



Short communication

Lithium iron phosphate with high-rate capability synthesized through hydrothermal reaction in glucose solution

Guangchuan Liang, Li Wang, Xiuqin Ou*, Xia Zhao, Shengzhao Xu

Institute of Power Source & Ecomaterials Science, Box 1055, Hebei University of Technology,
300130 Tianjin, China

ARTICLE INFO

Article history:

Received 4 January 2008

Received in revised form 20 February 2008

Accepted 22 February 2008

Available online 29 February 2008

Keywords:

Lithium iron phosphate

Hydrothermal reaction

Glucose

Carbon coated

Cathode material

ABSTRACT

Carbon-coated lithium iron phosphate (LiFePO₄/C) was hydrothermally synthesized from commercial LiOH, FeSO₄ and H₃PO₄ as raw materials and glucose as carbon precursor in aqueous solution at 180 °C for 6 h followed by being fired at 750 °C for 6 h. The samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and constant current charge–discharge cycling test. The results show that the synthesized powders are in situ coated with carbon precursor produced from glucose. At ambient temperature (25 ± 2 °C), the specific discharge capacities are 154 mAh g⁻¹ at 0.2 C and 136 mAh g⁻¹ at 5 C rate, and the cycling capacity retention rate reaches 98% over 90 cycles. The excellent electrochemical performance can be correlated with the in situ formation of carbon precursor/carbon, thus leading to the even distribution of carbon and the enhancement of conductivity of individual grains.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Lithium iron phosphate (LiFePO₄) has been recognized as a promising candidate to replace lithium cobalt oxide as the cathode material of lithium ion batteries, due to its lower cost, improved safety, highly reversible and repeatable property. However, the low ionic and electronic conductivity has constricted its commercial applications [1]. Improvements in conductivity have been achieved by carbon coating [2–4], supervalent cation doping [5–9] or conducting nanophase forming [10,11] and particle size reducing [12–16]. In these pioneer works, the LiFePO₄ composite was prepared by the common approach of solid-state reaction. The lengthy and complicated procedures require repeated grinding and calcination that produced material with varied performances between batches. The hydrothermal synthesis is a useful method for preparing fine particles. More recently, it has been preferentially chosen to prepare LiFePO₄ for its advantages: quick, easy to form, economical in energy and easy to expand [17–24]. Dokko et al. [20,21] synthesized LiFePO₄ through a hydrothermal process at 170 °C for 12 h, followed by annealing at 400 °C for 30 min in an argon atmosphere. The prepared sample (carbon free), with a particle size of 0.5 μm, exhibited a discharge capacity of 150 mAh g⁻¹ at 0.2 C,

80 mAh g⁻¹ at 2 C and 40 mAh g⁻¹ at 5 C in a potential range of 2.0–4.5 V. Franger et al. [17] hydrothermally synthesized LiFePO₄ powders at 220 °C for 1 h, then heat-treated in the presence of sucrose at 550 °C for 12 h. The sample with a carbon content of less than 5 wt% and a particle size of 1.3 μm showed a specific discharge capacity of 143 mAh g⁻¹ at 0.1 C in a potential range of 2.0–4.5 V. Meligrana et al. [22] developed a hydrothermal synthesis to prepare high surface area LiFePO₄ powders in the presence of a surfactant compound, cetyltrimethyl ammonium bromide (CTAB), with a high concentration at 120 °C for 5 h, then fired at 600 °C for 12 h in pure N₂. The obtained samples showed a grain dimension range from 100 nm to around 50 nm, which was strongly affected by CTAB content. The conductivity of the powders was improved by the in situ coated carbon film on the surface of the particles, resulting from the pyrolysis of CTAB during the firing step. The sample with 4.8 wt% carbon showed discharge capacities of 140 mAh g⁻¹ at 0.2 C and 115 mAh g⁻¹ at 5 C. Chen and Whittingham [23] and Lee and Teja [24] investigated the effects of hydrothermal synthesis conditions, such as temperature, reactant concentration, pH value and reaction time, on the particle size, purity and capacity of LiFePO₄.

