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A support layer for solid oxide fuel cells

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Abstract

The use of a perforated, ceramic layer, laminated on top of a porous electrode, as a support structure for solid oxide fuel cells is described. The support layer can be used on either the anode or cathode side and allows for the fabrication of mechanically robust, impregnated electrodes. Using fuel cells based on yttria-stabilized zirconia (YSZ), we demonstrate that the support layer can be made from YSZ or from a composite of YSZ and $La_{0.3}Sr_{0.7}TiO_3$ (LST). It is shown that there is no solid-state reaction between LST and YSZ, even after calcination at 1550 °C. Unlike pure LST, LST–YSZ composites can form a laminated structure on porous YSZ. Unlike pure YSZ, a dense LST–YSZ composite with 60-wt% LST exhibited an electronic conductivity of 7.6 S/cm at 700 °C after reduction in H_2 at 1000 °C, making the composite layer attractive for current collection in anode-supported cells.

Keywords: Solid oxide fuel cells; LST (La-doped $SrTiO_3$); Electrode support

1. Introduction

Fuel-cell components need to be handled without breaking during fabrication and assembly and need to survive operating conditions that include thermal cycling. To satisfy these requirements, one of the cell components must have sufficient strength to provide mechanical support. SOFCs are therefore generally categorized as electrolyte-, anode-, or cathode-supported. Electrolyte-supported cells are the simplest to fabricate, but thick electrolytes limit the performance due to their high resistance, particularly at low temperatures (less than 800 °C) with yttria-stabilized zirconia (YSZ) electrolytes.

To prepare electrode-supported cells, it is necessary either to work with materials that are compatible with high-temperature sintering or to attach a dense electrolyte film to the electrode at low temperatures. Because preparation of dense films at low temperatures tends to be difficult, most high-performance cells today are anode-supported, with a Ni–YSZ, ceramic–metallic (cermet) composite as the anode. NiO and YSZ can be calcined to very high temperatures without undergoing solid-state reactions, allowing the electrolyte and the Ni–YSZ cermet to be sintered together. However, co-firing of the electrode and electrolyte limits the choice of materials that can be used in the supporting electrode. For example, one cannot prepare Cu-based anodes in this manner because Cu oxides melt at the temperatures required for sintering YSZ electrolytes. Cathode-supported cells also cannot be supported in this way due to the fact that the perovskites typically used as the electronic components within the cathode undergo solid-state reactions with YSZ at the temperatures required for sintering of the electrolyte [1].

In our laboratory, we have developed an alternative method for preparing both anodes and cathodes of cells with thin electrolytes [2,3]. The method involves producing a two-layer structure from the electrolyte material (e.g. YSZ), with one side dense and the other side highly porous. This bilayer structure can be prepared by tape casting, with the laminated tapes calcined to temperatures sufficient to form a dense electrolyte. In the porous layer, the porosity is achieved through the use of pore formers, such as graphite or PMMA [4]. The electronically conductive component in the electrode is added to the porous layer only after firing the bilayer to high temperatures, thereby minimizing the compatibility issues associated with co-firing the electrodes and electrolytes.

In this design, the impregnated porous layer must provide the support if thin electrolytes are to be used. However, previous

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work has shown that the physical and mechanical properties of composite electrodes prepared by impregnation are very different than those of traditional composites. Impregnated composites have a non-random structure, with the electronic component essentially coating the YSZ backbone. Two beneficial manifestations of this structure are that the coefficient of thermal expansion (CTE) of impregnated composites is close to that of YSZ and that electronic conductivity can be achieved with less than 30-vol% (the percolation threshold in random media) of the electronic component [5–7]. Unfortunately, it is difficult to produce mechanically strong, impregnated composites due to the fact that the YSZ backbone must be highly porous, with relatively small pores, in order to achieve high electrochemical performance.

In this paper, we describe the fabrication of a support layer on top of a porous electrode layer that can be used to make mechanically strong cells with impregnated electrodes. The method is relatively general in that it can be applied to the fabrication of either anode-supported or cathode-supported cells. We will demonstrate the method by showing support layers made from YSZ and from a mixture of YSZ and La-doped $SrTiO_3$ (LST), a mixture that is electronically conductive when used at the anode. LST has a CTE that is close to that of YSZ and an electronic conductivity as high as 60 S/cm under reducing conditions [8].

