



Short communication

Synthesis and electrochemical properties of olivine LiFePO_4 prepared by a carbothermal reduction method

Hui-ping Liu, Zhi-xing Wang*, Xin-hai Li, Hua-jun Guo, Wen-jie Peng, Yun-he Zhang, Qi-yang Hu

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

ARTICLE INFO

Article history:

Received 14 January 2008

Received in revised form 28 February 2008

Accepted 29 February 2008

Available online 8 March 2008

Keywords:

Lithium ion battery

Lithium iron phosphate

Fe_2O_3

Carbothermal reduction

ABSTRACT

LiFePO_4/C composite cathode material was prepared by carbothermal reduction method, which uses $\text{NH}_4\text{H}_2\text{PO}_4$, Li_2CO_3 and cheap Fe_2O_3 as starting materials, acetylene black and glucose as carbon sources. The precursor of LiFePO_4/C was characterized by differential thermal analysis and thermogravimetry. X-ray diffraction (XRD), scanning electron microscopy (SEM) micrographs showed that the LiFePO_4/C is olivine-type phase, and the addition of the carbon reduced the LiFePO_4 grain size. The carbon is dispersed between the grains, ensuring a good electronic contact. The products sintered at 700°C for 8 h with glucose as carbon source possessed excellent electrochemical performance. The synthesized LiFePO_4 composites showed a high electrochemical capacity of 159.3 mAh g^{-1} at 0.1 C rate, and the capacity fading is only 2.2% after 30 cycles.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Lithium iron phosphate is a promising cathode material candidate for lithium rechargeable batteries. This material has many advantages compared with conventional cathode materials such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 . Among the several cathode materials, olivine-type LiFePO_4 proposed by Goodenough and co-workers [1] has a suitable theoretical capacity of 170 mAh g^{-1} , a flat discharge potential of 3.4 V (vs. Li^+/Li), and excellent thermal stability.

However, some problems that are concerned with the inherent low electronic conductivity and ionic diffusion coefficient are remaining to be solved. Recently, much effort has been devoted to improving the electronic conductivity of LiFePO_4 by means of coating of the particles with conductive carbon [2,3,4] dispersing metal powders of copper or silver powders [5,6], doping [7] and synthesizing small particles with high purity [8]. Some new methods have also been developed to prepare LiFePO_4 , such as spray pyrolysis method [2], mechanical activation process [9,10], microwave synthesis [11], hydrothermal method [12], emulsion drying approach [13,14], sol-gel method [15], co-precipitation technique [16,17], carbothermal reduction method [18], vacuum firing and water quenching technique [19]. The electrochemical properties of LiFePO_4 powder have achieved high specific capacity, which were prepared by the above approaches or by conventional

iron oxalate decomposition method. However, expensive raw material of iron oxalate limits the practical application of LiFePO_4 .

From the above reviews, in order to obtain a well-crystallized LiFePO_4 with relatively small particle size, cut down the cost, simplify the synthesis technology and enhance the specific capacity of the material, we introduced a carbothermal reduction method to synthesize LiFePO_4 by using ferric oxide as raw materials, and glucose as conductive additive and reducing agent.

2. Experimental

Carbon-containing LiFePO_4 was synthesized by adding carbon black or glucose through the following procedure: (1) Li_2CO_3 (99.9%), Fe_2O_3 (AR), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.5%) and reducing agent (carbon black or glucose) were mixed in a stoichiometric ratio. (2) Then the precursor was grinded by ball milling for 4 h. Liquid medium of ethyl alcohol was employed. (3) It was dried in oven at 80°C for 12 h in the air. (4) The mixture was transferred to a temperature-controlled tube furnace equipped with flowing argon and heated at 300°C for 2 h, then heated at 700°C and held for 8 h. The product was removed from the furnace after cooling.

Thermogravimetric (TG) analysis of the precursor was measured on a SDT Q600 TG-DTA apparatus at the temperature between 25 and 900°C with a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen flow. The morphologies of powders were observed by scanning electronic microscope (SEM, JSM-5600LV, JOAL Company). The structures of the as-prepared materials were characterized by X-ray powder diffraction (XRD, RINT-2500V, Rigaku Co.) using $\text{Cu-K}\alpha$ radiation in the range of $10\text{--}90^\circ$ with a scanning rate of 2° min^{-1} .

