



Short communication

# High performance proton-conducting solid oxide fuel cells with a stable $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{3-\delta}-\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ composite cathode

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## ABSTRACT

A  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{3-\delta}-\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  (SSC–SDC) composite is employed as a cathode for proton-conducting solid oxide fuel cells (H-SOFCs).  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) is used as the electrolyte, and the system exhibits a relatively high performance. An extremely low electrode polarization resistance of  $0.066\ \Omega\ \text{cm}^2$  is achieved at  $700\ ^\circ\text{C}$ . The maximum power densities are: 665, 504, 344, 214, and  $118\ \text{mW}\ \text{cm}^{-2}$  at 700, 650, 600, 550, and  $500\ ^\circ\text{C}$ , respectively. Moreover, the SSC–SDC cathode shows an essentially stable performance for 25 h at  $600\ ^\circ\text{C}$  with a constant output voltage of 0.5 V. This excellent performance implies that SSC–SDC, which is a typical cathode material for SOFCs based on oxide ionic conductor, is also a promising alternative cathode for H-SOFCs.

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## 1. Introduction

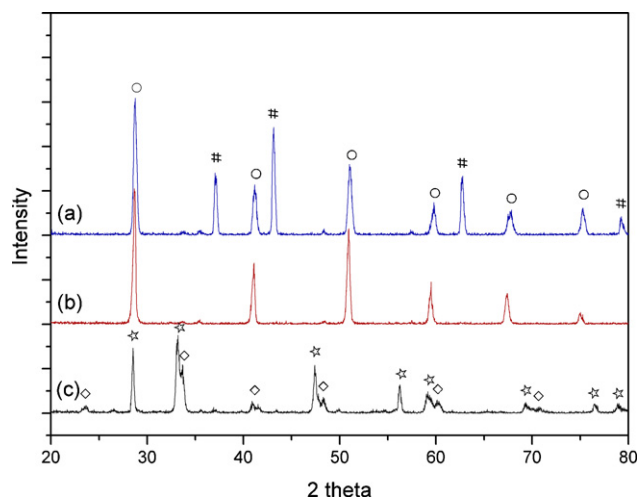
Recently, proton-conducting solid oxide fuel cells (H-SOFCs) have attracted much attention due to their unique properties. Compared with the oxide ionic conductors, the proton conductors possess several advantages, including a lower active energy of proton transport which ensures that the H-SOFCs operate at intermediate or lower temperatures. In addition, it ensures the production of water in the cathode which thus avoids the dilution of the fuel [1,2].

It is well known that the cathode polarization plays a critical role in the whole electrode reaction process, especially at low temperatures [3,4]. Therefore, it is crucial to develop efficient cathode materials for H-SOFCs to meet the demand for commercialization. Many useful cathode materials, which operate at lower temperatures, are based on compounds containing cobalt and include  $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$  (LSCF) [5],  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (SSC) [6], and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) [7]. These cobalt-based perovskite oxides often have high thermal expansion coefficients [8]. Therefore, if only the pure single phase materials are used, good adherence between the electrolyte and the cathode cannot be achieved, which obviously goes against the high performance output. Addition of a sufficient amount of electrolyte to the above materials, to prepare the composite cathode, results in a signifi-

cant improvement in the matching between the electrolyte and the cathode, without seriously compromising the electronic conductivity of the cathode [9]. Furthermore, the addition of the electrolyte can enlarge the triple phase boundary, especially for H-SOFCs [1,10].

