

THIN-FILM FUEL CELLS

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ABSTRACT

Bilayers consisting of highly porous substrates and dense thin-films of zirconia, ceria, and perovskite mixed conductors (SrZrO_3 , SrCeO_3 , and LaSrCoFeO_3) have been successfully fabricated using colloidal deposition techniques. The films are well bonded to the substrate, gas tight, and exhibit little interfacial resistance. Performance of solid oxide fuel cells (SOFCs) based on YSZ electrolytes of less than 10 μm have achieved power densities close to 2 watts/cm^2 at 800°C. Ceria based SOFCs exhibited excellent electrochemical performance over the temperature range of 600 to 800°C with peak power in excess of 650 mW/cm^2 at 750°C and close to 300 mW/cm^2 at 600°C. Bilayers of thin SrCeO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCF) suitable for gas separation or membrane reactors have been fabricated as well as fuel cells based on proton conducting SrZrO_3 films have also been fabricated and tested. The approach is generic and allows deposition of a variety of thin ceramic films on porous substrates. The methodology is scaleable and inexpensive, and should allow substantial cost-savings in the manufacture and operation of electrochemical devices in the intermediate temperature range of 500-800°C.

INTRODUCTION

Ionic and mixed-conducting ceramic devices such as solid-oxide fuel cells, gas separation membranes, and membrane reactors require a dense electrolyte and highly porous electrodes. The motivation to fabricate thin film ceramic electrolytes derives from the benefits associated with lowering of ohmic losses across ionic and mixed ionic-electronic conducting materials as membrane thickness is reduced. When films are very thin (5-15 μm) the resistance of the electrolyte at intermediate temperatures is almost negligible, for example a ~10 μm thick YSZ electrolyte has been shown to have an iR drop of 0.025 Ωcm^2 at 800°C¹. This allows the electrochemical device to operate at lower temperatures and higher thermodynamic efficiency where less expensive materials may be used in device construction. The technical challenge involves depositing pinhole and crack free dense layers of electrolyte 5 to 40 μm in thickness on substrates of high porosity. The film must be well bonded to the substrate without excessive infiltration into the electrode porosity and there must be minimal interface polarization.

Several approaches to thin film fabrication have been reported including physical vapor deposition techniques^{2,3}, tape calendaring⁴, sol-gel deposition⁵, sputtering⁶ and in our group colloidal deposition. Many of these approaches have allowed the fabrication of high quality films, however, the high cost of capital equipment and/or operating costs for several of these

approaches presents a considerable barrier to their commercialization. In our laboratory we have focused on the use of wet chemical techniques such as colloidal deposition wherein a fine powder is dispersed in solution, deposited onto a green substrate, and fired such that the film fully densifies and the substrate remains highly porous.

Colloidal deposition of dense electrolyte layers on porous substrates requires that the materials are chemically compatible at the processing temperature and there must be adequate thermal expansion match between the layers. It is critical to develop a thorough understanding of the sintering behavior of both film and substrate materials. Once compatible materials have been selected, fabricating dense films of 5-40 μm is achieved by careful control of the sintering profile (shrinkage vs. temperature) and the magnitude of the shrinkage of the materials. This is accomplished by systematically modifying the sintering profiles of film and substrate through control of particle size and morphology of green substrates. Poor understanding of these parameters often leads to electrolyte films of low density (pinholes) or cracked films composed of islands of high-density film. Even in cases where the shrinkage of film and substrate are sufficiently close to generate dense electrolyte films, residual stresses can lead to highly distorted films with significant curling. Importantly, the electrode substrate must be processed to yield continuous porosity and a high surface area microstructure, without compromising the strength of the bilayer.

At Lawrence Berkeley National Laboratory (LBNL) we have perfected the technique of colloidal deposition whereby high quality films of a wide variety of ionic and mixed ionic-electronic conductors can be deposited onto porous electrode substrates. Sintering profiles of films and substrates are matched to the extent that bilayers can be free sintered to a high degree of flatness with no compressive load (or with minimal load). Using these techniques, we have fabricated bilayers having dense electrolyte films of many electrolytes including yttria-stabilized zirconia (YSZ)^{1,7,8,9}, ceria¹⁰, strontium cerate¹⁰, and LSCF. Colloidal deposition is a flexible process in that a wide variety of materials can be deposited as thin films with no (or minimal) alterations to fabrication equipment. Further, only small amounts of material are needed for bilayer fabrication making this approach suitable for novel or expensive conductors. Thin-film solid oxide fuel cells (SOFCs) fabricated using these techniques have demonstrated exceptional performance at reduced temperatures relative to conventional thick-film SOFCs.

