



Short communication

Direct lamination of solid oxide fuel cell anode support, anode, and electrolyte by sequential tape casting of thermoreversible gel slips

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ABSTRACT

A novel direct lamination technique by tape casting thermoreversible gel-based slips is introduced for the production of solid oxide fuel cell anode support, anode, and electrolyte layers. Production of cells with controlled layer thicknesses of ~ 10 – $500\ \mu\text{m}$ and having well formed and relatively high toughness interfaces is demonstrated. Cells with maximum current density of $1.76\ \text{A}\cdot\text{cm}^{-2}$ and maximum power density $425\ \text{mW}\ \text{cm}^{-2}$ were achieved using 97% H_2 /3% H_2O fuel at $800\ ^\circ\text{C}$. Specific opportunities for further optimization of processing to improve electrochemical performance are highlighted.

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1. Introduction

Anode-supported solid oxide fuel cell (SOFC) designs have been widely developed owing to relatively straightforward processing and high performance [1,2]. Generally in anode-supported cells, a thick (~ 0.5 – $1\ \text{mm}$), highly porous anode acts as the mechanical support for a thinner anode active layer, electrolyte, cathode (each ~ 10 – $20\ \mu\text{m}$ thick) and current collector (~ 20 – $100\ \mu\text{m}$ thick). Cell performance is enhanced by the minimized ion transport distances compared to alternative cell designs requiring thicker electrolyte or active layers.

Producing composites having both thick and thin layers, as required in anode-supported cells, requires specialized procedures. One strategy often employed in research laboratories is to form the substrate separately – for example by pellet pressing – and then apply the thin film layers by a coating technique such as screen printing, blade coating, or spin coating [1]. A second strategy is to build up the substrate and thin film layers concurrently, as is often done by laminating multiple cast tapes [3] or through sequential tape casting [4]. A chronic problem faced with processing conventional tapes is the large amount of organic binder (typically on the order of 10–20 wt%) that must be removed, which limits the total laminate thickness [5]. Another disadvantage of lamination is

the formation of flaws, such as pores, that lead to poor interfacial strength and toughness [6].

The process described here addresses these forming limitations by utilizing thermoreversible gels as the basis for tape casting slips. Acrylic triblock copolymers in alcohol form thermoreversible gels that have a highly advantageous combination of properties for ceramic processing, described in detail elsewhere [7–9]. In short, these tailorable gels are comprised of 90–95 wt% solvent in a polymer network and undergo reversible elastic solid-to-viscous liquid transitions upon heating to mildly elevated temperatures (30 – $70\ ^\circ\text{C}$) [10]. Used as the base for ceramic slurries, these properties allow for casting of thick components and for direct lamination of multiple layers during sequential casting [7,11]. The direct lamination of thick anode supports and thin anode functional and electrolyte layers by sequential tape casting with thermoreversible gel slips is the foundation of this work.

2. Procedure

2.1. Anode support, anode, and electrolyte

Thermoreversible gel slips were produced using gel bases of poly(methyl methacrylate)-poly(*n*-butyl acrylate)-poly(methyl methacrylate) triblock copolymer with $9\ \text{kg}\ \text{mol}^{-1}$ endblocks and $53\ \text{kg}\ \text{mol}^{-1}$ midblock (Kuraray America, Houston, TX) dissolved in $\sim 70\ ^\circ\text{C}$ 2-ethylhexanol (Alfa Aesar, Ward Hill, MA). This composition had a gel point of ~ 30 – $35\ ^\circ\text{C}$ and viscosity of $\sim 0.01\ \text{Pa}\ \text{s}$ above $50\ ^\circ\text{C}$ [10,12]. Tape casting slips were produced by adding mixtures of NiO (Nickelous Oxide, J.T. Baker, Center Valley, PA), YSZ (TZ-8Y,

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Tosoh USA, Grove City, OH) and corn starch (Argo, ACH Food Companies, Cordova, TN) porogen for the anode substrate; mixtures of NiO and YSZ for the anode active layer; and YSZ for the electrolyte layer. Aerosol AY-65 (Cytec Industries, Arlington, TX) or polyethyleneimine ("PEI", Sigma–Aldrich, Milwaukee, WI) was used as the dispersant, and poly(ethylene glycol) and benzylbutylphthalate (Richard E. Mistler, Yardley, PA) were used as plasticizers in the anode support slip only. Slip compositions are shown in Table 1. In each case, solids and dispersant were ultrasonically mixed into heated ($\sim 70^\circ\text{C}$) gel bases in three batches, one-half in the first batch and one-quarter in the second and third batches. Plasticizers were added last. The slips were de-aired by applying vacuum for ~ 10 min prior to tape casting.

