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Hydrothermal Synthesis of Electrochemically Active $LiMnPO_4$

Haisheng Fang, Liping Li, and Guangshe Li*
State Key Lab of Structural Chemistry, Fujian Institute of Research on the Structure of Matter
and Graduate School of Chinese Academy of Sciences, Fuzhou 350002, P. R. China

(Received January 5, 2007; CL-070007; E-mail: guangshe@fjirsm.ac.cn)

Highly crystalline olivine-structured $LiMnPO_4$ was prepared by a simple hydrothermal method in a basic aqueous medium at 200 °C for 10 h. The particle shape of the as-prepared $LiMnPO_4$ was plate-like with the thickness of 100–200 nm. A capacity of 68 $mA\,h\,g^{-1}$ was reversibly achieved between 3 and 4.5 V vs. Li^+/Li.

Since the pioneering work on $LiFePO_4$ by Padhi et al.,[1] lithium transition-metal phosphates $LiMPO_4$ (M = Mn, Fe, Co, and Ni) with ordered olivine structure have attracted much attention as potential new cathode materials for lithium ion batteries owing to their low cost, low toxicity, and improved chemical stability. Among these compounds, $LiFePO_4$ shows a flat voltage plateau at 3.5 V vs. Li^+/Li and a theoretical specific capacity of 170 $mA\,h\,g^{-1}$ and, therefore, was previously considered as a candidate cathode material to replace the popularly used $LiCoO_2$. Many attempts have been performed to improve the rate capability of $LiFePO_4$ by minimizing the particle size, cation doping, or conductive coatings.[2–7] However, low gravimetric density and low-voltage plateau of $LiFePO_4$ limit the performance improvement for applications in lithium ion batteries. Another olivine-structured compound $LiMnPO_4$ is promising for this purpose because it offers the potential of Mn^{3+}/Mn^{2+} redox couple at 4.1 V vs. Li^+/Li, which is compatible with the system presently used in lithium ion batteries. Nevertheless, ab initio calculations indicated that $LiMnPO_4$ suffers from lower intrinsic electronic conductivity as compared to that of $LiFePO_4$[8] and may give rise to electrochemical inactivity. This seems to be verified by the previous experimental works in which Padhi et al.[1] and Yamada et al.[9] were unable to extract any lithium from $LiMnPO_4$. Contrary to these observations, Li et al.[10] achieved a large reversible capacity of 140 $mA\,h\,g^{-1}$ in $LiMnPO_4$ which was synthesized by a solid-state reaction. These controversial results clearly demonstrated that the electrochemical activity of $LiMnPO_4$ was strongly dependent on the preparation method.

Up to date, very limited methods were developed to achieve electrochemically active $LiMnPO_4$.[11–13] Hydrothermal synthesis is a versatile method for preparing crystalline particles.[14–18] Its advantages include simple synthetic process, easy scale-up production, energy efficient, and environmental friendly. In this work, we explored the synthesis of $LiMnPO_4$ via a hydrothermal route. $LiMnPO_4$ thus obtained achieved to show electrochemical activity.

Chemicals, $Li_2SO_4{\cdot}H_2O$, $MnSO_4{\cdot}H_2O$, and $NH_4H_2PO_4$, with a molar ratio of 3:1:1 were dissolved in 40 mL of distilled water at room temperature. The pH of the solution was adjusted to around 10 by addition of concentrated $NH_3{\cdot}H_2O$ (25 wt %) under vigorous stirring. The obtained suspension was transferred into a Teflon-lined stainless steel autoclave and heated in an oven at 200 °C for 10 h. The precipitated product was filtered off, washed several times with distilled water, and finally dried at 120 °C for 10 h. The yield was over 95%.

The crystalline phase was identified with powder X-ray diffraction (XRD, DMAX2500, Rigaku) with Cu Kα radiation. The lattice parameters were refined with peak positions that were calibrated by internal standard of silicon (99.9% pure). The morphology of the $LiMnPO_4$ powders was observed by a scanning electron microscope (JEOL, JSM-5600LV). An Oxford INCA energy dispersive X-ray spectrometer (EDXS) was applied to examine the compositions of the sample.

