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# $Ba_{1-x}Pr_xCo_{1-y}Fe_yO_{3-\delta}$ as cathode materials for low temperature solid oxide fuel cells

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#### 1. Introduction

In recent years, development of solid oxide fuel cells (SOFCs), operated in the low and intermediate temperature range of 500–800 °C, has received much attention for its potential in high efficiency power generation systems [1–3]. Lowering of the operation temperatures can suppress the degradation of components and extend the range of acceptable material selection, therefore improving cell durability and reducing the system cost. However, reducing the operating temperature decreases the electrode kinetics and results in large interfacial polarization resistances. This effect is most pronounced for the oxygen reduction reaction at the cathode [4,5]. Essential to the design of high performance electrodes are favorable electronic and ionic conductivities as well as high catalytic activities for oxygen reduction reactions in order to lower the polarization resistance of the cathode [6].

Perovskite-type oxides  $Ln_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$  (Ln = La, Sm, Nd, Gd, and Dy) are a few of the promising cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) [7]. For these materials, partial substitution of  $Ln^{3+}$  by  $Sr^{2+}$  at the A-site leads to the formation of oxygen vacancies and/or the reduction of B-site ions [8]. Among the perovskite-type cathode materials with different rare earth cations at the A-site, those incorporating  $Pr^{3+}$  ion exhibited the highest electrical conductivity and the lowest overpotential values due to the additional contribution

# ABSTRACT

 $Ba_{1-x}Pr_xCo_{1-y}Fe_yO_{3-\delta}$  (BPCF) perovskite oxides have been synthesized and investigated as cathode materials for low temperature solid oxide fuel cells (LT-SOFCs). Compared with those of  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF) and  $Sm_{0.5}Sr_{0.5}CoO_3$  (SSCo) cathode materials, BPCF has a lower polarization resistance at decreased temperatures. In particular,  $Ba_{0.5}Pr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  showed the lowest polarization loss among the different compositions as a cathode material for LT-SOFCs. The area specific resistance (ASR) of  $Ba_{0.5}Pr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  as a cathode material is 0.70 and 0.185  $\Omega$  cm<sup>2</sup> at 500 °C and 550 °C, respectively. The maximum power density of the cell BPCF/SDC/Ni–SDC with humidified hydrogen as fuel and air as oxidant reaches 860 mW cm<sup>-2</sup> at 650 °C.

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of the  $Pr^{3+}/Pr^{4+}$  valence change [9]. Shao et al. developed the  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF) cathode material for reduced temperature SOFCs. Although this potential cathode material showed excellent electrochemical performance, the obvious disadvantage of BSCF is the high thermal expansion coefficient (TEC), with a value of  $20 \times 10^{-6}$  K<sup>-1</sup> between 50 and  $1000 \degree C$  [10].

By substituting the La cation with an alternative cation, Gd or Pr, a favorable decrease in the ASR and TEC, due to a decreasing ionicity of the Ln–O bond, was observed as well as a suppression of the tendency to lose oxygen from the lattice with increasing temperature [11]. The TEC of  $Ln_{0.6}Sr_{0.4}CoO_{3-\delta}$  (Ln=La, Pr, Nd, Sm, and Gd) decreased from La to Gd, respectively. A similar trend was also observed in the analogous  $Ln_{1-x}Sr_xMnO_3$  and  $Ln_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$  systems [12,13]. Steele and co-workers [14] evaluated Ce–Pr oxides mixed conductors as cathodes for solid oxide fuel cells. Their results indicated that the electrical conductivity increases with increasing praseodymium content and the conductivity exceeds  $0.1 S cm^{-1}$  at 800 °C for compositions with 40–50 mol% PrO<sub>2-x</sub>.

In this work, we have studied  $Ba_{1-x}Pr_xCo_{1-y}Fe_yO_{3-\delta}$  (BPCF) (x=0.5; y=0.2, 0.5, 0.8) as a new cathode material for low and intermediate SOFCs [15]. The optimized composition was identified for BPCF and the electrochemical performance was compared with those of cathode materials used for IT-SOFCs, including BSCF and Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (SSCo).

#### 2. Experimental

The co-precipitation method was used to synthesize the BPCF powder. In a typical co-precipitation process, the nitrate

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precursors, Ba, Pr, Co and Fe, were mixed in the desired ratio; then they were dissolved in deionized water at 50 °C to obtain a 0.2 M solution. An equivalent volume aqueous solution of 2 M ammonium carbonate was slowly added into the BPCF precursor solution at a rate of  $5 \,\mathrm{ml}\,\mathrm{min}^{-1}$  with continuous stirring. The resulting precipitates were filtered, dried in an oven at 50 °C for 48 h and then calcined at 900 °C in air for 4 h. The same approach was also applied to the synthesis of SSCo and BSCF.

