



Short communication

A novel cobalt-free $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\alpha}$ composite cathode for solid oxide fuel cells

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ABSTRACT

A new series of cobalt-free perovskite-type cathode materials $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.2$) for proton conducting intermediate temperature solid oxide fuel cells (IT-SOFCs) are prepared by a citric-nitrate process. The conductivities of the cathode materials are measured as functions of temperature (300–800 °C) and oxygen partial pressure ($1-10^{-10}$ atm). It is found that partial substitution of Mo for Fe site obviously enhances the conductivities of the cathode materials. Among the series of samples, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ (BSFM10) has the highest conductivity to be 192 S cm^{-1} in air at 400 °C. The samples of $0 \leq x \leq 0.15$ are p-type electronic conductors in the oxygen partial pressure range tested. An anode-supported $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\alpha}$ (BZCY) electrolyte membrane is successfully fabricated by a simple, cost-effective spin coating process. Peak power densities of the hydrogen/air fuel cell using BZCY electrolyte membrane and BSFM10–BZCY composite cathode reach 153 mW cm^{-2} at 600 °C, 253 mW cm^{-2} at 650 °C and 420 mW cm^{-2} at 700 °C, respectively. The interfacial polarization resistance (R_p) for the fuel cell is as low as $0.15 \Omega \text{ cm}^2$ at 700 °C under open circuit conditions.

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1. Introduction

Solid oxide fuel cell as a new power generation device has attracted worldwide attention since it provides many advantages over traditional energy conversion systems including high power conversion efficiency, fuel adaptability, reliability, little environment pollution and so on [1–3]. A typical cell essentially consists of porous anode and cathode as well as dense ion conducting electrolyte. Yttria stabilized zirconia (YSZ) is often applied in SOFCs due to its high performance and good chemical stability. However, relatively high operating temperatures (between 800 °C and 1000 °C) not only lead to high fabrication costs for SOFCs systems, but also limit their practical application [4]. To make SOFCs technologies economically competitive, the operating temperature must be reduced so that less expensive materials may be used in the SOFCs systems. Therefore, there is much interest in developing proton conducting oxide based IT-SOFCs. The state-of-the-art proton conducting materials are BaCeO_3 -based oxides. Compared to YSZ oxide-ionic conductor, the doped BaCeO_3 exhibits lower activation energy and higher proton conductivity as well as higher energy efficiency at intermediate temperature of 300–800 °C. However, doped

BaCeO_3 displays poor chemical stability in water vapor and carbon dioxide containing atmospheres. Consequently, it is necessary to improve their chemical stability without much impairing conductivity. In contrast, BaZrO_3 -based oxides have sufficiently high chemical stability in spite of relatively low conductivity [5]. It was demonstrated that the cerates and the zirconates may form solid solutions in any fraction, which may have both adequate proton conductivity and sufficient chemical stability under IT-SOFC conditions. Recently, a new composition, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY), was reported to display both the highest ionic conductivity among all known cerate–zirconate based electrolyte materials at temperatures below 550 °C and sufficient chemical as well as thermal stability over a wide range of conditions relevant to fuel cell operations [6].

The cathode material is one of the most important components for determining the performance of IT-SOFCs. For a proton conducting electrolyte based IT-SOFC, a complex system including transport of three charge species, i.e., proton, oxide ion and electron, reduction of oxygen molecules and formation of water molecules on charging is formed at cathode side. Consequently, the development of proper cathode materials is critical for high performance IT-SOFCs. Many cobalt-containing perovskite-type cathode materials such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) [2], $\text{Ba}_{1-x}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (BCFN) [7], $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) [8] and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) [9] have been reported as possible cathodes due to the low polarization resistance and the high oxygen reduction activation. However, these cobalt-doped materials

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are faced with some problems like high thermal expansion coefficient and high cost of cobalt element [10]. For this reason, the cobalt-free cathode materials with sufficient catalytic activity for IT-SOFCs have attracted considerable attention [11,12].