Up to now, there have been many reports on the effects of particle size, electronic conductivity and crystallographic structural changes on the charge–discharge performance of LiFePO₄. However, there are few reports on the effect of the hydrothermal preparation method (actually concerning the carbon dispersion degree and intimate contact with LiFePO₄ particles) of LiFePO₄ with high-rate capability. And the high-rate capability of the active

* Corresponding author. Tel.: +86 22 60202406; fax: +86 22 26564850.

E-mail addresses: liangguanchuang@hebut.edu.cn (G. Liang),
tigerw129@yahoo.com.cn (L. Wang), ouxuqin@hebut.edu.cn (X. Ou),
qqw1wlwl@163.com (X. Zhao), xs283@163.com (S. Xu).

material reported so far is not up to expectation. It is believed that optimization of conducting phase coating on LiFePO_4 particles prepared through hydrothermal route is the most important thing to improve its high-rate capability.

Therefore, the emphasis was focused on increasing the conductivity of the hydrothermally synthesized LiFePO_4 particles in this work. Glucose was used to develop an in situ carbon precursor/carbon coating on LiFePO_4 powders synthesized by hydrothermal method. Preliminary results indicated that the addition of glucose resulted in uniform carbon precursor/carbon distribution, thus facilitating the discharge behavior at high discharge rate.

2. Experimental

LiFePO_4 was prepared by a hydrothermal process in a 10L stainless steel autoclave (Weihai Co., China, Model WHF-10L) equipped with a mechanical stirrer. After the addition of aqueous solution of LiOH , H_3PO_4 and glucose, the autoclave was purged with nitrogen to remove residual oxygen. Then the FeSO_4 aqueous solution was added with stirring. The molar ratio of $\text{Li}:\text{Fe}:\text{P}$ in the precursor solution was 3:0.98:1, the concentration of Fe^{2+} and glucose in the reaction solution were controlled to be 0.5 mol L^{-1} and 25 g L^{-1} , respectively. The autoclave was sealed and heated at 180°C for 6 h. After the hydrothermal reaction, the autoclave was cooled down to below 100°C . Afterwards, the precipitate was filtered and washed several times with deionized water. The filter cake was dried at 120°C for 12 h in a vacuum oven. In order to carbonize the caramel produced from the glucose, the dried sample was fired at 750°C for 6 h under a nitrogen atmosphere. The samples were hereafter reported as LFG for unfired LiFePO_4 and LFG/C for the fired. For comparison, LiFePO_4 was also prepared with the absence of glucose under the same conditions, hereafter reported as LF, which was carbon-coated by firing with glucose, hereafter reported as LF/C.

The structure and morphology of the samples were characterized by X-ray diffractometer (Rigaku D/max 2500 V/PC) with a $\text{Cu K}\alpha$ radiation source, scanning electron microscope (Philips XL 30) and high-resolution transmission electron microscopy (Philips, Tecnai F20). The carbon content of the samples was determined by gravimetric method.

The electrochemical performance of the samples was tested using a coin-type cell (size: 2430). The composite electrode was prepared by mixing LiFePO_4 , carbon (super P-MMM Carbon) conductive additive and polytetrafluoroethylene (PTFE) in a weight ratio of 8:1:1. The content of LiFePO_4 in the composite cathode was $12\text{--}15 \text{ mg cm}^{-2}$. These film-type LiFePO_4 electrodes assembled in coin cells were separated from the counter electrode (lithium metal) by a Celgard 2400 separator. The electrolyte was LiPF_6 dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate

