



Short communication

A novel layered perovskite cathode for proton conducting solid oxide fuel cells

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ABSTRACT

BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} (BZCY7) exhibits adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of SOFC operating conditions, while layered SmBa_{0.5}Sr_{0.5}Co₂O_{5+δ} (SBSC) perovskite demonstrates advanced electrochemical properties based on doped ceria electrolyte. This research fully takes advantage of these advanced properties and develops novel protonic ceramic membrane fuel cells (PCMFCs) of Ni-BZCY7|BZCY7|SBSC. The results show that the open-circuit potential of 1.015 V and maximum power density of 533 mW cm⁻² are achieved at 700 °C. With temperature increase, the total cell resistance decreases, among which electrolyte resistance becomes increasingly dominant over polarization resistance. The results also indicate that SBSC perovskite cathode is a good candidate for intermediate temperature PCMFC development, while the developed Ni-BZCY7|BZCY7|SBSC cell is a promising functional material system for next generation SOFCs.

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1. Introduction

Conventional SOFCs are developed based on oxygen ion conducting electrolyte, i.e., yttria-stabilized zirconia (YSZ), due to its high ionic conductivity and sufficient stability under high temperature conditions. While high operating temperature may provide several unique advantages for SOFCs, including high reaction kinetics, high power density, etc., it also imposes great challenges on the long term stability and durability of the state-of-the-art SOFC material systems. Recently PCMFC has emerged as a promising candidate for intermediate temperature (IT) SOFCs [1–3], and shows great advantages over its oxygen ion electrolyte based counterpart.

High performance PCMFC is largely dependent on the property of proton conducting oxide electrolytes. While many perovskite-type oxides show high proton conductivity in a reducing atmosphere, one of the technical barriers is how to properly tailor material properties, so that both high proton conductivity and chemical stability can be obtained simultaneously. Zuo et al. [4] developed a new composition for proton conducting electrolyte, BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} (BZCY7). The results show that both adequate proton conductivity as well as sufficient chemical and thermal stability are obtained over a wide range of SOFC operating conditions; whereas, at temperatures below 550 °C, it shows the highest ionic conductivity of all known electrolyte materials. It is worth noting that the electrolyte in the above investigation is relatively thick

(about 65 μm), obviously there is a great potential to reduce the electrolyte thickness and cell ohmic resistance. Consequently, the high power density of BZCY7 electrolyte based cell can be obtained, meanwhile remaining its chemical stability.

The development of compatible and low cost cathode materials for PCMFC is another challenging issue [5]. Simple perovskite-type mixed ionic–electronic conductors, such as doped LaCoO₃ [6], BaCoO₃ [7], or LaFeO₃ [8], have been extensively investigated as cathode material candidates. While the catalytic activity of these cathode materials are adequate for SOFCs, the thermal expansion mismatch between electrolyte and cathode materials may lead to structural issues such as cracks at elevated temperature. The double-layered perovskites may potentially overcome this problem. It is found that layered SmBaCo₂O_{5+δ} (SBCO) perovskite with an intermediate lanthanide-ion radius (Sm³⁺) may make an appropriate tradeoff between the values of the catalytic activity and TEC [9]; and has been employed as cathode materials for SOFCs [10,11]. Recently, Irvine and coworkers [12] reported a novel layered SmBa_{0.5}Sr_{0.5}Co₂O_{5+σ} (SBSC) perovskite that demonstrated advanced electrochemical properties based on doped ceria electrolyte, and can be potentially utilized as cathode materials for IT SOFC applications. It is anticipated that the high performance may be obtained using SBSC cathodes in BZCY7 electrolyte based PCMFCs.

This research aims at developing a high performance PCMFC by combining the advantages of both thin BZCY7 electrolyte and advanced property of novel layered SBSC perovskite cathode materials. The fabrication process and the high performance of BZCY7–SBSC based PCMFC are demonstrated using a series of experimental results.

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2. Experimental

2.1. Sample preparation, single cells fabrication, and X-ray diffraction measurement

The $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) powders were synthesized using modified Pechini method, where citrate and ethylenediamine tetraacetic acid (EDTA) were employed as parallel complexing agents. Y_2O_3 was first dissolved in nitric acid; the calculated amount of $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ was dissolved in EDTA– NH_3 aqueous solution under heating and stirring conditions. An appropriate amount of citric acid was then added in the solution. After converted into viscous gel under heating and stirring conditions, the solution was ignited to flame and result in ash. The resulted ash-like material was afterwards calcined in air at 1100°C for 5 h to form a pure perovskite oxide, and the synthesized BZCY7 powders were then obtained.

