

Preparation and electrochemical properties of LiFePO_4/C composite cathodes for lithium-ion batteries

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Abstract. Three kinds of LiFePO_4/C composites for lithium-ion batteries were prepared by solid-state reaction. The crystalline structure, morphology and specific surface area of the composites were investigated by X-ray diffraction, scanning electron microscopy and multi-point Brunauer, Emmett and Teller. The results showed that the samples were all well-ordered olivine structures. A network structure, LiFePO_4/C composite, was obtained using phenolic resin as carbon source. It possessed the highest specific surface area of $115.65 \text{ m}^2/\text{g}$, exhibited the highest discharge capacity of 164.89 and 149.12 mAh/g at 0.1 C and 1 C rates, respectively. The discharge capacity was completely recovered when 0.1 C rate was applied again.

Keywords. Lithium-ion batteries; LiFePO_4 ; cathode material; composite.

1. Introduction

LiFePO_4 is an interesting alternative cathode material for lithium-ion batteries, due to it being an inexpensive starting material having good environmental compatibility, excellent cycling stability and high temperature performance. The main drawback is its very low electronic conductivity and lithium-ion diffusion coefficient which lead to poor rate capability. This will hinder its commercialization as a cathode material for lithium-ion batteries. Efforts to increase the electronic conductivity of LiFePO_4 have focused on reducing particle size (Prosini *et al* 2003; Park *et al* 2004), coating carbon (Myung *et al* 2003) and doping metal cation (Chung *et al* 2002).

Carbon coating does not change its intrinsic conductivity, but it is very effective in enhancing capacity and rate capability. Carbon black and sugar are used as main carbon sources. The electronic conductivity of LiFePO_4/C composite prepared by adding sucrose reached 0.1 S/cm (Bewlay *et al* 2004). Prosini *et al* (2001) showed that by adding 10% carbon black in the starting materials, an improvement in its practical capacity and rate capability was seen. Carbon can control particle growth and enhance electronic conductivity, therefore, higher capacity and better rate capability can be obtained.

In this paper, LiFePO_4/C composites were prepared using various carbon sources and their properties were comparatively investigated.

2. Experimental

LiFePO_4/C composites were prepared by a solid-state reaction. Li_2CO_3 (AR, Taishan Chemical Plant), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (AR, Fluka) and $\text{NH}_4\text{H}_2\text{PO}_4$ (AR, Mingfeng Reagent Corporation) were used as the starting materials, in addition to adding acetylene black, glucose and phenolic resin, respectively. The starting materials were weighed in stoichiometric ratio and homogeneously mixed by ball grinding in anhydrous ethanol. To decompose the oxalate and the phosphate, the dried mixture was placed in a tubular furnace and treated at 350°C for 5 h in argon flow. The resultant powders were cooled to room temperature, and reground, then returned to the tubular furnace and calcined at 650°C for 18 h in argon flow. The remaining powders were cooled to room temperature. Thus the LiFePO_4/C composites containing 10% carbon were obtained and marked as A, B, C, respectively.

The crystalline structure has been confirmed by a powder X-ray diffractometer (XRD, D5000) with $\text{CuK}\alpha$ radiation. The XRD data was obtained over an angular 2θ range from 15 – 45° with a step size of 0.02° and a constant counting time of 0.2 s per step. XRD patterns were fitted and revised by Jade 5 analysis software and lattice parameters (a , b and c) were calculated. Cell volume is the product of a , b and c . The crystallite size of samples were calculated by the Scherrer equation, $D = K\lambda/(\beta \times \cos\theta)$, from the full width at half maximum β of the (131) reflection peaks, K value being 0.89. The morphology of the composites was observed by scanning electron microscopy (SEM, JMS-6700F). Multi-point Brunauer, Emmett

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and Teller method (BET, NOVA-1000) was used to measure the specific surface area of the powders.

LiFePO₄, conductive additive and polytetrafluorethylene (PTFE) were mixed homogeneously in a weight ratio of 75:20:5. The mixture was rolled into a 0.1 mm thin sheet with uniform thickness from which 12 mm diameter pellets were cut. The pellet was used as the cathode and the electrolyte was 1 mol/L LiClO₄ in ethylene carbonate and dimethyl carbonate (1:1 by volume). Lithium foil was used for the counter and reference electrodes. The separator was Celgard 2400 microporous membrane. The assembly of the cell was carried out in an argon glove box. The galvanostatic tests were run by Arbin instrument (BT-2000) between 2.5 V and 4.1 V vs Li/Li⁺ at various rates.

