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Abstract

Developing ceria-based solid oxide fuel cells (SOFCs) with low cost, high power density, and, in particular, high working efficiency is of great significance to practical applications. In this work, Ba- and Sr-containing composites ($\text{Ni-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$) were for the first time proposed and evaluated as anodes for $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC)-based SOFCs. Both Ba and Sr diffusion occurs at elevated temperatures during fabricating anode-supported half-cells; correspondingly, a thin electron-blocking interlayer is formed in situ at the anode/electrolyte interface. The presence of Ba ensures the formation of a BaCeO_3 -based electron-blocking layer, which has a very high ion transport number and completely eliminates the internal short circuit current across the SDC electrolyte. Sr incorporation can substantially promote the sintering activity of the anode and electrolyte and, hence, reduces the sintering temperature of the half-cells to 1150 °C. The electrochemical performance of the SDC-based cells varies significantly with the anode composition. $\text{Ni-Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ is demonstrated to be the optimal anode composition showing high open circuit voltages (1.038 V at 650 °C) and peak power densities (677 mW cm^{-2} at 650 °C). These results present substantial progress in developing leakage current-free ceria-based SOFCs and also provide new insight into designing new cathode materials/structures for efficient ceria-based solid oxide electrolyzer cells.

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**Barium- and Strontium-Containing Anode Materials toward Ceria-Based Solid
Oxide Fuel Cells with High Open Circuit Voltages**

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Abstract

Developing ceria-based solid oxide fuel cells (SOFCs) with low cost, high power density and in particular high working efficiency is of great significance to practical applications. In this work, Ba- and Sr-containing composites ($\text{Ni-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$) were for the first time proposed and evaluated as the anodes for $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC)-based SOFCs. Both Ba and Sr diffusion occurs at elevated temperatures during fabricating anode-supported half cells; correspondingly, a thin electron-blocking interlayer is formed *in situ* at the anode/electrolyte interface. The presence of Ba ensures the formation of BaCeO_3 -based electron-blocking layer, which has very high ion transport number and completely eliminate the internal short-circuit current across SDC electrolyte. Sr incorporation can substantially promote the sintering activity of the anode and electrolyte, and hence reduces the sintering temperature of the half cells to 1150 °C. The electrochemical performance of the SDC-based cells varies significantly with the anode composition. $\text{Ni-Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ is demonstrated to be the optimal anode composition showing high open circuit voltages (1.038 V at 650 °C) and peak power densities (677 mW cm^{-2} at 650 °C). These results present substantial progress in developing leakage current-free ceria-based SOFCs, and also provide new insight into designing new cathode materials/structures for efficient ceria-based solid oxide electrolyzer cells (SOECs).

Keywords: open circuit voltage, doped ceria, element diffusion, sintering, solid oxide fuel cells

1. Introduction

As a promising alternative energy technology for next generation of power supply devices, solid oxide fuel cells (SOFC) have received significant research attention worldwide because of some appealing advantages, such as high energy efficiency, low pollutant emission and excellent fuel flexibility allowing the utilization of various kinds of hydrocarbon fuels¹⁻³. However, high operating temperature usually causes severe performance degradation and requires long start-up time and expensive interconnectors/sealing materials, which is considered as a main obstacle that hinders SOFCs commercialization. Therefore, exploring SOFC operating at reduced temperatures and outputting high performance simultaneously is becoming very urgent. Employing highly conductive electrolyte materials plays a key role in lowering the operation temperature of SOFCs⁴. Among all types of well-established electrolyte materials, doped ceria (DCO) exhibits high ionic conductivity and remarkable chemical compatibility with electrode materials, and is considered to be one of the potential electrolyte materials for low-temperature SOFCs⁵. Regrettably, partial internal short-circuit behavior occurs when DCO electrolytes are exposed to fuel gas under operating conditions due to the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox reaction, which results in decreased open circuit voltages (OCVs) and hence low working efficiency⁶⁻⁷.

