Synthesis, Structure and Electrochemical Performance of LiFePO₄/C

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Olivine-type $LiFePO_4$ and $LiFePO_4/C$ cathode materials were synthesized by hydrothermal method. The crystal structure and morphology and electrochemical performance of the materials were characterized and analyzed by X-ray diffraction, scanning electron microscopy and electrochemical testing. The effects of three different carbon sources, *i.e.* critic acid, poly(vinyl alcohol) and glucose, on the performance of as-synthesized cathode materials were investigated. Then, $LiFePO_4/C$ cathode materials prepared using glucose as the carbon source were modified with polyaniline (PAn) as modifier. The results show that the carbon formed from the carbon resource during hydrothermal process has obviously improved the electrochemical performance of $LiFePO_4$, while it has no effect on the crystal structure of $LiFePO_4$. The initial discharge specific capacity of $LiFePO_4/C$ cathode with 5 % glucose as carbon resource achieves 151.2 mAh × g⁻¹ at 0.1 C and 87.3 mAh × g⁻¹ at 2C, respectively. After modified by 10 % PAn the $PAn_{0.1}$-$LiFePO_4/C_{0.9}$ delivers the capacity of 167.1 mAh × g⁻¹ at 0.1 C and has good reversibility and high capacity retention.

Key Words: LiFePO₄, Carbon resource, Hydrothermal method, Cathode material.

INTRODUCTION

The shortages of fossil fuel and the pollution of human survival environment promote the rapid development of solar, wind, hydropower and other clean sustainable energy. Converting the new energy into electrical energy and using it as driving force of power tools are causing the concern in the field of the world's energy and environment. Lithium-ion batteries for their high specific capacity, long life and less pollution have become new energy storage candidates for power source of electric vehicles. Recently, lithium iron phosphate ($LiFePO_4$) has been successfully developed as cathode material in lithium-ion battery with high security and long service life. Now, the $LiFePO_4$ has been prepared by solid-phase method and sol-gel method[1,2]. $LiFePO_4$ itself has inherent disadvantages, namely the low electronic conductivity and low Li^+ diffusion rate. So the modification and morphology control of $LiFePO_4$ have become the research focus[3,4]. Hydrothermal method can make the materials to achieve molecular-level mixing in the solution. And the prepared particle size can been controlled. Furthermore, relatively low synthesis temperature and short reaction time can help to reduce particles agglomeration[5-8]. In this paper, carbon sources were directly introduced into the process of hydrothermal synthesis. The effect of different carbon sources such as citric acid, poly(vinyl alcohol) (PVA) and glucose on the performance of $LiFePO_4$ was investigated.

With $LiFePO_4/C$ as parent material, polyaniline (PAn) coated PAn_x-$LiFePO_4/C_{1-x}$ particles were *in situ* synthesized.

EXPERIMENTAL

Raw materials such as $LiOH \cdot H_2O$, $FeSO_4 \cdot 7H_2O$ and H_3PO_4 were weighed according to n (Li): n (P): n (Fe) = 3:1:1. The aqueous solutions of LiOH and H_3PO_4 were mixed together first and then $FeSO_4$ solution and a certain amount of citric acid, polyvinyl alcohol or glucose was added subsequently. Finally they were put in an autoclave. The autoclave was sealed and heated at 180 ºC for 6 h. When the solution cooled down to room temperature the precipitate was filtered and washed several times with deionized water and ethanol. The filter cake was dried at 90 ºC for 3 h in a vacuum oven. The dried sample was treated at 650 ºC for 5 h under N_2 atmosphere. The $LiFePO_4$ without carbon was marked as sample **a**. The sample synthesized with 5 % (by the amount of substance of LiOH) citric acid, PVA or glucose was marked as b, c or d. PAn-$LiFePO_4/C$ composite was prepared using $LiFePO_4/C$ particles as crystal nuclear, sodium dodecylbenzenesulfonate as emulsifier, $FeCl_3$ as oxidative agent and aniline as monomer in aqueous solution at 0 ºC for 6 h. The final product PAn-$LiFePO_4/C$ was successively washed with distilled water and acetone, then dried at 60 ºC under vacuum overnight to obtain a homogeneous powder.

