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Anode-supported micro-tubular SOFCs made by aqueous electrophoretic deposition

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Abstract

Anode-supported micro-tubular solid oxide fuel cells (SOFCs) were manufactured by a novel method using aqueous electrophoretic deposition (EPD). The process of these micro-tubular SOFCs included consecutive aqueous EPDs of porous anode layer (NiO–YSZ), dense electrolyte layer (yttria-stabilized zirconia, YSZ) and porous cathode layer ($La_{0.8}Sr_{0.2}MnO_3$, LSM) onto a thin wire electrode (e.g., a Cu wire), followed by stripping, drying, and a single co-sintering. The microstructure of the micro-tubular SOFC, including the thickness and porosity of each layer, was controlled by the processing parameters such as solid loading, current density, deposition time, and sintering temperature. The electrochemical performance of such a micro-tubular SOFC was demonstrated by the *V–I–P* (voltage–current–power) measurement.

Keywords: Electrophoretic deposition; Micro-tubular SOFC; Yttria-stabilized zirconia

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1. Introduction

The relatively high operating temperature of solid oxide fuel cell (SOFC) not only greatly restricts the selection of useable materials and their manufacturing processes but also causes such problems as electrode sintering, interfacial diffusion between the electrolyte and electrodes, and thermal stresses because of operation cycle. This difficulty can be solved by improving the manufacturing technique to obtain a thinner yet gas-tight ZrO_2 electrolyte film. Kinds of methods have been employed to make the ZrO_2 electrolyte film, e.g., tape casting, dry pressing, electrochemical vapor deposition (EVD) [1], physical vapor deposition (PVD) [2], and more recently, electrophoretic deposition (EPD) [3]. Because both EVD and PVD are expensive, yet most of the cheaper processes do have difficulties of obtaining controllable precision and repeatable quality, EPD has become a prominent candidate with great practical potential. EPD employs a DC electric field to move and deposit charged particles in suspension onto an arbitrarily shaped electrode with opposite charge. This cheap and fast technique not only makes complicated shaped ceramic products possible for wide application, but also avoids such difficulties as de-binder compared to other wet processes when additives are inevitable. Most of all, the controllability of deposite thickness and uniformity, as well as the simplicity of process apparatus and feasibility to mass production, make EPD one of the best choices to fabricate the ZrO_2 electrolyte film.

A number of studies have been devoted to the use of EPD to produce ceramic films and coatings. Among them, some were focused on the fabrication of ZrO_2 electrolyte film onto porous anode or cathode substrates [4]. In spite of both the economic and environmental disadvantages, however, most of these researches employed organic solvents, instead of water, as the carrier of their suspensions in order to avoid the detrimental effects of electrolysis of water on the quality of deposited film. Although there are a few studies [5–9] focused on the development of aqueous EPD technique with suppressed/controlled hydrolysis problem, seldom has been found on the field of SOFC. By using a suitable dispersant, we had been able to make yttria-stabilized zirconia (YSZ) electrolyte films on a porous anode Ni–YSZ cermet via aqueous EPD [10].

On the other hand, by increasing the reactive area per unit volume, a class of so-called micro-tubular SOFC [11–19] has emerged as a new class of SOFC design which in principle can benefit both the intrinsically higher efficiency of planar design and easier packaging of tubular counterpart. In this paper, we

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propose a novel method to manufacture an anode-supported micro-tubular SOFC by consecutive aqueous EPDs and a single-step co-sintering.

2. Experimental

Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, and $Mn(CH_3COO)_2 \cdot 4H_2O$, according to a LSM formula of $La_{0.8}Sr_{0.2}MnO_3$, were dissolved in distilled water, to which $C_6H_8O_7 \cdot H_2O$ was added according to a molar ratio of 1:2 (metal ions:citric acid) during stirring. After a clear solution was obtained, it was heated via an oil bath to 85–90 °C while continuously stirring until gelation occurred. The gel was further dried at 100 °C in an oven for 10 h to get rid of the water before being ground into powder and then calcined at 1100 °C for 2 h to obtain the correct crystal structure.

NiO (NiO-F, Inco) and YSZ (HSY-3.0, Daiichi Kigenso) powders, according to a 1:1 ratio, were mixed and attrition milled in distilled water. Suspensions with various solid loading of such anode (Ni–YSZ cermet, upon reduction at work), electrolyte (YSZ) and cathode (LSM) ceramic powders, respectively, were made by mixing the powders with distilled water using a shear mixer and an ultrasonic sonicator. To prevent the colloids from agglomeration and sedimentation, suitable amount of ammonium polyacrylate ($PAA–NH_4$, Darvan 821A, R.T. Vanderbilt, USA) was added as dispersant. $PAA–NH_4$ would dissociate in water so that PAA^- ions would adsorb to YSZ particles to stabilize them electrosterically. Zeta potentials of these suspensions were determined by laser Doppler velocimetry (Zetasizer-3000HSA, Malvern Instruments, UK). The details of suspension preparation and evaluation, as well as the setup of constant-current EPD can be found elsewhere [10].

