



Short communication

Preparation of supported SrCeO₃-based membrane by spin coating method

Xinzhen Ding, Jinghua Gu*, Dong Gao, Guotao Chen, Yue Zhang

Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Xueyuan Road, Haidian District, Beijing 100191, China

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ABSTRACT

SrCe_{0.9}Y_{0.1}O_{3-δ} (SCY10) powder with a pure perovskite phase is prepared by solid-state reaction method. NiO is dispersed uniformly in SCY10 powder to fabricate NiO-SCY10 anode substrate. The starting powder, the mixture of SrCO₃, CeO₂ and Y₂O₃, is deposited directly on the green substrate instead of SCY10 powder by spin coating. After co-firing at 1300 °C for 3 h, the starting powder reacts to form SCY10 top layer on the substrate. SEM micrographs show that the top layer is defect-free and adheres well with the anode substrate without any delamination. A single fuel cell is assembled with anode-supported SCY10 membrane as electrolyte membrane and Ag as cathode. The electrochemical property of the fuel cell is tested with hydrogen as fuel in the temperature range of 600–800 °C. The open circuit voltage (OCV) reaches 1.05 V at 800 °C, and the maximum power density is 50 mW cm⁻², 155 mW cm⁻², 200 mW cm⁻² at 600 °C, 700 °C, 800 °C, respectively.

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1. Introduction

Solid oxide fuel cells (SOFCs) are promising power generation systems because of the potential of high-energy conversion efficiency, low environmental pollution and fuel flexibility [1–5]. The electrolyte is the heart of each fuel cell which effectively separates the anode gas and the cathode gas and mediates the electrochemical reaction occurring at the electrodes. Proton conductor, as a type of electrolyte, attracted more interest all over the world [6–8]. Proton conductors have become promising electrolyte candidates in the intermediate-temperature SOFC community due to their high protonic conductivity and low activation energy [9]. Besides, water forms at the cathode side where oxygen is the inlet gas in a proton conducting SOFC, so the fuel at the anode side remains pure and the outlet fuel can be reused without any treatment.

Protonic conductivity has been reported for many perovskite-type oxides such as doped BaCeO₃, SrCeO₃, BaZrO₃, and SrZrO₃. Doped BaZrO₃ and doped SrZrO₃ have good chemical stability, but are undesirable for their high sintering temperature and relatively low conductivity [10]. Compared with doped SrCeO₃ materials, doped BaCeO₃ materials have high proton conductivity and substantial oxygen ion conductivity in the presence of oxygen or water vapor [11]. Whereas, doped SrCeO₃ ceramics have higher proton transfer numbers than doped BaCeO₃ ceramics. Therefore, doped SrCeO₃ ceramics are competitive candidates for the electrolyte in the SOFC using hydrogen as fuel [12].

The electrolyte resistance is the decisive factor for the performance of fuel cell. In the cell that the electrolyte supports the electrode, the ohmic contribution is large due to high electrolyte resistance [13]. But, in the cell that an electrode supports the electrolyte, thin electrolyte layer is made to decrease the resistance of the electrolyte. The thickness of the electrolyte layer reduced to the range of 10–15 μm is a remarkable advantage in application [14,15]. Several methods were developed for preparation of electrolyte films on the anode substrates such as spray coating method [16], electrochemical vapor deposition [17]. Each method has its own advantages and disadvantages. Spray coating has a high deposition rate, but it is difficult to obtain a dense thin electrolyte film. Some of the fabrication methods are complicated and expensive such as electrochemical vapor deposition. Recently, spin coating process using slurry prepared from pre-fabricated powder as coating material was developed [18]. In spin coating method, some organic additives are used to adjust the solid loading, viscosity and volatility of the solvent system. Combining the advantages of particle coating and slurry coating, this method is expected to fabricate ultra thin ceramic film in an inexpensive way [19]. Although doped SrCeO₃ ceramics have many advantages as mentioned above, the publication on supported SrCe_{1-α}Y_αO_{3-δ} membrane for SOFCs has not been found. Also, no paper has reported the effect of the process parameters on the microstructure and the performance of doped SrCeO₃ films prepared by spin coating method.