Yang et al. [1] and Wu et al. [11] reported high performances from  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}-\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (SSC–BZCY) and  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}-\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$  (SSC–BCS) composite cathodes for SOFCs with  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) and  $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$  (BCS) being used as the respective electrolytes. It should be noted that water is produced in the cathode for H-SOFCs and that the cathode is also exposed to air; however, the  $\text{BaCeO}_3$ -based compounds show poor chemical stability standing against  $\text{H}_2\text{O}$  and  $\text{CO}_2$  [12,13]. Thus, the long-term stability of such composite cathodes containing  $\text{BaCeO}_3$  may not be reliable. In addition, He et al. have recently reported that oxygen ion diffusion is a notable limiting step in the cathodic process of H-SOFCs using SSC–BCS as the cathode in both dry and wet atmospheres [14]. Based on the above statement, we propose a new idea that the SSC–SDC composite cathode, which is widely used for SOFCs based on SDC oxide ionic conductors, should be employed for H-SOFCs. The addition of SDC to SSC also results in a good thermal matching to BZCY except for the high oxygen ion migration ability. Moreover, an excellent long-term stability is expected since SDC can endure corrosion by both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  [15]. In this work, H-SOFC, with BZCY used as the electrolyte was fabricated by co-pressing and co-firing at a relatively low temperature of  $1300\ ^\circ\text{C}$  for 5 h. SSC–SDC was employed as the cathode, and a high and stable performance was obtained.

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**Fig. 1.** XRD patterns of the NiO-BZCY anode substrate (a), the BZCY electrolyte membrane (b), and SSC-SDC composite cathode (c). (○) BZCY; (#) NiO; (◇) SSC; (☆) SDC.

## 2. Experimental

### 2.1. Powders syntheses and cell fabrications

SSC, SDC, and BZCY powders were synthesized via a citric acid-nitrate gel combustion process. As an example, the synthesis of the BZCY powders involved the following procedure. First,  $Y_2O_3$  was dissolved in  $HNO_3$ , then  $Zr(NO_3)_4 \cdot 5H_2O$  was added to the solution while stirring. Once the solution had cleared,  $Ba(CH_3COO)_2$  and  $Ce(NO_3)_3 \cdot 6H_2O$  were added. Subsequently, citric acid with a molar ratio of metal ions: citric acid of 1:1.5 was added and the pH value was adjusted to about 7 with ammonia. The solution was then heated and stirred continuously at 70–80 °C until ignition and com-

bustion occurred, giving the as-prepared powders. The as-prepared powders were then calcined at 1000 °C for 3 h in air to form a pure perovskite phase of BZCY. The as-prepared SSC and SDC powders were calcined at 950 and 700 °C for 3 h, respectively.

The NiO-BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> composite powders for the anode substrates were prepared by the citric acid-nitrate gel combustion process, and the synthesis procedure is the same as described above. The as-prepared powders were calcined at 750 °C for 3 h to ensure that no metallic nickel remained. The anode-supported half cell was fabricated by a co-pressing and co-firing method at a relatively low temperature of 1300 °C for 5 h. It should be noted that no pore-creating materials such as starch were added to the anode substrate.

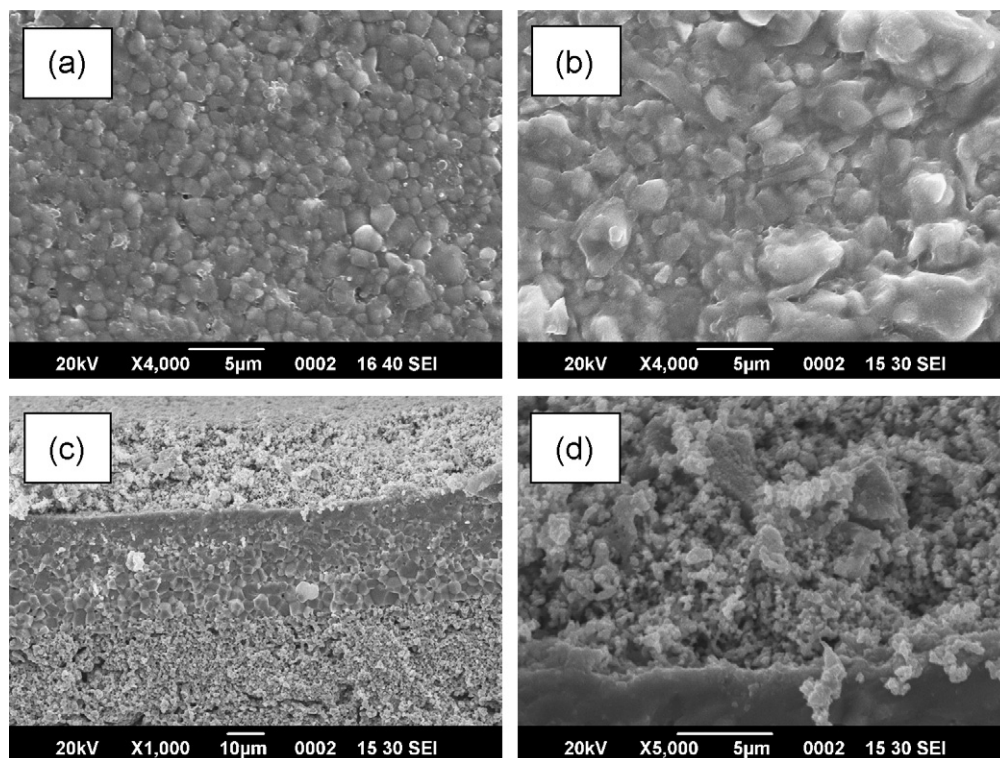
SSC and SDC powders in an appropriate proportion (weight ratio of 6:4) were mixed thoroughly together with a 6 wt. % ethylcellulose-terpineol binder, to prepare the cathode slurry. The slurry was then painted onto the BZCY electrolyte membrane and sintered at 950 °C for 3 h in air to form a porous cathode layer. Ag paste was then applied to the cathode as a current collector.

