



A mixed-conducting $\text{BaPr}_{0.8}\text{In}_{0.2}\text{O}_{3-\delta}$ cathode for proton-conducting solid oxide fuel cells

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ABSTRACT

A mixed ionic and electronic conductor, $\text{BaPr}_{0.8}\text{In}_{0.2}\text{O}_{3-\delta}$ (BPI), was synthesized and examined as a cathode material for proton-conducting solid oxide fuel cells (H-SOFCs). X-ray diffraction analysis revealed that BPI had a perovskite structure and showed satisfactory tolerance to CO_2 and H_2O and good chemical compatibility with $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) electrolyte. Test cells with a single-phase BPI cathode exhibited excellent electrochemical performances, demonstrating a peak power density of $\sim 688 \text{ mW cm}^{-2}$ at 750°C . Furthermore, the cells with a BPI cathode showed very stable power output at a cell voltage of 0.7 V at 600°C over 100 h, suggesting that BPI is a promising alternative cathode for H-SOFCs.

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1. Introduction

Proton-conducting solid oxide fuel cells (H-SOFCs) have attracted much attention for low-temperature operation because many oxide proton conductors display lower activation energy than oxygen-ion conductors, thus having potential for higher proton conductivity and faster surface reactions at lower temperatures [1–6]. However, the lack of efficient cathode materials which are compatible with the existing oxide proton-conducting electrolytes results in poor cell performance at reduced temperatures [5,7]. For example, mixed ionic and electronic conductors developed for oxygen-conducting SOFCs (e.g., $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [8], $\text{PrBaCo}_2\text{O}_{5+\delta}$ [9]) have been used as cathodes for H-SOFCs. Since these mixed-conducting cathodes conduct oxygen ions and electronic defects (electrons and/or holes), their performances are relatively low due to the lack of active sites for oxygen reduction reaction (ORR) at the interfaces between the proton-conducting electrolytes and the oxygen ion conducting cathodes [10]. It is noted that some materials allow simultaneous transport of proton, oxygen ion, and electronic defects under typical fuel cell operating conditions, including Pr and Y co-doped BaCeO_3 [3] and BaZrO_3 [11], Bi-doped BaCeO_3 [12], and Co-doped $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_3$ [7]. When these mixed conductors are used as the cathodes in H-SOFCs, they allow simultaneous transport of proton, oxygen vacancy, and electronic defects, thus offering potential to extend the “active” sites for ORR beyond the

cathode/electrolyte interface [10,12,13]. Furthermore, these mixed conductors often have excellent compatibility with the proton-conducting electrolytes [14].

In addition to the mixed-conducting cathode materials based on BaCeO_3 or BaZrO_3 , Gd- or Y-doped BaPrO_3 [15–17] also showed good mixed conductivity at intermediate temperatures. For examples, the conductivity of $\text{BaPr}_{0.7}\text{Gd}_{0.3}\text{O}_{3-\delta}$ could reach $\sim 0.1 \text{ S/cm}$ in humidified H_2 at 500°C and that of $\text{BaPr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ was 0.26 S cm^{-1} at 800°C in air [16]. However, most studies were focused on the feasibility of using these doped BaPrO_3 conductors for H-SOFCs, including the nature of conduction and stability under different conditions, [16–18] because the contribution of proton, oxide ion, and electron to the total conductivity is sensitive to testing conditions and the conduction mechanism is complex [16,18]. More importantly, the reported poor chemical stability of doped BaPrO_3 compounds hindered their practice applications [16–18]. For instance, it was reported that doped BaPrO_3 is susceptible to decomposition under both wet and dry reducing conditions, moist oxidizing conditions, in CO_2 -containing atmospheres, and even under processing conditions at high temperatures [16–18]. To date, accordingly, there is little information on the performance and stability of BaPrO_3 -based cathodes for H-SOFCs. Inspired by the significant enhancement in stability of In-doped BaCeO_3 [19] and BaZrO_3 [20], we have systematically examined In-doped BaPrO_3 . It is believed that the relatively smaller ionic radius ($r_i = 800 \text{ pm}$) and larger electro-negativity of In greatly enhanced the stability of the structure. In this paper, we report our findings on the development of a novel mixed conductor, $\text{BaPr}_{0.8}\text{In}_{0.2}\text{O}_{3-\delta}$ (BPI), as the cathode for H-SOFCs based on BZCYYb electrolyte.

