Short communication

A cobalt-free $Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ composite cathode for proton-conducting solid oxide fuel cells

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ABSTRACT

A cobalt-free composite $Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SSFCu–SDC) is investigated as a cathode for proton-conducting solid oxide fuel cells (H-SOFCs) in intermediate temperature range, with $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) as the electrolyte. The XRD results show that SSFCu is chemically compatible with SDC at temperatures up to 1100 °C. The quad-layer single cells of NiO–BZCYYb/NiO–BZCYYb/BZCYYb/SSFCu–SDC are operated from 500 to 700 °C with humidified hydrogen (~3% H$_2$O) as fuel and the static air as oxidant. It shows an excellent power density of 505 mW cm^{-2} at 700 °C. Moreover, a low electrode polarization resistance of 0.138 Ω cm^2 is achieved at 700 °C. Preliminary results demonstrate that the cobalt-free SSFCu–SDC composite is a promising cathode material for H-SOFCs.

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1. Introduction

Currently, much attention has been focused on the cathode materials for proton-conducting solid oxide fuel cells (H-SOFCs) due to their unique properties. The proton conductors have several advantages over the oxide ion conductors, including simpler fuel-recycling instruments and being able to avoid the dilution of the fuel [1,2]. More importantly, the low activation energy of proton transport is favorable for the H-SOFCs to operate at intermediate-to-low temperatures, thus leading to a prolonged operational lifetime and improved materials compatibility [3,4]. $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) has been found to be an excellent electrolyte in this temperature range, since it shows a rapid transport of both protons and oxide ion vacancies and high ionic conductivity. Besides, BZCYYb can resist deactivation by sulfur as well as hydrocarbon cracking and reforming [5].

As known, one key to improve the cell performance is reducing the polarization resistance of the cathode–electrolyte interface [6]. However, developing alternative cathode materials with low interface polarization losses and high stability for intermediate temperature solid oxide fuel cells (IT-SOFCs) remains a challenge [7]. Traditional cathode materials for IT-SOFCs include $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [1] and $La_{0.5}Ba_{0.5}Cu_{0.5}Co_{0.5}O_{3-\delta}$ [8]. However, cobalt-based perovskite oxides often suffer problems like high thermal expansion coefficients, easy reduction and evaporation of cobalt and the high cost of cobalt element, thus limiting the further applications [9,10]. Therefore, it is critical to develop cobalt-free cathode materials with good performance for IT-SOFCs. Fe-based perovskite oxides could well serve as promising alternatives to cobalt-based cathode materials, because of the less flexible redox behavior and low price of iron [11]. Recently, Ling et al. have reported a novel cobalt-free cathode $Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (SSFCu) for IT-SOFCs with advanced electrochemical properties based on doped ceria electrolyte [12]. The electrical conductivity of SSFCu reaches the maximum value of 82 S cm^{-1} at 450 °C, which meets the general required value of cathode material. And the result of symmetric cell (the area specific resistance as low as 0.084 Ω cm^2 at 700 °C) implies that SSFCu should be a potential IT-SOFCs cathode material with high electrocatalytic activity for oxygen reduction reactions. However, the electrochemical performance of SSFCu cathode for H-SOFCs has not been reported up to date.

Based on recent research [13], we propose adding $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) electrolyte which is widely used for SOFCs based on SDC oxide ion conductors, into SSFCu cathode to prepare the composite cathode for H-SOFCs, for the following four reasons. First, as SDC is an excellent oxide ion conductor and SSFCu is a mixed ionic–electronic conductor [12], the addition of SDC into SSFCu ensures the cathode layer having a high activity for oxygen

ion reduction and migration, while oxygen ion diffusion is a notable limiting step for the cathodic processes of H-SOFCs [14]. Second, composite cathode can enlarge the triple phase boundary of H-SOFCs [1,15]. Third, the addition of SDC helps achieve good thermal matching and adherence between SSFCu and BZCYYb electrolyte [12,13]. Last, a good long-term stability is expected, for SDC can endure corrosion by CO_2 and H_2O [16]. In this work, we investigated the SSFCu–SDC composite as a potential cathode in proton-conducting IT-SOFCs based on the BZCYYb electrolyte, and the chemical compatibility between SSFCu and SDC was evaluated.

