

Synthesis and electrochemical properties of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode material prepared from a sucrose-containing precursor

A. P. Tang · X. Y. Wang · S. Y. Yang ·
J. Q. Cao

Received: 12 December 2007 / Accepted: 7 May 2008 / Published online: 28 May 2008
© Springer Science+Business Media B.V. 2008

Abstract Monoclinic structure $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite powders are synthesized via a novel homogeneous mixing route followed by a one-step heat treatment. The composites were characterized by X-ray diffraction (XRD) and galvanostatic charge/discharge, CV measurements. The influence of the heat treatment on the electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites was investigated. To examine the effect of residual carbon content on the properties of the composites, six samples with 1.2, 2.3, 3.4, 4.4, 5.8, and 7.0 wt% carbon were prepared. The sample with 4.4 wt% carbon exhibited good cycling performance and rate capability in the range of 3.0–4.8 V.

Keywords $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite · $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ · Cathode material

1 Introduction

Recently, framework materials based on the phosphate polyanion have been identified as potential electroactive materials for lithium ion battery applications. The lithiated transition metal phosphates based on either the olivine or Nasicon structures, such as LiMPO_4 [$M = \text{Mn}, \text{Fe}, \text{Co}$] [1–12], $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [13–31], and LiVOPO_4 [32, 33], appear to hold particular promise. In comparison with lithiated transition metal oxides, they display high redox potentials,

good Li^+ transport, remarkable electrochemical and thermal stability, and comparable energy density [28]; however, their low electronic conductivity prevents full use of the total capacity even at slow rates, presenting a major drawback to practical implementation of these materials. Fortunately, this problem may be overcome by such methods as coating the particles with a thin carbon layer or minimizing the particle size [34].

Among these compounds, olivine structured iron phosphates are the most promising candidates as new cathode materials due to their abundant supply, low toxicity, and high theoretical capacity of 170 mAh g^{-1} . Vanadium phosphates are also appealing. Although vanadium is not as environmentally benign as iron, studies show that vanadium is somewhat tolerated by many animals [28]. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ for application in lithium ion batteries exists in two forms: the thermodynamically stable monoclinic form, isotypic with the form of several other monoclinic $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{Sc}, \text{Fe}, \text{and Cr}$) materials, and the rhombohedral or NASICON phase that can be formed by ion exchange from the stable sodium analogue or oxidizing NASICON $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ with Cl_2 in CHCl_3 to form $\text{V}_2(\text{PO}_4)_3$ and then reacting with LiI . Two lithium ions per $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ formula unit can be extracted from the rhombohedral form at 3.77 V (vs. Li/Li^+), and only 1.3 can be reinserted [25]. However, all the three Li ions per $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ formula unit in monoclinic form can be removed and reversibly intercalated; high capacity can then be expected in this system.

Usually, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ materials are obtained through high temperature solid-state reactions [15–27] or sol–gel methods followed by heat treatment [28–31]. These methods comprise a pre-sintering step and a subsequent final heating step. In this investigation, we developed a novel homogeneous mixing route to prepare a sucrose-

A. P. Tang · X. Y. Wang (✉) · S. Y. Yang · J. Q. Cao
School of Chemistry, Xiangtan University,
Hunan 411105, China
e-mail: wxianyou@yahoo.com

A. P. Tang
School of Chemistry and Chemical Engineering, Hunan
University of Science and Technology, Hunan 411201, China

containing precursor, in which sucrose acted not only as a chelating reagent, but also a carbon source, and successfully synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites without a pre-sintering treatment step. In addition, based on the influences of heat treatment methods on the electrochemical properties of the composite, the effect of the amount of residual carbon on the properties of the composites is also evaluated.

2 Experimental

The precursors were prepared as follows. First, stoichiometric V_2O_5 was added to the solution which contained the stoichiometric amount of H_3PO_4 and an appropriate amount of sucrose, with continued stirring at about $70\text{ }^\circ\text{C}$ until a clear blue solution formed. Second, stoichiometric LiOH was added to above mixture. Finally, the resultant solution was heated on a hot plate to dryness.

