



## Short communication

In situ screen-printed  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  electrolyte-based protonic ceramic membrane fuel cells with layered  $\text{SmBaCo}_2\text{O}_{5+x}$  cathodeBin Lin<sup>a</sup>, Yingchao Dong<sup>a</sup>, Ruiqiang Yan<sup>b</sup>, Shangquan Zhang<sup>a</sup>, Mingjun Hu<sup>a</sup>, Yang Zhou<sup>a</sup>, Guangyao Meng<sup>a,\*</sup><sup>a</sup> Department of Materials Science and Engineering, University of Science and Technology of China (USTC), Hefei, Anhui 230026, PR China<sup>b</sup> Department of Materials Engineering, Taizhou University, Linhai, Zhejiang 317000, PR China

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## ABSTRACT

In order to develop a simple and cost-effective route to fabricate protonic ceramic membrane fuel cells (PCMFCs) with layered  $\text{SmBaCo}_2\text{O}_{5+x}$  (SBCO) cathode, a dense  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) electrolyte was fabricated on a porous anode by in situ screen printing. The porous  $\text{NiO-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (NiO-BZCY) anode was directly prepared from metal oxide ( $\text{NiO}$ ,  $\text{BaCO}_3$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$  and  $\text{Y}_2\text{O}_3$ ) by a simple gel-casting process. An ink of metal oxide ( $\text{BaCO}_3$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$  and  $\text{Y}_2\text{O}_3$ ) powders was then employed to deposit  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) thin layer by an in situ reaction-sintering screen printing process on NiO-BZCY anode. The bi-layer with 25  $\mu\text{m}$  dense BZCY electrolyte was obtained by co-sintering at 1400 °C for 5 h. With layered SBCO cathode synthesized by gel-casting on the bi-layer, single cells were assembled and tested with  $\text{H}_2$  as fuel and the static air as oxidant. A high open-circuit potential of 1.01 V, a maximum power density of 382  $\text{mW cm}^{-2}$ , and a low polarization resistance of the electrodes of 0.15  $\Omega\text{cm}^2$  was achieved at 700 °C.

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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, the porous  $\text{NiO-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (NiO-BZCY) anode was directly prepared from metal oxide by a simple gel-casting process. Recently, gel-casting has gained attention as a new method in the preparation of electrode powders and electrode-supported substrates for SOFCs [5,6]. Then the 25  $\mu\text{m}$  dense BZCY electrolyte was fabricated in situ metal oxide on the anode support by an in situ reaction-sintering screen printing process, which is cost-effective, easy to realize, and suitable for mass-production.

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 simple perovskite-type mixed ionic–electronic conductors such as doped  $\text{LaCoO}_3$  [7],  $\text{BaCoO}_3$  [8] or  $\text{LaFeO}_3$  [9] have been extensively studied as possible cathodes, however not much attention has been paid to the perovskite related structures such as the double or layered perovskites. Layered  $\text{SmBaCo}_2\text{O}_{5+x}$  perovskite with an intermediate lanthanide-ion radius ( $\text{Sm}^{3+}$ ) may provide a compromise between the values of the catalytic activity and TEC [10]. Recently

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Zhou et al. [11] have shown the potential of layered  $\text{SmBaCo}_2\text{O}_{5+x}$  (SBCO) for cathode application and evaluated the performance of this material working as a cathode in SOFCs based on oxide ion conductors of  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (SDC) and  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM). However, to the best of our knowledge, the performance of SBCO cathodes as a part of protonic ceramic membrane fuel cells (PCMFCs) has not been reported to date. In this work, the layered SBCO synthesized by gel-casting were employed as a new PCMFCs cathode.