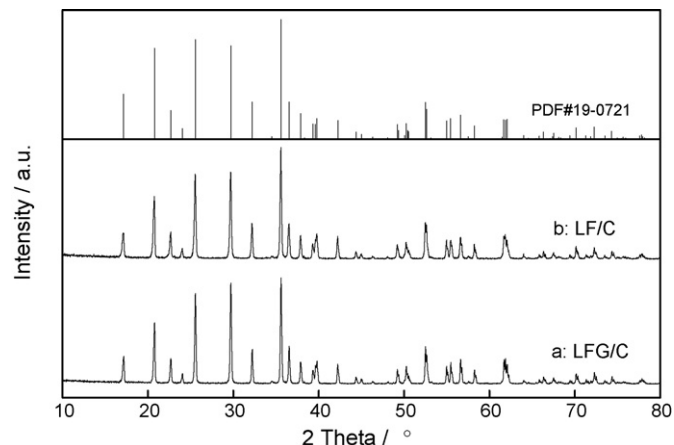


Fig. 1. X-ray powder diffraction patterns of LiFePO_4 samples, hydrothermally synthesized at 180°C for 6 h and fired at 750°C for 6 h in pure N_2 .

(DEC) and dimethyl carbonate (DMC) (1:1:1, by volume), and the concentration of the solution is 1.0 M. The assembly was carried out in an argon-filled glove box. The cathode performance was investigated in terms of charge–discharge curves and cycling capacity using an automatic charge–discharge instrument (Model CT2001A Land Co., China,) in the cut-off voltages of 2.3 V and 4.2 V. All the electrochemical measurements were carried out at ambient temperature ($25 \pm 2^\circ\text{C}$).

3. Results and discussion

Fig. 1 shows XRD patterns of the samples LFG/C and LF/C. The XRD patterns of both samples accord very well with that of phospho-olivine LiFePO_4 and no impurity phase is detected. Both samples have narrow diffraction peaks, indicating a high crystallinity degree. Weight analysis results show that the carbon contents are 4.94 wt% and 5.04 wt% for LFG/C and LF/C, respectively. Nevertheless, there is no evidence of carbonaceous or carbon phase in the diffraction patterns, probably due to its low content and/or its amorphous structure.

Fig. 2 displays SEM images of the prepared LFG and LF powders. Both samples are composed of slightly agglomerated particles. The primary particles show flat shape and grain dimensions of about $0.5\text{--}1 \mu\text{m}$ in edge and about $0.1 \mu\text{m}$ in thickness. The presence of glucose has no significant effect on the product morphology, as shown in Fig. 2a and b. Laser particle size analysis results show that the average sizes (D_{50}) are $1.15 \mu\text{m}$ and $1.28 \mu\text{m}$ for LFG and LF, respectively, which suggests that the presence of glucose in the synthesis process has minor effects on the prohibition of particle agglomeration.

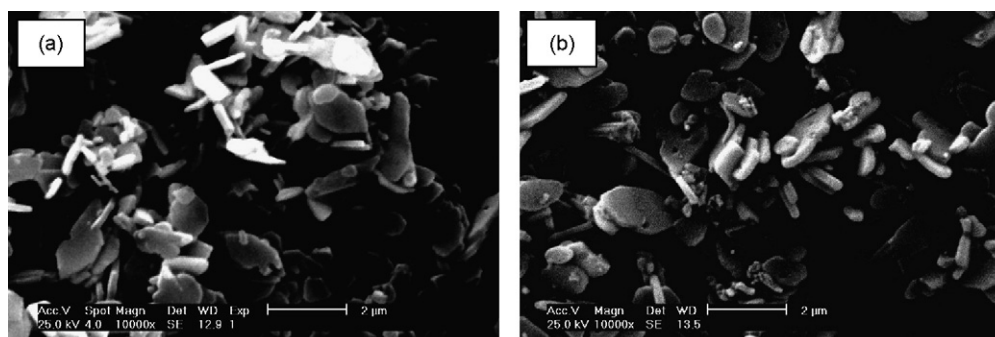


Fig. 2. SEM images of LiFePO_4 samples: (a) LFG and (b) LF, both were hydrothermally synthesized at 180°C for 6 h.

