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Thin-Film Electrolytes for Reduced Temperature Solid Oxide Fuel Cells

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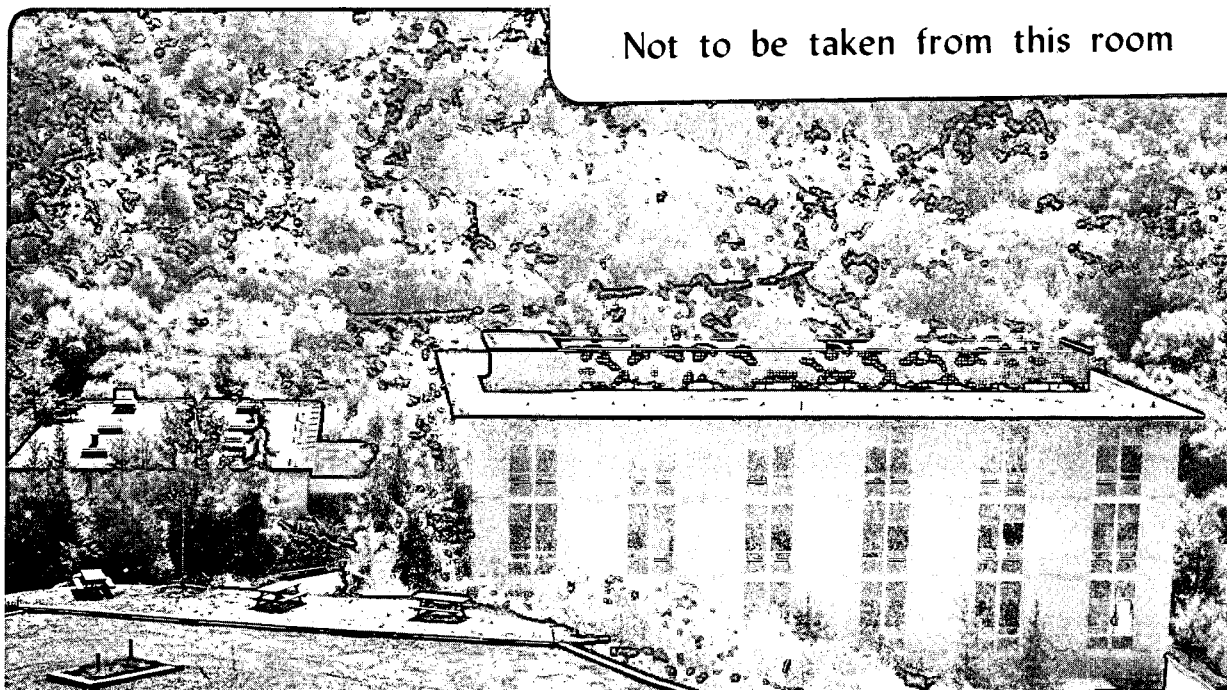## Thin-Film Electrolytes for Reduced Temperature Solid Oxide Fuel Cells

S.J. Visco, L.-S. Wang, S. De Souza, and L.C. De Jonghe

November 1994

DISCLAIMER

Thin-Film Electrolytes for Reduced Temperature
Solid Oxide Fuel Cells

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ABSTRACT

Solid oxide fuel cells produce electricity at very high efficiency and have very low to negligible emissions, making them an attractive option for power generation for electric utilities. However, conventional SOFC's are operated at 1000 °C or more in order to attain reasonable power density. The high operating temperature of SOFC's leads to complex materials problems which have been difficult to solve in a cost-effective manner. Accordingly, there is much interest in reducing the operating temperature of SOFC's while still maintaining the power densities achieved at high temperatures. There are several approaches to reduced temperature operation including alternative solid electrolytes having higher ionic conductivity than yttria stablilized zirconia, thin solid electrolyte membranes, and improved electrode materials. Given the proven reliability of zirconia-based electrolytes (YSZ) in long-term SOFC tests, the use of stabilized zirconia electrolytes in reduced temperature fuel cells is a logical choice. In order to avoid compromising power density at intermediate temperatures, the thickness of the YSZ electrolyte must be reduced from that in conventional cells (100 to 200 μm) to approximately 4 to 10 μm. There are a number of approaches for depositing thin ceramic films onto porous supports including chemical vapor deposition/electrochemical vapor deposition, sol-gel deposition, sputter deposition, etc. In this paper we describe an inexpensive approach involving the use of colloidal dispersions of polycrystalline electrolyte for depositing 4 to 10 μm electrolyte films onto porous electrode supports in a single deposition step. This technique leads to highly dense, conductive, electrolyte films which exhibit near theoretical open circuit voltages in H_2/air fuel cells. These electrolyte films exhibit bulk ionic conductivity, and may see application in reduced temperature SOFC's, gas separation membranes, and fast response sensors.

1. INTRODUCTION

Materials problems associated with operating electrochemical devices at temperatures of 1000 °C or more have limited the development of solid oxide fuel cells. The technical complexity and associated costs of fabricating fuel cell stacks require that these devices operate reliably for 30,000 or more hours. This places great demands on the mechanical and chemical stability of materials used in high temperature fuel cells. For these reasons, several research groups are pursuing the development solid oxide fuel cells that can operate at reduced temperatures, e.g. 700 to 850 °C. Clearly, as the temperature of the fuel cell is lowered, resistive losses across the solid electrolyte increase and overpotentials at the air and fuel electrode are similarly magnified. Still, the lower temperature of operation allows for a wider choice of electrode materials as well as decreasing the problem of electrode sintering. Approaches to minimize resistive losses across the electrolyte have included replacing the yttria stabilized zirconia electrolyte (YSZ) with alternative electrolytes having higher ionic conductivity, and/or reducing the thickness of the ceramic electrolyte from 100 - 200 microns to a few microns.