## 2. Experimental

The NiO–BZCY anode support was directly prepared using a gel-casting method with metal oxide (NiO,  $\text{BaCO}_3$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$  and  $\text{Y}_2\text{O}_3$ ) precursors in a certain proportion to make sure that the BZCY composition was  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  and the weight ratio of NiO:BZCY was 6:4. The precursors were mixed with organic monomer (mixture of acrylamide (AM) and *N,N*-methylene-bis-acrylamide (MBAM), AM:MBAM = 5:1) in an aqueous solution. The resulting slurry with the initiator ammonium bisulphate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) was poured into a mould, and subsequently heated in an oven at  $80^\circ\text{C}$  for 1 h. The gel was cut into discs, followed by drying at  $80^\circ\text{C}$  for 24 h. The as-prepared green anode-substrates were stored ready for use.

An ink of metal oxide ( $\text{BaCO}_3$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$  and  $\text{Y}_2\text{O}_3$ ) powders was then employed to deposit BZCY thin layer by an in situ reaction-sintering screen printing process on NiO–BZCY anode. The ink for screen printing consisted of metal oxide powder (50 wt.%) and ethyl cellulose-terpineol vehicle (50 wt.%). The prepared ink was screen printed on the as-prepared green anode-substrates through a Terylene screen. The mesh count of the screen was 500 wires  $\text{in}^{-1}$ . The bi-layer of green electrolyte and anode support were then co-fired at  $1400^\circ\text{C}$  for 5 h. Layered  $\text{SmBaCo}_2\text{O}_{5+x}$  powder was synthesized by an aqueous gel-casting method using  $\text{Sm}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{Co}_3\text{O}_4$  as precursors, followed by calcinations at  $1100^\circ\text{C}$  for 10 h. The SBCO slurry was applied to the electrolyte by printing and then fired at  $1000^\circ\text{C}$  for 3 h to form a porous cathode.

The phase identification of the sintered anode–electrolyte bi-layer and prepared cathode powders was studied with the powder X-ray diffraction by  $\text{Cu K}\alpha$  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. 1(a), the as-prepared powder of  $\text{SmBaCo}_2\text{O}_{5+x}$  exhibits a layered perovskite phase structure [11]. 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. 1(b)) and to NiO and BZCY in the anode substrate (Fig. 1(c)), which gave no evidence for the formation of other substance.

Fig. 2 is the SEM image of surface morphology of the as-prepared tri-layer cell of BZCY electrolyte on the porous anode support after testing. It can be seen that the BZCY membrane is completely dense. There is no obvious pores and cracks on the surface. The result

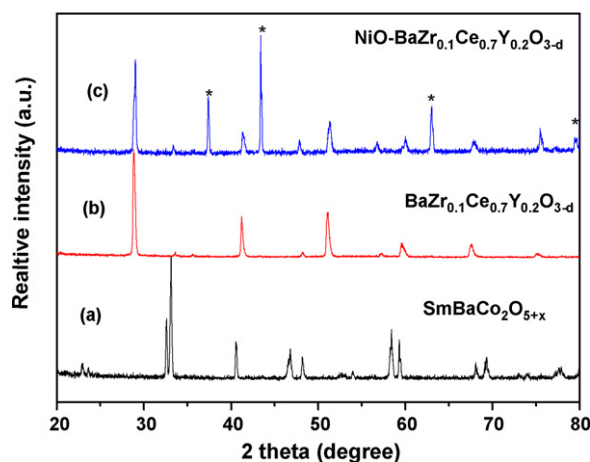


Fig. 1. XRD patterns for (a) the layered  $\text{SmBaCo}_2\text{O}_{5+x}$  powders, the bi-layer of (b) BZCY membrane and (c) NiO–BZCY anode substrate. \*NiO.

