



## Short communication

Intermediate-to-low temperature protonic ceramic membrane fuel cells with  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  composite cathode

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## ABSTRACT

The perovskite-type  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BSCF–BZCY) composite oxides were synthesized by a modified Pechini method and examined as a novel composite cathode for intermediate-to-low temperature protonic ceramic membrane fuel cells (ILT-PCMFCs). Thin proton-conducting  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) electrolyte and  $\text{NiO}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (NiO–BZCY) anode functional layer were prepared over porous anode substrates composed of  $\text{NiO}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  by a one-step dry-pressing/co-firing process. A laboratory-sized quad-layer cell of NiO–BZCY/NiO–BZCY (~50  $\mu\text{m}$ )/BZCY (~20  $\mu\text{m}$ )/BSCF–BZCY (~50  $\mu\text{m}$ ) was operated from 550 to 700 °C with humidified hydrogen (~3%  $\text{H}_2\text{O}$ ) as fuel and the static air as oxidant. A high open-circuit potential of 1.009 V, a maximum power density of 418  $\text{mW cm}^{-2}$ , and a low polarization resistance of the electrodes of 0.10  $\Omega \text{cm}^2$  was achieved at 700 °C. These investigations have indicated that proton-conducting BZCY electrolyte with BSCF perovskite cathode is a promising material system for the next generation solid oxide fuel cells (SOFCs).

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## 1. Introduction

The development of solid oxide fuel cells (SOFCs) has launched to a new stage characterized by thin electrolytes on porous electrode support, in which nearly all fabrication techniques developed are concerned with inorganic membranes, and hence it can also be named as ceramic membrane fuel cells (CMFCs) [1]. Protonic ceramic membrane fuel cells (PCMFCs) based on proton-conducting electrolytes exhibit more advantages than traditional CMFCs based on oxygen ion-conducting electrolytes, 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,  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) 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. BZCY, at temperatures below 550 °C, displayed the highest ionic conductivity of all known electrolyte materials for SOFC applications. The electrolytes in the above

cells, however, were rather thick (about 65  $\mu\text{m}$ ) and were made by co-pressing two kinds of ceramic powders, which is not suitable to fabricate cells with larger area for practical purpose. Thus, it is necessary to develop a simple and cost-effective route to fabricate PCMFCs with thinner electrolyte membrane on porous anode support, in order to reach higher performance. In this work, thin proton-conducting  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) electrolyte (~20  $\mu\text{m}$ ) and  $\text{NiO}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (NiO–BZCY) anode functional layer (~50  $\mu\text{m}$ ) were prepared over porous anode substrates composed of  $\text{NiO}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  by a one-step dry-pressing/co-firing process, which is a simple, reproducible, and cost-effective method for thin membrane fabrication, in which the thickness of the thin membrane can be easily controlled by adopting suitable amount of the powders.

The development of proper cathode materials for protonic ceramic membrane fuel cells (PCMFCs) in order to improve materials compatibility and reduce costs remains a challenge. Many perovskite-type mixed ionic–electronic conductors such as doped  $\text{LaCoO}_3$  [5],  $\text{BaCoO}_3$  [6],  $\text{LaFeO}_3$  [7] or  $\text{SrCoO}_3$  [8] have been extensively studied as possible cathodes. To make better use of the new proton conductors such as BZCY, efficient cathode materials must be developed. Recently Yang et al. [9] reported a perovskite-type  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (SSC–BZCY) composite cathode for low-temperature SOFCs based on oxide proton conductors. With higher performance than the  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (SSC) cathode,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) represents one of

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the most promising cathode materials that has attracted considerable attention for its excellent performance in SOFC based on oxygen ion-conducting electrolyte [10–14]. However, to the best of our knowledge, the performance of BSCF cathodes on BZCY electrolytes has not been reported to date. In this work, the perovskite-type  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BSCF–BZCY) composite oxides synthesized by a modified Pechini method were employed as a new composite cathode for intermediate-to-low temperature protonic ceramic membrane fuel cells (ILT-PCMFCs).