2. Experimental

The YSZ used in this study was obtained from Tosoh (8 mol% Y_2O_3, TZ-8Y). $La_{0.3}Sr_{0.7}TiO_3$ (LST) powder was synthesized by solid-state reaction from stoichiometric amounts of La_2O_3, $Sr(NO_3)_2$, and TiO_2 (all obtained from Aldrich). After ball milling the powders with ethanol for 24 h, the mixtures were dried and calcined in air at 1200 °C for 3 h to produce the LST. Because we were unable to get LST and YSZ structures to adhere to each other, we also examined an LST–YSZ composite. To prepare an LST–YSZ composite, the LST powder was mixed with YSZ at an LST–YSZ weight ratio of 0.6:0.4, so as to produce a dense structure that would be 64-vol% LST. The mixed powders were then ball milled for an additional 24 h.

The methods used to make the green tapes used in this study are described elsewhere [2,9,10]. The ceramic powders used in the tapes were initially ball milled for 20 h with water and a dispersant (Darvan C, R.T. Vanderbilt Company, Inc.) in order to break up agglomerates that may prevent formation of a dense structure. Emulsion-type binder solutions (Duramax HA-12 and B-1000, Rohm and Haas) were added to the slurry and stirred for 24 h before casting. The solutions and methods used for producing each layer in the fired structures were identical; however, pyrolyzable pore formers were added to those tapes used to produce the porous electrode layers. Graphite (<325 mesh, Alfar Aeser) was used to introduce smaller pores, while polystyrene–divinylbenzene (200–400 mesh, Alfa Aeser) was used to produce larger pores. Lamination of the ceramic tapes was performed using a uni-axial hydraulic press (Model C, Carver Inc.) equipped with heating platens (Model 2101, Carver Inc.). The laminating pressure and temperature were 8 MPa and 70 °C, respectively, and the tapes were held under these conditions for 10 min. After lamination, the tapes were fired at 1550 °C for 4 h.

To measure the properties of the LST–YSZ composites, the same slurry used in preparing LST–YSZ tapes were used to prepare a dense, 0.5 cm × 0.3 cm × 1.21 cm slab. This slab was initially light yellow in color, but became black upon heating in H_2 at 1000 °C for 48 h. Silver wires were attached to the slab using silver paste, and conductivity measurements were performed on the slab by conventional four-probe methods. The conductivity was measured from room temperature to 700 °C while heating the sample at 5 °C/min in dry H_2.

Phase purity of the powder and the pellet samples was examined using a Rigaku Geigerflex X-ray diffractometer (XRD) with Cu Kα radiation. The microstructures of the samples were investigated using a scanning electron microscope (JEOL 6400) with an accelerating voltage of 15 kV. To prevent electronic charging on the sample surfaces, specimens were coated with Au–Pd alloys, applied by sputtering.

For the fuel-cell measurements, the cathode was applied onto the dense electrolyte side by painting on a mixture of YSZ, $La_{0.6}Sr_{0.4}MnO_3$ (LSM), and graphite pore formers, followed by firing at 1250 °C for 2 h. The anode was prepared by impregnation of the porous YSZ with aqueous solutions of $Ce(NO_3)_3{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}6H_2O$ (Alfa Aesar) to achieve a final loading of 15-wt% CeO_2 and 30-wt% Cu [2,11]. CeO_2 was impregnated first and Cu was added to the anode using an aqueous solution containing $Cu(NO_3)_2$ and urea ($CO(NH_2)_2$, AlfaAesar) in a 1:1.5 molar ratio. Electronic contacts were formed using Ag wire and Ag paste at the cathode and Au wire and Au paste at the anode. Cells having a cathode area of 0.36 cm^2 were sealed onto a 1-cm diameter alumina tube using a ceramic adhesive (Aremco, Ceramabond 552). The cells were then placed inside a furnace and heated at 2 °C/min to the operating temperature, with flowing H_2 at the anode. Impedance data were obtained in the galvanostatic mode using a Gamry Instruments Potentiostat, with frequencies between 0.1 Hz and 100 kHz with an I_{rms} of 10 mA.

