Journal of Power Sources 293 (2015) 852–858

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Novel light-weight, high-performance anode-supported microtubular solid oxide fuel cells with an active anode functional layer

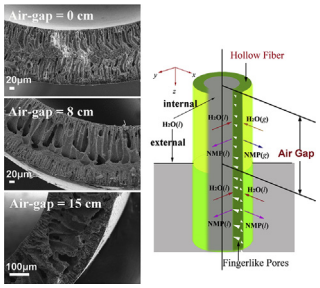
Tong Liu [a], Yao Wang [a, b], Cong Ren [a], Shumin Fang [a], Yating Mao [c], Fanglin Chen [a, *]

[a] Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA
[b] Department of Water Quality Engineering, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, PR China
[c] Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA

HIGHLIGHTS

- Air gap has significant influence on the microstructure evolution of hollow fibers.
- Microstructure evolution with different air gaps has been explained.
- With proper air gap, light weight high performance MT-SOFCs are achieved.
- MT-SOFCs exhibit robust resistance to thermal cycling.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 March 2015
Received in revised form
16 May 2015
Accepted 4 June 2015
Available online 12 June 2015

Keywords:
Microtubular SOFCs
Anode functional layer
Phase-inversion
Air-gap
Light-weight

ABSTRACT

Influence of the air-gap, the distance from the tube-in-orifice spinneret to the upper surface of the external coagulant bath during the extrusion/phase-inversion process, on the microstructure of nickel–yttria-stabilized zirconia (Ni–YSZ) hollow fibers has been systematically studied. When the air-gap is 0 cm, the obtained Ni–YSZ hollow fiber has a sandwich microstructure. However, when the air-gap is increased to 15 cm, a bi-layer Ni–YSZ hollow fiber consisting of a thin layer with small pores and a thick support with highly porous fingerlike macrovoids has been achieved. The output power density of microtubular solid oxide fuel cells (MT-SOFCs) with a cell configuration of Ni–YSZ/YSZ/YSZ–LSM increases from 594 mW cm^{-2} for the cells with the Ni–YSZ anode of sandwich microstructure to 832 mW cm^{-2} for the cells with the Ni–YSZ anode of bi-layer microstructure at 750 °C, implying that to achieve the same output power density, the weight of the cells with the bi-layer anode support can be reduced to 41.5% compared with that of the cells with the sandwich anode support. Thermal-cycling test shows no obvious degradation on the open-circuit-voltage (OCV), indicating that the MT-SOFCs have robust resistance to thermal cycling.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising next-generation energy conversion systems because of their high energy conversion efficiency and excellent fuel flexibility [1–4]. The design of the cell architecture and electrode microstructure may greatly influence the performance and the reliability of SOFC systems [5–10]. Compared with planar SOFC systems, tubular SOFCs exhibit higher mechanical integrity, better thermal-cycling behavior and simpler gas manifolding and sealing [1]. In particular, microtubular SOFCs

* Corresponding author.
E-mail address: chenfa@cec.sc.edu (F. Chen).

http://dx.doi.org/10.1016/j.jpowsour.2015.06.018
0378-7753/

(MT-SOFCs), with the outer diameter less than 2–3 mm, hold the promise for high volumetric power density, improved thermo-mechanical stability and rapid start-up [1,11–13]. Therefore, MT-SOFCs are attracting increased research interest not only for stationary applications such as combined heat and power systems but also for portable auxiliary power units [14,15].

Among the various cell configurations, anode-supported MT-SOFCs have been considered to be the most promising due to their excellent cell performance, sufficient mechanical strength, and less challenge for stack assembly [1]. Recently, phase-inversion process has been intensively explored for preparation of the anode support for MT-SOFCs [6–8,13,16–18]. To develop a low-weight but high performance MT-SOFCs, an anode support composed of a thick highly porous fingerlike-macrovoids layer (HPFML) near the inner surface and a thin small pore layer (SPL) near the outer surface with sufficient triple phase boundaries (TPBs) is expected to serve as the fast gas diffusion channels and active anode functional layer (AFL), respectively. During the extrusion/phase-inversion process, the spinning slurries are pressurized using the nitrogen gas, and then extruded through a tube-in-orifice spinneret and an air-gap into external coagulant bath, as schematically shown in Fig. 1. The air-gap is the distance between the tube-in-orifice spinneret/air interface and the air/external coagulant bath interface. Because the air-gap can efficiently affect the local viscosity of the spinning slurries near the outer surface of the extruded tube, the microstructure of the hollow fibers may be tailored by adjusting the air-gap during the extrusion/phase-inversion process. Kingsbury et al. reported that alumina (Al_2O_3) hollow fiber consisting of a SPL supported on a HPFML can be easily prepared in one step by manipulating the air-gap during the extrusion/phase-inversion process followed by high-temperature sintering [19]. From the literature, we can find that the pore size of the HPFML near the inner surface as well as the porosity and gas permeability of the whole membranes increased with increasing the air-gap, thus leading to reduced membrane weight per volume and gas transport resistance in the membrane, which may be an ideal microstructure for light-weight high-performance MT-SOFC application. However, no such ideal microstructure and its effect on the cell performance have been reported. Therefore, in this work, for the first time, air-gap has been controlled to prepare the bi-layer hollow fibers as anode for MT-SOFCs. The microstructure evolution as well as pore formation mechanism are studied, and then the correlation between the microstructure and the physical properties as well as the cell performance is performed. The thermal cycling capability of the optimal cells is also conducted.

