

Research Article

Synthesis of LiFePO_4 /Graphene Nanocomposite and Its Electrochemical Properties as Cathode Material for Li-Ion Batteries

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LiFePO_4 /graphene nanocomposite was successfully synthesized by rheological phase method and its electrochemical properties as the cathode materials for lithium ion batteries were measured. As the iron source in the synthesis, FeOOH nanorods anchored on graphene were first synthesized. The FeOOH nanorods precursors and the final LiFePO_4 /graphene nanocomposite products were characterized by XRD, SEM, and TEM. While the FeOOH precursors were nanorods with 5–10 nm in diameter and 10–50 nm in length, the LiFePO_4 were nanoparticles with 20–100 nm in size. Compared with the electrochemical properties of LiFePO_4 particles without graphene nanosheets, it is clear that the graphene nanosheets can improve the performances of LiFePO_4 as the cathode material for lithium ion batteries. The as-synthesized LiFePO_4 /graphene nanocomposite showed high capacities and good cyclabilities. When measured at room temperature and at the rate of 0.1C ($1\text{C} = 170\text{ mA g}^{-1}$), the composite showed a discharge capacity of 156 mA h g^{-1} in the first cycle and a capacity retention of 96% after 15 cycles. The improved performances of the composite are believed to be the result of the three-dimensional conducting network formed by the flexible and planar graphene nanosheets.

1. Introduction

Rechargeable lithium ion batteries have been considered as the next generation of power sources for electric vehicles, hybrid electric vehicles, and plug-in hybrid electric vehicles [1–3]. Due to its low cost, long cycle life, environmental friendliness, and thermal stability, olivine phase LiFePO_4 , with a theoretical capacity of 170 mA h g^{-1} and a flat voltage plateau at 3.4 V (versus Li^+/Li), has been considered as a promising electrode material for these rechargeable lithium-ion batteries [4]. However, along with the above-mentioned advantages, like another polyanion-type cathode materials, LiFePO_4 has also disadvantages of low electronic conductivity and slow diffusion rates of lithium ions. To overcome the low electronic conductivity of LiFePO_4 , a lot of methods have been made through different material processing approaches [5–8]. Among these approaches, coating LiFePO_4 with carbonaceous conductors is the easiest and most used method to improve the electronic conductivity of LiFePO_4 particles.

Graphene is a monolayer of graphite, consisting of sp^2 hybridized carbon atoms arranged in a honeycomb crystal

lattice. It is a nearly ideal two-dimensional (2D) material with extraordinary mechanical, electrical, thermal, and optical properties [9–12]. Owing to the outstanding electrical conductivity, graphene has recently been used to improve the performances of the cathode electrode materials in supercapacitors, fuel cells, solar cells, and lithium ion batteries [13–16]. In the application for lithium ion batteries, since graphene itself is electrochemically active as the anode materials, it has been used in most cases in the anode materials to restrict the volume expansion and to improve the electronic conductivity. Graphene has also been used to improve the performance of LiFePO_4 synthesized by solid-state reactions and sol-gel reaction [17–19].

In this paper, LiFePO_4 /graphene nanocomposite was synthesized by rheological phase method [20] with FeOOH nanorods as the precursor. The final products were LiFePO_4 nanoparticles anchored on graphene nanosheets. The electrochemical measurements showed that the 2D graphene nanosheets in the nanocomposites did improve the performances of LiFePO_4 as the cathode materials for lithium ion batteries.

2. Experimental Section

2.1. Synthesis of LiFePO₄/Graphene Nanocomposite

Synthesis of FeOOH Nanorods-Graphene Oxide Nanocomposite. Graphite oxide (GO) was obtained by ultrasonic treatment of graphite oxide, which was prepared using the traditional Hummers's method [21]. After 200 mg GO was stirred in 100 mL water-ethanol system (H₂O : C₂H₅OH = 1 : 1 in volume) for 1 h, 1.35 g FeCl₃·6H₂O was dissolved in the solution and refluxed at 100 °C for 2 h in oil bath. The mixture was then naturally cooled and centrifuged at 4800 r/min for 10 min. After being washed sequentially in deionized water and ethanol several times and dried in an oven at 60 °C for 24 h, the brown yellow FeOOH powder was obtained.