In this study, a new series of cobalt-free perovskite-type cathode materials $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.2$) for proton conducting IT-SOFCs were prepared by a citric-nitrate process. The conductivities of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ were measured as functions of temperature (300–800 °C) and oxygen partial pressure ($1-10^{-10}$ atm). An anode-supported $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte membrane was successfully fabricated by a simple, cost-effective spin coating process. The fuel cell with BSMF10-BZCY composite cathode was assembled and tested from 600 °C to 700 °C with hydrogen as the fuel and air as the oxidant.

2. Experimental

All the reagents used in the present study are analytical reagent grade. The BZCY powders used for electrolyte and composite electrode materials were prepared by a citric-nitrate process. $\text{Ba}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water at the stoichiometric ratio under stirring and citric acid was added as the complexant with a molar ratio of citric acid:total metal cations = 1.8:1. Then the solution was converted to a viscous gel under heating and stirring conditions, and the gel was ignited to flame. The BZCY powders with perovskite structure were obtained by calcining the resultant ash-like materials at 1100 °C for 10 h.

The as-prepared BZCY powders were blended with NiO and starch (as pore former) with a weight ratio of 35:65:10 using ball-milling in ethanol for 3 h. The well-mixed powders were pressed into a green pellet of 20 mm in diameter and 1 mm in thickness under 50 MPa, followed by pre-sintering at 1000 °C for 2 h as an anode substrate.

In addition, the as-prepared BZCY powders were passed through a sieve (200 mesh) to get uniform powders. Homogeneous and stable electrolyte (BZCY) slurry was prepared by mixing BZCY powders with a homemade organic binder consisting of ethyl cellulose and terpineol. The weight ratio of BZCY powders to the organic binder was 0.6. The BZCY slurry was spin-coated onto the pre-sintered NiO-BZCY anode substrate described above and sintered at 1400 °C for 5 h, the half cell was obtained.

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.2$) used as cathode materials for IT-SOFCs also were prepared by a citric-nitrate process. The required amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in deionized water under stirring and citric acid was added as the complexant with a molar ratio of citric acid: metal = 1.8:1. Then the solution was evaporated under heating and stirring to form a viscous gel, and ignited to flame. The resulting ash was pressed into pellets (1 mm in thickness and 20 mm in diameter) by a hydrostatic pressure of 200 MPa, and then sintered at 950 °C for 5 h. The relative densities of the obtained $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ceramic pellets were determined by geometrical measurements to be higher than 92% of theoretical density. Some of the ceramic pellets were used for the measurement of conductivity as functions of temperature (300–800 °C) and oxygen partial pressure ($1-10^{-10}$ atm) by AC impedance method using an electrochemical workstation (Zahner IM6ex). The applied frequency range was from 0.1 Hz to 100 kHz, and the signal amplitude was 20 mV. The oxygen partial pressures were adjusted by mixing O_2 , air, Ar and H_2 in the proper ratio. Some of the ceramic pellets were used as the cathode material for SOFCs. A typical single cell fabrication is as follows. The $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ (BSFM10) ceramic pellet was ground and mixed with the BZCY powders (weight ratio of 7:3) in ethanol by ball milling for 3 h,

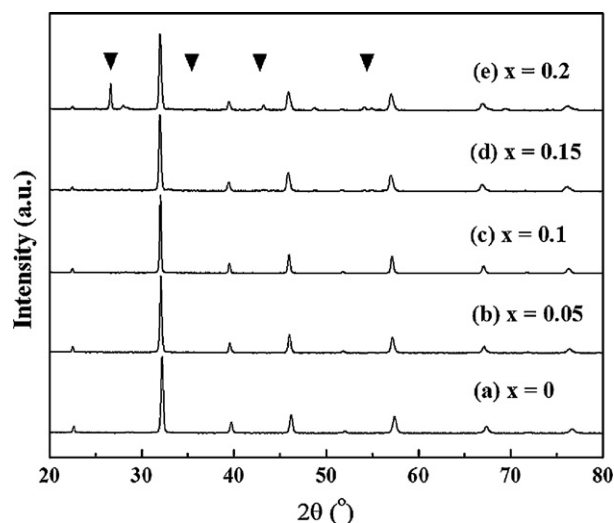


Fig. 1. XRD patterns for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.2$) ceramic cathode materials sintered at 950 °C for 5 h.