## 2. Experimental

The  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) powders were synthesized by a modified Pechini method with citrate and ethylenediamine tetraacetic acid (EDTA) as parallel complexing agents.  $\text{Y}_2\text{O}_3$  was dissolved in nitric acid first, and calculated amounts of  $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zr}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , were dissolved in EDTA– $\text{NH}_3$  aqueous solution under heating and stirring. An appropriate amount of citric acid was added in the solution. 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  $1100^\circ\text{C}$  for 5 h. The anode-supported BZCY bi-layer ( $\varphi 15$  mm) was prepared by a dry-pressing method. NiO + BZCY + starch mixture (60 wt. %:40 wt. %:20 wt. % in weight) was pre-pressed at 200 MPa as substrate. Then the anode functional layer (mixture of NiO and BZCY, NiO:BZCY = 60 wt. %:40 wt. % in weight) was pressed onto the substrate. Finally loose BZCY powder, calcined at  $1100^\circ\text{C}$  for 5 h to form a pure perovskite oxide, was uniformly distributed onto anode substrate, co-pressed at 250 MPa and sintered subsequently at  $1400^\circ\text{C}$  for 5 h to densify the BZCY membrane.  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) perovskite cathode powder was also synthesized by the modified Pechini method using  $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as precursors, followed by calcinations at  $950^\circ\text{C}$  for 5 h. Fine BSCF and BZCY powders (weight ratio of 3:2), were mixed thoroughly with a 6 wt. % ethylcellulose–terpineol binder to prepare the cathode slurry, which was then painted on BZCY electrolyte membrane, and sintered at  $1000^\circ\text{C}$  for 3 h in air to form cells.

The phase identification of the sintered anode–electrolyte bi-layer and prepared cathode powders was studied with the powder X-ray diffraction by Cu K $\alpha$  radiation (D/Max-gA, Japan). Single cells were tested from  $550$  to  $700^\circ\text{C}$  in a home-developed-cell-testing system with humidified hydrogen ( $\sim 3\%$   $\text{H}_2\text{O}$ ) as fuel and the static air as oxidant, respectively. The flow rate of fuel gas was about  $40\text{ ml min}^{-1}$ . 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  $550$  to  $700^\circ\text{C}$ . A scanning electron microscope (SEM) was used to observe the microstructure of the cells after testing.

## 3. Results and discussion

As shown in Fig. 1a, the as-prepared powder of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) exhibits a well-developed crystallization and all the peaks can be well indexed as a cubic perovskite structure. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at  $1400^\circ\text{C}$  for 5 h. It could be clearly seen that there were only peaks corresponding to  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) in electrolyte membrane (Fig. 1b) and to NiO and BZCY in the anode substrate (Fig. 1c), which gave no evidence for the formation of other substance.

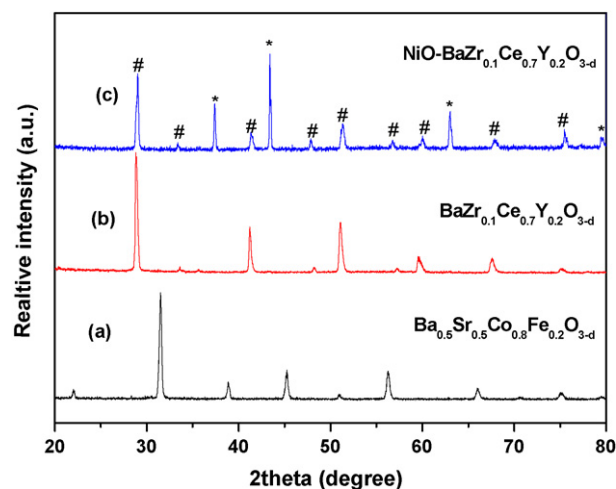


Fig. 1. XRD patterns for (a) the  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  powders, the bi-layer of (b) BZCY membrane and (c) NiO–BZCY anode substrate. (\*) NiO; (#) BZCY.

Fig. 2 is the SEM image of surface morphology of the as-prepared quad-layer cell of BZCY electrolyte on the porous anode support after testing. It can be seen that the BZCY membrane is fully dense. There is no obvious pores and cracks on the surface. The result demonstrates that the one-step dry-pressing/co-firing process followed by a heat treatment at a quite low temperature ( $1400^\circ\text{C}$ ) to fabricate dense BZCY electrolyte membrane on porous anode support was successful. From the cross-section view of the BZCY membrane (Fig. 3), it is found that the BZCY membrane is only about  $20\ \mu\text{m}$  in thickness.

Fig. 4 presents the  $I$ – $V$  and  $I$ – $P$  characteristics of the laboratory-sized quad-layer cell, the SEM image of which is shown in Fig. 3. 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 BZCY electrolyte because of both anode and cathode materials exhibiting much higher conductivity than electrolyte materials. The high open-circuit voltages (OCVs) of  $1.009\text{ V}$  at  $700^\circ\text{C}$ ,  $1.015\text{ V}$  at  $650^\circ\text{C}$ ,  $1.037\text{ V}$  at  $600^\circ\text{C}$  and  $1.048\text{ V}$  at  $550^\circ\text{C}$  indicate that the electrolyte membrane is sufficiently dense. Peak power densities were  $418$ ,  $351$ ,  $267$ , and  $179\text{ mW cm}^{-2}$  at  $700$ ,  $650$ ,  $600$ , and  $550^\circ\text{C}$ , respectively. Fig. 3 shows the cross-section view of the cell, NiO–BZCY/NiO–BZCY ( $\sim 50\ \mu\text{m}$ )/BZCY ( $\sim 20\ \mu\text{m}$ )/BSCF–BZCY ( $\sim 50\ \mu\text{m}$ ) after testing. As can be seen, the BZCY electrolyte

