Synthesis of LiFePO₄/ C composite electrode with enhanced electrochemical performance①

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Abstract: LiFePO₄/ C composite was synthesized by high temperature solid-state reaction using iron(II) oxalate, ammonium di-hydrogen phosphate and lithium carbonate with a kind of carbohydrate dissolved in the dispersant(ethanol) as carbon sources added to the synthetic precursor. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy observations(SEM), charge/ discharge test, cyclic voltammetry(CV) and carbon analysis. The results show that the synthesis of LiFePO₄/ C has ordered olivine structure. The carbon has two advantages: optimizing particle size of LiFePO₄ and increasing the electronic conductivity and high Li⁺ diffusivity. The cathode material can demonstrate a charge/ discharge flat voltage of 3. 4 V(vs Li⁺ / Li). Especially the active material with 15% and 20% carbohydrate added according to the final product of lithium iron phosphate shows very good electrochemical performance delivering about initial 150. 2 mA · h · g⁻¹ and 162. 0 mA · h · g⁻¹ specific capacity respectively at 0. 1 C rate and the carbon contents in the final production are only 5. 17% and 5. 29%, respectively.

Key words: Li-ion battery; cathode materials; LiFePO₄; carbon-coated

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1 INTRODUCTION

The ever-growing demand for portable batteries with high energy density is exerting pressure for the development of advanced lithium-ion batteries. Commercial Li-ion batteries rely on the application of one of the well-known lithium insertion hosts, i. e. LiCoO₂, LiMn₂O₄ and LiNiO₂. However the high cost of cobalt resource, low specific capacity of LiMn₂O₄ and LiNiO₂ is known to be difficult to synthesize and its multi-phase reaction during electrochemical cycling leads to structural degradation. For large-scale applications such as electric and hybrid vehicle systems, the vital issue is the availability of advanced materials. The high temperature performance is also critical because these batteries may be operated at elevated temperature.

LiMPO₄ as cathode materials (M = Fe, Mn, Feᵧ Mn₁₋ᵧ, Co, Ni, etc.) has attracted much attention as a candidate for the battery with high energy density since Padhi et al[1] established the baseline characteristics of LiFePO₄ cathodes for lithium-ion batteries in 1996. LiFePO₄ has a high lithium intercalation voltage (3. 4 V, vs Li / Li⁺), high theoretical capacity (170 mA · h · g⁻¹), excellence in a high temperature application[2], low cost[3], ease of synthesis, and stability when used with common organic electrolyte systems[4-7].

Unfortunately, it should be noted that there is an intrinsic negative aspects of olivine-type materials for lithium battery cathodes —very poor conductivity[1] and Li⁺ can only be partially extracted/ inserted at large charge/ discharge rates. About two years ago, Yamada et al[8] and MacNeil et al[9] considered that LiFePO₄ reacted very weakly with electrolyte at elevated temperatures compared with other common cathode materials and therefore it may be suitable for large cell applications. In recent optimization of LiFePO₄ is focusing on the increase of its electronic conductivity and the synthesis routes[10-12]. In recent years, improvements have been made to improve the conductivity of LiFePO₄ through optimization of synthesis techniques to minimize the particle size, doping to improve the intrinsic conductivity[13, 14], addition of metal powder[15] or carbon particles[16, 17] during synthesis or incorporating organic or polymeric additives[18] to form conductive carbon coatings on the particles during firing. In this paper, a study of pure and modified LiFePO₄ materials was described. The goal was to prepare active materials with excellent electrochemical performance.

2 EXPERIMENTAL

2. 1 Synthesis of cathode materials

The cathode materials were prepared by solid-

state reaction of $FeC_2O_4 \cdot 2H_2O$ (Aldrich), $NH_4H_2PO_4$(Aldrich), Li_2CO_3(Aldrich) and carbohydrate (Aldrich). The stoichiometric mixtures of the raw materials were mixed by ball-milling (500 r/min) for 12 h with agate balls in alcohol, followed by drying. Then these mixtures were ground with a mortar and pellets were calcined at 350 ℃ for 8 h in flowing Ar. Final firing for crystallization of the olivine phase was made at 750 ℃ for 24 h in Ar flowing ambience. The samples of L0, L1, L2, L3 and L4 correspond to $LiFePO_4$ with 0% (uncoated), 10%, 15%, 20% and 25% carbohydrate mixed respectively according to the product of $LiFePO_4$.