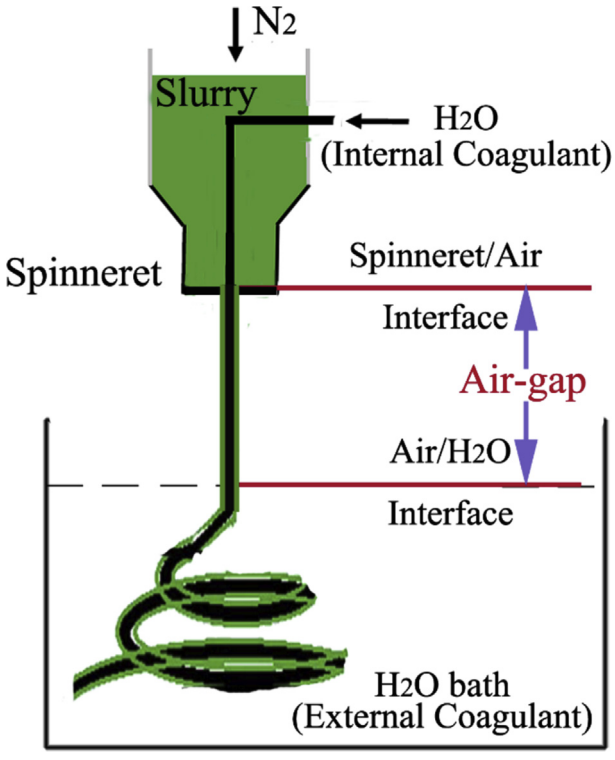


Fig. 1. Schematic diagram showing the air gap in the extrusion/phase-inversion process.

2. Experimental

The nickel oxide – yttria-stabilized zirconia (NiO–YSZ) hollow fibers are fabricated via a combined extrusion and phase-inversion method [7]. NiO (JT Baker, USA) and YSZ (8 mol% yttria-stabilized zirconia, Tosoh Corporation, Japan) powders at a weight ratio of 6:4 were mixed by ball-milled with ethanol for 24 h and then dried at 80 °C in the oven for 12 h. 4.7 wt% polyethersulfone (PESf) (Veradel 3000P, Solvay Specialty Polymers, USA) polymer binder and 1.1 wt% polyvinylpyrrolidone (PVP) (K30, CP, Sinopharm Chemical Reagent Co., China) dispersant were dissolved into 27.9 wt% N-methyl-2-pyrrolidone (NMP) (HPLC grade, Sigma–Aldrich, USA) solvent to form organic solution, and then 63.6 wt% NiO–YSZ powders were dispersed in the organic solution, followed by ball-milling for 2 days to form a uniform and stable suspension. The as-prepared suspension was degassed for 2 h and then extruded through a tube-in-orifice spinneret (O.D. 2.6 mm, I.D. 1.6 mm) using pressurized nitrogen (0.2 bar), and tap water was pumped through the bore of the spinneret at a speed of 10 mL min^{-1} using a digital mass flow controller (Alicat Scientific Inc., USA). After passing a given air-gap, the fibers were immersed into non-solvent (H_2O) for 24 h to complete the solidification. In this work, the air-gap is adjusted to be 0, 8, and 15 cm, respectively. For simplification, the fibers prepared were denoted as A0, A8, and A15, and the MT-SOFCs using the corresponding hollow fiber anode supports were denoted as cell A0, cell A8, and cell A15, respectively. The hollow fiber precursors were dried at room temperature in open air for a week, heated to 600 °C at a rate of 1 °C min^{-1} and maintained at that temperature for 2 h to remove the polymer binder, and then heated up to 1200 °C with 2 h dwell time in air to achieve sufficient mechanical strength for subsequent handling. YSZ film was coated on the pre-fired NiO–YSZ hollow fibers by a dip-coating method [20] and then co-sintered at 1450 °C for 5 h with a heating and cooling rate of 2 °C min^{-1}. YSZ and $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ (LSM, Fuel Cell Materials, USA) powders at a weight ratio of 50:50 were ground with terpilenol to form a cathode ink, which was then printed onto the surface of the YSZ electrolyte using a screen-printing method, followed by firing at 1100 °C for 2 h. The active cathode area is 0.3 cm^2. A sliver grid was printed on the surface of the cathode to collect the cathodic current, and sliver wire was used as the current lead, while two silver wires were directly attached to the two ends of the MT-SOFCs to collect the anodic current [7].

The microstructures of the pre-fired NiO–YSZ hollow fibers and anode-supported MT-SOFCs were examined using a scanning electron microscope (SEM, Zeiss Ultra Plus FESEM, Germany). Before testing the physical properties of Ni–YSZ anode support, NiO–YSZ hollow fibers were first sintered at 1450 °C for 5 h in air and then reduced at 750 °C for 5 h in humidified H_2. The porosity was measured using the Archimedes method in water. The gas permeability was measured using a home-made setup [7]. The electrical conductivity was tested at room temperature using the