



Short communication

Syntheses, characterizations and electrochemical properties of spherical-like LiFePO_4 by hydrothermal method

Zhongli Wang, Shaorui Su, Chunyang Yu, Yu Chen, Dingguo Xia*

College of Environmental and Energy Engineering, Beijing University of Technology, Pingleyuan 100, Chaoyang District, Beijing 100022, China

ARTICLE INFO

Article history:

Received 7 January 2008
 Received in revised form 7 April 2008
 Accepted 22 April 2008
 Available online 4 May 2008

Keywords:

LiFePO_4
 Hydrothermal
 Complexing-agent
 XPS
 Mössbauer spectra

ABSTRACT

Spherical-like LiFePO_4 was synthesized by hydrothermal synthesis method using Phenanthroline as a complexing-agent to avoid the Fe(II) ions from oxidation and control the growth of the crystal. Structural, electron valence state, morphology and particle size were investigated by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), Mössbauer spectra, scanning electron microscopy (SEM) and laser particle sizer. Charge–discharge cycling performances were used to characterize its electrochemical properties. The sample possesses uniformly distributed spherical-like particles with an average size of 0.5–1 μm . Test shows that the reversible capacity of spherical-like LiFePO_4 is about 140 mAh g^{-1} at 0.1 C. The capacity fading is neglectable.

© 2008 Published by Elsevier B.V.

1. Introduction

Lithium iron phosphate has become of great interest as a cathode for rechargeable lithium ion batteries in terms of its high theoretical capacity of 170 mAh g^{-1} , low cost, and environmental benignancy and safety [1–3]. Olivine-type LiFePO_4 has an orthorhombic unit cell, which accommodates four units of LiFePO_4 . In phosphor-olivine, all of the oxygen ions form strong covalent bonds with P^{5+} to form the PO_4^{3-} tetrahedral polyanion and stabilize the entire three-dimensional framework. This guarantees stable operation at higher temperatures and extreme safety under abusive conditions which adds greatly to the attractiveness of the olive-type cathode [4]. But the stable structure induces the decreasing of conductivity of LiFePO_4 , which is a disadvantage for the transferring of lithium ions. At this time, the main obstacle for reaching a perfect performance of LiFePO_4 at ambient temperature is its very low electronic conductivity and low lithium ions diffusion coefficient. Two possible means to overcome this major problem were recently explored: one is the synthesis of a LiFePO_4 /electronic conductor composite compound; the other is the achievement of a small and homogeneous particle size distribution to shorten the diffusion distance of lithium ions [5].

Hydrothermal synthesis is a better route to synthesize a small and homogeneous particle size distribution LiFePO_4 than solid-state reaction. What's more, hydrothermal synthesis is better at low-energy cost and readily scalable [6]. However, LiFePO_4 powders prepared by hydrothermal method are mostly plank shape, which is disadvantageous for the physical and chemical properties of LiFePO_4 . In this paper, spherical-like LiFePO_4 was synthesized by hydrothermal route using complexing-agents in the conditions of pH 9.5, 300 °C and 0.1 mol L^{-1} of Fe(II). The obtained spherical-like LiFePO_4 exhibits homogeneous microstructure and better electrochemical properties of materials in terms of capacity delivery, cycle life and discharge capability.

2. Experimental

The samples of LiFePO_4 were prepared by hydrothermal method in an autoclaved stainless steel reactor. The starting materials were $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (98% Aldrich), $(\text{NH}_4)_2\text{HPO}_4$ (98% Aldrich), $\text{LiC}_6\text{H}_5\text{O}_7 \cdot 4\text{H}_2\text{O}$ (98% Aldrich) and Phenanthroline (99% Aldrich). In a typical synthesis, the mol ratio of Fe:P is 1:1, and FeSO_4 of 0.3 mol L^{-1} was mixed with Phenanthroline of 0.1 mol L^{-1} . The resulting red solution was transferred into a 200 ml stainless steel autoclave. The pH values of solution was adjusted by dropping different amount of LiOH to be 6.0, 8.5, 9.0, 9.5, respectively, which were labeled as samples 1, 2, 3 and 4. The autoclave was sealed and heated to 240 °C for 2 h. Precipitates were collected by filtration and

* Corresponding author. Tel.: +86 10 67396158; fax: +86 10 67396158.
 E-mail address: dgxia@bjut.edu.cn (D. Xia).

