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Proton conducting solid oxide fuel cells with layered $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ perovskite cathode

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ABSTRACT

$\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) exhibits adequate protonic conductivity as well as sufficient chemical and thermal stability over a wide range of SOFC operating conditions, while layered perovskite $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (PBSC) has advanced electrochemical properties. This research fully takes advantage of these advanced properties and develops a novel protonic ceramic membrane fuel cell (PCMFC) of Ni-BZCY7|BZCY7|PBSC. Experimental results show that the cell may achieve the open-circuit potential of 1.005 V, the maximal power density of 520 mW cm^{-2} , and a low electrode polarization resistance of $0.12 \Omega \text{ cm}^2$ at 700°C . Increasing operating temperature leads to the decrease of total cell resistance, among which electrolyte resistance becomes increasingly dominant over polarization resistance. The results also indicate that PBSC perovskite cathode is a good candidate for intermediate temperature PCMFC development, while the developed Ni-BZCY7|BZCY7|PBSC cell is a promising functional material system for SOFCs.

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1. Introduction

Intermediate temperature SOFC (IT-SOFC) could potentially circumvent problems induced by high temperature operating conditions, such as long term stability and durability of material systems [1]. Two technical barriers have to be overcome in order for IT-SOFC performance to be comparable to its high temperature counterpart, e.g., high ohmic resistance of electrolyte and low catalytic activity of electrodes under intermediate temperature conditions ($550\text{--}750^\circ\text{C}$).

Recently, proton conducting SOFCs have attracted much attention and show great advantages compared with oxide-ion conducting SOFCs, such as low activation energy [2] and high energy efficiency [3]. The state-of-the-art proton conducting materials are barium-based perovskite-type ceramics, e.g., BaCeO_3 and BaZrO_3 . By suitable doping, these materials

may obtain both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of SOFC operating conditions, e.g., $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) [4]. This material can be used as an electrolyte for proton conducting SOFC development.

In a typical proton conducting SOFCs, hydrogen molecules release electrons and are dissociated to protons at anode active layer. The protons then migrate to cathode side through proton conducting electrolyte. At cathode side, oxygen molecules are changed to ions with a supply of external electrons; water molecules are then formed through the combination of protons and ions. Essentially three charge species are involved in cathode electrode, i.e., protons, ions, and electrons. Consequently, cathode electrode development is very critical for high performance proton conducting SOFCs. Furthermore, intermediate temperature operating condition imposes

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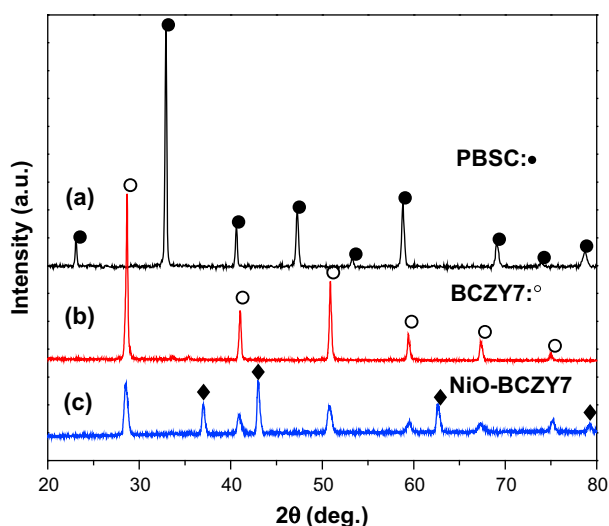


Fig. 1 – XRD patterns for (a) the layered $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (PBSC) perovskite powders, the bi-layer of (b) BZCY7 membrane and (c) NiO-BZCY7 anode substrate. Diamond (◆): NiO.

