



Short communication

Low-temperature protonic ceramic membrane fuel cells (PCMFCs) with $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ cubic perovskite cathode

Hanping Ding^a, Bin Lin^a, Yinzhu Jiang^b, Songlin Wang^a, Daru Fang^a,
Yingchao Dong^a, Shanwen Tao^b, Ranran Peng^a, Xingqiu Liu^{a,*}, Guangyao Meng^a

^a Department of Materials Science and Engineering, University of Science and Technology of China (USTC), Hefei 230026, PR China

^b Department of Chemistry, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK

ARTICLE INFO

Article history:

Received 17 June 2008

Received in revised form 14 July 2008

Accepted 15 July 2008

Available online 26 July 2008

Keywords:

Protonic ceramic membrane fuel cells

$\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$

Cathode

Cubic perovskite

$\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$

ABSTRACT

The $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (SCS) composite oxide with cubic perovskite structure was synthesized by a modified Pechini method and examined as a novel cathode for protonic ceramic membrane fuel cells (PCMFCs). At 700 °C and under open-circuit condition, symmetrical SCS cathode on $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) electrolyte showed low polarization resistances (R_p) of 0.22 Ωcm^2 in air. A laboratory-sized tri-layer cell of NiO–BZCY7/BZCY7/SCS was operated from 500 to 700 °C with humidified hydrogen (~3% H_2O) as fuel and the static air as oxidant. A high open-circuit potential of 1.004 V, a maximum power density of 259 mW cm^{-2} , and a low polarization resistance of the electrodes of 0.14 Ωcm^2 was achieved at 700 °C.

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1. Introduction

The development of solid oxide fuel cells (SOFCs) has reached its new stage characterized with thin electrolytes on porous electrode support, in which the most important fabrication techniques developed are almost all concerned with inorganic membranes, and so can be named as ceramic membrane fuel cells (CMFCs) [1]. Protonic ceramic membrane fuel cells (PCMFCs) based on proton-conducting electrolytes may exhibit more advantages than CMFCs based on oxygen-ion electrolytes in many respects, such as low activation energy [2] and high energy efficiency [3].

There is now considerable interest in proton-conducting oxide electrolytes for PCMFCs. Many perovskite-type oxides show high proton conductivity in a reducing atmosphere. One of the major challenges for this type of proton conductor is a proper compromise between conductivity and chemical stability. Zuo et al. [4] reported a new composition, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) that exhibited both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation. BZCY7, at temperatures below 550 °C, displayed

the highest ionic conductivity of all known electrolyte materials for SOFC applications.

The development of proper cathode materials for PCMFCs in order to improve materials compatibility and reduce costs remains a challenge. Many simple perovskite-type mixed ionic–electronic conductors such as doped LaCoO_3 [5], BaCoO_3 [6] or LaFeO_3 [7] have been extensively studied as possible cathodes, however not much attention has been paid to the perovskite structures such as doped SrCoO_3 . Recently, Aguadero et al. [8] have prepared a novel $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ perovskite, and shown its potential use as a MIEC in SOFCs. We have evaluated the performance of this material working as a cathode in SOFCs based on oxide ion conductors (SDC) [9]. In this work, the $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ cubic perovskite synthesized by a modified Pechini method was examined as a new cathode for PCMFCs based on proton BZCY7 electrolyte.

2. Experimental

The $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (SCS) powder was synthesized by Pechini method. Stoichiometric amounts of commercial Sb_2O_3 , SrNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in a citric acid aqueous solution containing some drops of HNO_3 . The solution was slowly evaporated, leading to an organic gel, which was dried at 120 °C and slowly decomposed at temperatures of up to 600 °C. A black phase-pure SCS powder was obtained after calcinating the precursor

* Corresponding author. Tel.: +86 551 3606249; fax: +86 551 3607627.
E-mail address: xqliu@ustc.edu.cn (X. Liu).