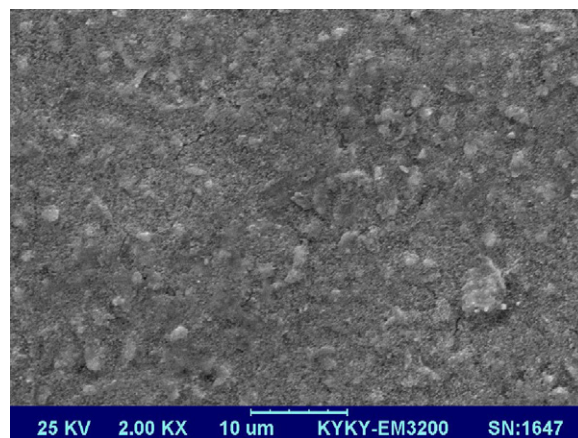


Fig. 2. SEM image of surface morphology of the as-prepared tri-layer cell of BZCY electrolyte on the porous anode support after testing.

demonstrates that the in situ reaction-sintering screen printing 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 in situ screen-printed BZCY7 membrane (Fig. 3), it is found that the BZCY membrane is only about  $25\ \mu\text{m}$  thick.

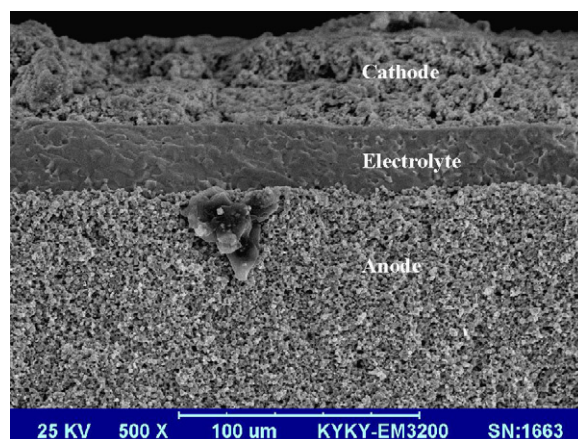


Fig. 3. SEM micrograph of the cross-sectional view of the as-prepared tri-layer cell, Ni–BZCY/BZCY ( $25\ \mu\text{m}$ )/SBCO after testing.

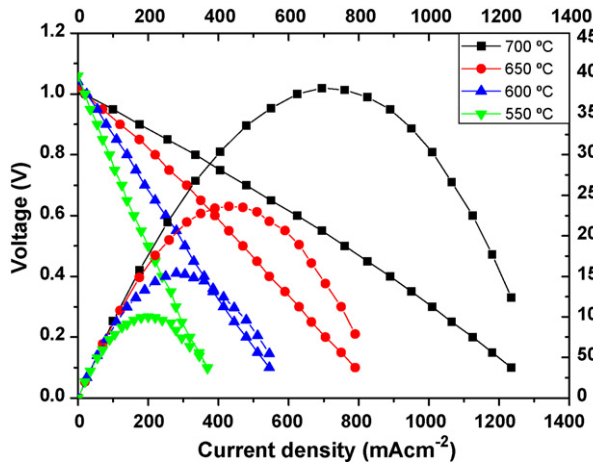


Fig. 4. Performance of the as-prepared cell with hydrogen at different temperatures.

Fig. 4 presents the  $I$ - $V$  and  $I$ - $P$  characteristics of the as-prepared 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 (OCV) of 1.01 V at 700 °C, 1.02 V at 650 °C, 1.04 V at 600 °C and 1.06 V at 550 °C indicate that the electrolyte membrane is sufficiently dense. Peak power densities were 382, 237, 154, and 100  $\text{mW cm}^{-2}$  at 700, 650, 600, and 550 °C, respectively. Fig. 3 shows the cross-section view of the cell, Ni-BZCY/BZCY/SBCO after testing. As can be seen, the BZCY electrolyte is about 25  $\mu\text{m}$  in thickness, quite dense and adhered very well to the layers of anode and cathode. The cells have higher power density than the values (270 and 148  $\text{mW cm}^{-2}$  at 700 and 600 °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 layered  $\text{SmBaCo}_2\text{O}_{5+x}$  working as a 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:

