

Development of Anode-Supported Solid Oxide Fuel Cell by Co-Tape Casting and Co-Sintering

L. N. Rodrigues, M. Machado, L. P. R. Moraes, V. V. Thyssen, and F. C. Fonseca

Nuclear & Energy Research Institute, IPEN-CNEN/SP, University of São Paulo, São Paulo, Brazil

Simple and cost-effective technologies to produce solid oxide fuel cells require control of microstructure, thickness, homogeneity, and reproducibility of the functional layers. The manufacturing of a solid oxide fuel cell (SOFC) involves significant ceramic processing challenges to obtain layers with controlled microstructure. Possibly the most common technique for large-scale production of SOFCs is tape casting. In this study, YSZ electrolyte and 60NiO/YSZ anode slurries were studied for the production of half-cells deposited by the sequential tape casting technique. A co-sintering procedure was developed for the half-cells and after cathode deposition the single cells were tested.

Introduction

The tape casting process is a low-cost and scalable technique to fabricate ceramic substrates for SOFCs (1,2). The process consists of producing a slurry that is deposited and spread on a surface using a doctor-blade to control the thickness. The slurry is composed of the ceramic powder of interest, a solvent, dispersants, binders, and plasticizers (3-5). The dispersants ensure an adequate viscosity and density, the binders increase the viscosity and change the Newtonian flow behavior, and the plasticizers provide some flexibility to the tape (5). The slurry requires preparation protocols to guarantee the homogeneity and proper viscosity for the tape-casting process (6,7). Procedures for drying and sintering the tapes are crucial to ensure the final shape and microstructural properties of the ceramic.

Tape casting is used either to produce thick electrolyte substrates for electrolyte supported cells (ESC) (6) or the anode substrate for anode supported cells (ASC) (7,8). Half-cells containing anode support and a thin electrolyte are widely prepared by combining the tape casting and lamination techniques, such as thermal iso-statistic pressing, adding complex steps to the procedure (9,10). Thus, sequential tape casting arises as an effective method in which functional layers are cast consecutively to obtain a multilayer tape (7,10-12). This method reduces the number of process steps and heat treatments, allowing good control over the microstructure and adherence between layers (9,13).

The thermo-mechanical mismatch and the distinct physical properties of each layer are the main challenges to the sequential tape casting and co-sintering of multilayered ceramic bodies (14-18). The different thermal behavior of the materials can lead to cracks and warping of the multilayer tape during the heating treatment. To prevent those issues and to obtain the desired shape and microstructure, the slurry composition has to be optimized and the thermal treatments fine-tuned (15).

In this study, a sequential tape casting method was developed to produce anode-supported half-cells of 60NiO/YSZ anode and YSZ electrolyte. The structural properties and thermal characterization of the green tape were evaluated, and the electrochemical properties of the fuel cell were accessed.

Experimental

Anode support and electrolyte half-cells were prepared by sequential tape casting. The anode ceramic powder NiO/YSZ (60/40 vol%), was previously prepared by liquid mixture (19,20) and the commercial yttria-stabilized zirconia (YSZ, TZ-8Y, Tosoh) was used as the electrolyte. To produce the slurries, the ceramic powders were mixed with polyvinylpyrrolidone (PVP, Synth) dispersant, ethanol (Synth, 99,5 %) solvent, polyvinyl butyral (PVB, Butvar-98) binder, and 2 plasticizers, polyethylene glycol (PEG) and dibutyl phthalate (DBP), both from Sigma Aldrich. For the anode tape, graphite (Micrograph) was added as a pore former (21).

The components were mixed and ball-milled for 30 h. Viscosity measurements of the slurries were performed on a viscometer (HAAKE Viscotester C), in the range of 0.5 to 200 rpm. The as-prepared slurry was then deposited on the polypropylene film using a doctor blade to control the thickness. The drying process was carried out at room temperature. For the half-cell, the YSZ electrolyte was deposited first, allowed to dry and the thick anode tape was deposited on the top of the electrolyte. After the sequential casting, the tapes were cut into button half-cells of 25 mm diameter for characterization.