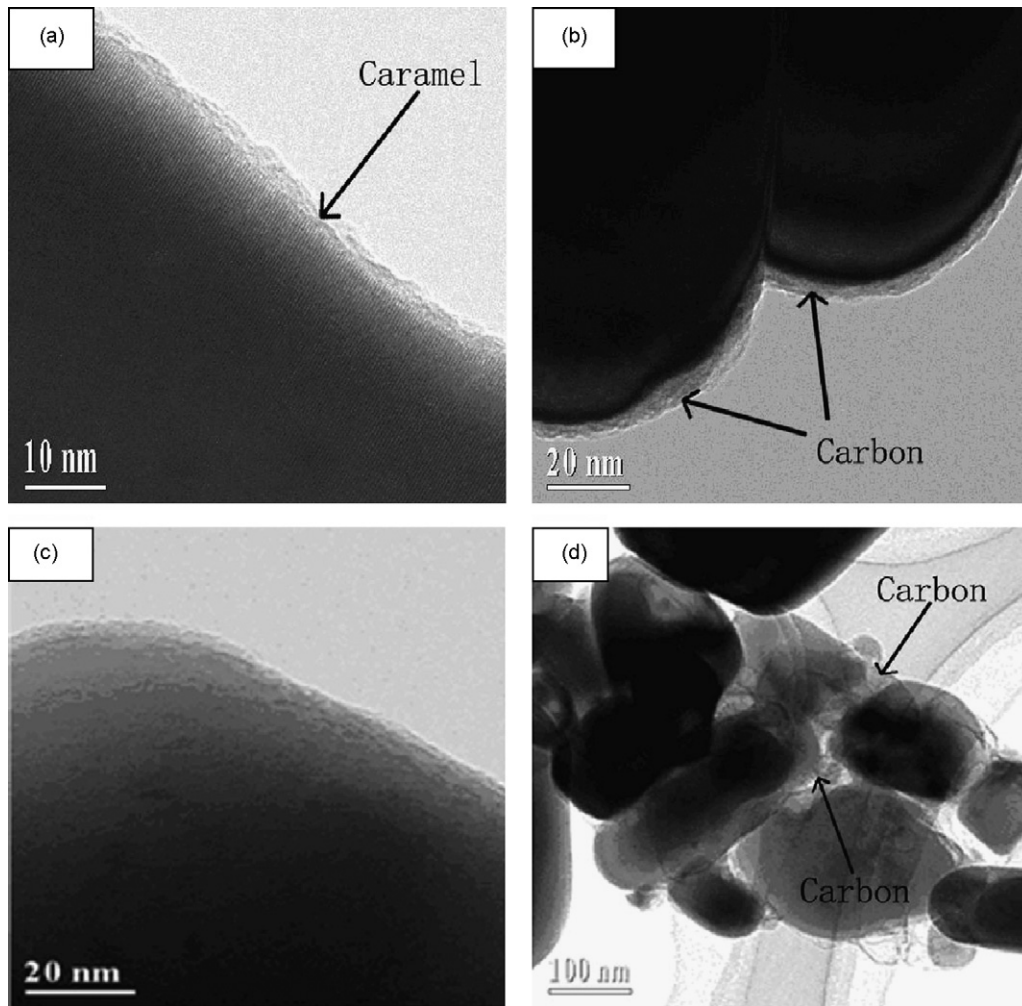


Fig. 3. TEM images of carbon-coated grains surface. (a) LFG; (b) LFG/C; (c) LF fired at 750 °C; (d) LF/C.