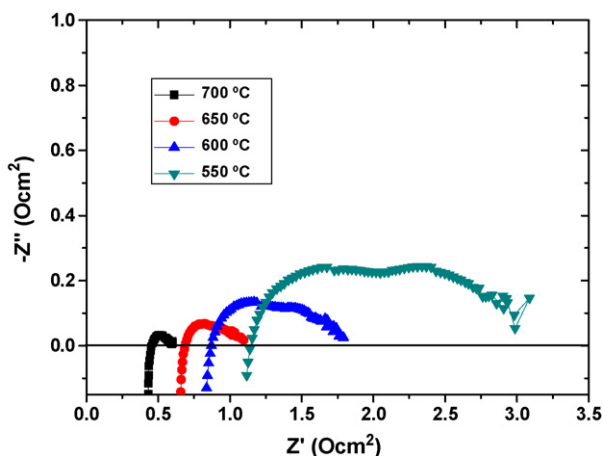


Fig. 5. Impedance spectra of the as-prepared cells under open-current conditions at different temperatures.

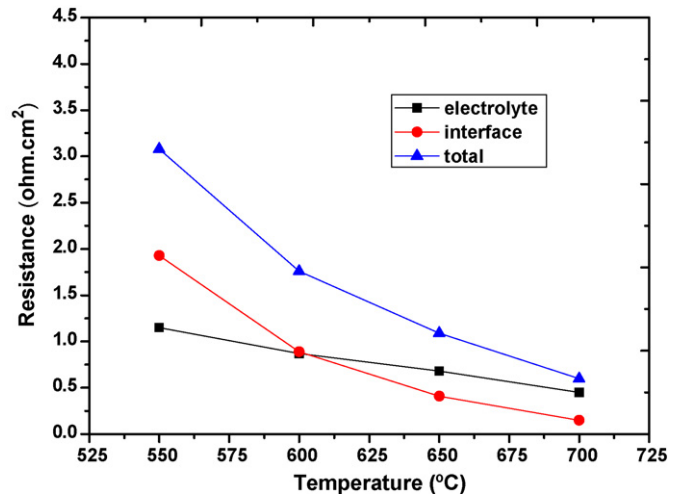


Fig. 6. The interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the tri-layer cell measured under open-circuit conditions at different temperatures.

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 1.93  $\Omega \text{cm}^2$  at 550 °C to 0.15  $\Omega \text{cm}^2$  at 700 °C. The results indicated that the layered SBCO cathode is a good candidate for operation at or below 700 °C. Further, Fig. 6 shows that the cell performance is influenced by the interfacial resistances, especially at temperatures below 550 °C, where the cell performance is essentially determined by the interfacial resistances. At 550 °C, the polarization resistance of the electrodes is about 1.93  $\Omega \text{cm}^2$  whereas the resistance of the electrolyte is only about 1.15  $\Omega \text{cm}^2$ . 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 a simple and cost-effective route to fabricate protonic ceramic membrane fuel cells (PCMFs) with layered  $\text{SmBaCo}_2\text{O}_{5+x}$  cathode, a dense  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) electrolyte was fabricated on a porous anode by in situ screen printing. A laboratory-sized tri-layer cell of NiO-BZCY/BZCY (25  $\mu\text{m}$ )/SBCO, not yet optimized for performance, was operated from 550 to 700 °C fed with humidified  $\text{H}_2$  ( $\sim 3\%$   $\text{H}_2\text{O}$ ). A high open-circuit potential of 1.01 V and a maximum power density of 382  $\text{mW cm}^{-2}$  was achieved at 700 °C. The polarization resistance of the electrodes was as low as 0.15  $\Omega \text{cm}^2$  at 700 °C. These results have indicated that the layered SBCO cathode is a good candidate for operation at or below 700 °C, and that in situ screen printing is a simple and potentially commercial prospective route for preparing the key components of SOFCs.

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