to PO_4^{3-} valence bonding modes is observed at 1050 cm^{-1}.[27] The characteristic peak of polyaniline assigned to N=Q=N stretching should be observed at around 1133 cm^{-1}, although it appears to be hidden by the PO_4^{3-} peak. According to the result of the thermogravimetric (TG) analysis, PANI is present in the prepared composite at about 3 wt. %.

The SEM image shown in Figure 2 b suggests that the typical size of the prepared $FePO_4$/PANI composite is in the range 20–40 nm. The TEM images of this composite indicate an agglomerate structure where a large number of $FePO_4$ particles are connected together by the amorphous PANI (Figure 2 c). The higher magnification image shown in Figure 2 d confirms that the typical size of the $FePO_4$/PANI composite is within the range 20–40 nm. It is interesting to note that changing the synthesis conditions to prepare different $FePO_4$/PANI composites by varying the aniline concentration in the reaction solution led to composites with almost identical PANI contents. It is

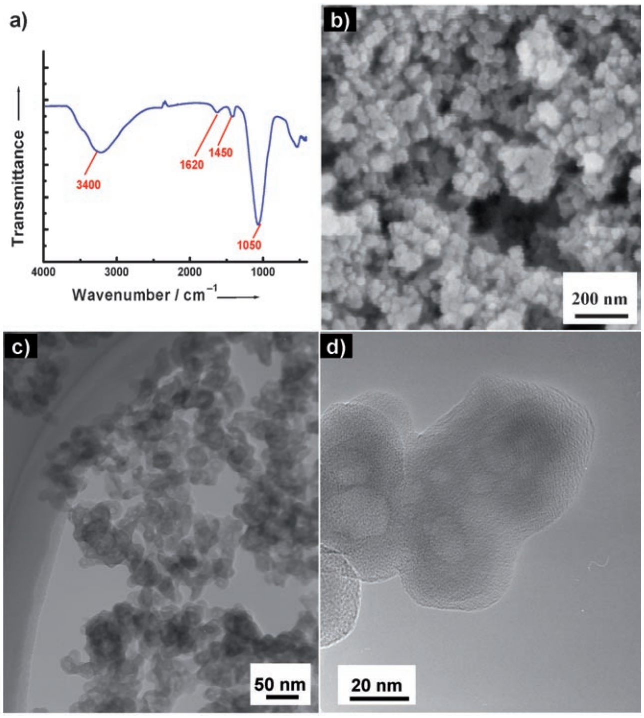

Figure 2. Characterization of the $FePO_4$/PANI composite: a) FTIR spectrum; b) SEM image; c) TEM image; d) HRTEM image.

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assumed that further polymerization of aniline is inhibited once the $FePO_4$ is fully coated with PANI.

Figure 3a shows an SEM image of the $LiFePO_4$/carbon composite prepared at 700 °C, which has an agglomerate structure. The TEM image shown in Figure 3b illustrates that the typical size of these $LiFePO_4$/carbon particles is still in the range 20–40 nm. The selected-area electron diffraction (SAED) pattern suggests that the prepared $LiFePO_4$ is highly crystalline (inset in Figure 3b). The carbon layer in the interstitial particle/boundary region, which is generated by carbonization of the sugar precursor, can also clearly be seen in Figure 3b (indicated by red arrows). The TEM image shown in Figure 3c shows a typical example of a particle made up of several primary crystallites with sizes ranging from 20–40 nm.

The high resolution TEM images shown as insets in Figure 3c (labeled by red arrows) clearly reveal that each primary crystallite is completely coated by a carbon layer to form a $LiFePO_4$/carbon core–shell structure where the carbon shell arises from carbonization of the PANI shell. Lithium ions can easily intercalate into the framework of $LiFePO_4$ through the partly graphitic carbon shell (thickness of about 1–2 nm).[28] Moreover, the $LiFePO_4$ crystallites with a carbon shell connect together, thereby further ensuring electrical continuity around the crystallites. The TEM image shown in Figure 3d shows a typical example of some primary particles where the $LiFePO_4$/carbon core–shell structure can clearly be observed. The average particle size of the prepared $LiFePO_4$/carbon composite, as deduced by applying Scherrer's equation to the XRD patterns, is 36 nm (Figure 3e), which is consistent with the TEM observations. The amount of carbon material within this prepared composite, as estimated from the TG analysis, is about 6 wt.%. The special BET surface of the prepared $LiFePO_4$/carbon composite is 50 $m^2 g^{-1}$.