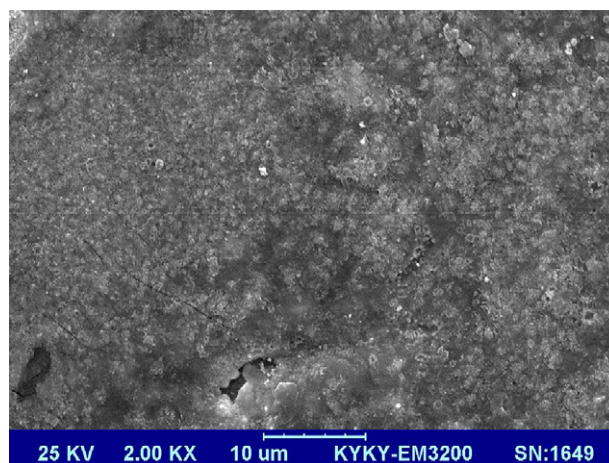


Fig. 2. SEM image of surface morphology of the as-prepared quad-layer cell of BZCY electrolyte on the porous anode support after testing.

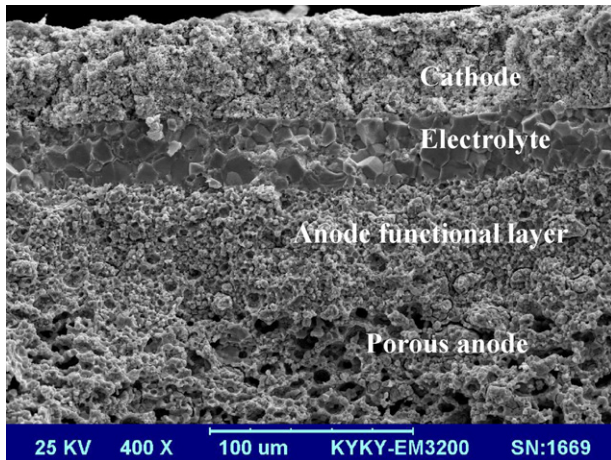


Fig. 3. SEM micrograph of the cross-sectional view of the as-prepared quad-layer cell, NiO–BZCY/NiO–BZCY( $\sim 50 \mu\text{m}$ )/BZCY( $\sim 20 \mu\text{m}$ )/BSCF–BZCY( $\sim 50 \mu\text{m}$ ) after testing.

is about  $20 \mu\text{m}$  in thickness, quite dense and adhered very well to the layers of functional anode and cathode. The cells have higher power density than the values (about  $270$  and  $148 \text{ mW cm}^{-2}$  at  $700$  and  $600^\circ\text{C}$ ) reported by Zuo et al. [4]. The result may mainly come from the lower resistances of electrolyte and cathode.

In order to evaluate the performance of the perovskite-type  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BSCF–BZCY) composite oxides working as a composite cathode in a PCMF, 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 resistance of the two interfaces: the cathode–electrolyte interface and the anode–electrolyte interface. As expected, the increase of the measurement temperature resulted in a significant reduction of the interfacial resistances, typically from  $1.48 \Omega \text{ cm}^2$  at  $550^\circ\text{C}$  to  $0.10 \Omega \text{ cm}^2$  at  $700^\circ\text{C}$ . Compared with  $\text{BaCe}_{0.4}\text{Pr}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BCPY) cathode, its interfacial resistances was  $\sim 0.4 \Omega \text{ cm}^2$  at  $700^\circ\text{C}$  on the  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) electrolyte [9]. The results indicated that the BSCF–BZCY composite cathode is a good candidate for operation at or below  $700^\circ\text{C}$ . Further, Fig. 6 shows that the

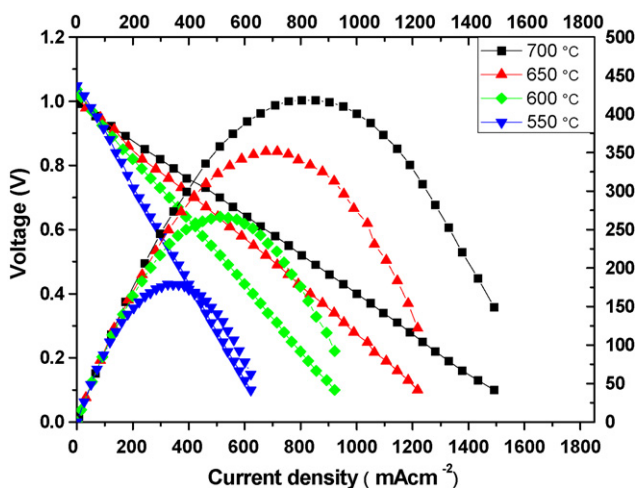


Fig. 4. Performance of the as-prepared cell with hydrogen at different temperatures.

