



Short communication

Novel Ni–Ba_{1+x}Zr_{0.3}Ce_{0.5}Y_{0.2}O_{3-δ} hydrogen electrodes as effective reduction barriers for reversible solid oxide cells based on doped ceria electrolyte thin filmYuanyuan Rao^a, Zhiquan Wang^a, Wei Zhong^a, Ranran Peng^{a,*}, Yalin Lu^{a,b,**}^a CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, Anhui, China^b Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, Anhui, China

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ABSTRACT

Samarium-doped ceria (SDC) is evaluated as electrolyte materials for intermediate temperature reversible solid oxide cells (RSOCs). The bulk resistances of cells with SDC thin-film electrolytes are 0.16 and 0.23 Ω cm² when operating in solid oxide electrolysis cell (SOEC) mode and in solid oxide fuel cell (SOFC) mode, respectively. This result suggests that the electrolyte is reduced to a greater extent in the SOEC mode. New Ni–Ba_{1+x}Zr_{0.3}Ce_{0.5}Y_{0.2}O_{3-δ} (x = -0.04, 0 and 0.04) composites are applied as hydrogen electrode for RSOCs to prevent SDC reduction. With the new hydrogen electrodes, the bulk resistances of the RSOCs are approximately 0.37 Ω cm² in both SOFC and SOEC modes, suggesting that reduction in the SDC electrolyte is successfully minimized. The energy dispersive X-ray mapping of the Ba element indicates that Ba cations partially transfer from the hydrogen electrode into the electrolyte layer.

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1. Introduction

Reversible solid oxide cells (RSOCs) have drawn increasing attention as a positive energy storage and regeneration system for renewable energy sources, a system that can be used to smooth out the intrinsic fluctuations and intermittence of those sources. RSOCs can work as solid oxide fuel cells (SOFCs) in an electricity shortage by converting the fuel's energy into electricity energy or as solid oxide electrolysis cells (SOECs) in a state of electricity excess by converting electricity energy into chemical energy [1]. Traditional RSOCs use stabilized zirconia as electrolytes and must operate at high temperatures (800–1000 °C) to achieve sufficient conductivity of the electrolytes [2,3]. Unfortunately, high operating temperature can lead to many material problems in RSOCs, including electrode sintering.

In recent years, doped ceria has drawn much attention as a promising electrolyte material for intermediate temperature SOFCs (500–700 °C) thanks to its high ionic conductivity. However, a reduction of Ce⁴⁺ to Ce³⁺ by hydrogen would occur above 450 °C, which lowers the open-circuit voltage (OCV) and the energy conversion coefficient, and causes a mechanical breakdown of the cells [4,5]. Moreover, Eguchi et al. [6] suggested that doped ceria would be unsuitable for SOECs because the H₂ evolution rate they observed was much lower than expected which might have been

caused by a severe reduction of the doped ceria electrolyte. Several techniques, such as fabricating a thin film of stabilized zirconia [5] or doped bismuth [7] over ceria-based electrolytes, have been developed to form electronic barriers. Hirabayashi et al. [4,8] proposed a simple and effective way to prevent SDC reduction by coating a BaO thin film over the surface of the SDC electrolyte. After the high-temperature solid reaction, a BaCe_{1-x}Sm_xO_{3-α} (BCS) layer was formed, which helped to improve the OCV from 0.7 V to 1.0 V at 950 °C [4,8]. However, in Hirabayashi's method, the SDC electrolyte close to hydrogen electrode was still reducible. In this work, SDC was intensively evaluated as a thin film electrolyte in RSOCs, and its conducting behaviors in different operation modes were systematically investigated. New Ni–Ba_{1+x}Zr_{0.3}Ce_{0.5}Y_{0.2}O_{3-δ} (x = -0.04, 0 and 0.04) composites were applied as the hydrogen electrode for RSOCs to prevent the reduction of the SDC electrolyte. The characteristics of cells with SDC as the electrolyte and Ni–Ba_{1+x}Zr_{0.3}Ce_{0.5}Y_{0.2}O_{3-δ} as the hydrogen electrode were also investigated.

