



# Fabrication of anode-supported microtubular solid oxide fuel cells by sequential dip-coating and reduced sintering steps

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## ABSTRACT

The expensive and time-consuming fabrication of microtubular solid oxide fuel cells (MT-SOFCs) is one of the main barriers for their commercialization. In this study, a sequential dip-coating coupled with co-firing process was developed to fabricate anode-supported MT-SOFCs using carbon rods as a sacrificial template. Both anode and electrolyte layers underwent co-firing at 1400 °C rather than conventional pre-sintering and co-sintering steps. The whole cell structure was fabricated through sequential dip-coating and drying cycles that are flexible to various tube sizes and fast in turnaround time. The fabricated MT-SOFCs were comprised of Ni–yttria-stabilized zirconia (3YSZ) anode support, scandia-stabilized zirconia (ScSZ) electrolyte, Ni–ScSZ anode functional layer, strontium-doped lanthanum manganite (LSM)–ScSZ cathode functional layer, and LSM cathode current collector layer, respectively. The electrochemical performance of the fuel cell was measured at temperatures between 650 and 800 °C. The MT-SOFC delivered stable performance for more than 50 h operation at 700 °C. The fabricated fuel cell also exhibited excellent thermal cycling stability. The results demonstrated that the sequential dip-coating coupled with co-firing is a simple, flexible and cost-effective fabrication process to produce reliable and robust MT-SOFCs.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) have attracted considerable attention owing to high-efficiency, pollution free operation, and flexible fuel power generation [1–3]. Two common SOFC designs are tubular and planar geometry. Planar SOFCs have exhibited higher peak power densities than those of tubular fuel cells [4]. The decrease in the diameter of the tubular cells improves the volumetric power density. This observation has led to the invention of the microtubular SOFCs (MT-SOFCs) [5]. One of the main challenges for the commercialization of MT-SOFCs is the fabrication process to achieve a trade-off between manufacturing costs and product quality [6]. In addition, the fabrication process affects the cell microstructure and performance [7]. Thus, an inexpensive, highly controllable and reproducible manufacturing technique is necessary.

The most common technique to fabricate MT-SOFCs is the traditional extrusion process [8]. Extrusion is the most promising

technology for the mass production of microtubular supports with the potential for high reproducibility [8], but the extruded ceramics require careful control over the drying operational parameters. Additionally, extrusion is subjected to drawbacks, including high capital cost and long lead time for the adjustment of processing parameters [9]. Other fabrication methods also have been used for preparing the MT-SOFCs including gel-casting [11], phase inversion [12], isostatic pressing [13], electrophoretic deposition [14], and dip-coating [15]. Among these techniques, dip-coating stands out as an appropriate technique for producing MT-SOFCs with the following attractive features: simple equipment and process [10], homogeneous product composition [16], capability of producing thin layers and tubes with one closed end [17], outstanding contact quality [18,19], promising reproducibility and controllable film thickness [6], capability of eliminating the influence of the supports' surface defects [20], and having the potential of being automated for mass production [10].

Dip-coating is commonly used for the coating of electrolytes on tubular anode supports [21–24], but only very few researchers have used dip-coating to fabricate the whole cell [15,25–28]. The whole cell structure can be fabricated by dip-coating. The thickness

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of different layers can be controlled by adjusting the solid content of the slurries, the withdrawal speed of the substrate, and the number of dipping-drying cycles [6]. However, a common structural issue with the layers produced by vertical dip-coating is the gradual increase of deposited layer thickness from the top to bottom of the substrate in the vertical direction. In the other words, the film thickness increases in the longitudinal direction of the substrate. The thickness variation can be minimized through using substrates with the lengths of less than several centimeters, lowering the substrate withdrawal speed, using organic solvents that evaporate rapidly, and decreasing the solid content of the slurry. The thickness variation could also be minimized by inverting the substrate just before each dip. The internal diameter and length of the cell support can be varied by changing the size and length of the core substrate, respectively. The core substrate used as a template can be a heat-shrinkable polymer tube, a steel wire core coated with polystyrene layer to release the core by polymer dissolution [10], a glass tube coated with paraffin wax to facilitate the removal of the glass tube after drying [29], or a sacrificial rod [26–28,30].

The sacrificial substrate can be removed through burning out; for instance, a carbon rod will burn out, and the dip-coated layers will be converted into a rigid ceramic body during the production process of the anode-supported SOFCs. The conventional fabrication process of Ni-YSZ anode-supported SOFCs with electrolyte usually requires three sintering steps, including the pre-sintering of anode at about 1000 °C [28], the densification of the deposited electrolyte through the co-sintering of anode/electrolyte bi-layers at about 1400 °C [31], and the cathode sintering with anode and electrolyte at about 1200 °C [32,33]. The co-firing temperature depends on the electrolyte densification temperature that is usually over 1300 °C, but the unfavorable reaction of the LSM-based cathode and the zirconia based electrolyte proceeds at around 1200 °C. Co-firing all the components, called single-step co-firing, was performed for planar cells by some researchers using the sintering aids to inhibit the reaction between the LSM cathode and YSZ electrolyte [34]. However, the cells with a separately fired cathode exhibited higher power densities than those of the single-step co-fired cells.