To suppress the electronic conduction across the DCO electrolyte, various approaches were proposed and investigated⁸⁻¹⁴. As a common strategy to protect DCO electrolyte from reduction, fabricating bi-layered electrolyte membranes have been suggested, including YSZ/SDC and BZCY/SDC, but the low oxygen ionic conductivity of YSZ and BZCY invalidate the merit of using DCO for developing low-temperature SOFCs^{9, 14}. In addition, for the case of YSZ/SDC, formation of $(\text{Zr,Ce})\text{O}_{2-x}$ solid solution during sintering may further decrease the ionic conductivity of the electrolyte membrane and hence degrade the cell performance. In order to suppress DCO reduction and meanwhile maintain high electrolyte conductivity, Hibino et al.¹⁵⁻¹⁶ prepared a very thin $\text{BaCe}_{1-x}\text{Sm}_x\text{O}_{3-\delta}$ layer on the SDC electrolyte surface via a solid-state reaction between SDC and BaO slurry. Following their work, Sun and Liu et al.^{10, 12} demonstrated that Ba-containing composites (doped

BaCeO₃-Ni) can be directly employed as the anodes for DCO-based SOFC, and a thin BaCeO₃-based electron-blocking layer is formed *in situ* during fabricating half cells. Besides, the thickness of the electron-blocking layer can be regulated by controlling the thickness of Ba-containing anode functional layer and/or the sintering temperature of half cells^{10, 17}.

In our previous work, we reported for the first time that SrCeO₃-like electron-blocking layer is formed via Sr diffusion induced *in-situ* solid-state reaction at elevated temperatures by using Ni-SrCe_{0.95}Yb_{0.05}O_{3-δ} anode for SDC-based SOFCs¹⁸. Notably, the densification temperature of SDC electrolyte membrane is remarkably reduced compared with the cell with Ba-containing anode possibly because Sr is a good sintering aid for SDC¹⁹. However, there is still considerable leakage current for the cell with SrCeO₃-based electron-blocking layer, which is due to the significant electronic conduction behavior of SrCeO₃ under fuel cell conditions. Meanwhile, the delivered power performance is not competitive as compared with the cells with Ba-containing composite anode. Herein, Ba- and Sr-containing composites (Ni-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ}) were proposed as the anodes for SDC-based SOFCs in order to achieve low-temperature fabrication, high power performance and high open circuit voltages (high working efficiency). This concept takes advantages of both Ba and Sr diffusion strategy for DCO-based SOFC. Besides, Sr doping can also increase the chemical stability of doped BaCeO₃²⁰⁻²¹. In this case, Ba diffusion ensures the formation of BaCeO₃-based electron-blocking layer with high ion transport number, while Sr diffusion helps to reduce the sintering temperature of the half cells. In addition, the dependence of electrochemical performance of the cells on the anode composition is investigated in detail, and an optimal anode composition is determined.

2. Experimental

2.1. Sample preparation

NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} (x=0, 0.1, 0.2, 0.3) composite powders with a weight ratio of 6:4 that are employed as the anodes for SDC-based SOFCs were all synthesized via a one-pot combustion process described in our previous work¹⁸.

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, BaCO_3 , $\text{Sr}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and Y_2O_3 are the reagents for synthesizing the composite powders. After combustion, the as-prepared composite powders were calcined at 1000 °C for 3 h in air.

Anode-supported half cells with $\text{NiO-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ anode supports and SDC electrolyte membranes were fabricated by a dry-pressing method. No pore-former was added into the composite anode. The diameter and the thickness of the green cells were about 15 and 1mm, respectively. Subsequently, the green half cells were sintered at 1250, 1200 or 1150 °C for 5 h in air. Finally, a typical $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ -SDC composite cathode slurry with a weight ratio of 6:4 used in our previous work was brush-painted on the SDC electrolyte surface of half cells, and then fired at 950 °C for 2 h to assemble a fuel cell with an active area of 0.195 cm². $\text{Ni-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ anodes will be obtained after $\text{NiO-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ anode supports are reduced by the fuel gas during cell testing.

In order to illustrate the different diffusion phenomena of Sr and Ba from anode to electrolyte during fuel cell sintering and clarify the reason for the reduced sintering temperature of SDC when Sr-containing anode was used for SDC-based SOFC, BaCO_3 and SrCO_3 suspensions were drop-coated on the SDC pellets pre-sintered at 800 °C for 3 h, and then annealed at 1300 °C for 5 h. Ba and Sr diffusion from BaCO_3 and SrCO_3 occur during high-temperature sintering, which is similar to the situation of Ba- or Sr-containing anode supported SDC-based fuel cells, respectively. The schematic diagram for this experiment is shown in **Figure S1** (Supporting Information). After annealing, the SDC pellets were collected for further characterization. To investigate the phase composition and the chemical states of the elements in the electron-blocking layer, SDC powders were placed between two green $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ ($0.1 \leq x \leq 0.3$) pellets and then annealed at 1300 °C for 10 h to simulate the sintering process of $\text{NiO-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ /SDC half cells, as described elsewhere^{18, 22}.