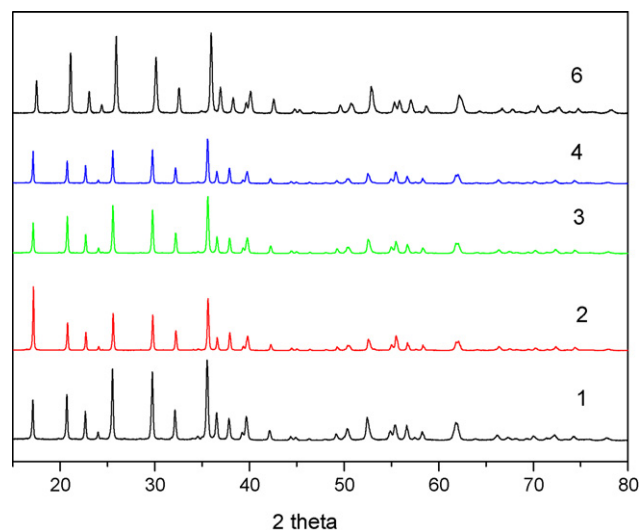


Fig. 1. XRD pattern for LiFePO₄ samples 1, 2, 3, 4 and 6.

Table 1
Results of Rietveld refinement of LiFePO₄ samples 1, 2, 3, 4 and 6

	Sample				
	1	2	3	4	6
pH	6.0	8.5	9.0	9.5	9.5
<i>a</i> (Å)	10.3441	10.3302	10.3304	10.3166	10.3275
<i>b</i> (Å)	5.9988	5.9953	5.9973	5.9912	5.9959
<i>c</i> (Å)	4.7046	4.6960	4.6957	4.6892	4.7001
Vol. (Å ³)	291.9	290.8	290.9	289.8	291.0
<i>R</i> _{wp}	10.34	11.6	11.6	11.09	9.16
<i>R</i> _p	7.85	8.63	7.96	8.19	7.67
<i>R</i> _F	5.93	6.13	4.65	5.47	5.13

Samples 1, 2, 3 and 4, synthesized in the pH value 6.0, 8.5, 9.0 and 9.5 deionized water solvent at 240 °C, and the concentration of all reaction agents is 0.3 mol L⁻¹. Sample 6, synthesized in pH value 9.5 glycol solvent at 300 °C, and the concentration is 0.1 mol L⁻¹.

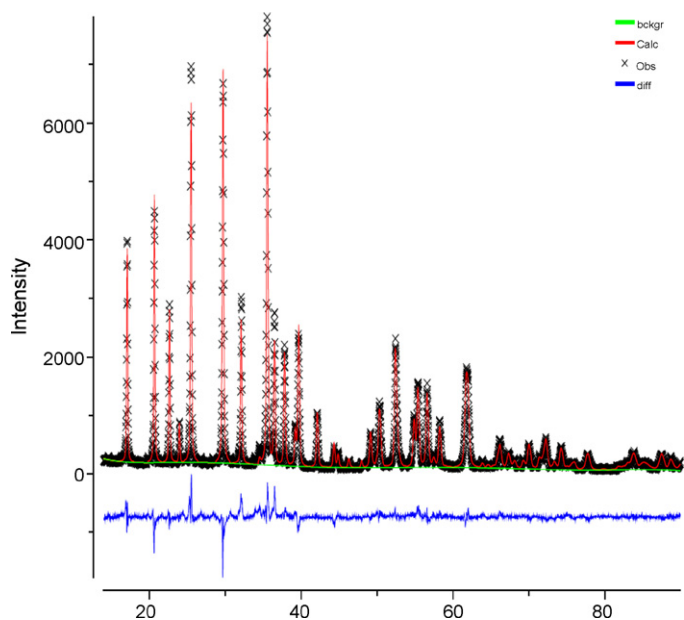


Fig. 2. Rietveld refinement of sample 1.