Detection method: Crystal structure of $LiFePO_4$ and $LiFePO_4/C$ and PAn-$LiFePO_4/C$ were identified with X-ray

diffraction with CuK_α radiation. XRD patterns were collected by a step-scanning mode in the range of 10º-80º with a step time of 0.014º/0.3 s. The powder morphologies were observed by the field emission scanning electron microscopy (FE-SEM). In the electrochemical test, the composite electrodes were fabricated using as-prepared cathode materials, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10 in NMP. The slurry was coated onto Al foil and dried at 120 ºC for 12 h under vacuum. The resulting electrode plates were pressed with a twin roller and cut into a round shape (Φ = 14 mm). Cells were assembled in argon-filled glove box using lithium as the anode and 1 M $LiPF_6$/EC-DEC (1:1 vol %) as the electrolyte. The charge-discharge cycle performance was examined in galvanostatic charge-discharge unit LAND-CT2001A battery cycler from 2.4 V to 4.2V.

RESULTS AND DISCUSSION

XRD analysis of LiFePO₄ and LiFePO₄/C and PAn-LiFePO₄/C: The XRD patterns of $LiFePO_4$ and $LiFePO_4$/C and PAn-$LiFePO_4$/C composites are shown in Fig. 1. The diffraction peaks of $LiFePO_4$/C and PAn-$LiFePO_4$/C are consistent with the standard diffraction peaks, indicating that they are the olivine-type structure. The diffraction peaks of impurities Li_3PO_4 and $Fe_2(PO_4)OH$ appear in the curve of $LiFePO_4$ and the peak intensity is relatively weak. On the other hand, the peak of carbon is not observed, indicating that the amount of carbon is little or most of which is amorphous carbon. It is well known that the added carbon sources during the hydrothermal synthesis process would conduct some chemical reactions at the temperature of hydrothermal synthesis, which offer a good dispersion and reducibility environment for growth of $LiFePO_4$ and contribute to well formed crystal $LiFePO_4$. The carbon prevents the oxidation of Fe^{2+} to Fe^{3+} and hinders the appearance of impurity during high temperature calcination of $LiFePO_4$/C composite material. Without carbon in $LiFePO_4$, the small amount of Fe^{2+} will be oxidized to Fe^{3+} during the hydrothermal synthesis and subsequent high-temperature roasting process. The formation of non-conductive layer on the surface of $LiFePO_4$ particles will influence the $LiFePO_4$ activity in the lithium battery. In addition, no evidence of diffraction peaks for crystalline carbon and polyaniline appear in the diffraction patterns, which indicates that the carbon and polyaniline have no influence on the olivine structure of $LiFePO_4$.

SEM analysis of LiFePO₄ and LiFePO₄/C and PAn-LiFePO₄/C samples: The morphology of $LiFePO_4$ and $LiFePO_4$/C and PAn-$LiFePO_4$/C observed by SEM are shown in Fig. 2. As can be seen from Fig. 2, hydrothermal synthesis environment with different carbon sources has a great effect on the morphology of samples. The agglomeration phenomenon of sample **a** is more serious than others and the particle size is larger and uneven. The particle size of sample **b** is about 600 nm, which is larger than that of sample **c** and **d**, whose are about 300 nm. The dispersion of sample **d** is better than that of sample **c**. It is acknowledged that different carbon sources have different effects on the grain growth and re-growth. The carbon formed in the hydrothermal and subsequent roasting process distributes between the particles or coats on the particle