2.2. Electrochemistry testing and other characterizations

The single cell was attached to a home-made cell testing equipment by using Ag paste for sealing. After drying at 80 °C for 6 h, the single cell was tested from 650 to

500 °C at 50 °C intervals with ~3% H₂O humidified hydrogen (40ml min⁻¹) as the fuel and the static air as the oxidant. The current-voltage curves of the cells were measured by using a DC electronic load (ITECH Electronics model IT8511). The OCVs of the fuel cells were obtained from both a DC Electronic Load and EIS measured under open circuit condition. The crystal structures of NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} composite powders were characterized by an X-ray diffractometer (Rigaku TTR-III) with Cu K α radiation. The microstructures and elemental distribution of the tested single cells and treated SDC pellets were investigated by a scanning electron microscope (SEM, JEOL JSM-6700F) equipped with an energy-dispersive X-ray spectroscopy system (EDS). The sintering shrinkage behaviors of NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} composite anode materials were examined using dilatometer measurement (Netzsch DIL 402E). The specimens were fabricated by die-pressing with dimensions of 30 mm × 4 mm × 2 mm. X-ray photon spectroscopy (XPS, Thermo ESCALAB 250) and inVia Raman Microscope (Renishaw) with 532 nm incident laser excitation were used to investigate the phase composition and the chemical states of the elements of the nominal SDC powders calcined between two Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} pellets.

3. Results and discussion

The XRD patterns of NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} (0 ≤ x ≤ 0.3) composites calcined at 1000 °C for 3 h are shown in **Figure 1**. The indexing of the XRD patterns clearly reveals all the samples present well crystallized perovskite (Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ}) and cubic (NiO) phase structures and no impurity diffraction peaks are detected over the range of Sr doping content (0 ≤ x ≤ 0.3). Shown in **Figure 2** are SEM images of the surface and cross-sectional morphology of the SDC electrolyte membranes in the NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ}/SDC (0.1 ≤ x ≤ 0.3) half cells sintered at 1150 °C for 5 h. One can see that the sintering ability of the SDC electrolyte membrane is closely associated with the NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} anode, and both the electrolyte density and grain size increase significantly with increasing Sr content in the anode. The SDC electrolyte membrane is fully dense for the cell with Ba_{0.7}Sr_{0.3}Ce_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} anode support, which also exhibits the largest

grain size. The results suggest that the densification temperature of the SDC electrolyte membrane can be well controlled by tuning Sr doping in the $\text{NiO-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ anode support. It should be noted that the densification temperature of the anode-supported SDC electrolyte membrane is decreased by nearly 200 °C without using additional sintering aids as compared with those SDC-based cells with traditional NiO-SDC or NiO-BZCY anode supports^{10, 23}.

The substantially decreased densification temperature might be ascribed to the improved sintering activity of anode and/or electrolyte. Basically, the shrinkage of anode support during sintering is one key driving force for the densification of the electrolyte membrane²⁴. To verify the formulated interpretation for the reduced sintering temperature of SDC electrolyte, the sintering shrinkage behaviors of $\text{NiO-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ ($0 \leq x \leq 0.3$) specimens were measured and shown in **Figure 3**. One can see that, when the temperature is increased to 1200 °C, the shrinkage of $\text{NiO-Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ (NiO-BSZCY91) and $\text{NiO-Ba}_{0.8}\text{Sr}_{0.2}\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ (NiO-BSZCY82) reaches 12.5% and 15.5%, respectively, and the corresponding value for $\text{NiO-BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ (NiO-BZCY) specimen is only 6.8%, indicating that Sr doping greatly promotes the sintering activity of the anode support. Similar sintering shrinkage behavior is also observed in $\text{NiO-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ /SDC half cells sintered at 1200 °C for 5 h, as shown in **Figure S2**(Supporting Information), further confirming the positive role that Sr plays in anode sintering. It has to be mentioned that, NiO-BSZCY73 shows similar shrinkage percentage to NiO-BSZCY82 at 1200 °C, but the electrolyte membrane of the cell with NiO-BSZCY73 anode support exhibits higher density and larger grain size (**Figure 3**). Therefore, it can be speculated that the improved sintering activity of the electrolyte might be another possible reason for the reduced sintering temperature of the cells with Sr-containing anode, which is in great part due to Sr diffusion from anode to SDC electrolyte.

