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Steam electrolysis in a solid oxide electrolysis cell fabricated by the phase-inversion tape casting method

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ABSTRACT

In this study, an asymmetric NiO–yttria-stabilized zirconia (YSZ) cathode substrate has been successfully fabricated by the phase-inversion tape casting method. 3-dimensional X-ray microscopy and subsequent analysis demonstrate that the NiO–YSZ substrates exhibit dual-layer structure: a thin sponge-like pore layer is supported on a thick finger-like macro-void layer. The electrochemical performance of the Ni–YSZ/YSZ/YSZ–LSM electrolyzer with this novel dual-layer cathode has been significantly enhanced. The electrolyzer exhibits an excellent current density of 2.3 A cm^{-2} and a high H_2 production rate of 958 mL cm^{-2} h^{-1} at 800 °C and 1.5 V, and a polarization resistance of 0.25 Ωcm^2 at the open circuit voltage when the cathode and anode are exposed to 33 vol.% H_2O–67 vol.% H_2 and ambient air, respectively, demonstrating that the thin sponge-like pore layer in the dual-layer cathode can provide sufficient electrochemical reaction sites for H_2O reduction, while the thick finger-like macro-void layer can serve as the support for the electrolyzer and facilitate H_2/H_2O transport in the cathode, reducing the cathode polarization resistance and enhancing the cell performance.

1. Introduction

Recently, hydrogen has been considered as a promising energy carrier for the sustainable future due to its clean, storable and transportable characteristics [1–3]. Steam electrolysis in a solid oxide electrolysis cell (SOEC) has attracted increasing attention due to its environmental friendliness and high efficiency in storing energy by converting electrical energy into hydrogen [4–7]. Currently, there are three basic designs for SOEC development: electrolyte-, anode- and cathode-supported configurations. Nickel-based composite cathode-supported SOEC [8–12], for example, Ni–yttria-stabilized zirconia (YSZ), has been considered as the most promising cell configuration since it provides excellent thermal and electrical conductivity, and high electrochemical catalytic activity for steam electrolysis. However, the polarization resistance, especially concentration polarization may rise significantly resulting from the gas transport resistance through the thick cathode, especially at high hydrogen production rate. In addition, insufficient transport of steam in the SOEC mode, especially at high steam concentration, may also result in irreversible metal Ni oxidation and agglomeration [13–16].

Suzuki et al. [8] and Othman et al. [9] have shown that both porosity and microstructure play important roles in dictating the performance of solid oxide fuel cells (SOFC), and the anode structure in SOFC can be modified to significantly minimize both activation and concentration polarization resistance and thus to enhance the cell performance. The traditional sponge-like porous anode prepared by the tape casting, uni-axial pressing or gel-casting method, has been investigated extensively and proven to be beneficial for the densification of electrolyte by the dip-coating method [17–19]. However, such morphology is not ideal for gas diffusion because of high tortuosity factor (usually 4–10) [17–19], consequently limiting the SOFC cell performance. It should be noted that an anode of an SOFC will work as the cathode when the cell is operated in an SOEC mode [20–22], and the concentration polarization tends to be more critical in SOEC mode due to the larger molecular size of H_2O than that of H_2 and higher steam concentration in the H_2–H_2O binary system [23,24]. Pore formers can be introduced to modify the electrode pore structure [25], however, its tortuous microstructure still limits the cell performance [9]. Recently, the phase-inversion method has been applied to fabricate high-performance micro-tubular SOEC/SOFC, but since the electrolyte film can only be coated on the finger-like macro-void layer near the outer surface of the tube, the active electrochemical reaction sites near the hydrogen electrode/electrolyte interface will be low, while the sponge-like pore layer near the inner surface is not beneficial to gas transport, resulting in lower cell performance than expected [26]. Meanwhile, phase-inversion tape casting (PITC) method has been intensively utilized to optimize the anode microstructure of the planar SOFC and thus the cell performance [27–31], in which the fabricated anode possesses a unique dual-layer structure, a thin sponge-like pore layer (10–50 μm) supported on a thick finger-like macro-void layer (>300 μm), holding the promise to serve as the active anode