3. Results and discussion

3.1. Support layer description

The concept of using a support layer is demonstrated in Fig. 1(a). The electrolyte, electrode, and support structures are prepared by laminating various green tapes together, followed by high-temperature firing. A picture of a cell made by these methods is shown in Fig. 1(b). In this example, the tape used for the perforated support layer had regularly spaced, 2-mm-diameter holes. The support layer was 300 μm thick, with the holes exposing approximately 20% of the underlying electrode. In this picture, the electrode is black because of the CuO has not yet been reduced. The thicknesses of the anode and electrolyte were 100 and 60 μm, respectively.

A simple punch was used to produce the holes in the tape for the support layer. Clearly, the hole shape, size, and spacing

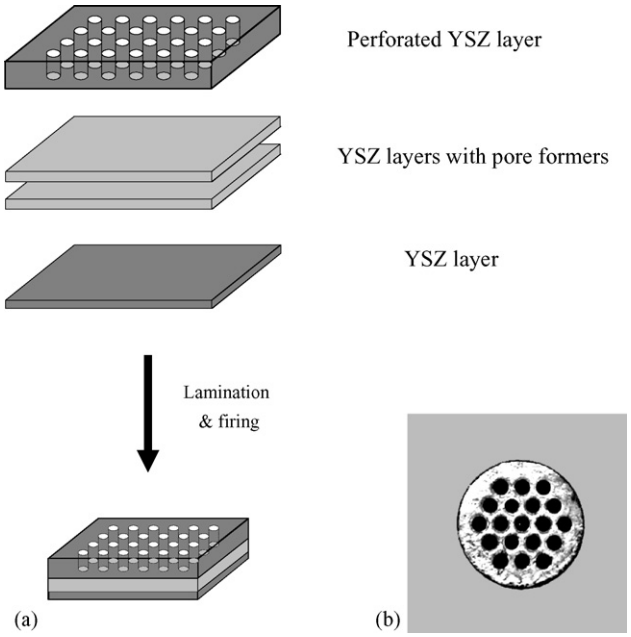

Fig. 1. (a) Schematic view of a cell having support layer. (b) Photograph of a cell with a YSZ support layer.

could be varied to allow more of the electrode to be exposed without significantly sacrificing mechanical properties. Because the support layer is separated from the region of the three-phase boundary at the electrode–electrolyte interface, it will have no impact on cell performance so long as care is taken with the hole spacing and geometry so as to avoid gas-phase diffusional limitations.

3.2. Characterization of LST

XRD results, shown in Fig. 2(a), demonstrate that the LST powder calcined at 1200 °C in air for 3 h had the cubic, perovskite structure. The lattice parameter calculated from the (2 0 0) peak in the XRD is 0.3907 nm, in good agreement with the JCPDS data for $La_{0.3}Sr_{0.7}TiO_3$.

The chemical compatibility of LST and YSZ against solid-state reactions was also examined, since the diffusion of La or Sr elements into the YSZ could form insulating phases, such as $SrZrO_3$ and $La_2Zr_2O_7$ [12,13]. The XRD pattern of the LST–YSZ mixture with 60-wt% LST and calcined at 1550 °C for 4 h in air, is shown in Fig. 2(b). The pattern is that expected for a physical mixture of LST and YSZ, with no evidence for the formation of additional phases. This agrees with an earlier study showing that Y-doped $SrTiO_3$ does not react with YSZ at high temperatures [14].