Synthesis of LiFePO₄-Graphene Nanocomposite. Firstly 200 mg PEG10000 was dissolved in 20 mL ethanol. Then 2 mmol FeOOH powder and 2 mmol LiH₂PO₄ were added in the solution. With ultrasonic treatment for 5 min, the LiH₂PO₄ was completely dissolved and the FeOOH powder was dispersed uniformly. After heating and stirring for overnight, the solvent was partially evaporated and the system was very viscous. After being adjusted into a rheological phase, the reactants were annealed at 650 °C for 10 h. The final dark brown powder was obtained after being cooled to room temperature naturally.

2.2. Characterization. The phase purity of the products was examined by powder X-Ray Diffraction on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The crystal size and morphology of the products were examined with a scanning electron microscope (SEM, QUANTA 200, Holland). The thermal analysis was determined by a Netzsch STA 449C (Germany) in oxygen at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. Transmission electron microscope (TEM) images and high-resolution transmission electron microscope (HRTEM) images were taken on a JEM 2010-FEF (JEOL Ltd., Japan) operating at 200 kV. The carbon contents in the composites were determined by VarioEL III elemental analyzer (Elementar Analysen System GmbH, Germany).

2.3. Electrochemical Property Measurements. The electrochemical measurements were carried out using CR2016 coin cells with lithium metal disks as the counter electrodes. The working electrodes were made by pressing mixtures of the synthesized LiFePO₄/Graphene composites, acetylene black (AB), and polyvinylidene fluoride (PVDF) binder with a weight ratio of 80 : 15 : 5 on Al meshes which were used as the current collectors. The electrolyte was composed with 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (1 : 1 v/v) solvents and the separator was Celgard 2300 microporous film. The cells were assembled in a glovebox filled with high purity Ar gas. The electrochemical tests were performed galvanostatically in the voltage window of 2.0–4.4 V on Neware battery test system (Shenzhen, China) at room temperature. All the charge-discharge specific capacities were calculated on

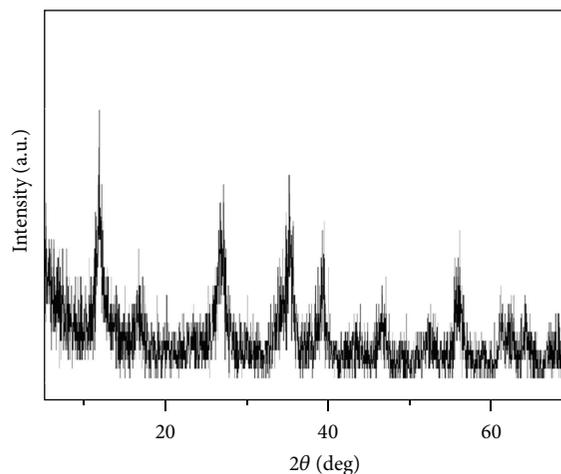


FIGURE 1: The XRD spectrum of the FeOOH precursors.

the net mass of LiFePO₄ excluding carbon content (both the amorphous carbon and the graphene).

3. Results and Discussion

Figure 1 showed the XRD spectrum of the FeOOH precursors obtained by the reflux reaction between graphite oxide and FeCl₃·6H₂O. All the reflection peaks can be indexed on the basis of FeOOH standard card without any reflection peak from impurity phases. Also, the low intensity and the big width of the reflection peaks in the XRD spectrum implied the nanoscale sizes of the FeOOH precursors.

Figure 2 shows the TEM images of the FeOOH precursors. It is clear that the FeOOH precursors have nanorods morphology, evenly distributed and anchored on the graphene nanosheets. The nanorods are 5–10 nm in diameter and 10–50 nm in length.

Figure 3 shows the XRD spectra of the LiFePO₄/graphene composites synthesized at 600 °C and 650 °C, respectively. All the diffraction peaks can be indexed on the base of olivine phase LiFePO₄ without any peaks from impurities. Compared with the XRD spectrum of the composite obtained at 600 °C, the peaks in the XRD spectrum of the composite obtained at 650 °C have much higher intensities, implying that the LiFePO₄ synthesized at 650 °C has better crystallinity. Since good crystallinity of LiFePO₄ is beneficial to the diffusion of Li⁺ and can thus improve the electrochemical performances of the materials, 650 °C was used as the annealing temperature in the experiment.

