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 $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ -BaCe_{0.8} $Sm_{0.2}O_{3-\delta}$ composite cathodes for proton-conducting solid oxide fuel cells

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Abstract

Electrochemical performance of composite cathodes consisted of an electron–oxygen–ion mixed conductor, $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC), and a proton conductor, $BaCe_{0.8}Sm_{0.2}O_{3-\delta}$ (BCS) was investigated for intermediate temperature solid oxide fuel cells with proton-conducing ceramics as the electrolytes. Interfacial polarization resistance of the composite decreased with SSC content to the minimum at 60 wt.% SSC and then increased. Firing temperature of the cathodes also affected the resistance, and high performance cathode could be obtained by firing at 1050 °C. The minimum interfacial polarization resistance was 0.21 Ω cm² at 700 °C, where powder density of 0.24 W/cm² was achieved with humidified hydrogen as the fuel and ambient air as the oxidant. The low interfacial polarization resistance suggests promise applications of SSC–BCS composites as the cathodes for SOFCs based on proton-conducting electrolytes.

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1. Introduction

High temperature proton conductors (HTPCs) might be the substitute electrolytes for intermediate temperature solid oxide fuel cells (SOFCs) in respect of their high ionic transferring numbers, low activation energies for proton conduction, and greater efficiency in fuel utilization [1-3]. Single cells based on the HTPC electrolytes, such as doped barium cerate, have been reported for their great power output [3-6]. With HTPC as the electrolyte, water is formed at the cathode. Such distinguished characteristic of cathode reactions calls for intensive study on their reaction mechanisms and might lead to some special demands on the cathode materials. Until now, attentions are focused on the modification of electrolyte materials and cell fabrication techniques, and few reports are available on the cathode characterization and their microstructure optimization.

For most cases, Pt was used as the cathode for the cell with HTPC electrolyte. Nowadays, perovskite oxides, such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ [3], Ba_{0.5}Pr_{0.5}CoO₃ [4], La_{0.6}Sr_{0.4}CoO₃

* Corresponding author. E-mail address: pengrr@ustc.edu.cn (R. Peng). [6], and La_{0.6}Ba_{0.4}CoO₃ [7], are also reported as the cathodes for fuel cells using doped-BaCeO₃ proton conductors. However, little work on cathode optimization was conducted. In this work, $Sm_xSr_{1-x}CoO_{3-\delta}(SSC)$, which has been intensively investigated as the cathodes for low-and-intermediate SOFCs using oxygen conductors as the electrolytes, was studied as the cathode for fuel cells based on HTPCs. To minimize the cathodic polarization resistance, a proton conductor, BaCe_{0.8}Sm_{0.2}O_{3- $\delta}$}, was mixed with SSC to form a composite cathode. The electrochemical performance of the composite cathodes was investigated as a function of SSC content and electrode firing temperature.

2. Experimental

The fuel cell component, $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC), $BaCe_{0.8-}Sm_{0.2}O_{3-\delta}$ (BCS) and NiO powders were all synthesized by a glycine–nitrate process (GNP). To prepare SSC powders, solutions of $Sm(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$ and $Co(NO_3)_2 \cdot 6H_2O$ were mixed at the molar ratio of 1:1:2, and then, glycine was added with the glycine/metal molar ratio of 2:1. This mixed solution was heated on a hot plate under stirring, converted to a

viscous gel, and ignited to flame, resulting in fine SSC 'ash' of brown in color. The 'ash' was calcined at 950 °C for 4 h to remove carbon residues and to form perovskite SSC. BCS and NiO powders were synthesized by GNP as described elsewhere [3,8].

NiO and BCS powders were mixed in the weight ratio of 65:35(about 1:1 in the volume ratio) as the composite anode. Di-layers of the anode substrate and BCS electrolyte were fabricated by a dry-pressing method. The thickness and the diameter of electrolyte were about 70 μ m and 11 mm, respectively, after the bi-layer was co-fired at 1400 °C for 5 h in air. The composite cathodes were prepared by mixing SSC and BCS powders, in which SSC content varied from 10 wt.% to 100 wt.%. The cathode layers about 40 μ m in thickness and 6 mm in diameter were formed by screen-printing process with ethocel and abietyl alcohol as binder, and then fired at 950~1100 °C for 5 h in air. Ag paste was applied onto the cathode surface as the current collector.

Single cells were tested from 600 °C to 700 °C with a homedeveloped cell-testing system. Humidified hydrogen (~3% H_2O) and air were fed to the anode and the cathode, respectively, at 50 ml min⁻¹. The impedance spectra were measured using an electrochemical workstation (IM6e, Zahner) under open circuit conditions in the typical frequency range from 0.01 Hz to 1 MHz. The current–voltage curves were obtained using a potentiostat/galvanostat (DJS-292, SPSIC).