The carbon content of the fired LFG, namely LFG/C, is 4.94 wt%, whereas that of the fired LF is 0 wt%, which indicates that the LFG/C powders are in situ coated with carbon precursor produced from caramelization of glucose. And the carbon precursor turns into carbon after calcination. The in situ carbon coating can also be confirmed by TEM images in Fig. 3. It can be seen that there is a thin film on the surface of the grains of LFG and LFG/C, which is considered as the carbon precursor/carbon. In contrast to sample LFG and LFG/C, the surface of LF grains fired at 750 °C is smooth and there is no carbon layer, which indicates that the grains are in situ coated with carbon precursor/carbon in the hydrothermal process in the presence of glucose. Since this in situ coating is carried out in liquid phase, carbon precursor can be evenly distributed on the surface of all particles. However, in the case of LF/C, the carbon is unevenly distributed on the particle surface due to the mixing of LF powders with glucose in solid phase, as shown in Fig. 3d.

To investigate the effect of different carbon coating methods on conductivity, the powders with varying carbon contents were prepared by in situ coating (for LFG/C) and mixed coating (for LF/C). The effect of carbon contents and carbon coating methods (in situ coating and mixed coating) on conductivity is shown in Fig. 4. When carbon content is less than 5 wt%, the bulk conductivity of the powders prepared through mixed coating is greater than

that of the powders prepared through in situ coating. However, when the carbon content is greater than 5 wt%, the bulk conductivity of the powders prepared through in situ coating is greater than that of the powders prepared through mixed coating, which

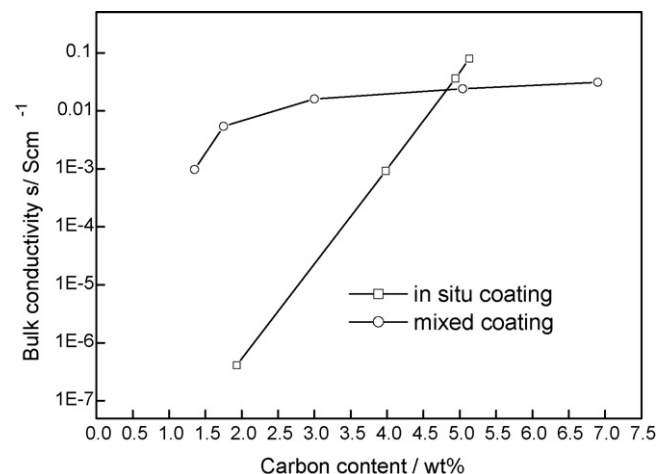


Fig. 4. Variation of bulk conductivity with carbon content.

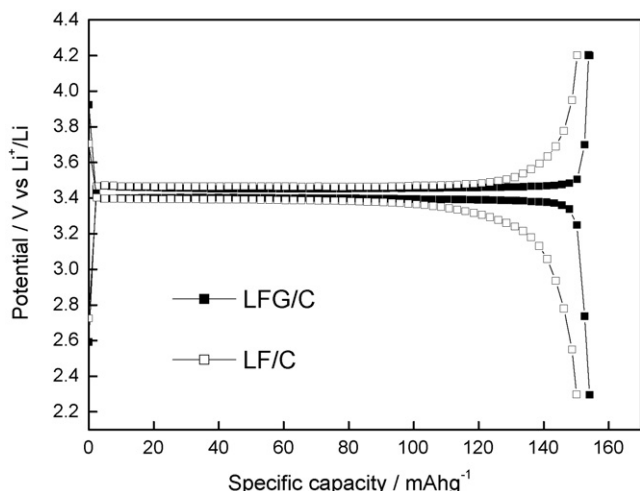


Fig. 5. Charge and discharge curves of the LiFePO_4 samples: (a) LFG/C and (b) LF/C. The charge and discharge measurements were carried out at 0.2 C rate. Current density = 15 mA g^{-1} .

can be interpreted as follows: in relation to the insulating particles coated with conducting phase, the parameter of bulk conductivity cannot represent the actual electronic conductivity of individual grains. Under the test conditions, the conducting phase among the uneven coating grains is more likely to form a circuit. As shown in Fig. 3, the carbon distribution of sample LF/C is not as uniform as that of LFG/C, thus leading to the increase of bulk conductivity when carbon content is less than 5 wt%. As for the sample LFG/C, the breakage of the thinner carbon film at the interface of the particles under the test pressure may lead to the decrease of bulk conductivity. Therefore, the enhancement of individual insulating grain's conductivity depends more on the distribution uniformity of conducting phase than on its total amount in the sample. The above conclusions can be verified by the electrochemical results of the samples.