Conductivity measurements were performed on a LST–YSZ slab that had been prepared with 60-wt% LST and fired in air to 1400 °C for 4 h. Assuming that the slab had no porosity, this weight fraction of LST corresponds to 64-vol% of the slab, a value well above the percolation threshold of 30-vol% expected for random media. Therefore, one should expect the composite to be conductive if the LST within the composite is conductive. In our measurements, the slab was first reduced in H_2 at 1000 °C, then cooled to room temperature. After attaching the

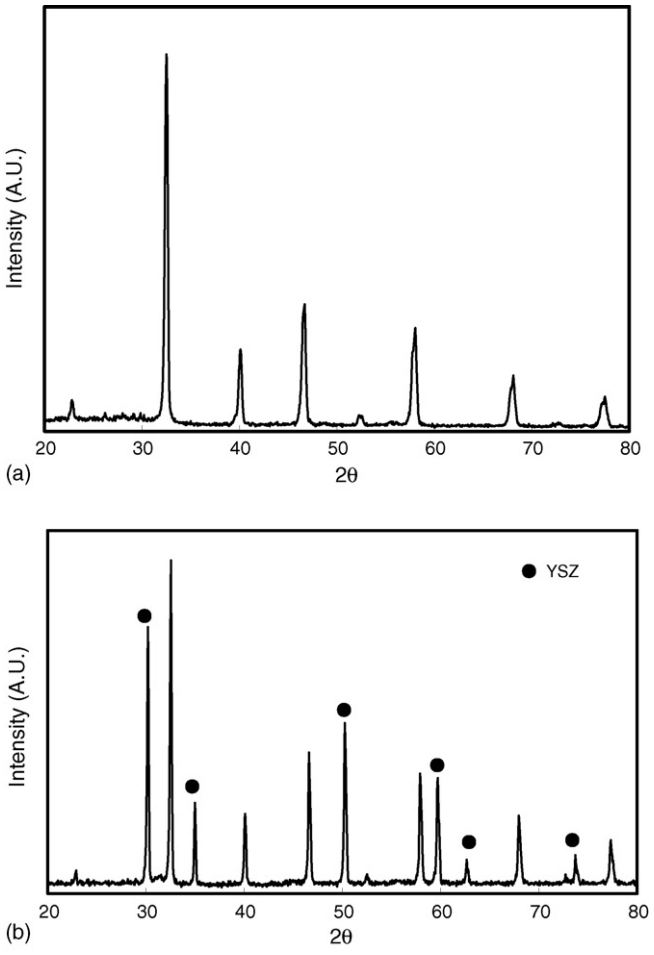

Fig. 2. (a) XRD pattern of $La_{0.3}Sr_{0.7}TiO_3$ calcined at 1200 °C for 3 h in air. (b) XRD pattern of a $La_{0.3}Sr_{0.7}TiO_3$–YSZ composite calcined at 1550 °C for 4 h in air.

Ag leads, the conductivity of the slab was determined to be 2.8 S/cm at room temperature in air. After heating at 5 °C/min to 700 °C in H_2, the conductivity of the slab increased to 7.6 S/cm. This is lower than the value of 40 S/cm reported by Canales-Vazquez et al. for pure $La_{0.3}Sr_{0.7}TiO_3$ in H_2 at 700 °C [8]. However, the presence of YSZ and the thickness of the slab used in these measurements (the bulk of the LST must be reduced in order to be electronically conductive) easily explain the lower value that we observed. In any case, this conductivity is sufficient for conduction of electrons in the direction perpendicular to the electrolyte surface.

It is interesting to consider the results of an earlier study in which porous composites of $Sr_{0.88}Y_{0.08}TiO_3$ (YST) and YSZ were used to make SOFC anodes [14]. The YST–YSZ composites in that case were also made by tape casting; however, the composites were attached directly to the dense YSZ electrolyte and were approximately 65% porous due to the inclusion of pore formers within the YST–YSZ tapes. Composites with 50-wt% YST and with 80-wt% YST were examined, but the cell performance in both cases indicated that the composites had insufficient conductivities. The reason for the low conductivity in that earlier work is almost certainly that the volume fraction of the conductive phase, the YST, was