2. Experimental

2.1. Powders synthesis

$Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (SSFCu), $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) and $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) powders were all synthesized by auto ignition process. Taking the synthesis of BZCYYb as an example, $Ba(NO_3)_2 \cdot 9H_2O$, $Zr(NO_3)_4 \cdot 4H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, Y_2O_3 and Yb_2O_3 as raw materials were dissolved in distilled water at stoichiometric ratio, citric acid and EDTA were then added as complexing agents, with the molar ratio of citric acid:EDTA:metal cations of 1.5:1:1. Under heating and stirring, the solution gradually changed into black foam and ignited to flame. The as-synthesized powders were subsequently calcined at 1000 °C for 3 h, to remove the carbon residue and achieve a pure perovskite phase of BZCYYb powders. Similarly, the as-synthesized SSFCu and SDC powders were calcined at 950 and 800 °C for 3 h, respectively.

2.2. Fabrication of the single cells

The anode-supported BZCYYb tri-layer half-cells (ψ15 mm) were fabricated by one-step dry-pressing method. The mixture of NiO + BZCYYb + starch as pore former (60 wt.%:40 wt.%:20 wt.%), was pre-pressed at 200 MPa to form into an anode substrate. Subsequently the anode functional layer (mixture of NiO:BZCYYb of 60 wt.%:40 wt.%) was pressed onto the substrate. Then loose BZCYYb powders were uniformly distributed onto the anode substrate, co-pressed at 250 MPa and co-sintered at 1350 °C for 5 h to obtain a dense BZCYYb electrolyte film.

Fine SSFCu and SDC powders (60 wt.%:40 wt.%) were mixed thoroughly together with a 6 wt.% ethylcellulose–terpineol binder, to prepare the composite cathode slurry. The cathode slurry was then painted on the BZCYYb electrolyte film and sintered at 950 °C for 3 h in air to form a quad-layer cell of NiO–BZCYYb/NiO–BZCYYb/BZCYYb/SSFCu–SDC. Finally Ag paste was painted onto the cathode layer as a current collector.

2.3. Characterization and electrochemical measurements

Phase composition of the sintered anode–electrolyte layer, SSFCu oxide and SSFCu–SDC composite cathode fired at various temperatures were identified with the X-ray diffraction (XRD) analysis by Cu Kα radiation (D/Max-gA, Japan). A scanning electron microscope (SEM, JEOL JSM-6400) was used to observe the microstructure of the cells after testing.

The single cells were tested in a home-developed-cell-testing system from 500 to 700 °C, with humidified hydrogen (~3% H_2O) as fuel and static air as oxidant, respectively. The flow rate of fuel gas was about 40 ml min^{-1}. The cell voltages and output currents were measured by digital multi-meters (GDM-8145). The electrochemical impedance spectra were measured under open-circuit conditions with an impedance analyzer (CHI604C, Shanghai Chenhua) from 500 to 700 °C.
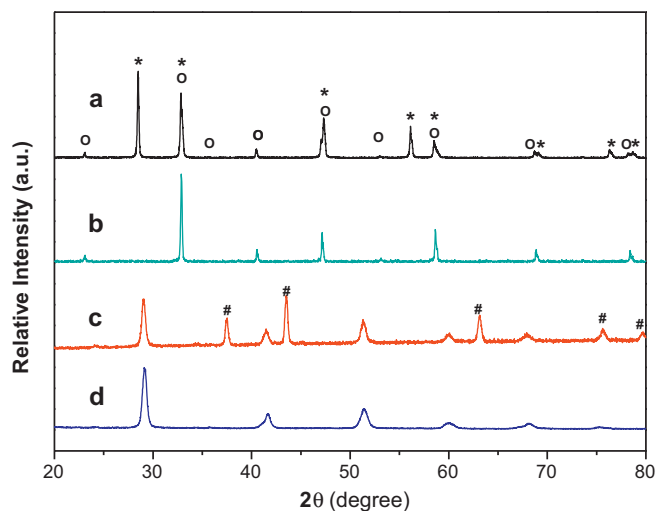

Fig. 1. XRD patterns of (a) $Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SSFCu–SDC) composite cathode, (b) SSFCu oxide, (c) NiO–$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (NiO–BZCYYb) anode substrate, and (d) BZCYYb electrolyte membrane: (O) SSFCu; (*) SDC; (#) NiO.