The EPD cell consisted of a Cu wire (Ø 100 μm) anode surrounded by a hollow cylinder Ni cathode in one of the aforementioned suspensions as shown in Fig. 1. The distance between these two electrodes was 1.5 cm. EPD was conducted under constant current control at various current levels. The voltage was registered during EPD. The process of a micro-tubular SOFC was carried out by EPD (NiO–YSZ) → drying → EPD (YSZ) → drying → EPD (LSM), then followed by stripping from the Cu wire, complete drying, and co-sintering at 1250 °C for 2 h in order to obtain a final structure consisting of a porous anode layer, a dense electrolyte layer and a porous cathode layer respectively. The microstructure was revealed by SEM, and the porosity was stereometrically measured by a linear intercept method from the micrograph.

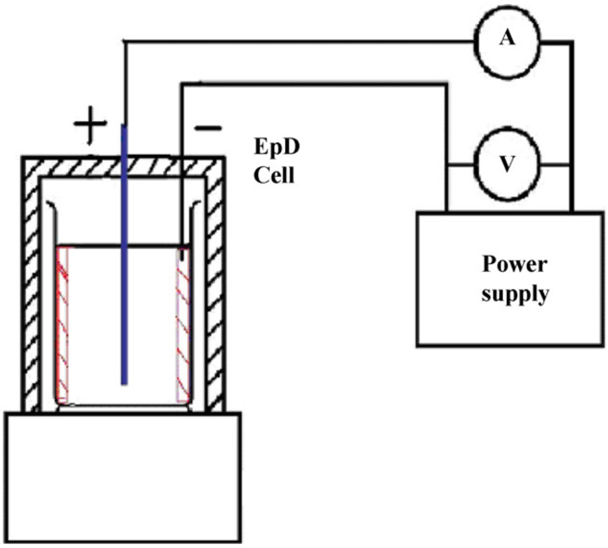

Fig. 1. A schematic of the EPD setup.

3. Results and discussion

3.1. Suspension

Fig. 2(a) shows the variations of zeta potential with pH value for slurries of YSZ, NiO and NiO–YSZ mixture respectively. It is obvious that NiO rather than YSZ controls the suspension behavior of the NiO–YSZ mixture. This fact can be further verified by the very similar variations of zeta potential with $PAA–NH_4$ addition for both NiO and NiO–YSZ mixture, as shown in Fig. 2(b). Note that the zeta potential of YSZ varies with the concentration of $PAA–NH_4$ in a different manner [10].

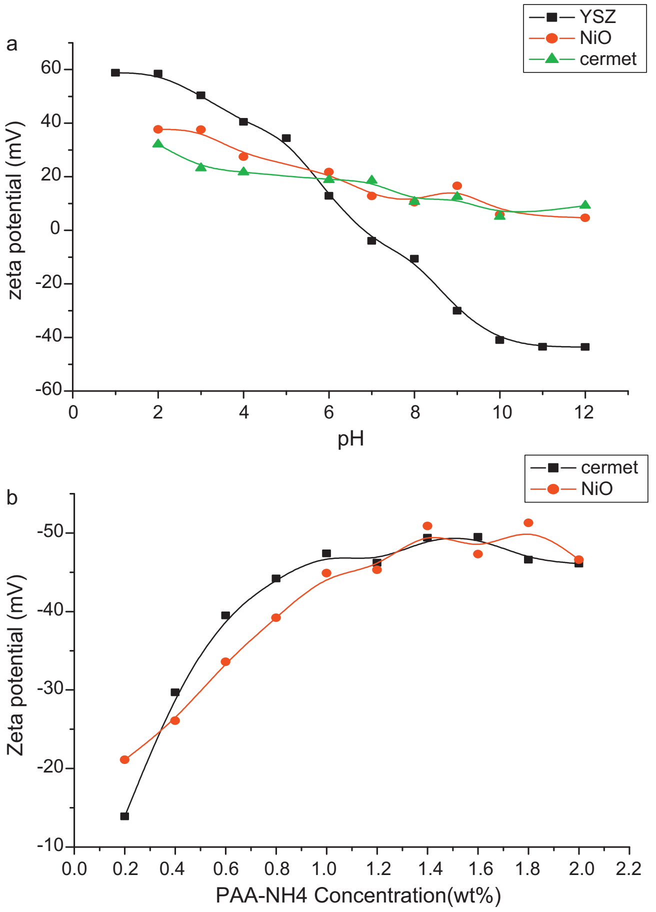

Fig. 2. Variations of zeta potential with (a) pH, and (b) $PAA–NH_4$ concentration for YSZ, NiO and their mixture.