The materials with the specific compositions of  $Ba_{0.5}Pr_{0.5}$ Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> (BPCF5582), Ba<sub>0.5</sub>Pr<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> (BPCF5555), and Ba<sub>0.5</sub>Pr<sub>0.5</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> (BPCF5528), were synthesized and characterized. The choice of composition at x = 0.5 is based on previous reports for perovskite materials with maximum electrical conductivity, such as  $Sm_0 Sr_0 CoO_3$  [16] and  $Ba_0 Sr_0 CoO_2 Fe_{0.8}O_3$ [3]. The properties of BPCF were compared with those of SSCo and the BSCF. In this study, the same processes were used to synthesize all cathode materials in order to compare their chemical and physical properties with similar microstructures and morphologies. For electrical conductivity measurements, the powder materials of BPCF5582, BPCF5555, BPCF5528, SSCo, and BSCF were pressed into pellets and sintered at 1250°C for 4h. However, BSCF was an exception, which was sintered at 1150 °C to avoid melting. The size of the sintered pellets was about 0.15 cm in thickness and 1.60 cm in diameter. For the characterization of electrochemical performance, anode-supported half-cells NiO-YSZ|SDC with SDC as electrolytes were prepared by tape-casting/screen-printing and co-firing at 1400 °C for 4 h. The as-synthesized cathode materials without further grounding were made into paste and screen-printed on the NiO-YSZ|SDC half-cells. The final fuel cells have the following geometries: diameter of 1.60 cm, anode thickness of 0.9 mm, electrolyte thickness of 15  $\mu$ m, cathode thickness of 12  $\mu$ m, and cathode active area of  $0.35\,\mathrm{cm}^2$ .

The phase of the synthesized materials were examined by Xray powder diffraction (XRD) performed on the Bruker AXS D8 Advance with Cu K $\alpha$  radiation. The morphology of the cross-section of the cell was observed by a scanning electron microscope (SEM, Hitachi S-3500N, Japan). Prior to the SEM examinations, the samples were coated with gold by sputtering to minimize the charging effects under SEM imaging conditions. The electrical conductivity was carried out by a dc four-probe measurement from room temperature to 900 °C in air. Thermal mechanical analysis (TMA) was employed for the measurement of the thermal expansion coefficient and the melting temperature, using a horizontal pushrod dilatometer (Setsys Evolution manufactured by Setaram) with an Al<sub>2</sub>O<sub>3</sub> reference in the temperature range of 20–1450 °C with a ramp rate of 3 °C min<sup>-1</sup> in air. The resolution of the devices for thermal mechanical analysis is 0.2 nm. The cells were maintained at 650 °C for 5 h while hydrogen was gradually introduced to reduce NiO to Ni in the anode. The hydrogen was then introduced to the anode with an increased concentration of 20%, 40%, 60%, 80%, and 100% balanced with nitrogen with a flow rate of 100 sccm. The electrochemical polarization curves were measured from 500 °C to 700 °C in 50 °C intervals. The electrochemical performance and the ac impedance measurements were performed twice at each temperature with hydrogen saturated water as a fuel at 21 °C and air as an oxidant. The flow rates of hydrogen and air used for the impedance measurements were both 100 sccm. The polarization characteristics were measured using a Solartron 1480A Multistat with a flow rate of 4 mV s<sup>-1</sup> in the potential range from open circuit voltage (OCV) to 0.3 V. The ac impedance spectra were obtained in the frequency range of 100 kHz to 0.1 Hz under OCV conditions with 50 mV AC amplitude using a Solartron 1260 frequency response analyzer (FRA) connected to the Solartron 1480A Multistat.



Fig. 1. X-ray diffraction patterns of BPCF with different compositions.

#### 3. Results and discussion

Fig. 1 shows the XRD patterns of BPCF5582, BPCF5555, and BPCF5528. All the peaks can be indexed to a pure phase with an orthorhombic perovskite-type structure; the same is observed for  $PrCoO_3$  (JCPDS no. 89-8415) [17]. The TMA indicated that the melting temperature of BPCF5582 was around 1309 °C. The preliminary sintering experiments showed that BSCF was partially melted at 1250 °C, a property that was not observed for BPCF and SSCo. Therefore, the sintering temperature for BSCF was adjusted to 1150 °C.

Fig. 2 shows the cross-sectional SEM images of the cells after the electrochemical testing. As seen from the images, it is clear that the three layers, cathode, electrolyte and anode, are well bonded together. From the magnified SEM image shown in Fig. 2b, it is clear that the cathode consists of nanostructured particles that result in the cathode layer exhibiting a high porosity. These nanostructured electrodes have the advantage of facilitating gas diffusion and extending the triple-phase boundary (TPB) length [18], which both significantly improve the electrochemical performance of cells.

The electrical conductivities of BPCF5582, SSCo, and BSCF were measured by a four-probe method in air. The temperature dependence of the electrical conductivities for these materials is shown in Fig. 3. The figure indicates that the electrical conductivity of BPCF5582 is close to that of SSCo, but much higher than that of BSCF.

Fig. 4 shows the electrical conductivity of BPCF with varied compositions, measured by the four-probe method at different temperatures. Electrical conductivities of BPCF increased with an increasing amount of Co at the B-site. As a result, among the three compositions studied, BPCF5582 showed the highest electrical conductivity. The conductivity of BPCF5582 reached  $1500 \, \text{s} \, \text{cm}^{-1}$  at  $600 \, ^\circ \text{C}$ , which is much higher than that of  $\text{BPrCo}_2\text{O}_{5.5+x}$  at  $600 \, ^\circ \text{C}$ ,  $200 \, \text{s} \, \text{cm}^{-1}$  [19], and  $\text{BaCoO}_3$  at  $850 \, ^\circ \text{C}$ ,  $10 \, \text{s} \, \text{cm}^{-1}$  [20].

