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Enhanced performance of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} based oxygen electrode for solid oxide electrolysis cells by decorating with Ag particles

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Abstract

To improve the performance of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) oxygen electrode in a solid-oxide electrolysis cell (SOEC), Ag particles were added to increase its conductivity and thus its electrochemical performance. The experiment results showed that the polarization resistance of Ag decorated BSCF-SDC oxygen electrode with the appropriate amount of Ag particles was lower than that of BSCF-SDC oxygen electrode. Especially, the polarization resistance of Ag decorated BSCF-SDC oxygen electrode with 1.3 wt.% Ag particles (noted as 1.3Ag-BSCF-SDC) was as low as 0.006 Ω cm². The 1.3Ag-BSCF-SDC oxygen electrode showed good stability in the short-term electrolysis durability test. The electrolysis cell based on 1.3Ag-BSCF-SDC oxygen electrode showed better performance than that based on BSCF-SDC oxygen electrode. Therefore, this method is an effective way to improve the performance of a BSCF-based oxygen electrode for an SOEC.

1. Introduction

Hydrogen is considered as an ideal energy to replace fossil fuels because of its light weight, high caloric value and clean combustion products [1, 2]. Therefore, the development of hydrogen production technology is highly valued world-wide. A solid oxide electrolysis cell (SOEC) is a solid oxide fuel cell that operates in reverse. Hence, the SOEC can produce hydrogen by electrolyzing steam with heat and electricity. Its operating temperature is usually above 700 °C, which increases its electrode reaction rate. The high-temperature working conditions also reduce the electrical energy required for the electrolysis reaction. Furthermore, during the entire electrolysis process, no pollutant is discharged. Therefore, an SOEC is an efficient, low-cost and environmentally friendly hydrogen production technology [3–6].

The oxygen electrode is where oxygen is produced in a SOEC. Its performance thus directly determines the hydrogen production efficiency. Ba_{x}Sr_{1-x}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) materials with high oxygen permeability and high catalytic activity have been shown to be suitable as oxygen electrodes for an SOEC [7–9]. For example, Yu Bo et al reported the use of BSCF as an SOEC oxygen electrode [7]. At 850 °C, the area-specific resistance of a BSCF electrode is only 0.077 Ω cm², and the hydrogen production rate of a BSCF/yttria-stabilized zirconia (YSZ)/Ni-YSZ-structured SOEC can reach 147.2 ml cm⁻² h⁻¹. Wen Qiang Zhang et al reported an SOEC study based on a BSCF/Sm_{0.2}Ce_{0.8}O_{1.9} (SDC)/YSZ/Ni-YSZ structure with a BSCF oxygen electrode, a YSZ electrolyte and an SDC isolation layer [8]. At 850 °C, the hydrogen production rate reached 177.4 ml cm⁻² h⁻¹. Dorna Heidari et al reported a study of a BSCF-SDC/YSZ-SDC/Ni-YSZ-structured SOEC using a BSCF-SDC composite material as the oxygen electrode [9]. At 800 °C and a 50% H₂O/H₂ atmosphere, the area-specific resistance of an 80% BSCF-20% SDC oxygen electrode was only 0.105 Ω cm², and the SOEC current was 0.622 A cm⁻².
However, BSCF has the disadvantage of low conductivity, which has been reported to be only 40–60 S cm$^{-1}$ [10]. As an oxygen electrode in an SOEC, its low conductivity will affect the oxidation reaction of oxygen ions transferred from the electrolyte, which then affects the water-vapor electrolysis. Furthermore, it will affect the collection of electrolys current from the oxygen electrode [11]. Therefore, the performance of a BSCF oxygen electrode can be improved by increasing its conductivity. For an SOFC, the BSCF oxygen electrode conductivity can be improved by adding Ag particles with high electronic conductivity [12–15]. For example, Wei Zhou et al reported that an area specific resistance of Ag-modified BSCF cathode with 3.0 wt.% Ag for IT-SOFC was as low as 0.042 Ω cm$^2$ at 600 °C [12]. Rensu et al reported on a nanostructured Ag-modified BSCF (Ag@BSCF) cathode for SOFCs [13]. By adding Ag, the ohmic resistance of the BSCF cathode was reduced, and its electrochemical performance was improved. Mosialelc et al reported that the SOFC performance based on the Ag-BSCF cathode was improved by 48% compared with the BSCF cathode [14]. Yuan Song Wang et al reported that the polarization resistance of BSCF/Gd-doped CeO$_2$ cathode was reduced by adding a small amount of Ag, which was lower than 0.1 Ω cm$^2$ at temperatures higher than 700 °C [15].