Simultaneous thermogravimetric and differential thermal analyses (TG/DTG), and dilatometry (TMA) were performed using Setaram Labsys apparatus. The analyzes were carried out from room temperature to 1200 and 1400 °C for TG/DTG and TMA, respectively, with 10 °C/min heating rates under synthetic air flow (3 L/h). The apparent densities of the tapes were measured by the Archimedes method according to the ASTM C 373-88 standard (22). X-rays diffraction (XRD) analysis of the tapes were carried out in the Rigaku MiniFlex II with Cu K α radiation. The microstructures of the as-prepared powders were analyzed by scanning electron microscopy (SEM - Jeol, JSM-6010LA).

A lanthanum-doped manganite cathode ink was prepared from the commercial material (Fuel Cell Materials) and deposited on the half-cell by spin coating (Laurell WS-400B) (23). The fuel cell sample was sintered at 1150 °C for 1 h under air.

The electrochemical characterization of the sample was carried out using an open flanges system (Fiaxell SOFC Technologies) connected to a potentiostat Parstat 3000A-DX for open circuit voltage (OCV) monitoring, polarization curves (I_xV) and electrochemical impedance spectroscopy (EIS) measurements. Fuel cell tests were carried out in the 650-850 °C temperature range under hydrogen and synthetic air, both at 12 L/h flow rate set by mass flow controllers

Results and Discussion

Fig. 1 shows the rheological behavior of both the electrolyte and the anode slurries. Viscosity analysis confirms the pseudoplastic behavior of slurries. As the flow rate increases, the viscosity decreases, consistent with the behavior of a non-Newtonian fluid, which is appropriate for the casting process.

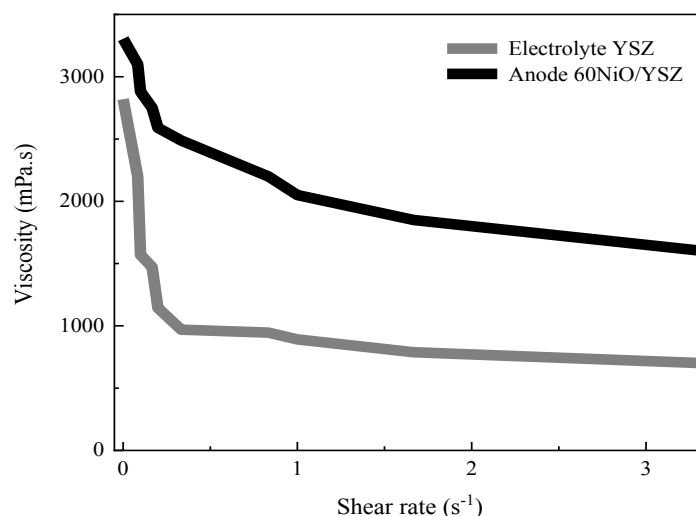


Figure 1. Viscosity analysis of slurries.

The TG data of the anode and electrolyte green tapes on Fig. 2a showed mass loss at temperatures 400 and 800 °C. In Fig. 2b the DTG allowed observe more clearly the mass loss at temperatures 80, 250, 300 and 350 °C, which are consistent with the decomposition temperatures of the organic components of the tape. The mass loss at 800 °C is due to graphite oxidation in the anode. Based on TG/DTG analyses, the calcining temperature of 850 °C was defined.