additional challenges on cathode material selections [5]. One of the essential requirements for IT-SOFC cathode material is a high oxygen reduction rate. The reduction reaction is strictly confined to triple phase boundary (TPB) sites. The mixed ionic and electronic conductors (MIEC) may potentially extend TPB active region over the entire cathode. In this respect, many simple perovskite-type MIEC such as doped LaCoO_3 [6], BaCoO_3 [7] and SmCoO_3 [8] have been extensively studied as cathode candidates for SOFCs. Recently layered perovskite oxide $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) with ordered A-cations has also been investigated as potential cathode material by G. Kim et al. [9–11]. This compound can be theoretically described with the stacking sequence of $\dots[\text{BaO}|\text{CoO}_2|\text{PrO}_x|\text{CoO}_2]\dots$. When $x < 1$, the ordered A-cations localizing oxygen vacancies appear within the rare earth layers [12,13]. This characteristic has a great potential to improve cathode performance. When a simple cubic perovskite with randomly occupied A-sites transfers into a layered crystal structure with ordered lanthanide and alkali-earth layers, it reduces the strength of oxygen binding and provides disorder-free channels for ionic migration. The high performance of layered perovskite oxides can be understood using general formula $\text{AA}'\text{B}_2\text{O}_{5+\delta}$ with the A' site being Ba element. When A' site is partially substituted by Sr, it could potentially improve the conductivity of layered perovskite oxides, this hypothesis have been confirmed by recent study from Irvine et al. [14], where Sr-doped oxide $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (PBSC) demonstrated excellent area-specific-resistance (ASR) values based on gadolinia-doped ceria (GDC) electrolyte, and could be potentially employed as cathode material for IT-SOFCs.

To the best of our knowledge, the performance of PBSC cathode on BZCY7 electrolyte has not been reported up to date. This paper aims to investigate PBSC performance as a cathode in proton conducting SOFC material system, i.e., PCMFC Ni-BZCY7/BZCY7/PBSC, under intermediate temperature operating conditions. The button cell is fabricated. The

electrochemical performance of the cell is characterized using complex impedance technique.

2. Experimental

2.1. Sample preparation, cell 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. After agitation for a certain time, a proper amount of citric acid was introduced, the molar ratio of EDTA: citric acid: total of metal cations was controlled around 1:1.5:1. After converted to viscous gel under heating and stirring conditions, the solution was ignited to flame and results in ash. The resulting 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 ($\phi = 15$ 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 at 50 MPa. Then loose BZCY7 powder synthesized above was uniformly distributed onto the anode functional layer, co-pressed at 250 MPa, and subsequently co-sintered at 1400°C for 5 h to obtain anode electrode/electrolyte assembly.

Layered $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (PBSC) powders were synthesized using Pechini process with Pr_6O_{11} , $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ 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 PBSC powders were then mixed thoroughly with a 6 wt% ethylcellulose-terpineol binder to prepare the cathode slurry. The slurry was painted

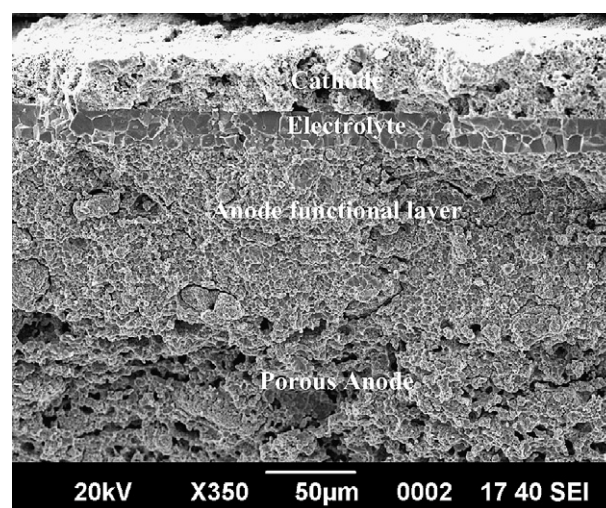


Fig. 2 – SEM micrographs of cell after testing: the cross-section of tri-layer cell with a $20\text{ }\mu\text{m}$ -thick BZCY7 membrane.

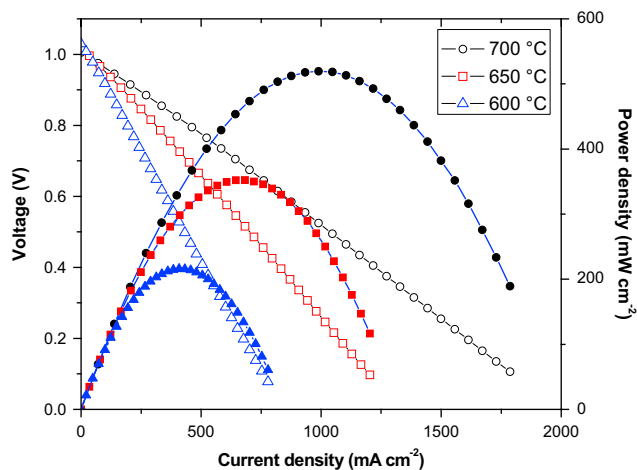


Fig. 3 – Performance of the as-prepared cell with hydrogen at different temperatures.