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functional layer and fast gas diffusion channels, respectively. However, no attention has been paid to this novel planar dual-layer Ni-based electrode for SOEC application, and its microstructural effects on the SOEC performance have not been studied. Therefore, in this work, PITC method has been employed to prepare the novel dual-layer Ni–YSZ cathode substrate for SOEC, and its electrochemical performance, including electrolysis current density and polarization resistance, is investigated.

2. Experimental

The asymmetric NiO–YSZ substrate was prepared by the PITC process [32,33] and the details of the phase-inversion slurry were described in a recent report [11]. After being degassed for 10 min using a vacuum pump, the slurry was casted on carrier film (Myler polymer film) using a doctor blade with a gap height of 0.7 mm, and then immersed into the water bath for 24 h to complete the solidification process. The NiO–YSZ substrate was punched into pellets with a diameter of about 20 mm and dried at ambient atmosphere for a week. The entire process is schematically shown in Fig. 1. These pellets were first pre-sintered at 1200 °C for 2 h, and YSZ electrolyte film was then dip-coated onto the NiO–YSZ substrate [34]. After firing the YSZ/NiO–YSZ bilayer at 1450 °C for 5 h, YSZ–$(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$(LSM) anode slurry at a weight ratio of 50:50 was screen-printed onto the YSZ film, followed by firing at 1100 °C for 2 h. The active anode area is 0.3 cm^2. A gold grid was printed on the anode surface to collect the anodic current, and silver wires were used as the current lead.

The as-prepared cells were sealed onto an alumina tube using a conducting paste (DAD-87, Shanghai Research Institute of Synthetic Resins) and a ceramic adhesive (552–1105, Aremco). Hydrogen flow rate was controlled using a digital mass flow controller (APEX, Alicat Scientific), while water vapor was added to the cathode via a humidifier by heating liquid water to a certain temperature, and the steam partial pressure was measured using a humidity sensor (Vaisala HMT 337). The current density–cell voltage (i-V) curves as well as the impedance spectra were measured with a four probe method using a multi-channel VersaSTAT (Princeton Applied Research) from 700 to 800 °C.

Microstructure of the cells was characterized by a scanning electron microscope (SEM, Zeiss Ultra Plus FESEM), while the cathode 3-dimensional (3D) microstructure was characterized using X-ray microscopy and analyzed by an in-house Matlab code.

3. Results and discussions

3.1. Microstructure and pore formation mechanism

Fig. 2A shows the cross-sectional SEM image of the porous NiO–YSZ substrate pre-sintered at 1200 °C for 2 h prepared through the PITC method. It can be seen that the NiO–YSZ substrate exhibits the typical dual-layer structure: a thin sponge-like pore layer supported on a thick finger-like macro-void layer, forming a characteristic asymmetric membrane typically formed by the phase-inversion process [9–11,27,28,31–33,35]. It should be pointed out that those finger-like macro-voids are initiated from the non-solvent (H_2O)/slurry interface where the initial exchange of solvent N-methyl-2-pyrrolidone (NMP) in the casted ceramic/polymer slurry (Step 1 in Fig. 1) with non-solvent (H_2O) bath takes places (Step 2 in Fig. 1), and then penetrates into the bulk (Step 3 in Fig. 1) until the solidification completes. Since the exchange rate between NMP and H_2O adjacent to the carrier film is lower than that for the formation requirement of the finger-like macro-voids, only the slow precipitation of the casted ceramic/polymer slurry can occur and thus those sponge-like pores adjacent to the carrier film are formed [10,35,36]. After being solidified, punched into circular sample and dried, the green NiO–YSZ substrate is ready for pre-sintering (Step 4 in Fig. 1).

