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A facile method to prepare hybrid $LiNi_{0.5}Mn_{1.5}O_4$/C with enhanced rate performance

Naiqing Zhang[a,b,*], Tongyong Yang[c], Ye Lang[c], Kening Sun[a,b,*]

[a] Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150001, PR China
[b] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China
[c] Department of Chemistry, Harbin Institute of Technology, Harbin 150001, PR China

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ABSTRACT

The hybrid $LiNi_{0.5}Mn_{1.5}O_4$/C cathode material is prepared with a facile method of pre-mixing and post-calcination treatment for enhancing the rate performance. The physical and electrochemical properties are discussed through X-ray diffraction (XRD), transmission electron microscopy (TEM), charge–discharge measurements in test cells and electrochemical impedance spectroscopy (EIS). The results show that the $LiNi_{0.5}Mn_{1.5}O_4$ particle can be partially surrounded and interconnected with each other by carbon black particles, therefore the electronic conductivity can be remarkably improved by over 5 times without degrading the spinel structure. The $LiNi_{0.5}Mn_{1.5}O_4$/C composite exhibits enhanced rate capability together with cycling performance compared to $LiNi_{0.5}Mn_{1.5}O_4$. EIS confirms that the significantly improved electrochemical property is due to the suppression of surface resistance and the enhanced electronic conductivity.

1. Introduction

Lithium ion batteries which are regarded as an available power source for meeting the ever increasing energy requirements and relieving the environmental pollution, have been commercially used in high power density devices such as electric vehicle (EV) or hybrid electric vehicle (HEV) [1–3]. The spinel $LiNi_{0.5}Mn_{1.5}O_4$ has been extensively studied as a promising cathode material for lithium ion battery due to its high capacity and distinctive high discharge potential (4.7 V vs. Li) [4,5]. The impressively high voltage can supply the battery with an extended working potential and hence a larger energy density. However, for EV or HEV application, the rate performance of $LiNi_{0.5}Mn_{1.5}O_4$ should be especially taken into consideration. Some efforts have been devoted to enhance the rate performance of $LiNi_{0.5}Mn_{1.5}O_4$ in the literatures. Liu et al. [6] and Katiyar et al. [7] centered their attention on chemical doping. The partial replacement of Ni^{2+} ions with Cr^{3+} ions could maintain the spinel structure, which led to the high capacities of 95 and 100 mAh g^{-1} at 5 and 1*C*, respectively. Similarly, Lafont et al. [8] substituted trace Mg^{2+} ions for Ni^{2+} sites in $LiNi_{0.5}Mn_{1.5}O_4$ for better rate behavior by increasing the electronic conductivity, and a high capacity of 90 mAh g^{-1} at 5*C* was obtained. Different from the doping strategy, Kunduraci and Amatucci [9] synthesized nano-$LiNi_{0.5}Mn_{1.5}O_4$ spinels at different preparation conditions and investigated the relationship between the electronic conductivity and the rate behavior. Based on the nanostructure which favored the Li^+ diffusion, the authors proved that the high electronic conductivity contributed to the excellent rate performance. It is reasonable because the cathode in lithium ion batteries is based on insertion reactions, in which lithium ions are accommodated into an open host structure with electron addition and followed by an extraction with electron removal during the cycling processes. Therefore, the electronic conductivity plays a significant role in rate property no matter which approach is adopted.

The conductive carbon is characterized by its fast electronic transport, which facilitates the intrinsically insulated electrode material to exhibit an improved high-rate performance, such as $LiFePO_4$ [10,11]. Following this idea, recently we successfully developed a facile method to fabricate the hybrid $LiNi_{0.5}Mn_{1.5}O_4$/C cathode material by partially surrounding the $LiNi_{0.5}Mn_{1.5}O_4$ with carbon black. This fabrication includes two procedures: the pre-mixing and the post-calcination. To our knowledge, there is no report on the enhancement in the rate performance of $LiNi_{0.5}Mn_{1.5}O_4$ via this technology, and it is of significance because a remarkable improvement in rate capability has gained. In this study, the $LiNi_{0.5}Mn_{1.5}O_4$/C composite was constructed and

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* Corresponding authors at: Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150001, PR China; State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China. Tel.: +86 451 8641 2153; fax: +86 451 8641 2153.
E-mail addresses: znqmww@163.com (N. Zhang), keningsun@yahoo.com.cn (K. Sun).