### 2.2. Characterization of the phase composition and microstructure of the cell components

Phase structures of the powders were identified by X-ray diffraction (XRD) analysis on a Philips PW 1730 diffractometer using  $CuK\alpha$  radiation. The microstructures of the tested cells were investigated by scanning electron microscopy (SEM, JEOL JSM-6700F).

### 2.3. Electrochemical measurements

Single cells were tested in a home-made cell testing system at temperatures of 500–700 °C with humidified hydrogen (~3%  $H_2O$ ) used as the fuel and static air used as the oxidant, respectively. The flow rate of the fuel gas was about 30 ml  $min^{-1}$ . The cell performances were measured with a DC Electronic Load (ITech Electronics



**Fig. 2.** SEM images of the surface morphology of the BZCY electrolyte before testing (a) and after testing (b), and the cross section of the tested cell (c and d).

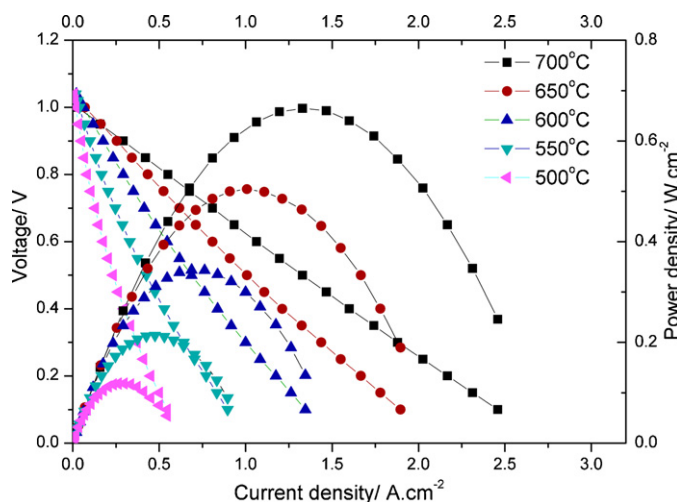


Fig. 3.  $I$ - $V$  and power density curves of the Ni-BZCY|BZCY|SSC-SDC single cell at different temperatures with hydrogen as the fuel.

model IT8511). Resistances of the cell under open circuit conditions were measured by an impedance analyzer (CHI604B, Shanghai Chenhua). A 5 mV AC signal was applied and the frequency was swept from 100 kHz–0.1 Hz.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the components of an as-prepared single cell. Only peaks corresponding to NiO and BZCY and to BZCY can be found in the anode substrate and electrolyte membrane, respectively. The SSC-SDC composite cathode was sintered at 950 °C for 3 h, and the pattern was identified to be SSC and SDC, except for a few minor unknown peaks, indicating a good chemical compatibility.