The tape casting system used was outfitted with a heated slip reservoir (~ 55 – 60°C) and water-cooled chilling bed ($\sim 10^\circ\text{C}$), instead of the room temperature slip reservoir and heated drying bed typically found in a traditional system. The chilled bed was necessary to rapidly cool the slips in order to induce gelling before significant thinning of the cast layer could occur and to limit solvent loss. As in traditional tape casting techniques, a silicone-coated Mylar[®] carrier film was pulled underneath the slip reservoir and past an adjustable doctor blade, which determined the layer thickness, at a rate of $\sim 0.5\text{ m min}^{-1}$. Target layer thicknesses (after firing) were 0.5–1 mm for the anode support and 10–20 μm for the anode functional layer and electrolyte. A single casting pass was used for each of the three layers, with the anode support layer cast first. The thermoreversible nature of the slips allowed the heat of the deposited layer to re-melt the surface of the previously cast layer, causing them to bind strongly with each other [11]. Bi-layer samples with $>50\ \mu\text{m}$ YSZ–NiO (anode composition) and YSZ (electrolyte composition) layers were also produced in the same manner for mechanical testing of the laminate interfaces.

After all layers were cast, disks ~ 22 mm in diameter were punched out of the tapes. In order to prevent curling or warping, the disks were dried slowly by sealing them alongside a small reservoir of 2-ethylhexanol in a container with a pinhole vent. After ~ 5 days the tapes were firm to the touch and allowed to dry fully under ambient atmosphere. It is worth noting here that alternative procedures have been developed for removing solvent from gels more quickly and/or with minimized curvature and warpage [11,13]. While the 1.5–2.3 wt% of triblock copolymer binder may be burned off in under an hour [11–13], the corn starch porogen used here requires a slower burnout (1°C min^{-1} to 150°C ; $0.5^\circ\text{C min}^{-1}$ from 150°C to 600°C ; 1 h dwell at 600°C), which was combined with a pre-fire step (2°C min^{-1} from 600°C to 1000°C ; 1 h dwell at 1000°C ; furnace cool). Samples were co-sintered in zirconia-coated alumina crucibles at 1400°C for 4 h ($10^\circ\text{C min}^{-1}$ ramp up and down). To prevent curvature from differential sintering, a zirconia-coated alumina plate was placed on top of the samples.

2.2. Cathode and current collector

The cathode and current collector were applied after firing the anode and electrolyte since these two halves of the cell require

significantly different firing schedules. A composite cathode was prepared by milling a 50–50 wt% mixture of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ ("LSM", Praxair, Danbury, CT) and YSZ in ethanol for 24 h. The slurry was dried, sieved to $125\ \mu\text{m}$ and suspended in V-737 screen printing vehicle (Heraeus, Hanau, Germany) using a three-roll mill. This cathode ink was applied to the cells using the doctor blade technique. In a similar fashion a pure LSM ink was prepared and applied to the cells as a cathode current collector. The complete cell was fired at 1175°C for 1 h. The cathode and cathode current collector target thicknesses were 20–30 μm ; the area was 0.5 cm^2 and defined the active area of the cells. A grid pattern of DAD-87 silver ink (Shanghai Research Institute of Synthetic Resins, Shanghai, China) was then applied to the cathode, and silver wires were used to establish electrical contact to the testing apparatus.

2.3. Electrochemical testing

The cells were prepared for testing by sealing the button cell to an alumina tube with silver ink. The silver ink also allowed for anode side current collection and two silver wires were connected to the silver seal to provide electrical contacts to the anode. The setup was placed in a horizontal tube furnace at 800°C , and 97% H_2 /3% H_2O fuel was supplied to the anode side via a second alumina tube inserted in the larger alumina tube as detailed elsewhere [1,2]. The NiO in the anode and anode support was reduced to Ni during the first phase of testing. Electrochemical measurements were made using an IM6 Electrochemical Workstation (Zahner–Elektrik, Kronach, Germany) and time-dependent voltage measurements were monitored and recorded with a 2420 SourceMeter (Keithley Instruments, Cleveland, OH) interfaced with a LabVIEW virtual instrument (National Instruments, Austin, TX) running on a PC.

