Journal of Power Sources 280 (2015) 446–452

Contents lists available at ScienceDirect

Journal of Power Sources

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

High-efficiency, nickel-ceramic composite anode current collector for micro-tubular solid oxide fuel cells

Tao Li, Zhentao Wu, K. Li*

Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

HIGHLIGHTS

- A low-cost, nickel-based composite as anodic current collector.
- The new design addresses manufacturability, morphology tailoring and low resistance towards fuel transport.
- Superior adhesion is achieved between anode and current collector, with dramatically reduced contact loss.
- The time & cost-effective fabrication technique is suitable for mass-scale production.

ARTICLE INFO

Article history:
Received 1 December 2014
Received in revised form
13 January 2015
Accepted 21 January 2015
Available online 21 January 2015

Keywords:
Anodic current collector
Micro-tubular SOFC
Contact loss
Co-extrusion/co-sintering

ABSTRACT

High manufacturing cost and low-efficient current collection have been the two major bottlenecks that prevent micro-tubular SOFCs from large-scale application. In this work, a new nickel-based composite anode current collector has been developed for anode-supported MT-SOFC, addressing reduced cost, manufacturability and current collection efficiencies. Triple-layer hollow fibers have been successfully fabricated via a phase inversion-assisted co-extrusion process, during which a thin nickel-based inner layer was uniformly coated throughout the interior anode surface for improved adhesion with superior process economy. 10 wt.% CGO was added into the inner layer to prevent the excessive shrinkage of pure NiO, thus helping to achieve the co-sintering process. The electrochemical performance tests illustrate that samples with the thinnest anodic current collector (15% of the anode thickness) displayed the highest power density (1.07 W cm^{-2}). The impedance analysis and theoretical calculations suggest that inserting the anodic current collector could dramatically reduce the percentage of contact loss down to 6–10 % of the total ohmic loss (compared to 70% as reported in literatures), which proves the high efficiencies of new current collector design. Moreover, the superior manufacturability and process economy suggest this composite current collector suitable for mass-scale production.

1. Introduction

Nowadays, how to convert fossil fuels into useful forms of energy via a clean, efficient and sustainable route has become the theme for modern energy generation. Solid oxide fuel cells (SOFCs) have been considered as a promising solution towards energy shortage and environmental pollution due to some interesting advantages, such as high efficiencies (>60%), considerable fuel flexibility and low or zero emission of pollutants (SO_2 and NO_x) [1–3]. Among different geometric designs of SOFCs, the micro-tubular (MT) design was first reported in early 1990s by Kendall's group [4], displaying some unique features, such as rapid start-up/shut-down, high volumetric power density, good cycling performance and thermal shock resistance [5]. It has received an increasing level of interest during the past two decades but current development is restricted in R&D phase due to several technical challenges, such as the lack of a cost-effective manufacturing route, which limits mass-scale production, and the difficulties in efficiently collecting current from electrodes, especially from the small lumen of micro-tubes.

In the MT design, various cell components are configured in the form a multi-layer cylindrical tube and conventional fabrication routes usually consist of repetitions of coating and sintering, which makes the overall process complicated and cost-consuming [6–8]. To achieve better process economy, the ram co-extruder developed by Kendall's group enables the extrusion of multiple pastes with

* Corresponding author.
E-mail address: Kang.Li@imperial.ac.uk (K. Li).

http://dx.doi.org/10.1016/j.jpowsour.2015.01.130
0378-7753/

matched rheology in a single-step process [9,10], which dramatically simplifies the manufacturing route. The main drawback of this process is the difficulties in individual thickness control and the inflexibility in morphology tailoring. Some other studies have reported the development of a phase inversion-based co-extrusion technique, which allows flexible process control and adjustable morphologies [11–13]. Moreover, this technique leads to a stronger adhesion between cell components, resulting in lower ionic resistance and over-potential loss. In terms of scale-up, a key challenge is how to effectively collect current, especially from the lumen side of individual cell, without creating further mass transfer resistance and ohmic loss. Various techniques have been reported for lumen-side current collection, such as wrapping metallic wires on one end of inner anode uncovered by electrolyte [6,14,15], with some additional silver or platinum paste to improve the contact. This approach has been widely applied especially for MT-SOFCs fabricated via multi-step processes. As for co-extruded micro-tubes, current collection is usually achieved by inserting nickel mesh and pin, or silver wires into the anodic lumen [16–18]. However, reproducibility and contact loss need to be considered when evaluating the overall cell performance. Some numerical calculations conducted have suggested that the contact loss, which is resulted from problematic adhesion between anode and wires, is the main contributor towards total ohmic loss (up to 70%) [18]. To sum up, a new current collection technique addressing process economy, reduced contact loss, and negligible mass transfer resistance is still of great interest.

