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Highly stable microtubular solid oxide fuel cells based on integrated electrolyte/anode hollow fibers

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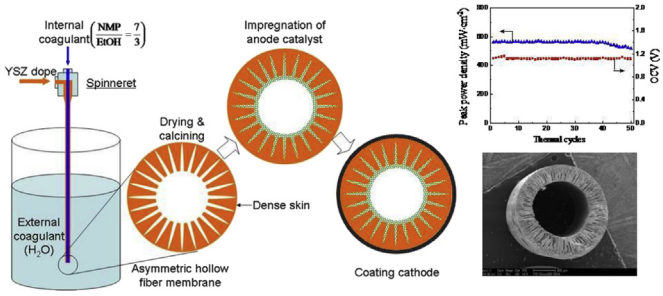
HIGHLIGHTS

- Integrated electrolyte/anode was fabricated with favorable structure for MT-SOFC.
- Anode Ni loading was reduced significantly via a vacuum-assisted impregnation.
- The MT-SOFC delivered a highly stable performance in 40 thermal cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The asymmetric YSZ hollow fibers have been prepared by a phase-inversion method, based on which, the integrated electrolyte/anode hollow fibers are fabricated via a vacuum-assisted impregnation of nickel nitrate. The content of NiO in the integrated hollow fibers enhances linearly from 0 to 42 wt.% with the impregnation cycles from 0 to 10. The porosity of the integrated electrolyte/anode hollow fibers decreases from 43% to 31% with the repeated impregnation and calcination of Ni catalyst. Its conductivity reaches up to 728 S cm^{-1} after 10 cycles of impregnation. And the mechanical strength of the integrated hollow fiber enhances from 128 to 156 MPa due to the increased NiO content. Based on the integrated electrolyte/anode hollow fibers, the prepared microtubular solid oxide fuel cells (MT-SOFCs) deliver a peak power density of 562 mW cm^{-2} after ten cycles of Ni impregnation. The cell stability has been verified in 40 thermal cycles with a steady OCV of 1.1 V and stable power density around 560 mW cm^{-2} operated at 800 °C.

1. Introduction

Microtubular solid oxide fuel cells (MT-SOFCs) have captured increasing attention from research communities due to their high volumetric power densities, rapid start-up and shut-down operations, low capital costs and relatively less challenging sealing requirements at high temperature [1–4]. Much work has been focused on the development of anode-supported MT-SOFCs since the nickel-based support can provide good catalytic activity towards the fuel oxidation and an electrolyte film can be facilely coated with very thin thickness leading to a reduced electrolytic resistance and thus ensuring a high power output [5–9]. However, the anode-supported MT-SOFCs are mainly prepared via multi-step layer-by-layer methods, a very complex fabrication process suffering from many uncertainties and the possible existence of defects between these layers. Based on this method to prepare

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these MT-SOFCs, the anode micro tubes are normally extruded and presintered firstly. Then the other cell components like anode functional layer (AFL), electrolyte membrane, cathode functional layer (CFL) and cathode are separately coated on these micro tubes. Finally, these components need to go through a co-sintering procedure again to guarantee the sufficient integration as a whole cell [3]. During the multi-layer preparation, defects in the boundaries between layers are often inherently existed leading to undesired physical/chemical changes at the interfaces for instance the mechanical and thermal delaminations during long-term or thermal-cycle operations. These delaminations or defects are main factors for the cell degradation. Therefore, the integrated electrolyte/electrode configuration, combining the electrolyte and electrode properly in the form of electrolyte skeleton, has been proposed to improve the cell mechanical stability against thermal shocks [10]. The skeleton is prepared with electrolyte material and sintered in one step to form a dense electrolyte membrane sandwiching between the two porous electrolyte networks. Subsequently, the electrode catalysts are impregnated into the electrolyte networks and co-sintered to form the whole cell. To obtain a well integrated electrolyte/electrode structure, the matrix controlling and the catalyst plating have been previously investigated [11–13]. However, no attempts have been reported on the studies of the thermal durability of the prepared MT-SOFCs to prove the mechanical stability of the integrated electrolyte/anode structure.

Phase-inversion process is an effective method to fabricate the highly asymmetric ceramic hollow fibers, which can be applied for chemical reactors, oxygen separators and microtubular SOFCs [14–17]. By tuning the spinning conditions, the resultant ceramic hollow fiber can be tailored into a structure with a dense skin layer supported by a porous substrate with finger voids [13,18]. If such asymmetric hollow fiber is made from the electrolyte, such as Y_2O_3 stabilized ZrO_2 (YSZ), the dense skin layer may be severed as the electrolyte membrane, and nickel catalyst can be impregnated inside the porous substrate layer to achieve a well integrated electrolyte/anode matrix. To prepare such a configuration, the skin and the finger-void support can be formed in one step leading to the integrated electrolyte/anode skeleton. Thus, many defects sourced from multi-step preparation like the interface defects or the mechanical delaminations can be avoided. The thermal-cycle fatigue of the cell would also be diminished since the thermal expansion coefficient (TEC) of the electrolyte is consistent with that of the electrodes.