3. Results and discussion

The X-ray diffraction patterns of the samples, A, B and C, are shown in figure 1. The profiles of the diffraction peaks are quite narrow and symmetric. Hence, well-crystallized samples are obtained. There is no evidence of crystalline or amorphous carbon. Carbon addition has no effect on crystal structure of LiFePO₄. The diffraction peak intensities of samples B and C are evidently weaker than that of sample A. The practical temperatures of samples B and C are slightly lower than that of sample A, because of heat absorption during decomposition of glucose and phenolic resin.

The results of cell volume, crystalline size and I_{200}/I_{131} (which is the ratio of the highest intensity theoretical/practical peaks) are shown in table 1. The cell volumes of samples B and C are smaller than that of sample A, which can prevent crystal structure from being destroyed during insertion and extraction of lithium ions. The crystalline sizes of samples A, B and C gradually turn small. The

lithium-ions have to diffuse for a longer distance between the boundary and the centre of the crystalline grain because of greater crystalline size. I_{200}/I_{131} is seen to approach that of ideal crystals. The value for sample C is the largest, and it is closest to that for the ideal crystal structure.

The SEM morphologies of samples A, B and C are shown in figure 2. Sample A has rhombus shaped particles with smooth surface. The particle size is not uniform. It is very easy to discern agglomerated carbon particles in figure 2a. The starting materials and acetylene black were not homogeneously mixed due to the difference in their density, which led to a partial growth of LiFePO₄ grains. The particle size of sample B was smaller, the grain surface was uniformly coated by the carbon produced *in situ*, because of uniform dispersal of glucose and starting materials. Carbon coating restrained the second crystallization and prevented grain growth. The particle surface of sample C is very rough. Since the starting materials with phenolic resin were uniformly dispersed in anhydrous ethanol, they got trapped in the polymeric network of this phenolic resin during solidification. The network structure of phenolic resin was preserved during heat treatment. The LiFePO₄/C composite possessed excellent porous network structure as shown in figures 2c and d.

The specific surface areas of samples A, B and C shown in figure 3 are 10.14, 18.25, 115.65 m²/g, respectively. The specific surface area of sample C is 10 and 6 times greater than those of samples A and B. The high specific surface area of sample C is mainly attributed to the porous network structure.

Figure 4 shows the charge and discharge curves of various LiFePO₄/C composites. The initial discharge specific capacity of samples A, B and C at the C/10 rate is 132.09, 153.77, 164.89 mAh/g, respectively. The charge and discharge plateaus are almost the same at 3.45 V and 3.40 V, respectively which indicates a typical two-phase reaction (Takahashi *et al* 2001). The difference between the charge and discharge plateaus is about 0.05 V, showing weak polarization. Carbon coating is very effective in enhancing the electronic conductivity of LiFePO₄/C composites. Specific capacity is very dependent on particle size. The discharge capacity of sample A is relatively low due to larger grains and asymmetric carbon coating. The capacity of sample B is greater due to uniform carbon coatings increasing the contact between the conductive additive and active materials. Sample C possesses the largest initial

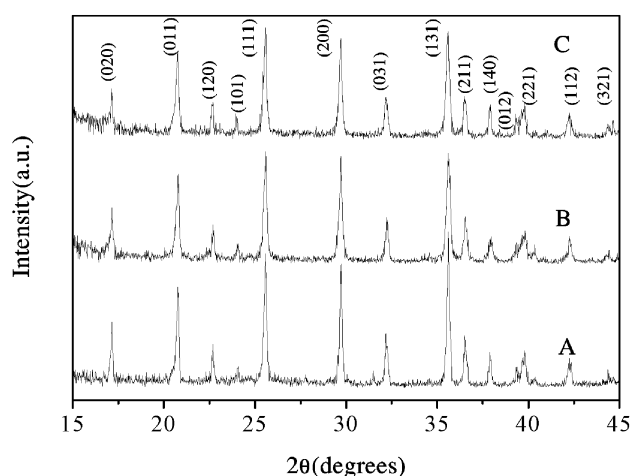


Figure 1. The XRD patterns of samples A, B and C.

Table 1. The comparison on the cell volume, crystalline size and I_{200}/I_{131} of samples.

