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Effect of Carbon Content on Electrochemical Properties of $LiFePO_4$/C Composite Cathode*

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Abstract Olivine-type $LiFePO_4$/C composite cathode materials were synthesized by a solid-state reaction method in an inert atmosphere. The glucose was added as conductive precursors before the formation of the crystalline phase. The effects of glucose content on the properties of as-synthesized cathode materials were investigated. The crystal structure and the electrochemical performance were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), laser particle-size distribution measurement and electrochemical performance testing. The material has a single crystal olivine structure with grain-sizes ca. 100—200 nm. SEM micrographs and the corresponding energy dispersive spectrometer (EDS) data confirm that the carbon particulates produced by glucose pyrogenation are uniformly dispersed among the $LiFePO_4$ grains, ensuring a good electronic contact. Impedance spectroscopy was used to investigate the ohmic and kinetic contributions to the cell performance. It is found that increasing the carbon content leads to a reduction of the cell impedance due to the reduction of the charge transfer resistance. The galvanostatically charge and discharge tests show that the material obtained by adding 10% C (by mass) gives a maximum discharge capacity of 140.8 $mA \cdot h \cdot g^{-1}$ at the same rate ($C/10$). The material also displays a more stable cycle-life than the others.

Keywords olivine-type, cathode material, conductive precursors, cycle-life

1 INTRODUCTION

The demand for high energy density rechargeable batteries for portable electronic devices and electric vehicle systems has promoted the development of lithium ion batteries. Many kinds of material have been investigated as the cathode material for lithium ion batteries[1]. Recently, novel materials based on lithiated transition metal polyanions have also been proposed, and olivine-structured $LiFePO_4$ appears to hold particular promise[2]. $LiFePO_4$, with a theoretical capacity of 170 $mA \cdot h \cdot g^{-1}$, shows good cycle stability due to the structural similarity between the charged and discharged states. In particular, it exhibits very good thermal stability[3]. These properties make it an attractive candidate for rechargeable lithium batteries.

However, the performance of $LiFePO_4$ is limited by the low electronic conductivity and/or slow diffusion of lithium ions across the two-phase boundary. To address these issues, some researchers have optimized synthesis techniques to minimize particle size[4] or have incorporated additives to increase conductivity. The latter approach includes coating $LiFePO_4$ particles with carbon by incorporating an organic or inorganic component with the precursors before calcination[5,6], adding metal particles to the mix[7], or solid-solution doping by metals supervalent to Li^+[8]. All improve the performance of $LiFePO_4$. Recently, it has been pointed out, however, that the presence of carbon, even below 1% (by mass), causes a significant tap density decrease[9], while Barker *et al.* controvert that large quantities of excess carbon, in the order of 100% excess carbon, are useable in the compound formation[10]. It is imperative to optimize carefully the carbon content in composite $LiFePO_4$ materials. To this end, we prepare a series of samples with variable active material/carbon ratios by using glucose as conductive precursors to investigate the influence of carbon content on the electrochemical performance of $LiFePO_4$. Various experimental techniques are employed to characterize the composite samples, such as crystal structure, surface morphology, and particle size distribution.

2 EXPERIMENTAL

Conventional solid-state reaction was employed to synthesize $LiFePO_4$ powders. $LiCO_3$ (99.5%), $FeC_2O_4 \cdot 2H_2O$ (>99%) and $NH_4H_2PO_4$ (>99.5%) were prepared as the precursor reagents, and the glucose was added as conductive precursor. Stoichiometric precursors (Li:Fe:P=1:1:1) with different glucose content, namely 5%, 10%, 15%, 20%, 30%, 40% (by mass), were grounded for 1 h using an agate mortar and pestle. The mixtures were preheated at 350℃ for 10 h in flowing nitrogen (20 $ml \cdot min^{-1}$), regrinded for 30 min, followed by heat treatment at 750℃ for 24 h.

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To determine the carbon content, a known amount of sample was dissolved in hydrochloride acid. The solution was filtered and the residue was washed with distilled water, dried and weighed.