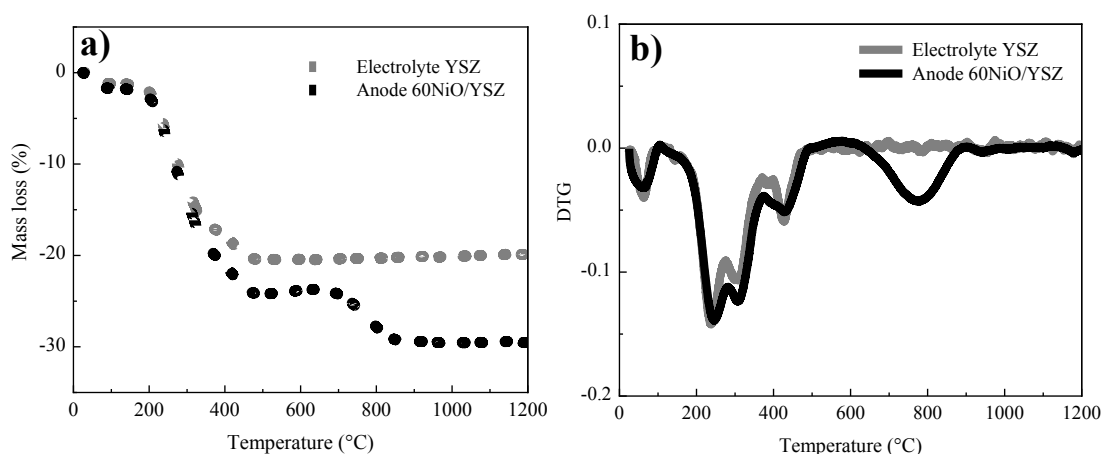


Figure 2. (a) TG and (b) DTG analysis of YSZ and 60NiO/YSZ tapes.

Fig. 3 shows the linear retraction profiles of both the electrolyte and the anode green tapes from 850 to 1400 °C. The dilatometry curves show that the retraction of the tape starts

at 1200 °C. The YSZ electrolyte reaches about 88 % of relative density close to 1400 °C, while the NiO/YSZ anode reaches 57 % of relative density.

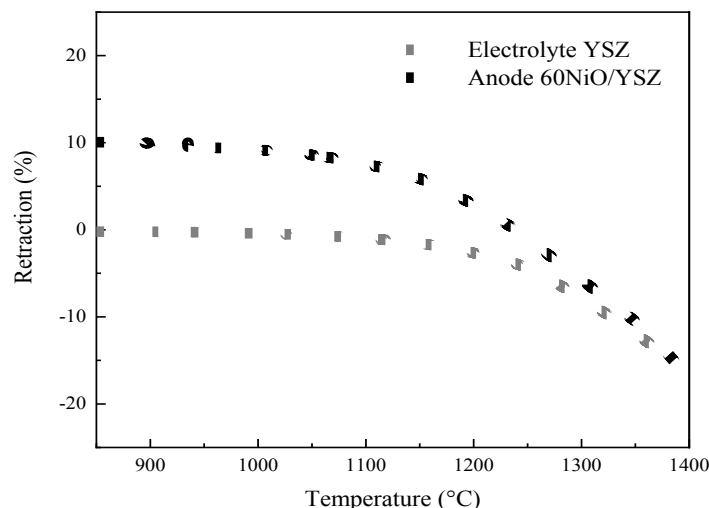


Figure 3. Dilatometric curves of YSZ and 60NiO/YSZ tapes.

Samples were sintered at 1450 °C for 1 hour to attain an appropriate relative density for YSZ electrolyte (~ 95 %) and an adequate porosity for 60NiO/YSZ anode (~ 39 %).

The XRD analyses of the sintered tapes (Fig. 4), were indexed, and only the peaks corresponding to the cubic phases YSZ and NiO were observed.

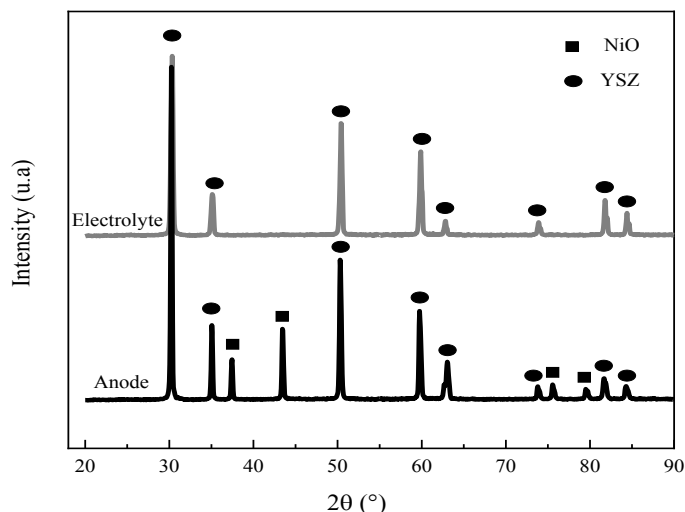


Figure 4. XRD analyses of YSZ and 60NiO/YSZ tapes sintered at 1450 °C for 1 h.

