

Synthesis and characterization of LiFePO_4/C composite used as lithium storage electrodes^①

HU Guo-rong(胡国荣)¹, ZHANG Xin-long(张新龙)¹, PENG Zhong-dong(彭忠东)¹,
LIAO Gang(廖刚)², YU Xiao-yuan(禹筱元)¹
(1. College of Metallurgical Science and Engineering,
Central South University, Changsha 410083, China;
2. Institute of Material and Chemical Engineering,
China University of Geosciences, Wuhan 430074, China)

Abstract: LiFePO_4/C composites with good rate capability and high energy density were prepared by adding sugar to the synthetic precursor. A significant improvement in electrode performance was achieved. The resulting carbon contents in the sample 1 and sample 2 are 3.06% and 4.95% (mass fraction), respectively. It is believed that the synthesis of LiFePO_4 with sugar added before heating is a good method because the synthesized particles having uniform small size are covered by carbon. The performance of the cathodes was evaluated using coin cells. The samples were characterized by X-ray diffraction and scanning electron microscope observation. The addition of carbon limits the particles size growth and enables high electron conductivity. The LiFePO_4/C composites show very good electrochemical performance delivering about 142 mAh/g specific capacity when being cycled at the C/10 rate. The capacity fade upon cycling is very small.

Key words: Li-ion battery; positive material; lithium iron phosphate; carbon-coated

CLC number: O 646.54; TM 911.1

Document code: A

1 INTRODUCTION

The ever-growing demand for portable batteries with high energy density is exerting pressure for the development of advanced lithium-ion batteries. Transition-metal oxides have tended to be the most attractive candidates for active cathode materials due to their high potential Li^+/Li ; in many of them, a large proportion of the lithium can be inserted/extracted reversibly. 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 temperatures. In recent years, there has been considerable effort devoted to developing high energy density, safe and reliable new materials to use as the cathodes in lithium-ion batteries. Since the pioneering study on LiFePO_4 by Padhi et al.^[1], significant efforts have been made to improve this material^[2-14]. The overwhelming advantage of iron-based compounds is that, in addition to being inexpensive and naturally abundant, they are less toxic than Co, Ni and Mn. On the other hand, this cathode may be affected by a loss of capacity with increasing current density, associated with diffusion-controlled kinetics of the electrochemical process^[1].

Ways to improve the rate performance of the LiFePO_4 material is enhancing its ionic/electronic conductivity by suitable preparation procedures. Recently, Yamada et al.^[3] and MacNeil et al.^[15] discovered that LiFePO_4 reacts very weakly with electrolyte at elevated temperatures compared with other common cathode materials and therefore it may be suitable for large cell applications. Research efforts on the Fe-based phosphate are centered around: 1) the synthesis of LiFePO_4 particles with well-defined morphology and texture by means of "soft chemistry"; 2) the use of conducting coatings to indirectly enhance the electronic conductivity of the composite electrode; and 3) the cationic/anionic substitution to enhance its intrinsic electrochemical properties. Items 1) and 2) have already resulted in exiting effect as recently reported by Ravet et al.^[16]. Item 3) is rapidly advancing as well^[13].

2 EXPERIMENTAL

2.1 Materials preparation

LiFePO_4 was prepared by solid-state reaction of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and Li_2CO_3 . A stoichiometric mixture of the raw materials and the measured amount of white table sugar were mixed by ball-

① Received date: 2003 - 05 - 22; Accepted date: 2003 - 08 - 27

Correspondence: HU Guo-rong, Professor, PhD; Tel: + 86-731-8830532; E-mail: hgrhsj@263.net

milling for 12 h using zirconia milling media in alcohol. After drying, and then grinding with a mortar and pestle, the mixture was calcined at 320 °C for 8 h in flowing Ar. Final firing for crystallization of the olivine phase was done at 700 °C for 20 h in Ar.

2.2 Characterization

X-ray powder diffraction was used to confirm the phases of the materials made by the methods described. Scanning electron microscope (SEM) was used to study the morphology of the materials. The carbon content of the powders was analyzed using CS-444 carbon/sulfur determinator (LECO Co. USA).

2.3 Electrochemical tests

The electrochemical cycling performances of the LiFePO_4 powders were evaluated at room temperature (20 °C) with laboratory-scale Li/LiFePO₄ button cells including a lithium metal foil as counter electrode, a composite of 80% LiFePO₄ (mass fraction), 10% acetylene black (AB), and 10% polytetrafluoroethylene (PTFE) binder as a cathode. A microporous polypropylene film (Celgard 2400) was used as a separator and 1 mol/L LiPF_6 solution with the 1:1 volumetric ratio of ethylene carbonate-dimethyl carbonate (EC-DMC) was used as the electrolyte. All cells were assembled inside a glove box filled with ultrapure argon. Charge/discharge characteristics of the cells were recorded in the potential range of 2.5–4.1 V using a LAND CT2001A computer-controlled galvanostat and potentiostat. Currents and specific capacities were calculated based on the mass of LiFePO₄, not that of LiFePO₄/C, in the electrode.