The thermal expansion coefficient of BPCF5582 was also measured by thermal mechanical analysis as shown in Fig. 5. The TEC of BPCF5582 was found to be  $17.183 \times 10^{-6} \text{ K}^{-1}$  between 20 °C and 500 °C and 28.311 ×  $10^{-6} \text{ K}^{-1}$  from 500–1200 °C, respectively. As a comparison, the TEC of SSCo was also plotted in Fig. 5, which was  $18.122 \times 10^{-6} \text{ K}^{-1}$  in the temperature range of 20–550 °C and  $34.310 \times 10^{-6} \text{ K}^{-1}$  in the temperature range of 600–1200 °C, respectively. These results show that the TEC of BPCF5582 is much higher than those of electrolyte materials even though it is lower than that of BSCF [10]. In order to decrease the TEC of the cathode, a composite electrode consisting of BPCF and electrolyte materials should be used in the future study.



Fig. 2. Cross-sectional SEM images of a single cell with a BPCF cathode, a SDC electrolyte, and a NiO-YSZ composite anode.

Fig. 6 shows the cell voltages and power densities as a function of current density for a single cell tested at different temperatures. The maximum power densities of cells with a BPCF cathode are 110, 250, 480, 860 mW cm<sup>-2</sup> at 500, 550, 600, and 650 °C, respectively. As shown in Fig. 7, the electrolyte resistance was much higher than that of the electrode–electrolyte interfacial polarization resistance. Therefore, the cell performances were mainly limited by the ohmic loss rather than the electrode polarization. The ASR of the BPCF



Fig. 3. The electrical conductivity of BPCF5582 compared with two well-known cathode materials, BPCF and SSCo.



Fig. 4. Temperature dependence of the electrical conductivity of  $Ba_{1-x}Pr_xCo_{1-y}Fe_yO_{3-\delta}$  with different compositions.



Fig. 5. Thermal expansion coefficients of BPCF5582 compared with that of SSCo.

cathode is as low as 0.70 and 0.185  $\Omega\,cm^2$  at 500 °C and 550 °C, respectively, which is lower than those of BSCF and SSCo (not shown here).

The electrochemical performance of the BPCF5582 as a cathode material was evaluated and compared with those of SSCo and BSCF. Fig. 8 shows the cell voltages and power densities, as a function of



Fig. 6. Cell voltages and power densities as a function of current density for the cell BPCF5582/SDC/Ni-YSZ at different temperatures.



**Fig. 7.** Total cell resistance ( $R_c$ ), electrode polarization resistance ( $R_p$ ), electrolyte and contact resistance ( $R_e$ ) as determined from the impedance spectra for the cell BPCF5582/SDC/Ni–YSZ under open circuit voltage conditions.



**Fig. 8.** Comparison of I-V polarization curves with different cathode materials at 650 °C.



**Fig. 9.** Impedance spectra of cells with different cathode materials measured at 650 °C using three-electrode configuration.

current density, for cells with different cathode materials at 650 °C. The maximum power densities of cells with BSCF, SSCo and BPCF cathodes are 660, 770, 860 mW cm<sup>-2</sup>, respectively. This indicates that the electrochemical performance of BSCP5582 was better than those of SSCo and BSCF.

To figure out the performance difference between the abovementioned three cells, the impedance spectra were measured, as shown in Fig. 9. Since identical materials and microstructure of the anode and the electrolyte was used in each cell, it was assumed that the difference of the electrode polarization-resistance obtained from Cole–Cole plots was contributed by the difference of the cathode materials only. From Fig. 9, it can be seen that the polarization resistance of BPCF5582 is close to that of BSCF, but lower than that of SSCo at 650 °C. Similar results were observed for the electrode polarization at operation temperature from 500 °C to 650 °C.

#### 4. Conclusions

The physical properties and electrochemical performances of  $Ba_{1-x}Pr_xCo_{1-y}Fe_yO_{3-\delta}$  (BPCF) (x=0.5; y=0.2, 0.5, 0.8) as cathode materials have been investigated. All the samples have a single orthorhombic phase. The  $Ba_{0.5}Pr_{0.5}Co_{0.8}Fe_{0.2}O_3$  (BPCF5582) showed the highest electrical conductivity among all compositions. The ASR of the electrode for the cell BPCF5582/SDC/Ni-YSZ is as low as 0.70 and 0.185  $\Omega$  cm<sup>2</sup> at 500 °C and 550 °C, respectively, which is lower than those of BSCF and SSCo. The maximum power densities of cells with BSCF, SSCo and BPCF5582 as cathodes are 660, 770, 860 mW cm<sup>-2</sup> at 650 °C, respectively. All these results have demonstrated that BPCF is a promising cathode material, especially for lower temperature SOFCs.

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