and dried by an infrared lamp, then passed through a sieve (200 mesh) to get uniform powders. The composite cathode slurry was obtained by mixing as-prepared BSMF10-BZCY powders with a 6 wt% ethyl cellulose-terpineol binder thoroughly. The composite cathode slurry was coated onto the pre-sintered membrane with a cathode surface area of ca. 0.5 cm² and co-sintered with the BZCY membrane at 900 °C for 2 h. Thus, a single cell based on BSMF10-BZCY composite cathode and BZCY electrolyte membrane was obtained. Ag-Pd paste was painted on two surfaces (ca. 0.5 cm²) of the cell, dried by an infrared lamp and then fired at 900 °C for 20 min as current collectors.

The single cell was tested from 600 °C to 700 °C with hydrogen as fuel and air as oxidant, respectively. The flow rates of gases were 50 ml min⁻¹. The electrochemical impedance spectra (EIS), *I*-*V* and *I*-*P* curves of the fuel cell were determined by an electrochemical workstation (Zahner IM6ex). The applied frequency range and the signal amplitude were the same as the above. The phase structure analysis of the samples was carried out by powder X-ray diffraction (XRD) with Ni filter using $\text{Cu K}\alpha$ radiation on a Panalytical X'pert Pro MPD diffractometer under tube voltage of 40 kV and tube current of 40 mA. The scanning range and rate were 20–80° and 2.00° min⁻¹, respectively. Morphologies of the fuel cell were observed by field-emission scanning electron microscopy (FESEM, Hitachi S-4700).

3. Results and discussion

The XRD patterns of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.20$) ceramic samples sintered at 950 °C for 5 h are shown in Fig. 1. As shown, the ceramic samples of $0 \leq x \leq 0.15$ are the perovskite-type cubic phase structure, whereas for the ceramic sample of $x = 0.20$, some diffraction peaks of impurity appear, which is identified to be molybdenum oxide (▼). Obviously, the solid solution limit in the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ceramic samples is $x = 0.15$.

Fig. 2 shows the electrical conductivities of ceramic samples $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.15$) in the temperature range from 300 °C to 800 °C in air. All the samples reveal the same trend, i.e., the conductivity increases with increasing temperature up to 400 °C and decreases with further increasing temperature. The trend may be attributable to the reason that the samples display a semi-conductor conduction behavior between 300 °C and 400 °C, whereas a metallic-like conduction behavior above 400 °C. This trend is similar to that reported by Chen et al. [13]. It can be seen that electrical conductivity increases in the order: $\sigma(x=0.1) > \sigma$

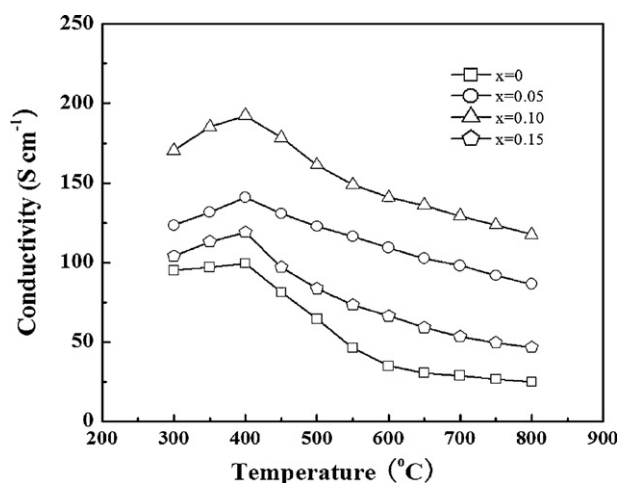


Fig. 2. Conductivities of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.15$) measured by the AC impedance method in air from 300 °C to 800 °C.

($x=0.05$) $>\sigma$ ($x=0.15$) $>\sigma$ ($x=0$). Among the measured samples, the sample of $x=0.1$ has the highest conductivity (192 S cm^{-1} at 400 °C). In addition, the sample of $x=0.1$ has much higher conductivity of 140 S cm^{-1} in air at 600 °C than that (32 S cm^{-1}) for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ cathode material under same conditions reported by Jung et al. [14].