Although only the electrostatic part of, rather than the whole electrosteric, stabilization is measured by zeta potential, the data in Fig. 2 (b) nevertheless suggests that 1.0 wt% of PAA–NH_4 is required for a good suspension of the NiO–YSZ mixture. A relatively regular suspension behavior of LSM is also identified by zeta potential study, and a PAA–NH_4 concentration of 0.4 wt% is thus selected for slurry preparation.

3.2. Aqueous EPD

Both of the deposition rate and porosity increase with solid loading for the cermet layer deposited at 5 mA, as shown in Fig. 3(a). The former is attributed to the agglomeration at higher solid loading which in turn lowers the specific adsorption amount of the PAA ions and thus demands more particles to be deposited at the same current level [20], whereas the latter could be due directly to the worse EPD density at higher agglomeration. On the other hand, Fig. 3(b) shows that at a solid loading of 10 wt% both the deposition rate and porosity increase with the EPD current too. It is reasonable that a higher current dictates more charge transferred per unit time, thus more cermet powder deposited within a certain period. At a higher deposition rate the packing density of EPD worsens, therefore a higher porosity is realized. Both Fig. 3(a) and (b) thus vividly demonstrate that the porosity of the anode cermet layer is controllable via aqueous EPD. It is worth noting at this point that the aqueous EPDs of subsequent electrolyte (dense YSZ) and cathode (porous LSM) layers have also been successfully conducted but with more complexity. In fact, it is found that the density of the YSZ electrolyte actually improves when deposited on the porous cermet and sintered together. The detailed study will be included in an accompanying paper.

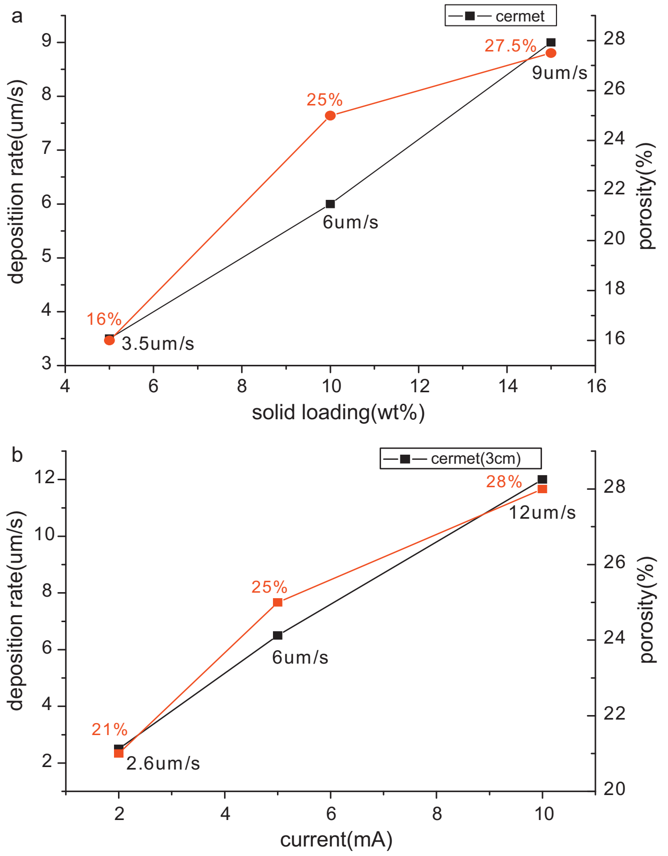

Fig. 3. Variations of deposition rate and porosity with (a) solid loading, and (b) current for the NiO–YSZ layer.

3.3. Micro-tubular SOFC

Fig. 4(a) shows typical scanning electron micrograph of a micro-tubular SOFC electrophoretically deposited at 10 wt% solid loading for all slurries but at 5, 1 and 10 mA for cermet,