Figure 4 shows the SEM and TEM images of the LiFePO₄/graphene composite. From the low magnification SEM image of the LiFePO₄/C (Figure 4(a)), we can see that the LiFePO₄/C powder is comprised of many aggregations of microplanes. When the image is magnified 10000 times (Figure 4(b)), it is clear that there are many nanoscale particles anchored on the microplanes. In the TEM image of the LiFePO₄/C (Figure 4(c)), the graphene is obvious. And we can see that the phosphate particles are not very uniform, with large particles having about 100 nm in size and small

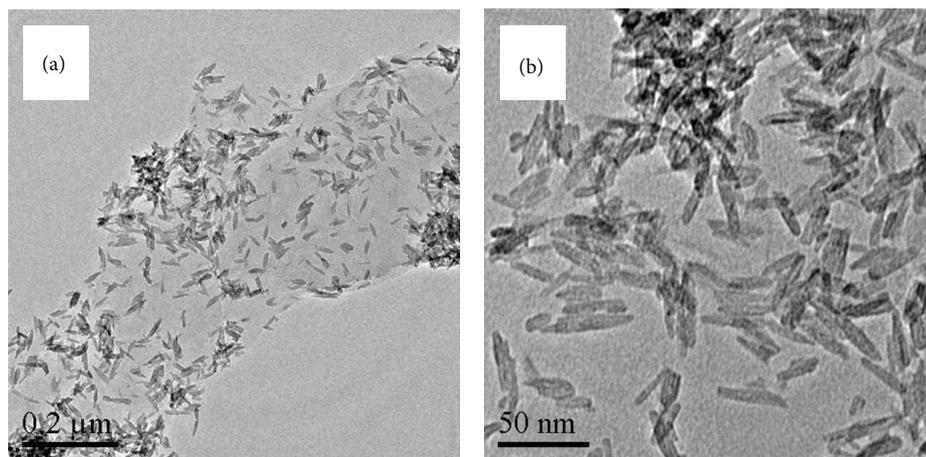


FIGURE 2: The TEM images of the FeOOH nanorod precursors with different magnifications. The images showed that the FeOOH nanorods are evenly distributed and anchored on the graphene nanosheets.

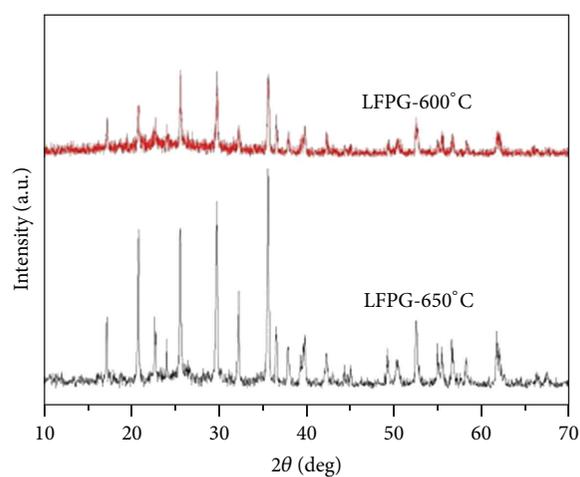


FIGURE 3: The XRD spectra of the LiFePO_4 -graphene composites synthesized at 600°C and 650°C , respectively.

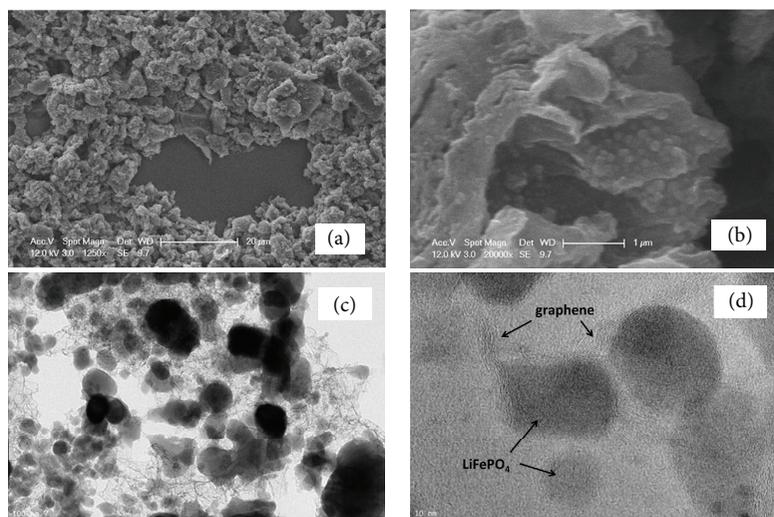


FIGURE 4: The SEM (a, b) and TEM (c, d) images of the LiFePO_4 /graphene composite.