In order to investigate the conduction nature, we measured the conductivities of the samples as functions of oxygen partial pressure ($p\text{O}_2 = 1-10^{-10}$ atm). Typical $\log\sigma$ vs. $\log p\text{O}_2$ curves at 600 °C for the samples of $x=0$ (BSF) and $x=0.1$ (BSFM10) are presented in Fig. 3. It can be seen from Fig. 3 that both samples display a similar conduction. In the oxygen partial pressure range tested, the conductivities increase with $p\text{O}_2$ increasing, indicating that the samples are p-type electronic conductors. It can also be seen from Fig. 3 that the conductivity for the sample with Mo (BSFM10) is about four times as high as that for the sample without Mo (BSF). The possible interpretation is as follows. Mo^{6+} ions may be reduced to Mo^{5+} ions to some extent with oxygen partial pressure decreasing in the range of $p\text{O}_2 = 1-10^{-10}$ atm. Similarly, Fe^{4+} ions may be also reduced to Fe^{3+} ions to some extent. Mo^{6+} , Mo^{5+} , Fe^{4+} and Fe^{3+} ions have close ionic radii to be 73 pm, 75 pm, 72.5 pm and 78.5 pm in six-coordination, respectively [15]. Hence, both Mo^{6+} and Mo^{5+} ions can enter into the lattice of BSF in a solid solution form as confirmed by XRD. The existence of multivalent $\text{Fe}^{4+}-\text{Fe}^{3+}$

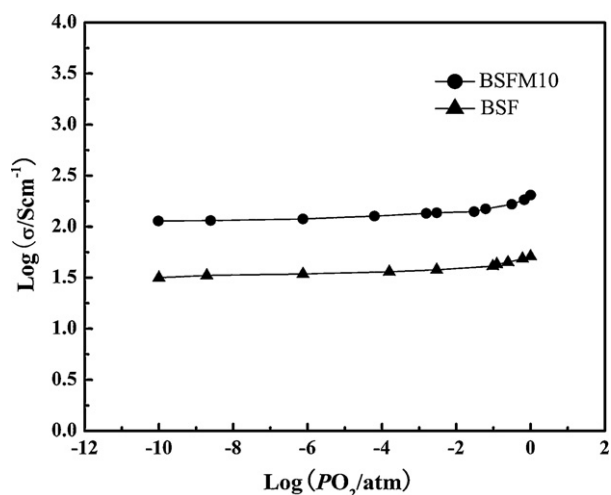


Fig. 3. Conductivities of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (BSF) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ (BSFM10) as a function of oxygen partial pressure at 600 °C.

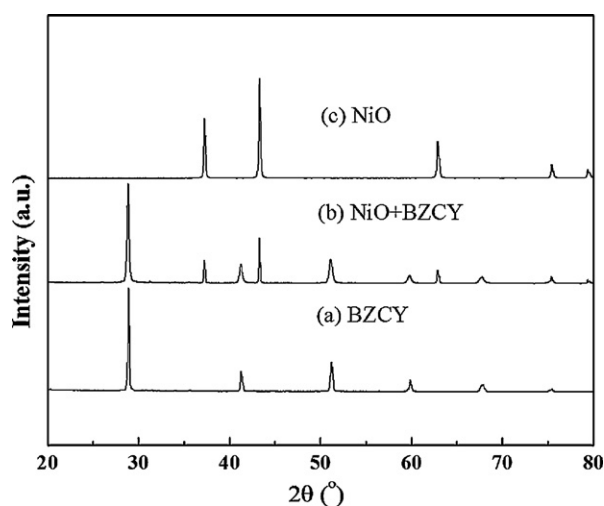


Fig. 4. XRD patterns for (a) BZCY electrolyte membrane sintered at 1400 °C for 5 h, (b) NiO-BZCY anode substrate sintered at 1400 °C for 5 h and (c) NiO.

is responsible for the p-type electronic conduction in both the samples without Mo (BSF) and with Mo (BSFM10). For the sample with Mo (BSFM10), the existence of $\text{Mo}^{6+}-\text{Mo}^{5+}$ further enhances the p-type electronic conduction, resulting in higher conductivity than the sample without Mo (BSF). This is similar to the case of $\text{Fe}^{3+}-\text{Fe}^{4+}$ and $\text{Co}^{3+}-\text{Co}^{4+}$ existing in $\text{La}_{0.6}\text{Sr}_{0.4-z}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ [8].