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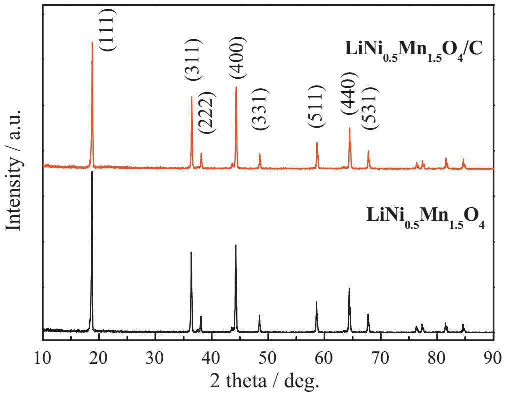

Fig. 1. XRD patterns of the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$/C powders.

characterized through the physical and electrochemical measurements.

2. Experimental

2.1. Synthesis procedure

The $LiNi_{0.5}Mn_{1.5}O_4$ powder was synthesized by sol–gel method as reported before [12]. All chemical reagents used in this study were A.R. grade. In brief, stoichiometric $LiOH{\cdot}H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, and $Mn(CH_3COO)_2{\cdot}4H_2O$ were successively dissolved in a continuously stirred aqueous solution of citric acid. After adjusting the pH of solution to 7.0 using ammonium hydroxide, the solution was evaporated at 75 °C until obtaining a wet gel. The as-prepared gel was dried at 90 °C under a vacuum atmosphere for overnight, and then pre-sintered at 450 °C for 5 h in air. Thereafter, the obtained powder was calcined at 850 °C for 6 h. For preparing the $LiNi_{0.5}Mn_{1.5}O_4$/C composite, the gelatin (1 g) was firstly dissolved in distilled water (100 ml) by stirring at 50 °C for 2 h, and then the carbon black (0.01 g) and the as-prepared $LiNi_{0.5}Mn_{1.5}O_4$ powder (1 g) were added. After ultrasonic treatment for 15 min, the obtained mixture was stirred at 50 °C for 1 h. Finally, the $LiNi_{0.5}Mn_{1.5}O_4$/C was obtained by filtering and drying the mixture at 300 °C for 3 h.

2.2. Physical characterization

The crystal structure of materials was identified by XRD (Rigaku D/max-γB) using monochromated Cu Ka radiation (45 kV, 50 mA). The particle morphology of $LiNi_{0.5}Mn_{1.5}O_4$/C was observed using TEM (Hitachi, 7650). The electronic conductivity of the prepared samples was measured by a four-point probe method and combined with a Keithley 2400 source meter.

2.3. Electrochemical test

The cathode film was prepared by mixing active cathode material ($LiNi_{0.5}Mn_{1.5}O_4$/C or $LiNi_{0.5}Mn_{1.5}O_4$), carbon black and polyvinylidene fluoride with a weight ratio of 8:1:1 in N-methyl pyrrolidinone. The slurry was coated onto an aluminum foil using doctor blade technique. CR2025 test cells used for electrochemical measurements were assembled in a glove box (MBraun, 200B). The cell consisted of a cathode and a lithium metal anode separated by two porous polypropylene films. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate and dimethyl carbonate solution (EC:DMC = 1:1, volume). The charge–discharge measurement was carried out galvanostatically at the desired current density (1*C* corresponding to 148 mA g^{-1}) in the range between 3.0 and 4.95 V at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed using an advanced electrochemical system (Parstat 2273). The amplitude of the a.c. signal was 10 mV over the frequency range between 1 MHz and 9 mHz. The spectra were analyzed by Z-view software. Before EIS measurements, all samples were charged to the same voltage of 4.75 V. The Li foil served as both the counter and reference electrodes during EIS measurements. Every electrochemical measurement was carried out with more than two cells, only the reliable data were compared in this study.