There are several reported methods for fabricating thin electrolyte films including electrochemical vapor deposition (EVD), sputter deposition, sol-gel film processing, and recently tape-calendaring of ceramic filled plastic tapes. Among the various thin-film techniques, the sol-gel and bilayer extrusion techniques are probably the most cost effective approaches. Although it has been shown in this laboratory and others that sol-gel deposition of ceramic films can be accomplished on porous substrates, the upper limit to thickness for a single coating step is typically 0.5 microns. Electrolytes of these dimensions have a high probability of pinholes and rarely demonstrate acceptable open circuit voltages in completed fuel cells. Furthermore, when the film thickness approaches the grain boundary thickness, the film becomes

inherently unstable at temperature. Accordingly, in order to deposit practical electrolytes on porous substrates (> 2 μm), multiple sol-gel coatings are required. The necessity of building up multiple sol-gel coatings in order to achieve adequate electrolyte performance clearly increases the processing time which may diminish the attractiveness of the sol-gel approach. Thus, we modified our approach to allow deposition of dense, pinhole-free, electrolyte films of 2 microns or more in thickness with a single pass. Fuel cells fabricated with these new films exhibit close to theoretical open circuit voltage, and high current densities.

| Tape-calendaring | Sol-gel film | Reverse-slip coat |
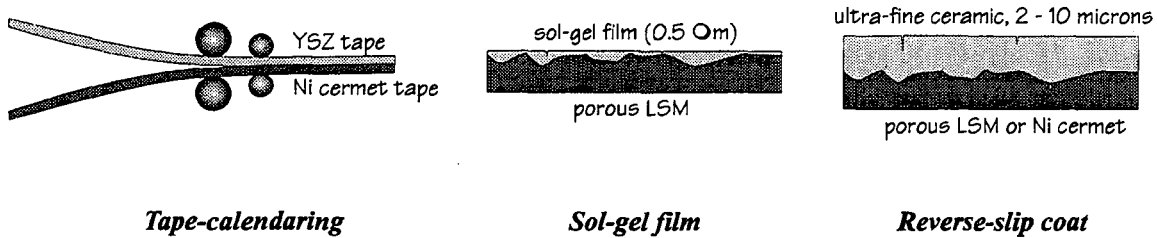
Fig. 1 Some of the approaches used to fabricate thin-film electrolyte fuel cells.

The performance of thin-film fuel single-cells can rival that observed for high temperatures SOFC's. This has been demonstrated by the work of Nguyen Q. Minh at Allied Signal[1], Scott Barnett at Northwestern University[2], and by our group at Lawrence Berkeley Laboratory[3]. It is not known at this time whether the high performance of thin-film single SOFC's will be realized in multi-cell stacks, and whether thin-film cells will exhibit long life operation. A goal of reduced temperature operation of SOFC's is to decrease the cost of the multi-cell stack while still delivering high performance and long life. A perceived means of achieving this goal is through the use of metal interconnects. This remains to be shown for thin-film fuel cell stacks, and is clearly a priority in the evolution of thin-film SOFC technology.

2. BACKGROUND

Initial work in our group on electrolyte membranes utilized metal alkoxide chemistry as a route to thin ceramic films[4]. First, zirconium alkoxide films were applied to continuous substrates either by spin or dip-coating techniques. In order to avoid cracking of the hydrolyzed alkoxide thin films, the metal alkoxides were first reacted with chelating agents such as diethanolamine. In this way, 1-dimensional polymeric chain structures are favored upon water hydrolysis of the chelated alkoxide, imparting elastomeric properties to the hydrolyzed film, allowing it to relieve stress on drying. This technique was quite successful, allowing us to routinely coat a variety of continuous substrates (Pt, Ni, Si, SiO$_2$, etc.) with dense crack-free films at firing temperatures below 700 °C. It was found that an upper limit of approximately 0.5 microns could be deposited in a single pass without cracking. In order to achieve films thicknesses above 0.5 microns on a continuous substrate, multiple coatings would be necessary.
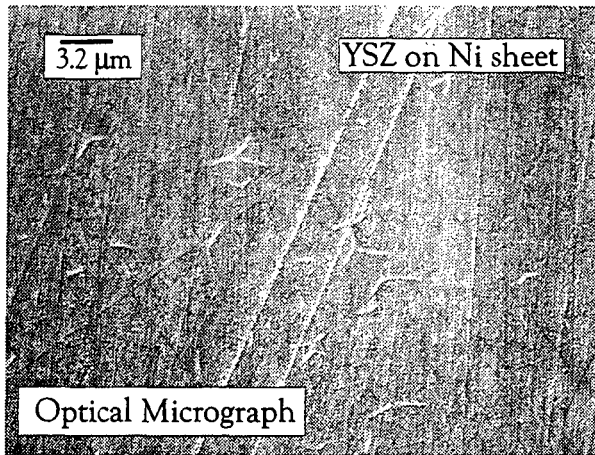
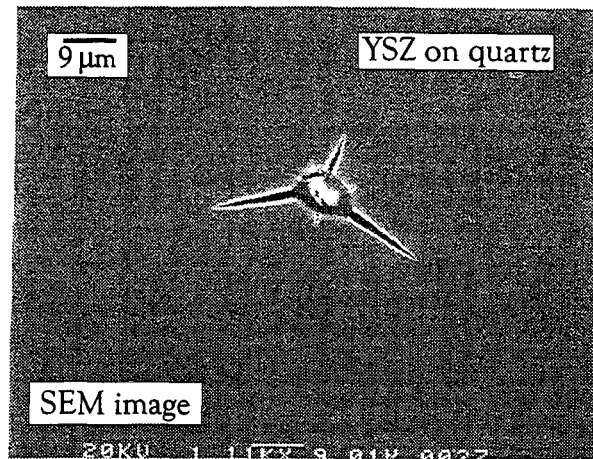Fig. 2 Metal alkoxide sol-gel film on Ni sheet

Fig. 3 Sol-gel film on quartz substrate

The second phase of the alkoxide work involved demonstration of the feasibility of applying dense, crack-free, coatings on porous substrates. In order to achieve that goal, model substrates were employed. The substrates chosen were Anotec™ alumina membranes; ceramic filters of well defined porosity. Chelated metal alkoxide solutions were spun onto ceramic membranes having pore sizes of 0.2, 0.1, and 0.02 microns. Thin, crack-free films of yttria stablized zirconia (YSZ) were successfully deposited onto the porous ceramic membranes[4]. To our knowledge, this was the first time a dense ceramic electrolyte was successfully deposited from solution onto a porous substrate. Interestingly, it was observed that the critical thickness above which cracking occurred was reduced to 0.2 microns. Also, the critical pore size above which the films could not bridge the pore was found to be approximately 0.02 microns. In other words, high quality YSZ thin films were obtained for Anotec membranes having 0.02 micron pores, but for membranes with larger pore sizes, open porosity films were obtained.