2.2 Characteristic of cathode materials

2.2.1 Phase identification and particle size analysis

The phase analysis and particle size of all samples were determined by using X-ray diffraction (XRD, D/max-r A type Cu $K_{\alpha 1}$ 140 kV, 300 mA, $10°$-$70°$, $8°$/min, Japan).

2.2.2 Microstructures of cathode material

Scanning electron microscope(SEM) was used to examine the microstructures of the cathode material(SEM, KYKY 2800, Japan).

2.2.3 Electrochemical measurements

The electrochemical cycling performances of the $LiFePO_4$ powders were evaluated at room temperature (20 ℃) with laboratory-scale Li/$LiFePO_4$ button cells including a lithium metal foil as counter electrode, a composite of 80% $LiFePO_4$, 10% acetylene black (AB) and 10% (mass fraction) polytetrofluornethelene(PTFE) binder as a cathode. A micro-porous polypropylene film (Celgard 2 400) was used as a separator and 1 mol/L $LiPF_6$ solution with the 1 : 1 volume ratio of ethylene carbonate-dimethyl carbonate (EC-DMC) was used as the electrolyte. All cells were assembled inside a glove box filled with ultra-pure argon. Charge/discharge characteristics of the cells were recorded in the potential range of 2.5 V and 4.1 V using a LAND computer-controlled galvanostat. Currents and specific capacities were calculated based on the mass of $LiFePO_4$ but not $LiFePO_4$/C in the electrode.

The cyclic voltammgram of the powder microelectrode test cell was performed between 2.2 V and 4.2 V vs lithium using a Potentiostat/Galvanostat system, Model 273A, EG&G instrument. The scan rate was chosen to be 0.5 mV/s to 20 mV/s. A piece of Pt wire (100 μm in diameter) was embedded in glass tubing. Part of the Pt wire was etched by aqua regia, so that a micro-cavity was packed with powders of the cathode material. By using the powder microelectrode as the working electrode, lithium metal foils were chosen as the

counter electrode and 1 mol/L $LiPF_6$/EC+ DMC (1 : 1 in volume) as the electrolyte solution, and the test cells were assembled in argon on dry box. As the surface area of the counter electrode was 200 times larger than that of the working microelectrode, the counter electrode could also be used as the reference electrode without serious error.

2.2.4 Carbon concentration

The carbon concentration of the composite was analyzed using CS-444 carbon/sulfur determinator (LECO Co. USA).

3 RESULTS AND DISCUSSION

The phases of all the samples L0, L1, L2, L3 and L4 are shown in Fig. 1. From the powder X-ray diffraction (XRD) patters, it can be seen that the synthetic $LiFePO_4$ phase belongs to ordered olivine-type structure. From Table 1, it can be seen that the diffraction intensity of 311 peak of $LiFePO_4$ compound declines with the more carbohydrate mixed in the $LiFePO_4$/C composites. This means that with the increasing amount of carbon coated the amorphous phases in the composite also increase. But their diffraction peaks are in the same positions indicating that carbon coating does not have effect on the inner crystal structure of $LiFePO_4$.
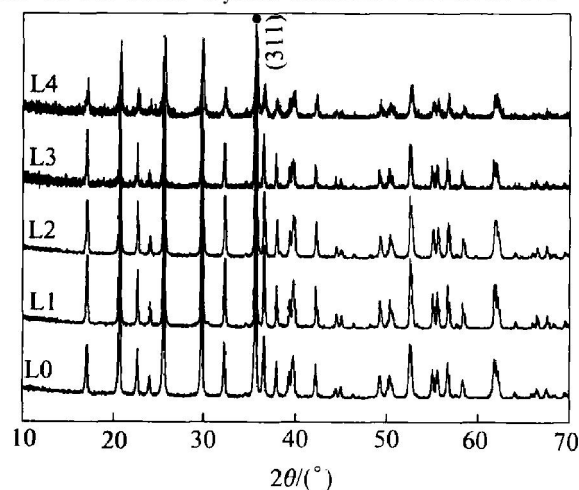

Fig. 1 XRD patterns of samples L0, L1, L2, L3 and L4

Table 1 Relative intensity of 311 peak

Sample No.	I_{311}/(CPS)	Sample No.	I_{311}/(CPS)
L0	28 250	L3	14 253
L1	18 013	L4	12 853
L2	15 643		

From the SEM photographs of Fig. 2, it can also be known that the addition of carbohydrate has an evident effect on controlling the growing particles of cathode powder, and the particle size of