In this paper, the mixture of SrCO₃, CeO₂ and Y₂O₃ was directly deposited on the anode substrate by spin coating method. Dense SrCe_{0.9}Y_{0.1}O_{3-δ} (SCY10) membrane formed on NiO-SCY10 anode substrate in situ by the solid-state reaction. The fuel cell with the

* Corresponding author. Tel.: +86 10 8231 6500; fax: +86 10 8231 6500.
E-mail address: gujh@buaa.edu.cn (J. Gu).

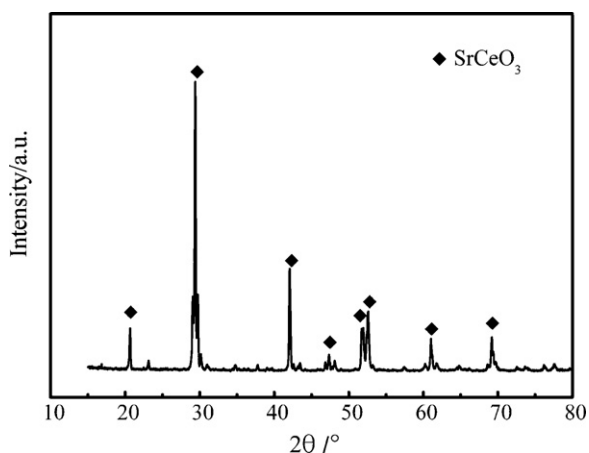


Fig. 1. XRD pattern of SCY10 powder prepared by the solid-state reaction at 1200 °C for 10 h.

obtained SCY10 membrane as electrolyte was assembled and the electrochemical properties of the cell were studied.

2. Experimental

SCY10 powder was prepared by solid-state reaction method. SrCO_3 , CeO_2 and Y_2O_3 powders were mixed in the molar ratio of 1:0.9:0.05 by ball-milling for 3 h in deionized water media. After the resultant mixture was dried, a part of the mixture was kept as precursor powder, and the rest part was calcined at 1200 °C for 10 h in air to obtain perovskite-type SCY10 powder. The synthesized SCY10 powder was ground and mixed with NiO powder. The volume ratio of SCY10 powder to nickel was 1.5:1. NiO-SCY10 mixture was then pressed uniaxially under 250 MPa into green compacts with a diameter of 1.8 cm, which were used as anode substrates for the spin coating process.

Homogeneous and stable slurry was prepared by mixing the precursor powder with a binder (mass ratio, 4:5) in an agate mortar for 1 h. The binder consisted of terpeneol (A.R.) and ethyl cellulose (A.R.) in a volume ratio of 97:3. SCY10 layer was deposited on NiO-SCY10 anode substrate by spin coating at 4.4 krpm for 60 s followed by heat treatment. Spin coating was carried out three times in order to obtain the dense SCY10 top layer. The samples were calcined at 600 °C for 30 min after each coating to remove the organic binder, then co-fired at 1300 °C in air for 3 h.

The phases of SCY10 powder and the membranes were studied with X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (D/max-2200PC, Japan). Scanning electron microscope (SEM) was used to observe the microstructure of the membranes.

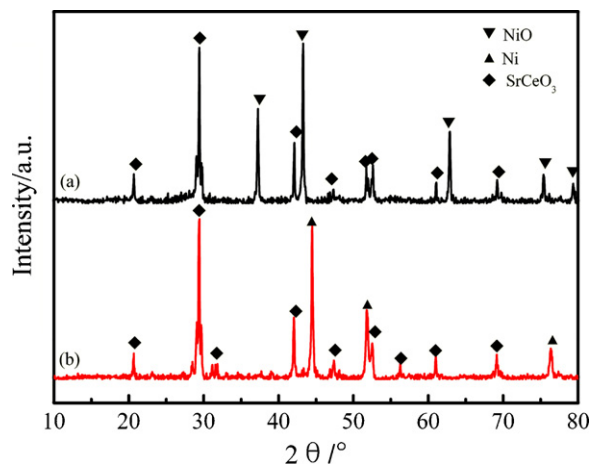


Fig. 2. XRD patterns of the anode substrate. (a) Before hydrogen reduction and (b) after hydrogen reduction.