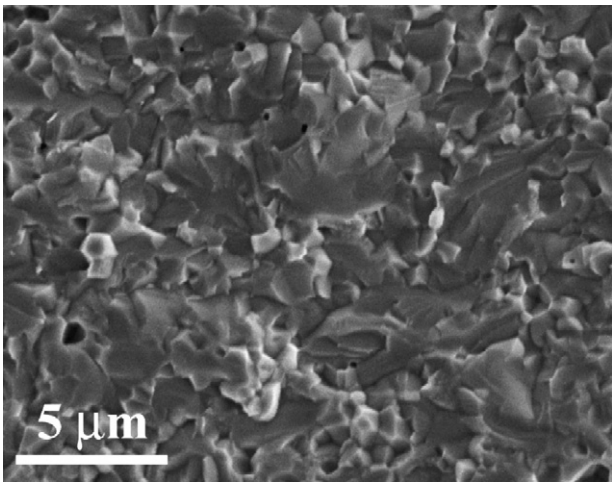

Fig. 3. SEM image of the $La_{0.3}Sr_{0.7}TiO_3$–YSZ composite after firing at 1400 °C for 4 h in air.

below 30-vol%, the percolation threshold. Given that any electrode based on doped $SrTiO_3$ must be porous and also contain an ionically conductive component, the development of electrodes in which most of the conductivity is derived from the doped $SrTiO_3$ phase will be challenging.

SEM was used to investigate the microstructure of the LST–YSZ composite with 60-wt% LST. Fig. 3 shows a cross-sectional image after firing at 1400 °C for 4 h in air. Image analysis suggests that the porosity of the composite was less than 2%. EDS analysis confirmed that the composite layer consisted of LST and YSZ but could not distinguish individual crystallites.

3.3. Adhesion of LST–YSZ composites to YSZ

In order to achieve the structure shown in Fig. 1, it is necessary for the ceramic support layer to adhere to the porous YSZ layer. This is straightforward when the support layer is made from YSZ. However, we found that support layers made from pure LST completely de-laminated from YSZ upon calcination. This is likely a consequence of the fact that there is no solid-state reaction between these two oxides, even at high temperatures.

Adhesion was achieved between the porous YSZ (region A) and the LST–YSZ (region B) composite, as demonstrated by the SEM of the cross-sectional image of the interface in Fig. 4(a). Apparently, the YSZ within the LST–YSZ layer is able to sinter to the YSZ in the porous layer, providing a physical connection. Fig. 4(b) shows the EDS spectra of the YSZ and LST–YSZ regions from Fig. 4(a). The EDS shows no evidence for Sr or La within the YSZ region, consistent with the fact that there is no solid-state reaction between LST and YSZ. Note that Zr peaks overlap with that from the Au that was used as a coating material during SEM sample preparation.

3.4. Electrochemical performance of cells with support structures

To determine whether the support structure affects performance, model fuel cells were prepared without a support structure, with a YSZ support structure, and with an LST–YSZ support structure. In each case, the porous YSZ that is adjacent to the electrolyte was impregnated with Ce and Cu salts so as to achieve a loading of 15-wt% CeO_2 and 30-wt% Cu. The performance levels in H_2 at 700 °C for the cell without the support structure and the cell with the LST–YSZ support structure are shown in Fig. 5. Results for the cell with the YSZ support are not shown because they were indistinguishable from the results obtained from the cell with the LST–YSZ support. Fig. 5 shows that the *V–I* polarization curves for cells with and without the support layer are linear and the maximum power density for both cases was approximately 200 mW/cm^2, a value that is determined by the materials used in this example. In both cells, the OCV is lower than the theoretical Nernst potential, ~1.2 V at 700 °C, due to imperfect sealing.

Impedance data for the LST–YSZ supported cell at 300 mA/cm^2 are shown in Fig. 6. The total cell impedance was approximately 1.5 Ω cm^2, consistent with the slope of *V–I* curve. The ohmic resistance of the cell, determined from the intercept on the real axis at high frequencies in the Cole–Cole plot, is 0.6 Ω cm^2. Earlier work in our laboratory showed that the semicircles with the peak frequencies of 2 kHz and 4 Hz are associated with LSM–YSZ cathodes and Cu–CeO_2 anodes, respectively [15]. The impedance plot in Fig. 6 indicates that cathode and anode polarization are about 0.2 and 0.7 Ω cm^2, which is consistent with the data in previous work [15]. All of the data indicate that neither the YSZ support nor the LST–YSZ support structures have a significant effect on the cell performance.