Upon comparing the results shown in Figures 2 and Figure 3 we can clearly see that the crystallite size of the prepared $LiFePO_4$/carbon composite calcined at 700 °C for 15 h is close to the particle size of its precursor $FePO_4$/PANI composite, thereby suggesting that the formed carbon shell effectively restricts the crystallite growth of $LiFePO_4$. This result could lead to the development of a new method for the synthesis of nano-sized lithium intercalated compounds that complements conventional methods based on lowering the synthesis temperature. Inspired by this finding, we also successfully prepared nano-sized $Li_4Ti_5O_{12}$ particles completely coated with carbon by calcining a PANI-coated TiO_2 precursor in the presence of CH_3COOLi at 800 °C (See Figure 3f). More importantly, the in situ polymerization restriction method introduced in this paper can be used directly for synthesis of other nano-sized metal oxides such as Mn_3O_4 (see Figure 3g and the Supporting Information for the syntheses of $Li_4Ti_5O_{12}$ and Mn_3O_4).

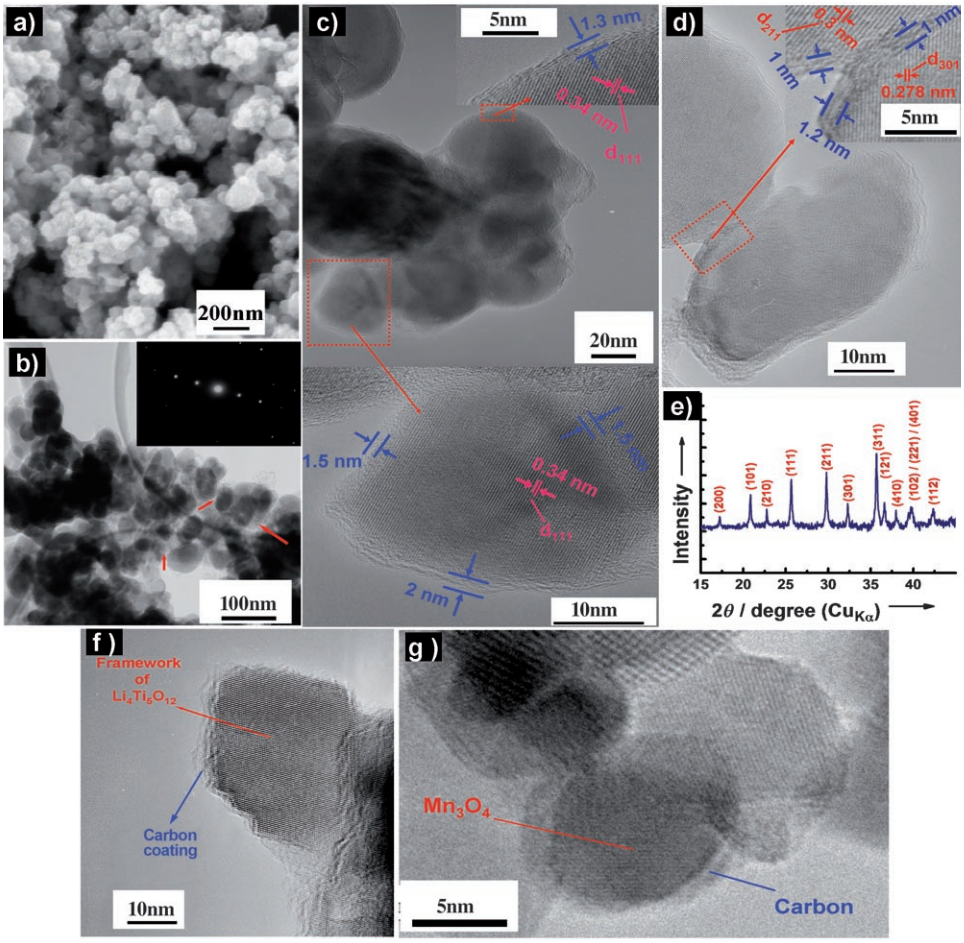

Figure 3. Characterization of the $LiFePO_4$/carbon composite: a) SEM image; b) TEM image; c) typical TEM image for an $LiFePO_4$/carbon particle containing several primary crystallites; d) typical TEM image for some $LiFePO_4$/carbon primary particles (each primary particle includes only one $LiFePO_4$ crystallite); e) XRD pattern of the prepared $LiFePO_4$/carbon composite; f) selected TEM image of prepared $Li_4Ti_5O_{12}$/carbon composite; g) selected TEM image of prepared nano-sized Mn_3O_4.