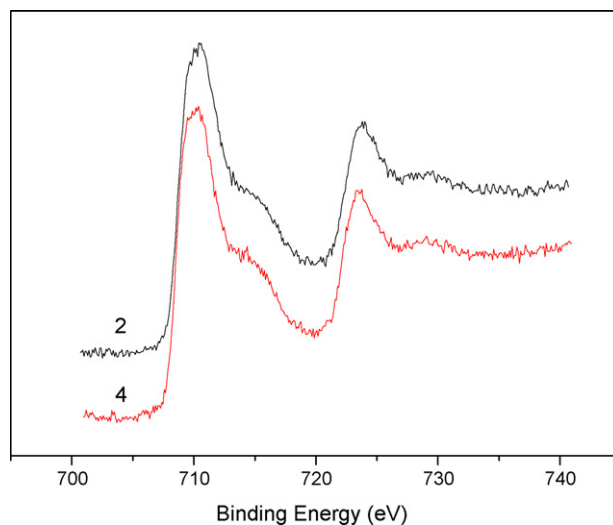


Fig. 3. XPS for LiFePO₄ samples 2 and 4.

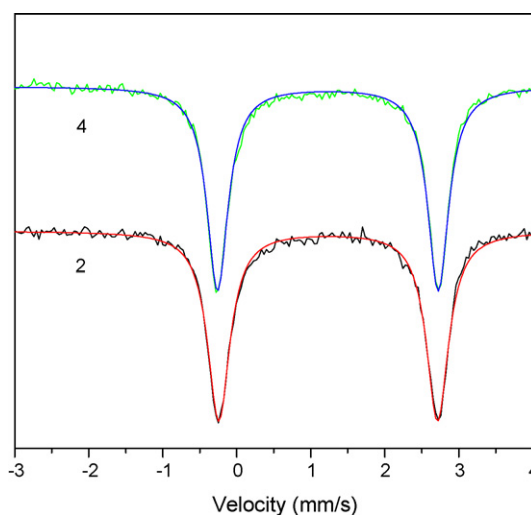


Fig. 4. Mössbauer spectra for samples 2 and 4.

dried at 120 °C for 5 h in the vacuum oven. XRD measurements of the LiFePO₄ materials were carried out using D8 X-ray diffraction (XRD) with Cu K α radiation at room temperature. Particle morphology of the LiFePO₄ powders was observed using a SEM (JEOL, JSM 6400). XPS (AXIS ULTRA DLD) was done to determine the valence of Fe. The cathodes were prepared by pressing a mixture of the active materials acetylene black and binder (PTFE) in a weight ratio of 70/20/10. The Li metal was used as the counter electrodes. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cells were assembled in an argon-filled dry box. The electrochemical properties of the cells were measured at a current of 0.1 C (17 mA g⁻¹), with a charge–discharge voltage limit of 2.0–4.2 V.

Table 2
Particle size, capacity and conductivity of LiFePO₄ samples

	Sample				
	1	2	3	4	6
pH	6.0	8.5	9.0	9.5	9.5
Particle size (<i>D</i> ₅₀) (μm)	10.4	30.2	25.4	16.4	0.5
Capacity (mAh g ⁻¹)	26.7	41.2	64.8	82.3	143.5
Conductivity/logs (S cm ⁻¹)	–10.1		–9.9		–9.6