As-prepared precursors were heat-treated according to two different methods as follows:

- (i) The precursor was pressed into pellets and heated at $350\text{ }^\circ\text{C}$ in a tubular furnace with flowing argon gas for 5 h. After slowly cooling to room temperature, the pellets were ground for 30 min, pressed into pellets again, then heated to $700\text{ }^\circ\text{C}$ and held at this temperature for 3 h under flowing argon to yield the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite.
- (ii) After grinding for 30 min, the precursor was pressed into pellets and sintered at $700\text{ }^\circ\text{C}$ for 3 h under flowing argon to yield the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite.

Structural and crystallographic analysis of the reaction product was taken from powder diffraction data obtained using diffractometer (D/MAX-3C) with $\text{Cu K}\alpha$ radiation. The thermal behavior of the sucrose-containing precursor was examined by thermogravimetric (TG) analysis using a WRT-3P instrument at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ in a nitrogen atmosphere.

The electrochemical characterization of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders as cathode of two-electrode electrochemical cells were measured using a Neware battery tester (BTS-51, Shenzhen, China). The cathodes of the two-electrode electrochemical cells were fabricated by blending the prepared powder with polyvinylidene fluoride (PVDF) binder and acetylene black in a weight ratio of 80:5:15 in *N*-methyl-2-pyrrolidone. The obtained slurry was coated on Al foil and dried at $70\text{ }^\circ\text{C}$ for 24 h in a vacuum. Two-electrode electrochemical cells were assembled in a glove box filled with high-purity argon, where the lithium metal foil were used as anode, Celgard2400 as separator, and 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volumetric ratio of 1:1 as

electrolyte. The electrochemical capacity measurements were performed in the voltage range between 3.0 and 4.8 V, and the electrochemical capacity of samples was evaluated on the active materials. Cyclic voltammetry (CV) tests were conducted using a CHI 660 electrochemical analyzer. CV tests were performed between 3.0 and 4.8 V at a scan rate of 0.05 mV s^{-1} at about $25\text{ }^\circ\text{C}$.

3 Results and discussion

3.1 Effect of heat treatment on sucrose-containing precursor

The TG curve of the sucrose-containing precursor is shown in Fig. 1. For the sucrose-containing precursor, there is an initial loss of lattice water from the precursor decomposing at $<236\text{ }^\circ\text{C}$. In the temperature range $236\text{--}420\text{ }^\circ\text{C}$, there is a weight loss due to the pyrolysis of sucrose and its possible derivatives that were formed during preparing precursor. A slight weight loss is observed above $420\text{ }^\circ\text{C}$ because pyrolysis of the remaining sucrose and its possible derivatives continues until $540\text{ }^\circ\text{C}$. After pyrolysis of sucrose and its possible derivatives, the product weight decreases due to the formation of carbon oxides in carbothermal reaction between 540 and $600\text{ }^\circ\text{C}$. The temperature of the carbothermal reaction is in accordance with that reported by Fu et al. [22] and Li et al. [35].

On the basis of TG analysis, we were able to determine the sintering temperature at which $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was prepared by heat treatment of the sucrose-containing precursor. First, we attempted a simple one-step heat treatment at $700\text{ }^\circ\text{C}$. Second, a pre-sintering temperature, namely $350\text{ }^\circ\text{C}$, was applied to a two-step heat treatment which consisted of the pre-sintering step and a subsequent