3 RESULTS AND DISCUSSION

The electrochemical insertion-deinsertion of lithium ions into LiFePO₄ can be described as:



This reaction occurs on a flat plateau at 3.45 V (vs Li), as a two-phase process, and the complete extraction of lithium ($x = 1$) corresponds to a theoretical specific capacity of 170 mAh/g.

The crystal phase of all the samples was identified from the X-ray powder diffraction (XRD) experiments to be LiFePO₄ phase with ordered olivine structure indexed by orthorhombic Pnmb (as shown in Fig. 1).

This structure is based on a hexagonal-packed oxygen array with Li and Fe occupying the octahedral sites in the alternate planes (chains of edge sharing Fe-centered octahedral connected by a phosphate tetrahedral). There is a good correspondence with the

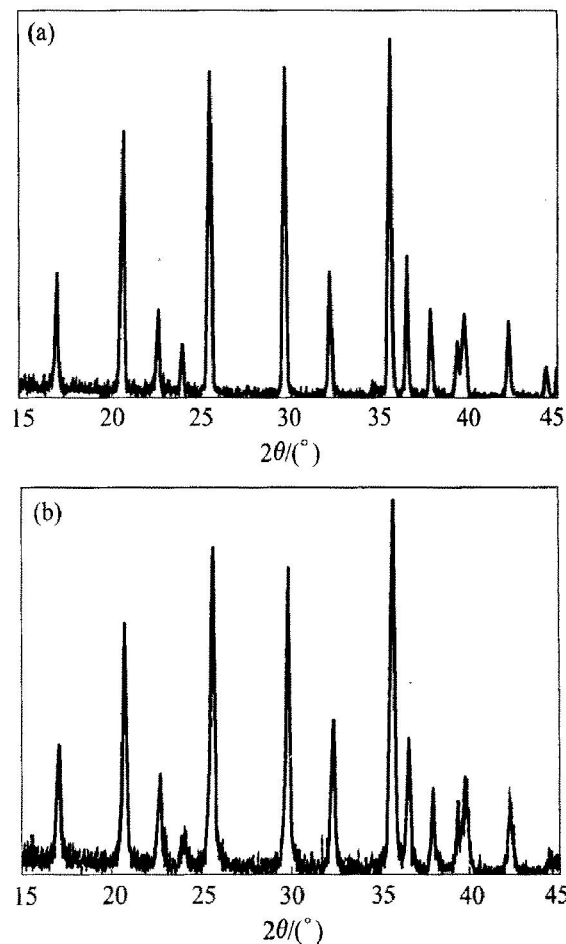


Fig. 1 XRD spectra of uncoated LiFePO₄ (a) and carbon-coated LiFePO₄ (b)

reference LiFePO₄ pattern, demonstrating that single phase is obtained with no evidence of impurities. The peak intensity of carbon-coated LiFePO₄ are lower than that of the uncoated LiFePO₄ due to the amorphous phases addition. Their peaks are in the same positions, indicating that carbon coating doesn't affect the inner olivine structure of LiFePO₄.

The carbon contents in the final LiFePO₄ powders were determined to be 3.06% and 4.96% for sample 1 and sample 2, respectively.

Fig. 2 shows SEM images of the samples of LiFePO₄ coated with 3.06%, 4.95% carbon and uncoated. One can clearly see that the particle size decreases as the amount of carbon increases. Therefore, there is clear evidence that adding sugar during the first heating dramatically slows the particle growth.

According to Figs. 2(b) and (c), this material has a uniform small particle size and all particle may be uniformly covered by carbon. Thus, it is an effective method to improve the rate capacity of LiFePO₄.