In order to further investigate the conduction nature, we measured the oxide-ionic transference numbers of the BSF and BSFM10 samples in an oxidizing atmosphere by oxygen concentration cell method [16]. It was found that the oxide-ionic transference numbers of both BSF and BSFM10 samples were all less than 0.01, further confirming that the samples were all the p-type electronic conductors.

Fig. 4a shows that the BZCY electrolyte membrane sintered at 1400 °C for 5 h was well-crystallized as a single phase with perovskite-type structure. Fig. 4b displays the XRD pattern of anode substrate NiO-BZCY (weight ratio of 65:35) sintered at 1400 °C for 5 h. It is clear that there are only peaks corresponding well to BZCY in electrolyte membrane (Fig. 4a) and NiO (Fig. 4c), which gives no evidence for the formation of other substance.

Fig. 5a shows surface FESEM image of BZCY membrane deposited on the anode substrate after sintering at 1400 °C for 5 h. It can be seen that the membrane is sufficiently dense, uniform and crack-free with an average grain size of 2–5 μm . It can also be seen from the cross-sectional image of the cell after tested (Fig. 5b) that the thickness of the electrolyte membrane is about 35 μm , and the membrane adheres to the anode substrate and the cathode firmly.

The electrochemical performance of single cell is shown in Fig. 6, including $I-V$ and $I-P$ curves. The open circuit voltages (OCVs) of the single cell are 1.058 V at 600 °C, 1.03 V at 650 °C and 1.01 V at 700 °C, respectively. Obviously, they are close to the theoretical open-circuit voltage values, indicating the electrolyte membrane (thickness: 35 μm) is sufficiently dense. The maximum power densities of the single cell are 420 mW cm^{-2} at 700 °C, 253 mW cm^{-2} at 650 °C and 153 mW cm^{-2} at 600 °C, respectively. In spite of larger BZCY electrolyte membrane thickness for the cell, the power density is higher than that for the cell with a $\text{SmBaCo}_2\text{O}_{5+x}$ cathode and BZCY electrolyte thickness of 25 μm reported by Lin et al. [17]. The desirable performance at intermediate temperatures in this study is mainly attributed to the low interfacial polarization resistance of the single cell.

In order to evaluate the performance of composite cathode (BSFM10-BZCY) in the single cell, the impedance spectra for the cell under open-current conditions at different temperatures are