While the pure YSZ support structure will provide more strength to the cell, especially if YSZ is replaced with partially stabilized zirconia, the electronic conductivity provided by the LST–YSZ composite could have significant advantages for current collection in larger systems. With the YSZ support, electrical contact can only be made in the regions near the holes, while no such restrictions are placed on the cells with LST–YSZ supports.

Finally, it should be noted that a similar approach to that used here for the preparation of conductive supports on the anode side could be applied to supports on the cathode side. The support material in this case would need to be conductive under oxidizing conditions and again have a CTE similar to that of YSZ. Porous LSM tubes have been used in cathode-supported SOFC for many years [16,17]; but, because of the tendency for LSM to undergo solid-state reactions with YSZ at the temperatures necessary to sinter the YSZ electrolyte, these cells do not exhibit high performance at low temperatures. However, it should be possible to insert a porous YSZ layer between the LSM tube and the dense YSZ, then impregnate the porous with a perovskite, such as Sr-doped $LaFeO_3$ [18], after the high-temperature treatments have been performed. So long as the high-temperature treatments do not cause diffusion of La or Sr all the way through the porous YSZ to the YSZ electrolyte interface, there should be no effect of solid-state reactions on cell performance.

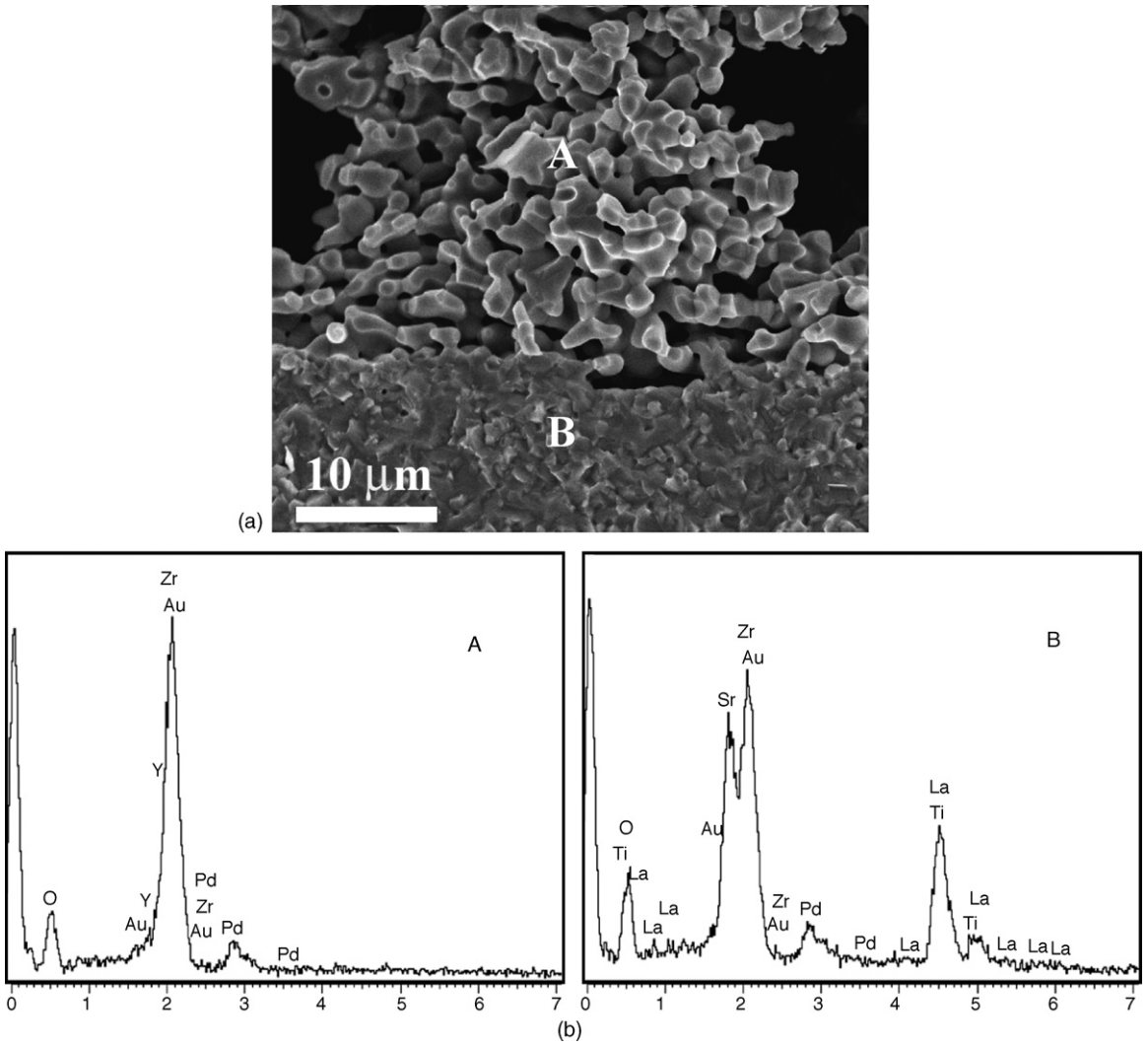

Fig. 4. (a) SEM image of the interface between a porous YSZ layer (A) and a $La_{0.3}Sr_{0.7}TiO_3$–YSZ layer (B). (b) EDS spectra obtained from porous YSZ (A) and from the $La_{0.3}Sr_{0.7}TiO_3$–YSZ composite (B).

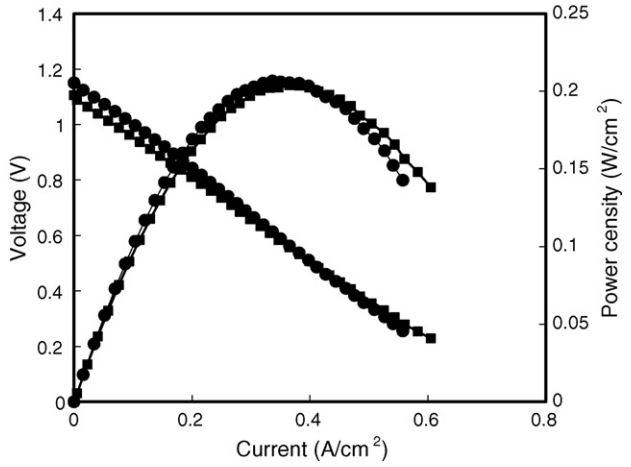

Fig. 5. *V–I* curves from cells prepared without a support layer (circles) and with an $La_{0.3}Sr_{0.7}TiO_3$–YSZ support layer (square). The data was taken at 700 °C in H_2.

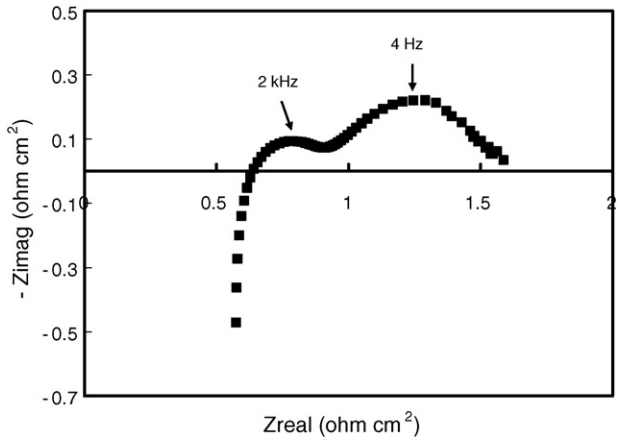

Fig. 6. A Cole–Cole plot for the cell with an $La_{0.3}Sr_{0.7}TiO_3$–YSZ support layer. The data was taken at 700 °C in H_2, at 300 mA/cm^2.

4. Conclusion

Perforated ceramic layers can provide excellent support structures for SOFC. Particularly when used in combination with electrodes prepared by impregnation of the electroactive components, this method allows the fabrication of cells with thin electrolytes. The choice of electronically conductive ceramics for the support structure can also assist in current collection.

Acknowledgement

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