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2. Experimental

2.1. Powder fabrication

BaPr_{0.8}In_{0.2}O_{3-δ} (BPI) powder was prepared by the solid-state reaction method using BaCO₃, Pr₆O₁₁, and In₂O₃ powders (all from Alfa) as precursors. A mixture of these powders in stoichiometric ratio was ball-milled for 24 h in ethanol, dried, crushed, and calcined at 1100 °C for 10 h. The process was repeated to achieve pure perovskite phase. To determine the conductivity and evaluate the stability of BPI exposed to CO₂ and H₂O, the as-prepared BPI powders were iso-statically pressed into pellets at 200 MPa, followed by sintering at 1450 °C for 10 h to form dense pellets of ~8.7 mm in diameter and ~0.8 mm in thickness.

2.2. Single cell fabrication

NiO-BZCYYb/BZCYYb bi-layer was fabricated as described elsewhere [4]. A cathode slurry, consisting of BPI, V006 thinner (from Heraeus), and acetone, was brush-painted on the BZCYYb electrolyte surface, followed by firing at 1000 °C for 2 h. The functional cathode area was about 0.3 cm². Thicknesses of the anode (NiO-BZCYYb), electrolyte (BZCYYb), and cathode were about 500, 15, and 20 μm, respectively. The button cells were mounted on an alumina supporting tube for fuel cell testing at 600–750 °C with humidified hydrogen (3 vol.% H₂O) as fuel and stationary air as oxidant.

2.3. Characterizations

The phase compositions of the samples were examined by X-ray diffraction (XRD) analysis (PW-1800 system). The electrochemical performance of the cells was examined with an Arbin multi-channel electrochemical testing system (MSTAT, which is used to control and measure current/voltage responses with time). Impedance spectra were acquired using a Solartron 1255 frequency response analyzer interfaced with an EG&G PAR potentiostat (model 273A) with a signal amplitude of 10 mV in the frequency range from 100 kHz to 0.1 Hz.

3. Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) patterns of the as-prepared BPI powders. It should be noted that the BPI had a quasi-cubic perovskite structure with orthorhombic distortions, which was similar to those of BaPr_{0.7}Gd_{0.3}O_{3-δ} [17] and BaPr_{1-x}Yb_xO_{3-δ} [18]. After the powders were pressed into pellets and then sintered at 1450 °C for 10 h, the crystal

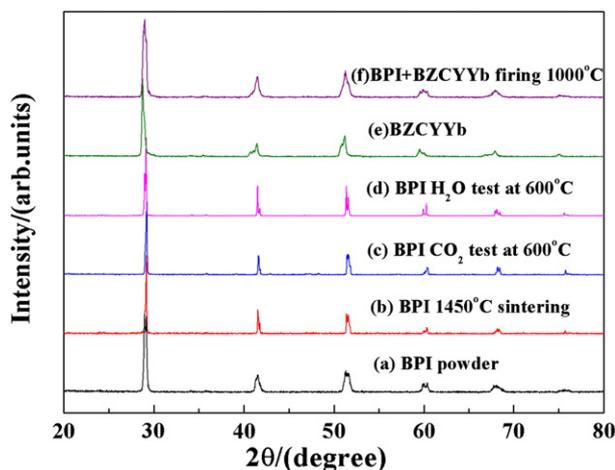


Fig. 1. XRD patterns of (a) BPI powders, (b) after sintering 1450 °C for 10 h, (c) after exposed to 2% dry CO₂ at 600 °C for 2 h, (d) after exposed to 3% H₂O at 600 °C for 20 h, (e) BZCYYb powders, and (f) BPI-BZCYYb mixtures after calcination at 1000 °C for 2 h.

structure remained, as shown in Fig. 1b. In contrast, BaPr_{0.7}Gd_{0.3}O_{3-δ} was reported to be unstable under similar processing conditions and segregation of gadolinia from the perovskite after firing at 1500 °C was observed [17]. Moreover, it was reported that BaPr_{0.7}Gd_{0.3}O_{3-δ} is reactive with CO₂ to form BaCO₃, even sensitive to ~0.03% CO₂ in the atmosphere [17]. When BaPr_{0.7}Gd_{0.3}O_{3-δ} was exposed to a humidified gas, barium and praseodymium hydroxides were formed [16,17]. To investigate the chemical stability of BPI against CO₂ and H₂O, the BPI samples were exposed to air containing 2% CO₂ at 600 °C for 2 h and to humidified air (with ~3% H₂O) at 600 °C for 20 h, respectively. XRD analysis of the samples after the exposure (Fig. 1c and d) indicated that there were no secondary phases observed and BPI had satisfactory tolerance to CO₂ and H₂O.

Further, comparison of the XRD data shown in Fig. 1f with those in Fig. 1a and e suggested that there were no observable chemical reactions between BPI and BZCYYb when the BPI-BZCYYb mixture was fired at 1000 °C for 2 h, indicating that BPI cathode material and BZCYYb electrolyte were chemically compatible during the cathode fabrication process.