Since the research on film coating of Anotec membranes showed that very fine surface pore sizes were necessary for successful deposition of high quality YSZ films from alkoxide solutions, fabrication of suitable electrode structures was attempted. An established technology for ultrafiltration (Ceraver membranes) involves sol-gel coating of graded porosity alumina tubes to yield pore sizes on the order of 40 to 200 A°. Similarly, if planar Ni/YSZ cermets or perovskite electrodes could be graded to a fine surface pore size, the above metal alkoxide procedure for YSZ thin-film deposition could be utilized to generate a fuel cell structure. Graded $LaSrMnO_3$ substrates were successfully fabricated using sedimentation casting and filtration casting. YSZ films were applied to the electrodes by dip-coating with the metal alkoxide solutions. Although continuous films were observed locally on the substrate, surface defects such as large pores, gave rise to pinholes in the film. Since it appeared unlikely that graded porosity electrodes could be fabricated defect-free, a slightly different technique was employed to coat the electrode. In order to raise the viscosity of the coating solution the metal alkoxide solutions were replaced by chelated glycine-nitrate solutions. Metal nitrates were dissolved in aqueous glycine solutions, and concentrated with heat to yield highly viscous solutions. These solutions were cast onto release sheets, allowed to dry to tacky films, and then transferred to the porous LSM substrates. The tape-transfer technique allowed us to coat virtually any porous substrate in a single step. The fired films were continuous and adherent. However, a critical thickness of about 0.5 μm was still observed. This was expected to present practical difficulties since surface topography of the porous LSM substrate exhibited variations of greater than 0.5 μm. The YSZ/LSM bilayers were subsequently coated with Ni/YSZ paint, and fuel cells were constructed. Low open circuit voltages were observed for the thin-layer fuel

cells. Most likely, this was due to short-circuiting of the cell by surface defects penetrating the thin YSZ films. Two possible solutions to this problem were envisaged. The YSZ film thickness could be increased by using multiple tape-transfer coating, however, this would increase the complexity of the process, and the cost. Therefore, a different approach was taken, which proved to be highly successful.

3. APPROACH

The technical approach used in this work involved the use of colloidal dispersions of metal oxides to coat porous substrates with thin, fully dense, electrolyte films. In order to deposit YSZ films on the order of 4 to 10 microns in a single step, a technique of reverse slip-coating was employed. Ceramic powders were calcined at various heating schedules in order to tailor the shrinkage profiles of electrode substrates. Porous anode or cathode substrates were then pre-fired to strengthen the electrode structures. Colloidal dispersions of 0.18 μm YSZ powders were prepared and found to be stable for several days. Porous electrode substrates were then immersed in the colloidal dispersion, removed, and allowed to dry. The green bilayers were subsequently fired, yielding dense, pinhole free YSZ films of 4 to 10 μm on the porous electrode supports. Films could be successfully deposited onto porous cathodes or cermet anodes. Fuel cell structures were completed by screen printing of the complementary electrode onto the bilayer, and mounting of the single cell onto a zirconia tube. Single-cell fuel cells exhibited near theoretical OCV's and high power densities. The approach is quite general and allows us to deposit fully dense YSZ thin films 4 to 10 μm on a variety of porous substrates in a single step.

4. COLLOIDAL YSZ ROUTES TO HIGH QUALITY THIN-FILM ON POROUS SUBSTRATES

In this approach a solution of colloidal YSZ particles is deposited on a partially sintered porous anode or cathode structure. The colloidal YSZ film is deposited in a single step onto the substrate and attains a final thickness of approximately 4 to 10 μm after sintering. In order to avoid cracking of the YSZ thin film due to stresses built up by the 2-D confinement of the sintering film, the substrate is pre-fired to the extent that the shrinkage of the substrate matches the shrinkage profile of the YSZ thin film. In this way, the film is under compression rather than tension while sintering, and highly dense, crack-free films having thicknesses of 4 to 10 μm can be deposited in a single step onto porous substrates. This approach has been very successful. Furthermore, it does not require the use of graded porosity substrates, and consequently substrate preparation is straightforward. The YSZ films deposited in this way lead to near theoretical open circuit voltages and high power densities in single cell fuel cells.

4.1 Experimental: colloidal YSZ

4.1.1 NiO-YSZ anode substrate processing:

YSZ (Tosoh) was pre-calcined at 1200 °C for 4 hours and attritor milled for 1 hour. NiO powder (J.T. Baker) was attritor milled for 1 hour. The milled NiO and YSZ powders were mixed with corn starch in isopropanol or acetone and attritor milled for an additional 3 hours in isopropanol. The powders were mixed approximately as 40 wt% NiO, 40 wt% YSZ, and 10 wt% corn starch. After milling, the anode powders were collected and mixed with approximately 3 wt% binder, and 1 wt% dispersant in isopropanol. The mixture was well stirred on a magnetic stirring plate until the solvent had evaporated and then the powder were sifted using a 100 μm sieve. The anode powders were then compacted under uniaxial pressure in a 1"

die at a pressure of 4000 lbs. Green anode disks were subsequently fired at 950 °C for 10 hours to coarsen the microstructure.

4.1.2 LSM-YSZ cathode substrate processing:

$La_{0.85}Sr_{0.15}MnO_3$ powders were made by the glycine-nitrate process as described earlier. LSM and YSZ were mixed in a ratio of 50/50 wt% with 3% binder and 1% dispersant in isopropanol. The mixture was stirred on a magnetic stir plate until the solvent evaporated. The LSM powder was then passed through a 100 μm sieve. The LSM powder was then pressed uniaxially at 4000 lbs. in a 1" diameter die. The green LSM disks were then coarsened at 1250 °C for 2 hours. For the case where LSM was applied to a Ni-cermet/YSZ bilayer, the sieved LSM/YSZ powders were mixed with ethylene glycol to form a paste.