In the present work, the above hypothesis has been verified. To this end, electrolyte/anode skeleton in the geometry of an asymmetric YSZ hollow fiber with high mechanical strength was prepared via an improved phase-inversion method. Nickel, the anode component, was infiltrated with assistance by a vacuum into the framework of the finger-void porous structure. Based on the configuration of the integrated electrolyte/anode, the resultant MT-SOFC is expected to possess a high stability under many thermal cycles.

2. Experimental

2.1. Materials

Commercially available yttria-stabilized zirconia (YSZ) powder with a purity of 99.9% and a particle size of 20–30 nm (Yitong Co. Ltd., Weifang, China) was used as the electrolyte material. The cathode material, $La_{0.8}Sr_{0.2}MnO_{3-\alpha}$ (LSM), was synthesized via the Pechini method, mixed with YSZ powder in a weight ratio of 8:2. Nickel nitrate (AR grade, Sinopharm Chemical Reagent Co., Ltd.) was used as the anode precursor. Polyethersulfone (PESf, Radel A-300, Ameco Performance, USA), *N*-methyl-2-pyrrolidone (NMP, >99.8%, Kermel Chem Inc., Tianjin, China) and Polyvinylpyrrolidone (PVP) (AR grade, Sinopharm Chemical Reagent Co., Ltd.) were used as the polymer binder, solvent and additive, respectively, for the preparation of the spinning dopes. Deionized water and mixed ethanol/NMP solution (70 wt% of NMP) were used as the respective external and internal coagulants.

2.2. Preparation of the integrated electrolyte/anode hollow fiber

The integrated electrolyte/anode hollow fiber was fabricated via a combined phase inversion with vacuum-assisted impregnation method. The spinning dope was prepared with the following steps as below. The calculated amount of PESf pellets (7.4 wt% in the spinning dope) and PVP powder (3.7 wt% in the spinning dope) were dissolved by the solvent NMP (29.6 wt% in the spinning dope) in a 250 cm^3 wide-neck bottle under stirring condition to form a polymer solution. YSZ powder (59.3 wt% in the spinning dope), which had been pre-dried at 120 °C for 12 h, was added gradually into the PESf-PVP-NMP polymer solution under mixing. The spinning dope was mixed continuously for 48 h to ensure the uniform YSZ dispersion in the polymer solution. After degassing at room temperature for 2 h, the spinning dope was transferred to a stainless steel syringe. Meanwhile, the internal coagulant (EtOH/NMP = 3/7 in weight) was prepared and transferred to another syringe. Pushed by the syringe pumps (LSP01-1BH, Longer Precision Pump Co., Ltd., Baoding, China), the spinning dope and the internal coagulant were pressed simultaneously through a spinneret with an annular orifice, passing through a 10 cm air gap, into a water coagulant bath. The process is shown in Fig. 1. The spinning rates of the spinning dopes and the internal coagulant were set at 10 and 8 mL min^{-1}, respectively. The green hollow fibers were immerged in the external coagulation bath to complete the solidification process. After 24 h, the hollow fiber precursors were taken out from the water bath, cut into pieces of 20 cm in length, straightened and dried at room temperature successively. Finally the precursors were sintered at 1500 °C for 4 h to form YSZ hollow fibers with a dense outer skin and a porous inner surface (Fig. 1).

The anode was prepared via a vacuum-assisted impregnation process and the setup is schematically shown in Fig. 2(a). Firstly, valve 1 was opened but with valve 2 closed. The prepared YSZ hollow fiber was vacuumed by a vacuum pump. Next, valve 1 was switched off and valve 2 was switched on prudently. The anode solution (Table 1) was sucked into the hollow fiber. After both valves were switched off, the hollow fiber was taken out and dried at room temperature and calcined at 700 °C for 4 h under the ambient atmosphere. The heating rate should be controlled under 2 °C min^{-1}. The impregnation and calcination processes were repeated for 10 times, and the weight of the cell increased with the impregnation cycles. Meanwhile, the conventional impregnation was also applied to compare the results (Fig. 2(b)) [19].

2.3. Fabricating and testing of MT-SOFCs

After impregnation of anode catalyst, the cathode ink [14] was dip-coated on the out surface of the YSZ hollow fiber and calcined at 1200 °C for 2 h to form the microtubular SOFC with a configuration of integrated anode/electrolyte (Fig. 1). The performance of the prepared MT-SOFC was tested in accordance with the previous method [9,14]. The diluted silver paste was both injected into the lumen side of microtubular SOFC and brushed on the outer surface as current collector. The spiral Ag wires were pasted on the cathode and anode to lead out current. Prior to the measurement, the anode was reduced by flowing hydrogen at 700 °C for 2 h. The cell was tested at 800 °C using hydrogen as the fuel and air as the oxidant. The flow rates of hydrogen and air were fixed at 40 and