Letter

Pervoskite-type $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ cathode for proton conducting IT-SOFC

Kui Xie [a,b,*], Jianer Zhou [a], Guangyao Meng [b]

[a] National Engineering Research Center for Domestic & Building Ceramics, Jingdezhen Ceramic Institute, Jingdezhen, Jiangxi 333403, China
[b] Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China

ARTICLE INFO

ABSTRACT

This paper presents Pervoskite-type $BaCo_{0.7}Ta_{0.1}Fe_{0.2}O_{3-\delta}$ (BCTF) cathode for intermediate temperature proton conducting solid oxide fuel cells (SOFCs). BCTF with cubic phase shows excellent structural stability and adequate chemical stability against CO_2/H_2O in contrast to $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$. Conductivity of BCTF reaches above $10\,S\,cm^{-1}$ in air at intermediate temperatures. Composite cathode polarization resistance ($BCTF/BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$) in a symmetric cell based on proton conducting $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BCZY) electrolyte was as low as $0.1\,\Omega\,cm^2$ at $700\,°C$. The maximum output of anode-supported thin-film SOFC with BCTF/BCZY composite cathode and BCZY electrolyte reaches $255\,mW\,cm^{-2}$ when employing humidified H_2 as fuel and static air as oxidizer.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Solid oxide fuel cells (SOFCs) have been extensively studied as advanced power generation devices because of their high energy conversion efficiency, low environment impact, and good fuel flexibility [1–3]. Considerable efforts have been devoted to reduce SOFC operation temperature by lowering cathode polarization resistance [4–6]. Perovskite-type cobalt-containing cathodes display the most excellent catalytic activity to oxygen as well as desirable conductivity around intermediate temperatures in contrast to manganese- and chromium-based cathodes [7–12]. A-site fully occupied by Ba^{2+} with large ionic size allows fast surface oxide–oxide exchange reaction as studied by several researchers [13–16], which is crucial to high performance SOFC cathode due to the catalytic activity to oxygen and ionic conductivity.

However, the structural stability of these cathodes have been questioned because of the transition from cubic phase to hexagonal phase at room temperatures which is simultaneously accompanied by the change of oxygen vacancy from disordering to ordering and the decrease of catalytic activity to oxygen [13,16]. Additionally, cathode materials for proton conducting cells have to possess desirable stability against steam as H_2O is produced as product of cell reaction in cathode compartment. On the other hand, $BaCoO_3$-based cathode materials are not stable in air where trace CO_2

would react with them to result in degradation in fuel cell performance [17]. Su and his co-worker reported that the structural stability could be improved by partially replacing cobalt cation with high-valance Nb^{5+} [8]. High-valance ion increases oxygen non-stoichiometry in Pervoskite oxide which is closely and positively related to the structure stability. Tong and his co-worker reported that the incorporation of Zr^{4+} with higher electro-negativity in B-site is an effective way to modify the chemical stability of $BaCoO_3$ [17]. The mechanism could be roughly attributed to the increase in acidity of Pervoskite oxide when doping with higher electronegative cations.

Up to date, alternative cathode based on cobaltite with adequate structure stability and chemical stability is still a continuous incentive for searching and developing high performance cathodes. In this work, we are trying to use Ta^{5+} as a cation dopant in B-site to improve the structural and chemical stability. Of course, we are not the first to investigate +5 cation dopant as Nb doped $BaCoO_3$ was already studied for oxygen-ion conducting SOFC cathode [18], however, the chemical stability and cathode performance were not reported for proton conducting SOFCs. The similar ionic size of Ta^{5+} (0.68 Å) to Co^{3+} (0.63 Å) leads to a reasonable assumption for cation doping. Ta^{5+} with higher electro-negativity than Co^{3+}/Co^{4+} increases the acidity of ceramic oxide and makes oxide not sensitive to CO_2/H_2O. In this study, 10% Ta^{5+} and 20% Fe^{3+} were co-doped in B-site, where the doping of Ta modifies the structural and chemical stability while the Fe dopant makes the thermal expansion coefficient compatible with electrolytes [19]. In this work, the structural and chemical stability, mixed conductivity, cathode polarization of $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ and the corresponding fuel cell

* Corresponding author at: National Engineering Research Center for Domestic & Building Ceramics, Jingdezhen Ceramic Institute, Jingdezhen, Jiangxi 333403, China.
E-mail address: xiekui@mail.ustc.edu.cn (K. Xie).

performance based on proton conducting electrolyte were studied, respectively.