4.1.3 YSZ thin-film coating

High quality YSZ powders (Tosoh) were mixed in distilled water and sonicated with a high intensity ultrasonic probe for 15 minutes. The solution was allowed to settle for 1 hour to allow the large particles to sediment out. The supernatant was decanted, placed in a large diameter evaporating dish, and allowed to dry. The finer particles deposited on the outer edges of the evaporating dish. These particles were collected, redispersed in isopropanol, and sonicated with the ultrasonic probe. This formed a very stable colloidal dispersion of fine YSZ particles suitable for casting thin films. YSZ thin films could be obtained either by dip-coating or direct casting onto the porous substrate.
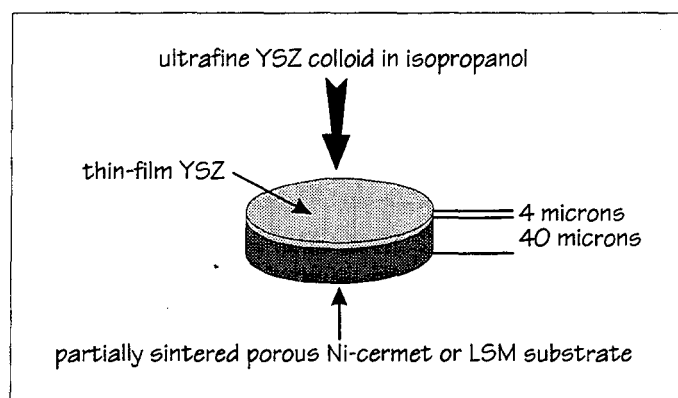

Fig. 4 Schematic representation of colloidal deposition of YSZ on porous substrates

The electrolyte/electrode bilayer is fired below 1350 °C in the case for YSZ/LSM to avoid reactions at the interface that would degrade fuel cell performance. For the Ni-cermet/YSZ bilayer, the structure is fired at 1400 °C for approximately 1 hour to achieve full density of the YSZ thin-film. After the bilayer is fired at the appropriate temperature, the corresponding anode or cathode is screen printed onto the bilayer and refired at 1250 °C for about 1 hour.

4.1.4 Current collector

Platinum mesh was bonded to the anode and cathode surfaces using platinum paste. Two leads were spot-welded to each Pt mesh current collector to compensate for ohmic drop from the galvanostat to the fuel cell. The current collectors were then fired onto the electrode surfaces at 700 °C for 1 hour.

4.1.5 Seals

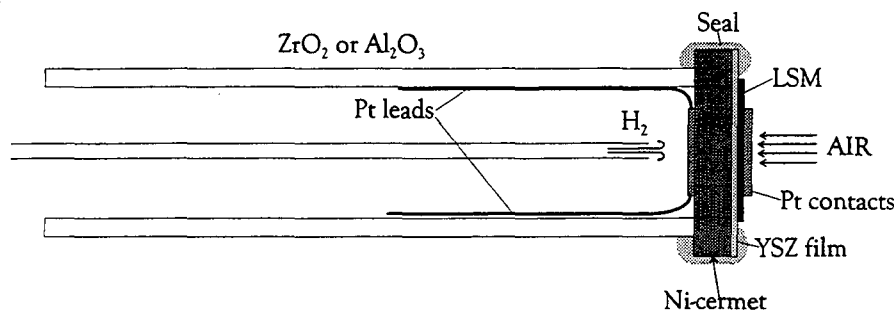Ceramic seals were used to bond the fuel cell/current collector structure to a zirconia or alumina tube.

Fig. 5 Schematic of thin-film fuel cell test apparatus.

Although glass seals were also successful, the ceramic seals were far easier to fabricate, and did not appear to compromise fuel cell performance. The seals between the Ni-cermet and alumina tube was accomplished with a thin layer of Aremco 571 and this seal was encapsulated by a thick Aremco 516 (zirconia based) cement seal. The seals were cured as the fuel cell structure was brought to temperature for testing.

4.1.6 Impedance Spectroscopy Analysis

Impedance analysis of thin YSZ films, bilayers, and fuel cells based on them was accomplished with a Shlumberger Solartron 1260 Frequency Response Analyzer. Measurements to date were obtained with a two probe setup. Since the porous Ni-cermet was completely covered by the thin YSZ film, the use of 2 reference electrodes for 4-probe impedance analysis is not possible. Instead, 3-probe testing is used to accurately determine the YSZ/LSM interfacial impedance.
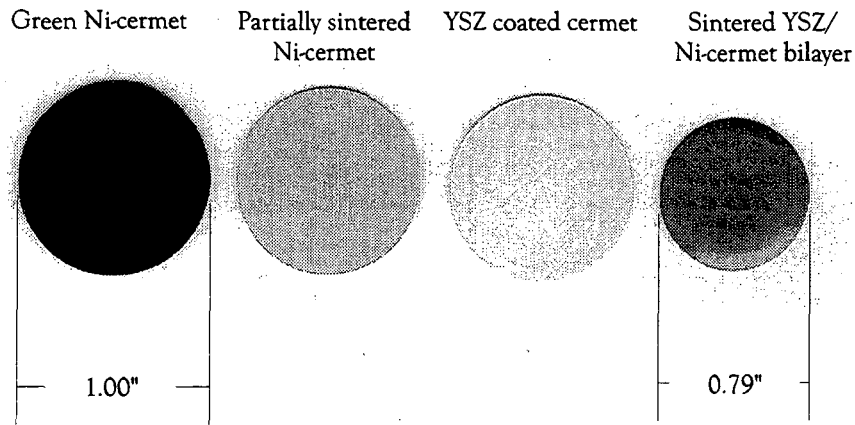
4.1.7 Fuel Cell Testing

Humidified hydrogen (4% H_2O) was supplied to the Ni-cermet anode at a rate of 0.5 ccm. Oxygen was supplied to the cathode by ambient air. Initially, fuel cells were operated galvanostatically with 2-wire connections to cell. However, ohmic drop across the leads must be separately measured and corrected for in the fuel cell performance curves. The cell was then fabricated using a 4-wire construction, allowing 2 wires for power, and 2 wires for sensing. On cell heat-up, argon gas is supplied to the anode. Once the cell has thermally equilibrated at the operating temperature of 700 to 800 °C, the anode gas is switched to H_2 and the NiO/YSZ anode is reduced to the Ni-cermet.

4.2 Results

4.2.1 LSM/YSZ and Ni-cermet/YSZ bilayers

In order to deposit thin YSZ films on the order of 4 to 10 μm in a single step without cracking, it was imperative to control the shrinkage profile of the porous substrate to match that of the film. As can be seen in the shrinkage profiles for YSZ and LSM, both materials exhibit similar sintering properties. The progression from Ni-cermet to sintered Ni-cermet/YSZ bilayer is seen below in Fig. 6.

| Green Ni-cermet | Partially sintered Ni-cermet | YSZ coated cermet | Sintered YSZ/ Ni-cermet bilayer |

├— 1.00" —┤   ├— 0.79" —┤

Fig. 6 Optical image of Ni-cermet, coated cermet, and sintered electrode/electrolyte bilayer.