on BZCY7 electrolyte of sintered anode electrode/electrolyte assembly, which was then sintered at 1000 °C for 3 h in air to form a single cell. The final geometry of cell pellet is approximately 12 mm in diameter and 0.8 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 α radiation (D/Max-gA, Japan).

2.2. Electrochemical characterization

The single cell was tested from 600 to 700 °C with humidified hydrogen ($\sim 3\%$ H $_2$ O) as a fuel and the static air as an oxidant. The flow rate of fuel was about 30 ml/min. The voltage–current curves were recorded by Scribner 890ZV at the scanning rate of 30 mV s $^{-1}$. The electrochemical impedance spectra (EIS) were obtained using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 potentiostat over the frequency range from 0.01 Hz to 10 5 Hz under open-circuit conditions. A scanning electron microscope (SEM) was used to observe the microstructure of the post-test cell.

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of PBSC exhibits a pure layered perovskite phase structure without any peaks attributable to impurities [14]. 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 BaZr $_{0.1}$ Ce $_{0.7}$ Y $_{0.2}$ O $_{3-\delta}$ (BZCY7) in electrolyte membrane (Fig. 1(b)) and to NiO and BZCY7 in anode substrate (Fig. 1(c)). 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 that the BZCY7 electrolyte membrane is completely dense, and there are no pores or cracks. It can also be seen from the cross-section view of tri-layer cell Ni–BZCY7/BZCY7/PBSC that the thickness of fabricated BZCY7 membrane is

only about 20 μ m, and the thickness of PBSC cathode layer is about 50 μ m. The membrane adheres 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. In general, the open-circuit voltage (OCV) of the cell should be close to its theoretic value of 1.1 V, and is slightly influenced by operating conditions. Since BZCY7 electrolyte is a mixed conductor membrane, a slight electron cross flow (current leakage) might exist through the membrane, consequently it leads to that the practical OCV is lower than its theoretical value. The higher the current leakage exists, the lower the cell OCV will be. On the other hand, if the electrolyte membrane is not dense, fuel/gas cross flow might take place, causing lower OCV value as well. One can see from Fig. 3 that peak power densities are 520, 353 and 216 mW cm $^{-2}$ at 700, 650 and 600 °C, respectively; whereas the high open-circuit voltages (OCV) of 1.005 V at 700 °C, 1.018 V at 650 °C, 1.03 V at 600 °C indicate that the electrolyte membrane is sufficiently dense, and the current leakage is negligible. It is worth noting that I–V curves are almost linear implying that there is a little activation loss related to the high catalytic activity of PBSC.

The performance of PBSC perovskite as cathode material in PCMFC settings is examined using electrochemical impedance spectra. The impedance spectra of the as-prepared cell are obtained under open-circuit conditions at different temperatures, and are shown in Fig. 4(a). The impedance spectra consisted of two arcs at 600 °C, which indicate that there are at least two electrode processes during oxygen molecule reduction. The high frequency arc could be attributed to the polarization during charge transfer process. The low frequency arc could be attributed to the oxygen adsorption and desorption on the cathode surface as well as the diffusion of the oxygen ions [15]. When operating temperature increases to 650 °C and 700 °C, low frequency arc disappears, implying that the resistance of oxygen diffusion in porous electrode can be neglected at relative high temperatures. The total cell resistance (R_t), ohmic resistance (R_o), as well as interfacial polarization resistance (R_p) were then determined from the impedance spectra in Fig. 4(a), the results are shown in Fig. 4(b). In these spectra, the intercept with the real axis at low frequency represents R_t and the value of the intercept at high frequency is R_o , while the difference between these two values corresponds to R_p . It can be seen that increasing operating temperature may lead to significant reduction of interfacial polarization resistance R_p , typically from 0.69 Ω cm 2 at 600 °C to 0.12 Ω cm 2 at 700 °C, respectively. For cells with different cathode material, e.g., Ni–BZCY7/BZCY7/SrCo $_{0.9}$ Sb $_{0.1}$ O $_{3-\delta}$, the corresponding R_p values are 1.2 Ω cm 2 and 0.14 Ω cm 2 at 600 °C and 700 °C respectively [16]. As shown in Fig. 4(b), the cell resistance contributed from polarization resistance R_p is larger than that from ohmic resistance (R_o) when the cell is operated at the temperature below 625 °C. At 600 °C, the polarization resistance of the electrodes is 0.69 Ω cm 2 whereas the resistance of the electrolyte is only 0.5 Ω cm 2 . The ratio of R_p to R_t increases with the decrease of the operating temperature, from 25% at 700 °C to 58% at 600 °C respectively.