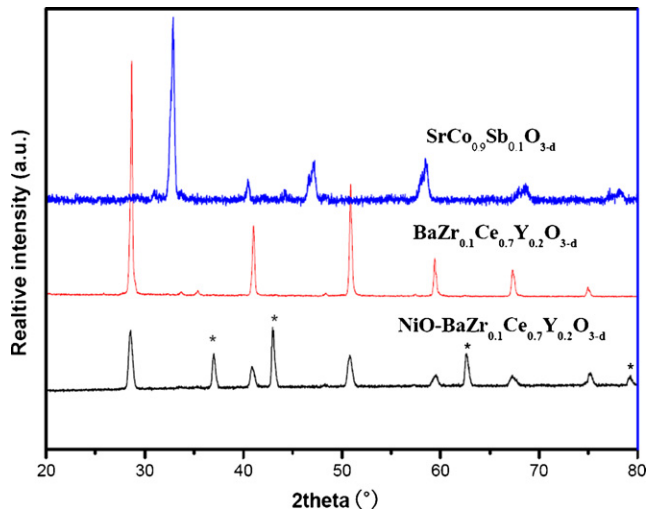


Fig. 1. X-ray diffraction patterns of (a) the SrCo_{0.9}Sb_{0.1}O_{3-delta} (SCS) powder, the bi-layer of (b) BZCY7 membrane and (c) NiO–BZCY7 anode substrate (*: NiO).

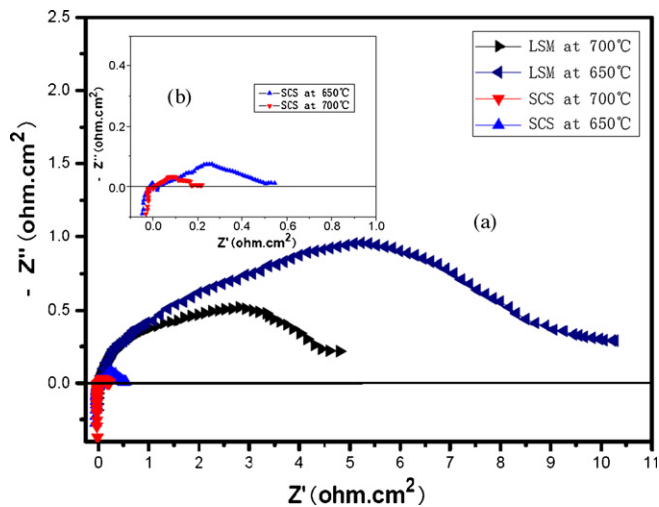


Fig. 2. Comparison of the impedance spectra for (a) the La_{0.8}Sr_{0.2}MnO_{3-delta} (LSM) cathode and (b) the SrCo_{0.9}Sb_{0.1}O_{3-delta} (SCS) cathode in air.

at 1000 °C for 10 h. The BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-delta} (BZCY7) powders were synthesized by a modified Pechini method with citrate and ethylenediamine tetraacetic acid (EDTA) as parallel complexing agents. Y₂O₃ was dissolved in nitric acid first, and calculated amounts of Ba(NO₃)₂·9H₂O, Ce(NO₃)₃·6H₂O, Zr(NO₃)₄·4H₂O were dissolved in EDTA–NH₃ aqueous solution. After agitation for a certain time, a proper amount of citric acid was introduced, with the molar ratio of EDTA: citric acid: total of metal cations controlled at around 1:1.5:1. The solution was heated under stirring, converted to a viscous gel and ignited to flame, resulting in the ash. The resulting ash-like material was afterwards calcined in air at 1100 °C for 5 h. Fine SCS powder was mixed thoroughly with a 6wt% ethylcellulose–terpineol binder to prepare the cathode slurry, which was then painted on both sides of dense BZCY7 pellets, forming SCS/BZCY7/SCS symmetric cells. The cathodes were calcined at 1000 °C for 3 h in air. For comparison, a conventional La_{0.8}Sr_{0.2}MnO_{3-delta} (LSM) cathode was also fabricated (calcined at 1150 °C for 3 h) and characterized.