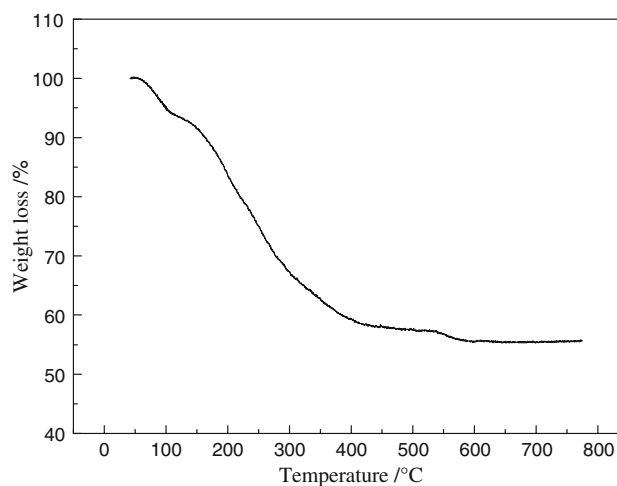


Fig. 1 TG curve of sucrose-containing precursor

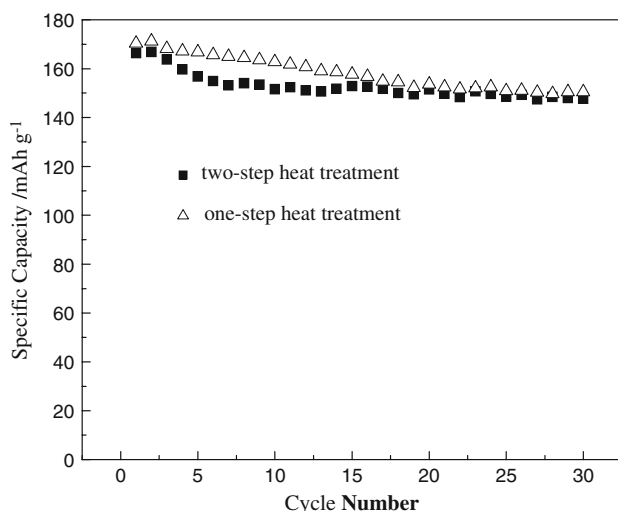


Fig. 2 Cycling performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite with 4.4 wt% carbon at C/5 rate in voltage range of 3.0–4.8 V

final heating at 700 °C for the formation and crystallization of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

The discharge capacities of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ prepared with two kinds of process at the C/5 rate in the voltage range of 3.0–4.8 V are given as a function of cycle number in Fig. 2. The materials prepared by the one-step heat treatment and by the two-step heat treatment with pre-sintering at 350 °C deliver a first discharge capacity of 170 and 166 mAh g^{-1} , and their corresponding discharge capacity after 30 cycles remain about 151 and 148 mAh g^{-1} , respectively.

The material synthesized by the one-step heat treatment is equivalent to that material prepared using the two-step heat treatment in terms of specific capacity and capacity retention. The latter prepared route is, however, considerably more complicated. Therefore, the one-step heat treatment is a promising $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite preparation technique.

3.2 Effect of carbon content on $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite materials

In order to study further the performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites prepared by one-step heat treatment, it is necessary to investigate the effect of residual carbon content on the properties of the composites. Six samples with different amounts of sucrose added to the precursors were synthesized by the one-step heat treatment. It was found by TG and chemical analysis that the amount of remaining carbon in the composites is 1.2, 2.3, 3.4, 4.4, 5.8, and 7.0 wt%, respectively.

The XRD patterns of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites with various amounts of residual carbon are shown in Fig. 3, where all samples are $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with an ordered

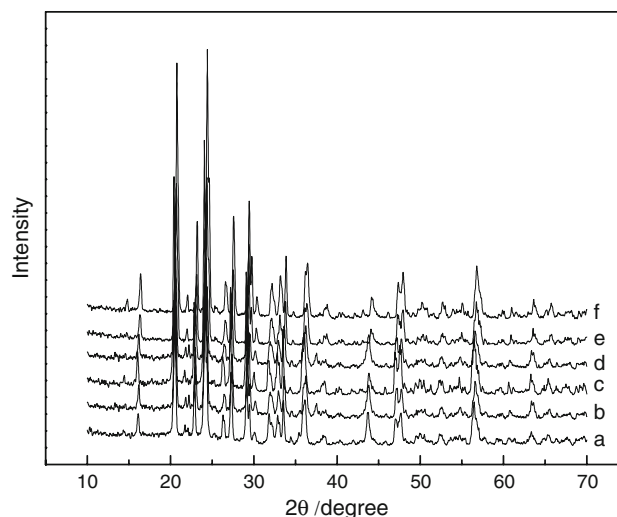


Fig. 3 XRD patterns for $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites with various carbon content. (a) 1.2 wt%; (b) 2.3 wt%; (c) 3.4 wt%; (d) 4.4 wt%; (e) 5.8 wt%; (f) 7.0 wt%

monoclinic structure (space group $P2_1/n$). There is no evidence of the formation of crystalline or amorphous carbon in the XRD curves. As shown in Fig. 3f, the diffraction peaks are broadened and the crystallinity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powder is decreased due to suppression of the formation of crystalline $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ by the excessive carbon content. A similar observation in LiFePO_4/C composite was reported by Yun et al. [34].