2. Experimental

2.1. Powders preparation

Ba_{1+x}Zr_{0.3}Ce_{0.5}Y_{0.2}O_{3-δ} (here x = -0.04, 0, 0.04, respectively) powders were synthesized by a modified citric acid combustion method. A suitable amount of EDTA was dissolved into distilled water with ammonia added to obtain a transparent solution. A mixed nitrate solution of Ba²⁺, Zr⁴⁺, Y³⁺ and Ce³⁺ in the designed ratio was blended with the EDTA solution, and then added with citric acid as a chelator to form a precursor solution. The molar ratio

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of the metallic cations, EDTA and citric acid was set as 1:1.2:1.2. The precursor solution was heated and stirred on a hot plate, and then burned into a black sponge after evaporation. The black sponge was calcined at 1100 °C for 2 h to form perovskite powders. In this paper, powders of $\text{Ba}_{1+x}\text{Zr}_{0.3}\text{Ce}_{0.5}\text{Y}_{0.2}\text{O}_{3-\delta}$ are denoted as BZCY/*M*, where *M* is the mole percentage of the Ba element. For example, $\text{Ba}_{0.96}\text{Zr}_{0.3}\text{Ce}_{0.5}\text{Y}_{0.2}\text{O}_{3-\delta}$ is denoted as BZCY/96. Other powders such as $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SDC), NiO and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) were all synthesized by the glycine-nitrate process, as previously reported in Refs. [9,10].

2.2. Fabrication of single cells

NiO and SDC (BZCY/*M*) powders were mixed in a weight ratio of 65:35 to form composite hydrogen electrodes, with 5% graphite added as a pore former. The bi-layer hydrogen electrode and SDC electrolyte were fabricated by the co-pressing method. The thickness of the electrolyte thin films was approximately 35 μm after they were co-sintered at 1350 °C for 5 h in air. SSC powders were blended with SDC powders in a weight ratio of 70:30, and then applied to the surface of the electrolyte using a screen-printing technology. The cells were sintered at 950 °C for 2 h to complete the fabrication process. Silver paste was painted onto the surface of the air electrodes to act as the current collector.

2.3. Characterizations of the RSOCs

Single cells were tested at 700 °C in a home-developed cell testing system with 10% H_2O –90% H_2 and air as a reactant injected into the hydrogen electrode and the air electrode, respectively. The flow rate of hydrogen was 80 ml min^{-1} . The AC impedance spectra of single cells were measured under open circuit conditions (OCC) and bias voltages (OCV +0.3 V for the SOEC mode, and OCV –0.3 V for the SOFC mode) using an electrochemical workstation (IM6e, Zahner). The measurements were conducted in the range of 1 MHz–0.1 Hz with a 10 mV amplitude. The fracture microstructure of the tested cells was analyzed using a JEOL scanning electron microscope (SEM, JXA-8100) equipped with an energy dispersive X-ray (EDX) microanalyzer.

3. Results and discussion

3.1. Electro-performance of RSOCs with an SDC electrolyte

Fig. 1(a) shows the I–V curve of RSOCs measured at 700 °C using SDC as the electrolyte and NiO-SDC as the hydrogen electrode. The

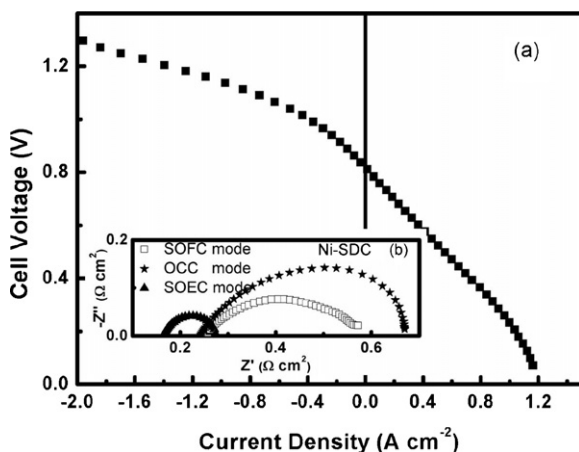


Fig. 1. I–V curve (a) and A.C. impedance spectra (b) of a RSOC with a structure of Ni-SDC || SDC || SSC-SDC.

positive current density applies to the SOFC operation, and the negative current density applies to the SOEC operation. As shown in Fig. 1(a), the open circuit voltage (OCV) of RSOC was 0.84 V, close to previously reported results [11]. The low OCV indicates partial electron conduction in the SDC electrolyte. The discharging and electrolysis current densities were 0.189 A cm^{-2} at 0.7 V and 2.0 A cm^{-2} at 1.3 V. Fig. 1(b) shows the AC impedance spectra of the cells under OCC, the SOEC mode and the SOFC mode. The bulk resistance in the SOEC mode, with a value of 0.16 $\Omega \text{ cm}^2$, was much lower than that measured in SOFC (OCC) mode, which is approximately 0.23 $\Omega \text{ cm}^2$. This difference clearly suggests that the high voltage applied in the SOEC mode will strengthen the reduction of Ce^{4+} to Ce^{3+} , which is consistent with Eguchi's observation [6]. Moreover, the different valence status of ceria cations under the two operating mode would lead to a severe degradation in RSOCs.