It is desirable to have slightly more shrinkage of the substrate relative to the film, in order to put the film in compression. In some cases this would actually heal visible cracks that occurred after drying of the sol film and prior to densification. Control of the substrate sintering profile was accomplished through careful calcination of the glycine-nitrate derived powders. Typically a bimodal distribution of coarsened powders was used to control shrinkage. For the case of Ni-cermet substrates, systematic control of particle size and mixing was necessary to create a highly porous and homogeneous substrate suitable for coating. In the absence of careful control of substrate fabrication, single-step deposition would not close the surface porosity of the substrate and several coatings were necessary. Since it is highly desirable to achieve one-step deposition, control of substrate homogeneity is important. Furthermore, it is expected that control of cermet morphology will be critical in achieving desired electrochemical and mechanical properties of the bilayer structure and will govern fuel cell performance. Fortunately, control of particle size and cermet homogeneity is not an expensive proposition, but rather requires systematic investigation of the process parameters controlling these properties. This was accomplished in our case by methodical studies of the effects of attritor milling of as-received and as-synthesized metal oxide powders, and binder/dispersant concentrations, on the morphology of the substrate as determined by optical and scanning electron microscopy (SEM). The relationship between morphology and thin-film quality was determined in a similar fashion. Finally, the relationship between substrate morphology and fuel cell performance was examined, and is part of the ongoing research program.
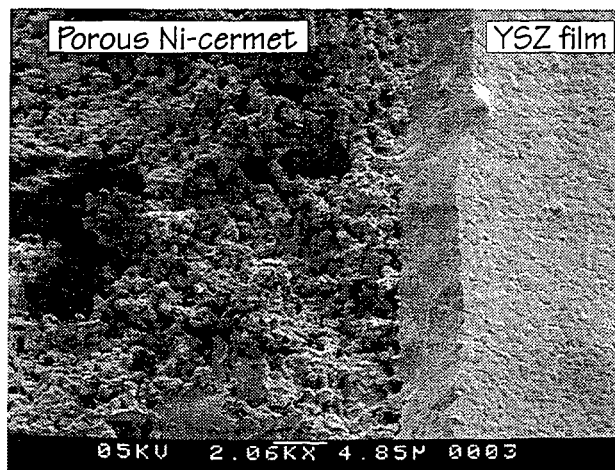
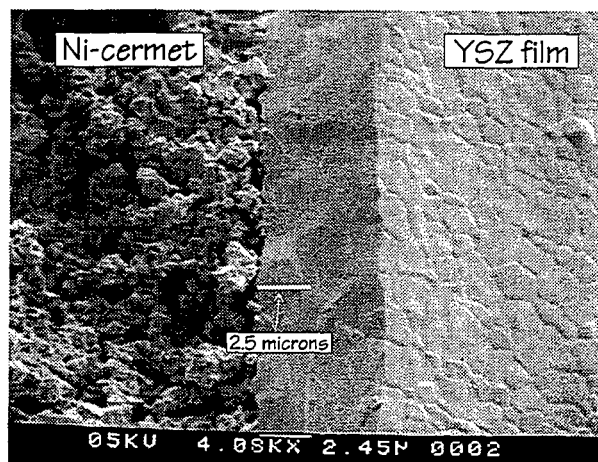**Fig. 7 SEM micrograph of thin YSZ film on porous Ni-cermet**

Fig. 8 Higher magnification SEM micrograph of Ni-cermet/YSZ bilayer structure

Successful deposition of fully dense, 4 to 10 μm thick, YSZ films has been routinely achieved on highly porous LSM and Ni-YSZ cermets. As stated above, the quality of the film was largely determined by the quality of the substrate. Subtle changes in particle size as a result of changes in attritor milling and/or coarsening schedule were shown to adversely affect the homogeneity of the compact and lead to poor film quality on deposition. Conversely, by controlling process parameters carefully, high quality substrates are routinely obtained. Accordingly, single-step deposition of crack-free YSZ is relatively simple on such substrates. The high degree of homogeneity of the LSM and Ni-cermet substrates also leads to good mechanical strength and good adhesion of the YSZ film to the substrate. Although thin YSZ films could be deposited on either porous LSM or Ni-YSZ cermets, the reactivity of the LSM/YSZ interface reported in numerous studies implies that the Ni-cermet is probably is more desirable as a substrate. This is clearly supported by the diffraction patterns shown in Fig. 9 and Fig. 10. In the case where a LSM/YSZ bilayer was sintered at 1325 °C there was no indication of second phase formation, however, at 1350 °C the reaction of LSM and YSZ is clearly evidenced by the appearance of $La_2Zr_2O_7$ in the xray diffraction pattern (Fig. 10).

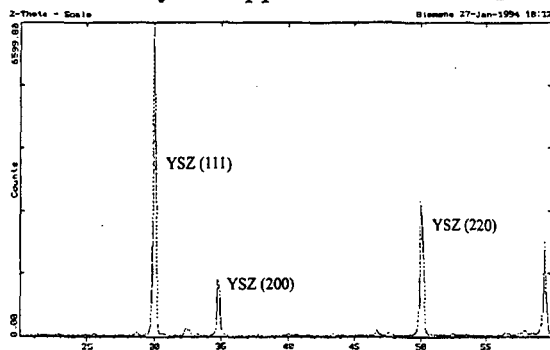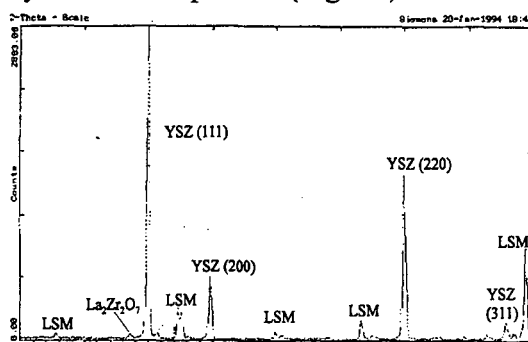**Fig. 9 Thin YSZ film sintered on LSM substrate at 1325 °C for 1 hour.**

Fig. 10 Thin YSZ electrolyte film sintered onto LSM substrate at 1350 °C for 1 hour.