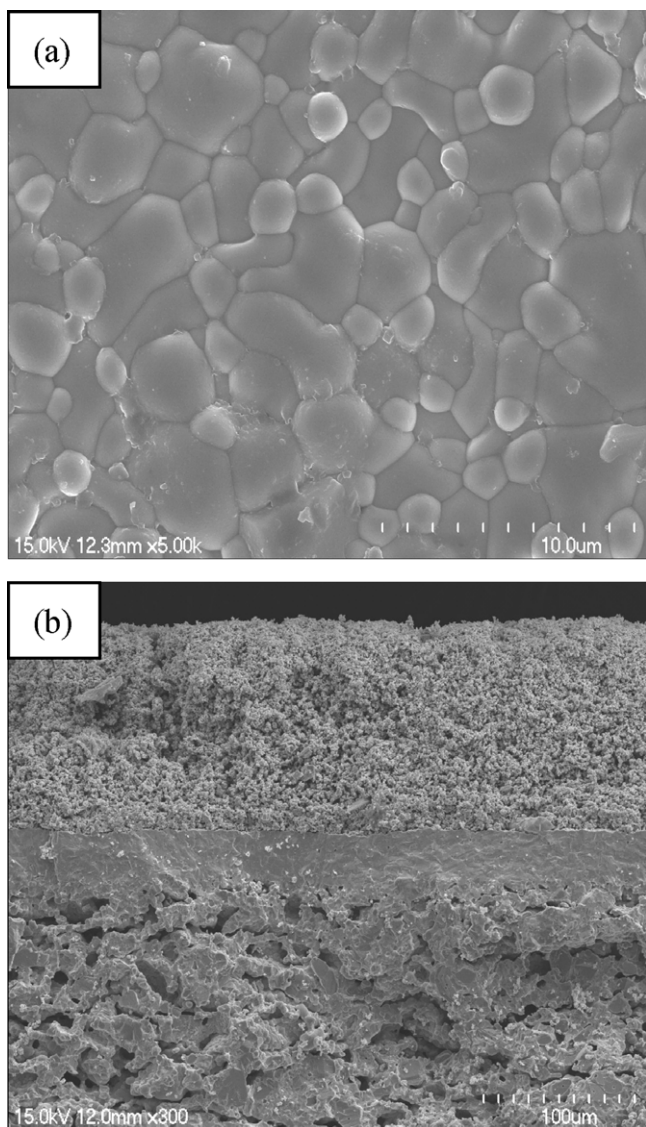


Fig. 5. Microstructures for (a) the surface of BZCY electrolyte membrane sintered at 1400 °C for 5 h and (b) the cross-section of the single cell after testing.

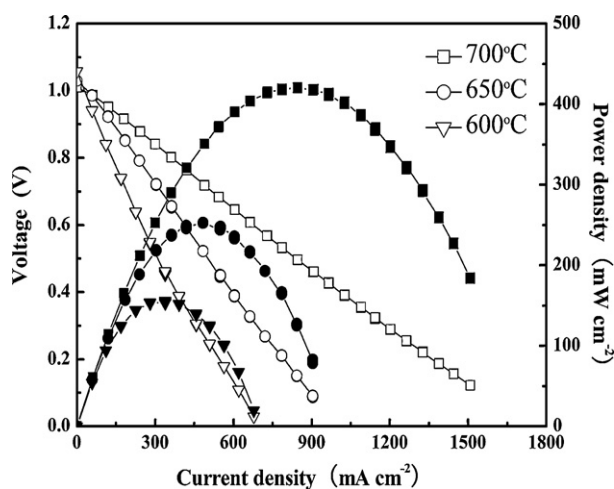


Fig. 6. *I*-*V* and *I*-*P* curves of single cell NiO-BZCY|BZCY|BSFM10-BZCY using hydrogen as the fuel and air as the oxidant at different temperatures.

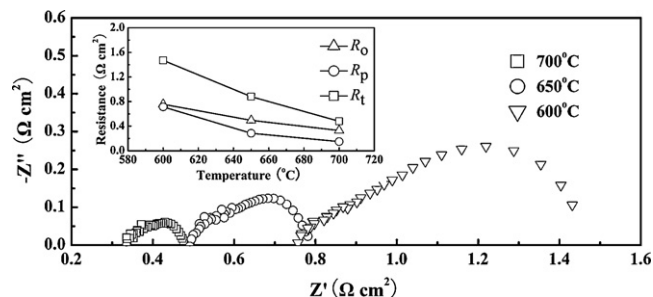


Fig. 7. Impedance spectra of the tested cell under open-current conditions at different temperatures. The inset expresses the dependence of R_0 , R_p and R_t of the cell on the temperature.

shown in Fig. 7. The impedance spectra consist of two depressed semicircles. The high-frequency semicircle is related to the ohmic resistance (R_0) of the electrolyte, while the low-frequency semicircle is relevant to the resistance of the interfacial polarization resistance (R_p) of the cell. The R_0 and the total resistance R_t may be obtained from the intercepts with the real axis at high and low frequencies in the spectra, respectively. The difference between the R_0 and R_t represents the R_p of the cell. As shown in Fig. 7, the R_0 and R_p are 0.756 $\Omega \text{ cm}^2$ and 0.714 $\Omega \text{ cm}^2$ at 600 °C, 0.495 $\Omega \text{ cm}^2$ and 0.285 $\Omega \text{ cm}^2$ at 650 °C, 0.33 $\Omega \text{ cm}^2$ and 0.15 $\Omega \text{ cm}^2$ at 700 °C, respectively. The R_p (0.15 $\Omega \text{ cm}^2$) in this study is lower than the values of 0.35 $\Omega \text{ cm}^2$ for the cathode of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ [18] and 0.18 $\Omega \text{ cm}^2$ for the cathode of $\text{GdBaFe}_2\text{O}_{5+\delta}$ [19] at 700 °C with same electrolyte and anode. It is also clear from Fig. 7 that the R_0 is higher than the R_p , indicating the R_0 is dominant in determining the performance of the anode-supported BZCY membrane fuel cell. So we can deduce that development of proper cathode materials is a grand challenge for IT-SOFCs.