The charge-discharge plots (Fig. 3) at low current density and at room temperature for the optimized carbon-coated materials show a gain in term of faradaic balance with more than 0.8 lithium ions extracted and reversibly reinserted between 4.1 V and 2.5 V (vs Li). Moreover, the amount of carbon in

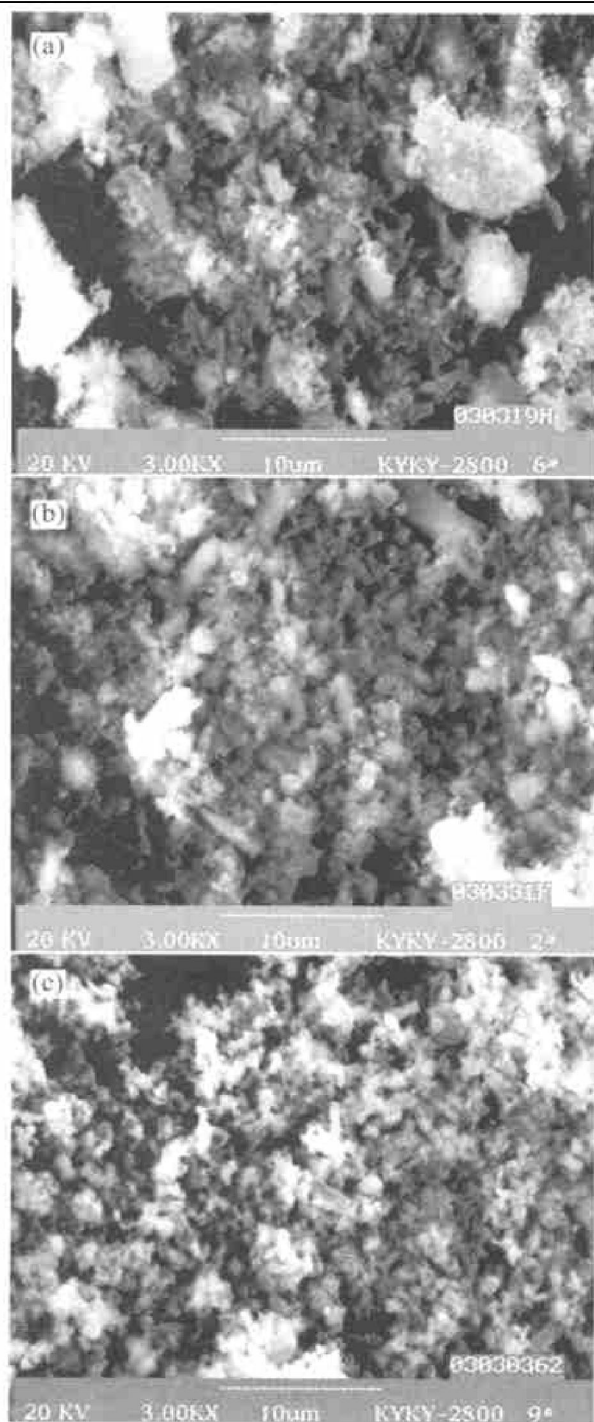


Fig. 2 Morphologies of uncoated (a), 3.06% carbon-coated (b) and 4.95% carbon-coated LiFePO_4 (c)

these compounds is less than 5%, which is less than that of reported literature, and the source of this carbon (sugar) is a simple, cheap, and environmentally friendly compound (not always the case for many authors who propose formaldehyde or resorcinol as precursors).

These different behaviors between pure (uncoated) and composite (carbon coated) LiFePO_4 are obviously associated with the presence of intimate carbon dispersion, thus confirming its role in optimizing the morphology of the LiFePO_4 electrode material and, thus, enhancing the kinetics of its electrochemical

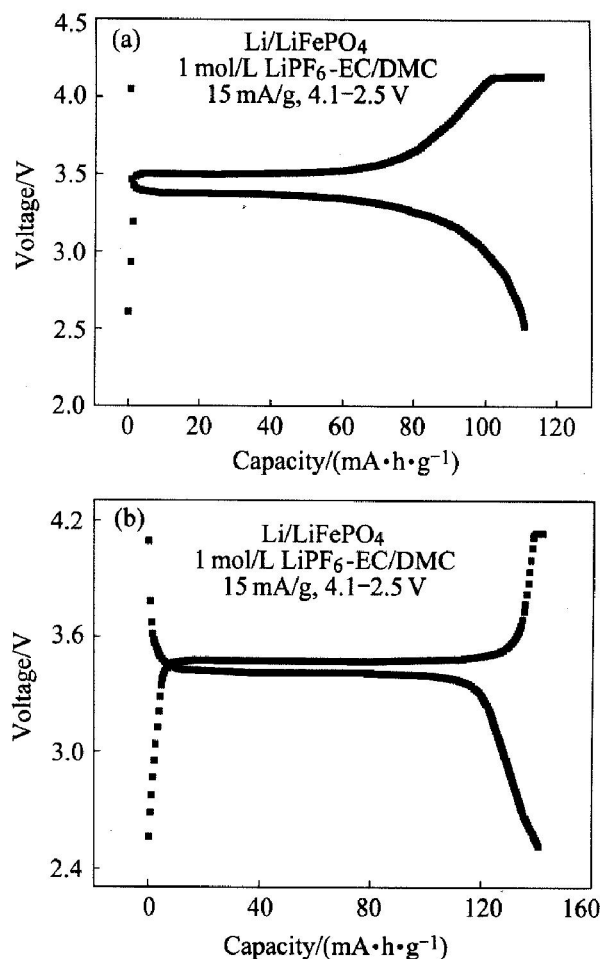


Fig. 3 Charge-discharge curves of $\text{Li}/\text{LiFePO}_4$ cell cycled between 4.1 V and 2.5 V at room temperature
(a) —Uncoated LiFePO_4 ; (b) —Carbon coated LiFePO_4