2. Experimental

$BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCTF) powder was synthesized by a solid-state reaction method [20]. In this process, $BaCO_3$, $CoCO_3$, Ta_2O_5 and Fe_2O_3 were ball-milled in ethanol for 24 h and then dried at 100 °C. The obtained precursor was then pressed into disc with 15 mm in diameter and 3 mm in thickness under 250 MPa followed by a heat treatment at 1000 °C for 10 h in air. XRD was performed to analyze the phase formation. For comparison, $BaCo_{0.8}Fe_{0.2}O_3$ (BCF) with Ta doping was prepared under the same conditions followed by a XRD test. After that, BCTF and BCF powder with the same particle size were heat-treated at 700 °C for 10 h in ($3\%CO_2/3\%H_2O/94\%Ar$), respectively. XRD was performed to detect the phase changes. Some BCTF powder was exposed in the same atmosphere at 700 °C for 20 h to check the stability. Some fresh BCTF powder was pressed into disk and then sintered in air at 1200 °C for 5 h for direct current conductivity test. The polarization of composite cathode $BCTF/BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BCZY) (65:35 in weight ratio) in a symmetric cell based on proton conducting BCZY electrolyte was recorded from 600 to 700 °C in air with electrochemical impedance spectroscopy (CHI604C). In this experiment, BCZY powder was fabricated by a combustion method as described elsewhere [21] and then the fresh powder was pressed into disk with thickness of 2 mm and diameter of 25 mm followed by heat treatment at 1400 °C for 5 h to prepare the electrolyte for symmetric cell. Single SOFC with BCTF/BCZY cathode based on BCZY and nickel anode was assembled as described in elsewhere [21]. Silver paste was printed onto both cathode surfaces and fired at 550 °C for 30 min to form current collectors. Single SOFC was tested at 700 °C with humidified hydrogen as fuel and static air as oxidizer.

3. Results and discussions

It is deemed that the structure of $BaCoO_3$ oxide changes from cubic phase at higher temperature to hexagonal structure at room temperature [13]. This transformation process is simultaneously accompanied by the transition of oxygen vacancy from disordering to ordering [16] which significantly decreases the catalytic activity and ionic conductivity. As reported by several researchers, the oxygen nonstoichiometry in Pervoskite closely relates to structural stability which could be enhanced by introducing high-valance cations into B-site [8,13,16,17].

The doping of Ta^{5+} results in the decrease of the oxygen vacancy concentration and the increase of oxygen nonstoichiometry according to electrostatic neutrality as shown in chemical reaction (1), which according increases the structural stability.

$$Ta_2O_5 + 2V_O^{\bullet\bullet} \xrightarrow{Co_2O_3} 2Ta_{Co}^{\bullet\bullet} + 5O_O^x \qquad (1)$$

The mechanism of Ta stabilization effect for cubic phase could be attributed to the distinctness between cubic and hexagonal structures. The BO_6 octahedra as the skeleton of the cubic structure is corner shared in Pervoskite while the BO_6 octahedra in hexagonal structure is face-shared. The distance between B-site cations in hexagonal structure is therefore shorter than that in cubic pervoskite. The doping of Ta^{5+} increases the average valance of B-site cation and then increases the oxygen nonstoichiometry, which accordingly raise the electrostatic repulsion and destabilize the hexagonal structure. This is why the higher valance cations in B-site could increase the stability of cubic phase. $BaCoO_3$ oxide is hexagonal structure at room temperature [13]. As shown in Fig. 1(a), $BaCo_{0.8}Fe_{0.2}O_3$ (BCF) is also hexagonal structure even it is doped with 20% Fe^{3+} in B-site, which could be due to the same valance of Fe and Co. BCTF cathode, as shown in Fig. 1(b), is a single cubic phase with space group $Pm\bar{3}m$ and cell parameter 4.086 Å. The substitution of 10% Ta for Co demonstrates excellent stabilization effect for cubic Pervoskite structure. However, the valance change of Co^{4+}/Co^{3+} and $Fe^{3+}/^{2+}$ could arise with the doping of Ta^{5+} as shown in chemical reactions (2) and (3).