X-ray diffraction (XRD) was performed on Rigaku D/Max 2500 V/PC powder diffractometer using Cu Kα radiation (wavelength $\lambda = 0.15405$ nm) from $2\theta = 10°$ to 80° at a count rate of 1 s per step of 0.02°. The morphological change of the material with different carbon content was examined using XL-30 ESEM surrounding scanning electron microscope (PHILIPS, the Netherlands). Particle sizes were determined with MASTERSITER 2000 laser particle size analyzer (Marlwin Apparatus Company, England). The electrochemical impedance spectroscopy (EIS) tests (frequency range: 100 kHz—0.001 Hz) and cyclic voltammetry measurement (scan rate: 0.1 $mV \cdot s^{-1}$) were performed with a CHI 660B Electrochemical Analyzer (CH Instruments, Inc., China).

Electrochemical experiments were operated on coin cells with lithium metal pellets as negative electrodes, using 1 $mol \cdot L^{-1}$ $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1/1) as electrolytes and American Cellgard 2400 membrane as separators. The positive electrodes were prepared by mixing 80% active material with 15% acetylene black as conductive additives and 5% polytetrafluoroethylene as binder. The mixture was coated onto an aluminum foil and then dried in a 120℃ vacuum oven for 12 h. All cells were fixed in the Ar_2 filled glove box (ZKX3, Nanjing University Instrument Plant, China). The galvanostatically charge and discharge experiments were performed on PCBT-138-320-A battery program-control test system (Wuhan Lixing Power Corporation, China) with a constant current of 0.1 C in the potential range of 2.8—4.0 V.

3 RESULTS AND DISCUSSION

3.1 Crystal structure

Figure 1 shows the X-ray diffraction patterns of the active material with different carbon content. The comparison with published spectra of Li-Fe-P-O (40-1499 card JCPDS Data Base) reveals the presence of single phase $LiFePO_4$ for composite cathode containing 5%, 10% and 15% C (by mass). With increasing carbon content, some peaks attributed to a second phase (Li_3PO_4) are observed. When the carbon content is increased to 30% and 40% (by mass), the undesirable conversion of iron (Fe_2P) begins to appear. This may be due to the reducing environment produced by excess carbon.

The grain size (D) was calculated with the Scherrer formula $\beta \cos(\theta) = k\lambda/D$, where β is the full-width-at-half-maximum length of the diffraction peak on a 2θ scale and k is a constant here close to unity. The mean value of D is about 100 nm, which is also comparable with the reported results[11].

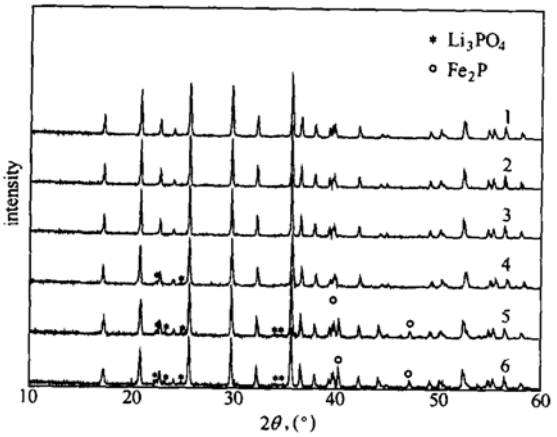

Figure 1 XRD patterns of $LiFePO_4$ with different amount of carbon

w, %: 1—5; 2—10; 3—15; 4—20; 5—30; 6—40

A series of scanning electron microscopy (SEM) micrographs (Fig. 2) reveals the morphological changes of the samples with different amount of carbon. As shown in Fig. 2, as the carbon content increases, the particle size of the powder becomes smaller and the surface microstructure of the powder is denser. The presence of loosely-agglomerated spherical particle with an average grain size of about 100—200 nm was observed from the powder with 10% C (by mass). For the sample with 20% C (by mass), it is not as regular as the former. Some particles are in smaller size while others are larger. This can be further verified by the following particle size distribution pattern. The samples with 30% C (by mass) and 40C (by mass) also have uneven particle size, but it is obviously smaller than the sample with 10% C (by mass).

The energy dispersive spectrometer (EDS) data corresponding to the above SEM micrographs were employed to investigate whether the carbon particulates produced by glucose pyrogenation were uniformly dispersed among the $LiFePO_4$ grains. The result shows that the distribution is uniform, whereas an evident non-uniform distribution of carbon in the sample with the lowest carbon content is observed.