3. Results and discussion

As shown in Fig. 1, SSFCu oxide calcined at 950 °C crystallizes in a cubic perovskite structure of the Pm3m (2 1 1) space group, without any peaks attributable to impurities. From the XRD spectra of anode–electrolyte layer, it is obvious that there are only peaks corresponding to BZCYYb in the electrolyte membrane (Fig. 1c) and to NiO and BZCYYb in the anode substrate (Fig. 1d), with no evidence for the formation of other substances. Fig. 2 shows the XRD spectra of the SSFCu–SDC composite cathode fired at three temperatures of 900, 1000, and 1100 °C for 5 h in air, to evaluate the chemical compatibility between SSFCu and SDC. There are only peaks corresponding to SSFCu with a cubic perovskite structure and SDC with a fluorite structure can be found after sintering at temperatures up to 1100 °C, with no new identifiable peaks or shift of peaks, thus indicating an excellent chemical compatibility.

SEM images show the cross-sectional views of the BZCYYb electrolyte and the quad-layer cells after testing. From Fig. 3a, it can be seen that BZCYYb membrane is completely dense and grains are quite uniform in size of around 1 μm, without obvious pores
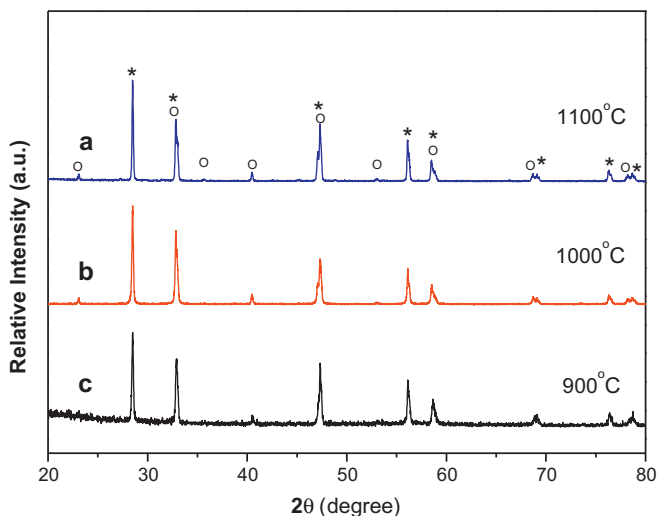

Fig. 2. XRD patterns of the SSFCu–SDC composite cathode layer sintered at 900, 1000 and 1100 °C for 5 h: (O) SSFCu; (*) SDC.
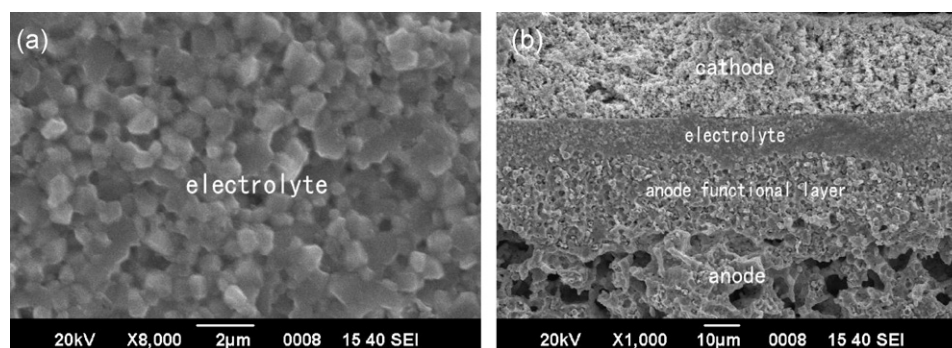
Fig. 3. SEM images of the cross-sectional views of (a) the BZCYYb electrolyte and (b) the quad-layer cells after testing.

or cracks. As shown in Fig. 3b, the porous SSFCu–SDC cathode displays good adhesion to the BZCYYb electrolyte membrane, while their thicknesses are about 30 μm and 15 μm, respectively. This good configuration can promote gas transport and electrochemical reactions, leading to a lower polarization resistance and a higher performance. The results demonstrate that a dense BZCYYb electrolyte membrane can be successfully fabricated on the porous anode support via the combined dry-pressing/co-firing process at a relatively low temperature (1350 °C). Moreover, optimizing the microstructure of SSFCu–SDC cathode will further enhance the cathode performance.