Based on the above discussion, it can be inferred that the conductivity and performance of a BSCF oxygen electrode in an SOEC can be improved by adding Ag. However, to the best of our knowledge, there are no reports on this. In our work, we will verify it experimentally, and then present an effective method to improve the performance of a BSCF oxygen electrode in an SOEC.

2. Experimental

2.1. Preparation of the samples

The oxygen electrode materials were a BSCF-SDC composite with a mass ratio of 7:3. The BSCF was prepared by a sol-gel method [16], and the SDC was prepared by a glycine nitrate method [17]. The YSZ \((\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}\) electrolyte was purchased from SOFCman Energy Technology Co., Ltd (China). The hydrogode electrode material was an NiO-SDC composite with a mass ratio of 6:4; the NiO was prepared by a glycine nitrate method. The Ag particles were nanoscale silver colloids purchased from the XianFeng company (China). The Ag particle diameters were 15 ± 5 nm, the concentration was 10 mg ml$^{-1}$, and the solvent was water. The SOEC was supported by the YSZ electrolyte, which was pressed into 13 mm diameter pieces with a tablet press and then sintered at 1400 °C for 4 h to form compact ceramic sheets. The YSZ ceramic sheets were then thinned to a 300 μm thickness. The SDC interlayer material dispersed in a mixture of terpineol and ethylcellulose was coated on one side of the YSZ electrolyte ceramic sheet via screen printing, and then sintered at 1250 °C for 4 h [18]. The NiO-SDC composite hydrogen electrode material was coated on the other side of the YSZ electrolyte ceramic sheet via screen printing, and then sintered at 1100 °C for 5 h. The BSCF-SDC composite oxygen electrode material was coated upon the SDC interlayer via screen printing, and then sintered at 950 °C for 5 h. The area of the coated oxygen electrode was 0.4 cm $\times$ 0.4 cm. Then, 0.6 ul, 1.1 ul, 1.6 ul, 2.1 ul of the Ag colloid was dropped on the surface of the BSCF-SDC composite oxygen electrodes with a pipette gun, respectively. Four BSCF-SDC oxygen electrodes with different Ag content were fabricated, in which Ag content was 1.3, 2.3, 3.4, 4.5 wt.%, respectively. They were noted as 1.3Ag-BSCF-SDC, 2.3Ag-BSCF-SDC, 3.4Ag-BSCF-SDC, and 4.5Ag-BSCF-SDC, respectively. As shown in figure 1, the SOEC structure was Ag-decorated BSCF-SDC/YSZ/NiO-SDC. Ag paste was used to encapsulate the cell on one side of the ceramic tube. It was also used as the collector for the oxygen and hydrogen electrodes, while Ag was used for the cell wiring. Besides, the symmetrical cells were fabricated with the configuration of oxygen electrode|SDC interlayer|YSZ electrolyte | SDC interlayer|oxygen electrode.
2.2. Sample measurements

The crystal structures of BSCF-SDC and Ag-decorated BSCF-SDC oxygen electrode materials were obtained with a Japan Rigaku-D-Max Ra x-ray diffractometer (XRD). Scanning electron microscope (SEM, FEI Quanta 250 FEG) coupled with energy disperse x-ray (EDX) detector was adopted to check the morphologies of the BSCF-SDC and Ag-decorated BSCF-SDC oxygen electrodes, and Ag element distribution in the Ag-decorated BSCF-SDC oxygen electrode. AC impedance measurements of the symmetrical cells were carried out in ambient air under open cell voltage (OCV) conditions with an electrochemical workstation (CHI 760E, Shanghai Chenhua Instrument Corporation, China). The electrochemical performance of the SOEC was tested with the above electrochemical workstation. During the tests, a mixture of water vapor, oxygen and nitrogen was introduced into the hydrogen electrode. The water vapor was produced by a 76 °C constant-temperature water bath. Hydrogen was used as a reducing gas for the hydrogen electrode, and its flow rate was 40 ml min\(^{-1}\). Nitrogen was used as a carrier gas, at a flow rate of 50 ml min\(^{-1}\). The relative humidity of the mixture was 40 vol \%. The electrochemical impedance spectra of the symmetrical cells and SOECs were measured over the frequency range 0.1 Hz to 1 MHz at a signal amplitude of 50 mV. Twelve points were collected every cycle. The current density-voltage characteristic curve of the SOEC was measured by a linear voltage sweep at a scanning rate of 9 mV s\(^{-1}\).