3. Results and discussion

3.1. Structural and morphological characterizations

The XRD patterns of the $LiNi_{0.5}Mn_{1.5}O_4$ powders with and without addition of carbon black are illustrated in Fig. 1. Both the prepared samples present diffractions of a cubic $LiNi_{0.5}Mn_{1.5}O_4$ spinel structure without any peaks for carbon black due to its amorphous nature and/or low quantity. Quite weak peaks positioned at 43.7° and 63.3° are indexed to the NiO impurity in both samples. No other impurity phases are observed in XRD patterns for the $LiNi_{0.5}Mn_{1.5}O_4$/C composite. The crystal lattice parameters are 8.176 Å and 8.170 Å for $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$/C, respectively, which are very close to each other and consistent with the previously reported result [13]. All results illustrate that the spinel structure is not affected by the introduction of carbon black.

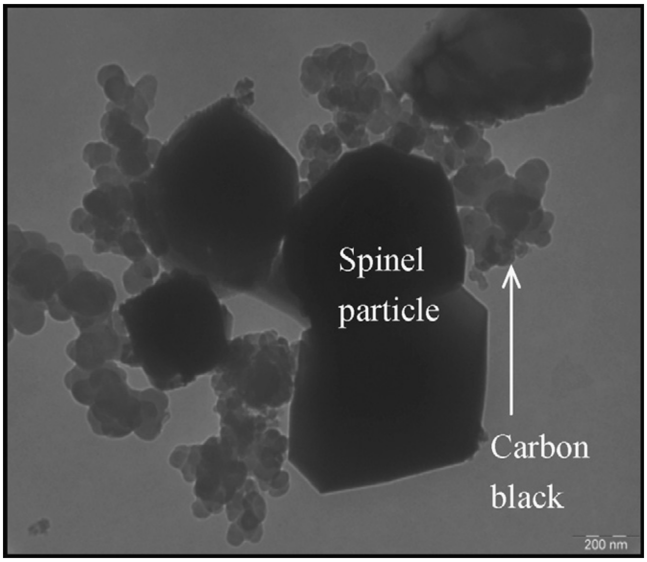

Fig. 2. TEM image of the $LiNi_{0.5}Mn_{1.5}O_4$/C composite.

Fig. 2 shows the TEM image of the $LiNi_{0.5}Mn_{1.5}O_4$/C. As can be seen, carbon black particles present an average grain size of approximate 70 nm and are slightly agglomerated. The $LiNi_{0.5}Mn_{1.5}O_4$ can be partially covered and interconnected with each other by carbon black particles. Since the carbon additive can provide pathways for electron transfer and enhance the electronic connection among $LiNi_{0.5}Mn_{1.5}O_4$ particles, the electronic conductivity of $LiNi_{0.5}Mn_{1.5}O_4$/C is improved from 7.23×10^{-7} S cm^{-1} for $LiNi_{0.5}Mn_{1.5}O_4$ to 4.11×10^{-6} S cm^{-1}. Furthermore, the partial covering can suppress the side reaction of the active cathode material with the electrolyte through reducing their direct contact interface, which favors the cyclability. The effectiveness of this similar covering with ZnO has been confirmed by Morales and co-workers [14] (Fig. 3).

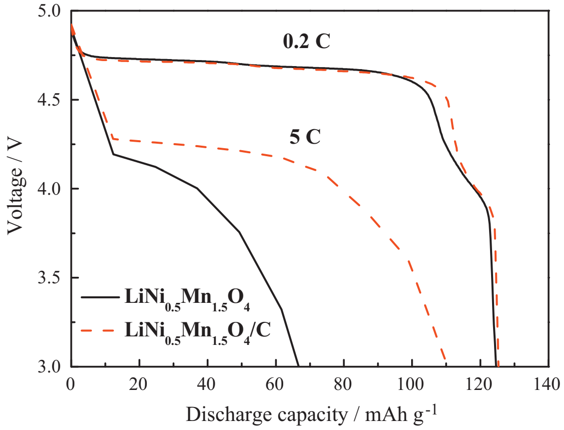

Fig. 3. Discharge profiles of the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$/C electrodes at the discharge rate of 0.2*C* and 5*C*.