To determine the electrochemical performance of the quad-layer NiO–BZCYYb/NiO–BZCYYb/BZCYYb (~15 μm)/SSFCu–SDC (~30 μm) single cell in real fuel cell conditions, the I–V and I–P characteristics were measured from 500 to 700 °C, with humidified hydrogen (~3% H_2O) as fuel and the static air as oxidant. As known, if the BZCYYb electrolyte membrane is not dense, fuel/gas cross flow may take place to cause a lower open-circuit voltage (OCV). As shown in Fig. 4, the maximum power densities were 505, 398, 289, 195 and 121 mW cm^{-2}, and the OCV values were 0.992, 1.017, 1.035, 1.053 and 1.065 V at 700, 650, 600, 550 and 500 °C, respectively. High open-circuit voltages indicate a sufficiently dense BZCYYb electrolyte membrane, which is in good agreement with the SEM images above. This single cell exhibits higher power densities than those using cobalt-free SrFe$_{0.9}$Sb$_{0.1}$O$_{3-\delta}$ (428 mW cm^{-2} at 700 °C) [17] and PrBaFe$_2$O$_{5+\delta}$ (452 mW cm^{-2} at 700 °C) cathodes [18], even the cobalt-based La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$–BZCYYb (260 mW cm^{-2} at 600 °C) cathode [19]. The high performance can mainly be attributed to three aspects. First, the excellent oxygen ion conductivity of SDC and its good chemical compatibility with SSFCu [1,3], increase the activity of SSFCu–SDC cathode for oxygen ion migration and reduction, while oxygen ion migration serves as a notable speed-limiting step for the cathodic processes of H-SOFCs [14]. In the same way, for the cathode, partly replacing Fe ions with divalent and trivalent Cu ions in a perovskite lattice can increase the oxygen vacancies [12]. Third, the good configuration, especially the excellent interface contact between electrodes and electrolyte favors a low polarization resistance.

In order to further investigate the different contributions to the total resistance of single cells, electrochemical impedance spectroscopy are performed under open-circuit conditions from 500 to 700 °C. As shown in Fig. 5, the low-frequency intercept on the real axis is the total cell resistance (R_t) and the high-frequency intercept is the ohmic resistance (R_{ohm}), while the difference between the two values corresponds to the polarization resistance (R_p) of both cathode–electrolyte and anode–electrolyte interfaces. A quite low polarization resistance of 0.138 Ω cm^2 is achieved at 700 °C, which is lower than those using SrFe$_{0.9}$Sb$_{0.1}$O$_{3-\delta}$ (0.154 Ω cm^2 at 700 °C) [17] and PrBaFe$_2$O$_{5+\delta}$ (0.18 Ω cm^2 at 700 °C) cathodes [18], agreeing with the power densities above. The cobalt-free SSFCu–SDC cathode exhibits high electrochemical activity for operation at intermediate temperature range. Fig. 6 shows the estimated resistance from the impedance spectra, it can be observed that R_p increases much faster than R_{ohm} during the decrease of measurement temperature. The ratio of R_p/R_t as a function of temperature is also provided for comparison. At temperatures lower than 650 °C, R_p has gradually played a predominant role in the total cell resistance. A decrease in the operating temperature from

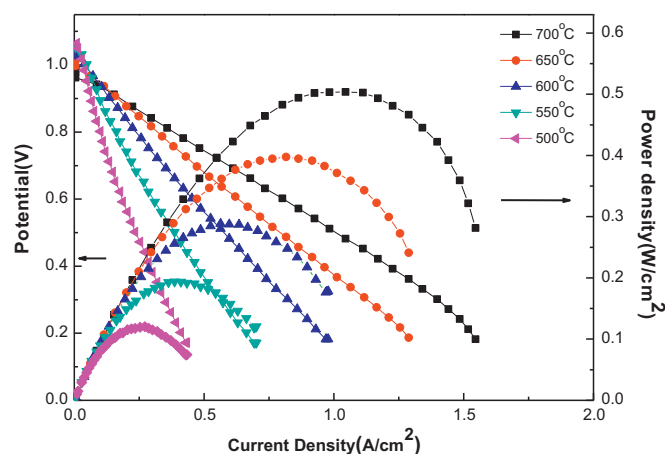**Fig. 4.** The I–V and I–P curves of the NiO–BZCYYb/NiO–BZCYYb/BZCYYb/SSFCu–SDC single cell with humidified hydrogen as the fuel at 500–700 °C.