$$2Co_{Co}^x + 2O_O^x \rightarrow 2Co_{Co}' + V_O^{\bullet\bullet} \qquad (2)$$

$$2Fe_{Fe}^x + 2O_O^x \rightarrow 2Fe_{Fe}' + V_O^{\bullet\bullet} \qquad (3)$$
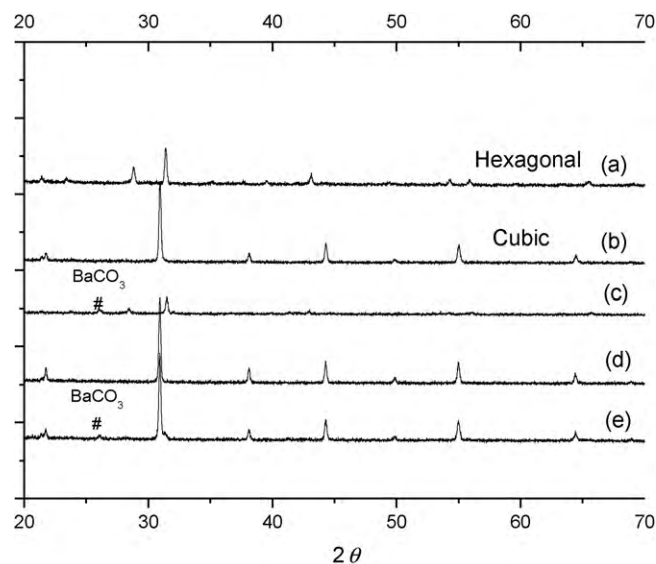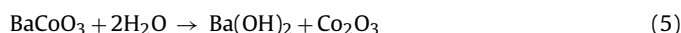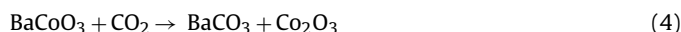

Fig. 1. XRD spectra of $BaCo_{0.8}Fe_{0.2}O_3$ (BCF) and $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCTF) (a) BCF powder prepared with solid state reaction at 1000 °C; (b) BCTF powder prepared with solid state reaction at 1000 °C; (c) BCF after heat treatment in $3\%CO_2/3\%H_2O/94\%Ar$ at 700 °C for 10 h; (d) BCF after heat treatment in $3\%CO_2/3\%H_2O/94\%Ar$ at 700 °C for 10 h; (e) BCTF after heat treatment in $3\%CO_2/3\%H_2O/94\%Ar$ at 700 °C for 20 h.

Actually, cathode is working in strongly oxidizing atmosphere with P_{O_2} of 0.2 atm, which may result in a possibility of ignoring the valance change to some extent. Further investigation of valance change is still worth to continue in future. On the other hand, as presented in the introduction part, the chemical stability of $BaCoO_3$-based cathode for proton conducting SOFC is another challenging problem. As shown in Fig. 1(c) and (d), a peak corresponding to barium carbonates appears for BCF while BCTF is still single cubic phase after a heat treatment at 700 °C in $3\%CO_2/3\%H_2O/94\%Ar$ for 10 h. Partial substitution of Ta^{5+} for Co^{4+} decreases the sensitivity to CO_2/H_2O. The small amount of Ta^{5+} introduced into lattice provides adequate benefit to overall thermodynamics to render carbonation unfavorable in short-term performance. However, a weak peak corresponding to barium carbonates appears for BCTF, as shown in Fig. 1(e), after being heat-treated in $3\%CO_2/3\%H_2O/94\%Ar$ for 20 h, which means BCTF is not completely stable in the presence of CO_2/H_2O at intermediate temperature for long time. The reason why Ta^{5+} could stabilize BCTF cathode against carbonation could be understood as follows. For ABO_3 Pervoskite BCTF cathode, the electro-negativity of B-site element is important to its chemical stability in the presence of CO_2/H_2O. The reaction between cathode and CO_2/H_2O takes place like this:

$$BaCoO_3 + CO_2 \rightarrow BaCO_3 + Co_2O_3 \qquad (4)$$

$$BaCoO_3 + 2H_2O \rightarrow Ba(OH)_2 + Co_2O_3 \qquad (5)$$

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O \qquad (6)$$

The real process of the above reactions is a separation of BaO from BCTF oxide. Higher electro-negativity of B-site cation brings on stronger B-O band in Pervoskite structure and then make it more difficult for BaO separation.

Fig. 2 shows the conductivity of BCTF in air as function of temperatures. The conductivity reaches about 20 S cm^{-1} at intermediate temperature, which is a little bit lower than that of reported Co-based cathode under the same conditions [11,12]. This could be attributed to that the highly electronegative Ta^{5+} decreases the conductivity. Cathode polarization is considered as the performance including catalytic activity and mixed conductivity. Fig. 3 shows the cathode polarization in a symmetric cell at 700 °C. In this model
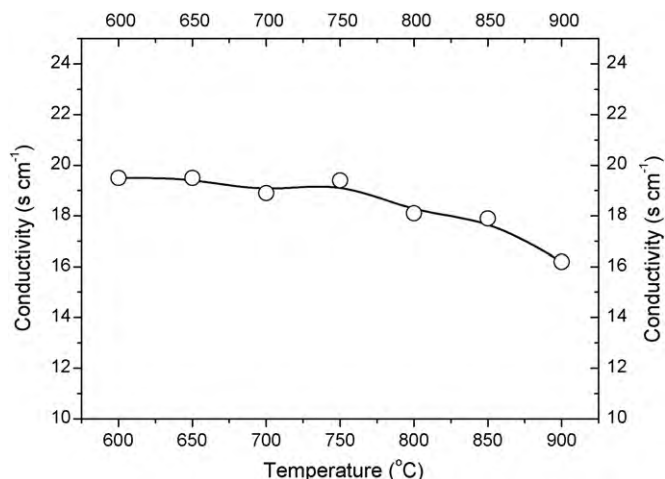
Fig. 2. Conductivity of $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCTF) in air as function of temperature.

circuit, theoretical intercept with real axis at high frequency represents the series resistance (R_1) of the symmetric cell and the other intercept at low frequency corresponds to the total resistance (R_2) of cell. Thus, 50% of the difference between R_1 and R_2 was considered as the BCTF cathode polarization. As shown in Fig. 3, R_p (cathode polarization) is just 0.1 Ω cm^2 at 700 °C which is much lower than the reported values for traditional $La_{0.5}Sr_{0.5}MnO_3$ [22] and comparable to other reported cobalt-based cathodes [23]. The BCTF polarization resistance slightly increases to 0.4 Ω cm^2 at 650 °C and then significantly increases to 1.2 Ω cm^2 at 600 °C, which may be due to the loss of catalytic activity and mixed conductivity at low temperature. The BCTF cathode polarization is however still encouraging at such low temperatures compared with reported Mn- or Cr-based cathodes [24,25].