surfaces to prevent the growth of grain and refine grains. The SEM observation has shown that there is an appropriate amount of carbon resource especially for the glucose in the morphology and shape control of $LiFePO_4$/C. From Fig. 2 (e) and Fig. 2(f) it can be seen that the $PAn_{0.1}$-$LiFePO_4$/$C_{0.9}$ composite looks homogeneous. Fig. 2(f) further demonstrated that polyaniline is well coated on the surface of the $LiFePO_4$/C particles. Most of the particles congregated each other by the connection of sticky polymers, which could benefit to reduce the particle-to-particle contact resistance and enhance the electrical conductivity of the composites.
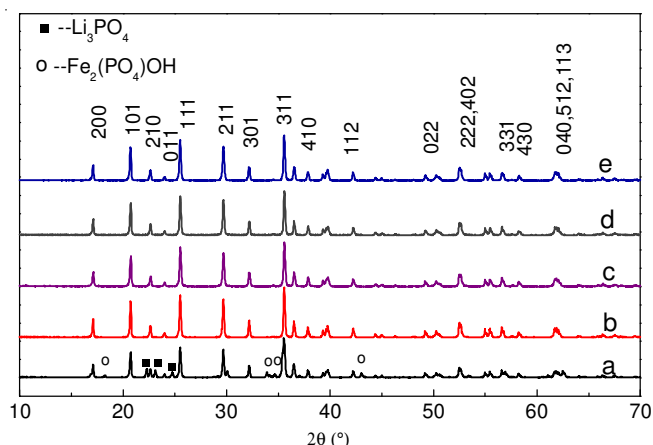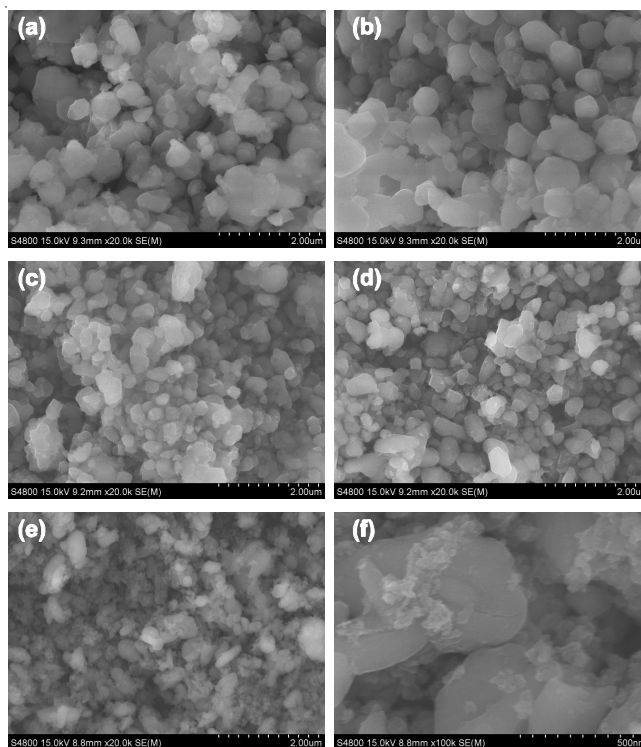

Fig. 1.　XRD patterns of LiFePO₄ and LiFePO₄/C and PAn-LiFePO₄/C samples (**a**) LiFePO₄; (**b**) LiFePO₄/C with 5 % critic acid as carbon resource; (**c**) LiFePO₄/C with 5 % poly(vinyl alcohol) as carbon resource; (**d**) LiFePO₄/C with 5 % glucose as carbon resource; (**e**) PAn₀.₁-LiFePO₄/C₀.₉ with 5 % glucose as carbon resource

Fig. 2.　SEM patterns of LiFePO₄ and LiFePO₄/C and PAn-LiFePO₄/C samples (**a**) LiFePO₄; (**b**) LiFePO₄/C with 5 % critic acid as carbon resource; (**c**) LiFePO₄/C with 5 % PVA as carbon resource; (**d**) LiFePO₄/C with 5 % glucose as carbon resource; (**e**) (**f**) PAn₀.₁-LiFePO₄/C₀.₉ with 5 % glucose as carbon resource