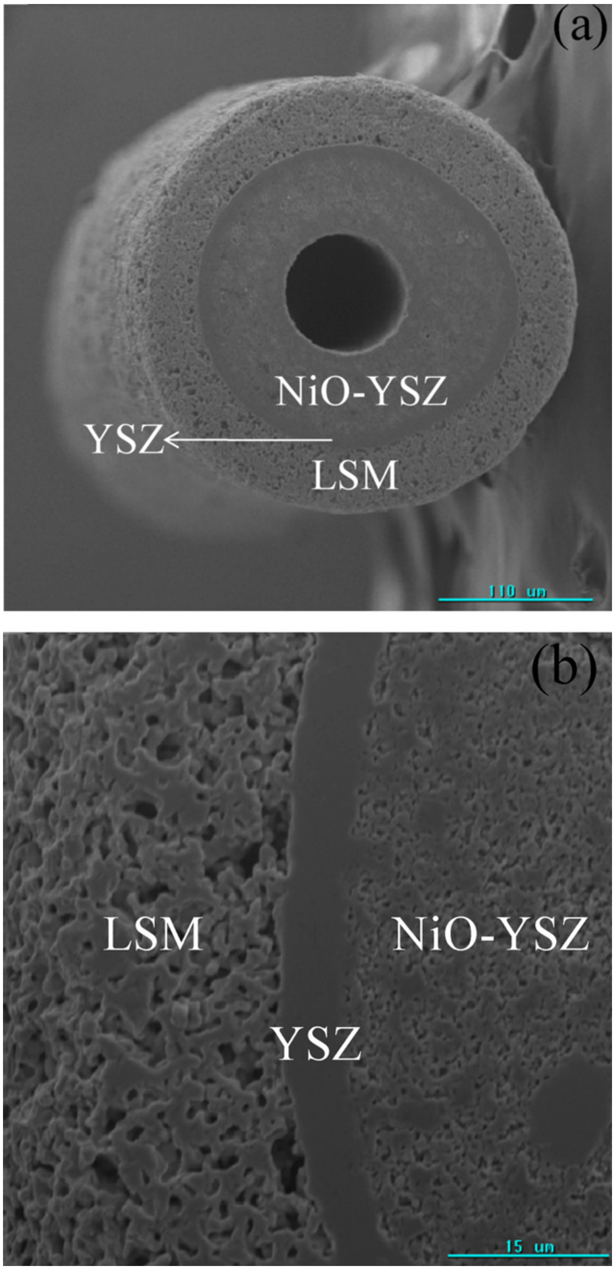

Fig. 4. (a) A typical scanning electron micrograph of a micro-tubular SOFC electrophoretically deposited at 10 wt% solid loading for all slurries but at 5, 1 and 10 mA for cermet, YSZ and LSM layers, respectively. (b) A close-up showing a dense YSZ electrolyte layer as thin as 6 μm, a cermet anode layer with 25% porosity, and a cathode LSM layer with 35% porosity.

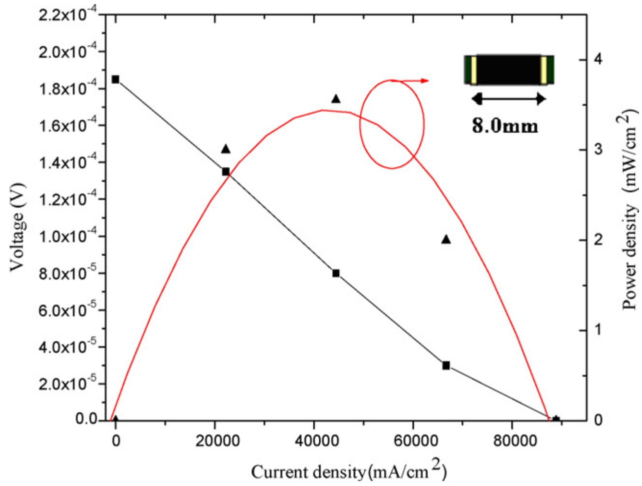

Fig. 5. Electrochemical performance of such a micro-tubular SOFC with a 6 μm YSZ electrolyte layer. The *V–I–P* analysis is carried out at 800 °C with a 50 sccm fuel of 20% H_2 in N_2 flowing inside the tube and air outside.

YSZ and LSM layers, respectively. A dense YSZ electrolyte layer as thin as 6 μm, a cermet anode layer with 25% porosity and a cathode LSM layer with 35% porosity are observed in Fig. 4(b). The electrochemical performance of such a micro-tubular SOFC is demonstrated in Fig. 5, where the *V–I–P* analysis is carried out at 800 °C with a 50 sccm fuel of 20% H_2 in N_2 flowing inside the tube and air outside. Although only a relatively low power density of 3.5 mW/cm^2 is realized in the test, one should keep in mind that 3 mol% yttria stabilized zirconia was employed for its cheaper and easier to handle in this preliminary study. Future developments with 8 mol% yttria stabilized zirconia and with optimized microstructure and improved process control are expected to deliver a much higher efficiency.

4. Conclusions

This study successfully demonstrates the feasibility of using consecutive aqueous EPD and single co-sintering to produce an anode-supported micro-tubular SOFC with a thin (down to 6 μm) YSZ electrolyte film sandwiched by a porous NiO–YSZ anode layer and a porous LSM cathode layer. The deposition rate and porosity of the NiO–YSZ layer both increase with current density and with solid loading, while its suspension behavior is governed by NiO.

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