3.2. RSOCs with Ni-BZCY/*M* hydrogen electrode

A possible way to reduce or even stop the reduction of SDC electrolyte is to use BZCY/*M*, substituting for SDC, in the hydrogen electrode. As shown in Fig. 2, the OCVs of the RSOCs when using Ni-BZCY/*M* were 0.94, 1.00 and 1.00 V at 700 °C for *M* = 96, 100 and 104, respectively, much higher than when using a Ni-SDC hydrogen electrode. This indicates that BZCY/*M* in the hydrogen electrode helps to reduce electron conduction in the electrolyte. For *M* = 96, 100 and 104, the discharging current densities at 0.7 V are 0.246, 0.246 and 0.163 A cm^{-2} , and the electrolysis current densities at 1.3 V are 0.694, 0.357 and 0.198 A cm^{-2} . These values are all larger than those obtained when using a YSZ electrolyte (12 μm), which were 0.17 A cm^{-2} at 1.3 V and 0.15 A cm^{-2} at 0.7 V at 850 °C [3].

Fig. 3 shows SEM and EDX pictures of fractured tested cells with Ni-BZCY/*M* hydrogen electrodes. As shown in Fig. 3(a), (d) and (h), the electrolyte films adhere well to the three hydrogen electrodes. Comparing the element maps of Ba (Fig. 3(b), (e), and (i)) with Ni (Fig. 3(c), (f) and (j)), it can be clearly seen that Ba cations have partially crossed the interface into electrolyte layer. Because BaO is not stable at the high fabrication temperature (1350 °C), the transferred BaO would react with doped ceria to form a transition layer of BaCeO_3 based oxides. This might be the reason for the improved OCV of the cells. The thickness of the transition layer could be determined from the relative height between the Ba element and the Ni element in their respective mappings. The thicknesses of the transition layers were approximately 2, 4, and 8 μm for *M* = 96, 100, and 104, respectively.

Fig. 4 shows the impedance spectra of the RSOCs with Ni-BZCY/*M* hydrogen electrodes. In OCC, the bulk resistances of all

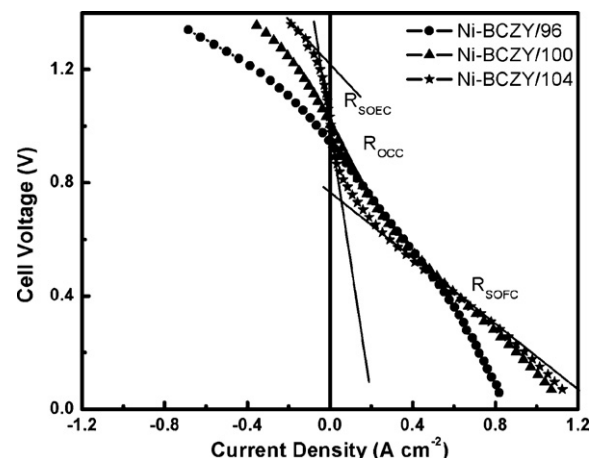


Fig. 2. I–V curves of single cells with different hydrogen electrodes.