Electrochemical performances of LiFePO$_4$ and LiFePO$_4$/C and PAn-LiFePO$_4$/C: The initial charge-discharge performances of LiFePO$_4$ and LiFePO$_4$/C (sample **a**, **b**, **c** and **d**) at 0.1 C are shown in Fig. 3. It can be seen from Fig. 3 that carbon sources have important effects on the charge-discharge performances of these LiFePO$_4$/C composites. There is no obvious platform on the charge and discharge curves of sample **a**. For sample **b** there is a short platform. Sample **c** and **d**, however, have stable charge and discharge platform at the 3.5 V and 3.3 V respectively. The sample **d** prepared by glucose as the carbon source has the maximum discharge capacity, which is 151.2 mAh × g^{-1} and sample **c** used poly(vinyl alcohol) as carbon source is the second one, but the discharge capacity of sample **b** used citric acid as carbon source does not increase obviously. The reason may be that irregular LiFePO$_4$/C particles have been formed in citric acid precursor solution, moreover, the particle size is large. These factors are the disadvantages to Li$^+$ diffusion in the process of charging and discharging. The poly(vinyl alcohol) and glucose are hydroxyl-rich compounds. They can be used as good dispersants and reducing agents in the precursor solution. Therefore the oxidation of Fe^{2+} into Fe^{3+} can be inhibited and small size particles of LiFePO$_4$/C have been obtained. Furthermore, the particle size decreases after roasting at high temperature and the grain shape becomes more regular. Small particles help Li$^+$ to reach the redox center of the cathode and improve the utilization of active materials, thereby enhancing the discharge capacity. But the sample **c** has a little agglomerating pheno-menon, which contributes to the lower discharge capacity than that of sample **d**.
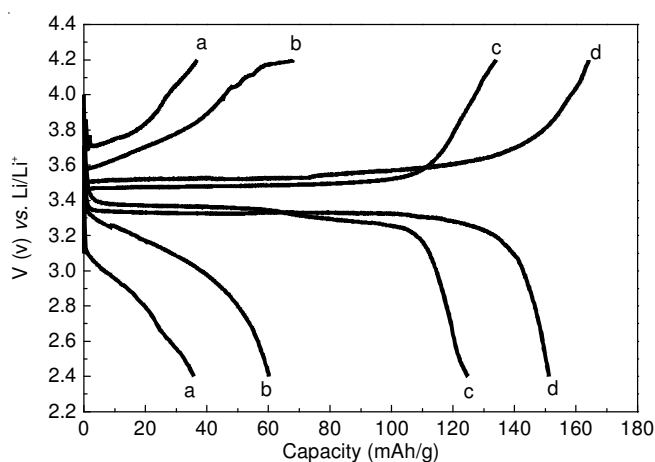

Fig. 3.　Initial charge-discharge curves of samples at 0.1 C (**a**) LiFePO$_4$; (**b**) LiFePO$_4$/5 % critic acid; (**c**) LiFePO$_4$/5 % PVA; (**d**) LiFePO$_4$/5 % glucose

Fig. 4 displays initial discharge curves of LiFePO$_4$/C samples with various contents of glucose at 0.1 C rate. It can be seen from Fig. 4 that initial discharge specific capacity of sample doped with 3 % glucose is 106.3 mAh × g^{-1}, while the sample **d** with 5 % glucose has the maximum initial discharge specific capacity. Then as the content of glucose increases the discharge specific capacities of samples decrease. There is an appreciate amount of glucose used as carbon resource. Under the same carbon source conditions, particle morphology and agglomeration level are the main factors to reduce the discharge

specific capacity. In addition, the high carbon content resulting in low effective active substance content may also affect the discharge specific capacity of materials.
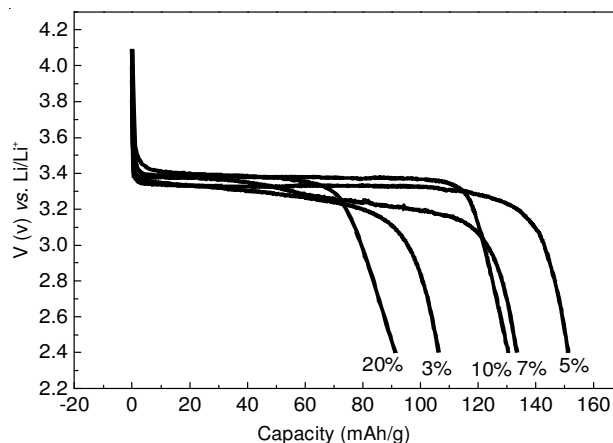