EXPERIMENTAL

Porous Substrate: Yttria-stabilized zirconia (YSZ) powders were obtained from Tosoh Corporation and nickel oxide powders (NiO) from J.T. Baker Inc. Ceria powders, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.8}$ (CGO), were supplied by NexTech Materials, 720 Lakeview Plaza Blvd., Worthington, OH, 43085. The substrate mixture containing approximately 45 w/o electrolyte (YSZ or CGO), 45 w/o NiO and a 10 w/o pore former (cornstarch) was attritor milled in acetone. The finely ground mixture was then dried, re-ground using a mortar and pestle, and sieved to $<100\ \mu\text{m}$. Samples were weighed out and pressed in a 3.81 cm diameter steel die. The green disks were then heated and held at the decomposition temperature of the pore former for 1 hour to ensure complete burnout of the cornstarch. The green disks were then partially fired to a green body strong enough to be handled for electrolyte deposition. Porous ceria or YSZ substrates were made in a similar manner, without NiO additions.

Thin-film Electrolyte: Electrolyte powders were obtained commercially (YSZ from Tosoh Corporation, CGO from NexTech Materials) or prepared by the glycine nitrate combustion process¹¹. Electrolyte powders were dispersed in isopropanol with an ultrasonic probe and applied to the anode substrate. To avoid cracking of the thin film or warping of the substrate due to the 2D confinement of the film during sintering, the shrinkage of the substrate was carefully matched to that of the electrolyte. The electrolyte/electrode bilayer was fired at 1400-1500°C to fully densify the electrolyte film.

Cathode: Cathode powders of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.98}\text{Ni}_{0.02}\text{O}_3$ (LSCN) and $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM) powders were prepared by the glycine nitrate process using a glycine to nitrate ratio of 0.5. These were mixed with the electrolyte material in approximately 50/50 weight percent ratio and applied to a 1 cm^2 masked off area of the bilayer. The structure was then fired at 1000-1250°C.

Current Collectors: Platinum paste (Heraeus OS3) was applied to both anode and cathode and fired to 950°C for 30 min. Platinum screens were then applied to the electrodes and bonded using Pt paste; Pt wires were spot-welded to these screens.

Cell Test Rig: The thin-film cell was sealed to the end of an alumina tube with Aremco cement. A type K thermocouple was fixed at the surface of the cathode current collector to obtain accurate fuel cell temperatures as a function of furnace temperature and current density during fuel cell operation. Hydrogen gas was saturated with water vapor at room temperature. Fuel cell temperature was monitored and controlled remotely through software written at LBNL.

Electrical Measurements: A high current galvanostat/potentiostat (PAR 371) was controlled by the use of an external voltage signal generated by software written in our lab using LabVIEW by National Instruments. This software allows current to be incremented monotonically for defined time increments as determined by the user. The program also automates current interrupt measurements across a cell with or without reference electrodes. Typically, currents were increased in 50 mA increments and the experiment was terminated when the cell potential dropped below 0.1 volt. The current interrupt method was used to separate the ohmic losses across the cell from other polarization losses. The interrupt current was typically greater than 750 mA/cm^2 and a minimum of two current interrupts were performed at each temperature.

RESULTS AND DISCUSSION

Thin Ceramic Films: Thin films of oxygen conductors (YSZ), mixed conductors (CGO, LSCF), and proton conductors (SrZrO_3) were successfully fabricated on porous substrates. A SEM micrograph of the fracture surface of a YSZ thin-film on a porous Ni-YSZ substrate is shown in Figure 1. The sample is at slight tilt so the top surface of the YSZ film can be seen along with the edge of the film and a portion of the porous substrate. Since the electrolyte is cofired onto the electrode, intimate bonding of electrode and electrolyte occurs leading to very low polarization of the bilayer under current load^{1,10}. In Figure 2 the fracture surface of a CGO thin film on a porous Ni-Ceria substrate is shown. Thin films of $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ were also successfully fabricated and the SEM micrographs of fracture surfaces of these films are shown in Figures 3 and 4.