Electrochemical characterization of the sample was performed using CR2025 coin-type cell. For cathode fabrication, the as-prepared powders were ball-milled with 20 wt % of carbon black for 4 h to form a $LiMnPO_4/C$ composite. The $LiMnPO_4/C$ composite was mixed with 5 wt % of carbon black and 5 wt % of polyvinylidene fluoride in *N*-methyl pyrrolidinone. The slurry thus obtained was pasted onto an Al foil and dried at 100 °C for 10 h in vacuum. The test cell consisted of cathode and lithium foil anode which were separated by a porous polypropylene film and electrolyte of 1 M $LiPF_6$ in EC:EMC:DMC (1:1:1 in volume). The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged between 3 and 4.5 V at a current density of 1.5 $mA\,g^{-1}$ at room temperature.

It is well recognized that the pH value of the precursor solution has a significant effect on the formation of final products under hydrothermal conditions. Weak acidic, neutral or weak basic precursor solutions favor to the crystallization of single-phase $LiFePO_4$,[14,17] while high alkalinity is in favor of obtaining $LiCoPO_4$ phase.[18] In this work, the preparation of $LiMnPO_4$ was first attempted by hydrothermal reaction at about pH 6. A few pink precipitate was obtained, and this precipitate was an unknown phase, showing a complicated XRD pattern. Further increasing pH value of the solution up to about 10 led to the successful formation of pure phase $LiMnPO_4$. Similarly, an

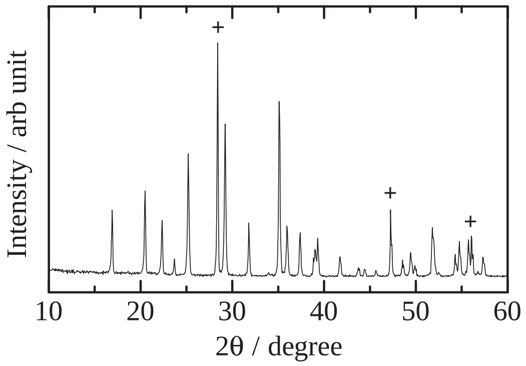

Figure 1. Powder XRD pattern of the as-prepared $LiMnPO_4$. Symbol “+” denotes the internal standard of silicon.

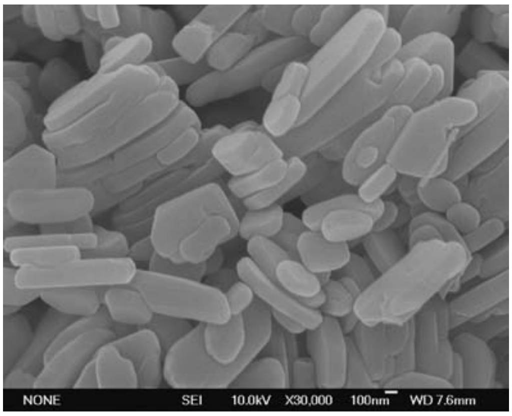

Figure 2. SEM image of $LiMnPO_4$ prepared at pH 10.

alkaline condition has already been employed to precipitate $LiMnPO_4$ using other preparation methods.[11] Figure 1 shows the XRD pattern of the product that was obtained at 200 °C for 10 h. All diffraction peaks were fully indexed in a space group of *Pnma* with the cell parameters $a = 10.4474$, $b = 6.1017$, and $c = 4.7427$ Å, and no impurity phase was detected. The sharp diffraction peaks in Figure 1 indicated that the as-prepared $LiMnPO_4$ was highly crystalline, and hence no extra heat treatments are needed to improve the crystallinity. Figure 2 shows the SEM image for the as-prepared $LiMnPO_4$. It is seen that the particles were slightly agglomerated and adopted a plate-like morphology with a thickness of about 100–200 nm. The fine texture of the particles also demonstrated the high crystallinity of the as-prepared $LiMnPO_4$. EDXS results indicated that the Mn/P ratio for the as-prepared sample was well consistent with the stoichiometric value of $LiMnPO_4$.

