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Short Communication

Millimeter tubular solid oxide electrolysis cells with modified asymmetric hydrogen electrode

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ABSTRACT

Asymmetric structure with pore gradient is fabricated as the hydrogen electrode for millimeter tubular solid oxide electrolysis cells (SOECs). The gradient electrode is achieved with a graphite-assistant phase inversion process using an additional graphite layer to remove the relative dense skin layer. The electrode has demonstrated higher gas permeability than that with normal composite structure. Consequently, the steam starvation (concentration polarization) is successfully eliminated when SOEC is operated at relatively high voltage and low steam concentration. In addition, reduced interfacial polarization resistance and elevated current density are achieved for the tubular SOEC with the unique electrode.

Introduction

In recent years, there has been an increased focus on hydrogen as an alternative energy carrier for a future low carbon economy and to mitigate heavy dependence on finite fossil fuels [1]. However, hydrogen is currently produced from natural gas by steam reforming, which depletes a valuable fossil fuel and emits green house gases. An environmentally friendly means of hydrogen production is electrolysis process using intermittent renewable energy sources such as solar energy and wind power. Compared with the widely developed low-temperature alkaline cells for water electrolysis technologies, high-temperature solid oxide electrolysis cells (SOECs) are of particular interest [2,3] due to both thermodynamic and kinetic reasons at elevated temperature [4,5]. Moreover, electricity and heat generated from the nuclear power systems and waste heat from high temperature industrial processes can be utilized for electrolysis in SOECs [5–7].

The tubular design of SOEC is popular due to its good mechanical property, greater tolerance to thermo-cycling and simple sealing [8–10]. A tubular SOEC usually consists of a dense thin film of yttria-stabilized zirconia (YSZ) as the electrolyte, a porous thin layer of strontium doped lanthanum manganite as the air electrode and a porous thick layer of Ni-

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YSZ cermet as the hydrogen electrode, where steam is electrochemically reduced to hydrogen. The hydrogen electrode also serves as the mechanical support, so it should be thick enough to achieve proper mechanical strength. This thick structure could lead to concentration polarization when SOEC is operated at high current density and low steam concentration. While lots of research have been conducted to reveal the relation between the electrode materials and their electrochemical activity [8,9,11–13], there is very few reports available to study the microstructure effect on steam concentration polarization.

The concentration issues could be minimized using an asymmetric structure with porosity gradient decreasing from the electrode surface to the electrode-electrolyte interface, which is capable to allow for adequate gas transportation and electrochemical steam reduction. This asymmetric structure for tubular cells is usually realized using a simple immersion induced phase-inversion method. The phase-inversion process often results in a multilayer structure with a highly porous layer sandwiched in two relatively dense layers. Thus, the electrode consists of three different layers: the layer connected to the electrolyte is a porous sponge layer, which is rich in three-phase boundaries for electrochemical reaction. The next one is the highly porous layer with finger-like regular pores for fast gas delivery. And the skin layer exposed to the gas is relatively dense [14,15]. Comparing with the symmetric electrode, improved performance is observed with the three-layer asymmetric structure. However, the gas (H_2O and H_2) delivery capability could be limited by the skin layer due to its much lower porosity than the finger-like layer. As a result, concentration polarization is observed at higher current density or applied voltage, and the steam starvation become more serious in high temperature electrolysis mode [16–18] since the diffusion coefficient of the heavier steam molecule is much smaller than hydrogen [19]. For example, Yang et al. [16] have reported serious steam starvation phenomenon occurred at higher voltage in micro-tubular SOECs, which were tested in an absolute humidity range from 30 to 80 vol. %.

The skin layer is formed inevitably in the phase inversion process. Our previous study has shown that the skin layer could be removed with a modified process [20]. In this process, an additional graphite layer is deposited as the skin layer, which can be completely removed by the subsequent high-temperature calcination. In this work, the graphite-modified phase inversion process is employed to fabricate tubular NiO-YSZ with continuous porosity gradient for SOEC. Concentration polarization can be effectively eliminated when the single tubular SOEC is tested at 800 °C under external voltage up to 1.5 V.