3. Results and discussion

3.1. Microstructure and interface toughness

Fig. 1 shows resulting microstructures after firing and before NiO reduction of the three tape cast layers and of the complete cell. In both cases, it can be seen that the interfaces between layers are well formed. A significant microstructural difference is observed when Aerosol AY-65 is used as dispersant (Fig. 1(a)) and when PEI is used (Fig. 1(b) and (c)). With Aerosol AY-65 dispersant, the electrolyte and anode layers are ~ 10 – $20\ \mu\text{m}$ thick, which was the targeted thickness range. With PEI dispersant, the layer thicknesses were significantly larger than desired and much less uniform. It is clear that dispersant chemistry plays an important role in the castability of these slips. Some dispersant chemistries including Aerosol AY-65 – a sodium diamylsulfosuccinate solution – were found to poison electrochemically active regions of the cell, in this case by the presence of sodium and sulfur.

A major concern for any lamination technique is the fidelity of the interfaces, vital for both mechanical integrity and electrochemical performance. Using the methodology of He and Hutchinson [14] for examining the toughness of a laminate interface, 10 N Vickers indentations were imparted in the anode-type or electrolyte-type layer of thick bilayers near their interface, as shown in Fig. 2. Cracks were induced at the corners of the indentations and propagated straight through the interface. No significant change in propagation direction was observed, which illustrates the elastic similarity between the two layers [14]. More importantly, no deflection into the interface is observed, even when cracks approached at low angles, showing that the interfaces have high toughness. A lower limit for interfacial toughness can be estimated using the graphical approach of Bhattacharya et al. [15] to the He–Hutchinson scheme. Using mechanical

Table 1
Slip compositions (wt%).

	Anode support	Anode	Electrolyte
2-ethylhexanol	17.0	22.0	23.0
Acrylate triblock copolymer	2.3	1.5	1.5
YSZ	34.8	37.5	74.0
NiO	34.8	37.5	–
Corn starch	7.6	–	–
Polyethyleneimine or Aerosol AY-65	1.5	1.5	1.5
Poly(ethylene glycol)	1.0	–	–
Benzylbutylphthalate	1.0	–	–