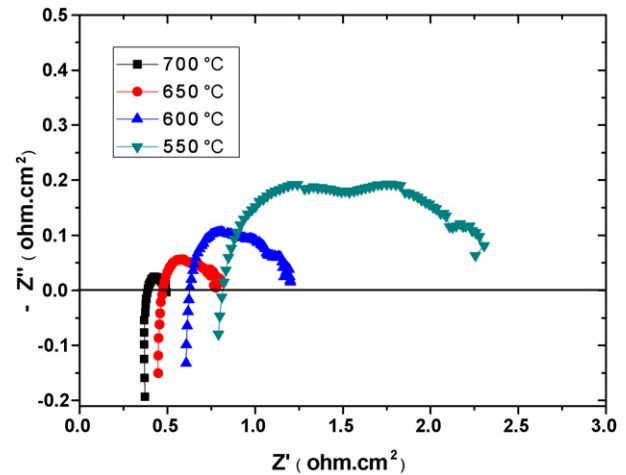


Fig. 5. Impedance spectra of the as-prepared cells under open-current conditions at different temperatures.

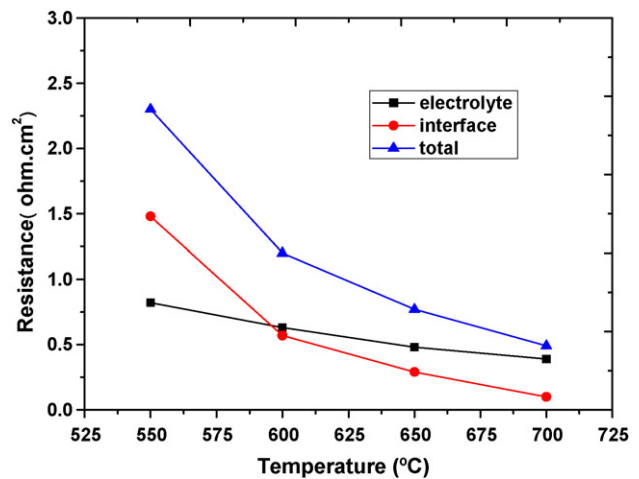


Fig. 6. The interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the quad-layer cell measured under open-circuit conditions at different temperatures.

cell performance is influenced by the interfacial resistances, especially at temperatures below  $550^\circ\text{C}$ , where the cell performance is essentially determined by the interfacial resistances. At  $550^\circ\text{C}$ , the polarization resistance of the electrodes is about  $1.48 \Omega \text{ cm}^2$  whereas the resistance of the electrolyte is only about  $0.82 \Omega \text{ cm}^2$ . So we can deduce that development of proper cathode materials is a grand challenge for developing the low-temperature PCMFs.

#### 4. Conclusions

In order to develop protonic ceramic membrane fuel cells (PCMFs) with  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BSCF–BZCY) composite cathode, a dense  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) electrolyte was fabricated on porous anode support by a simple dry-pressing/co-firing process. A laboratory-sized quad-layer cell of NiO–BZCY/NiO–BZCY( $\sim 50 \mu\text{m}$ )/BZCY( $\sim 20 \mu\text{m}$ )/BSCF–BZCY( $\sim 50 \mu\text{m}$ ) was operated from  $550$  to  $700^\circ\text{C}$  with humidified hydrogen ( $\sim 3\% \text{ H}_2\text{O}$ ) as fuel and the static air as oxidant. A high open-circuit potential of  $1.009 \text{ V}$  and a maximum power density of  $418 \text{ mW cm}^{-2}$  was achieved at  $700^\circ\text{C}$ . The polarization resistance of the electrodes was as low as  $0.10 \Omega \text{ cm}^2$  at  $700^\circ\text{C}$ . The results have indicated that the perovskite-type BSCF–BZCY composite

cathode is a good candidate for operation at or below 700 °C, and that the one-step dry-pressing/co-firing process is a simple and cost-effective route for preparing the key components of SOFCs.

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