* Corresponding author. Tel.: +86 731 8836633; fax: +86 731 8836633.
E-mail address: zxwang@mail.csu.edu.cn (Z.-x. Wang).

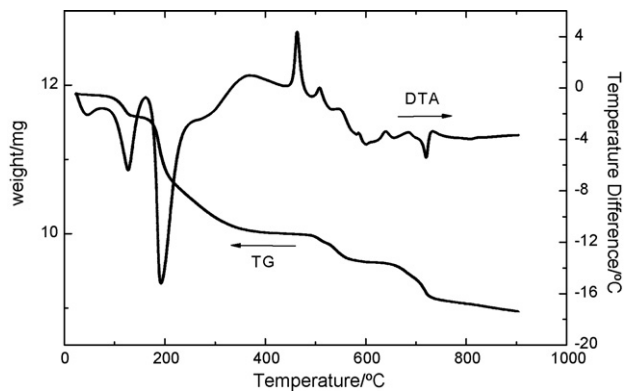


Fig. 1. TG and DTA profiles for precursor of LiFePO_4/C using acetylene black as carbon sources in argon atmosphere.

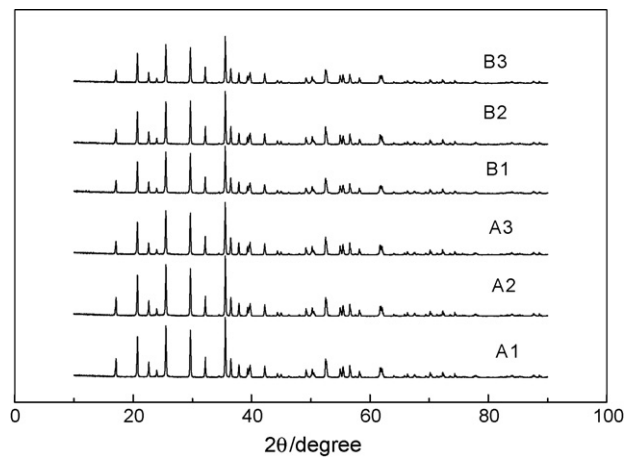


Fig. 2. XRD patterns of the LiFePO_4/C composite (Ax: carbon black, A1:3.46%, A2:4.74%, A3:10.80%, Bx: glucose, B1:3.10%, B2:4.80%, B3:10.10%).