3. Results and discussion

3.1. The effect of cathode composition on interfacial polarization resistance

The triple phase boundaries (TPBs) are essential for cathode reaction with HTPC electrolyte, since they are the right place for generated water to be released from, as given in equip. (1). In SSC–BCS composite cathode, the TPBs are extended from the electrolyte/cathode interface to the bulk of composite cathode, and might help to improve the cathode performance. In this work, the effect of SSC content on the cathode electrochemical performance was firstly investigated, and the cell performance was also studied.

$$4OH_{O}^{\cdot} + O_{2} + 4e \rightarrow 2H_{2}O + 4O_{O}^{x}$$

$$\tag{1}$$

Fig. 1 shows typical impedance spectra measured at 600 °C for single cells with cathodes containing different amount of SSC and fired at 1100 °C for 5 h. The total resistance (R_t), electrolyte resistance (R_e) and interfacial polarization resistance (R_p) are schematically shown in Fig. 1. It should be noted that although R_p here includes the interfacial polarization resistance from both the cathode and the anode, the change of R_p should be attributed to the variation of cathode polarization resistance, R_c , since the anode is fabricated with an identical process, and the anodic interfacial polarization resistance, R_a , is reasonably assumed to be the same for all the cells.

The spectrum for pure SSC cathode (Fig. 1(e)) appears to be two arcs, a high-frequency arc and a low-frequency arc. The high-frequency arc is larger than the low-frequency arc, indicating that ionic conduction probably limits the electrode reaction [9], and here the ionic might be proton. As the SSC concentration decreases and BCS increases, shown as Fig. 1 (d)-(a), the low-frequency arc becomes more dominant. The lowfrequency arc is generally deemed to characterize the exchange reaction of O to O⁻ and the diffusion of O⁻ to the reaction zone inside the solid cathode material. So the dominating of lowfrequency arc might indicate that mass transfer becomes the primary rate-limiting processes. There is also a small medium frequency arc in the spectrum of SSC 10 wt.% (8 vol.%), as shown in Fig. 1(a). Since the SSC content is far below its percolation threshold, the medium frequency might correspond to the low electron conductivity of the composite cathode. And more details about the cathode reaction mechanism with HTPC electrolyte are still under investigations.

It can be seen that the overall length of the impedance arcs decreases to a lowest value, and then increased with the SSC content. In order to clearly describe this variation, R_t , R_e and R_p measured at 600 °C and 700 °C by A.C. impedance are shown in Fig. 2 as a function of SSC content. To compare with R_t , the cell resistances simulated from I-V curves, R_s , are also shown in Fig. 2. It is obvious that R_t agrees well with R_s , implying negligible activation process taking place on the electrodes.

The interfacial polarization resistance, R_p , reduces with SSC content, and reaches its minimum at 60 wt.% (53 vol.%). The



Fig. 1. Nyquist impedance plots for single cells with cathodes with different amount of SSC. The measurement was conducted at 600 °C under open circuit conditions with humidified hydrogen as the fuel and air as the oxidant.



Fig. 2. Area specific resistances obtained from impedance spectra measured with single cells as a function of SSC content in the composite cathodes: a) 600 °C, b) 700 °C. R_e , the electrolyte, resistance, R_p , the interfacial polarization, resistance, R_t total resistance of the cell determined by impedance spectra, and R_s the cell resistance simulated from I-V curves.

lowest R_p is 0.67 Ω cm² at 600 °C and 0.21 Ω cm² at 700 °C. The low interfacial polarization resistance suggests that a high performance cathode is developed for intermediate temperature SOFCs base on HTPC electrolytes.

The electrolyte resistances, $R_{\rm e}$, remain stable with the cathode composition. The average resistance is about 1.1 Ω cm² at 600 °C and 0.72 Ω cm² at 700 °C, and the corresponding conductivity is calculated to be 0.00636 S cm⁻¹ and 0.00972 S cm⁻¹, respectively, which goes well with the value reported previously [3].

High interfacial polarization resistance of pure SSC clearly identifies the importance of the proton conduction within the electrode, which effectively extends the length of TPBs. At optimized composition in the cathode, the electrolyte resistance is higher than the interfacial polarization resistance and becomes the major source of the cell resistance. Especially at 700 °C, the lowest R_p is only 1/4 of R_t . Therefore, optimizing the cathode composition to enlarge the TPBs is very important for the improvement of cell performance when an electron–oxygen ion mixed conductor is used as the cathode material.