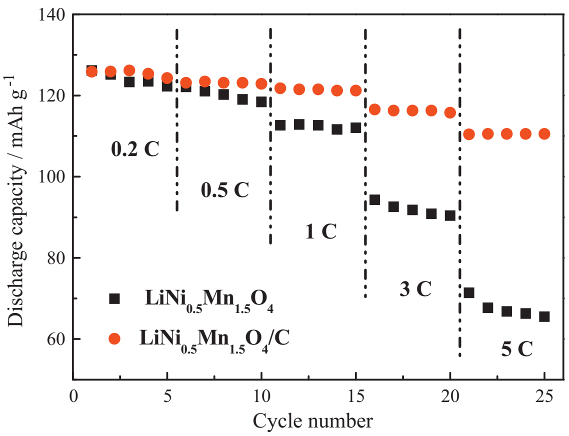

Fig. 4. Discharge capacities of the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4/C$ electrodes as a function of cycle number and discharge rate.

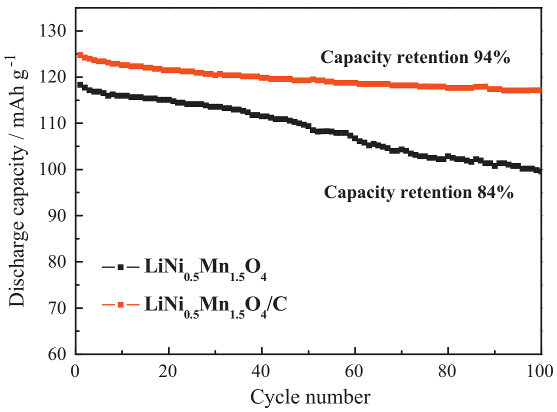

Fig. 5. Cycling performances of the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4/C$ electrodes with 0.2C charge and 1C discharge rates.

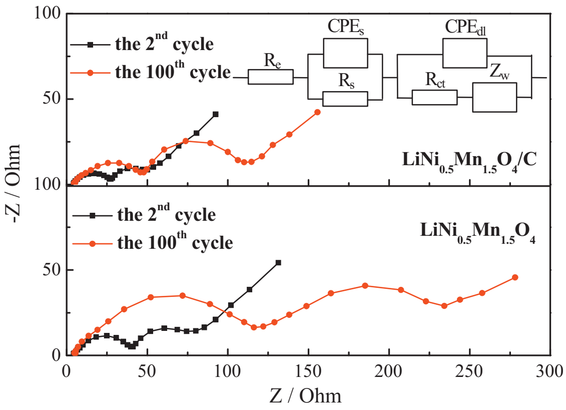

Fig. 6. EIS spectra of the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4/C$ electrodes after 2 and 100 cycles. The insert represents the equivalent circuit.

3.2. Electrochemical characterizations

The discharge curves of the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4/C$ electrodes are compared in Fig. 3. All test cells were charged at 0.2C and discharged at the rates of 0.2 and 5C, respectively. It is clear that the voltage profiles of both electrodes recorded at 0.2C present two ambiguously flat plateaux around 4.7 V which correspond to the reduction processes of Ni^{4+}/Ni^{2+} via Ni^{3+}, and also have a small voltage region at 4.1 V which corresponds to Mn^{4+}/Mn^{3+} reduction process [15]. The discharge capacities of the cells based on $LiNi_{0.5}Mn_{1.5}O_4/C$ and $LiNi_{0.5}Mn_{1.5}O$ are almost identical to 125 mAh g^{-1}. Therefore, although the electrochemically inactive carbon black is introduced, the effect on the discharge capacity can be ignored. In addition, while the 4.7 V plateaux of both electrodes are shortened and lowered down when increasing the discharge rate to 5C, a greatly serious deterioration caused by polarization is observed in the $LiNi_{0.5}Mn_{1.5}O_4$ electrode [16]. The $LiNi_{0.5}Mn_{1.5}O_4$ electrode delivers half of the capacity obtained at 0.2C without a flat discharge plateau, whereas the $LiNi_{0.5}Mn_{1.5}O_4/C$ can discharge at 4.3 V with a high 88% of its original capacity at 0.2C. The reduced polarization and better discharge performance of the $LiNi_{0.5}Mn_{1.5}O_4/C$ are ascribed to the improvement in electronic conductivity.

