doi:10.1246/cl.2012.232

Low-temperature Electrochemical Performance of $LiFePO_4/C$ Cathode with 3D Conducting Networks

Jun-chao Zheng,[1] Bao Zhang,*[1] Ming Zhang,[2] and Ling Wu[1]
[1]*School of Metallurgical Science and Engineering, Central South University, Changsha 410083, P. R. China*
[2]*School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China*

(Received October 18, 2011; CL-111025; E-mail: jczheng@csu.edu.cn)

The low-temperature electrochemical performance of $LiFePO_4/C$ cathode with 3D conducting networks is reported. XRD results show the sample is olivine-type structure. SEM and TEM images indicate that the particles consist of nanocrystalline $LiFePO_4$ and are coated by nanocarbon webs and form conducting 3D networks. The 3D networks contained two effectively mixed conducting networks, one on the nanoscale and the other on the microscale. It is useful to shorten the distance of Li^+ diffusion and e^- transport and to improve the electrochemical performance. The $LiFePO_4/C$ cathodes show excellent capacity retention and cycling performance at −20 °C for lithium-ion batteries.

$LiFePO_4$ has received much attention as a next-generation cathode material for lithium-ion batteries in applications such as power tools and hybrid electric vehicles because of its thermal stability and low cost.[1,2] However, $LiFePO_4$ suffers from the limitations of poor electronic conductivity and slow lithium-ion diffusion and hence performs unsatisfactorily at lower temperature.[3,4] Much attention has been given to the development of synthetic routes for this material and to the improvement of its basic electrochemical performance at ambient and high temperatures.[5–7] However, few papers are concerned with the low-temperature electrochemical performance of $LiFePO_4$. Because many high-technology applications, such as military and aerospace missions, require Li-ion batteries to be capable of operating at low temperatures (e.g., −20 °C, −30 °C, or even lower) with appropriate energy density and capacity,[8] it is necessary to evaluate the low-temperature performance. Fortunately, some researchers have done some useful work on the low-temperature performance of $LiFePO_4$ cathodes. Rui et al.[8] did a comparative study on the low-temperature performance of $LiFePO_4/C$ and $Li_3V_2(PO_4)_3/C$ cathodes for lithium-ion batteries. Li et al.[9] researched the low-temperature electrochemical performance of $LiFePO_4$ with Mn^{2+} doping. Liao et al.[10] reported low-temperature performance of $LiFePO_4/C$ cathode in a quaternary carbonate-based electrolyte. Zhang et al.[11] reported an improved electrolyte for the $LiFePO_4$ cathode working in a wide temperature range.

In this paper, we reported an excellent low-temperature electrochemical performance of $LiFePO_4/C$ cathode with 3D conducting networks.

The $LiFePO_4$ compound was synthesized from $FePO_4 \cdot xH_2O$, $(NH_4)H_2PO_4$, Li_2CO_3 and $(COOH)_2 \cdot 2H_2O$ (all 99% purity) taken in stoichiometric amounts. The process steps were: (1) initial mixing by magnetic stirring of all ingredients together as a slurry in alcohol at room temperature for 1 h, (2) high energy ball milling for 4 h (speed: 180 rpm, ball: powder ratio (in g): 5:1), (3) oven drying at 80 °C for 6 h in air, and (4) sintering at 600 °C for 12 h in argon atmosphere.

Structural and crystalline phase analyses of the products were taken from the powder X-ray diffraction (XRD, Rint-2000, Rigaku) using Cu Kα radiation. The samples were observed by SEM (JEOL, JSM-5600LV) and a Tecnai G12 transmission electron microscope (TEM). Elemental carbon analysis of samples was performed by C–S analysis equipment (Eltar, Germany).

The electrochemical characterizations were performed using Al-laminated pouch cells. Typical positive electrode loadings were in the range of 300 g m^{-2}. The cathode consisted of $LiFePO_4/C$ (90%), acetylene black (5%), and poly(vinylidene difluoride) (PVdF) binder (5%) on an Al foil current collector. The anode consisted of graphite (95%) and PVdF binder (5%) on a Cu foil current collector. These electrodes were dried under vacuum at 120 °C for 12 h before assembly inside an Ar atmosphere glovebox. Electrodes were cut and assembled into Al-laminated pouch cells with Celgard separator and 1 mol L^{-1} $LiPF_6$ in ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonitril (1:1:1 in volume) as the electrolyte. Electrochemical tests were carried out using an automatic galvanostatic charge–discharge unit, NEWARE battery cycler. The voltage range of 2.0–3.65 V was used for 100% depth of discharge (DOD) cycling.