Experimental

The NiO-YSZ millimeter tubes were prepared with the graphite-assisted phase-inversion method [20], which is briefly described here. NiO (Jinchuan Group, China) and YSZ (Sichuan, China) powders were mixed with a weight ratio of 1:1 and ball-milled for 24 h, followed by drying for 12 h. A polymer solution containing 1-Methyl-2-pyrrolidone (NMP, solvent, Chemical Pure, Sinopharm Chemical Reagent Co., Ltd, China), polyethersulfone (PESf, polymer, Radel A-100, Solvay Advanced Polymers) and polyvinylpyrrolidone (PVP, dispersant, K30, Chemical Pure, Sinopharm Chemical Reagent Co., Ltd, China) were prepared with a weight ratio of 20:4:1. Two different slurries were prepared by stirring the polymer solution and the powder for 6 h. One was graphite slurry (S1) containing 30 wt. % graphite powder (average size: 20 μm) and the other was NiO-YSZ ceramic slurry (S2) with 60 wt. % ceramic powder. After the slurry was pumped under vacuum for about 10 min, a glass tube (diameter of 0.50 cm) with bottom sealed was immersed into S1 for 5 s and then immersed into tap water for 5 min to solidify graphite slurry, resulting in a porous adhesive graphite layer. After drying, the glass tube was immersed into S1 again to form a transitional layer and subsequently immersed into S2. Lastly, the glass tube with the three layers was immersed into ethanol for 1 min and tap water for 12 h to complete the phase inversion process while the glass tube was separated with the coated layers. The dried raw tubes were pre-heated at 1200 °C for 2 h to achieve NiO-YSZ substrate with certain structural strength, as well as to burn off the graphite layer and organic components.

Thin YSZ (TZ-8Y Tosoh, Japan) electrolyte layer was deposited on the NiO-YSZ tube by a dip-coating method, then sintered at 1400 °C for 5 h. A-site non-stoichiometric $(La_{0.85}Sr_{0.15})_{0.9}MnO_3$ (LSM)-YSZ composite with 40wt.% YSZ was painted on YSZ and sintered at 1200 °C for 2 h as the air electrode. The active cathode area was about 0.7 cm^2. Tubular cells with the skin layers were also fabricated as a comparison. The fabrication processes were similar with the above mentioned but the graphite layer was not applied.

The microstructures were characterized with a scanning electron microscope (SEM, JSM-6700F). The SEM images were used to estimate the porosity with image analysis software Image J. The porosity was also measured using the Archimedes method. The mercury injection apparatus (Quantachrome PM60GT-17) was employed to measure the pore size distributions of the Ni-YSZ substrates. Gas permeation properties were measured through a home-made pilot plant. Tubular Ni-YSZ samples were fixed on the base of a male connector, and sealed off with epoxy resin, and then covered by a refined cylinder. Nitrogen was fed into the cylinder at different pressures. The gas permeation through the samples was measured by a soap bubble flow meter and the inlet gas pressure was also recorded. The electrochemical performance was measured using an Electrochemical Workstation (Solartron1287A-1260A). The hydrogen electrode was fed with 20 ml min^{-1} of H_2 containing different steam concentration, which was controlled through a humidifier. The steam partial pressure (P_{H2O}) in the gas mixture was evaluated with absolute humidity. Heating tapes were wrapped around the inlet gas pipes in order to prevent steam condensation.

Results and discussion

Fig. 1 shows the SEM microstructures of the tested Ni-YSZ substrates, which are ~450 μm thick. Fig. 1a–b clearly demonstrates an asymmetric distribution in porosity. The whole cross-sectional view for the sample with the skin layer can be roughly divided into three part (Fig. 1a). Different non-solvents can obtain various pore morphologies [21]. In this