The anode-supported BZCY7 bi-layer ($\varphi 15$ mm) was prepared by a dry-pressing method. The mixture of NiO + BZCY7 + starch (60%:40%:20% in weight) was pre-pressed at 200 MPa and formed into an anode substrate. The anode functional layer (mixture of NiO and BZCY7, NiO:BZCY7 = 60%:40% in weight) was then pressed onto the substrate. Finally loose BZCY7 powder synthesized above was uniformly distributed onto the anode substrate, co-pressed at 250 MPa, and subsequently sintered at 1400°C for 5 h to obtain densified BZCY7 membrane.

Layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\sigma}$ (SBSC) powder was synthesized using Pechini process with $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursors, followed by calcinations at 1000°C for 10 h. Fine SBSC powders were then mixed thoroughly with a 6-wt% ethylcellulose–terpineol binder to prepare the cathode slurry. The slurry was painted on BZCY7 electrolyte films, which was then sintered at 1000°C for 3 h in air to form single cells. The final geometry of cell pellets is approximately 12 mm in diameter and 0.76 mm in thickness.

The phase identification of the sintered anode–electrolyte bi-layer and prepared cathode powders were studied with the powder X-ray diffraction by Cu $K\alpha$ radiation (D/Max-gA, Japan).

2.2. Electrochemical characterization

Single cells were tested from 550 to 700°C using a home-developed cell-testing system with humidified hydrogen ($\sim 3\%$ H_2O) as fuel and the static air as oxidant, respectively. The flow rate of fuel was about 40 ml min^{-1} . The cell voltages and current were measured with digital multi-meters (GDM-8145). AC impedance spectroscopy was obtained over the frequency range from 0.01 to 10^5 Hz under open-circuit conditions with operating temperature from 550 to 700°C . A scanning electron microscope (SEM) was used to observe the microstructure of the cells after electrochemical test.

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\sigma}$ (SBSC) exhibits a layered perovskite phase structure without any peaks attributable to impurities [12]. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at 1400°C for 5 h. It can be clearly seen that there are 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(c)) and to NiO and BZCY7 in anode substrate (Fig. 1(b)). There is no evidence pointing to the formation of other substance.

After electrochemical test, the microstructure of as-prepared tri-layer cell is examined using SEM. One can see from Fig. 2(a) that the BZCY7 electrolyte membrane is completely dense, there is no pores and cracks on the surface. It can also be seen from the cross-

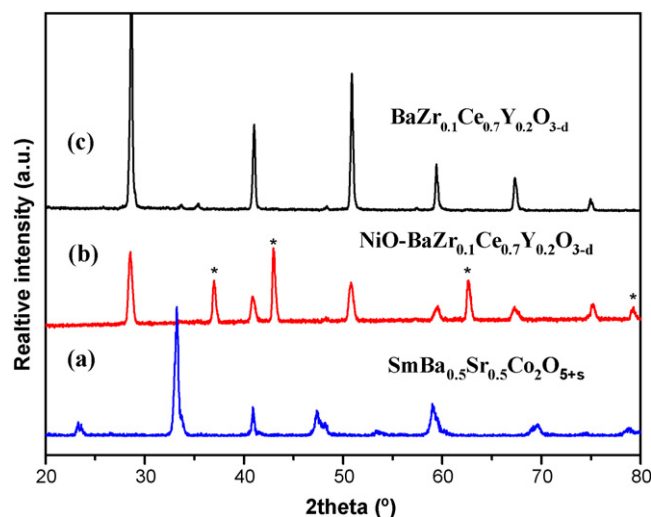


Fig. 1. XRD patterns for (a) the layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\sigma}$ (SBSC) perovskite powders, the bi-layer of (b) NiO–BZCY7 anode substrate and (c) BZCY7 membrane. Asterisk (*): NiO.

section view of tri-layer cell Ni–BZCY7|BZCY7|SBSC (Fig. 2(b)) that the thickness of fabricated BZCY7 membrane is only about $15 \mu\text{m}$, it adhered to the layers of functional anode and cathode fairly well.