Fig. 5 shows the cross-sectional SEM images of the fuel cell produced by sequential tape-cast. The SEM images show a homogeneous and dense electrolyte layer (~ 25 μm thick) with some residual closed porosity. The bottom part of the SEM image shows the anode support layer with ~ 350 μm thickness. The porous at the anode have an equivalent diameter of around $(3.5 \pm 1.5) \mu\text{m}$. The anode support shows well distributed porosity. The SEM analyses also exhibit a good adhesion between the electrolyte and anode layer, which

was attained without cracks or delamination. The spin coated cathode (LSM) layer is observed on the top of the dense YSZ layer with an estimated thickness of $\sim 8 \mu\text{m}$.

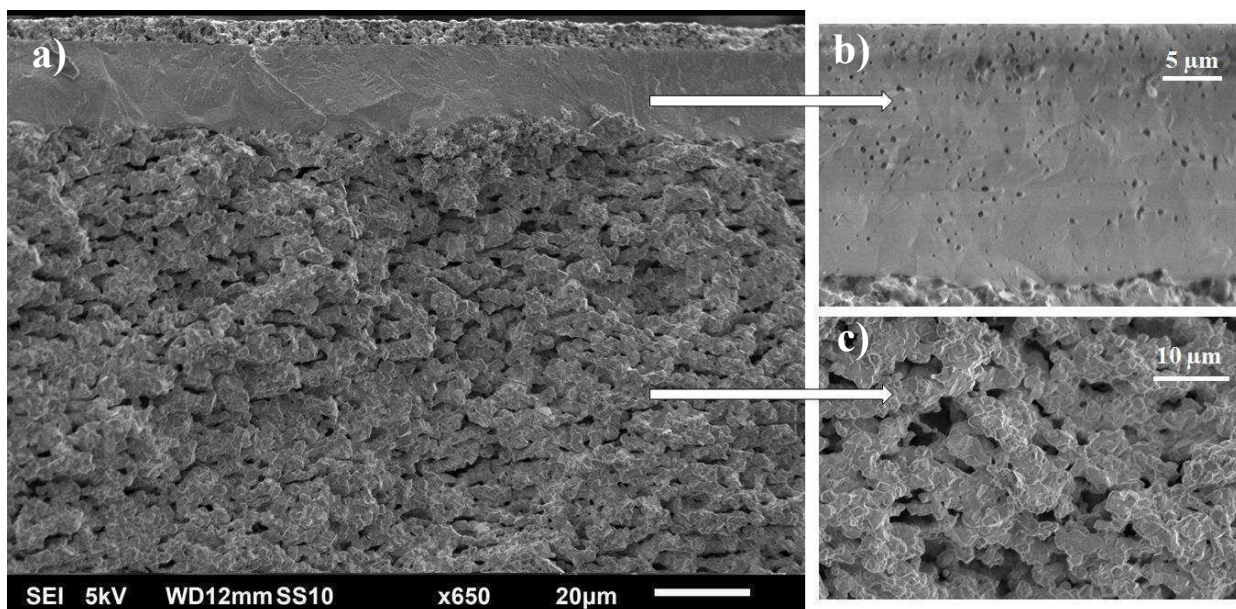


Figure 5. Scanning electron micrographs of sintered cell (1450°C for 1 h). (a) cross section of the unit cell, (b) YSZ electrolyte and interface, and (c) NiO/YSZ anode support.

The electrochemical performance tests were carried out at 650 , 750 and 850°C . Fig. 6 shows the open circuit cell voltage (OCV) values with time as temperature is increased. An OCV from 1.015 to 0.925V occurs as the temperature increases from 650 to 850°C .

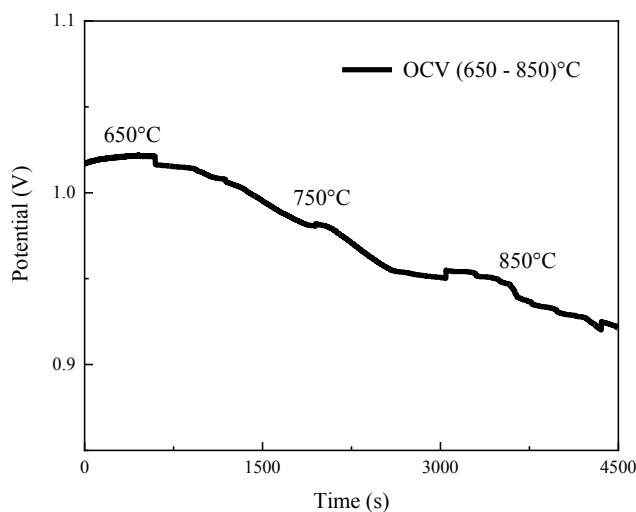


Figure 6. Curve showing the OCV with time and increase in temperature of the tape-cast and co-sintered single cell measured under hydrogen and synthetic air.