Electrochemically active $LiMnPO_4$ is difficult to achieve since $LiMnPO_4$ shows poor inherent electronic conductivity. In order to provide an efficient conductive carbon coating on the surface of the active materials, a generally adopted ball-milling procedure was employed to produce a homogeneous $LiMnPO_4$/C composite. Figure 3 shows the charge–discharge curves of $LiMnPO_4$/C composite cycled between 3 and 4.5 V at a current density of 1.5 mA g^{-1}. As can be seen in Figure 3, the cathode clearly exhibited electrochemical activity with charge and discharge plateaus around the voltage of 4.1 V vs. Li^+/Li with a relatively small polarization.[11] These plateaus corresponded to the redox of Mn^{3+}/Mn^{2+} that accompanied with lithium ion extraction and insertion in $LiMnPO_4$. A large irreversible capacity observed especially during the first cycling is most likely due to the oxidation of the electrolyte at relatively high cut-off voltage. A capacity of 68 mA h g^{-1} can be reversibly achieved, which is comparable to that reported by Delacourt et al.[11] This limited capacity could be the result of extremely low intrinsic electronic conductivity and slow lithium diffusion kinetics within the $LiMnPO_4$ grains. Several previous literatures have proved that small particle size is helpful for improving the performance of $LiMnPO_4$,[11,12] and further work for tailoring the preparation of small particles was in progress. Anyway, the above results demonstrated that electrochemically active $LiMnPO_4$ can be obtained by a simple hydrothermal method.

In conclusion, phase-pure and well-crystallized olivine-structured $LiMnPO_4$ was successfully prepared by a simple hydrothermal method. A reversible capacity of 68 mA h g^{-1} was obtained when cycled between 3 and 4.5 V.

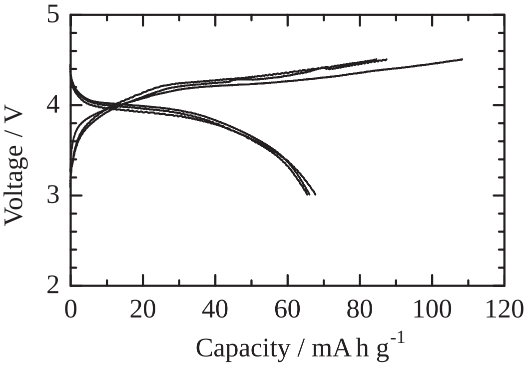

Figure 3. Charge–discharge curves of $LiMnPO_4$ at a current density of 1.5 mA g^{-1}.

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References

1 A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* **1997**, *144*, 1188.
2 A. Yamada, S. C. Chung, K. Hinokuma, *J. Electrochem. Soc.* **2001**, *148*, A224.
3 H. Huang, S. C. Yin, L. F. Nazar, *Electrochem. Solid-State Lett.* **2001**, *4*, A170.
4 S. Y. Chung, J. T. Bloking, Y. M. Chiang, *Nat. Mater.* **2002**, *1*, 123.
5 N. Ravet, Y. Chouinard, J. F. Magnan, S. Besner, M. Gauthier, M. Armand, *J. Power Sources* **2001**, *97–98*, 503.
6 Z. Chen, J. R. Dahn, *J. Electrochem. Soc.* **2002**, *149*, A1184.
7 S. T. Myung, S. Komaba, N. Hirosaki, H. Yashiro, N. Kumagai, *Electrochim. Acta* **2004**, *49*, 4213.
8 A. Yamada, M. Hosoya, S. C. Chung, Y. Kudo, K. Hinokuma, K. Y. Liu, Y. Nishi, *J. Power Sources* **2003**, *119–121*, 232.
9 A. Yamada, Y. Kudo, K. Liu, *J. Electrochem. Soc.* **2001**, *148*, A1153.
10 G. Li, H. Azuma, M. Tohda, *Electrochem. Solid-State Lett.* **2002**, *5*, 135.
11 C. Delacourt, P. Poizot, M. Morcrette, J. M. Tarascon, C. Masquelier, *Chem. Mater.* **2004**, *16*, 93.
12 N. H. Kwon, T. Drezen, I. Exnar, I. Teerlinck, M. Isono, M. Graetzel, *Electrochem. Solid-State Lett.* **2006**, *9*, A277.
13 J. S. Yang, J. J. Xu, *J. Electrochem. Soc.* **2006**, *153*, A716.
14 S. Yang, P. Y. Zavalij, M. S. Whittingham, *Electrochem. Commun.* **2001**, *3*, 505.
15 K. Dokko, K. Shiraishi, K. Kanamuraa, *J. Electrochem. Soc.* **2005**, *152*, A2199.
16 T. Kanasaku, K. Amezawa, N. Yamamoto, *Solid State Ionics* **2000**, *133*, 51.
17 K. Dokko, S. Koizumi, K. Kanamuraa, *Chem. Lett.* **2006**, *35*, 338.
18 X. Huang, J. F. Ma, P. W. Wu, Y. M. Hu, J. H. Dai, Z. B. Zhu, H. Y. Chen, H. F. Wang, *Mater. Lett.* **2005**, *59*, 578.