In order to gain more insights into understanding the effect of Sr diffusion on the densification of SDC and the different sintering promotion behavior of Ba and Sr, 150 μL BaCO_3 and SrCO_3 suspension was coated on the pre-sintered SDC pellets,

respectively, and then samples were sintered at 1300 °C for 5 h to simulate the sintering process of SDC-based SOFCs with Ba- or Sr-containing anode supports, as schematically illustrated in **Figure S1**. Sr and Ba from the coated BaCO₃ and SrCO₃ films will diffuse into SDC pellets and react with SDC accordingly during the sintering process. Shown in **Figure 4** are the SEM-EDS analysis in line-scan mode and element mapping results of the sintered SDC pellets. It can be clear seen that both Ba and Sr elements diffuse into the SDC pellets, but show substantially different diffusion kinetics. The diffusion distance of Sr (greater than 220 μm) is nearly double that of Ba (120 μm). The faster diffusion kinetics of Sr can be ascribed to the smaller ionic radius of Sr than that of Ba²⁵. It is worth noting that both Sr and Ba diffusion into the SDC pellets can promote the sintering activity, and Ba even appears to be more effective (**Figure S3** Supporting Information). Given Sr diffuses much faster than Ba, more Sr would be incorporated into SDC electrolyte membrane during cell sintering, and consequently the SDC membrane would get densified more easily. Therefore, it can be concluded that Sr diffusion should also play a critical role in reducing the sintering temperature of the cells with Sr-containing anode supports.

The electrochemical performance of the cells with different NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} (0 ≤ x ≤ 0.3) anode supports were evaluated with humidified hydrogen (~3% H₂O) as the fuel and static air as the oxidant. The temperature dependence of the OCVs of the cells with different anodes sintered at 1200 or 1150 °C are shown in **Figure 5**. For the cells sintered at 1150 °C, the OCV increase significantly with increasing Sr content in the anode, which is in good agreement with the density of the sintered SDC electrolyte membrane as shown in **Figure 2**. Although the OCVs of the cells with NiO-BSZCY91 and NiO-BSZCY82 anode supports are higher than the typical DCO-based cells, the OCVs are still obviously lower than the theoretical values, which can be ascribed to the ununiformity of these electron-blocking layers and the porosity of the electrolyte membranes (**Figure 2**). In contrast, the OCVs of the cell with NiO-BSZCY73 anode support sintered at 1150 °C achieve as high as 1.043, 1.056, 1.072, and 1.082 V at 650, 600, 550, and 500 °C, respectively, which is very close to the theoretical OCV values. The

elimination of the internal short-circuit current should be attributed to the formation of the electron-blocking layer together with the dense electrolyte membrane of the cell with NiO-BSZCY73 anode support. As can be seen from **Figure 5**, the internal short-circuit behavior is effectively suppressed for the cells with NiO-BSZCY91, NiO-BSZCY82 and NiO-BSZCY73 as anodes with further increasing sintering temperature to 1200 °C, correspondingly OCVs are 1.038, 1.065 and 1.057 V at 650 °C, respectively, while the cell with NiO-BZCY anode sintered at 1200 °C still exhibits inferior OCVs, which is caused mainly by the porous SDC electrolyte membrane (**Figure S4** Supporting Information) due to the poor sintering ability of NiO-BZCY and no Sr elements diffusion promoting the sintering of SDC electrolyte. The results demonstrate that, as compared with the previously reported cell with NiO-SrCeO₃ anode support¹⁸, the incorporation of Ba can substantially improve the electron-blocking capability of the in-situ formed interlayer. Meanwhile, Sr is critically important to get fully dense SDC electrolyte membranes at reduced temperatures.

The formation of the electron-blocking interlayer was investigated by SEM-EDS analysis and element mapping. As expected, a Ba- and Sr-containing electron-blocking layer, around 2 μm in thickness, can be observed at the anode/SDC electrolyte interface as shown in **Figure S5** (Supporting Information), which is similar to the previous reports with NiO-BaCeO₃ or NiO-BaZrO₃ anode supports^{10, 12, 22}. To further investigate the phase composition and the chemical states of the elements in the electron-blocking interlayer, SDC powders were placed between two green Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} pellets and then annealed at 1300 °C for 10 h to simulate the diffusion behaviors of Ba and Sr during sintering NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ}/SDC half cells. Ba and Sr will diffuse and then react with SDC powders at elevated temperatures. The collected SDC powders named SDC-BS91, SDC-BS82, and SDC-BS73 for x=0.1, x=0.2, and x=0.3, respectively, were then characterized by Raman spectroscopy and X-ray photoelectron spectra (XPS). The Raman spectra of the annealed SDC powders in comparison with as-prepared BaCe_{0.8}Sm_{0.2}O_{3-δ}, SrCe_{0.95}Sm_{0.05}O_{3-δ} and SDC powders are shown in **Figure 6a**. The most intense