LiFePO$_4$/C (L2, L3) is more well-proportioned than that of the pure LiFePO$_4$ (L0). The refined LiFePO$_4$ particle coated by carbon can help to increase the diffusivity of lithium ion during the electrode process. A wide size distribution ranging from 0.5 μm to 5 μm for the LiFePO$_4$ particles can be recognized in Fig. 2(a). And the distribution is not uniform, which will make the Li$^+$ of the larger particle not be discharged completely during the electrode process and leads to the low specific capacity of sample L0.
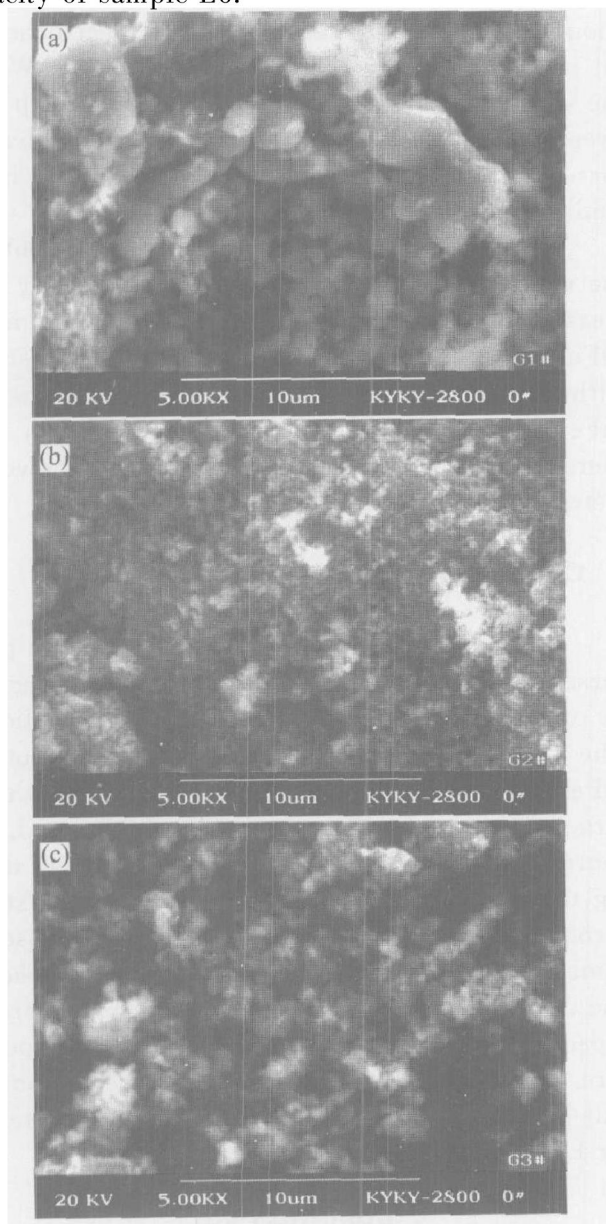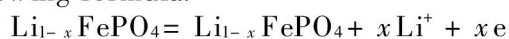

Fig. 2   SEM micrographs for samples
(a) —L0; (b) —L2; (c) —L3

The electrochemical insertion/ deinsertion of lithium ions into LiFePO$_4$ can be described as the following formula:

$$Li_{1-x}FePO_4 = Li_{1-x}FePO_4 + xLi^+ + xe$$

This reaction occurs on a flat plateau at 3.4 V vs Li, as a two-phase process of FePO$_4$/ LiFePO$_4$, and the complete extraction of lithium($x = 1$) corresponds to a theoretical specific capacity of 170

mA $\cdot$ h $\cdot$ g^{-1}.

From Fig. 4, it can be clearly known that the initial capacity decreases with the more than 20% carbohydrate added according to the product of LiFePO$_4$. It can be seen that the pure LiFePO$_4$ (L0) can only keep the specific capacity of 70.5 mA $\cdot$ h $\cdot$ g^{-1} after 20 cycles with the initial specific capacity of 120.4 mA $\cdot$ h $\cdot$ g^{-1} owing to the low electric conductivity[1]. The specific capacity loss is more than 40% while the LiFePO$_4$/C composites show excellent electrochemical behavior. Sample L3 can retain 156.90 mA $\cdot$ h $\cdot$ g^{-1} after 20 cycles with the initial capacity of 162.0 mA $\cdot$ h $\cdot$ g^{-1} and the carbon mass fraction is only 5.29% (Table 2). The capacity loss is very small. The reason is that the carbohydrate as the carbon precursor can improve the active material conductivity and the Li$^+$ diffusivity.