Figure 4 shows the electrochemical performance of the $LiFePO_4$/carbon composite. As shown in Figure 4a, a couple of redox peaks are observed between 3.2 and 3.6 V (vs. Li/Li^+) in the cyclic voltammetry curve obtained at a scan rate of 0.5 $mV s^{-1}$. These peaks correspond to the extraction and insertion of lithium ions and can still be clearly observed at a scan rate of 10 $mV s^{-1}$. The discharge capacity of the prepared composite is 168 $mA h g^{-1}$ at a current density of 0.1 $A g^{-1}$ (rate of about 0.6 C), and it still delivers a capacity of 90 $mA h g^{-1}$ at the current density of 10 $A g^{-1}$ (rate of about

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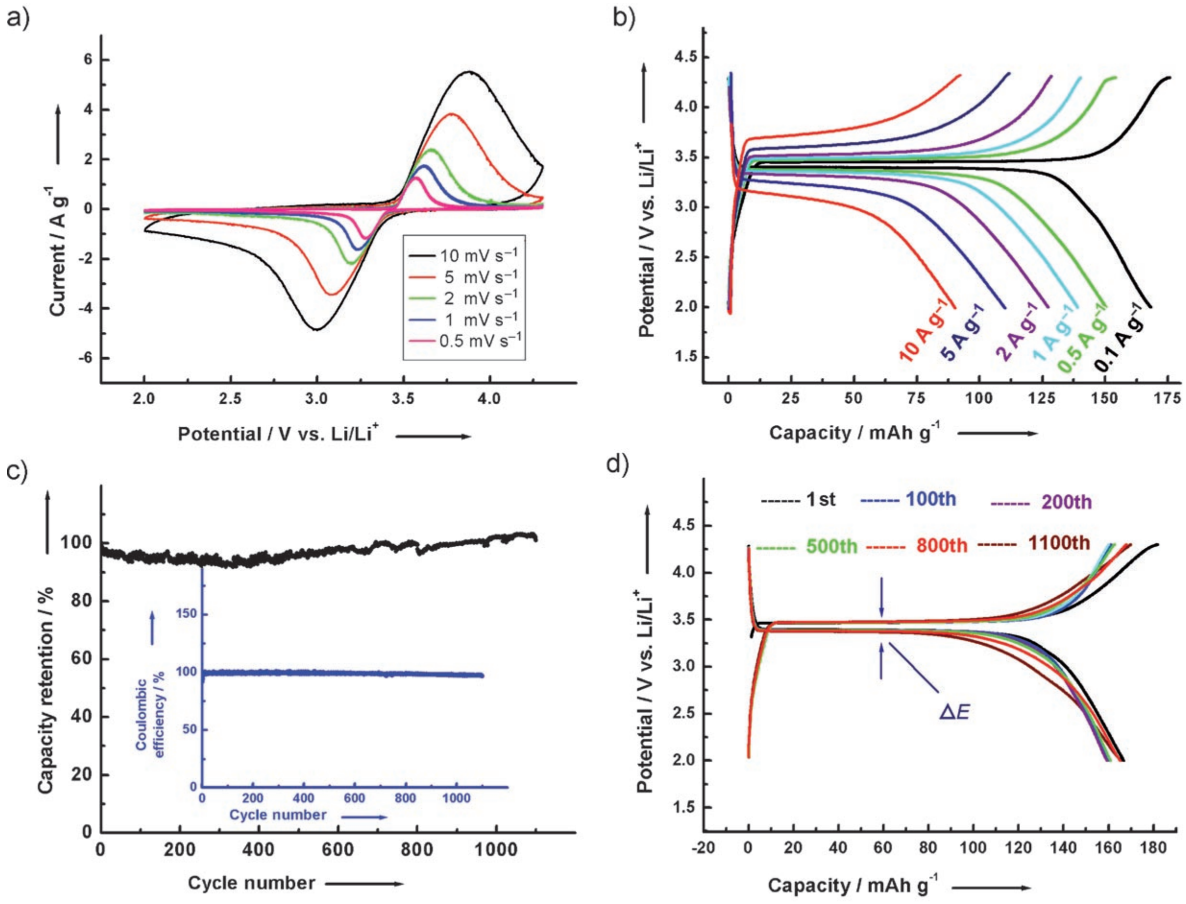