In this study, a cost-effective nickel-based composite anodic current collector has been developed for anode-supported MT-SOFCs, addressing manufacturability and current collection efficiencies. Some precious metal-ceramic composites have been investigated as current collector in addition to metallic wires and it has been reported that a certain concentration of metallic phase needs to be reached to change the insulating characteristic of the ceramic phase to the metallic conductive behaviour [2]. Moreover, the adhesion and conductivity strongly depends on the particle sizes of each component. Anodic current collector/anode/electrolyte triple-layer hollow fibers have been successfully fabricated via a phase inversion-assisted co-extrusion process, during which a thin nickel-based inner layer was uniformly coated throughout the interior anode surface for improved adhesion with superior process economy. The compositions of ceramic materials have been adjusted and investigated via dilatometry to help realize the co-sintering process. The effects of thicknesses of anodic current collector on cell performance have been systematically studied after a complete MT-SOFC was delivered, including I–V characterization and impedance analysis. Moreover, numerical calculations on ohmic loss contribution have been conducted to study the effectiveness of this new anodic current collector.

2. Experimental

2.1. Materials

Commercially available cerium–gadolinium oxide ($Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO), surface area 35.5 $m^2\ g^{-1}$, mean particle size (d50) 0.1–0.4 μm) and nickel oxide (NiO, surface area 3.7 $m^2\ g^{-1}$, mean particle size (d50) 0.5–1.5 μm) were purchased from NexTech Materials Ltd and used as supplied. Polyethersulfone (PESf) purchased from Radel A-300, Ameco Performance (USA), polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema), and dimethyl sulfoxide (DMSO) purchased from VWR International, LLC were used as the polymer binder, dispersant and solvent of spinning suspensions, respectively.

2.2. Fabrication of anode/anodic current collector dual-structured hollow fibers

Spinning suspensions of anode, anodic current collector and electrolyte were prepared separately by mixing ceramic powders, solvent, polymer binder and additives, details of which are described elsewhere [13,17]. CGO and NiO were applied in current collector (weight ratio 1:9) and anode (weight ratio 4:6), while the electrolyte is composed of 100% CGO, as shown in Table 1. Prior to the co-extrusion, all suspension were degassed under vacuum to eliminate any air bubbles trapped inside and then transferred into individual stainless steel syringes. Triple-layer precursor fibers were fabricated via a phase inversion-based co-extrusion process, in which all suspensions, together with the internal coagulant (H_2O), were extruded simultaneously through a custom-designed quadruple-orifice spinneret. An air gap of 25 cm was adapted to guarantee sufficient time for the lumen-side phase inversion process before the precursor enters the external coagulant bath. The extrusion rates of internal coagulant and three suspensions were precisely controlled by syringe pumps (Harvard PHD22/200 HPsi and KDS410) to achieve independent adjustment of layer thicknesses. The extrusion rates of internal coagulant, anode and electrolyte were maintained at 10, 7 and 1.5 ml min^{-1}, respectively, while the extrusion rate of anodic current collector was reduced from 5 to 1 ml min^{-1}. Precursor fibers were left in the external coagulant bath overnight to complete the solidification of polymer binder, before being cut to a length of 15 cm.

The co-sintering was conducted in static air to yield triple-layer ceramic hollow fibers using a tubular furnace (CARBOLITE). The temperature was first increased to 600 °C at a rate of 2 °C min^{-1} and held for 2 h, then to 1500 °C at a rate of 15 °C min^{-1} and dwelled for 12 h. The furnace was then cooled down to room temperature at the rate of 3 °C min^{-1}. A reduction that converts NiO into Ni is needed for hollow fibers samples prior to some post-sintering characterizations. The reduction was conducted at 550 °C in a pure hydrogen atmosphere for 2 h.

2.3. Characterizations

Prior to the co-sintering, shrinking behaviours of all three components were studied using a dilatometer (NETZSCH, model DIL 402C). Powder mixtures that have identical ratios as spinning suspensions were compressed into cubes with a dimension of 6 mm × 6 mm × 6 mm by using a house-developed die. The measurements were carried out in static air and the system was heated up to 1500 °C at 5 °C min^{-1}.

The morphology of the triple-layer hollow fibers was investigated using scanning electron microscopy (SEM) characterization (JEOL JSM-5610). Samples were gold-coated under vacuum for 2 min at 20 mA (EMITECH Model K550) and images with varied magnifications were obtained using both secondary electrons imaging (SEI) mode and backscattered electrons (BSE) mode.

Mechanical property was investigated using a tensile tester

Table 1
Compositions of the spinning suspensions for triple-layer hollow fibers.

Materials	Current collector (wt.%)	Anode (wt.%)	Electrolyte (wt.%)
NiO	63.0	40.8	/
CGO	7.0	27.2	55.7
Polymer binder (PESf)	7.0	6.8	5.57
Dispersant (Arlacel P135)	0.5	0.5	0.5
Solvent (DMSO)	22.4	24.7	38.2