Cell Performance: The performance of cells (porous substrate/electrolyte/ cathode) were evaluated under current control using flowing $H_2 + 3$ volume percent H_2O at the anode and static air at the cathode. Figure 5 shows the open circuit voltage of three different electrolyte systems. Figure 6 shows the current-voltage (i - V) curves for single cells of YSZ tested at $800^\circ C$ and of CGO at $750^\circ C$. The performance of a thin-film Ni-YSZ/YSZ/LSM-YSZ fuel cell over the intermediate temperature range of 650 - $800^\circ C$ is shown in Figure 7. As can be seen from the power density curves, the cell achieves a maximum power output of close to 2 watts/cm^2 at $800^\circ C$. The performance of thin-film cells having LSM-YSZ cathodes is a strong function of temperature, due to polarization of the air electrode at temperatures below $800^\circ C$. Mechanical integrity of YSZ thin films has been demonstrated by fuel cell tests lasting 1000's of hours at $800^\circ C$. Thin-film ceria based fuel cells also demonstrate excellent performance. In figure 8 the observed power density for a Ni-CGO/CGO/LSCN-CGO thin-film fuel cell is shown as a function of operating temperature. As can be seen from figure 8, thin-film ceria based cells achieve peak power densities of over 650 mW/cm^2 at $750^\circ C$ and close to 300 mW/cm^2 at $600^\circ C$.

Figure 9 shows the fracture surface of a $SrZr_{0.95}Y_{0.05}O_3$ thin film fuel cell after testing. Though the open circuit voltages (OCVs) were high the initial test performance of these proton conductors has been poor and the large resistive loss is attributed to a reaction layer between the electrolyte and cathode.

Voltage Losses: Due to the constraints of thin-film fuel cell geometry, only one reference electrode can be used in electrochemical testing (Figure 10). The use of a reference electrode allows separation of voltage losses into contributions from the anode and electrolyte/cathode components of the cell. For thin film cells tested in our laboratory at $800^\circ C$ the ohmic resistance across the entire thin-film cell measured by current interrupt is typically in the range of 0.05 to $0.20 \text{ }\Omega\text{cm}^2$ dependent on the electrolyte. The cell resistance across a fuel cell is shown in Figure 11. The exceptionally low values for the area specific resistance (ASR) observed for thin-film fuel cells also highlights the impact of resistive interfaces in SOFCs due to interface instability and/or poor electrode processing. For state-of-the-art planar SOFCs where the YSZ electrolyte is about $200 \text{ }\mu\text{m}$ in thickness, values of the ASR are typically in the range of 0.8 to $1 \text{ }\Omega\text{cm}^2$ at $950^\circ C$. Remarkably, at operating temperatures $150^\circ C$ lower than for thick-film cells, thin-film fuel cells exhibit almost an order of magnitude improvement in ASR. Notably, deterioration in the ASR for thick-film cells of 0.05 to $0.2 \text{ }\Omega\text{cm}^2$ would result in degradation of performance by 6 to 20%. However, this increase in ASR for a thin-film cell would effectively double the ASR and half the thin-film cell performance. In other words, as the electrolyte thickness in a SOFC is reduced to zero, ohmic losses across the electrolyte vanish, and interface/contact resistance and electrode polarization limit cell performance. Clearly, to attain and maintain high levels of performance in thin-film SOFCs, critical attention must be paid to electrode microstructure and processing in order to preclude formation of resistive interfaces.

Improving Device Performance: At $800^\circ C$ YSZ thin film cells demonstrated excellent performance, achieving power densities of 800 mW/cm^2 at 0.8 volts and exhibiting maximum power densities of close to 2000 mW/cm^2 . However, as can be seen in Figure 12, the ohmic drop (as measured by current interrupt) across the cell increased rapidly below $800^\circ C$ compared with

ceria electrolyte based cells. Improvement of the low temperature performance of YSZ based cells could be accomplished by replacing the LSM electrode with a cathode having better low temperature oxygen reduction kinetics such as LSC. In this case, a reaction barrier such as a 1 μm layer of ceria might be necessary between the YSZ and LSC to prevent the formation of a resistive interface through chemical reaction. As can be seen from Figure 12, thin film ceria based cells have very low resistive losses. Still, in order to attain power densities greater than 650 mW/cm^2 (at 750°C) it might be necessary to reduce voltage losses due to electronic conductivity in the ceria electrolyte. This could be accomplished by either choosing a dopant composition that reduces the electronic conductivity of the ceria electrolyte, or by depositing a very thin (<1 μm) layer of YSZ to block electronic transport.