Fig. 4 shows the microstructure of a single SOFC with composite BCTF/BCZY cathode based on BZCY. The cathode layer adheres to electrolyte very well indicating the desirable thermal compatibility. The cathode layer is not porous enough as the BCTF powder was prepared by solid-state reaction method, which may lead to higher cathode polarization resistance. The BCZY electrolyte with thickness of 60 μm is quite dense and uniform; and adheres very well to anode substrate according to the cross-sectional view. Fig. 5 shows the performance of SOFC with BCTF/BCZY cathode. The Open circuit
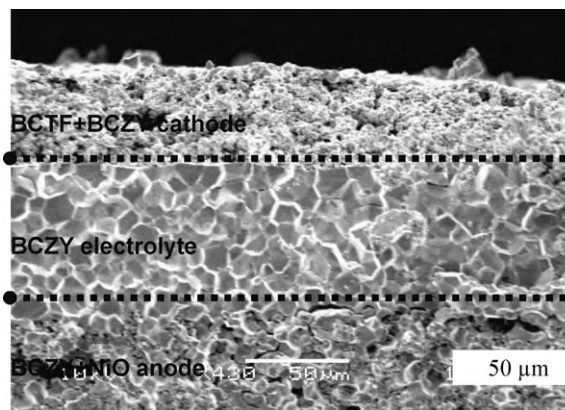

Fig. 3. Impedance spectra of $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCTF) and $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ composite cathode in symmetric cell based on $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte from 600 to 700 °C.

Fig. 4. Microstructure of solid oxide fuel cell with $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCTF) and $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ composite cathode after testing.
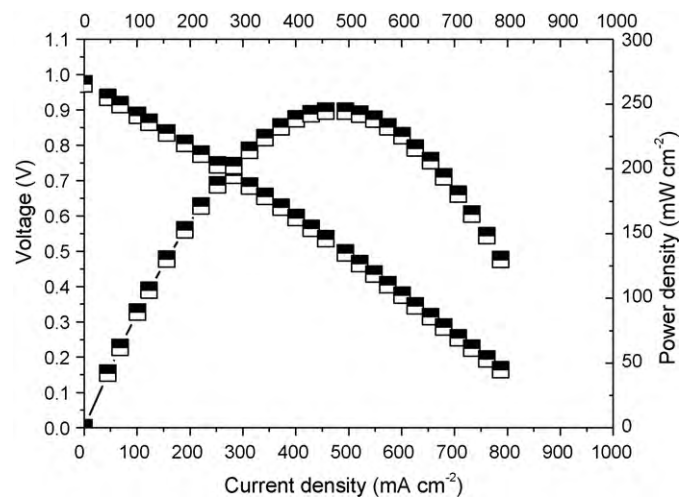
Fig. 5. Performance of fuel cell with $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ and $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ composite cathode.

voltage and maximum power density respectively reach 0.99 V and 255 mW cm^{-2} at 700 °C, which is comparable to the reported values based on $BaCe_{0.7}Sn_{0.1}Y_{0.2}O_{3-\sigma}$ electrolyte [26].

4. Conclusion

In this study, we aimed to provide a novel cathode $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCTF) for intermediate temperature proton conducting solid oxide fuel cells. BCTF cathode demonstrates excellent structural stability in cubic Pervoskite and adequate chemical stability against CO_2/H_2O. Cathode polarization and conductivity tests revealed that BCTF is a high performance cathode at intermediate temperatures. A proton conducting solid oxide fuel cell cathode with $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ and $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ composite cathode generates maximum power density of 255 mW cm^{-2} at 700 °C with humidified hydrogen as fuel and static air as oxidizer.