process.

4 CONCLUSION

LiFePO_4/C composites used as lithium storage electrode were prepared by adding sugar to the synthesis precursor. The addition of sugar, which is changed into carbon, enhances the electronic conduction of LiFePO_4 and also greatly improves its electrochemical performance. The cathode can be discharged at C/10 rate at 20 °C with a utilization of about 83% (141 mAh/g). The results indicate that LiFePO_4/C composites will be an attractive candidate as cathode material for Li-ion battery.

REFERENCES

- [1] Padhi A K, Najundaswamy K S, Goodenough J B. Phosphorolivines as positive electrode materials for rechargeable lithium batteries [J]. J Electrochem Soc, 1997, 144: 1188 - 1194.
- [2] Huang H, Yin S C, Nazar L F. Approaching theoretical capacity of LiFePO_4 at room temperature at high rates [J]. Electrochem Solid State Lett, 2001, 4: A170 - A172.

- [3] Yamada A, Chung S C, Hinokuma K. Optimized LiFePO_4 for lithium battery cathodes[J]. *J Electrochem Soc*, 2001, 148: A224 - A229.
- [4] Ravet N, Chouinard Y, Magnan J F, et al. Electroactivity of natural and synthetic triphylite[J]. *J Power Sources*, 2001, 97 - 98: 503 - 507.
- [5] Croce F, Epifanio A D, Hassoun J, et al. A novel concept for the synthesis of an improved LiFePO_4 lithium battery cathode[J]. *Electrochem Solid State Lett*, 2002, 5(3): A47 - A50.
- [6] Prosini P P, Zane D, Pasquali M. Improved electrochemical performance of a LiFePO_4 -based composite cathode[J]. *Electrochim Acta*, 2001, 46: 3517 - 3523.
- [7] Chen Zhaohui, Dahn J R. Reducing carbon in LiFePO_4/C composite electrodes to maximized specific energy, volumetric energy, and tap density[J]. *J Electrochem Soc*, 2002, 149: A224 - A229.
- [8] Yang Shoufeng, Zavalij P Y, Whittingham M S. Hydrothermal synthesis of lithium iron phosphate cathodes[J]. *Electrochem Comm*, 2001, 3: 505 - 508.
- [9] Yang S, Song Y, Zavalij P Y, et al. Reactivity, stability and electrochemical behavior of lithium iron phosphates[J]. *Electrochem Comm*, 2002, 4: 239 - 244.
- [10] Procini P P, Carewska M, Scaccia S, et al. A new synthetic route for preparing LiFePO_4 with enhanced electrochemical performance[J]. *J Electrochem Soc*, 2002, 149: A886 - A890.
- [11] Franger S, Cras F L, Bourbon C, et al. LiFePO_4 synthesis routes for enhanced electrochemical performance[J]. *Electrochem Solid State Lett*, 2002, 5(10): A230 - A233.
- [12] Li Guohua, Azuma H, Tohda M. Optimized $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ as the cathode for lithium batteries[J]. *J Electrochem Soc*, 2002, 149: A743 - A747.
- [13] Chung S Y, Blocking J T, Chiang Y M. Electronically conductive phosphor olivines as lithium storage electrodes[J]. *Nature Mater*, 2002, 2: 123 - 128.
- [14] Baker J, Saidi M Y, Swoyer J L. Lithium iron(II) phosphor olivines prepared by a novel carbonthermal reduction methods[J]. *Electrochem Solid State Lett*, 2003, 6(3): A53 - A55.
- [15] MacNeil D D, Lu Zhonghua, Chen Zhaohui, et al. A comparison of electrode/electrolyte reaction at elevated temperatures for various Li^+ ion battery cathodes[J]. *J Power Sources*, 2002, 108: 8 - 14.
- [16] Ravet N, Magnan J F, Gauthier J M, et al. Abstract A2-02-IN. International Conference on Materials for Advanced Technologies[C]. Singapore, 2001.

(Edited by YUAN Sai-qian)