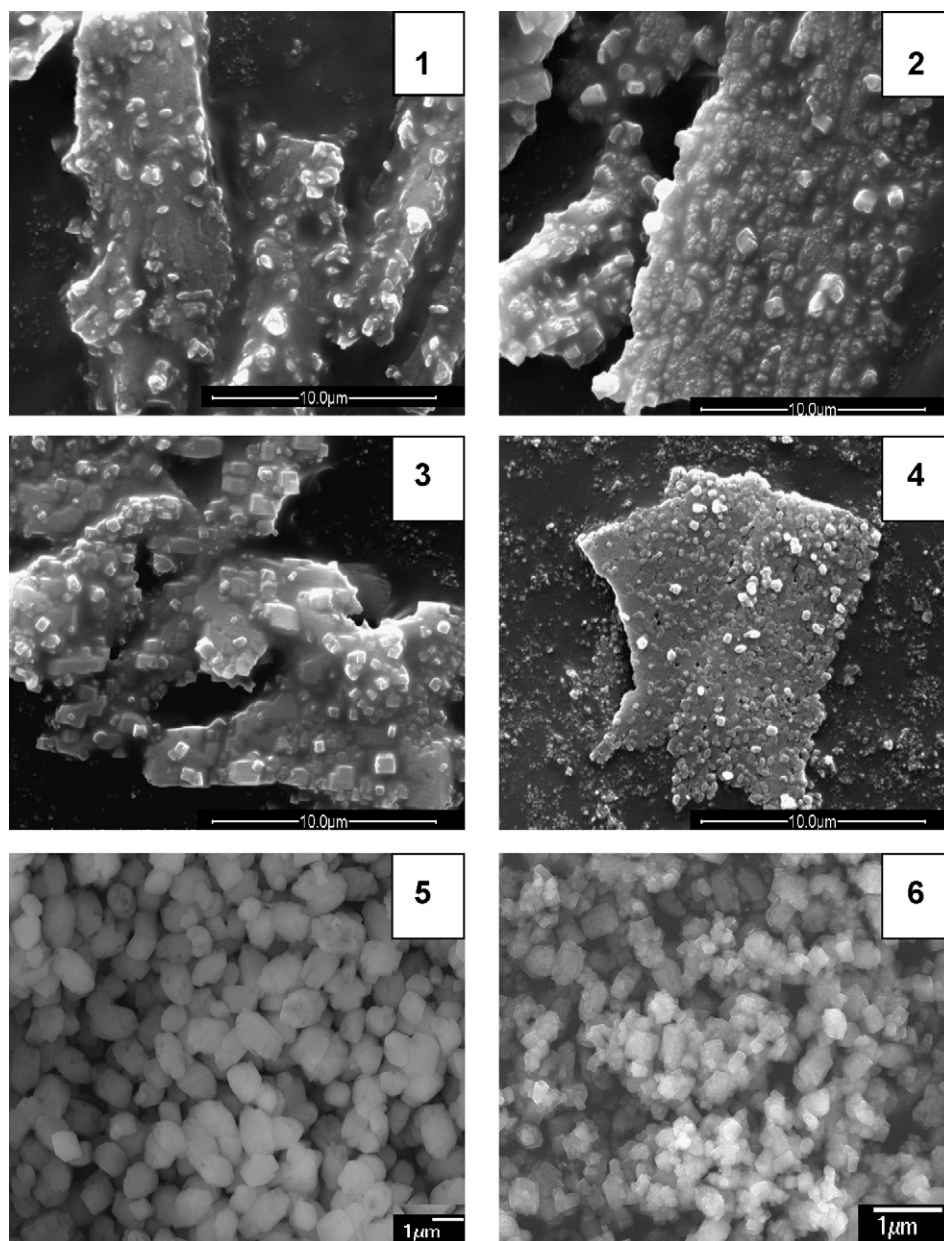


Fig. 5. SEM for LiFePO_4 samples 1, 2, 3, 4, 5 and 6; samples 1, 2, 3 and 4, synthesized in the pH value 6.0, 8.5, 9.0 and 9.5 deionized water solvent at 240°C , and the concentration of all reaction agents is 0.3 mol L^{-1} . Sample 5, synthesized in the pH value 9.5 in the deionized water solvent at 300°C , and the concentration is 0.1 mol L^{-1} . Sample 6, synthesized in pH value 9.5 glycol solvent at 300°C , and the concentration is 0.1 mol L^{-1} .

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of the samples prepared using Phenanthroline as complexing-agent under different pH value by hydrothermal method. The samples preserve a single ordered olivine structure indexed by orthorhombic $Pnma$. No impurity phases are detected in the XRD pattern. Additionally, the peak profiles are quite narrow, indicating a well-crystallized phase. The structural parameters obtained from X-ray Rietveld refinement of the material are listed in Table 1. The reliability factor (R_{wp}) is around 10%, which indicates a good solution. The lattice parameters and atomic coordinates are in agreement with the ones obtained by other authors with other techniques [7]. The cell volumes of LiFePO_4 samples at different pH value are among $291.9\text{--}289.8\text{ \AA}^3$. This is consistent with the previous cell volume reported by other reference [3]. In this work, we found that the cell volumes of these

samples decrease with the increase of pH value. It may be related to a better crystallinity of the sample at higher pH value. The Rietveld refinement pattern of LiFePO_4 sample 1 was shown in Fig. 2. The crystallite size was calculated for $[1\ 3\ 1]$, $[0\ 2\ 1]$ and $[0\ 2\ 0]$ crystallographic directions using the Sherrer's formula, giving a mean value of 48 nm.

