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Microstructure tailoring of the nickel–yttria stabilised zirconia (Ni–YSZ) cermet hollow fibres

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Abstract

Nickel–yttria stabilised zirconia (Ni–YSZ) hollow fibres have been prepared by the phase inversion/sintering technique followed by a reduction process with hydrogen. This work is particularly focussed on tailoring the microstructure and the properties of hollow fibres by ethanol addition into the spinning hollow fibre suspension. Microstructure evolution change is demonstrated by increasing the amount of ethanol from 0 to 35 wt% e.g. the hollow fibre cross-section is modified from a sponge-like structure sandwiched by two thin finger-like layers to the sponge-like structure only. Higher ethanol content translates to denser hollow fibres. This trend also correlates with the shrinkage, mechanical strength and electrical conductivity of the hollow fibres. As the ethanol content is increased, shrinkage reduces, mechanical strength improves and electrical conductivity increases. The Ni–YSZ hollow fibres made from suspensions containing 15–25 wt% ethanol are considered the best option as anode supports for micro-tubular solid oxide fuel cells in terms of their median porosity values, since insufficient porosity would hinder the fuel and product transport, whereas excessive porosity would deteriorate the mechanical strength of the fibres.

Keywords: Hollow fibre; Solid oxide fuel cell; Anode; Phase inversion

1. Introduction

Fuel cells are attractive to convert chemical energy to electrical energy due to their high conversion efficiency. Since the conversion is performed without involving heat, the fuel efficiency for some fuel cells like solid oxide fuel cells (SOFCs) can reach up to 80% [1–4]. Among various fuel cells, polymer-electrolyte-membrane fuel cell (PEMFC) and SOFC have currently attracted most attention. PEMFCs are limited by their lower operating temperatures. SOFC, on the contrary, is an all solid-state device which conventionally operates between 600 and 1000 °C. Moreover, SOFCs also offer fuel flexibility (allows different fuel options such as hydrogen, natural gas, methane, gasoline and other hydrocarbons) as well as high tolerance to fuel impurities [1–4]. In recent years, hollow fibre or micro-tubular SOFCs (MT-SOFCs) featuring high volumetric power density, good mechanical properties, good thermo-cycling behaviour and quick start-up and shut-down operations have been developed [5–8]. Such MT-SOFCs are normally fabricated using a three-step process, i.e. preparation of anode micro-tubes, formation of a thin electrolyte film on the micro-tube outer surface and the deposition of cathode layers on the electrolyte film [6]. Yttria-stabilised zirconia (YSZ) is the most commonly used electrolyte material considering its high oxygen ionic conductivity, strong mechanical properties

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and good chemical compatibility. Accordingly, numerous MT-SOFCs have been prepared using Ni–YSZ as anode and YSZ as an electrolyte [9–12].

In MT-SOFC, anode micro-tube's architecture has a substantial role in fuel cell performance. While typical anode tubes are designed to have a thick wall layer to support the additional deposited layers with sufficient mechanical strength, this design, undoubtedly, leads to a large resistance to the diffusion of gaseous fuel and products during operation. To this end, an immersion induced phase inversion technique has been developed to fabricate ceramic hollow fibre membranes with a thin wall layer and an asymmetric structure [13–15]. The main advantages of this method lie primarily within the usage of inexpensive equipment and simple procedures which are of interest particularly towards reduced production costs of MT-SOFCs.

The phase-inversion method is a technique to prepare asymmetric membranes for gas separation applications [13–14]. The asymmetric membrane has a continuous sandwich microstructure consisting of a layer dominated by finger-like voids followed by a sponge-like layer and another layer dominated by finger-like voids [15–18]. Here, finger-like voids provide transport channels for gaseous fuel and products. The sponge-like structure, on the other hand, acts as three phase boundaries (TPB) required for electrochemical reactions while also providing necessary mechanical strength into the hollow fibres [19]. The optimum balance between finger-like voids and sponge-like structure is of interest since an excess amount of finger-like voids would interrupt the percolative path of electronically conductive Ni metal required to maintain stable anode performance. Therefore, microstructure tailoring of the anode hollow fibres is crucial to enhance the performance of MT-SOFCs.

In this work, phase inversion and sintering are used to prepare Ni/YSZ hollow fibres with different microstructures. The effect of the resultant microstructure on the mechanical strength, porosity and electronic conductivity of SOFC anodes is studied. These hollow fibre anodes are then utilised as base layers upon which further electrolyte and cathode layers are deposited to make micro-tubular fuel cells.

2. Experimental

2.1. Materials

Commercially available NiO and 8 mol% yttria-stabilized zirconia (8YSZ) powders with 99.9% purity and particle size diameters of 20–30 nm (Weifang Yitong Co. Ltd., Weifang, China) were used as the anode materials. Polyethersulfone (PESf) ((Radel A-300), Ameco Performance, USA), *N*-methyl-2-pyrrolidone (NMP) (AR Grade, $>99.8\%$, Kermel Chem Inc., Tianjin, China) were used as the polymer binder and the solvent to prepare the spinning solution.

2.2. Spinning of the NiO/YSZ hollow fibres

A starting solution was first prepared to spin the hollow fibre precursors. A calculated quantity of PESf was dissolved in the NMP/ethanol mixture solution in a 250 cm^3 bottle. The composition of NMP/ethanol solution was varied from 0 to 35 wt% (of NMP) with the increment of 5 wt%. After the polymer solution formed, a mixture of NiO and YSZ powders (which were dried at 120 °C for 12 h previously), were then added gradually under stirring. The stirring was carried out continuously for at least 48 h to ensure that all powders were dispersed uniformly in the polymer solution. The starting solution was de-gassed at room temperature for an hour and the solution was then transferred to a stainless steel reservoir and pressurised to 0.10 MPa (absolute pressure) using nitrogen. A spinneret with the orifice diameter/inner diameter of 3.0/1.5 mm was used to spin the hollow fibre precursors. De-ionised water and tap water were used as the internal and external coagulants, respectively. The formed hollow fibre precursors were immersed in a water bath for more than 24 h to complete the solidification process. The hollow fibre precursors were heated in a furnace at 800 °C for 200 min to remove the organic polymer binder followed by sintering at 1400 °C in ambient non-flowing air atmosphere for 5 h to allow the sufficient fusion and bonding. After cooling to room temperature, the resulting NiO/YSZ hollow fibres were kept in a dry place for subsequent characterisation and reduction. The operating conditions employed to prepare NiO/YSZ hollow fibres are summarised in Table 1.

2.3. Reduction of the Ni/YSZ anodes

To obtain Ni/YSZ anode tubes, the sintered NiO/YSZ hollow fibres were reduced using hydrogen. A quartz tube was used as the holder for the 4 cm-long NiO/YSZ hollow fibre samples. Argon was used as purge gas during ramping up to 200 °C; above which pure hydrogen was then passed through the chamber with a flow rate of 20 $cm^3\ min^{-1}$. The reduction was performed at 700 °C for 5 h. After cooling down to 200 °C, the samples were then purged again with argon until the temperature reached room temperature. The resultant porous Ni/YSZ anode tubes were characterised.

Table 1
Preparation conditions of the NiO/YSZ hollow fibres.

Experimental parameters	Values
Compositions of the starting solution (wt%)	
NiO/YSZ	58.3
PESf	8.3
NMP+ethanol	33.3
Spinning temperature (°C)	20
Nitrogen pressure (absolute pressure) (MPa)	0.1
Injection rate of internal coagulant ($cm^3\ min^{-1}$)	20
Air gap (cm)	1
Sintering time (h)	5