characteristic peaks of $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.95}\text{Sm}_{0.05}\text{O}_{3-\delta}$ locate at around 348 and 343 cm^{-1} , respectively^{18, 22, 26}, and these peaks can be assigned to Ce-O stretching vibration of the CeO_6 octahedra^{18, 22, 26}. As can be seen, the characteristic peak appears for all the annealed SDC samples, suggesting the formation of the (Ba, Sr) CeO_3 -like phase^{18, 22}. Notably, the characteristic peak tends to shift negatively with increasing Sr doping in $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$, indicating that the (Ba, Sr) CeO_3 -like phase contains more Sr. **Figure 6b** shows the full survey XPS spectra of SDC-BS91 powders. Peaks corresponding to oxygen (O 1s at ~530 eV), cerium (Ce 3d at ~ 882 eV), strontium (Sr 3d at ~ 134 eV) and barium (Ba 3d at 780 eV) can be clearly detected. The Sr 3d spectra for SDC-BS91, SDC-BS82, and SDC-BS73 powders can be fitted with three peaks, as shown in **Figure 6c**. The peaks with binding energies of ~132.9 and ~134.8 eV are attributed to Sr^{2+} in the perovskite oxide^{25, 27}, which is consistent with the result of BSZCY91, and this is also good evidence to support the formation of (Ba, Sr) CeO_3 -like phase. The peak with a binding energy of ~130.2 eV likely corresponds to SrO_{1-x} species deposited on the surface of the annealed SDC powders²⁷⁻²⁹. In addition to be involved in the chemical reaction with SDC, the residual strontium oxide would also act as an effect sintering aid for the SDC electrolyte membrane as discussed previously¹⁹. High-resolution O 1s spectra of SDC, SDC-BS91, and BSZCY91 can be fitted with four peaks (**Figure 6d**). The peaks centered at ~528.7, ~530.3, ~531.2 and ~532.3 eV are attributed to the lattice oxygen species O^{2-} , reactive oxygen species, chemisorbed H_2O or CO_3^{2-} , and $-\text{OH}^-$ or O^2 , respectively³⁰⁻³². Compared to SDC, SDC-BS91 shows a significantly enhanced peak corresponding to chemisorbed H_2O or CO_3^{2-} , which is similar to that of BSZCY91. Basically, BaCeO_3 -based proton conductors are easily to adsorb moisture and CO_2 ^{13, 25, 33}, and hence the O 1s spectra further indicate the presence of (Ba, Sr) CeO_3 -like phase.

Figure 7 shows the SEM images of the cross-sectional morphologies of the tested single cells with different anodes sintered at 1200 °C for 5 h. One can see that the tested anode-supported fuel cells have almost identically thick cathode (~12 μm) and electrolyte (~15 μm). The thickness of anode substrate is about 1 mm, and all the

electrolyte membranes are fully dense except for the cell with the NiO-BZCY anode support. Besides, all the electrolyte membranes are closely bonded with the electrodes, suggesting good compatibility of the electrolyte and electrodes. The I-V and I-P curves of the single cells with different anodes at 650 °C are shown in **Figure 8a**. In addition to the densification temperature of SDC electrolyte membrane, the power density of the cells also shows high dependence on the anode composition. At 650 °C, the maximum power densities (MPD) are 677, 562, 464, and 275 mWcm⁻² for the cells with Ni-BSZCY91, Ni-BSZCY82, Ni-BSZCY73 and Ni-BZCY anodes, respectively. The cell with Ni-BSZCY91 anode outputs the highest peak power density, which is obviously greater than that of the cell with NiO-BZCY anode sintered at the same temperature. Although the power performance decreases with increasing the Sr-doping content, the MPD are still higher than that of the cell with NiO-BZCY anode. Considering the relatively low sintering temperature (low fabrication cost) and high OCVs (high working efficiency), the new SDC-based cell has great potential for practical application. According to the above results, Ni-BSZCY91 composite is demonstrated to be the optimal composition as anode for SDC-based SOFCs towards high power density, high OCVs and low densification temperature. **Figure 8b** shows the electrochemical performance of the cell with NiO-BSZCY91 anode at low operating temperatures. Besides, the cell also shows a good stability. As shown in **Figure 9**, no obvious performance degradation can be observed during the period of testing.