In Fig. 7 the $I \times V$ curves show the increase in current and power as the temperature rises. The analysis indicates strong ohmic polarization with maximum current and power density of 221 mA and $\sim 92 \text{ mW}$ at 850°C under 12 L/h of synthetic air and hydrogen.

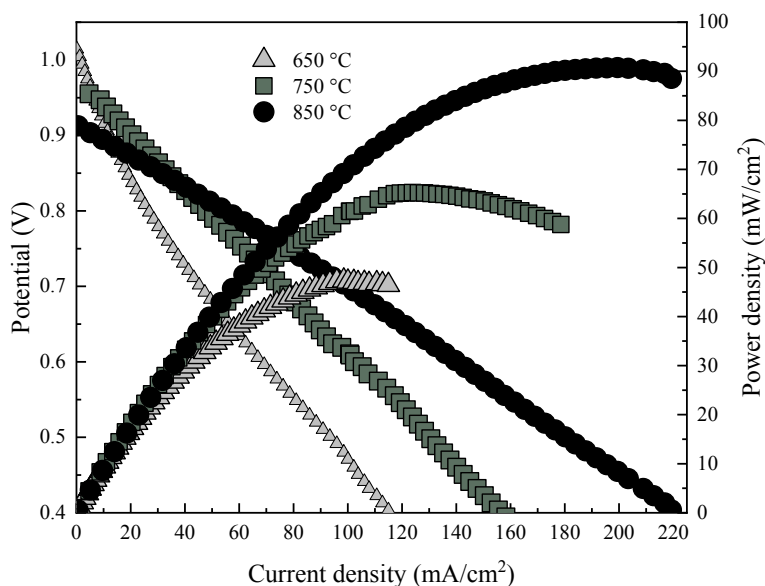


Figure 7. I x V curves of the tape-cast and co-sintered single cell measured under hydrogen and synthetic air.

The impedance measurements of the single-cell were performed in the frequency range from 100 kHz to 1 Hz at temperatures of 650, 750 and 850°C. The diagram shows a strong decrease in ohmic and the polarization resistances with increasing temperature due to the improvement in the mechanisms of diffusion and transport of gases at higher temperatures. At 850 °C reached 1.15 $\Omega\cdot\text{cm}^2$ of ohmic resistance and 0.77 $\Omega\cdot\text{cm}^2$ of polarization resistance.

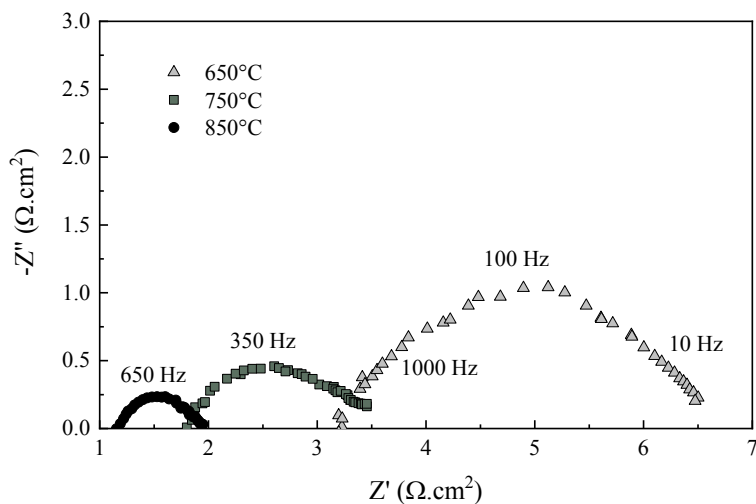


Figure 8. Impedance spectroscopy data of the co-sintered single cell.

Conclusion

A single cell was successfully produced by the sequential tape casting and co-sintering of electrolyte /anode half-cells. Such method allowed a good control of the microstructure of both layers by controlling the processing parameters. The preliminary electrochemical

characterization tests indicate that the developed method is promising for the cost-effective production of solid oxide fuel cells.

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