Fig. 4.　Initial discharge capacity curves at 0.1 C of LiFePO$_4$/C with various contents of glucose

Fig. 5 shows the initial discharge profiles of the PAn$_x$-LiFePO$_4$/C$_{1-x}$ composites. As can be seen, all the composites show similar flat voltage plateaus at around 3.4 V. The electro-chemical properties of the PAn$_x$-LiFePO$_4$/C$_{1-x}$ composite with different polyaniline contents were compared. Fig.5 shows a capacity of 139.5 mAh × g^{-1}, 142.5 mAh × g^{-1}, 167.1 mAh × g^{-1}, 162.8 mAh × g^{-1}, 150.4 mAh × g^{-1} at the 0.1 C rate for x = 0.03, 0.05, 0.10, 0.15 and 0.20 % respectively. PAn$_{0.1}$-LiFePO$_4$/C$_{0.9}$ exhibits a excellent discharge specific capacity of 168.9 mAh × g^{-1}. It is evident that modification with proper content of conductive polyaniline in LiFePO$_4$/C can effectively enhance discharge profiles.
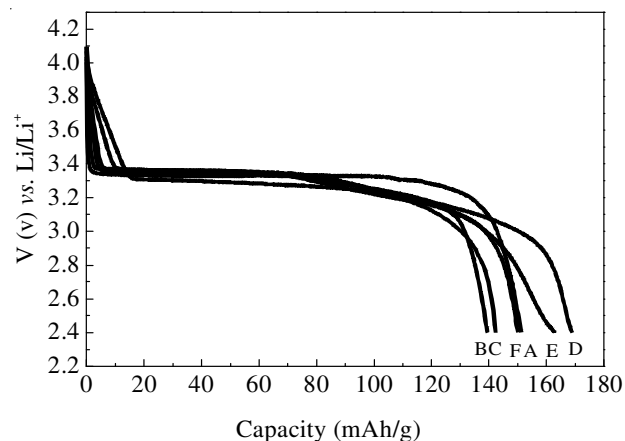

Fig. 5.　Initial discharge capacity curves at 0.1 C of PAn$_x$-(LiFePO$_4$/C)$_{1-x}$ with 5 % glucose as carbon resource (A x = 0; B x = 0.03 ; C x = 0.05; D x = 0.1; E x = 0.15; F x = 2)

Fig. 6 presents the cycle performances of LiFePO$_4$/C with 5 % glucose as carbon resource and PAn$_{0.1}$-LiFePO$_4$/C$_{0.9}$ at different rates. It can be seen from Fig. 6 that the samples have stable cycle performance and the first initial discharge specific capacities are 103.7 mAh × g^{-1} and 87.3 mAh × g^{-1} at 1 C and 2 C rate respectively for the prior sample. Compared with LiFePO$_4$/C the composite modified with 10 % polyaniline can significantly improve the high-rate discharge performance.
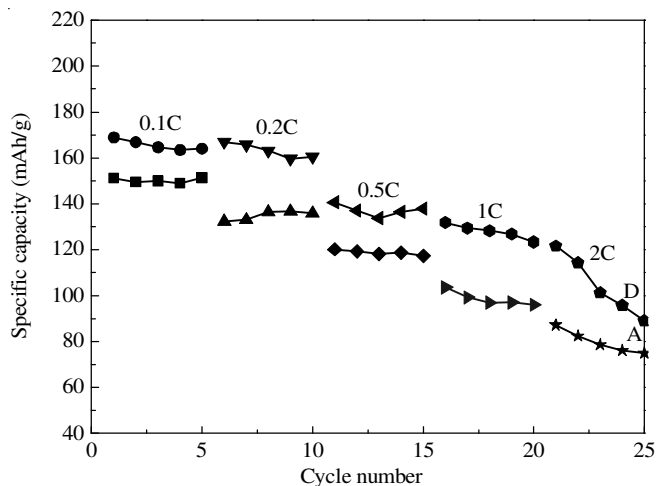
Fig. 6.   Rate capacity of LiFePO$_4$/C and PAn-LiFePO$_4$/C (**A** LiFePO$_4$/C with
          5 % glucose as carbon resource; **D** polyaniline (10 %)-LiFePO$_4$/C
          with 5 glucose as carbon resource)