The anode-supported BZCY7 bi-layer (Ø15 mm) was prepared by a dry-pressing method. NiO + BZCY7 + corn starch mixture (60%:40%:20% in weight) was pre-pressed at 200 MPa as substrate about 0.95 mm. Then the anode functional layer (mixture of NiO + BZCY7, NiO: BZCY7 = 50%:50%) was pressed onto the substrate. Finally loose BZCY7 powder, calcined at 1100 °C for 5 h to form a pure perovskite oxide, was uniformly distributed onto anode substrate, co-pressed at 250 MPa and sintered subsequently at 1400 °C for 5 h to densify the BZCY7 membrane. The cathode slurry was then painted on BZCY7 electrolyte films, and sintered at 1000 °C for 3 h in air to form cells.

The phase identification of the prepared SCS powders was studied with the powder X-ray diffraction by Cu Kα radiation (D/Max-gA, Japan). For electrochemical measurements, a silver paste was painted on the surfaces of SCS/BZCY7/SCS symmetric cells as a current collector. Electrochemical impedance spectroscopy (EIS) was measured by a frequency response analyzer (Chi604c, Shanghai Chenhua) in the temperature range of 600–800 °C in air. Single cells were tested from 550 to 700 °C in a home-developed cell testing system with humidified hydrogen (~3% H₂O) as fuel and the static air as oxidant, respectively. The flow rate of fuel gas was about 40 ml min⁻¹. The cell voltages and output current of the cells were measured with digital multi-meters (GDM-8145). AC impedance spectroscopy (Chi604c, Shanghai Chenhua) was performed on the cell under open-current conditions from

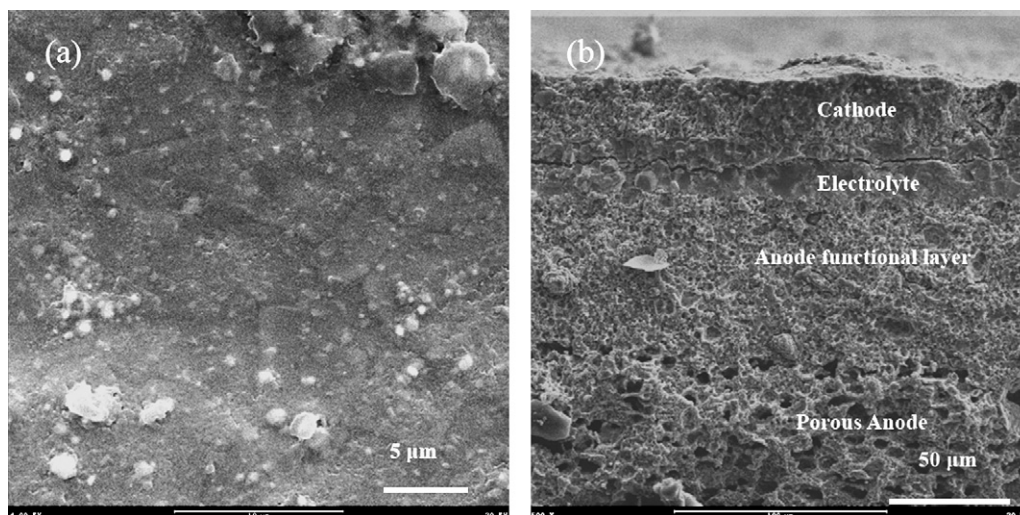


Fig. 3. SEM micrographs of as-prepared cells after testing: (a) the surface of BZCY7 electrolyte and (b) the cross-section of tri-layer cell of NiO–BZCY7/BZCY7/SCS.