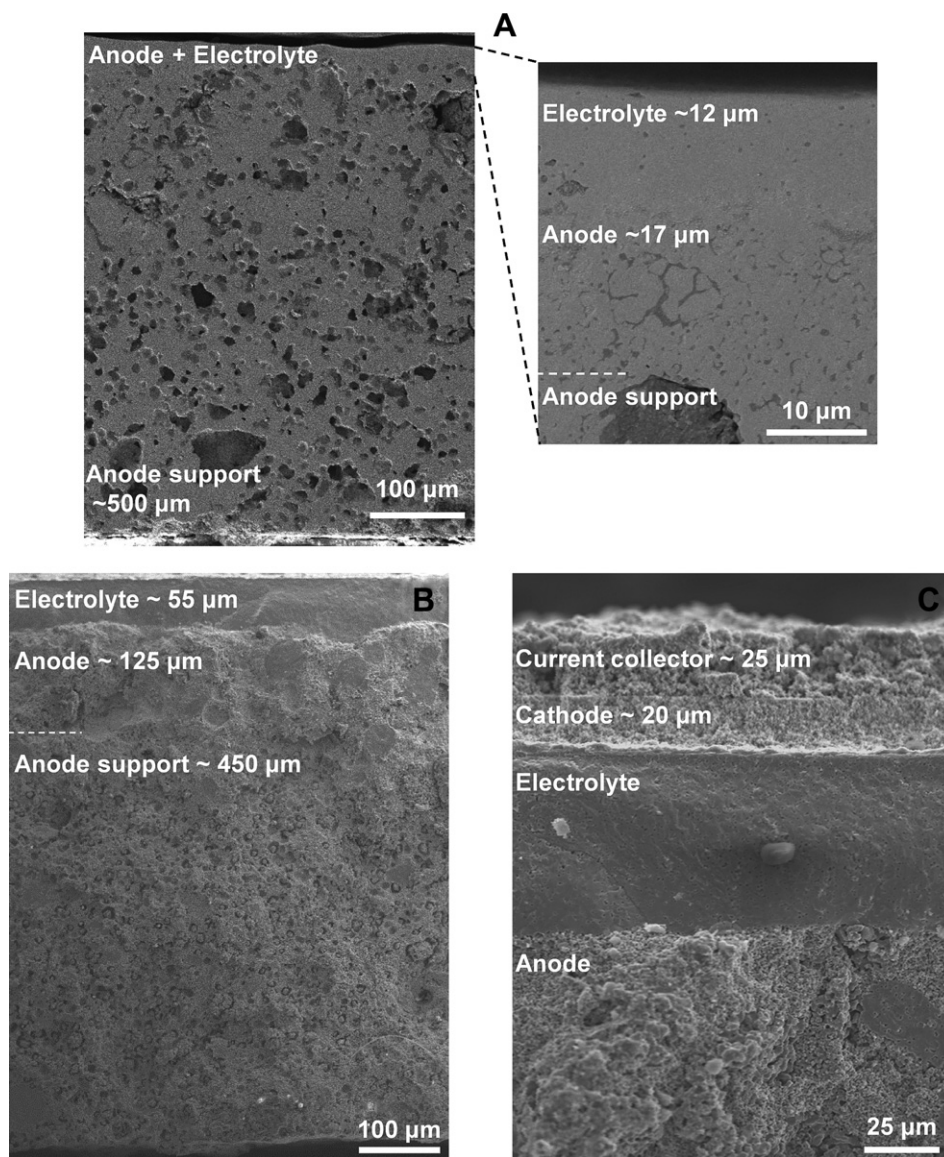


Fig. 1. SEM micrographs of fired SOFC structures. (a) Polished cross section of anode support, anode and electrolyte produced by tape casting using Aerosol AY-65 dispersant. Layer thicknesses are in the target range. (b) Fracture surface of anode support, anode and electrolyte produced by tape casting using PEI dispersant. Layer thicknesses are not optimal and porosity is visible in the electrolyte layer. (c) Fracture surface of same structure as in (b) after application of cathode and current collector and second firing step.

property data for YSZ and NiO-YSZ reported by Atkinson and Selcuk [16] and Pihlatie et al. [17] it is determined that the energy release rate of a crack deflected into the interface, and therefore the lower limit of the interface toughness, is 15.3 J m^{-2} [12]. This relatively high toughness serves to demonstrate that the interface is sufficiently robust that the electrical and ionic conductivities across the interfaces in these laminated systems are expected to be reasonably high.

3.2. Electrochemical performance

As discussed above, cells produced using Aerosol AY-65 dispersant were almost completely inactive, presumably due to the presence of poisoning sodium and sulfur. Current-voltage characteristics and impedance spectra for SOFCs produced using PEI dispersant are shown in Fig. 3. The target values for this material system are an open circuit voltage (OCV) of $\sim 1.1 \text{ V}$, maximum current density of $\sim 3\text{--}4 \text{ A cm}^{-2}$ and maximum power

density of $\sim 1 \text{ W cm}^{-2}$, which are typical for SOFCs of this material and fuel system using conventional processing techniques [18]. Fig. 3 shows the OCV was close to the target value ($\sim 1.04 \text{ V}$), while the maximum current density and power density were about half the target values (1.76 A cm^{-2} and 425 mW cm^{-2} respectively). The slightly depressed OCV is likely caused by the small amount of porosity in the electrolyte layer, visible in Fig. 1, or imperfect sealing. The lower than expected current and power densities are attributed primarily to the higher resistance of the electrolyte layer due to a relatively high thickness ($\sim 55 \mu\text{m}$ vs. target thickness of $10\text{--}15 \mu\text{m}$). This conclusion is supported by the impedance spectrum in Fig. 3(b) which shows $Z_{\Omega} \sim 0.33 \Omega \text{ cm}^2$ compared to a more typical value of $\sim 0.025 \Omega \text{ cm}^2$ for a high performance cell [18]. The polarization resistance of the cell ($0.35 \Omega \text{ cm}^2$) was also slightly higher than the $0.2\text{--}0.3 \Omega \text{ cm}^2$ typically observed for similar electrodes.