Sample	Cell volume (nm ³)	Crystalline size (nm)	I_{200}/I_{131}
A	0.2930	41.274	0.8489
B	0.2915	38.099	0.8585
C	0.2918	37.525	0.9418

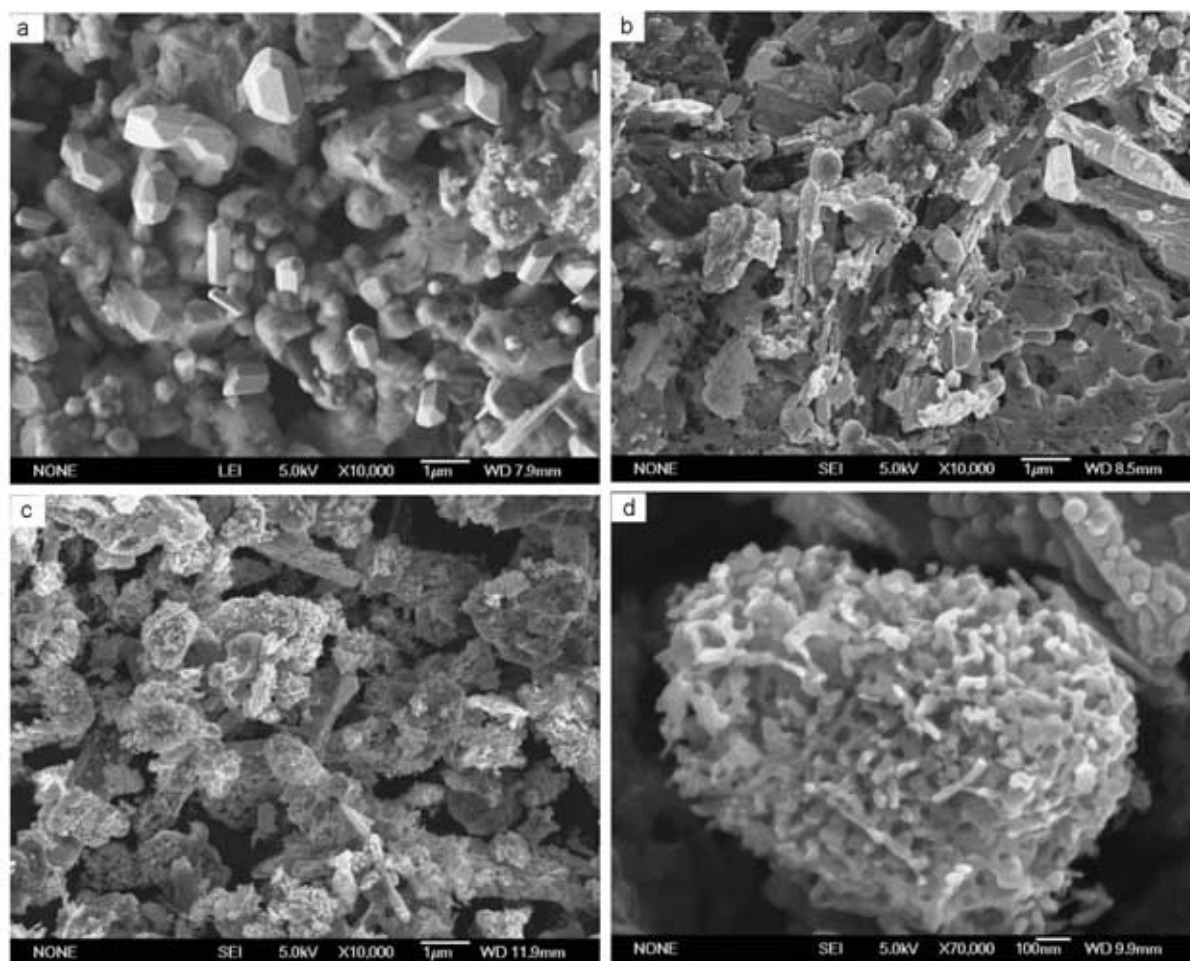


Figure 2. SEM morphology of samples: **a.** sample A, **b.** sample B, **c.** and **d.** sample C.