The electrochemical performance of the as-prepared cell is experimentally obtained and shown in Fig. 3 under different operating temperature conditions, including I – V curve and I – P curve. One can see from Fig. 3 that peak power densities are 533, 377, 245 and 128 mW cm^{-2} at 700, 650, 600 and 550°C , respectively; whereas the high open-circuit voltages (OCV) of 1.015 V at 700°C , 1.029 V at 650°C , 1.05 V at 600°C , 1.067 V at 550°C indicate that the electrolyte membrane is sufficiently dense, current leakage is negligible. It is worth pointing out that I – V curves are almost linear implying that there is a little activation loss related to the high catalytic activity of SBSC. Since the conductivity of both anode and cathode materials is higher than that of electrolyte in the as-prepared cell, it can be deduced that the voltage drop of the cell is mainly attributed to the IR loss across the BZCY7 electrolyte.

The performance of SBSC perovskite as cathode material in PCMF settings is examined using electrochemical impedance spectra. The impedance spectra of the as-prepared cells are obtained under open-circuit conditions at different temperatures, and are shown in Fig. 4(a). The impedance spectra consisted of two arcs. This indicates that there are at least two electrode processes corresponding to the two arcs during oxygen molecule reduction. The high frequency arc can be attributed to polarization during charge transfer process. On the other hand, the low frequency arc can be attributed to the oxygen adsorption and desorption on the cathode surface and the diffusion of the oxygen ions [13]. The total cell resistance (R_t), ohmic resistance (R_o), as well as interfacial polarization resistance (R_p) are then determined from the impedance spectra in Fig. 4(a), the results are shown in Fig. 4(b). As one can see that increase operating temperature may lead to significant reduction of interfacial polarization resistance R_p , typically from $1.13 \Omega \text{ cm}^2$ at 500°C to $0.08 \Omega \text{ cm}^2$ at 700°C , respectively. It is worth noting that R_p value of the cell with SBSC cathode is lower than that of the cell with a BSCF–BZCY7 composite cathode at operating temperature 700°C [14]. It turns out that SBSC cathode is a potential good candidate for high performance intermediate temperature PCMF development. One can also see from Fig. 2(b) that the cell resistance contributed from interfacial polarization resistance R_p is larger than that from ohmic resistance (R_o) when the cell is operated at the temperature below 650°C ; above 650°C , electrolyte resistance becomes increasingly dominant with

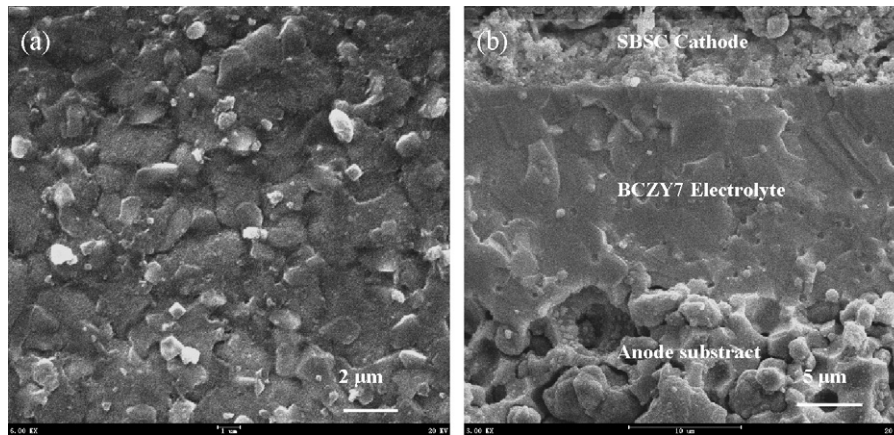


Fig. 2. SEM micrographs of cell after testing: (a) the surface of electrolyte and (b) the cross-section of cell with a 15- μm thick BZCY7 membrane.

temperature increase. At 550 °C, the polarization resistance of the electrodes is 1.13 Ωcm^2 whereas the resistance of the electrolyte is only 0.55 Ωcm^2 . The ratio of R_p to R_t increases with the decrease of the operating temperature, from 20% at 700 °C to 67% at 550 °C, respectively.