The XRD pattern of $LiFePO_4/C$ is shown in Figure 1. The sample shows a single phase that can be indexed on the olivine structure with the space group *Pmnb*, in agreement with a well crystalline $LiFePO_4$ according to the JCPDS (No. 83-2083). The Rietveld refinement on the XRD pattern was performed to obtain the cell parameters ($a = 1.0338$ nm, $b = 0.6040$ nm, $c = 0.4680$ nm), indicating a highly crystalline $LiFePO_4$ phase (JCPDS 81-1173, $a = 1.0330$ nm, $b = 0.6010$ nm, $c = 0.4692$ nm). There are no diffraction peaks for crystalline carbon, so the carbon in the composite is amorphous. According to elemental analysis the carbon content in the composite was about 0.8 wt %.

Figure 2a shows the SEM image of $LiFePO_4/C$ composite. The particles are near-spherical with the particles size ranging from 100 to 500 nm and are homogeneous. TEM investigation was also conducted to examine the $LiFePO_4/C$ particles. As

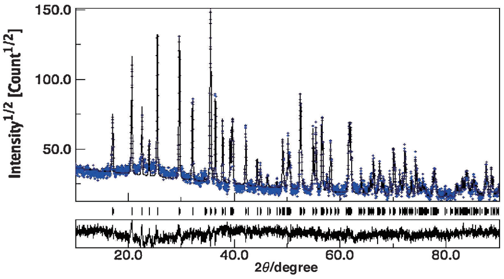

Figure 1. Rietveld refinement of the $LiFePO_4/C$ XRD data.

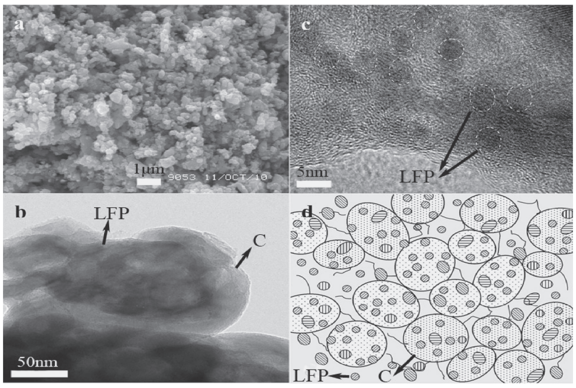

Figure 2. (a) SEM image of $LiFePO_4/C$; (b), (c) TEM images of $LiFePO_4/C$; (d) schematic illustration of the conducting 3D networks formed by nanocrystalline $LiFePO_4$ and nanocarbon webs.

shown in Figure 2b, the dark region is $LiFePO_4$ particle, and the light gray region is carbon, indicating that the $LiFePO_4$ particles are coated by conductive carbon tightly. The $LiFePO_4$ particle is encapsulated with an amorphous carbon shell, similar to the previously reported carbon-coated $Li_3V_2(PO_4)_3$.[12] It can be seen that the thickness of the carbon shell is about 30–50 nm. The high-resolution TEM image in Figure 2c clearly demonstrates the $LiFePO_4$ particle consisted of nanocrystalline $LiFePO_4$ and nanocarbon webs. This structure is very helpful to improve the electrochemical performance of $LiFePO_4$ cathode material.

Figure 3a shows the discharge capacity retentions of a cell at various C rates under 25 °C. The cell shows good capacity retention, and the capacity retention at 20 °C is 96.02%. Figure 3b is the discharge profiles of $LiFePO_4$ at different temperature. As the temperature decreased, the discharge plateau voltage and the discharge capacities slightly decreased. At a lower temperature of −20 °C, the cell was able to deliver 85.4% of the capacity at 25 °C, as shown in Figure 3c. The cycle performance of $LiFePO_4$ at −20 °C is shown in Figure 3d, the cell retains 100.38% of its initial discharge capacity after 340 cycles at 1 C under −20 °C. The energy density are about 120, 107.7, and 93.2 $\mathrm{W\,h\,kg^{-1}}$ at 25, 0, and −20 °C, respectively. The results are better than commercial batteries. According to data reported at the 45th Battery Symposium in Japan, at a temperature of 0 °C, the Sanyo 18650 battery can only deliver 42.2% of its capacity at 25 °C,[13,14] the low-temperature electrochemical performance is much worse than our results. Besides, our results are much better than those by Rui et al.,[8] Li et al.,[9] and Liao et al.[10] previously reported.