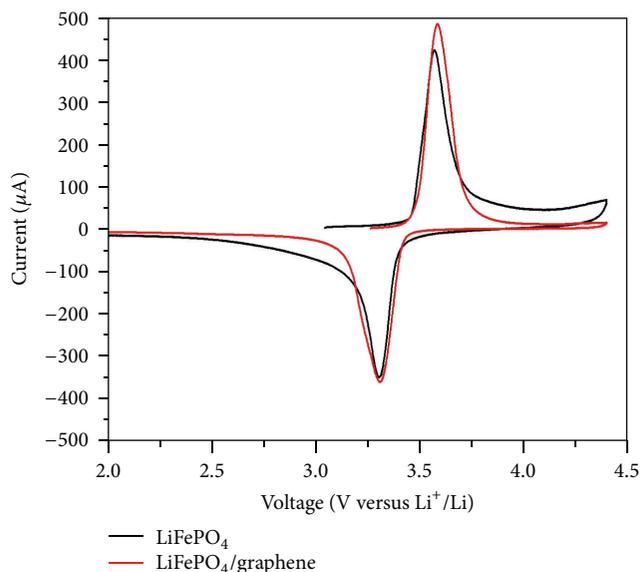


FIGURE 5: The cyclic voltammograms curves of LiFePO_4 and the $\text{LiFePO}_4/\text{graphene}$ composite for the first charge-discharge cycle at scanning rate of 0.1 mV s^{-1} between 2.0 and 4.4 V (versus Li^+/Li).

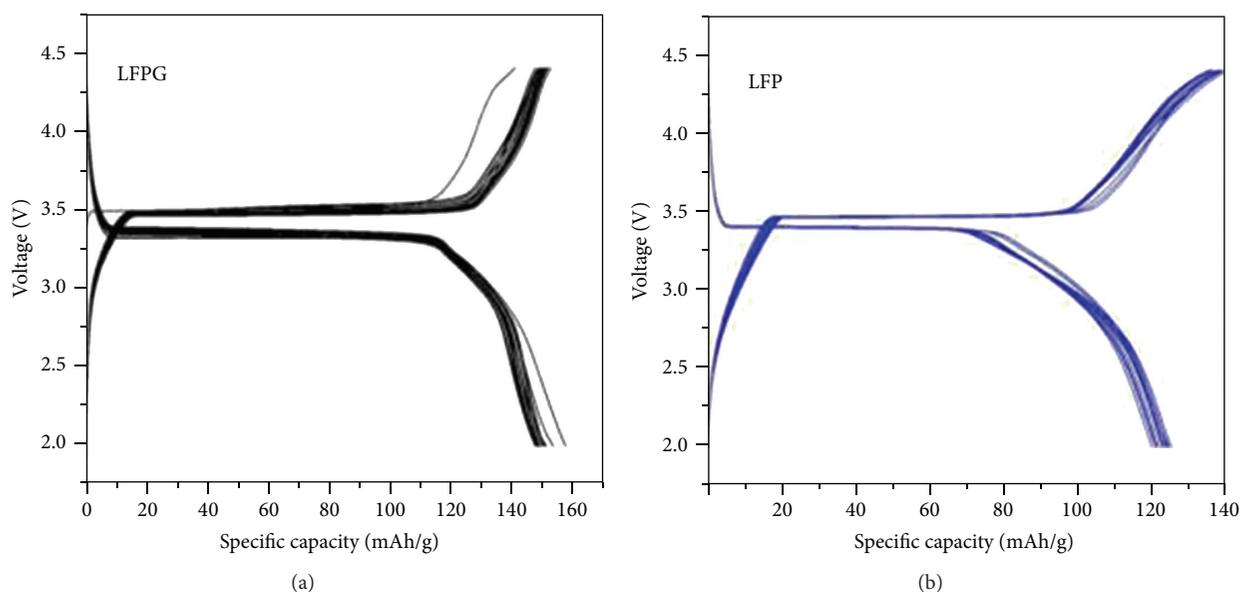


FIGURE 6: The charge-discharge curves of the first ten cycles for the LiFePO_4 and the $\text{LiFePO}_4/\text{graphene}$ composite.

particles at about 20 nm in size. In the high-resolution TEM image (Figure 4(d)), the layers of the graphene nanosheets and the crystal planes of the LiFePO_4 nanocrystals can be observed.