The discharge capacities measured at 0.2C charge and various discharge rates as a function of cycle number for both the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4/C$ electrodes are compared in Fig. 4. It is obvious that the $LiNi_{0.5}Mn_{1.5}O_4/C$ electrode exhibits enhanced rate capability compared with the $LiNi_{0.5}Mn_{1.5}O_4$. In details, when the discharge rate increases from 0.2 to 1C, there is only a small capacity decrease of about 3 mAh g^{-1} (i.e., from 126 to 123 mAh g^{-1}) for $LiNi_{0.5}Mn_{1.5}O_4/C$. With further increasing the discharge rate up to 5C, a capacity of 111 mAh g^{-1} is still delivered. While the $LiNi_{0.5}Mn_{1.5}O_4$ electrode degenerates greatly and the capacity remains only around 70 mAh g^{-1} at 5C rate. The results demonstrate that the added carbon black allows a greater utilization in capacity of the $LiNi_{0.5}Mn_{1.5}O_4$ particles at high discharge rates.

Fig. 5 shows the cycling performances of the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4/C$ electrodes under 0.2C charge and 1C discharge rates. The discharge capacity, the capacity retention and the cycling performance of the $LiNi_{0.5}Mn_{1.5}O_4/C$ electrode remarkably outperform those of the $LiNi_{0.5}Mn_{1.5}O_4$ electrode. The initial capacity of $LiNi_{0.5}Mn_{1.5}O_4/C$ reaches 125 mAh g^{-1} which is much higher than that of the other one (118 mAh g^{-1}). The capacity loss of the $LiNi_{0.5}Mn_{1.5}O_4/C$ electrode is only 6% of its initial capacity after 100 cycles, while the discharge capacity of the $LiNi_{0.5}Mn_{1.5}O_4$ shows a faster decline with a capacity loss of 16%.

To understand the improvement of electrochemical property in depth, EIS was carried out using the cells containing the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5}O_4/C$. The data were collected from the above cycling performance (Fig. 5) after 2 and 100 cycles. As shown in Fig. 6, all spectra consist of a semicircle in the high frequency range, another semicircle in the medium-to-low frequency range and a sloping line at the low frequency range, being ascribed to the resistance of Li^+ ion migration through the surface layer, the charge transfer resistance, and the diffusion of Li^+ in the solid electrode, respectively [17]. The impedance spectra can be explained on the basis of an equivalent circuit which is also presented in Fig. 6 and the fitting results are summarized in Table 1. Here, R_e is the electrolyte resistance, R_s is the surface resistance, R_{ct} is the charge transfer resistance, Z_W is the Warburg impedance, and CPE_s and CPE_{dl} are constant phase elements [18]. It is obvious that R_s and R_{ct} at the second cycle of the $LiNi_{0.5}Mn_{1.5}O_4/C$ electrode are smaller than those of $LiNi_{0.5}Mn_{1.5}O_4$, explaining for the higher initial capacity of $LiNi_{0.5}Mn_{1.5}O_4/C$ in Fig. 5. After 100

Table 1
Impedance parameters calculated from equivalent circuit.

Sample	Cycle number	R_s (Ω)	R_{ct} (Ω)
$LiNi_{0.5}Mn_{1.5}O_4$	2	39.08	31.88
	100	120.40	114.20
$LiNi_{0.5}Mn_{1.5}O_4/C$	2	23.12	23.15
	100	46.92	55.39

cycles, the R_s and R_{ct} of $LiNi_{0.5}Mn_{1.5}O_4$ increase drastically, while those of the $LiNi_{0.5}Mn_{1.5}O_4/C$ do not change much. The less R_s of the $LiNi_{0.5}Mn_{1.5}O_4/C$ compared with the $LiNi_{0.5}Mn_{1.5}O_4$ attests to the suppression of surface resistance which is caused by the side reactions between the active cathode material and the electrolyte [15]. This result is consistent with the analysis in Fig. 2. Since the charge transfer kinetics of the electrode material is inversely proportional to the surface resistance, it is reasonable that the smaller R_{ct} of $LiNi_{0.5}Mn_{1.5}O_4/C$ than the $LiNi_{0.5}Mn_{1.5}O_4$ stems from the suppression of R_s as well as the enhanced electronic conductivity. Therefore, the significant improvements in rate capability and cyclability are ascribed to the suppression of surface resistance and the enhanced electronic conductivity.