The much improved electrochemical performance at low temperature of the nanocrystalline $LiFePO_4$ could be attributed to 3D conducting networks, as shown in the TEM images and the schematic illustration in Figure 2d. The 3D networks contained two effectively mixed conducting networks, one on the nanoscale (nanocrystalline LFP) and the other on the microscale (carbon-coated LFP particles), so the Li^+ diffusion and e^- transport lengths will be shortened, as well as quick liquid electrolyte penetration and guarantee good low-temperature performance.[15]

$LiFePO_4/C$ cathode with conducting 3D networks was synthesized, and the low-temperature electrochemical performance was discussed. The $LiFePO_4/C$ cathode show excellent capacity retention and cycling performance at −20 °C for lithium-ion batteries. The cell can still deliver 85.4% of the capacity at 25 °C and retains 100.38% of its initial discharge capacity after 340 cycles at 1 C under −20 °C. The excellent capacity retention and cycling performance are attributed to the 3D conducting networks.

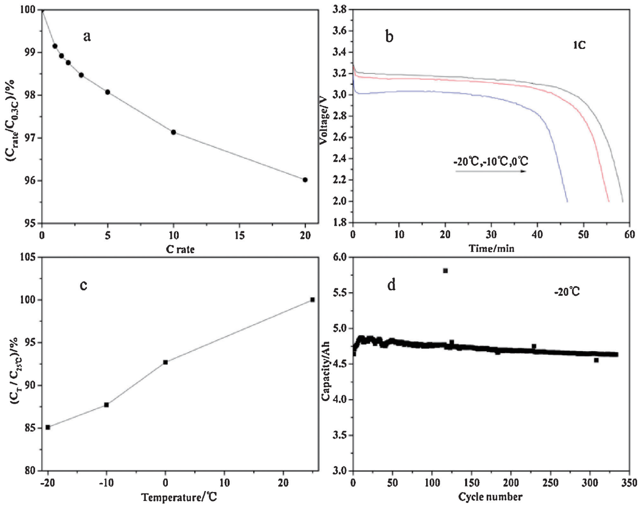

Figure 3. (a) Capacity retention of $LiFePO_4$/graphite cell at various C rates; (b) discharge profiles of $LiFePO_4$/graphite under different temperature; (c) capacity retention of $LiFePO_4$/graphite cell at various temperatures; (d) cycling performance of $LiFePO_4$/graphite cell.

This study was supported by National Natural Science Foundation of China (Grant No. 51072233), the Freedom Explore Program of Central South University (No. 2011QNZT070), and Postdoctoral Sustentation Fund of Central South University, China.

References

1 A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* **1997**, *144*, 1188.
2 H. Huang, S.-C. Yin, T. Kerr, N. Taylor, L. F. Nazar, *Adv. Mater.* **2002**, *14*, 1525.
3 S.-Y. Chung, J. T. Bloking, Y.-M. Chiang, *Nat. Mater.* **2002**, *1*, 123.
4 B. Zhang, X. Wang, Z. Liu, H. Li, X. Huang, *J. Electrochem. Soc.* **2010**, *157*, A285.
5 Q. Chen, J. Wang, Z. Tang, W. He, H. Shao, J. Zhang, *Electrochim. Acta* **2007**, *52*, 5251.
6 K. Amine, J. Liu, I. Belharouak, *Electrochem. Commun.* **2005**, *7*, 669.
7 H.-H. Chang, H.-C. Wu, N.-L. Wu, *Electrochem. Commun.* **2008**, *10*, 1823.
8 X. H. Rui, Y. Jin, X. Y. Feng, L. C. Zhang, C. H. Chen, *J. Power Sources* **2011**, *196*, 2109.
9 C. Li, N. Hua, C. Wang, X. Kang, T. Wumair, Y. Han, *J. Alloys Compd.* **2011**, *509*, 1897.
10 X.-Z. Liao, Z.-F. Ma, Q. Gong, Y.-S. He, L. Pei, L.-J. Zeng, *Electrochem. Commun.* **2008**, *10*, 691.
11 S. S. Zhang, K. Xu, T. R. Jow, *J. Power Sources* **2006**, *159*, 702.
12 M. M. Ren, Z. Zhou, X. P. Gao, W. X. Peng, J. P. Wei, *J. Phys. Chem. C* **2008**, *112*, 5689.
13 K. Danoue, T. Inoue, M. Fujimoto, Presented at 45th Battery Symposium, Kyoto, Japan, November, **2004**.
14 L.-X. Yuan, Z.-H. Wang, W.-X. Zhang, X.-L. Hu, J.-T. Chen, Y.-H. Huang, J. B. Goodenough, *Energy Environ. Sci.* **2011**, *4*, 269.
15 F.-F. Cao, Y.-G. Guo, L.-J. Wan, *Energy Environ. Sci.* **2011**, *4*, 1634.