The electrochemical performance of the samples LFG/C and LF/C are shown in Figs. 5 and 6. Both the bulk conductivity of LFG/C and that of LF/C are $10^{-1} \text{ S cm}^{-1}$. The carbon contents of LFG/C and LF/C are 4.94 wt% and 5.04 wt%, respectively. The cycling curves in Fig. 6 indicate the superior performance of LFG/C in specific discharge capacity, especially the high-rate capability compared with

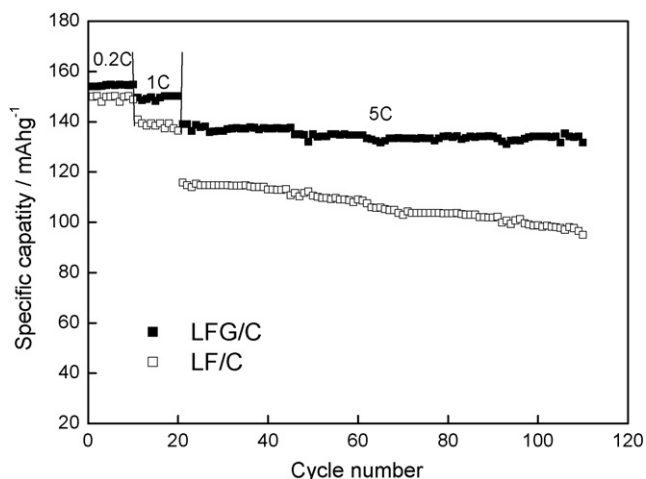


Fig. 6. Cycling performance of LFG/C and LF/C at various C rates (from 0.2 C to 5 C).

LF/C. The discharge capacity of LFG/C is 154 mAh g^{-1} at 0.2 C rate, which is 90% of the theoretical value and slightly greater than that of LF/C. From Fig. 5, it can be seen that sample LFG/C shows a steep potential decay at the end of the discharge step. With similar particle size, morphology, and comparable carbon content, the better rate capability of LFG/C, compared with that of LF/C, can be attributed to the increase of conductivity of the well carbon-coated grains.

Fig. 6 shows the cycling behaviors of the samples LFG/C and LF/C at room temperature at the rates of 0.2 C, 1 C and 5 C. The electrode was charged up to 4.2 V at 0.2 C, 1 C, 1 C rate and discharged at 0.2 C, 1 C, 5 C rate, respectively. The sample LFG/C shows a high-rate capability. From 0.2 C to 5 C, the capacity loss of LFG/C is about 14%, while that of LF/C is 36%. The sample LFG/C shows a capacity retention rate close to 100% (vs. the first-cycle corresponding C-rate capacity) over 90 cycles at 5 C.

The experimental results show that the addition of glucose in the hydrothermal process significantly improves the electrochemical performance of LiFePO_4 mainly due to the increase of conductivity of individual grains, rather than the bulk conductivity of the powders. During the synthesis process, glucose is changed to caramel, which is composed of more than one hundred organic compounds containing a lot of cyclocompounds with high viscosity. It can be in situ adhered to the surface of particles. The calcination stage results in the pyrolysis of the organic species and the formation of nanoscale carbon film on the surface of particles, leading to the enhancement of conductivity of the individual grains, which is believed to be favorable to the permeation of the electrolyte and transfer of Li ions. All of these are helpful to overcome the problem of poor ionic conductivity.