Fig. 2B displays the 3D X-ray microscopic image of the pre-sintered cathode substrate with dimensions of 3.03 × 3.75 × 0.35 mm. The upper part in Fig. 2B is the area close to the carrier film during the PITC process, similar to that shown in Fig. 2A. To further characterize the cathode structure, a 3D microstructure has been reconstructed by directly stacking the raw X-ray gray images along the *x*-axis in sequence (Fig. 2C), and the porosity and tortuosity factor of the finger-like macro-voids along the *z*-axis are calculated to be ~28% (Fig. 2D) [17] and 1.7 [17,37], respectively, further confirming that the substrate contained elongated finger-like pores, which is beneficial to H_2/H_2O transport in the cathode. From the cross-sectional SEM images of the electrolyzer (Fig. 2E–F), it can be found that good adherence between the YSZ electrolyte and the electrodes (cathode and anode) is obtained, and the thickness of the cathode, electrolyte, and anode is estimated to be 350, 10, and 20 μm, respectively.

3.2. Electrochemical performance

Fig. 3A shows the i-V curves for the dual-layer cathode-supported Ni–YSZ/YSZ/YSZ–LSM electrolyzer measured in the electrolysis mode under 33 vol.% H_2O–67 vol.% H_2(33% AH)/air condition. 40-sccm (standard cubic centimeters per minute) hydrogen is used as the carrier gas. Current density is recorded from open circuit voltage (OCV) to OCV + 0.6 V with the voltage sweeping rate of 0.03 V s^{-1}, while H_2 production rate corresponding to the electrolysis current density is calculated using the Faraday's law. As shown in Fig. 3A, the OCV (cell voltage at zero current density) is 0.885, 0.875 and 0.865 V at 700, 750 and 800 °C, respectively. Voltage higher than the OCV needs to be applied to generate the steam electrolysis process. It can be seen from Fig. 3A that the increase in both the operating temperature and the applied voltage can lead to the increment of the electrolysis current density. At 800 °C and under a cell voltage of 1.5 V, a cell current density of 2.3 A cm^{-2} and a hydrogen production rate of 958 mL cm^{-2} h^{-1} are obtained, much better than the previous results on solid oxide electrolyzer with similar cell materials and cell configurations but with the cathode fabricated by uni-axial pressing or even freeze-drying tape casting method [34,38,39], as listed in Table 1. Note that relatively high current density can also be achieved under different AH (inset of

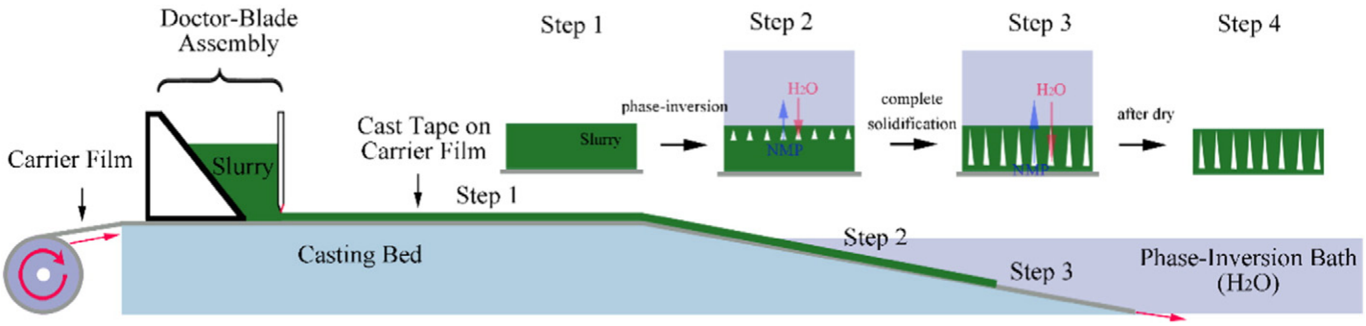

Fig. 1. Schematic diagram of the phase-inversion tape casting process.