4. Conclusions

In this study, a new series of cobalt-free cathode materials $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.2$) for proton conducting IT-SOFCs have been prepared by a citric-nitrate process. The solid solution limit in the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ceramic samples is $x = 0.15$. The partial substitution of Mo for Fe site obviously enhanced the conductivity of the cathode materials. Among the series of samples, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ (BSFM10) has the highest conductivity of 192 S cm^{-1} in air at 400 °C. The samples were p-type electronic conductors in the oxygen partial pressure range tested. The dense BZCY electrolyte membrane was fabricated on a porous anode substrate by a simple slurry spin coating process. The performance of single cell NiO-BZCY|BZCY|BSFM10-BZCY was tested at 600–700 °C with hydrogen as the fuel and air as the oxidant. The OCVs of cell were close to the theoretical values, and the peak power densities reached 153 mW cm^{-2} at 600 °C, 253 mW cm^{-2} at 650 °C and 420 mW cm^{-2} at 700 °C, respectively. A low interfacial polarization resistance was observed to be 0.15 $\Omega \text{ cm}^2$ at 700 °C. The results indicate that the BSFM10 is a promising cobalt-free cathode material for proton conducting IT-SOFCs.

Acknowledgments

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References

- [1] E.P. Murray, T. Tsai, S.A. Barnett, *Nature* 400 (1999) 649.
- [2] Z. Shao, S.M. Haile, *Nature* 431 (2004) 170.
- [3] W. Wang, Z. Yang, H. Wang, G. Ma, W. Gao, Z. Zhou, *J. Power Sources* 196 (2011) 3539.
- [4] K. Chen, Y. Tian, Z. Lu, N. Ai, X.Q. Huang, W. Su, *J. Power Sources* 186 (2009) 128.
- [5] K.H. Ryu, S.M. Haile, *Solid State Ionics* 125 (1999) 355.
- [6] C. Zuo, S. Zha, M. Liu, M. Hatano, M. Uchiyama, *Adv. Mater.* 18 (2006) 3318.
- [7] Z. Liu, L.-Z. Cheng, M.-F. Han, *J. Power Sources* 196 (2011) 868.
- [8] A. Mineshige, J. Izutsu, M. Nakamura, K. Nigaki, J. Abe, M. Kobune, S. Fujii, T. Yazawa, *Solid State Ionics* 176 (2005) 1145.
- [9] C. Xia, W. Rauch, F. Chen, M. Liu, *Solid State Ionics* 149 (2002) 11.
- [10] H. Ding, B. Lin, X. Liu, G. Meng, *Electrochem. Commun.* 10 (2008) 1388.
- [11] L. Zhao, B. He, Y. Ling, Z. Xun, R. Peng, G. Meng, X. Liu, *Int. J. Hydrogen Energy* 35 (2010) 3769.
- [12] B. Wei, Z. Lu, X. Huang, Z. Liu, J. Miao, N. Li, W. Su, *J. Am. Ceram. Soc.* 90 (2007) 3364.
- [13] Z. Chen, R. Ran, W. Zhou, Z. Shao, S. Liu, *Electrochim. Acta* 52 (2007) 7343.
- [14] J.I. Jung, S.T. Mixture, D.D. Edwards, *Solid State Ionics* 181 (2010) 1287.
- [15] R.D. Shannon, *Acta Cryst. A* 32 (1976) 751.
- [16] G. Ma, F. Zhang, J. Zhu, G. Meng, *Chem. Mater.* 18 (2006) 6006.
- [17] B. Lin, Y. Dong, R. Yan, S. Zhang, M. Hu, Y. Zhou, G. Meng, *J. Power Sources* 186 (2009) 446.
- [18] 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.
- [19] H. Ding, X. Xue, *J. Power Sources* 195 (2010) 4139.