It should be pointed out that although the experimental results have proved that the conductive carbon black is responsible for the improved electrochemical property, further investigations should be carried out, including the content and the homogeneous dispersion of carbon black, or even the carbon sources and their introducing methods. Consequently, much better electrochemical performance can be expected through these optimizations.

4. Conclusions

The hybrid $LiNi_{0.5}Mn_{1.5}O_4/C$ cathode material was successfully prepared by a facile method, in which the spinel $LiNi_{0.5}Mn_{1.5}O_4$ was partially covered with carbon black through a combined treatment of pre-mixing and post-calcination. Carbon black particles can not only reduce the side reaction between the $LiNi_{0.5}Mn_{1.5}O_4$ and the electrolyte, but also remarkably increase the electronic conductivity due to the electronic connection among $LiNi_{0.5}Mn_{1.5}O_4$ particles. The hybrid $LiNi_{0.5}Mn_{1.5}O_4/C$ can deliver a reversible capacity of 125 $mAh\,g^{-1}$ when discharged at 1*C* with capacity retention of 94% after 100 cycles and a high capacity of 111 $mAh\,g^{-1}$ at 5*C* discharge rate. The remarkably improved rate capability and cycling performance are due to the suppression of surface resistance and the enhanced electronic conductivity. The $LiNi_{0.5}Mn_{1.5}O_4/C$ is experimentally proved as a promising cathode for lithium ion batteries, and much better results could be expected via necessary optimizations in the following investigation.

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References

[1] G. Derrien, J. Hassoun, S. Panero, B. Scrosati, Adv. Mater. 19 (2007) 2336.
[2] X.L. Wu, L.Y. Jiang, F.F. Cao, Y.G. Guo, L.J. Wan, Adv. Mater. 21 (2009) 2710.
[3] H.M. Xie, R.S. Wang, J.R. Ying, L.Y. Zhang, A.F. Jalbout, H.Y. Yu, G.L. Yang, X.M. Pan, Z.M. Su, Adv. Mater. 18 (2006) 2609.
[4] Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 205.
[5] T. Ohzuku, S. Takeda, M. Iwanaga, J. Power Sources 81–82 (1999) 90.
[6] G.Q. Liu, L. Wen, G.Y. Liu, Y.W. Tian, J. Alloys Compd. 501 (2010) 233.
[7] R.K. Katiyar, R. Singhal, K. Aamar, R. Valentin, R.S. Katiyar, J. Power Sources 194 (2009) 526.
[8] U. Lafont, C. Locati, W.J.H. Borghols, A. Łasińska, J. Dygas, A.V. Chadwick, J. Power Sources 189 (2009) 179.
[9] M. Kunduraci, G.G. Amatucci, J. Electrochem. Soc. 153 (2006) A1345.
[10] X.K. Zhi, G.C. Liang, L. Wang, X.Q. Ou, L.M. Gao, X.F. Jie, J. Alloys Compd. 503 (2010) 370.
[11] S.T. Myung, S. Komaba, N. Hirosaki, H. Yashiro, N. Kumagai, Electrochim. Acta 49 (2004) 4213.
[12] T.Y. Yang, K.N. Sun, Z.Y. Lei, N.Q. Zhang, Y. Lang, J. Alloys Compd. 502 (2010) 215.
[13] Y.Y. Sun, Y.F. Yang, H. Zhan, H.X. Shao, Y.H. Zhou, J. Power Sources 195 (2010) 4322.
[14] J.C. Arrebola, A. Caballero, L. Hernán, J. Morales, J. Power Sources 195 (2010) 4278.
[15] J. Liu, A. Manthiram, Chem. Mater. 21 (2009) 1695.
[16] T. Ohzuku, R. Yamato, T. Kawai, K. Ariyoshi, J. Solid State Electrochem. 12 (2008) 797.
[17] J. Liu, A. Manthiram, J. Electrochem. Soc. 156 (2009) A66.
[18] H.M. Wu, I. Belharouak, A. Abouimrane, Y.K. Sun, K. Amine, J. Power Sources 195 (2010) 2909.