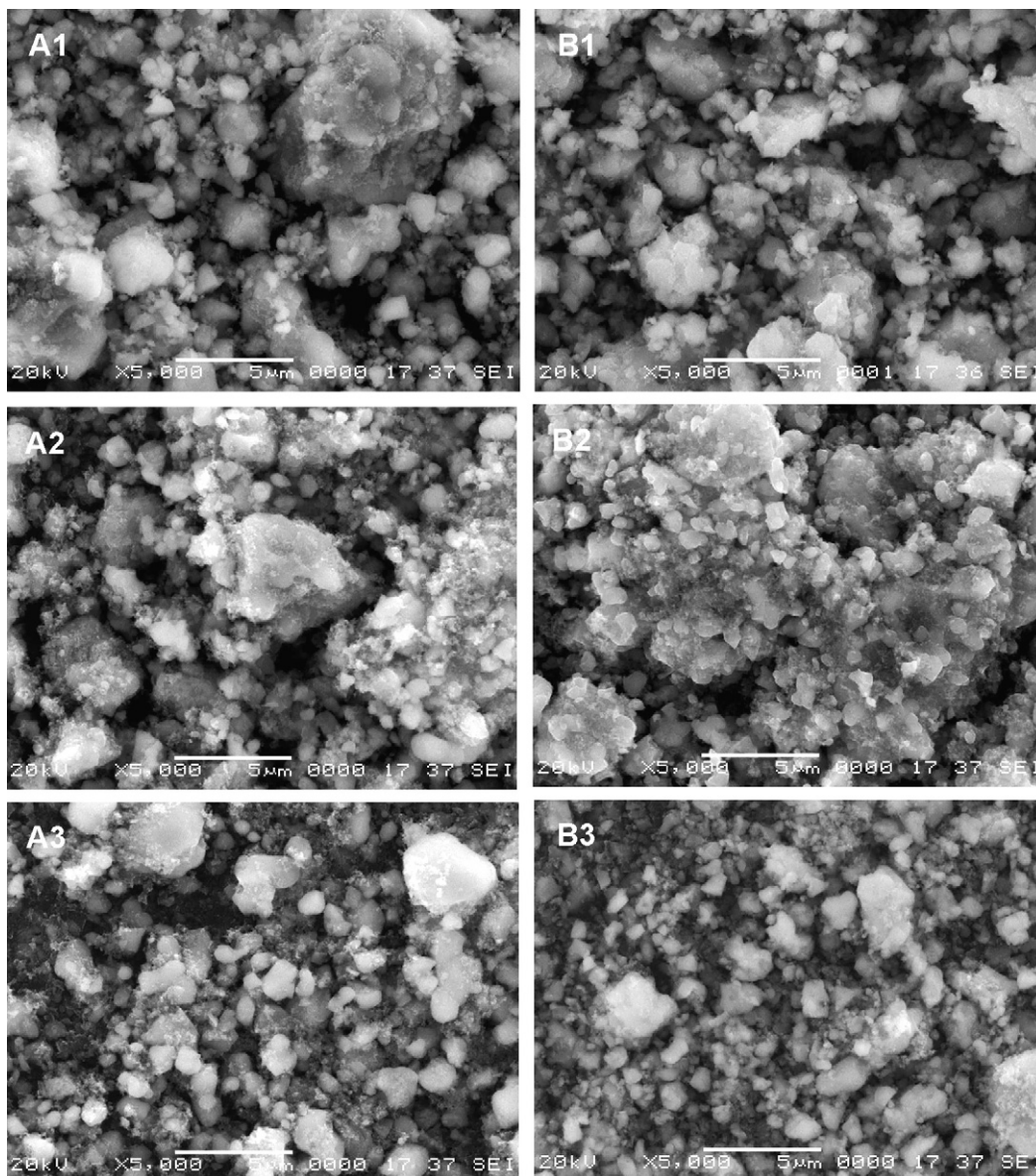


Fig. 3. SEM photographs of LiFePO_4/C composite (Ax: carbon black, A1: 3.46%, A2: 4.74%, A3: 10.80%, Bx: glucose, B1: 3.10%, B2: 4.80%, B3: 10.10%).