XPS spectra of the Fe 2p of samples 2 and 4 are reported in Fig. 3. The Fe 2p signal derives from the contribution of two doublets. The main species can be related to Fe^{2+} at a binding energy (BE) at 710.40, 723.80 eV and 710.37, 723.77 eV for LiFePO_4 [8,9].

Mössbauer measurements provide direct in sight into the content of Fe(III) in LiFePO_4 . The Mössbauer spectra of LiFePO_4 is simple to interpret as two quadrupole-split doublets; one doublet from Fe^{2+} in LiFePO_4 and a second doublet from Fe^{3+} in FePO_4 [10,11]. Fig. 4 shows the Mössbauer spectra of the LiFePO_4 sam-

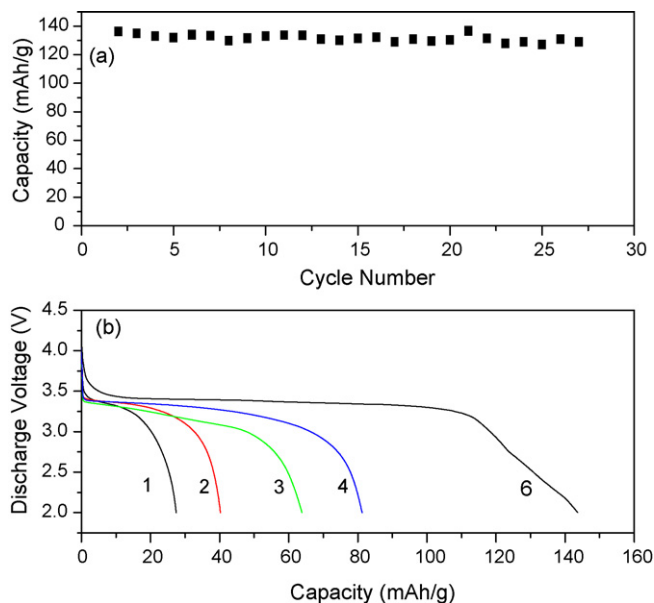


Fig. 6. (a) The cycling test of sample 6; (b) The discharge curves of samples 1, 2, 3, 4, and 6.

ples 2 and 4 taken at room temperature. Fe(II) are characterized by Mössbauer parameters of $CS = 1.2 \text{ mm s}^{-1}$, $QS = 3.0 \text{ mm s}^{-1}$. The analysis indicates the hyperfine parameters characteristic of high-spin ($S = 2$ Fe(II)) ferrous ions, suggesting the reduction of Fe(III) during the preparation. No iron cluster or Fe^{3+} is observed in the spectrum.

SEM images of the LiFePO_4 particles are presented in Fig. 5. There are two types, plank and spherical-like, of the particles. From the results of SEM mapping (not shown here), it is found that Fe is distributed uniformly in the plank and spherical particles. As an example, for 240°C , pH 6.0 and Fe(II) concentration of 0.3 mol L^{-1} , plank of approximately $15\text{--}20 \mu\text{m}$ length and $5\text{--}10 \mu\text{m}$ width can be obtained (Fig. 5(1)). Increasing the pH value to 8.5, 9.0 and 9.5, morphology remains the same (Fig. 5(2–4)). To compare the particle size, D_{50} of LiFePO_4 samples with different pH value were measured by laser particle sizer Winner2000 in deionized water. It can be seen that the particle size D_{50} obviously becomes small with the increase of pH value with the exception of sample 1 (shown in Table 2). Decreasing the Fe(II) concentration to 0.1 mol L^{-1} , the morphology of the particles obtained at 240°C also remains the same, while the temperature increases to 300°C , spherical-like particles of $2\text{--}3 \mu\text{m}$ (sample 5) are obtained (Fig. 5(5)). The spherical-like particles of LiFePO_4 of $0.5\text{--}1 \mu\text{m}$ (sample 6) are synthesized when the deionized water solvent is replaced by glycol (Fig. 5(6)). Compared with sample 5, the particle size of sample 6 decreases. This could be due to the higher viscosity of glycol.