Since SBSC cathode is layered perovskite material, where the oxide ion vacancies are exclusively located in the Sm^{3+} layer because of the smaller ionic radius of Sm^{3+} compared with that of Ba^{2+} ion, this microstructure characteristic can potentially increase oxygen surface exchange and oxide ionic diffusivity [9]. As a result, polarization resistance is low as observed in above experimental results. Operating temperatures influence both electrolyte and cathode performance, but in different ways. The increase of operating temperatures will lead to high migration activity of protons in electrolyte and reduced electrolyte resistance (Fig. 4(a)). Within cathode, the increased operating temperatures influence several processes, e.g., migration of charge (protons and electrons) increases; gas transport within porous cathode will be enhanced; the electrochemical reactions at TPB sites will be enhanced as well. The combinational effects of above processes will lead to the decrease of polarization resistance at elevated temperatures. The experimental results also indicate that the cell performance is mainly limited by interfacial polarization resistance at low temperature range. It is worthwhile to reduce cathode–electrolyte interfacial resistance for cell performance improvement in future studies.

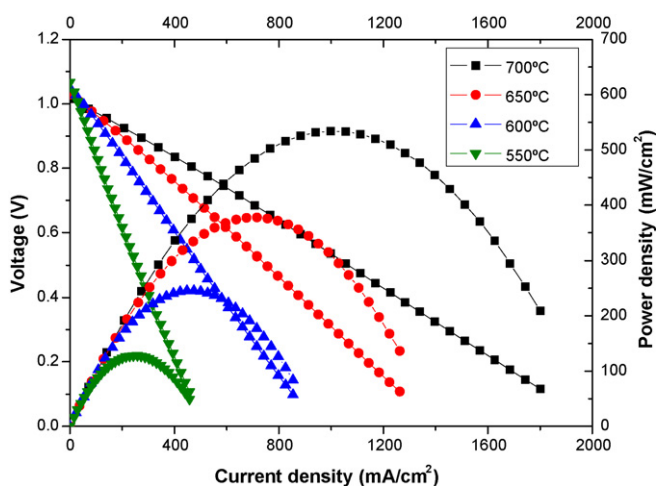


Fig. 3. Performance of the as-prepared cell with hydrogen at different temperatures.

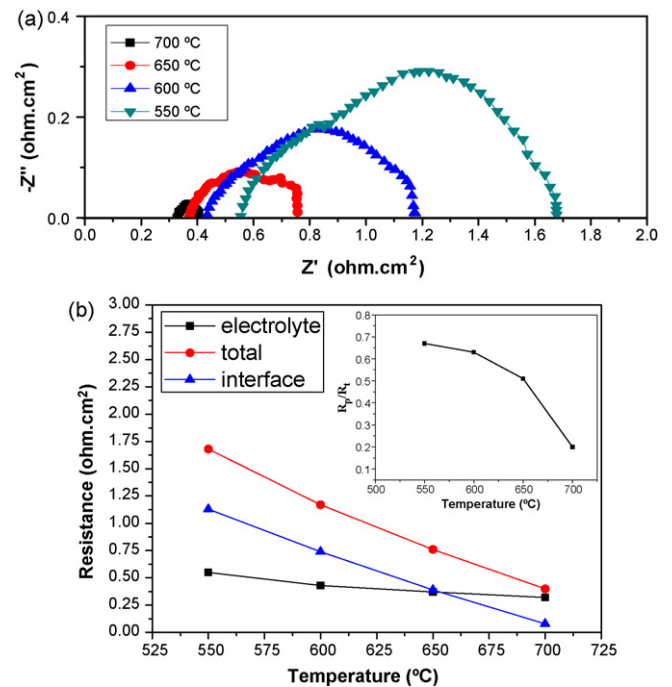


Fig. 4. (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures. R_p/R_t is also shown in (b).

4. Conclusions

A novel PCMF is successfully fabricated with layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\sigma}$ (SBSC) as cathode, thin $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) as electrolyte. The performance of the lab-scale tri-layer cell Ni-BZCY7|BZCY7|SBSC is tested and characterized under intermediate temperature range from 550 to 700 °C. The results show that the open-circuit potential of 1.015 V and maximum power density of 533 mW cm^{-2} are achieved at 700 °C. With temperature increase, the total cell resistance decreases, among which electrolyte resistance becomes increasingly dominant over polarization resistance. The results also indicate that SBSC perovskite cathode is a good candidate for intermediate temperature PCMF development, while the developed Ni-BZCY7|BZCY7|SBSC is a promising functional material system for next generation SOFCs.

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