3. Results and discussion

The XRD crystal structures are studied for SDC, BSCF, BSCF-SDC, and the Ag-decorated BSCF-SDC powders calcined at 950 °C for 2 h. In Supplementary figure 1 (available online at stacks.iop.org/MRX/8/035502/mmedia), the BSCF has a perovskite structure and the SDC has a cubic fluorite structure. In figure 2, BSCF-SDC is composed of BSCF and SDC phases. The XRD pattern of Ag-decorated BSCF-SDC in figure 2 contains all the diffraction peaks of the BSCF-SDC sample. In addition, there are Ag diffraction peaks (marked by hollow rectangles), but no peaks of an Ag-related heterophase are observed. Thus, the method of preparing Ag-decorated BSCF-SDC oxygen electrodes is feasible.

The surface morphologies of BSCF-SDC and Ag-decorated BSCF-SDC oxygen electrodes imaged with the SEM can be seen in figures 3(a), (b), respectively. In the BSCF-SDC composite oxygen electrode, the BSCF material has a large particle size and forms a porous network. This can be seen in the SEM of the BSCF oxygen electrode prepared under the same conditions (supplementary figure 2). The SDC material has a smaller particle size and is adsorbed on the BSCF skeleton. This creates a large specific surface area on the oxygen electrode, which will increase the active sites of the oxygen evolution reaction and improve the electrochemical reaction activity. To clearly observe the distribution of Ag particles in the Ag-decorated BSCF-SDC oxygen electrode, we choose the 4.5Ag-BSCF-SDC oxygen electrode as an example to study. In figure 3(b), the Ag particles have distinct and recognizable surfaces and are evenly distributed on the surface of BSCF-SDC oxygen electrode. The average diameter of the Ag particles is 2.36 ± 0.71 μm. Figure 3(c) shows EDX line-scan of Ag element in the cross-section of 4.5Ag-BSCF-SDC oxygen electrode. It can be noted that Ag particles are distributed in the bulk.
of 4.5Ag-BSCF-SDC oxygen electrode. Therefore, it can be concluded that Ag particles in the Ag-decorated BSCF-SDC oxygen electrode are distributed on the surface as well as in the bulk of the oxygen electrode.