4. Conclusion

Well-crystalline LiFePO_4 particles were successfully synthesized through hydrothermal reaction in glucose solution. At ambient temperature ($25 \pm 2^\circ \text{C}$), LiFePO_4/C exhibits the discharge capacities of 154 mAh g^{-1} at 0.2 C and 136 mAh g^{-1} at 5 C rate, and the cycling capacity retention rate could reach 98% over 90 cycles. The excellent electrochemical performance can be correlated with the in situ formation of carbon precursor/carbon, which leads to the even distribution of carbon and the enhancement of conductivity of individual grains.

References

- [1] A.S. Andersson, J.O. Thomas, *J. Power Sources* 97–98 (2001) 498.
- [2] Z. Chen, J.R. Dahn, *J. Electrochem. Soc.* 149 (2002) A1184.
- [3] F. Crose, A.D. Epifanio, J. Hassoun, A. Deptula, T. Olczac, B. Scrosati, *Electrochem. Solid-State Lett.* 5 (3) (2002) A47.
- [4] Z. Chen, J.R. Dahn, *J. Electrochem. Soc.* 149 (9) (2002) A1184.
- [5] S. Shi, L. Liu, C. Ouyang, D.S. Wang, Z. Wang, L. Chen, X. Huang, *Phys. Rev. B* 68 (2003) 195108.
- [6] D. Wang, H. Li, S. Shi, X. Huang, L. Chen, *Electrochem. Acta* 50 (2005) 2955.
- [7] G.X. Wang, S.L. Bewlay, K. Konstantinov, H.K. Liu, S.X. Dou, J.-H. Ahn, *Electrochem. Acta* 50 (2004) 443.
- [8] M.R. Yang, W.H. Ke, S.H. Wu, *J. Power Sources* 165 (2007) 646.
- [9] S. Franger, C. Benoit, C. Bourbon, F. Le Cras, *J. Phys. Chem. Solids* 67 (2006) 1338.
- [10] P.S. Herle, B. Ellis, N. Coombs, L.F. Nazar, *Nat. Mater.* 3 (2004) 147.
- [11] C. Delacourt, C. Wurm, L. Laffont, J.B. Leriche, C. Masquelier, *Solid State Ionics* 177 (2006) 333.
- [12] H.S. Kim, B.W. Cho, W.I. Cho, *J. Power Sources* 132 (2004) 235.
- [13] M.R. Yang, W.H. Ke, S.H. Wu, *J. Power Sources* 146 (2005) 539.
- [14] S.H. Wu, K.M. Hsiao, W.R. Liu, *J. Power Sources* 146 (2005) 550.
- [15] G. Arnold, J. Garche, R. Hemmer, S. Strobele, C. Vogler, M. Wohlfahrt-Mehrens, *J. Power Sources* 119–121 (2003) 247.
- [16] T.H. Cho, H.T. Chung, *J. Power Sources* 133 (2004) 272.
- [17] S. Franger, F. Le Cras, C. Bourbon, H. Rouault, *J. Power Sources* 119–121 (2003) 252.

- [18] S. Tajimi, Y. Ikeda, K. Uematsu, K. Toda, M. Sato, *Solid State Ionics* 175 (2004) 287.
- [19] J. Lee, A.S. Teja, *Mater. Lett.* 60 (2006) 2105.
- [20] K. Dokko, S. Koizumi, K. Shiraishi, K. Kananura, *J. Power Sources* 165 (2007) 656.
- [21] K. Dokko, K. Shiraishi, K. Kanamura, *J. Electrochem. Soc.* 152 (11) (2005) A 2119.
- [22] G. Meligrana, C. Gerbaldi, A. Tuel, S. Bodoardo, N. Penazzi, *J. Power Sources* 160 (2006) 516.
- [23] J. Chen, M.S. Whittingham, *Electrochem. Commun.* 8 (2006) 855.
- [24] J. Lee, A.S. Teja, *J. Supercrit. Fluids* 35 (2005) 83.