The initial charge–discharge voltage curves of prepared samples at the C/5 rate in the voltage range of 3.0–4.8 V are shown in Fig. 4. Four charge plateaus around 3.6, 3.7, 4.1, and 4.6 V appear in the charge process, which correspond to the complicated phase transition processes between the single phases $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ ($x = 2.5, 2.0, 1.0$, and 0) [17, 24]. On the other hand, the discharge profiles display an S-shaped curve, which exhibits an electrochemical signature of solid-solution behavior, and two plateaus around 3.5 and 3.6 V, which correspond to the two phase transition in the reinsertion of the last lithium, $\text{Li}_2\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_3\text{V}_2(\text{PO}_4)_3$.

The CVs of $\text{Li}/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cells between 3.0 and 4.8 V at a scan rate of 0.05 mV s^{-1} are presented in Fig. 5. Four anodic peaks, indicative of lithium ion extraction from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, occur at 3.60, 3.69, 4.11, and 4.59 V (vs. Li/Li^+), and three reduction peaks are located around 3.57, 3.64, and 3.93 V (vs. Li^+/Li), respectively, in good agreement with the charge/discharge curves shown in Fig. 4 and previously published results [20, 24, 30, 31]. On the other hand, the large irreversibility of the materials in the first cycle, shown in Fig. 4, is reflected in the voltammograms.

The discharge capacities of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites at the C/5 rate are presented in Fig. 6. Although there is

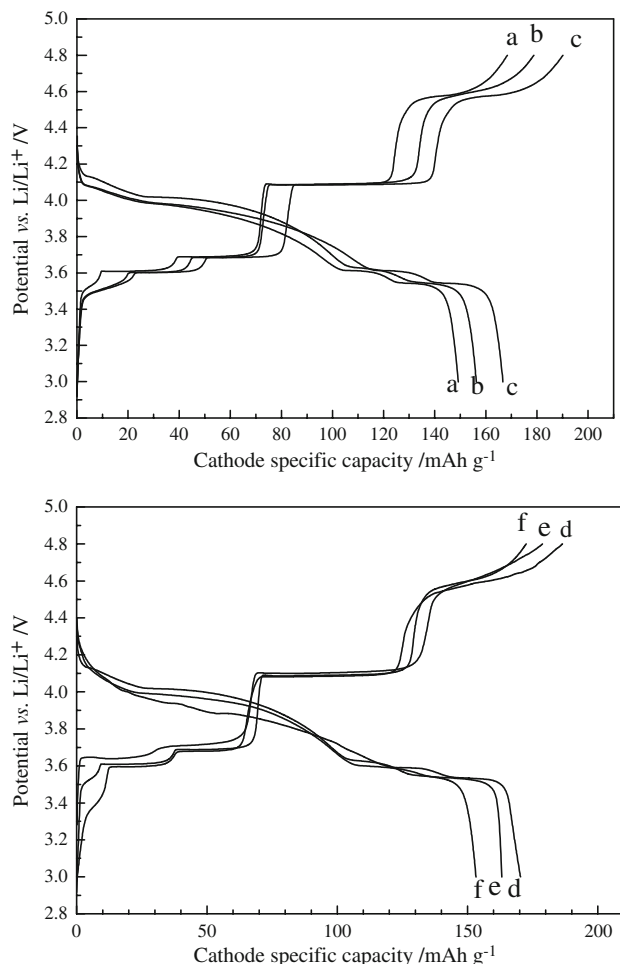


Fig. 4 The first charge/discharge profiles of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites with various carbon content. (a) 1.2 wt%; (b) 2.3 wt%; (c) 3.4 wt%; (d) 4.4 wt%; (e) 5.8 wt%; (f) 7.0 wt%