Fig. 2(a) and (b) shows the SEM images of the surface morphology of the BZCY electrolyte before and after testing, respectively. From both images, we can easily see that the electrolyte membrane of the cell fabricated in this work is very dense and the electrolyte retains this density after the cell run for 25 h at 600 °C. This suggests that a dense and crack-free BZCY electrolyte membrane can be successfully fabricated at temperatures as low as 1300 °C by employing the new preparation process for NiO-BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> anode composite powders. In addition, the BZCY electrolyte shows a high chemical stability. Fig. 2(c) and (d) shows the SEM images of the cross sections of the tested cell. It can be seen that the BZCY membrane and SSC-SDC cathode are about 30 and 20 μm in thickness, respectively. From Fig. 2(c), it can be observed that the adhesion of the SSC-SDC cathode to the BZCY electrolyte seems to be excellent and the cathode layer is porous. This excellent configuration favors an increase in the electrochemical reaction rate and a decrease in polarization of the cathode.

Fig. 3 shows the  $I$ - $V$  and power density curves of the single cell. The open circuit voltages (OCVs) were 1.010, 1.038, 1.060, 1.077, and 1.089 V, and the maximum power densities were 665, 504, 344, 214, and 118 mW cm<sup>-2</sup> at 700, 650, 600, 550, and 500 °C, respectively. In addition, the power densities can be further improved by optimizing the anode microstructure with pore-creating materials [16]. The high performance of the SSC-SDC can be attributed to its increased ability for oxygen reduction and oxygen ion migration, since oxygen ion migration is a notable limiting step for cathodic processes of H-SOFC [14]. Compared with SSC-BZCY, SSC-SDC only allows the simultaneous transport of oxygen vacancies and electronic defects, and hence the active sites mainly exist at the interface between the electrolyte and cathode. However, since SDC

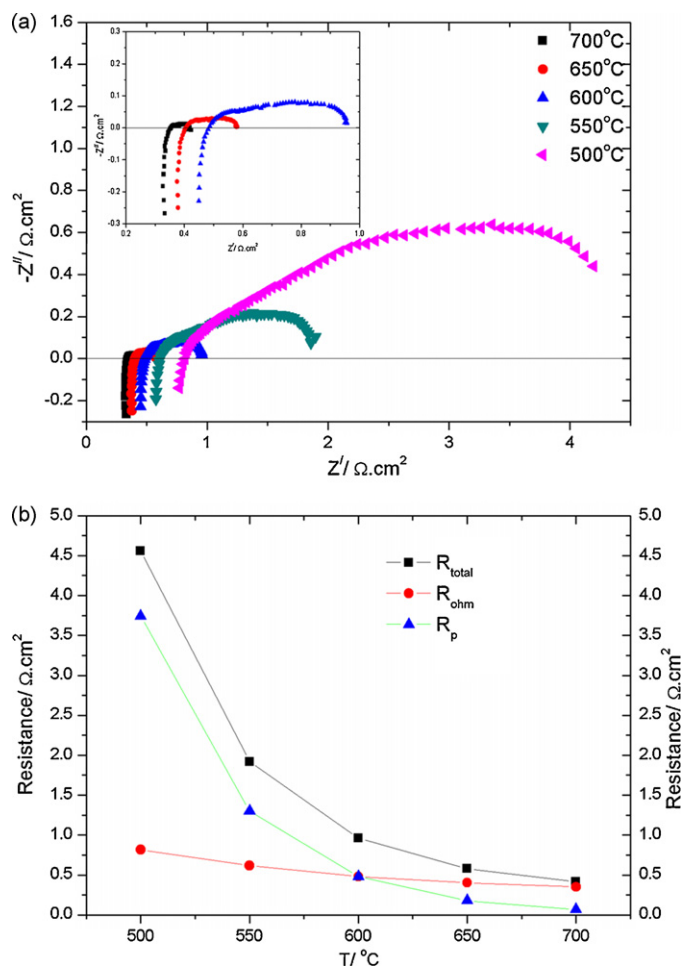
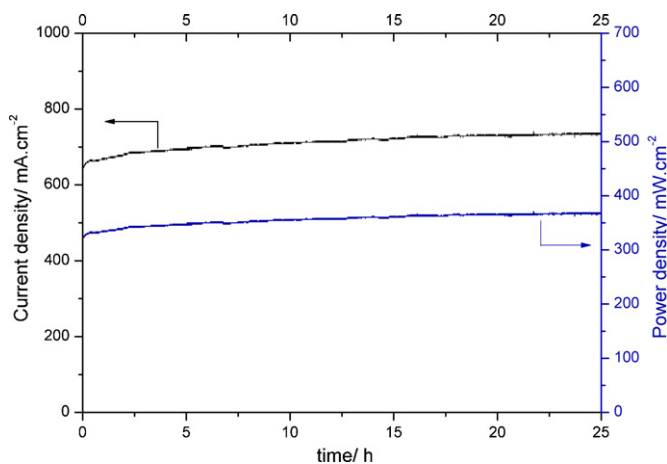