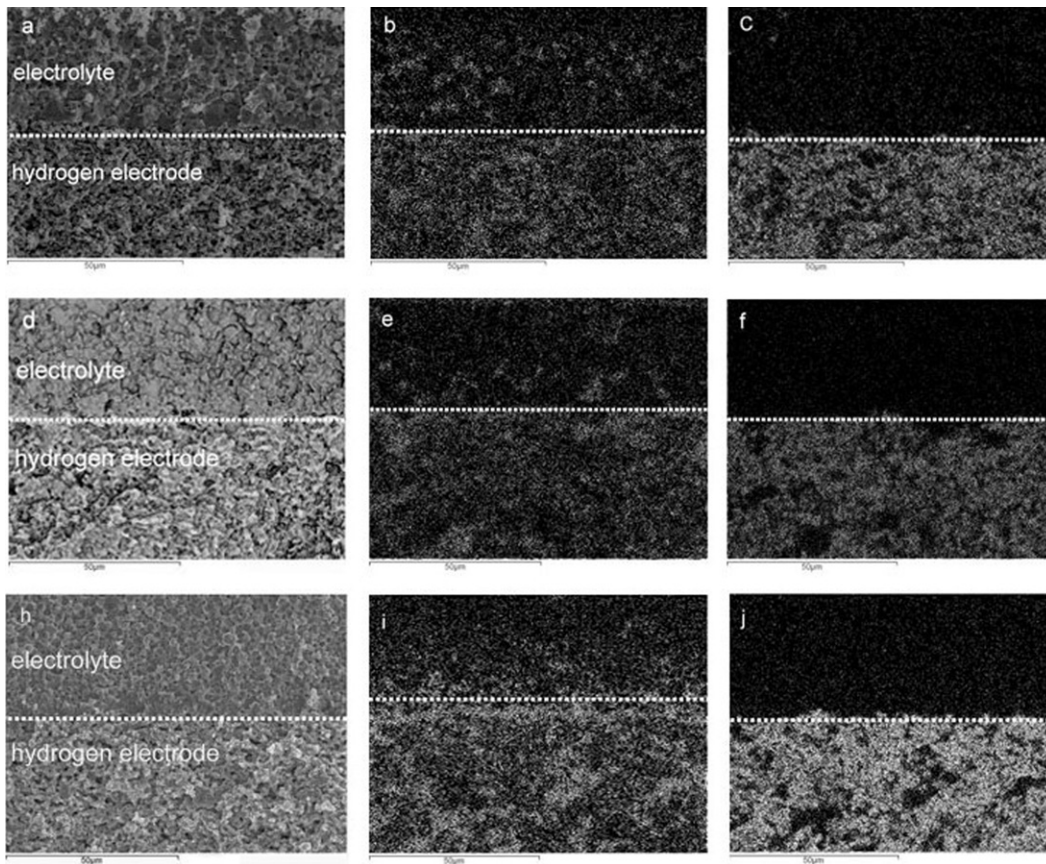


Fig. 3. SEM and EDX images of single cells using: (1) Ni-BCZY/96 ((a)–(c)); (2) Ni-BCZY/100 ((d)–(f)); and (3) Ni-BCZY/104((h)–(j)) as the hydrogen electrode. (a), (d) and (h) are SEM images of fractured single cells; (b), (e) and (i) are the Ba elemental maps; and (c), (f) and (j) are the Ni elemental maps of the cells. The broken lines represent the outer boundaries of the hydrogen electrodes, Ba and Ni in the SEM images, and Ba elemental map and Ni elemental maps, respectively.

three cells were almost the same, approximately $0.37 \Omega \text{ cm}^2$, indicating that the thickness of the transition layers hardly affects the electrolyte conduction. The SDC conductivities without electron conduction were calculated to be 0.027 S cm^{-1} , which is close to that measured in air [12]. It should also be noted that the bulk resistances of the cells using Ni-BZCY/M hydrogen electrodes changed very little in all three operating modes, suggesting a significant minimization of ceria reduction, especially in the SOEC mode.

The polarization resistances of the cells increased with increasing M in Ni-BZCY/M, approximately 0.62, 0.97 and $2.31 \Omega \text{ cm}^2$ in

OCC mode for M=96, 100, and 104, respectively. This is consistent with the literature findings that a slight A-Site deficiency in doped barium cerates helps to improve their conduction and thus the rate of electrode reaction [13,14]. It should also be noted that the polarization resistances with Ni-BZCY/M hydrogen electrodes are all larger than that using Ni-SDC hydrogen electrode. Possible reasons for this phenomenon include the following: (1) electron conduction in SDC may be beneficial to the electrode reaction [6]; and (2) different conducting ions in the transition layers (OH^\bullet) and SDC layers ($\text{V}_\text{O}^{\bullet\bullet}$) might partially lower the electrode reactions, as shown in Eq (A).



4. Conclusion

An easy and effective way to prevent the reduction of doped ceria electrolytes in RSOCs was suggested in this work. The OCV of the RSOCs when using the Ni-BZCY/M as hydrogen electrodes was 0.94, 1.00 and 1.00 V at 700°C for M=96, 100 and 104, respectively, which was much higher than that using a Ni-SDC hydrogen electrode. The bulk resistances of cells with these new hydrogen electrodes were all approximately $0.37 \Omega \text{ cm}^2$, and they hardly changed with the operating mode, suggesting a minimized reduction of doped ceria. Transfer of Ba cations from the hydrogen electrode to the electrolyte was observed from the Ba elemental map, which explains the minimized reduction and the improved open circuit voltage.

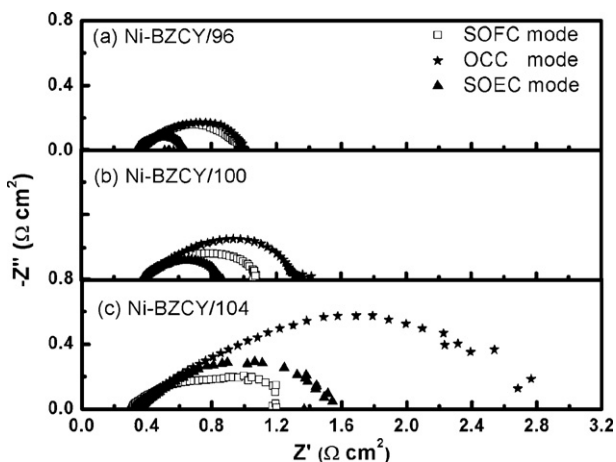


Fig. 4. AC impedance spectra of single cells with different hydrogen electrodes.

Acknowledgements

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