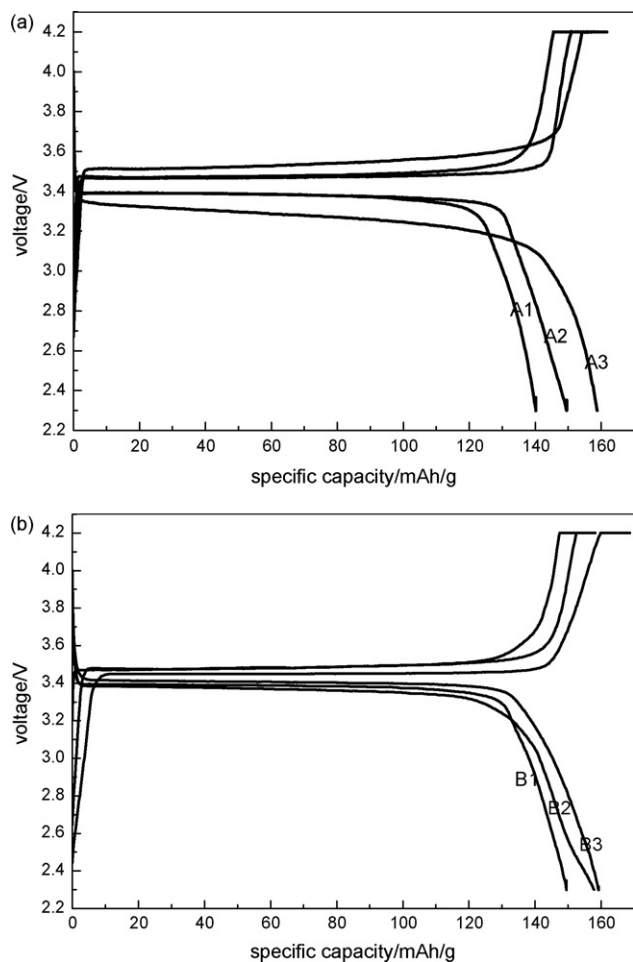


Fig. 4. (a) The charge–discharge profiles of the LiFePO₄/C composite (A1, A2, A3) at 0.1 C (Ax: carbon black, A1: 3.46%, A2: 4.74%, A3: 10.80%), (b). The charge–discharge profiles of the LiFePO₄/C composite (B1, B2, B3) at 0.1 C (Bx: glucose, B1: 3.10%, B2: 4.80%, B3: 10.10%).

Electrochemical performance of LiFePO₄ was characterized using CR2025 coin-type cell. The as-prepared powder was blended with acetylene and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1, following the mixing with *N*-methylpyrrolidinone (NMP) to form slurry. The slurry was then pasted onto an Al foil and the solvent was evaporated at 120 °C for 12 h under vacuum. A disk cut from Al foil pasted with LiFePO₄ was used as the tested electrode. The electrolyte was 1 mol L⁻¹ LiPF₆ dissolved in ethyl carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (volume ratio 1:1:1). The coin cell was composed of LiFePO₄ as the cathode, lithium metal as the anode and a microporous polypropylene sheet (Celgard2400, Celgard Inc., USA) as the separator. The cells were charged and discharged between 4.2 and 2.3 V at room temperature and 0.1 C rate with a charge/discharge apparatus (BTS-51, Neware, China).

3. Results and discussion

The carbon-containing LiFePO₄ was synthesized by a carbothermal reduction reaction with a two-step process. The process was assumed to be carried out according to the following steps:

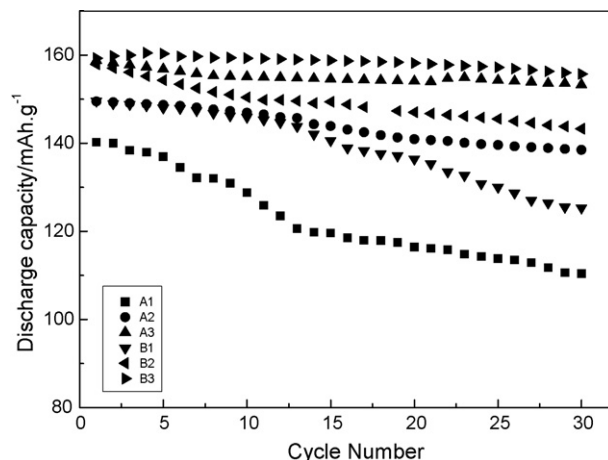
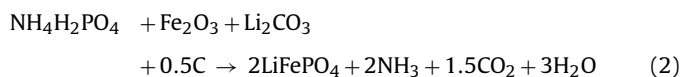
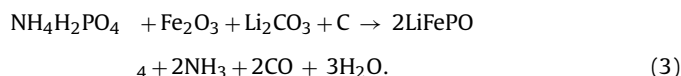


Fig. 5. Cycle performance of the samples at room temperature (Ax: carbon black, A1: 3.46%, A2: 4.74%, A3: 10.80%, Bx: glucose, B1: 3.10%, B2: 4.80%, B3: 10.10%).

or



The TG and DTA plots for stoichiometric mixtures of the powders by ball milling are shown in Fig. 1. It shows that there are various stages of weight loss. In the range of 60–136 °C, an initial weight loss of 2.55% and an endothermic peak are observed. This corresponds to volatilization of volatile such as water or ethyl alcohol. As the temperature increases to 192 °C, a second strong endothermic peak and the weight loss of 12.99% appear in the DTA and the TG plots, respectively. It seems that NH₄H₂PO₄ is decomposed into ammonia (NH₃) and phosphoric acid (shown as Eq. (1)). As the temperature increases to 464–550 °C, the TG shows a weight loss of 3.34% and the DTA plot exhibits several exothermic peaks. This indicates that the Fe₂O₃ is reduced to bivalent iron. In the range of 580–723 °C, the weight loss appears again in the TG plot, and an apparent endothermic peak appears at 720 °C, which corresponds to the decomposition of Li₂CO₃ (Li₂CO₃ → Li₂O + CO₂) and formation of LiFePO₄. A continuous weight loss is detected up to 900 °C in the TG plot.