The particle size distribution of the $LiFePO_4$ samples was analyzed and the results are shown in Fig. 3 and Table 1. It should be pointed out that the particle of $LiFePO_4$ containing 40% C (by mass) is the smallest. Fig. 3 indicates that $LiFePO_4$ containing 5% C (by mass) has larger particles and distributes wider. $LiFePO_4$ containing 10% C (by mass) has the smallest particles and shows a sharp peak in the particle distribution graph.

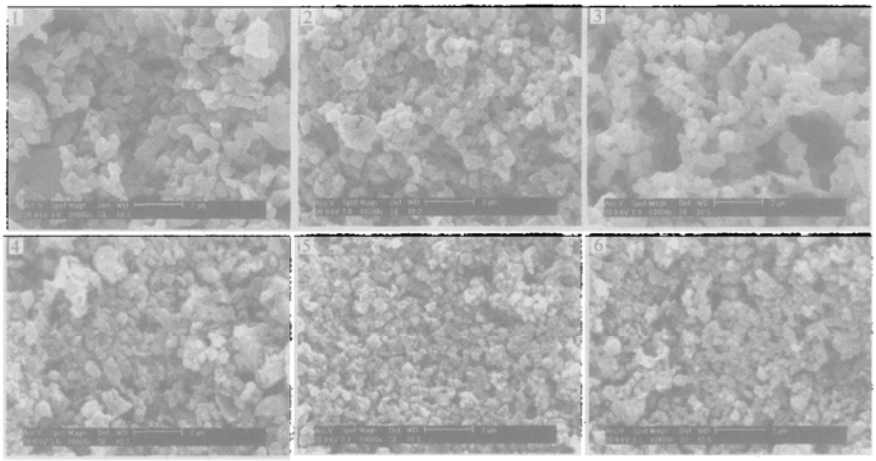

Figure 2 SEM graphs of $LiFeO_4$ with different amounts of carbon
w, %: 1—5; 2—10; 3—15; 4—20; 5—30; 6—40

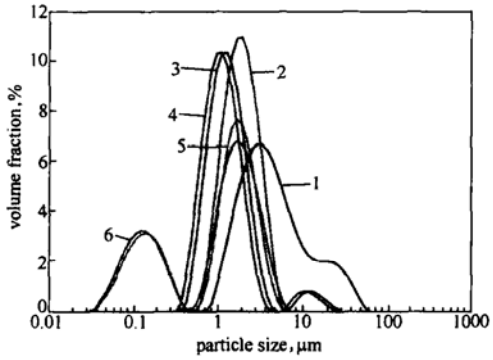

Figure 3 Particle size distribution of $LiFePO_4$ with different amount of carbon
w, %: 1—5; 2—10; 3—15; 4—20; 5—30; 6—40

Table 1 Particle size of $LiFePO_4$ with different amount of carbon

Carbon content (by mass), %	Particle size of $LiFePO_4$, D, μm		
	uniformity	volume weighted mean D	surface weighted mean D
5	1.27	7.855	3.479
10	0.399	2.191	1.791
15	0.486	2.543	1.868
20	0.842	2.572	1.887
30	0.764	1.535	0.331
40	0.782	1.486	0.3

3.2 Electrochemical properties

Figure 4 shows comparisons of the initial specific discharge capacity for the olivine $LiFePO_4$ powder with different amount of carbon. It can be easily seen that the $LiFePO_4$ sample with 10% C (by mass) has the maximal specific discharge capacity due to its highly crystallized microstructure and uniform surface morphology. This can be seen in its XRD pattern and SEM photo. The sample with 15% C (by mass) also has a high specific discharge capacity, which is a little inferior to the former probably due to its uneven particles (Fig. 3). The sample with 20% C (by mass) has a little lower specific discharge capacity because of the impurities in its structure (Fig. 1). The least value of specific discharge capacities which is as low as 100 $mA \cdot h \cdot g^{-1}$ belongs to the sample with 40% C (by mass). According to Fig. 4, it can be concluded that the discharge capacity increases and then decreases as the carbon content increases from 5% to 10% and then to 40%. Excessively increasing the carbon content leads to a reduction of the specific discharge capacities of the samples as a consequence of the increase of impurity contents.