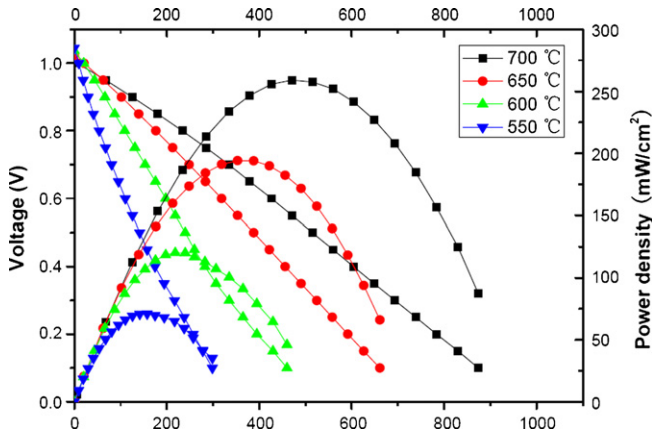


Fig. 4. Performance of the tri-layer cell with hydrogen at different temperatures.

550 to 700 °C. A scanning electron microscope (SEM) was used to observe the microstructure of the cells after testing.

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of SCS exhibits a subtle tetragonal distortion of a simple perovskite unit cell, with $a=b \sim 3.87 \text{ \AA}$ and $c \sim 3.90 \text{ \AA}$ [8]. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at 1400 °C for 5 h. It could be clearly seen that there were only peaks corresponding to $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) in electrolyte membrane (Fig. 1(b)) and to NiO and BZCY7 in the anode substrate (Fig. 1(c)), which gave no evidence for the formation of other substance.

Fig. 2 shows a comparison of typical impedance spectra of LSM and pure SCS cathodes under open-circuit conditions in air. The observed polarization resistances for the SCS cathode are as low as $0.22 \text{ } \Omega\text{cm}^2$ and $0.54 \text{ } \Omega\text{cm}^2$ at 700 °C and 650 °C, respectively. For the LSM cathode, its corresponding resistances are $4.8 \text{ } \Omega\text{cm}^2$ and $10.3 \text{ } \Omega\text{cm}^2$. Obviously, the SCS electrode exhibits a much higher electrochemical activity for O_2 reduction, and the polarization resistance of SCS is only 4.6–5.2% of the LSM at the measured temperatures.

Fig. 3(a) is the SEM image of surface morphology of the as-prepared tri-layer cell of BZCY7 electrolyte on the porous anode support after testing. It can be seen that the BZCY7 membrane

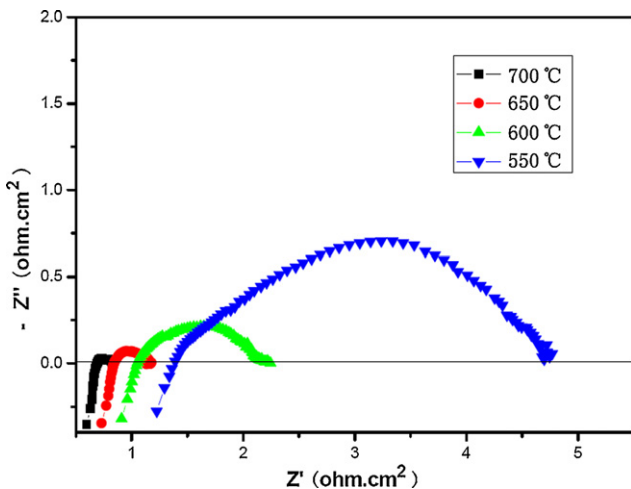


Fig. 5. Impedance spectra of the as-prepared cells under open-current conditions at different temperatures.

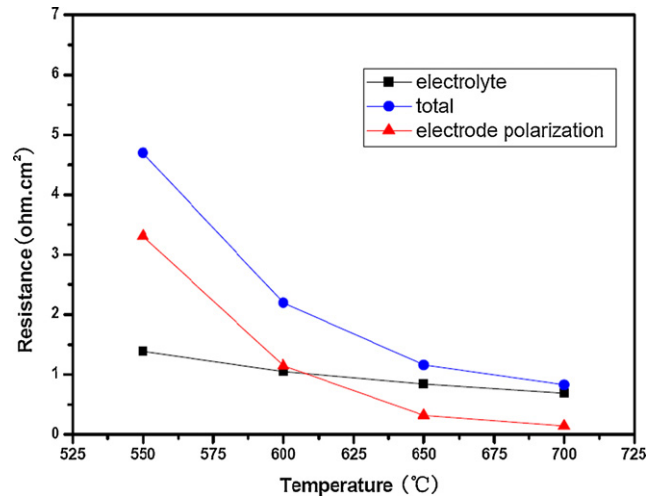


Fig. 6. The interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the tri-layer cell measured under open-circuit conditions at different temperatures.