To further figure out the power performance dependence on the anode composition of the fuel cells, electrochemical impedance spectra (EIS) were measured under open circuit conditions at 650 °C and are shown in **Figure 10**. One can see that both ohmic resistance (R_o) and polarization resistance (R_p) increase with increasing Sr content from 0.1 to 0.3. The R_o values are determined to be 0.223, 0.244, and 0.291 Ω cm² and R_p values are 0.516, 0.627, and 0.658 Ω cm² at 650 °C for the cells with Ni-BSZCY91, Ni-BSZCY82, and Ni-BSZCY73 anodes, respectively. It was reported that the ionic conductivity of Ba_{1-x}Sr_xCe_{0.6}Zr_{0.2}Y_{0.2}O_{3- δ} decreases with increasing Sr doping content²¹. Therefore, the increased R_p should be ascribed to the decreased

ionic conductivity of $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ in the anodes, which basically hinders ion transport and eventually decrease electrode reaction kinetics. XPS results (Figure S6 Supporting Information) show that Sr can easily diffuse into the SDC electrolyte and the amount of Sr diffusion is proportional to Sr content in the anode. Given all the fuel cells were fabricated and tested under same conditions, the increased R_o should be due to the decreased ionic conductivity of the electrolyte because the ionic conductivity of the electrolyte is affected by the diffused Sr elements¹⁹ and ionic resistance of the electrolyte dominate the R_o of the cell, suggesting Sr diffusion into the SDC electrolyte is detrimental to the electrolyte conductivity. The high R_o value of the cell with Ni-BZCY anode can be ascribed to the lower density of the SDC electrolyte membrane.

4. Conclusions

Ba- and Sr-containing composites were successfully demonstrated as potential anodes for SDC-based SOFCs to achieve low-temperature fabrication, high efficiency and power performance. Ba diffusion improved the electron-blocking capability of the *in-situ* formed anode/electrolyte interlayer while Sr diffusion reduced the sintering temperature of the SDC-based half cells. It turns out that $\text{Ni-Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ is the optimal anode composition, and the internal short circuit was effectively eliminated by an *in-situ* formed Ba- and Sr-containing thin electron-blocking layer at the temperature as low as 1200 °C, which was composed of SDC and (Ba, Sr) CeO_3 -like phase. As a result, the OCV of the fuel cell achieved 1.038 V at 650 °C with a peak power density of 677 mW cm⁻². The excellent electrochemical performance suggests that the Ba- and Sr-containing composites are promising electrodes for DCO-based SOFCs and SOECs with high working efficiency.

ASSOCIATED CONTENT

Supporting Information

Schematic diagram of the procedure for preparing Ba/Sr containing SDC and additional experimental results of linear shrinkage of half cells, SEM images,

SEM-EDS and XPS analysis available.

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Figure 1 The XRD patterns of NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} (0 ≤ x ≤ 0.3) composites calcined at 1000 °C for 3 h

Figure 2 SEM images of the surface (a) and cross-sectional (b) morphology of SDC electrolyte in the NiO-Ba_{1-x}Sr_xCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ}/SDC (0.1 ≤ x ≤ 0.3) half cells sintered at 1150 °C for 5 h.

Figure 3 The shrinkage behaviors of $\text{NiO-Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ ($0 \leq x \leq 0.3$) specimens

Figure 4 The SEM-EDS analysis in line-scan mode and element mapping results of the post-annealed SDC pellets closed to the coated (a, c) BaCO_3 and (b, d) SrCO_3 side.

Figure 5 The temperature dependence of the OCV of the cells with different anodes sintered at 1200 or 1150 °C

Figure 6 (a) The Raman spectra and (b) XPS full survey spectra of the SDC-BS91 powders, the survey spectra of (c) Sr 3d and (d) O 1s on the surface of the SDC, BSZCY91, SDC-BS91 powders.

Figure 7 SEM images of the cross-section of the tested single cells with (a) NiO-BSZCY91, (b) NiO-BSZCY82, (c) NiO-BSZCY73, and (d) NiO-BZCY anodes.

Figure 8 The I-V and I-P curves of the single cells with (a) different anode at 650 °C and (b) NiO-BSZCY91 anode tested at different temperatures.

Figure 9 Power density as a function of time for the cell with optimal anode composition tested at 600 °C, 0.7 V.

Figure 10 Electrochemical impedance spectra (EIS) of the cells with different anodes sintered at 1200 °C measured under open circuit conditions at 650 °C

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