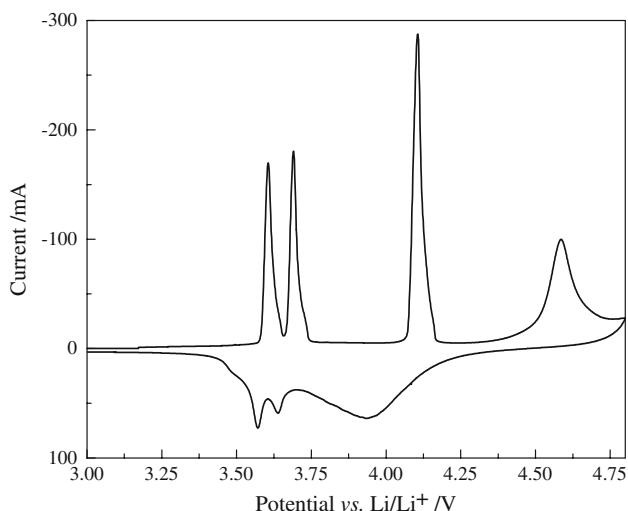


Fig. 5 CV curve for $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite with 4.4 wt% carbon

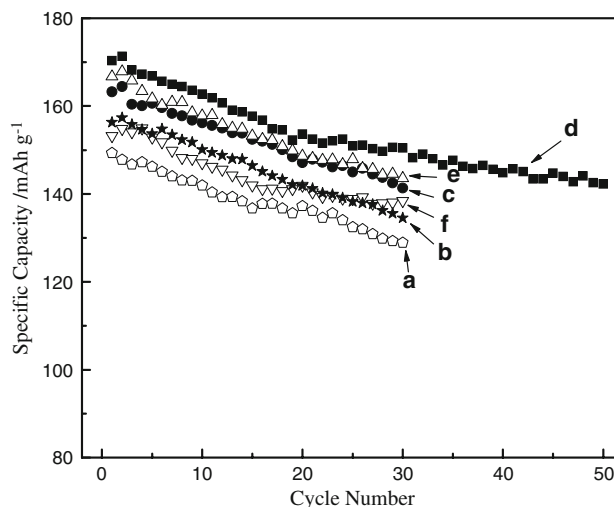


Fig. 6 Discharge capacities versus cycle number at C/5 rate between 3.0 and 4.8 V for $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites with various carbon content. (a) 1.2 wt%; (b) 2.3 wt%; (c) 3.4 wt%; (d) 4.4 wt%; (e) 5.8 wt%; (f) 7.0 wt%

little difference in the XRD patterns of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites, the cell performance of the cathode materials is dependent on the amount of residual carbon in the composites. Samples with 3.4 and 5.8 wt% carbon deliver higher initial discharge capacities, but their reversible capacities fade as cycling proceeds, indicating poor capacity retention. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ material with 4.4 wt% carbon gives the highest initial capacity (170 mAh g^{-1}), and after 50 cycles, the discharge capacity is 142 mAh g^{-1} , which reaches the previously published results for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples prepared by conventional high-temperature solid-state reactions [24] and the sol-gel route based on $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel [30]. Samples with a low carbon amount deliver low initial discharge capacities and have diminished capacity retention. On the other hand, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite with 7.0 wt% carbon displays good capacity retention, although a small reversible discharge capacity is observed. A reduced discharge capacity originates from the thicker carbon coating layer, and may be attributed to difficulty in lithium ion diffusion through the thicker carbon coating layer.

4 Conclusion

Monoclinic structured $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites were synthesized successfully via a novel homogeneous mixing route followed by one-step heat treatment at 700°C . All as-prepared samples with various carbon contents were $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with an ordered monoclinic structure. For materials with a low carbon content, the $\text{Li}/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ gives a small discharge capacity and displays poor capacity

retention. For materials with high carbon contents, Li/Li₃V₂(PO₄)₃ gives a small reversible discharge capacity, although good capacity retention is observed. Therefore, it is found that a Li₃V₂(PO₄)₃/C composite with 4.4 wt% carbon content displays the best electrochemical properties, e.g., the highest initial discharge capacity (170 mAh g⁻¹) and good capacity retention (142 mAh g⁻¹ after 50 cycles).

Acknowledgments This work was funded by the National Natural Science Foundation of China under project No. 50472080 and the Natural Science Foundation of Hunan Province under project No. 06JJ50078.