Figure 4. Electrochemical characterization of the prepared $LiFePO_4$/carbon composite: a) Cyclic voltammetry tests at different scan rates in the potential window 2.0–4.3 V (vs. Li/Li^+); b) charge–discharge tests at different current densities in the potential window 2.0–4.3 V (vs. Li/Li^+); c) cycling profile tested at a current density of 0.1 Ag^{-1} between 2.0 and 4.3 V; d) charge-discharge curves at different cycle number.

60 C), thereby indicating its high power performance (Figure 4 b). The results shown in Figure 4 b clearly demonstrate the remarkably improved electrochemical properties with respect to previously reported compounds. To the best of our knowledge, the highest value ever reported for the power performance of $LiFePO_4$ is 80 mA h g^{-1} at a discharge rate of about 60 C.[29] The prepared composite also exhibits an excellent cycling performance, with less than 5 % discharge capacity loss over 1100 cycles (see Figure 4 c). The coulombic efficiency shown in the inset of Figure 4 c (calculated from the discharge capacity/charge capacity) stays at about 100 %.

Figure 4 d shows the charge–discharge curves of the prepared $LiFePO_4$/carbon composite at different cycle numbers. As shown in Figure 4 d, the ΔE evaluated from the difference between charge potential and discharge potential remains almost constant, thus indicating its high cycling ability. Although nano-sized $LiFePO_4$ has been widely studied over recent years, similarly impressive cycle life data have rarely been reported. We believe that this phenomenon could boost the study of olivine $LiFePO_4$, particularly the effect of particle-size and/or the full carbon coating on the cycling ability of olivine.

In summary, a facile method has been developed for the synthesis of nano-sized $LiFePO_4$ completely coated with carbon from a low-cost Fe^{3+} salt. This method is likely to be easy to scale up for industrial production. The unique structure of this nano-size olivine $LiFePO_4$, combined with its full coating of conductive carbon, effectively enhances its electrochemical performance. The results reported herein provide a new basis for the synthesis of nanomaterials besides reducing the preparation temperature, and several other nano-sized materials have been successfully prepared by this method.

Experimental Section

The starting materials for synthesizing the $FePO_4$/PANI composite were $FeCl_3$, $NH_4H_2PO_4$, and aniline. In a typical synthesis, 100 mL of a distilled water solution containing 3.7 g of $FeCl_3$ was slowly added, with stirring, to 200 mL of distilled water solution containing 2.62 g of $NH_4H_2PO_4$ and 1 mL of aniline. The reaction mixture was then stirred for 5 h at room temperature and the resulting $FePO_4$/PANI composite was filtered and washed several times with distilled water.

The $LiFePO_4$/carbon composite was synthesized from the prepared $FePO_4$/PANI composite by mixing it with an equimolar amount of CH_3COOLi (with respect to the amount of $FePO_4$ in the prepared composite) and some sucrose (25 wt. % in these precursors). After mixing and milling for about 1 h, the precursors were heated at 400 °C for 4 h under argon containing 5 % H_2. The precursors were then re-

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milled for about 1 h and finally calcined at 700 °C for 15 h under argon containing 5 % H_2 to obtain the $LiFePO_4$/carbon composite.

FTIR data were obtained with an FT/IR-6200 spectrometer. Powder X-ray diffraction (XRD) data for the prepared materials were collected with a Bruker D8 Advance diffractometer using $Cu_{K\alpha}$ radiation. SEM images were recorded with a TOPCON DS-720 instrument, and TEM images with a Hitachi 800 TEM operating at 200 kV.

A composite electrode was used for electrochemical measurements. This electrode was prepared as follows. A mixture containing 83 wt. % of composite, 12 wt. % of acetylene black, and 5 wt. % of polytetrafluoroethylene (PTFE) was well mixed and then pressed onto a nickel mesh (100 mesh) which served as a current collector. The mass loading of the $LiFePO_4$ within the prepared composite electrode was 5 mg cm^{-2}. Lithium metal was used as both counter electrode and reference electrode. The electrolyte was 1 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate (1/1 by volume). The cyclic voltammetry (CV) and charge-discharge tests were performed with a Solartron Instrument Model 1287 controlled by a computer.

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