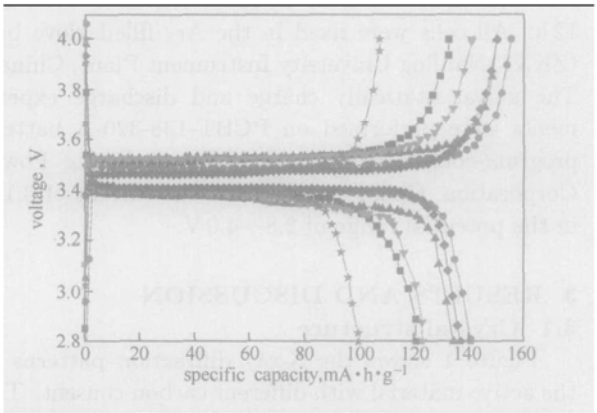

Figure 4 The initial charge-discharge curves of $LiFePO_4$ with different amount of carbon
w, %: ■ 5; ● 10; ◆ 15; ▲ 20; ▼ 30; ★ 40

The cycle performance of these samples is shown in Fig. 5. The capacity fading affecting the electrodes can also be related to the carbon content. It is more apparent that the specific discharge capacity of the sample with 10 % C (by mass) has the most excellent cycle ability among all the samples. It may be explained by that this sample has well-proportioned particle size distribution, leading to higher lithium ion diffusion coefficient. It should be specially pointed out that the one with 5% C fades most seriously, with

14.3% loss from the initial discharge capacity in 30 cycles, while the cells with higher carbon content (with 30 % and 40 % C) show a reduced fading. It may be caused by that the former has less carbon content and thus a loss of contact between the active material particles and the conductive additive.

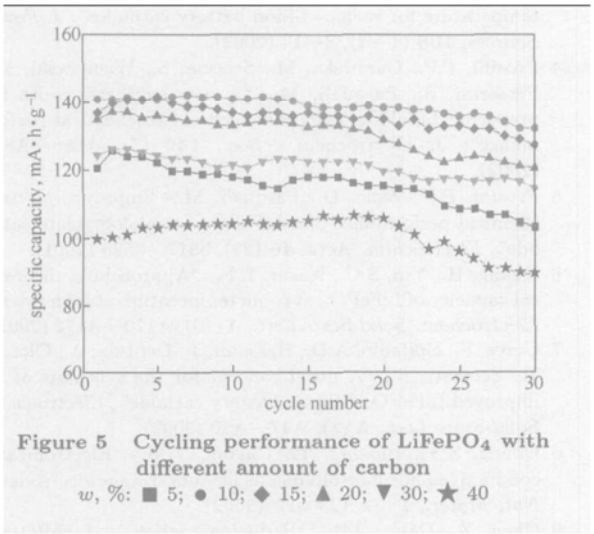

Figure 5 Cycling performance of $LiFePO_4$ with different amount of carbon
w, %: ■ 5; ● 10; ◆ 15; ▲ 20; ▼ 30; ★ 40

The above explanation can also be testified by considering the effect of the charge transfer resistance, R_{ct}, on the performance of the electrode. Fig. 6 shows a comparison of the impedance spectra before test cycles and after 10 cycles. It is found that increasing the carbon content leads to a reduction of the cell impedance due to the reduction of the charge transfer resistance. Compared with the spectra before test cycles, the R_{ct} values of most samples show a large decrease after 10 cycles. This may be related to the destruction of the passivation layer on the lithium metal surface[12]. The sample with the lowest carbon content is exceptive. The large value of R_{ct} can be ascribed to the slow kinetics of lithium ion intercalation/deintercalation, which may be caused by the loss of contact between the active material particles and the conductive additive upon cycling. Increasing the amount of carbon increases the probability of preserving the contact upon cycling. Considering the disadvantage of the excessive carbon (impurities), the optimal carbon content is 10%.

Figure 7 shows the cyclic voltammogram of the sample with 10% C (by mass) at a scanning rate of $0.1\,mV{\cdot}s^{-1}$. A pair of redox reaction peaks appears in the CV curves. The sharp oxidation and reduction peaks indicate that strong lithium intercalation and de-intercalation reactions occur for $LiFePO_4$ electrode. During anodic sweep, the lithium ions are extracted from Li_xFePO_4 structure. An oxidation peak forms at 3.61 V, and the corresponding reduction peak forms at 3.25 V. The separation between the anodic and cathodic peaks is 0.36 V. In the second cycle, the separation is decreased, which indicates the reversibility of the electrode is improved. From the second cycle to the tenth one, the reproducibility of the peaks is representative of the reversibility of the electrode. The low separation (0.3 V) between the anodic and cathodic peaks is representative of its good kinetics, especially considering that the electrochemical process involves diffusion of lithium ions in a solid phase and electron jumping across a poorly conducting compound.