Anode-supported cells are conventionally prepared by co-sintering meaning the pre-sintered anode and electrolyte are sintered together to form a dense electrolyte layer [31]. The pre-sintering of anode controls the shrinkage and reduces the thermal stresses during the co-firing of anode/electrolyte [17]. However, the pre-sintering step has the following disadvantages [35]: (i) increases the manufacturing cost, (ii) extends the fabrication period, and (iii) reduces the ratio of final products because the pre-sintered anode substrates are still fragile and require cautious treatment during coating of the electrolyte film. Thus, the pre-sintering of NiO-YSZ support microtubes leads to a longer manufacturing process with higher energy consumption.

The purpose of this study was to couple the sequential dip-coating with co-firing that shortens the manufacturing time and lowers the manufacturing cost of MT-SOFC. Employing an anode functional layer could help to reduce the shrinkage mismatch and also the thermal expansion mismatch between the anode support and electrolyte. Thus, the successful fabrication of the microtubular half-cells by co-firing was demonstrated. 3YSZ (TZ-3Y, 3 mol% yttria stabilized zirconia) that has the highest mechanical strength among stabilized zirconia with the different content of yttria was used for the preparation of the Ni-3YSZ anode supports [36]. The ZrO<sub>2</sub> stabilized with 10 mol% Sc<sub>2</sub>O<sub>3</sub> and 1 mol% CeO<sub>2</sub> (ScSZ) was used as the electrolyte and also as the ion-conducting phase in the electrodes due to the higher ionic conductivity of ScSZ than that of YSZ [37]. The performance of prepared MT-SOFC was evaluated by

electrochemical characterization, and the structure of the produced cell was characterized by scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Reagents and apparatus

3YSZ (TZ-3Y) powder was purchased from Tosoh, Japan. ScSZ (10Sc1CeSZ) and LSM (LSM-80F) powders were provided by Daiichi Kigenso Kagaku Kogyo, Japan. Microcrystalline cellulose (PH-301) was provided by FMC BioPolymer, PA, USA. Coarse nickel oxide powder (NiO-601) and fine nickel oxide powder (NiO-F) were purchased from Atlantic Equipment Engineers, NJ, USA, and Fuel Cell Materials Co., OH, USA, respectively. Polyvinyl butyral (B-76), Hypermer KD-1, and butyl benzyl phthalate (S-160) were obtained from Tape Casting Warehouse, Inc., PA, USA. Methyl ethyl Ketone (MEK, ≥99.0%) was purchased from Sigma-Aldrich. Ethyl-alcohol (EtOH, 200 proof) was obtained from Pharmaco-Aaper, CT, USA. The alumina-based sealant (Ceramabond 617) was prepared from Are-mco Products, NY, USA. The silver conductor paste (Heraeus C8728) was provided by Heraeus Materials Technology LLC, PA, USA. A silver wire (0.5 mm dia., annealed, 99.9%, Alfa-Aesar, MA, USA) was used for collecting current from the anode and cathode. A jar-mill (801CVM, U. S. Stoneware, OH, USA) and yttria stabilized zirconia milling media (5 × 5 mm, Inframat Advanced Materials) were used for the ball milling of slurries. Dip-coating was performed using a lab scale dip-coater (PTL-MM01 dip-coater, MTI Corp., CA, USA). A CF1600 muffle furnace and a CF1400 muffle furnace were used for the co-firing and cathode sintering of samples, respectively. A split tube furnace (STF 1200) was used for the testing of samples. All furnaces were purchased from Across International, NJ, USA. The alumina tubes for testing were purchased from McMaster-carr, OH, USA. The electrochemical performance of the MT-SOFC was characterized using a lab-designed fuel cell testing system consisting of an Autolab electrochemical workstation (Metrohm 302 N and 20 A current booster), and a set of mass flow controllers (P4B, MKS Instruments). The S-2600N scanning electron microscope that was used to take the SEM images is from Hitachi, Japan.

### 2.2. Fuel cell fabrication

The slurries were prepared by a dual-step process including the dispersion step and thickening step using a ball-mill for the anode support, anode functional layer, electrolyte, cathode functional layer, and cathode current collection layer slurries. Fig. 1 illustrates the preparation procedure of the slurries. Table 1 lists the composition of the anode support, anode functional layer, electrolyte, cathode functional layer, and cathode current collection layer slurries. The dip-coating process was performed using a carbon rod as a sacrificial core.

A sequential dip-coating method was developed and applied to prepare the microtubular half-cells within one step. Fig. 2(a) illustrates the schematic fabrication process of anode-supported MT-SOFC using the sequential dip-coating method. The carbon rod was dip-coated with anode support, anode functional layer, and electrolyte slurries successively at a withdrawing speed of 2 mm per second after an immersion time of 1 s. The dip-coated rod was dried in air for 5 min and the dip-coating and drying procedure was repeated several times until the required thickness was achieved.

Fig. 2(b) displays the co-firing temperature profile. The temperature was increased and held at 120 °C for 1 h, and it was increased to 450 °C at a rate of 0.5 °C min<sup>-1</sup>, followed by a dwelling step of 1 h to remove the organic additives introduced during the fabrication process. Then the temperature was increased to 1400 °C at a rate of 1.5 °C min<sup>-1</sup> and was held for 2 h. Finally, the samples

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