The influence of the scan rate on electrochemical performance of sample L0 and sample L3 was investigated by using power micro-electrode cycle voltammetry. The pair of peaks, consisting of an anodic and a cathodic peak, observed around 3.4 V vs Li/ Li$^+$ corresponded to the two-phase charge/
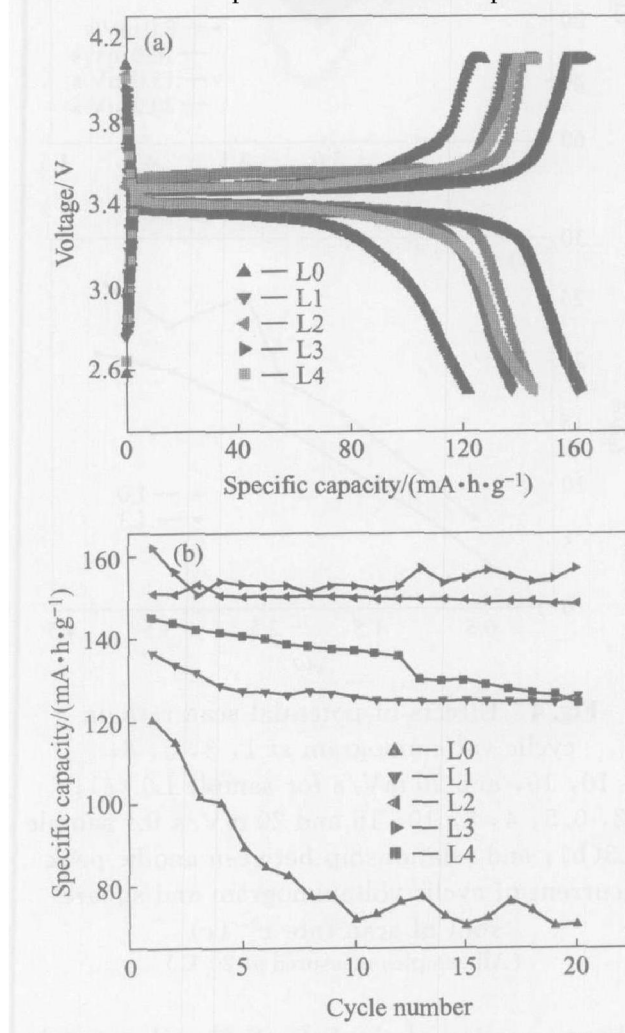

Fig. 3   Initial charge-discharge(a) and cycling behaviors(b) profiles of samples L0, L1, L2, L3 and L4