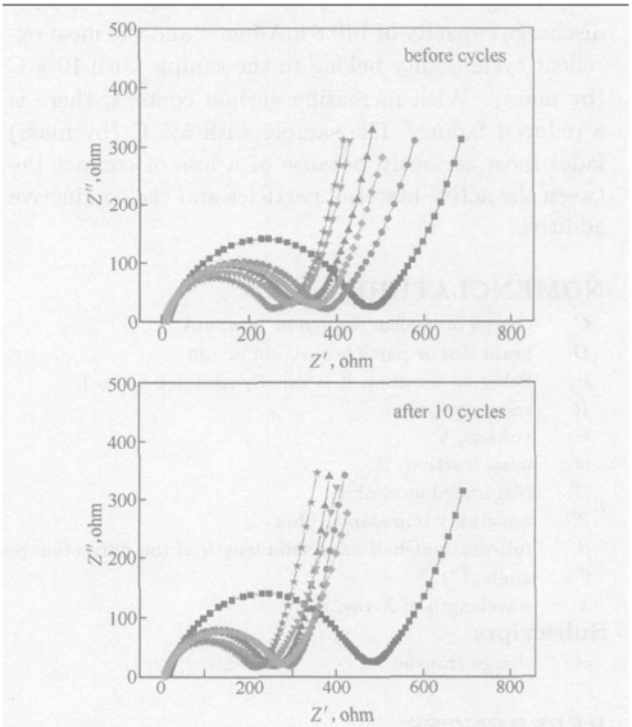

Figure 6 Comparision of the impedance spectra of the samples with different carbon content
w, %: ■ 5; ● 10; ◆ 15; ▲ 20; ▼ 30; ★ 40

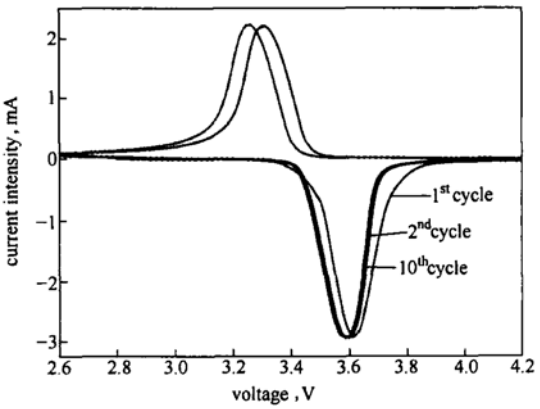

Figure 7 Cyclic voltammogram of the sample with 10% C measured at 20℃ and $0.1\,mV{\cdot}s^{-1}$

4 CONCLUSIONS

The influence of carbon content on the performance of $LiFePO_4/C$ composite compound was in-

vestigated. The physical properties of the samples were studied by means of XRD, SEM and particle size distribution analysis. The results illustrate that the $LiFePO_4$ sample with 10% C (by mass) has pure and complete olivine structure, uniform surface morphology and better particle-size distribution. With increasing carbon content, some peaks attributed to impurities appear, while the surface microstructure of the samples becomes denser. The electrochemical properties were also investigated by the galvanostatically charge and discharge tests. The highest specific discharge capacity of 140.8 $mA \cdot h \cdot g^{-1}$ and the most excellent cycle ability belong to the sample with 10% C (by mass). With increasing carbon content, there is a reduced fading. The sample with 5% C (by mass) fades most seriously because of a loss of contact between the active material particles and the conductive additive.

NOMENCLATURE

C	charge or discharge current rate, mA
D	grain size or particle size, nm or μm
k	Scherrer constant, it is usually assumed to be 1
R	resistance, ohm
V	voltage, V
w	mass fraction, %
Z'	real impedance, ohm
Z''	imaginary impedance, ohm
β	full-width-at-half-maximum length of the diffraction peak
θ	angle, (°)
λ	wavelength of X-ray, nm

Subscripts

ct	charge transfer

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