In this work, the effect of different carbon sources and carbon contents on LiFePO₄ was investigated. The nominal carbon contents and the actual carbon contents with acetylene black and glucose as carbon source are listed in Table 1.

Fig. 2 shows the X-ray diffraction pattern for the as-prepared LiFePO₄. Each sample with different carbon sources and carbon contents reveals a single-phase of LiFePO₄ with olivine structure (space group: Pnma). XRD results demonstrate that this method is suitable to produce pure LiFePO₄. But the intensity of diffraction peak for the carbon-containing LiFePO₄ gradually reduces along with the increase of carbon contents. It indicates that carbon plays an important role in restricting the growth of the particles, as is proved by SEM. The formation of relatively small grains is what we expected. As reported [20,21], the diffusion coefficient of lithium ion for LiFePO₄ (1.8 × 10⁻¹⁴ to 2.2 × 10⁻¹⁶ cm² s⁻¹) is much less than that of commercial product, such as LiMn₂O₄ (4.89 × 10⁻⁹ cm² s⁻¹).

Table 1

The carbon contents of the samples (Ax: carbon black as carbon source, Bx: glucose as carbon source, x=1, 2, 3)

Samples	A1	A2	A3	B1	B2	B3
Nominal carbon content (wt.%)	2	5	10	2	5	10
Actual carbon content (wt.%)	3.46	4.74	10.80	3.10	4.80	10.10

The small particle size is in favor of the insertion/deintercalation of lithium ions, which is also demonstrated by charge/discharge performance.

LiFePO₄ prepared with Fe₂O₃ as iron source at 700 °C for 8 h is expected to have the advantages of energy saving and cost reduction. The fact that LiFePO₄ synthesis using a relatively short time and low temperature was possible also implies that the ball milling could increase the reaction kinetics of the mixture.

Scanning electron micrographs of LiFePO₄ are presented in Fig. 3. It is observed that small particles less than one micrometer are congregated to form secondary particles. We can also distinguish two different particles, the relatively large particles with the size of approximately 300–1000 nm, and the fine intergranular particles with size of about 100–300 nm. Decreasing the carbon contents leads to large particle size of LiFePO₄. The results indicate that the addition of carbon is beneficial to the control of the particle size.

The charge–discharge curves of the LiFePO₄ between 2.3 and 4.2 V at 0.1 C rate are shown in Fig. 4a and b. The charge voltage plateau is around 3.5 V, while the discharge voltage plateau is between 3.3 and 3.4 V for samples with different carbon sources and different carbon contents. It can be found that all of LiFePO₄ show a single charge–discharge plateau. The electrochemical reaction of other iron phosphate [22], such as Li₃Fe₂(PO₄)₃, LiFeP₂O₇, Fe₄(P₂O₇)₃, occurs at potential of 2.8, 2.9 and 3.1 V (vs. Li/Li⁺), respectively. So the as-prepared materials should be pure LiFePO₄. Among the LiFePO₄/C composites, the sample B3 (Fig. 4b) exhibited the highest discharge capacity of 159.3 mAh g⁻¹, about 93.7% of the theoretical capacity of LiFePO₄. As seen in the figures the electrochemical capacity of the LiFePO₄/C composite is apparently affected by the carbon content, and higher carbon content results in a rapid increase of discharge capacity. This phenomenon may be attributed to that LiFePO₄ cannot be fully utilized at lower carbon content due to the low conductivity and larger particle size of the material such as samples A1 and B1 (Fig. 3a and b).

Fig. 5 shows the cycle performance of LiFePO₄/C composite at 0.1 C rate. For samples A1 and B1, the initial discharge capacity decreases rapidly from 140.2 and 149.6 mAh g⁻¹ to 110.4 and 125.3 mAh g⁻¹ at 30th cycle, showing the poorest cycling performance. It may attribute to the formation of cracks and subsequent pulverization of the material because of the volumetric change of the LiFePO₄ particles during Li⁺ insertion/deintercalation cycling [23]. However, samples A3 and B3 show much better cycling ability. The capacity fading of sample B3 with glucose as carbon source is only 2.2% after 30 cycles. This improved cycling stability for the sample with higher carbon content is possibly due to the buffering effect of the coated carbon layer, which buffers the volumetric change of LiFePO₄ during cycling.