References

[1] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563.
[2] K. Xie, Q.L. Ma, B. Lin, Y.Z. Jiang, J.F. Gao, X.Q. Liu, G.Y. Meng, J. Power Sources 170 (2007) 38.
[3] R.M. Ormerod, Chem. Soc. Rev. 32 (2003) 17.
[4] C. Torres-Garibay, D. Kovar, A. Manthiram, J. Power Sources 192 (2009) 736.
[5] T. Xia, N. Lin, H. Zhao, L. Huo, J. Wang, J. Grenier, J. Power Sources 192 (2009) 291.
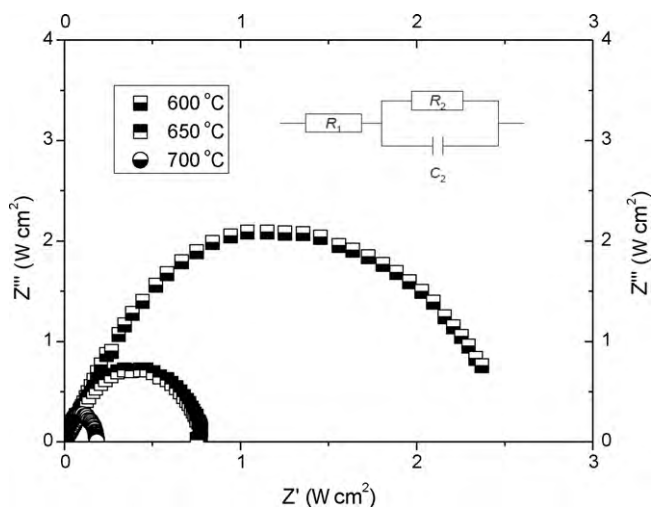[6] C. Bonhomme, S. Beaudet-Savignat, T. Chartier, P. Geffroy, A. Sauvet, J. Eur. Ceram. Soc. 29 (2009) 1781.

[7] C. Yang, X. Wu, S. Fang, C. Chen, W. Liu, Mater. Lett. 63 (2009) 1007.
[8] C. Zhu, X. Liu, C. Yi, L. Pei, D. Yan, J. Niu, D. Wang, W. Su, Electrochem. Commun. 11 (2009) 958.
[9] F. Liang, J. Chen, S. Jiang, B. Chi, J. Pu, L. Jian, Electrochem. Commun. 11 (2009) 1048.
[10] Y. Tao, H. Nishino, S. Ashidate, H. Kokubo, M. Watanabe, H. Uchida, Electrochim. Acta 54 (2009) 3309.
[11] J. Tulloch, S. Donne, J. Power Sources 188 (2009) 359.
[12] J. Li, S. Wang, Z. Wang, R. Liu, X. Ye, X. Sun, T. Wen, Z. Wen, J. Power Sources 188 (2009) 453.
[13] T. Nagai, W. Ito, T. Sakon, Solid State Ionics 177 (2007) 3433.
[14] T. Ishihara, S. Fukui, H. Nishiguchi, Y. Takita, Solid State Ionics 152–153 (2002) 609.
[15] Z. Shao, G. Xiong, J. Tong, H. Dong, W. Yang, Sep. Purif. Technol. 25 (2001) 419.
[16] Y. Cheng, H. Zhao, D. Teng, F. Li, X. Lu, W. Ding, J. Membr. Sci. 322 (2008) 484.

[17] J. Tong, W. Yang, B. Zhu, R. Cui, J. Membr. Sci. 203 (2002) 175.
[18] S. Lü, Y. Ji, X. Meng, G. Long, T. Wei, Y. Zhang, T. Lü, Electrochem. Solid-State Lett. 12 (2009) B103.
[19] W. Zając, K. Świerczek, J. Molenda, J. Power Sources 173 (2007) 675.
[20] K. Xie, R. Yan, X. Liu, J. Alloys Compd. 479 (2009) L40.
[21] K. Xie, R. Yan, D. Dong, S. Wang, X. Chen, T. Jiang, B. Lin, M. Wei, X. Liu, G. Meng, J. Power Sources 179 (2008) 576.
[22] J.W. Kim, A.V. Virkar, K.Z. Fung, K. Mehta, S.C. Singhal, J. Electrochem. Soc. 146 (1999) 69.
[23] H.Y. Tu, Y. Takeda, N. Imanishi, O. Yamamoto, Solid State Ionics 117 (1999) 277.
[24] Y. Sakaki, Y. Takeda, A. Kato, N. Imanishi, O. Yamamoto, M. Hattori, M. Iio, Y. Esaki, Solid State Ionics 118 (1999) 187.
[25] L. Zhang, X.B. Chen, S.P. Jiang, H.Q. He, Y. Xiang, J. Power Sources 180 (2009) 1076.
[26] K. Xie, R.Q. Yan, X.Q. Liu, J. Alloys Compd. 479 (2009) L36.