Fig. 2 shows the total conductivities of BPI samples measured in different atmospheres at 500–750 °C. As can be seen, the conductivity increased dramatically with increasing the oxygen partial pressure, which was a typical characteristic of p-type behavior. The conductivity reached 0.20, 0.15, 0.09, and 0.06 S cm⁻¹ at 750 °C in dry oxygen, dry air, wet and dry nitrogen, respectively. The total conductivity of BPI was comparable to that of BaPr_{0.9}Y_{0.1}O₃ (0.23 S cm⁻¹ at 800 °C in air) [16]. Additionally, the apparent activation energies varied in the range of 0.18 to 0.26 eV, which were very close to the value for Yb-doped BaPrO₃ (~0.4 eV) [18]. The observed high conductivity and low activation of BPI were attributed to the p-type electronic conduction. However, it should also be noted that the actual oxygen ionic and protonic conductivities for the BPI compounds were still quite high. As reported, the ionic and protonic conductivities for BaPr_{0.9}Y_{0.1}O₃ were 0.074 and 0.037 S cm⁻¹ at 604 °C, respectively, which were several times higher than those for BaCeO₃-based materials at the same doping level [16]. When BPI is used as cathode for H-SOFCs, the high ionic conductivity of BPI should be beneficial to facilitating charge transfer and extending the active sites beyond the triple phase boundary (TPB) near the cathode/electrolyte interface.

Fig. 3a presents the current–voltage (*I*-*V*) and current–power (*I*-*P*) characteristics of test cells using BPI cathodes, demonstrating peak power densities of ~688, ~552, ~435, and ~306 mW cm⁻² at 750, 700, 650, and 600 °C, respectively. These performances are by far the best

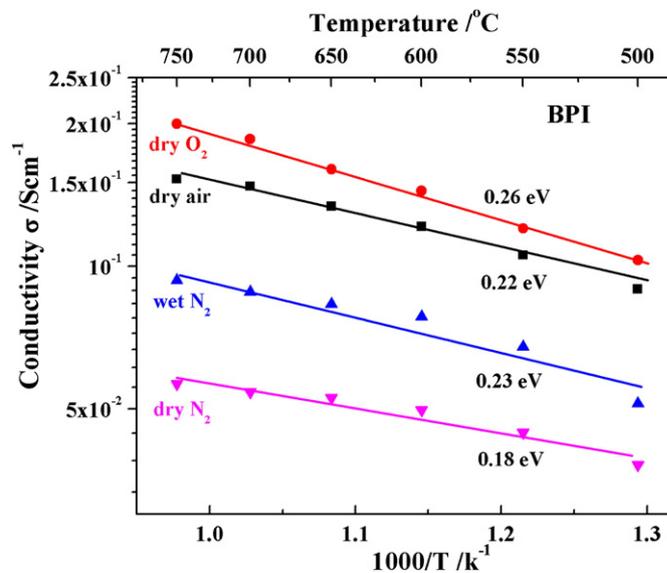


Fig. 2. The total conductivity of BaPr_{0.8}In_{0.2}O₃ in dry oxygen and air, dry and wet nitrogen at 500–750 °C.