4.2.2 Electrical Properties of bilayers

Although partially sintered porous LSM substrates were easily coated with a dense crack-free YSZ film using this approach, the LSM/YSZ interfacial impedance was found to be larger than for Ni-cermet coated substrates. When LSM/YSZ bilayers were sintered at 1325 °C, acceptable interfacial properties were obtained, however, by raising the sintering temperature

8

merely 25 °C the appearance of $La_2Z_2O_7$ (above) could be detected in the xray diffraction data, and bilayer impedance was compromised. The instability of this interface at elevated temperatures is yet another reason to reduce the operating temperature of fuel cells based on these materials. Whether deposited onto porous Ni-cermets or LSM substrates, the ionic conductivity of the YSZ thin film as well as the activation energy for conduction matched that of bulk YSZ. In light of the temperature at which the thin-film electrolytes are fired, it is not surprising that binder burnout is complete, and the thin-film materials attain bulk properties.
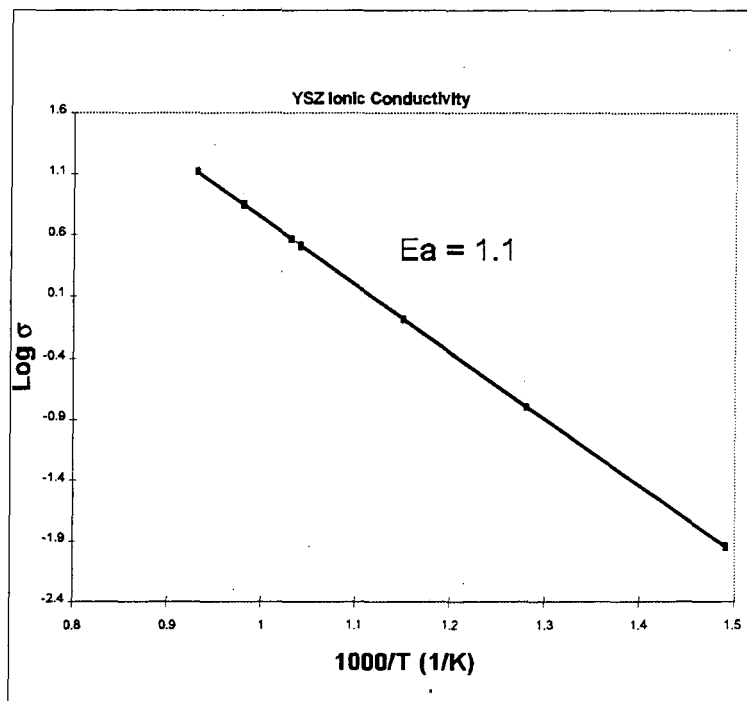

Fig. 11 Ionic conductivity of thin-film YSZ as a function of temperature.

Although the resistance of the electrolyte has been greatly reduced by limiting the thickness of this component to a few microns, the performance of the bilayer structures and fuel cells based on them depends critically on the nature of the electrode/electrolyte interface and its stability over time at the operating temperature of the device. To determine interfacial impedance of the LSM/YSZ bilayer, Pt leads were attached to the structure with Pt paste, and the impedance of the device was determined over the frequency range of 0.01 Hz to 65 kHz. The interfacial impedance of this device was found to be approximately 3.2 Ω cm^2. The impedance response was also determined for a fuel cell where a Ni/YSZ cermet was applied to the electrolyte face of the LSM/YSZ bilayer. The impedance spectrum can be seen in Fig. 12 below. The total impedance for this fuel cell was approximately 8 Ω cm^2, of which 1.8 Ω cm^2 was lead resistance, and 6.2 Ω cm^2 was interfacial contact resistance (3.2 Ω cm^2 for LSM/YSZ and 3.0 Ω cm^2 for Ni-cermet/YSZ). The interfacial impedances clearly dominate the electrical response of this fuel cell, and must be reduced. The cathode in this fuel cell was porous LSM. The interfacial impedance could be improved through the inclusion of YSZ in the cathode formulation. Several groups have claimed that the use of LSM/YSZ cathodes not only reduce the interfacial impedance at the (LSM/YSZ)/YSZ interface, but also improve the long-term stability of this interface. This is due presumably to spreading the LSM/YSZ reaction layer out over a large surface area, as opposed limiting the reaction layer to the electrode/electrolyte

interface where it presents a large series resistance. The current/voltage profile of this fuel cell is presented in the next section.
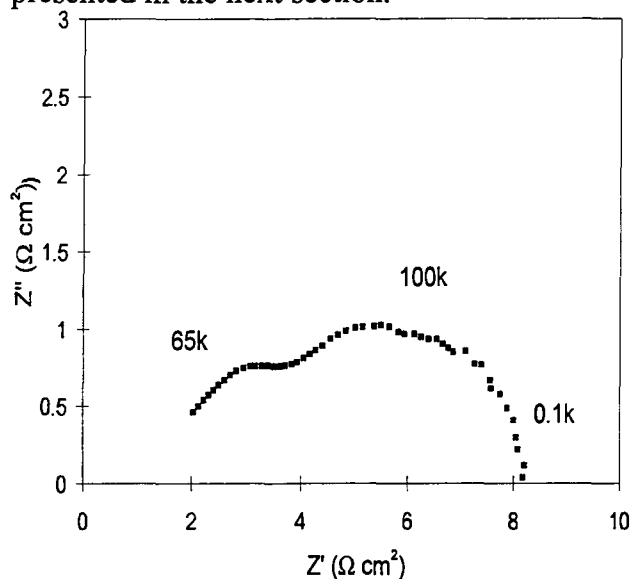

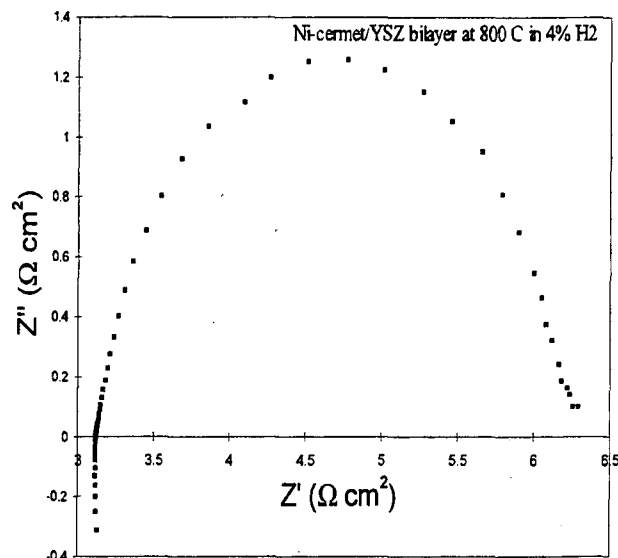**Fig. 12 Impedance spectra for LSM/YSZ bilayer**

Fig. 13 Impedance spectrum for Ni-cermet/YSZ bilayer.