is completely dense. There is no pores and cracks on the surface. Fig. 3(b) shows the cross-sectional view of the as-prepared tri-layer cell, Ni–BZCY7/BZCY7/SCS after testing. As can be seen, the BZCY7 electrolyte is about $20 \text{ } \mu\text{m}$ in thickness, quite dense and adhered very well to anode functional layer and cathode. The anode functional layer is used to optimize the interface of anode and electrolyte which is about $70 \text{ } \mu\text{m}$ in thickness.

Fig. 4 presents the I – V and I – P characteristics of the as-prepared cell. The almost linear I – V curve implies little electrode polarization. And also, we can deduce that the voltage drop of the cell is mostly from IR fall across the BZCY7 electrolyte because of both anode and cathode materials exhibiting much higher conductivity than electrolyte materials. The high open-circuit voltages (OCV) of 1.004 V at 700 °C, 1.024 V at 650 °C, 1.037 V at 600 °C and 1.045 V at 550 °C indicate that the electrolyte membrane is sufficiently dense. Peak power densities were 259, 194, 120 and 71 mW cm^{-2} at 700, 650, 600 and 550 °C, respectively.

In order to evaluate the performance of SCS cubic perovskite working as a cathode in a whole protonic ceramic membrane fuel cell, the impedance spectra of the as-prepared cells under open-current conditions at different temperatures as shown in Fig. 5. In these spectra, the intercept with the real axis at low frequencies represents the total resistance of the cell and the value of the intercept at high frequency is the electrolyte resistance, while the difference of the two values corresponds to the sum of the electrode polarization resistances of the cell. As expected, the increase of the measurement temperature resulted in a significant reduction of the electrode polarization resistances, typically from $3.31 \text{ } \Omega\text{cm}^2$ at 550 °C to $0.14 \text{ } \Omega\text{cm}^2$ at 700 °C. The results indicated that the SCS cathode is a good candidate for operation at or below 650 °C. Further, Fig. 6 shows that the cell performance is influenced by the electrode polarization resistances, especially at temperatures below 600 °C, where the cell performance is essentially determined by the interfacial resistances. At 550 °C, the polarization resistance of the electrodes is $\sim 3.31 \text{ } \Omega\text{cm}^2$ whereas the resistance of the electrolyte is only $\sim 1.39 \text{ } \Omega\text{cm}^2$. So we can deduce that development of proper cathode materials is a great challenge for developing the low-temperature PCMFCS.

4. Conclusions

In this study, cubic perovskite-type oxide SCS was successfully synthesized by a modified Pechini method and characterized as a

novel cathode for the low-temperature PCMFCS. The polarization resistances of symmetrical SCS cathode in air were as low as 0.22 and 0.54 Ωcm^2 at 700 and 650 °C, respectively. A laboratory-sized tri-layer cell of NiO–BZCY7/BZCY7/SCS, not yet optimized for performance, was operated from 550 to 700 °C fed with humidified H_2 (~3% H_2O). A high open-circuit potential of 1.004 V and a maximum power density of 259 mWcm^{-2} was achieved at 700 °C. The polarization resistance of the electrodes was as low as 0.14 Ωcm^2 at 700 °C. These results have indicated that the SCS cubic perovskite cathode is a good candidate for operation at or below 700 °C, and that proton-conducting electrolyte BZCY7 with SCS cathode is a promising materials system for the next generation solid oxide fuel cells.

Acknowledgement

The authors gratefully acknowledge the support of this research by National Natural Science Foundation of China under Contract

No. 50572099 and No. 50730002 and Chinese Research Foundation for the Doctors (20060358034).

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