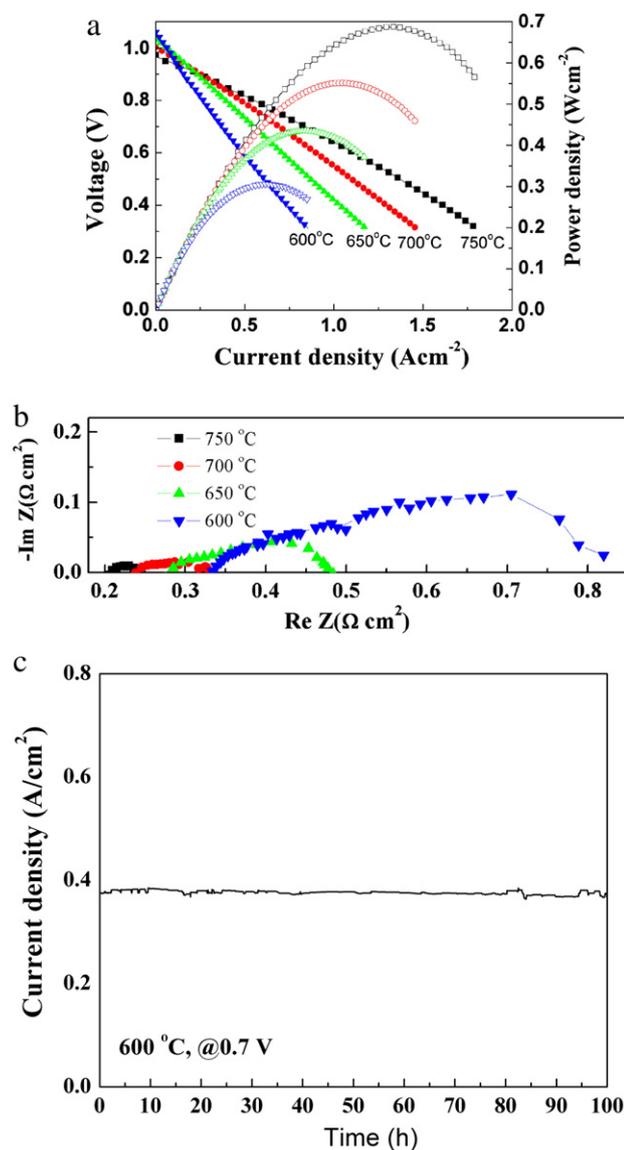


Fig. 3. (a) *I*-*V* and *I*-*P* characteristics for cell based on BPI cathode, (b) typical impedance spectra of the cell under open circuit conditions and (c) long-term stability of the cell tested at 600 °C under constant voltage of 0.7 V.

for proton-conducting SOFCs with mixed proton, oxygen ion, and electron conducting single phase cathodes, such as BaCe_{0.4}Pr_{0.4}Y_{0.2}O_{3-δ} (BCPY) [1], BaCe_{0.5}Bi_{0.5}O_{3-δ} (BCB) [15], and BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ} (BZCC) [17], as summarized in Table 1. The demonstrated performances were even better than those achieved by the cells using cobalt-based cathodes (such as PrBaCo₂O_{5+δ} [9] and SmBa_{0.5}Sr_{0.5}Co₂O_{5+δ} [21]) and only slightly lower than those using typical Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} cathode [8].

Further, the polarization resistances (R_p , $\Omega \text{ cm}^2$) of the cells were determined from impedance spectra: difference between the high frequency and the low frequency intercepts with the real axis. The average R_p of the cells based on BPI cathodes under open-circuit condition (Fig. 3b) were 0.03, 0.09, 0.20, and 0.49 $\Omega \text{ cm}^2$ at 750, 700, 650, and 600 °C, respectively. As compared to fuel cell with other cathode material in Table 1, the R_p values for the cells with BPI cathodes at 650 °C are almost the lowest ones.

To evaluate the durability of the cells with a BPI cathode, the cell performances were recorded as a function of time at 600 °C at a constant cell voltage of 0.7 V for 100 h. The current response of the cell remained relatively constant at $\sim 0.38 \text{ A cm}^{-2}$ and no obvious

Table 1

Main cathode material, peak power density output (PPD, mW cm^{-2}), and polarization resistance (R_p , $\Omega \text{ cm}^2$) at 650 °C reported in literature for proton-conducting SOFCs based on doped-BaCeO₃ electrolytes.

Cathode	Electrolyte	Anode	PPD	R_p	Ref.
BaPr _{0.8} In _{0.2} O _{3-δ} (BPI)	BZCYyb	Ni-BZCYyb	435	0.20	This work
BaCe _{0.5} Bi _{0.5} O _{3-δ} (BCB)	BZCY	Ni-BZCY	218	~ 0.75	[12]
BaCe _{0.4} Pr _{0.4} Y _{0.2} O _{3-δ} (BCPY)	BZCY	Ni-BZCY	270 ^a	–	[3]
BaZr _{0.1} Ce _{0.7} Co _{0.2} O _{3-δ} (BZCC)	BZCY	Ni-BZCY	370	0.35	[7]
PrBaCo ₂ O _{5+δ} (PBCO)	BZCYyb	Ni-BZCY	358	~ 0.21	[9]
SmBa _{0.5} Sr _{0.5} Co ₂ O _{5+δ} (SBSC)	BZCY	Ni-BZCY	377	~ 0.40	[21]
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} (BSCF)	BCY	Ni-BCY	~ 450	~ 0.1	[8]

^a Present PPD of the cell tested at 700 °C.

degradation was observed, as shown in Fig. 3c. This result demonstrated that BPI has great potential as a stable cathode material for H-SOFCs.

4. Conclusions

In this study, BaPr_{0.8}In_{0.2}O_{3-δ} was examined as a potential cathode material for H-SOFCs. The test cells based on BPI cathodes demonstrated a peak power density of $\sim 688 \text{ mW cm}^{-2}$ at 750 °C. Further, the cells with BPI cathodes displayed very stable performance at 0.7 V for 100 h at 600 °C, suggesting that BPI is a promising alternative cathode material for H-SOFCs. Moreover, properly doped BaPrO₃ or derived compounds have potential to be active electrode materials for other applications involving proton transport such as mixed-conducting membranes for hydrogen separation and purification.

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