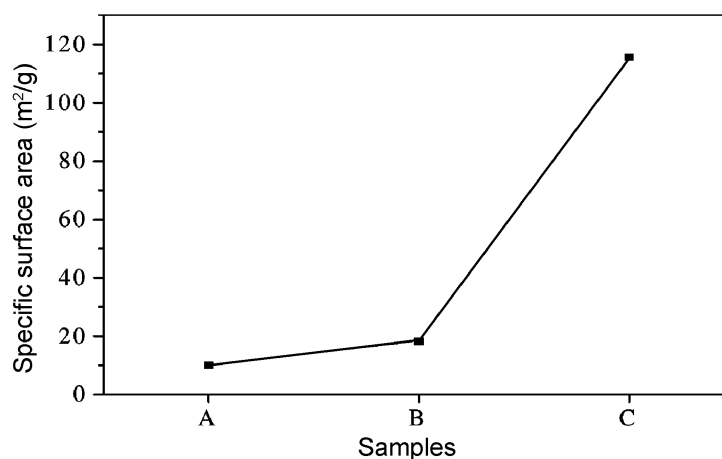


Figure 3. The specific surface area of samples.

discharge capacity, close to the theoretical capacity (170 mAh/g). The porous network structure contributes to the highest specific surface areas increasing the contact between carbon and LiFePO₄ and providing multi-dimension channels for insertion and extraction of lithium ions.

Figure 5 shows the rate and cycling capability of all samples. To investigate the rate capability, different current densities corresponding to C/10, C/2 and 1 C were applied. All samples showed excellent cycling stability in spite of the 1 C rate applied. When the rate was increased from

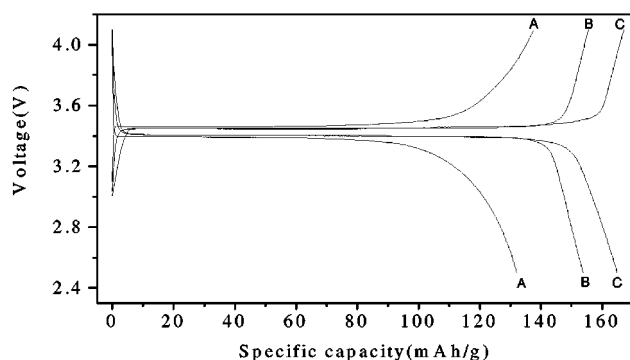


Figure 4. The initial charge and discharge capacity of samples at C/10 rate.

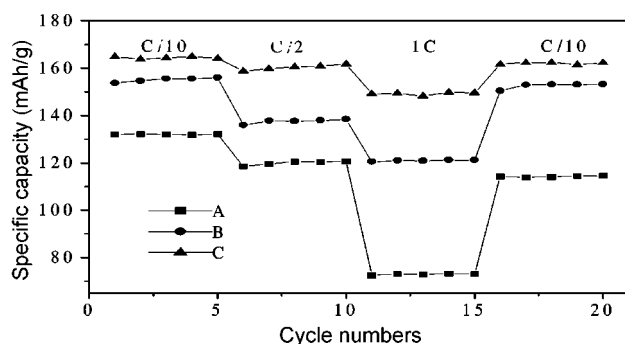


Figure 5. The rate capability of samples at C/10, C/2 and 1C rates.

C/10 to 1 C, the discharge specific capacity of sample A abruptly decreased from 132.09 mAh/g to 72.44 mAh/g, while those of samples B and C decreased by only 21.6% and 9.5%, respectively. The discharge capacity of sample C was 149.12 mAh/g at 1 C rate. The best rate performance of sample C is attributed to the porous network structure which provides multi-dimension channels for insertion and extraction of lithium ions and reduces the resistance for lithium-ion diffusion. When C/10 rate was applied again, the discharge capacity of sample A could not recover completely, the carbon and LiFePO_4 grains were separated

due to impact of large current, which possibly led to an interruption of the conductive network. The capacities of samples B and C could recover completely, which means that it is very difficult to separate the carbon and LiFePO_4 grains after the impact of large current when the carbon produced *in situ* is tightly bound to LiFePO_4 grains.

4. Conclusions

Three types of LiFePO_4/C composites from different carbon sources were prepared by solid-state reaction. Structural analysis shows that all materials are well-crystallized olivine structures. SEM observations and BET tests reveal that phenolic resin is the best carbon source to obtain excellent LiFePO_4/C composite with porous network structure and the highest specific surface area. This composite exhibits excellent cycling and rate capability. Therefore, it is concluded that the LiFePO_4/C composite with network structure is a promising cathode material for lithium ion batteries.

Acknowledgements

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