Table 2　Carbon content in samples L2 and L3

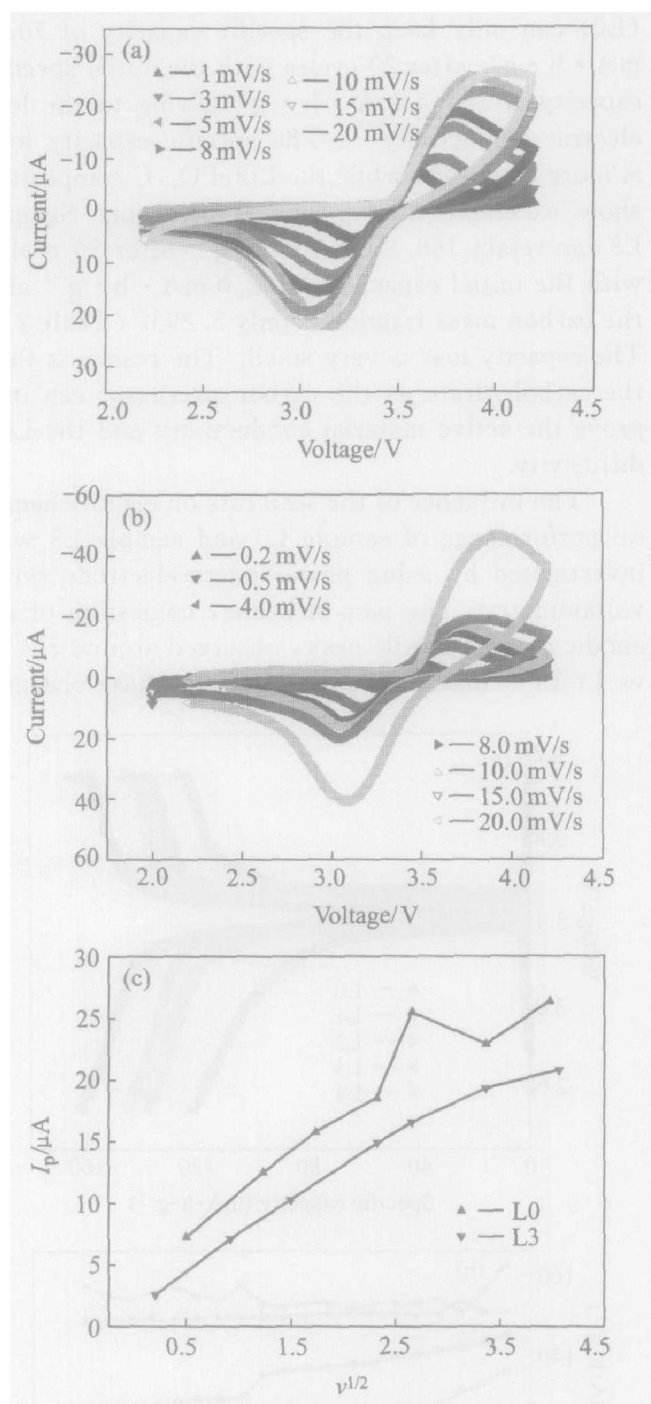| Sample No.	$w(C)/\%$	Sample No.	$w(C)/\%$
L2	5. 17	L3	5. 29

Fig. 4　Effects of potential scan rate on
cyclic voltammogram at 1, 3, 5, 8,
10, 15, and 20 mV/s for sample L0 (a);
0. 2, 0. 5, 4, 8, 10, 15 and 20 mV/s for sample
L3(b); and relationship between anodic peak
current of cyclic voltammogram and square
root of scan rate $v^{0.5}$(c)
(All samples measured at 20 ℃)

discharge reaction of the Fe^{2+}/Fe^{3+} redox couple.
This voltammogram indicates only one electro-
chemical reaction. Figs. 4(a) and (b) show the
effect of the potential scanning rate on the cycle

voltammograms measured at 1. 0, 3. 0, 5. 0, 8. 0,
10. 0, 15. 0 and 20. 0 mV/s for sample L0 and 0. 2,
0. 5, 4. 0, 8. 0, 10. 0, 15. 0 and 20. 0 mv/s for sam-
ple L3 respectively. Although the wave shape of
the anodic and cathodic peak is almost symmetri-
cal, the potential separation between the two peaks
increases as the scanning rate increases. This re-
sult means that the Fe^{2+}/Fe^{3+} redox reaction is a
quasi-reversible process. Fig. 4(c) shows the rela-
tionship between the peak current and the square
root of the scan rate($v^{0.5}$). The peak current is
proportional to $v^{0.5}$ with the scan rate is less than
about 10 mV/s. This means that the electrochemi-
cal process is limited by lithium diffusion. When
the scan rate exceeds 10 mV/s the relationship be-
tween I_p and $v^{0.5}$ is not proportional. This indicates
that the electrochemical process is controlled by a
similar blend process[19].

　　While with the increase of the carbon content
the volumetric energy density and tap density de-
crease unfortunately[20]. Huang et al[21] made
LiFePO₄/C composite by mixing raw materials
with carbon gel before heating. In this composite,
LiFePO₄ has a particle size of 100 ～ 200 nm and
there is about 15% carbon. Consequently the volu-
metric energy density decreases greatly.

4　CONCLUSIONS

　　The adding carbohydrate to the synthetic pre-
cursor can help to improve the electrical conductiv-
ity of LiFePO₄ and prevent growth of the particle.
The most important thing is that the production of
LiFePO₄ will be covered by refined carbon uni-
formity after the precursor has been sintered. It
contributes to the transfer of electron and Li^+ dur-
ing the electrode process. Meanwhile the existing
carbon can prevent the production of Fe^{3+} phase to
some extent. Sample L3 shows excellent capacity
and cycle capability exhibiting about 95% theoretic
capacity, 162. 0 mA·h·g^{-1}, at room tempera-
ture. This indicates that LiFePO₄/C composite
will be an attractive candidate as cathode material
for Li-ion battery.

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