The experimental results of the cell Ni–BZCY7/BZCY7/PBSC can be understood using the microstructure characteristic of

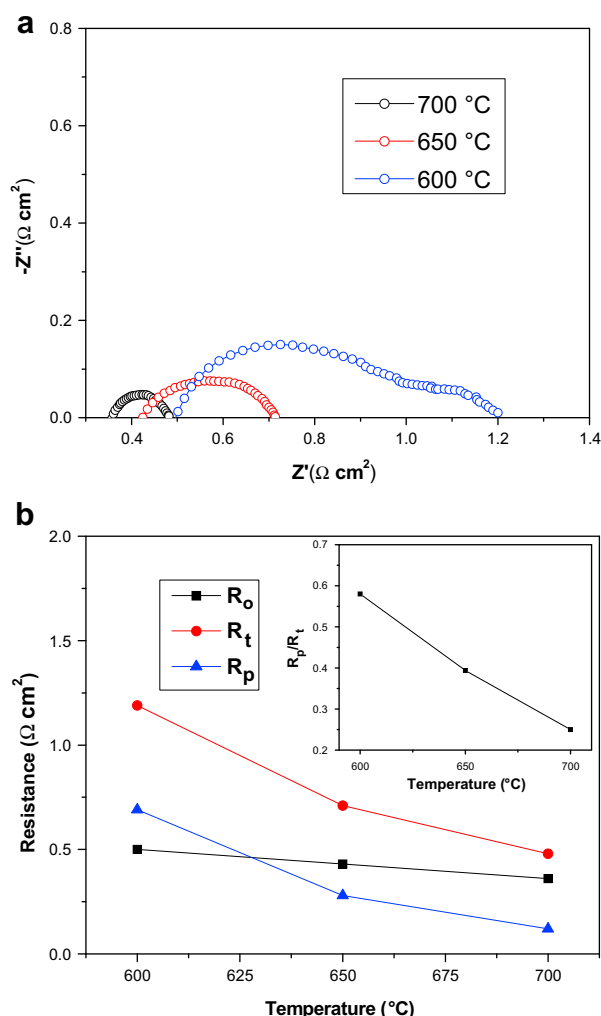


Fig. 4 – (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures. R_p/R_t is also shown in Fig. 4(b).

layered perovskite cathode PBSC. Due to the ordering A-sites in the layered perovskite oxides of PBSC, the rate of the oxygen up-taking is much faster than that in simple ABO_3 -type perovskite [17]. Similarly it is also much easier to release oxygen from layered oxides. The ordering of the A-site sublattice in layered structure significantly enhances the oxygen relaxation rate since oxygen atoms can be partially or even completely removed from the Pr^{3+} planes, generating numerous oxygen vacancies in the crystal lattice [17].

4. Conclusions

A novel PCMFC is fabricated with layered $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (PBSC) as a cathode, thin $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) as an electrolyte. The performance of the lab-scale tri-layer cell $\text{Ni-BZCY7|BZCY7|PBSC}$ is tested and characterized under intermediate temperature range from 600 to 700 °C. The results show that the open-circuit potential of 1.005 V and maximum

power density of 520 mW cm^{-2} are achieved at 700 °C. When temperature increases, the total cell resistance decreases, among which electrolyte resistance becomes increasingly dominant over polarization resistance. The results also indicate that PBSC perovskite cathode is a good candidate for intermediate temperature PCMFC development, while the developed $\text{Ni-BZCY7|BZCY7|PBSC}$ is a promising functional material system for SOFCs.

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