Figure 5 shows the cyclic voltammograms curves of the LiFePO_4 with and without graphene in the first charge-discharge cycle. Both the electrodes exhibit the redox peaks of $\text{Fe}^{2+}/\text{Fe}^{3+}$ at a scan rate of 0.1 mV s^{-1} . For the $\text{LiFePO}_4/\text{graphene}$ composite, the anodic peak at 3.5 V corresponds to the oxidation of Fe^{2+} to Fe^{3+} , and the cathodic peak at 3.3 V corresponds to the reduction of Fe^{3+} to Fe^{2+} , with a potential interval of 0.2 V between these two redox

peaks. The separation observed between the oxidation and reduction peaks is often used to differentiate the electrochemical reversibilities of the electrode materials, with larger separation indicating lower reversibility. This narrow separation of the redox peaks implies that the $\text{LiFePO}_4/\text{graphene}$ composite has very good electrochemical kinetics.

Galvanostatic charge-discharge measurements were carried out with lithium cells at a current density of $0.1C$ ($1C = 170 \text{ mA g}^{-1}$) to evaluate the electrochemical properties of the LiFePO_4 with and without graphene nanosheets. Figure 6 shows the initial 10 cycling profiles of the phosphate electrodes with (Figure 6(a)) and without (Figure 6(b)) graphene

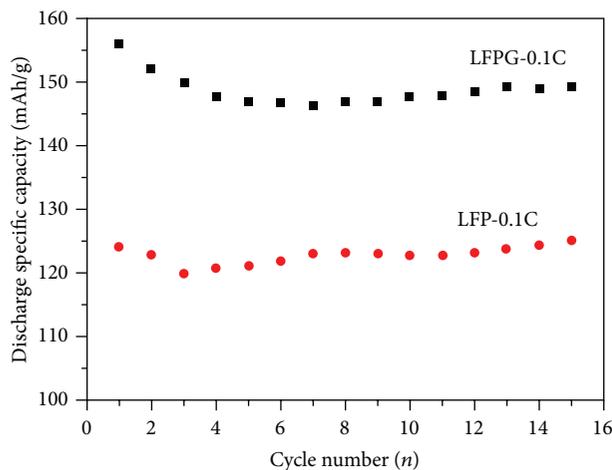


FIGURE 7: The cycling performances of the LiFePO_4 and the $\text{LiFePO}_4/\text{graphene}$ composite at the rate of 0.1C.

at room temperature. In the charge-discharge curves of the $\text{LiFePO}_4/\text{graphene}$ composite (Figure 6(a)), the charge profile of the first cycle exhibits a voltage plateau at 3.5 V (versus Li^+/Li), which should correspond to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. The discharge profile of the first cycle shows a voltage plateau at 3.3 V (versus Li^+/Li), with a very small separation (0.2 V) to the plateau in the charge profile. The specific discharge capacity in the first cycle is 158 mA h g^{-1} , which is around 93% of the theoretical specific capacity of LiFePO_4 . Also, the charge-discharge profiles have showed very stable cycle life. Although the charge-discharge curves for LiFePO_4 (Figure 6(b)) also show stable cycle life, the LiFePO_4 has much smaller discharge capacities when compared to the $\text{LiFePO}_4/\text{graphene}$ composite. The specific discharge capacity is only 125 mA h g^{-1} for LiFePO_4 when no carbon or graphene is present.

Figure 7 shows the cycling performances of the $\text{LiFePO}_4/\text{graphene}$ composite (labelled as LFPG in the figure) at the rate of 0.1C. The discharge specific capacity in the first cycle is 158 mA h g^{-1} . And the discharge capacity in the fifteenth cycle is 149 mA h g^{-1} , which is about 95.5% of the capacity in the first cycle. It shows that the $\text{LiFePO}_4/\text{graphene}$ composite has very good cyclability. The LiFePO_4 without graphene (labelled as LFP in the figure), though having much lower discharge capacities than the $\text{LiFePO}_4/\text{graphene}$ composite, also shows very good cycling performances. This implies that the good cyclability of the material comes from the very stable crystal structure of LiFePO_4 and has no relations with graphene.