4. Conclusion

In order to cut down the cost and simplify the synthesis technology, pure LiFePO₄/C was synthesized by using ferric oxide as iron source. It is demonstrated that olivine structure of the powder is not affected by the introduction of carbon, and the particle size reduced with the increase of carbon amount. The LiFePO₄/C composite shows higher charge/discharge capacity and more stable cycle ability as the carbon content increases. LiFePO₄/C synthesized at optimized carbon amount with glucose as carbon source delivers a capacity of 159.3 mAh g⁻¹, and the capacity fading is only 2.2% after 30 cycles.

Acknowledgement

The project was sponsored by National Basic Research Program of China (973 Program, 2007CB613607).

References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (4) (1997) 1188–1194.
- [2] Y.S.L. Bewla, K. Konstantinov, G.X. Wang, et al., *Mater. Lett.* 58 (2004) 1788–1792.
- [3] S.F. Yang, G.Y. Son, I.J.P.Y. Zaval, et al., *Electrochem. Commun.* 4 (2002) 239–244.
- [4] B.L. Cushing, J.B. Goodenough, *Solid State Sci.* 4 (11–12) (2002) 1487–1493.
- [5] K.S. Park, J.T. Son, H.T. Chung, *Solid State Commun.* 129 (2004) 311–314.
- [6] F. Croce, A.D. Epifanio, J. Hassoun, *Electrochem. Solid State Lett.* 5 (3) (2002) A47–A50.
- [7] G.X. Wang, Y.S. Bewla, J. Yao, et al., *Electrochem. Solid State Lett.* 7 (12) (2004) A503–A506.
- [8] A. Yamada, S.C. Chung, K. Hinokuma, *J. Electrochem. Soc.* 148 (3) (2001) A224–A229.
- [9] A. Yamada, S.C. Chung, *J. Electrochem. Soc.* 148 (8) (2001) A960–A967.
- [10] M. Takahashi, S. Tobishina, K. Takeik, et al., *J. Power Sources* 97–98 (2001) 508–511.
- [11] M. Higuchi, K. Katayama, Y. Azuma, et al., *J. Power Sources* 119–121 (2003) 258–261.
- [12] S.F. Yang, I.J.P.Y. Zaval, M.S. Whittingham, et al., *Electrochem. Commun.* 3 (2001) 505–508.
- [13] E.M. Bauere, C. Belitto, I.M. Pasupual, et al., *Electrochem. Solid State Lett.* 7 (4) (2004) A85–A87.
- [14] G.S.T. Myun, S. Komaba, N. Hirotsaki, et al., *Electrochem. Acta* 49 (2004) 4213–4222.
- [15] J. Yang, J.J. Xu, *Electrochem. Solid State Lett.* 7 (12) (2004) A515–A518.
- [16] G. Arnold, J. Garche, R. Hemmer, et al., *J. Power Sources* 119–121 (2003) 247–251.
- [17] B.Q. Zhu, X.H. Li, Z.X. Wang, H.J. Guo, *Mater. Chem. Phys.* 98 (2006) 373–376.
- [18] J. Barker, M.Y. Saidi, J.L. Swoyer, *Electrochem. Solid State Lett.* 6 (3) (2003) A53–A55.
- [19] X.G. Gao, G.R. Hu, Z.D. Peng, K. Du, X.R. Deng, *Chin. Chem. Lett.* 18 (2007) 1256–1260.
- [20] P.P. Prosini, M. Lisi, D. Zane, M. Pasquali, *J. Solid State Ionics* 148 (2002) 45–51.
- [21] Y.Y. Xia, H. Takeshige, H. Noguchi, et al., *J. Power Sources* 56 (1) (1995) 61–67.
- [22] A.K. Padhi, K.S. Nanjundaswamy, C. Maspuelier, et al., *J. Electrochem. Soc.* 144 (5) (1997) 1609–1613.
- [23] D. Wang, X.D. Wu, Z.X. Wang, L.Q. Chen, *J. Power Sources* 140 (2005) 125–128.