Reducing the electrolyte thickness is expected to significantly reduce resistance and improve power density [19]. Assuming

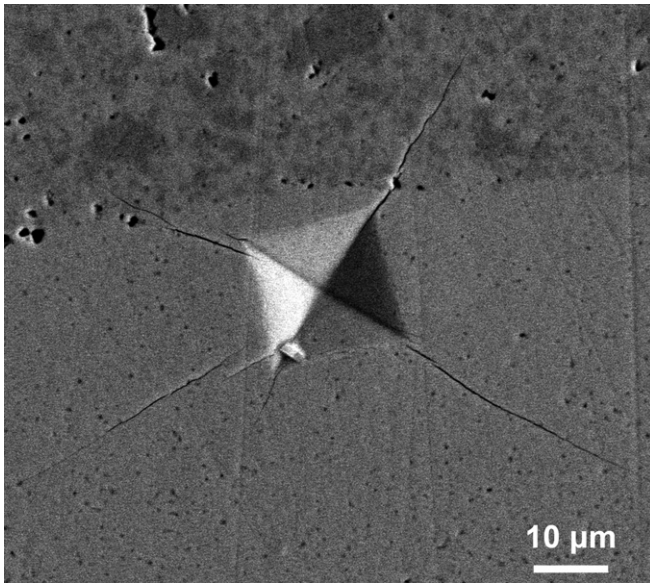


Fig. 2. SEM micrograph of Vickers indentation in YSZ (electrolyte composition) layer with corner cracks propagating into NiO-YSZ (anode composition) layer. Propagation directly through the interface between layers demonstrates the toughness of the interface.

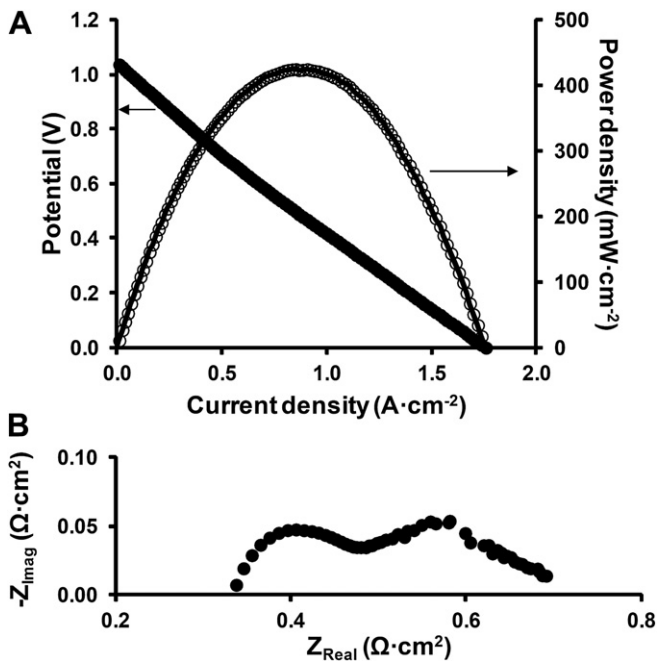


Fig. 3. (a) Voltage–current characteristics and (b) impedance spectrum of cell operating at 800 °C with 97% H_2 /3% H_2O fuel. Open circuit voltage is 1.04 V, maximum current density is 1.76 A cm^{-2} , maximum power density is 425 mW cm^{-2} , and ohmic resistance is 0.33 $\Omega \text{ cm}^2$.

a linear current–voltage characteristic, reduction of the cell ohmic resistance from the present 0.33 $\Omega \text{ cm}^2$, to a more typical value of $\sim 0.025 \Omega \text{ cm}^2$, should increase the cell power density to 0.8 W cm^{-2} , close to the goal of 1 W cm^{-2} [18].

4. Conclusions

A novel direct lamination technique for the production of SOFC anode support, anode, and electrolyte layers by sequential tape casting of thermoreversible gel-based slips was introduced. Multiple layers with thickness ranging from ~ 10 –500 μm were produced with a single tape casting step for each layer. The thermoreversible nature of the gels allowed for good bonding between layers, leading to high interfacial toughness. Dispersant chemistry greatly affected both the ability to finely control layer thickness as well as electrochemical performance. In the initial cells made using this technique, the greater than desired thickness of the electrolyte layer, and therefore higher ohmic resistance, caused significant depression of maximum current density and power density (1.76 A cm^{-2} and 425 mW cm^{-2} respectively). It is fully expected that higher performance cells can be produced by further optimization of this newly introduced processing method.

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