The AC response of a Ni-YSZ/YSZ cermet is shown in Fig. 13. The interfacial impedance of the cermet is approximately 3.0 Ω cm^2. One would expect this impedance to be significantly smaller than that observed for the LSM/YSZ cermet. It has been suggested that if hydrogen reduction of the NiO-YSZ/YSZ bilayer is not done carefully, deterioration of the Ni-YSZ/YSZ interface results. Consequently, the Ni-cermets are presently being brought to temperature under argon, and then reduced at 800 °C with hydrogen. Impedance spectroscopy has not yet been performed on these samples.
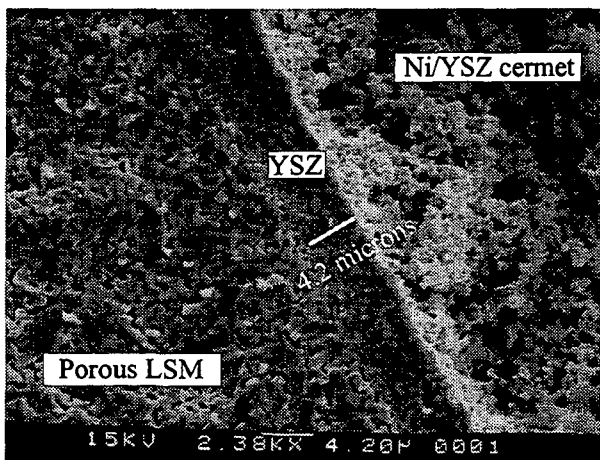
4.2.3 Fuel Cell Testing and Evaluation

Fig. 14 SEM micrograph of fracture cross-section of thin-film fuel cell.
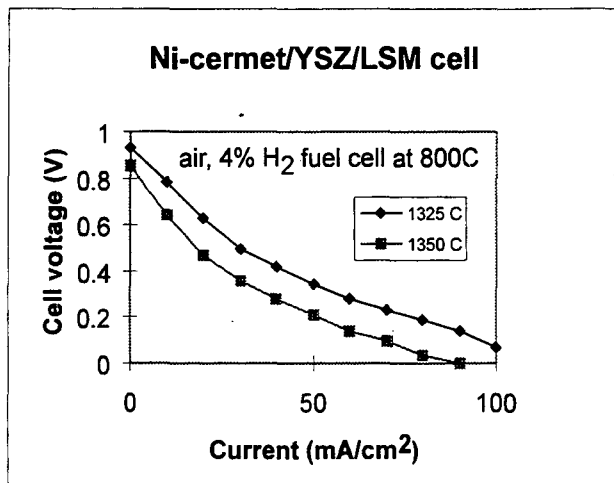
Fig. 15 Current-voltage profile for thin-film LSM/YSZ bilayer-based fuel cell.

Thin-film fuel cells were constructed as described in the experimental section. The completed cells were then slowly brought to temperature and the NiO electrode reduced to Ni metal *in situ*. As expected, the performance of the fuel cells based on LSM/YSZ bilayers was fair, but not outstanding. The cell exhibited near theoretical OCV, but exhibited a steeply sloping voltage/current profile with a short circuit current of approximately 100 mA/cm^2. This was most likely due to the presence of a reaction layer during firing of the bilayer, as detected in the xray, and impedance spectroscopy. The performance of the Ni-cermet/YSZ/LSM cell based on a LSM/YSZ bilayer is shown in Fig. 15. As would be expected, the cell fabricated from a LSM/YSZ bilayer fired at 1350 °C performed worse than the cell where the bilayer was fired at 1325 °C. This correlates well with the xray observation of La$_2$Zr$_2$O$_7$ for bilayers formed at 1350 °C.

Although high quality porous LSM substrates had proven to be relatively simple to fabricate and coat, the instability of the interface at temperatures above 1350 °C prompted us to focus efforts towards fabrication of highly homogeneous porous NiO/YSZ substrates. This effort was successful, and enabled routine coating of these substrates with 4 to 10 micron thick, fully dense YSZ. These cells easily outperformed cells based on LSM/YSZ bilayers. Fig. 16 and Fig. 17 below shows the performance of one such fuel cell.
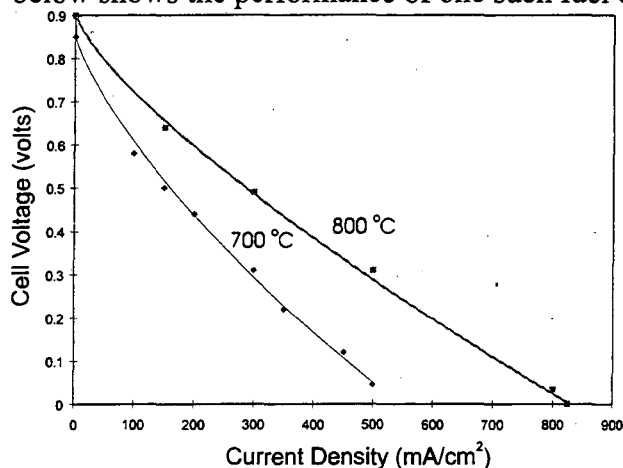

Fig. 16 Current-voltage profile for Ni-cermet/YSZ bilayer fuel cell with LSM cathode
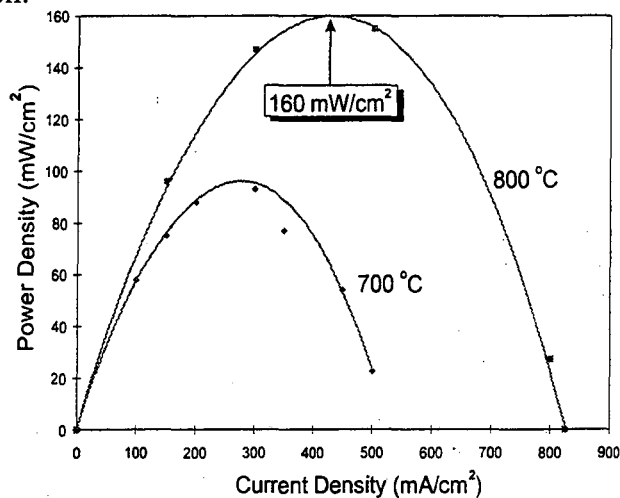
Fig. 17 Power-current profile for Ni-cermet/YSZ thin-film bilayer fuel cell with LSM cathode.