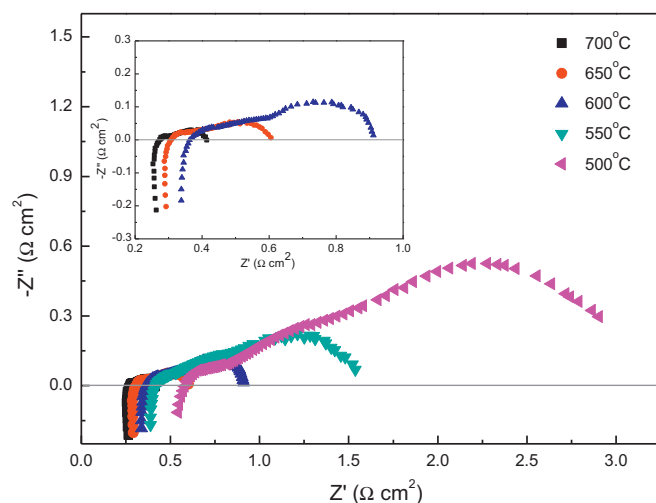**Fig. 5.** Electrochemical impedance spectra of the tested cell under open circuit conditions at 500–700 °C.
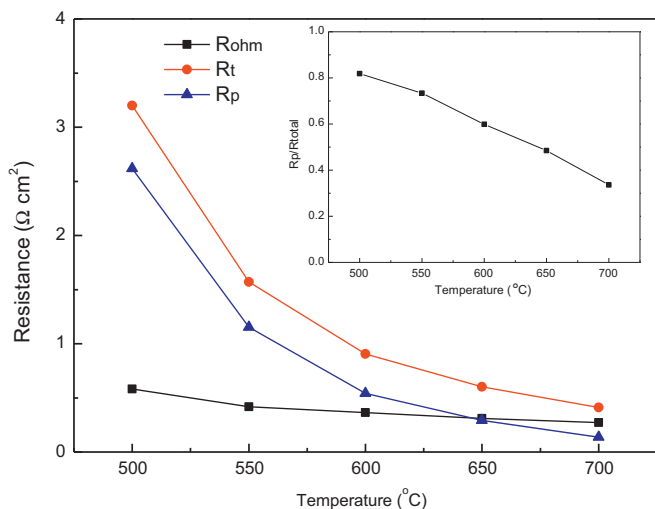
Fig. 6. The total cell resistances (R_t), interfacial polarization resistances (R_p), and ohmic resistances (R_{ohm}) obtained from the impedance spectra at different temperatures. Inset: the ratio of R_p/R_t.

700 to 500 °C, results in the R_p of the single cell increasing from 0.138 to 2.62 Ω cm², while the R_{ohm} only increasing from 0.273 to 0.581 Ω cm². It implies that the interfacial polarization resistance, which is dominated by the cathode–electrolyte interface greatly, has limited the cell performance in low temperature conditions [20]. For example, after the temperature decrease below 600 °C, the power density of single cell with SSFCu–SDC cathode will gradually exceed those with $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$–SDC and $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$–SDC cathodes, when the R_p of SSFCu–SDC cathode cell will be gradually exceeded by R_p of the later two cells, which increases relatively faster as the temperature decreasing [13,21]. The R_p of SSFCu–SDC cathode cell were 2.62, 1.15 and 0.54 Ω cm² at 500, 550 and 600 °C, while the R_p of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$–SDC cathode cell were 3.74, 1.27 and 0.48 Ω cm², and the R_p of $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$–SDC cathode cell were 3.66, 1.06 and 0.444 Ω cm², respectively. Other than the cathode materials, the electrode configuration of single cells also deserves further optimizing to achieve higher performance.