Silver was employed as cathode and current collector. Silver paste was printed on the two faces of the membrane prepared, and Ag wires were attached as terminal leads to form an electrochemical cell, which was fired at 550 °C for 30 min. The single cell was sealed to one end of an alumina tube with a glass sealant. Ni-SCY10 anode was formed by hydrogen reduction in situ at 800 °C for 3 h. The anode side was fed with hydrogen in a flow rate of 100 mL min^{-1} and the cathode side exposed to air. V - I characteristics of the fuel cell were tested using hydrogen as fuel at 600 °C, 700 °C and 800 °C, respectively.

3. Results and discussion

3.1. Preparation of supported SCY10 membranes

Fig. 1 shows XRD pattern of SCY10 powder prepared by solid-state reaction method. There exist only peaks corresponding to SrCeO_3 perovskite phase in Fig. 1. It means that no impurity phase forms. XRD patterns of the anode substrate before and after reduction are shown in Fig. 2. This figure indicates that Ni phase formed by reduction of NiO, and Ni-SCY10 substrate is obtained after hydrogen reduction. As shown in Fig. 3, the surface morphology of the anode substrate after reduction is quite different from that before reduction. There were some closed pores before reduction (see Fig. 3a). Whereas, the substrate became porous after reduction since oxygen in NiO was lost (see Fig. 3b). Porous Ni particles are uniformly dispersed in the anode substrate.

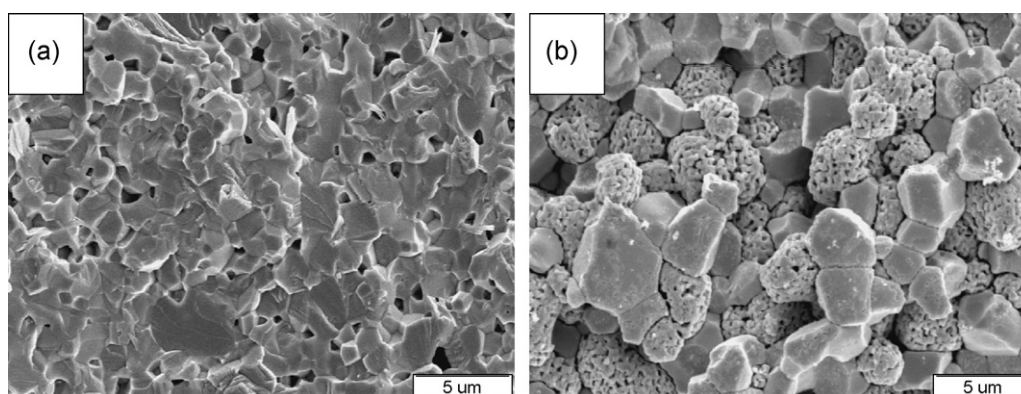


Fig. 3. The surface morphology of the anode substrate. (a) Before hydrogen reduction and (b) after hydrogen reduction.

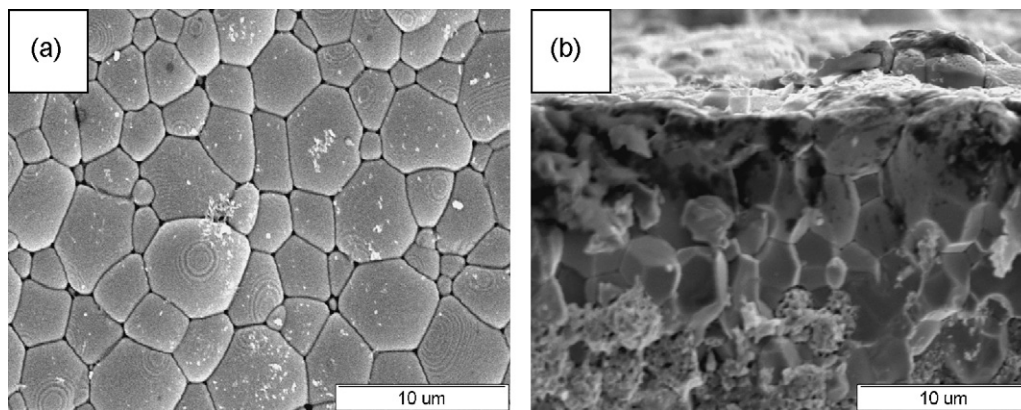


Fig. 4. The morphology of Ni-SCY10 anode-supported SCY10 membrane. (a) Top layer surface and (b) cross-section.