As can be seen from the current/voltage curves, at 800 °C the fuel cell based on a Ni-cermet/YSZ thin film electrolyte demonstrated short circuit currents of approximately 820 mA/cm^2. The power output for this cell is shown in Fig. 17. The cell attained an output of approximately 160 mW/cm^2 at 800 °C. It is quite likely that the cell performance exceeded that shown Fig. 18 and Fig. 19, since the temperature of operation was taken using the furnace controller thermocouple. Hydrogen was supplied directly to the Ni-cermet anode without pre-heating of the gas, and consequently it is possible that the anode was appreciably cooled by the fuel gas. The fuel cell test apparatus has been redesigned with a thermocouple at the Ni-cermet surface to monitor the actual operating temperature of the cell. In any event, the output shown in the figures above represents a minimum for the thin-film based cells.

The open circuit voltage of the thin-film electrolyte cell in Fig. 16 is about 100 mV less than theoretical. In order to realize maximum efficiency and power output of the fuel cell, this loss must be must be eliminated. The slight depression of cell voltage may be due to either a leak in cell seals, the presence of pinholes in the thin-film electrolyte, or both factors. Improvement of cell sealing has been accomplished recently through the use of a dual layer seal. The presence of

11

pinholes has been detected in some sintered bilayers by penetration of a low viscosity organic solvent. This has been corrected by further improvements in the Ni-cermet preparation, and by increasing the solids loading in the colloidal YSZ coating solution.
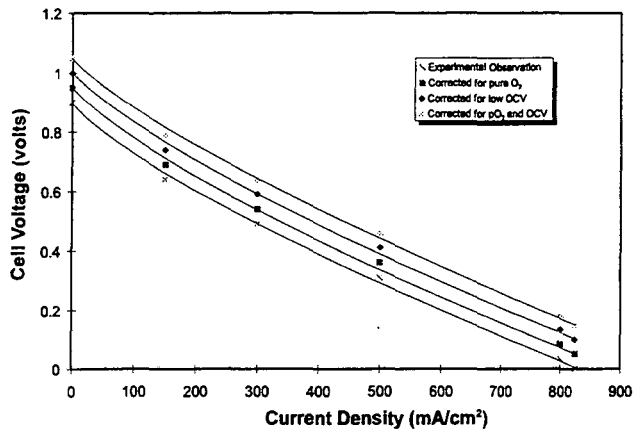

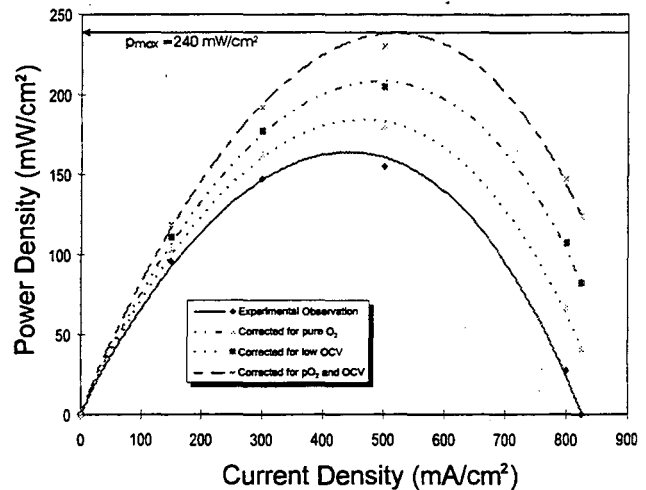**Fig. 18 Estimated thin-film fuel cell I-V curves corrected for leaks, etc.**

Fig. 19 Estimated thin-film power densities corrected for leaks, etc.

The performance of the Ni-YSZ/YSZ bilayer based fuel cells can be roughly corrected for the depressed OCV and for higher O_2 concentrations than were used experimentally. The oxygen atmosphere corrections were estimated from published data for actual fuel cell performance[5] as a function of pO_2. As can be seen from the above figures, maximum power densities of 240 mW/cm^2 at 800 °C should be attainable. It is expected that these results will be verified shortly with the improved Ni-cermet bilayers, and the redesigned fuel cell test apparatus.

5. CONCLUSIONS

A highly successful thin-film deposition procedure was developed through systematic elucidation of the shrinkage profiles for thin-film electrolytes and the porous electrode substrates to be coated. Colloidal dispersions of submicron polycrystalline electrolyte powders were used as the coating solutions. Partially sintered porous substrates (anodes or cathodes) were coated with the colloidal dispersions, and the resulting bilayers were co-fired to yield fully dense, crack-free electrolyte films of 4 to 5 μm in thickness in a single depositions step. In order to avoid reaction of the YSZ with LSM at the co-firing temperature, Ni-cermets were typically used as the porous substrate. The thin electrolyte films exhibited ionic conductivities of the bulk material.

LSM cathodes were screen-printed on the Ni-cermet/YSZ electrolyte bilayers and fired to yield single cell thin-film devices. Upon mounting into fuel cell test rigs, the thin-film cells were tested in H_2/air environments at the intermediate temperatures of 700 to 800 °C. The cells exhibited near theoretical open circuit voltages, and high power densities under load. Importantly, the goal of using thin-film techniques to reduce the operating temperature of SOFC's while maintaining excellent performance was realized.

Thin-film electrolytes of the order of 4 to 10 μm can be deposited on highly porous substrates in a single deposition step. The electrolytes are fully dense and crack-free, and exhibit ionic conductivity comparable to bulk material. The colloidal sol approach is a generic means of depositing thin-films and was found to work equally well for porous LSM or Ni-YSZ substrates. The quality of the deposited film depends largely on the homogeneity of the porous substrate,

and careful matching of film and substrate sintering profiles. In this way the electrolyte film is allowed to shrink in 3 dimensions as it sinters to full density. It was found that even in the case of poor films where visible cracking could be seen prior to the final firing, the substrate shrinkage would heal the cracks and high quality electrolyte films were obtained. It was observed that for the case where LSM substrates were coated with YSZ, a $La_2Zr_2O_7$ film could be observed in the xray if the sintering temperature exceeded 1350 °C. The presence of this film is deleterious to fuel cell performance, and for this reason it was decided that a preferable avenue was to coat Ni-YSZ substrates with thin electrolyte films. Impedance spectroscopy of the Ni-YSZ/YSZ bilayer showed a lower interfacial impedance relative to the LSM/YSZ bilayer. Furthermore, performance of the Ni-YSZ/YSZ thin-film fuel cell was far improved relative to the performance seen when LSM was used as a substrate for film deposition. The Ni-YSZ/YSZ/LSM fuel cell exhibited power densities of approximately 160 mW/cm^2 at 800 °C. It is expected that power densities well over 240 mW/cm^2 will be demonstrated shortly.

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