Figure 8 shows the discharge-cyclability profiles for the LFPG and LFP samples at different rates. At all the charge/discharge rates, the LFPG shows better performances than the LFP samples. In particular, at the rate of 5C, while the LFP shows discharge capacity of 78 mA h g^{-1} , the LFPG shows discharge capacity of 107 mA h g^{-1} , which is about 37% more than the LFP material. Although both materials have very good cyclability, the LiFePO_4 with graphene always shows larger capacities than the pristine LiFePO_4 without graphene,

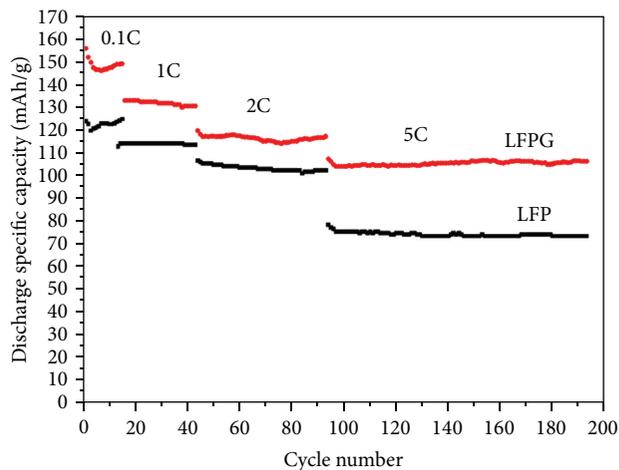


FIGURE 8: The typical discharge-cyclability profiles at different rates.

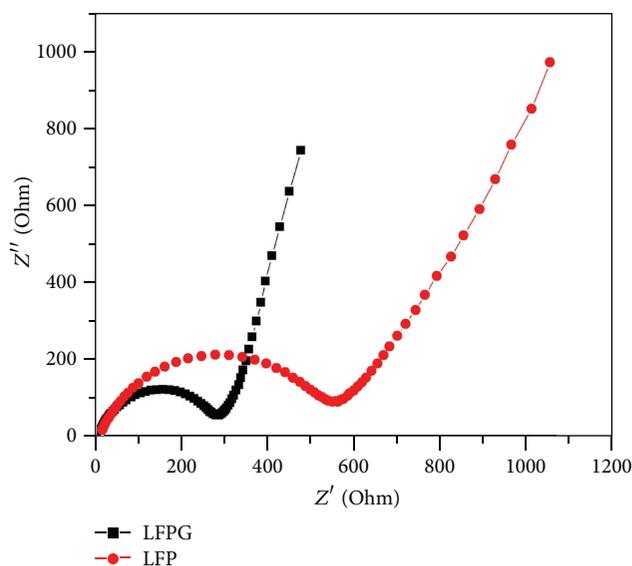


FIGURE 9: The electrochemical impedance spectroscopies (EIS) for LFPG and LFP.

especially at high charge/discharge rates. The phenomenon probably is due to the great electronic conductivity of the graphene monolayers. Also the existence of the graphene monolayer may also restrict the growing up of the LiFePO_4 particles and the small sizes of the LiFePO_4 are beneficial to the high-rate performances of the cathode materials.

To prove that the graphene monolayers in the LFPG composite increased the electronic conductivity of the material, we measured the electrochemical impedance spectroscopies (EIS) of both LFPG and LFP and showed the EIS profiles in Figure 9. From comparing the diameters of the semicircles of the EIS profiles, we can see that the charge-transfer resistance for the LFPG cathode ($\sim 270 \text{ ohm}$) is much smaller than the resistance for the LFP cathode ($\sim 550 \text{ ohm}$). This much smaller solid-electrolyte interface resistance should be owing to the existence of graphene layers in the LFPG composite, which has very good electronic conductivity.

4. Conclusion

In summary, LiFePO₄-graphene composite was successfully synthesized by rheological phase method, with FeOOH nanoparticles anchored on graphene nanolayers as the iron source. The obtained materials were characterized by XRD, SEM, TEM, charge-discharge tests, and electrochemical impedance spectrum measurements. Although both the LiFePO₄ with and without graphene showed excellent cyclabilities, the LiFePO₄-graphene composite showed higher capacities than the LiFePO₄ without graphene at all the charge/discharge rates measured. These better performances should be owing to the good electronic conductivity of the graphene nanolayers in the LiFePO₄-graphene composite.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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