4. Conclusions

The present study demonstrated that cobalt-free SSFCu–SDC composite oxide, which was prepared by an auto ignition process, can be employed as a high performance cathode for proton-conducting IT-SOFCs. Thin BZCYYb electrolyte membrane and NiO–BZCYYb anode functional layer were prepared over porous anode substrate composed of NiO–BZCYYb by one-step dry-pressing/co-firing process. The laboratory-sized quad-layer NiO–BZCYYb/NiO–BZCYYb/BZCYYb/SSFCu–SDC single cell with about 15 μm thick electrolyte, exhibited high power densities of 505, 398, 289, 195 and 121 mW cm^{-2} at 700, 650, 600, 550 and 500 °C, respectively, which can be mainly attributed to several factors. And the polarization resistance (R_p) is low as 0.138 m² at 700 °C, agreeing with the cell performance well. The above results indicate the SSFCu–SDC composite to be a promising candidate cathode for proton-conducting IT-SOFCs.

References

[1] L. Yang, C.D. Zuo, S.Z. Wang, Z. Cheng, M.L. Liu, Adv. Mater. 20 (17) (2008) 3280.
[2] A.F. Sammells, R.L. Cook, J.H. White, J.J. Osborne, R.C. MacDuff, Solid State Ionics 52 (1992) 111.
[3] N.P. Brandon, S. Skinner, B.C.H. Steele, Annu. Rev. Mater. Res. 33 (2003) 183.
[4] L. Bi, S. Zhang, B. Lin, S. Fang, C. Xia, W. Liu, J. Alloys Compd. 473 (2009) 48.
[5] L. Yang, S.Z. Wang, K. Blinn, M.F. Liu, Z. Liu, Z. Cheng, M.L. Liu, Science 326 (2009) 126.
[6] L. Zhao, B.B. He, B. Lin, H.P. Ding, S.L. Wang, Y.H. Ling, R.R. Peng, G.Y. Meng, X.Q. Liu, J. Power Sources 194 (2009) 835.
[7] T. Horita, K. Yamaji, N. Sakai, Y. Xiong, T. Kato, H. Yokokawa, T. Kawada, J. Power Sources 106 (2002) 224.
[8] Y.H. Ling, L. Zhao, B. Lin, X.Z. Zhang, J. Yu, R.R. Peng, G.Y. Meng, X.Q. Liu, J. Alloys Compd. 493 (2010) 252.
[9] X.Y. Chen, J.S. Yu, S.B. Adler, Chem. Mater. 17 (2005) 4537.
[10] X.L. Dong, Z. Xu, X.F. Chang, C. Zhang, W.Q. Jin, J. Am. Ceram. Soc. 90 (12) (2007) 3923.
[11] Y. Teraoka, H. Shimokawa, C.Y. Kang, H. Kusaba, K. Sasaki, Solid State Ionics 177 (2006) 2245.
[12] Y.H. Ling, L. Zhao, B. Lin, Y.C. Dong, X.Z. Zhang, G.Y. Meng, X.Q. Liu, Int. J. Hydrogen Energy 35 (2010) 6905.
[13] W.P. Sun, L.T. Yan, B. Lin, S.Q. Zhang, W. Liu, J. Power Sources 195 (2010) 3155.
[14] F. He, T.Z. Wu, R.R. Peng, C.R. Xia, J. Power Sources 194 (2009) 263.
[15] E. Fabbri, S. Licoccia, E. Traversa, E.D. Wachsman, Fuel Cells 9 (2) (2009) 128.
[16] B.R. Sneha, V. Thangadurai, J. Solid State Chem. 180 (10) (2007) 2661.
[17] Y.H. Ling, X.Z. Zhang, S.L. Wang, L. Zhao, B. Lin, X.Q. Liu, J. Power Sources 195 (2010) 7042.
[18] H.P. Ping, X.J. Xue, J. Power Sources 195 (2010) 7038.
[19] F. Zhao, C. Jin, C.G. Yang, S.W. Wang, F.L. Chen, J. Power Sources 196 (2011) 688.
[20] T.Z. Wu, Y.Q. Zhao, R.R. Peng, C.R. Xia, Electrochim. Acta 54 (2009) 4888.
[21] W.P. Sun, Z. Shi, S.M. Fang, L.T. Yan, Z.W. Zhu, W. Liu, Int. J. Hydrogen Energy 35 (2010) 7925.