In order to study the electrochemical performance of Ag-decorated BSCF-SDC oxygen electrodes, AC impedance measurements of the symmetrical cells based on BSCF-SDC and Ag-decorated BSCF-SDC oxygen electrodes have been carried out in ambient air under OCV conditions, which is shown in figure 4(a). Note that the ohmic resistances of the symmetrical cells have been subtracted from the impedance spectra. Equivalent circuit of L0R0 (Rp/C) is carried out to fit the spectra, where L is the inductance, R0 is the ohmic resistance, Rp is the polarization resistance, C is the capacitance. At 800 °C, the polarization resistance of BSCF-SDC, 1.3Ag-BSCF-SDC, 2.3Ag-BSCF-SDC, 3.4Ag-BSCF-SDC and 4.5Ag-BSCF-SDC oxygen electrode is 0.019, 0.006, 0.012, 0.024, and 0.023 Ω cm², respectively. It can be seen that the polarization resistance of 1.3Ag-BSCF-SDC and 2.3Ag-BSCF-SDC oxygen electrode is obviously lower than that of BSCF-SDC oxygen electrode. The results illustrate that the electrochemical performance of BSCF-SDC oxygen electrode can be significantly improved by
adding appropriate amount of Ag particles. This is because the addition of Ag particles increased the conductivity of the BSCF-SDC oxygen electrode, thus improving its electrochemical properties. The polarization resistance of 3.4Ag-BSCF-SDC and 4.5Ag-BSCF-SDC oxygen electrode is higher than that of BSCF-SDC oxygen electrode. The reason may be that the surface of BSCF-SDC oxygen electrode is covered by too many Ag particles and the active sites of oxygen oxidation reaction are reduced. Symmetrical cells based on BSCF-SDC and 1.3Ag-BSCF-SDC oxygen electrodes are tested for 30 h under 0.4 A cm\(^{-2}\) electrolysis current in order to study the short-term stability of the oxygen electrodes. During the short-term electrolysis durability test, AC impedance measurements of the symmetrical cells are carried out per 5 h under OCV conditions with interrupting the electrolysis test. Figure 4(b) shows the polarization resistance \((R_p)\) stability curves with error bars of BSCF-SDC and 1.3Ag-BSCF-SDC oxygen electrodes in the short-term electrolysis durability test. It can be noted that both oxygen electrodes show good stability. The polarization resistance degradation rate of the BSCF-SDC and 1.3Ag-BSCF-SDC oxygen electrodes is 0.098 and 0.073 mΩ cm\(^2\) h\(^{-1}\), respectively. It can be seen that the stability of the two oxygen electrodes is similar, which indicates that the durability of the BSCF-SDC oxygen electrode is not affected by the addition of Ag particles. SEM images of BSCF-SDC and 1.3Ag-BSCF-SDC oxygen electrodes after the durability test are shown in the supplementary figure 3. For the BSCF-SDC oxygen electrode, it can be observed that the surface grains agglomerate and grow up obviously, and the surface pores become less, thus reducing the surface active sites and degrading the performance of the oxygen electrode. For the 1.3Ag-BSCF-SDC oxygen electrode, the Ag particles on the surface of the electrode agglomerate obviously, which may lead to the reduction of active sites and degradation of the oxygen electrode performance.
The electrochemical properties of SOECs based on BSCF-SDC and 1.3Ag-BSCF-SDC oxygen electrodes are characterized. Figure 5(a) shows the voltage-current density characteristic curves of SOECs based on the BSCF-SDC and 1.3Ag-BSCF-SDC oxygen electrodes at 800 °C. At an electrolytic voltage of 1.5 V, the electrolytic current densities are 0.2 A cm$^{-2}$ and 0.4 A cm$^{-2}$, respectively. Hence, the addition of Ag particles improves the electrochemical performance of the BSCF-SDC oxygen electrode, and enhances the electrolysis performance of the SOEC. Figure 5(b) shows the AC impedance spectra of both SOECs at 800 °C. Their polarization resistances were 1.05 Ω cm$^2$ and 0.27 Ω cm$^2$, respectively, as determined by equivalent circuits (supplementary figure 4). The polarization resistance of the SOEC based on the 1.3Ag-BSCF-SDC oxygen electrode is significantly lower than that based on the BSCF-SDC oxygen electrode. Since the two SOECs had the same Ni hydrogen electrode, the difference in polarization resistance can be attributed to the oxygen electrode [19, 20]. The above results once again prove that the electrochemical performance of BSCF-SDC oxygen electrode can be remarkably improved by adding appropriate amount of Ag particles.

4. Conclusions

Ag particles were added to a BSCF oxygen electrode in an SOEC to improve its electrochemical performance. The Ag-decorated BSCF-SDC material included the Ag phases in which no Ag-related heterophase was found. Ag particles in the Ag-decorated BSCF-SDC oxygen electrode were distributed on the surface as well as in the bulk of the oxygen electrode. The polarization resistance of Ag decorated BSCF-SDC oxygen electrode with the appropriate amount of Ag particles was lower than that of BSCF-SDC oxygen electrode. Especially, the polarization resistance of 1.3Ag-BSCF-SDC was as low as 0.006 Ω cm$^2$. The 1.3Ag-BSCF-SDC oxygen electrode showed good stability in the short-term electrolysis durability test. The electrolysis cell based on 1.3Ag-BSCF-SDC oxygen electrode showed better performance than that based on BSCF-SDC oxygen electrode. In conclusion, the addition of high-conductivity Ag particles to the BSCF-SDC oxygen electrode is an effective way to improve its performance.

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