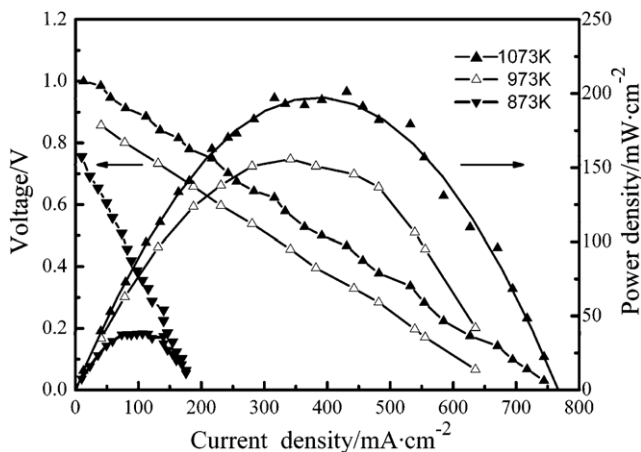


Fig. 5. Performance of the as-prepared cell with hydrogen as fuel.

Defect-free supported SCY10 membranes were fabricated. Neither pin hole nor crack is observed in the top layer by SEM. The top layer adheres well with the anode substrate without any delamination between them after hydrogen reduction. Fig. 4 shows the microstructure of a supported SCY10 membrane including top layer surface (Fig. 4a) and the cross-section (Fig. 4b). It can be clearly seen that SCY10 top layer is quite dense and the grain size is in the range of 2–6 μm . The top layer can be prepared as thin as 10 μm .

3.2. Electrochemical properties

A fuel cell was assembled with a 10 μm thick SCY10 layer supported by the anode as the electrolyte membrane. V – I curves and power density curves of the cell are shown in Fig. 5. The open circuit voltage (OCV) of the fuel cell fabricated in this research reaches 1.05 V at 800 °C. The maximum power density is 50 mW cm^{-2} , 155 mW cm^{-2} , 200 mW cm^{-2} at 600 °C, 700 °C, 800 °C, respectively. The electrochemical data become noisier with temperature increasing. This is caused by the fluctuation of the cell temperature during test. The polarization curve of 800 °C is approximately linear. It implies that the voltage loss is mainly caused by the ohmic resistance of the cell. Therefore, the power density curve of 800 °C is drawn according to the parabola fitting.

The experimental OCV is very close to the theoretical value when the testing temperature is higher than 700 °C. This result indicates that SCY10 top layer prepared by spin coating is dense. The powder density reaches 200 mW cm^{-2} at 800 °C, which is relatively high among those of the proton conductive fuel cells reported [12,15,18].

The cell shows good performance in the electrochemical test. It has been confirmed that defect-free supported $\text{SrCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ membrane can be prepared by spin coating method.

4. Conclusion

Dense $\text{SrCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (SCY10) membrane supported by a home-made Ni-SCY10 anode is successfully prepared from the slurry of SrCO_3 , CeO_2 and Y_2O_3 by spin coating. Ni particles are uniformly dispersed in the anode substrate. The dense SCY10 layer adheres well with the anode substrate. The open circuit voltage (OCV) of the fuel cell with 10 μm thick SCY10 membrane as the electrolyte membrane reaches 1.05 V at 800 °C. The maximum power density is 50 mW cm^{-2} , 155 mW cm^{-2} , 200 mW cm^{-2} at 600 °C, 700 °C, 800 °C, respectively, utilizing hydrogen as fuel. The experimental OCV is very close to the theoretical value when the testing temperature is higher than 700 °C.

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