The first cycle charge–discharge curves of LiFePO_4 samples are shown in Fig. 6(b). With the increase of pH value, the specific capacity of LiFePO_4 increases. From Fig. 6, the material with smaller cell volume synthesized at pH 9.5 delivered better capacity of 81 mAh g^{-1} at room temperature. The morphology of sample 5 is fine and uniform, but the electrochemical performance is about 80 mAh g^{-1} (not shown here), not better than that of sample 4 which showed the sheet of morphology. However,

the sample 6 with spherical-like morphology delivers a higher capacity, about 140 mAh g^{-1} , and shows a perfect cycling ability.

To compare the electronic conductivity of LiFePO_4 samples with different particle size, electronic conductivity measurements at room temperature for sample 1, samples 3 and 6 were carried by the two-point dc methods using a Picoammeter/Voltage Source (Keithley 2400). 0.15 g of LiFePO_4 powders were pressed into a slice with a diameter of 13 mm by a pressure of 20 MPa for 1 h . Table 2 shows the electronic conductivity of sample 6 does not increase greatly [12,13] relative to sample 3. The high discharge capacity of sample 6 is mainly due to the smaller particle size which provides a short diffusion distance for lithium ions.

4. Conclusions

Spherical-like LiFePO_4 was prepared by hydrothermal method using Phenanthroline as the complexing-agent to avoid the Fe(II) ions from oxidation and control the growth of the crystal. Morphology of LiFePO_4 synthesized by hydrothermal was mainly dependent on temperature and the concentration. XRD pattern, XPS profile and Mössbauer spectra were applied to characterize the structure, electron state and component of LiFePO_4 synthesized by hydrothermal route in different pH value solution. The decrease of particle size cannot improve the electronic conductivity but can obviously reduce the diffusion distance of lithium ions. Because of the smaller particles forming at higher pH value, the specific capacity of the sample increases with the increase of the pH value, especially, the resulted small spherical-like LiFePO_4 showing a better electrochemical properties. That means that the particle size and morphology plays an important role on the electrochemical performance enhancement.

Acknowledgements

This work was financially supported by the Beijing Natural Science Foundation (Grant No. 207001), Funding Project for Academic Human Resources Development in Institutions of Higher Learning under the Jurisdiction of Beijing Municipality and the National 973 Program of China (Grant No. 2002CB211807).

References

- [1] A.S. Andersson, J.O. Thomas, J. Power Sources 97/98 (2001) 498–502.
- [2] S. Yang, Y. Song, P.Y. Zavalij, M.S. Whittingham, Electrochem. Commun. 4 (2002) 239.
- [3] J.J. Chen, M.S. Whittingham, Electrochem. Commun. 8 (2006) 855–858.
- [4] C.Y. Ouyang, S.Q. Shi, Z.X. Wang, X.J. Huang, L.Q. Chen, Phys. Rev. B 69 (2004) 104303.
- [5] A. Yamada, M. Hosoya, S.-C. Chung, Y. Kudo, K. Hinokuma, K.-Y. Liu, Y. Nishi, J. Power Sources 119–121 (2003) 232–238.
- [6] S. Franger, F.L. Cras, C. Bourbon, H.L. Rouault, J. Power Sources 119–121 (2003) 252–257.
- [7] A.S. Andersson, B. Kalska, L. Haggstrom, J.O. Thomas, Solid State Ionics 130 (2000) 41.
- [8] X. Huang, J.F. Ma, P.W. Wu, Y.M. Hu, J.H. Dai, Z.B. Zhu, H.F. Wang, Mater. Lett. 59 (2005) 578–582.
- [9] C.V. Ramana, A. Ait-Salanh, S. Utsunomiya, J. Phys. Chem. C 111 (2007) 1049–1054.
- [10] B. Ellis, L.K. Perry, D.H. Ryan, L.F. Nazar, J. Am. Chem. Soc. 128 (2006) 11416–11422.
- [11] J.L. Dodd, I. Halevy, B. Fultz, J. Phys. Chem. C 111 (4) (2007) 1563–1566.
- [12] S.-Y. Chung, J.T. Bloking, Y.-M. Chiang, Nat. Mater. 1 (2002) 123.
- [13] D.-K. Kim, H.-M. Park, S.-J. Jung, Y.U. Jeong, J.-H. Lee, J.-J. Kim, J. Power Sources 159 (2006) 237–240.