Of course, when the cathode composition is optimized, reducing the electrolyte thickness will dramatically improve the cell performance. For example, when the electrolyte thickness decreases from 70 μ m to 20 μ m, the cell resistance at 700 °C will decrease from 0.7 Ω cm² to 0.4 Ω cm², which improves the maximum power density from 0.24 W cm⁻² to 0.48 W cm⁻².

3.2. The effect of cathode composition on cell performance

Shown in Fig. 3 is the change of open circuit voltage (OCV) and maximum power density with cathodic composition. At 600 °C, the tested OCVs are between 1.05 and 1.07 V, which are very close to the theoretical value 1.18 V, indicating the gastight of the electrolyte and also the negligible electronic conducting



Fig. 3. The effect of cathodic composition on open circuit voltage (solid) and maximum power density (hollow) measured at 600, 650 and 700 $^{\circ}$ C.

in the BCS solid solution. It should be noted that OCV increases slightly with SSC content, as shown in Fig. 3. This possibly indicates that high electronic conductivity is favorable to improve OCV, since the BCS–SSC composite with high SSC loading corresponding to large electronic conductivity.

The maximum power densities, as shown in Fig. 3, increase with SSC content to its highest value at 60 wt.% SSC and then decrease, in agreement well with the cell resistance. The maximum power density is about 0.15 and 0.24 W cm⁻² at 600 and 700 °C, respectively.

3.3. The effect of cathode morphology on cell performance

The length of TPBs is not only affected by the cathode composition, but also by its microstructure, which is determined by the starting powders, the fabrication process, and specially the firing temperature. Fig. 4 presents the impedance spectra measured at 700 °C for cathode with 50 wt.% SSC and fired at 950 °C–1100 °C in air for 5 h. Both the bulk resistance and the interfacial resistance decrease with firing temperature. The well contact of particles fired at higher temperature accounts for the decrease of cell resistance at the first stage, which effectively fortifies the bonding between the electrolyte and cathode, thus increases the length of the TPBs, and facilitates the transfer of input and output species, resulting in the reduction in both bulk resistance and polarization resistance. That is to say, a high firing temperature could elevate the electrode performance. However, firing at temperature above 1050 °C has no obvious



Fig. 4. Nyquist impedance plots of cells with the SSC–BCS composite cathodes fired at 950 °C, 1000 °C, 1050 °C and 1100 °C. The measurement was conducted at 700 °C under open circuit conditions with humidified hydrogen as the fuel and ambient air as the oxidant.

effect on the resistances. The electrolyte resistance is 0.68 and 0.69 Ω cm², while the electrode polarization resistance is 0.28 and 0.27 Ω cm² for cells with cathode fired at 1050 °C and 1100 °C, respectively. This suggests that 1050 °C is high enough for firing the cathode. Further increase of firing temperature might lead to the increase of cell resistance due to the coarsening of particles. The average particle diameter increases from about 0.5 μ m at 1000 °C to 2 μ m at 1100 °C. Much high firing temperature might result in the decrease of porosity and specific surface area, thus the decrease of TPBs length. The maximum power density is about 0.12, 0.19, 0.22 and 0.23 W cm⁻² for those fired at 950, 1000, 1050 and 1100 °C, respectively.

4. Conclusions

 $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC), an electron–oxygen ion mixed conductor, was investigated as the cathode materials for SOFCs with proton-conducting electrolytes. To enlarge the TPBs, $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BCS), a proton conductor, was mixed with SSC to form a composite cathode, and the effect of SSC content in the composite on its electrochemical performance was studied. The interfacial polarization resistance of the cell decreased with the SSC ratio, reached the lowest at SSC 60 wt.%, about 0.67 Ω cm² at 600 °C, and then increased; while the bulk resistance remains almost stable. The open circuit voltage of the cells was also affected by SSC content, which went up slightly with the SSC weight ratio, about 1.050, 1.063 and 1.070 V at 600 °C with SSC weight ratio of 10%, 60% and 100%, respectively. Moreover, firing temperature of the cathodes had a great effect on the cell resistance, and high performance cathode could be obtained by firing at 1050 °C. Tested at 700 °C, the minimum interfacial polarization resistance and the maximum powder density was achieved as 0.21 Ω cm² and 0.24 W cm⁻², respectively, with humidified hydrogen as the fuel and ambient air as the oxidant. The high electrochemical performance of the SSC–BCS composites suggests the potential application of the mixed conductors as cathode materials for SOFC based on proton-conducting electrolytes.

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