Fig. 4. Impedance spectra of the tested cell under open current condition at different temperatures (a), and the estimated resistances of the tested cell as a function of the temperature (b).

shows higher oxygen ion conductivity and better chemical compatibility with SSC than BZCY [1,17–19], we can conclude that the oxygen ion migration in SSC-SDC is faster than in SSC-BZCY which can effectively compensate for the lack of active sites in the cathode body. Therefore, the performance of SSC-SDC is comparable with that of SSC-BZCY.

The impedance spectra of the tested cells under open current conditions at different temperatures are shown in Fig. 4(a). In these spectra, the intercepts with the real axis at low and high frequencies represent the total resistance ( $R_{total}$ ) and the ohmic resistance ( $R_{ohm}$ ) of the cell, respectively. The difference between the above two values represents the polarization resistance ( $R_p$ ) of the interfaces between the electrodes and the electrolyte [20]. It can be observed that the resistances all dramatically decrease with an increase in temperature. Fig. 4(b) shows the estimated resistances ( $R_{total}$ ,  $R_{ohm}$ , and  $R_p$ ) obtained from the impedance spectra at different temperatures. A very low area-specific polarization resistance  $R_p$  of 0.066 Ω cm<sup>2</sup> is achieved at 700 °C, which is highly beneficial to an output high performance. A decrease in the cell operating temperature from 700 to 500 °C, results in the  $R_{ohm}$  of the single cell increasing from 0.35 Ω cm<sup>2</sup> (700 °C) to 0.82 Ω cm<sup>2</sup> (500 °C), while  $R_p$  increases from 0.066 Ω cm<sup>2</sup> (700 °C) to 3.74 Ω cm<sup>2</sup> (500 °C). When the temperature decreased from 700 to 500 °C,  $R_{ohm}$  doubled, while  $R_p$  increased by about 56 times. This confirms that at low operating temperatures the effect of the polarization resistance is predominant in the total cell resistance.



**Fig. 5.** Long-term stability of the Ni-BZCY|BZCY|SSC-SDC single cell with a constant output voltage of 0.5 V at 600 °C.

Moreover, the cell exhibits an essentially stable performance for 25 h at 600 °C with a constant output voltage of 0.5 V, as shown in Fig. 5. The current density increased gradually in the initial 15 h and then stabilized with increasing operating time, indicating that the electrode was initially activated and no substantial decline in the cell performance was observed within the 25 h operating time. The long-term stable performance indicates that SSC-SDC should prove to be a stable candidate material for the practical application of H-SOFCs at 600 °C.

#### 4. Conclusions

H-SOFCs with BZCY proton conductor used as an electrolyte, were fabricated by a combined co-pressing and co-firing process at a temperature of 1300 °C. The present study demonstrated that the SSC-SDC composite oxide, which is a typical cathode material for SOFCs based on oxide ionic conductors, can also be employed as a high performance cathode for H-SOFCs. The maximum power

densities were 665, 504, 344, 214, and 118 mW cm<sup>-2</sup> at 700, 650, 600, 550, and 500 °C, respectively, and a relatively low polarization resistance of 0.066 Ω cm<sup>2</sup> of the electrode was achieved at 700 °C. Moreover, the single cell with an SSC-SDC composite cathode exhibited an extreme long-term stability at 600 °C. These results show that it might be a novel way to find highly active and stable cathode materials for H-SOFCs from composite cathode materials for SOFCs based on oxide ionic conductors.

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