Fig. 7 presents the cyclic voltammetric (CV) behaviours of the LiFePO$_4$/C and PAn$_{0.1}$- LiFePO$_4$/C$_{0.9}$ composite at a sweep rate of 0.1 mV/s. Curve (**A**) shows a typical CV for the LiFePO$_4$/C. The broad oxidation and reduction peaks centered at 3.59 V and 3.259 V, respectively. Curve (**D**) shows a typical CV for the PAn$_{0.1}$- LiFePO$_4$/C$_{0.9}$. The broad oxidation and reduction peaks centers at 3.589 V and 3.262 V, respectively. The midpoint between the oxidation and reduction peaks which corresponds to the open-circuit voltage (OCV) of the electrode is about 3.4V. In the CV profiles, higher peak current means better electrode reaction kinetics and consequently, better rate performance of the PAn$_{0.1}$- LiFePO$_4$/C$_{0.9}$.

Conclusion
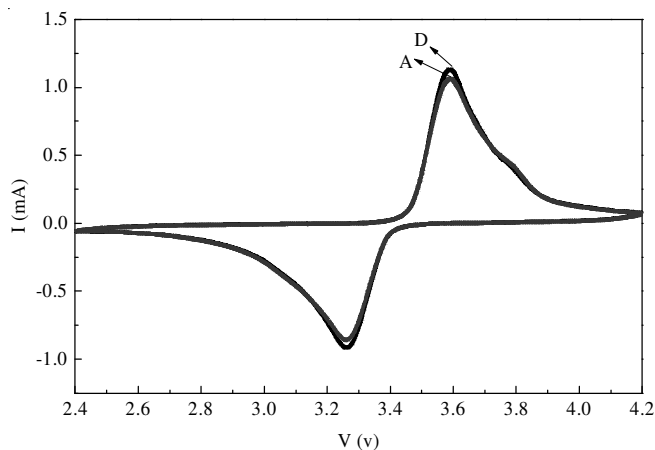
Olivine-type LiFePO$_4$ and LiFePO$_4$/C materials were synthesized by hydrothermal method. Carbon sources, *i.e.* critic acid, polyvinyl alcohol and glucose, were directly introduced in the process of hydrothermal method to provide an appropriate crystal growth environment for LiFePO$_4$ and LiFePO$_4$/C. The LiFePO$_4$/C cathode material synthesized with 5 % glucose as carbon resource has small particle size and even regular shape. The initial discharge specific capacity reaches 151.2 mAh $\times$ g^{-1} and 87.3 mAh $\times$ g^{-1} at 0.1 C and 2 C rate, respectively. LiFePO$_4$/C grains have been successfully coated with *in situ* polymerized PAn. The PAn$_{0.1}$-LiFePO$_4$/C$_{0.9}$ composite exhibits excellent initial discharge capacity, rate capability and cyclability. It delivers a discharge specific capacity of 167.1 mAh $\times$ g^{-1} at 0.1 C.

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Fig. 7.   Cyclic voltammetry curves of LiFePO$_4$/C and PAn-LiFePO$_4$/C (**A**
          LiFePO$_4$/C with 5 % glucose as carbon resource; **D** PAn (10 %)-
          LiFePO$_4$/C with 5 glucose as carbon resource)