References

1. Yamada A, Hosoya M, Chung SC, Kudo Y, Hinokuma K, Liu KY, Nishi Y (2003) *J Power Sources* 119–121:232
2. Yamada A, Chung SC (2001) *J Electrochem Soc* 148:A960
3. Chang XY, Wang ZX, Li XH, Kuang Q, Peng WI, Guo HJ, Zhang YH (2004) *Acta Phys-Chim Sin* 1249–1252:20
4. Li G, Azuma H, Tohdam M (2002) *Electrochem Solid State Lett* 5:A135
5. Amine K, Yasuda K, Yamachi M (2000) *Electrochem Solid State Lett* 3:178
6. Huang X, Ma JF, Wu PW, Hu YM, Dai JH, Zhu ZB, Chen HY, Wang HF (2005) *Mater Lett* 578–582:59
7. Okada S, Sawa S, Uebo Y, Egashira M, Yamaki J, Tabuchi M (2003) *Electrochemistry* 71:1136
8. Sides CR, Croce F, Young VY, Martin CR, Scrosati B (2005) *Electrochem Solid State Lett* 8:A360
9. Gabrisch H, Wilcox JD, Doeff MM (2006) *Electrochem Solid State Lett* 9:A360
10. Doeff MM, Hu YQ, McLarnon F, Kosteckib R (2003) *Electrochem Solid State Lett* 6:A207
11. Chen ZH, Dahna JR (2002) *J Electrochem Soc* 149:A1184
12. Hu YQ, Doeff MM, Kosteckib R, Finones R (2004) *J Electrochem Soc* 151:A1279
13. Yin SC, Grondy H, Strobel P, Anne M, Nazar LF (2003) *J Am Chem Soc* 125:10402
14. Yin SC, Grondy H, Strobel P, Anne M, Nazar LF (2003) *J Am Chem Soc* 125:326
15. Barker J, Saidi MY, Swoyer JL (2003) *J Electrochem Soc* 150:A684
16. Fu LJ, Liu H, Li C, Wu YP, Rahm E, Holze R, Wu HQ (2005) *Prog Mater Sci* 50:881
17. Barker J, Saidi MY, Huang H, Adamson G (2002) *Electrochem Solid State Lett* 5:A149
18. Sato M, Ohkawa H, Yoshida K, Saito M, Uematsu K, Toda K (2000) *Solid State Ionics* 135:137
19. Morcrette M, Leriche JB, Patoux S, Wurm C, Masquelier C (2003) *Electrochem Solid State Lett* 6:A80
20. Ren MM, Zhou Z, Li YZ, Gao XP, Yan J (2006) *J Power Sources* 162:1357
21. Morgan D, Ceder G, Saidi MY, Barker J, Swoyer J, Huang H, Adamson G (2003) *J Power Sources* 119–121:755
22. Fu P, Zhao YM, Dong YZ, An XN, Shen GP (2006) *Electrochim Acta* 52:1003
23. Morgan D, Ceder G, Saidi MY, Barker J, Swoyer J, Huang H, Adamson G (2002) *Chem Mater* 14:4684
24. Saidi MY, Barker J, Huang H, Swoyer JL, Adamson G (2003) *J Power Sources* 119–121:266
25. Gaubicher J, Wurm C, Goward G, Masquelier C, Nazar L (2000) *Chem Mater* 12:3240
26. Fu P, Zhao YM, Dong YZ, An XN, Shen GP (2006) *J Power Sources* 162:651
27. Burba CM, Frech R (2007) *Solid State Ionics* 177:3445
28. Huang H, Yin SC, Kerr T, Taylor N, Nazar LF (2004) *Adv Mater* 14:1525
29. Li YZ, Zhou Z, Ren MM, Gao XP, Yan J (2006) *Electrochim Acta* 51:6498
30. Li YZ, Zhou Z, Ren MM, Gao XP, Yan J (2007) *Mater Lett* 61:4562
31. Li YZ, Zhou Z, Gao XP, Yan J (2007) *Electrochim Acta* 52:4922
32. Barker J, Saidi MY, Swoyer JL (2004) *J Electrochem Soc* 151:A796
33. Azmia BM, Ishihara T, Nishiguchi H, Takita Y (2005) *J Power Sources* 146:525
34. Yun NJ, Ha HW, Jeong KH, Park HY, Kim K (2006) *J Power Sources* 160:1361
35. Li YZ, Zhou Z, Gao XP, Yan J (2006) *J Power Sources* 160:633