Table 1 - Summary of Systems Investigated

THIN FILM	SUBSTRATE	CATHODE
YSZ*	YSZ-NiO*	LSM-YSZ*
YSZ	Ce _{0.8} Gd _{0.2} O ₂ -NiO	LSCN-CGO LSCN-CGO
Ce _{0.9} Y _{0.1} O ₂ Ce _{0.8} Gd _{0.2} O ₂ *	Ce _{0.9} Y _{0.1} O ₂ -NiO Ce _{0.8} Gd _{0.2} O ₂ -NiO*	LSM- CYO LSCN-CGO*
Ce _{0.85} Sm _{0.15} O ₂ *	Ce _{0.9} Y _{0.1} O ₂ -NiO Ce _{0.85} Sm _{0.15} O ₂ -NiO* Ce _{0.85} Sm _{0.15} O ₂ -NiO*	LSCF-CGO LSCN-CGO* LSM-CSO*
SrCe _{0.9} Y _{0.1} O ₃ SrZr _{0.95} Y _{0.05} O ₃	Ce _{0.8} Gd _{0.2} O ₂ -NiO Ce _{0.85} Sm _{0.15} O ₂ -NiO YSZ-NiO	LSCN-SrCeYO LSM-SrZrYO
La _{0.8} Sr _{0.2} Co _{0.8} Fe _{0.2} O ₃	Ce _{0.85} Sm _{0.15} O ₂	
LaSrGa ₃ O ₇ (note: reacted with Ni)	YSZ-NiO with ceria barrier layer	

*Denotes systems that exceeded 500 mW/cm^2

CONCLUSIONS

The broad application of bi-layer fabrication by colloidal techniques has been demonstrated by making and testing several ionic and mixed ionic-electronic ceramic thin film devices. Systems investigated are summarized in Table 1. Thin film SOFCs fabricated using these techniques demonstrate excellent performance; YSZ based cells have achieved maximum power densities of close to 2000 mW/cm^2 at 800°C and CGO based cells have achieved power densities above 650 mW/cm^2 at 750°C. Current interrupt techniques indicate that the majority of the efficiency loss is due to ohmic losses associated with the cathode or cathode/electrolyte interface resistance. The goal of improving fuel cell performance at lowered temperatures by reducing the electrolyte thickness has been realized. Electrochemical characterization of the thin film fuel cells has indicated that ohmic drop across the electrolyte layer is almost negligible. Clearly, limitations to performance have been shifted from the electrolyte to interfacial and charge transfer resistance as well as mass transfer polarization at high current densities. Improved performance of thin film SOFCs, particularly at further reduced temperatures, will be

accomplished through systematic studies of alternative cathode materials and electrode microstructures.

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FIGURES

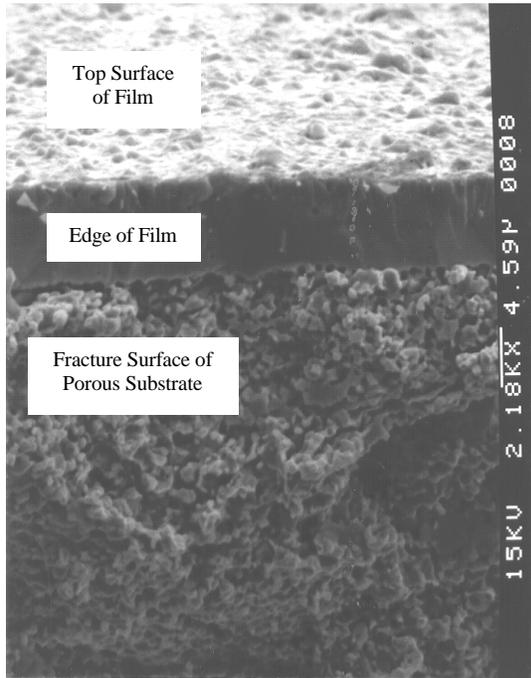


Figure 1. 7 μm YSZ on Ni-YSZ Substrate

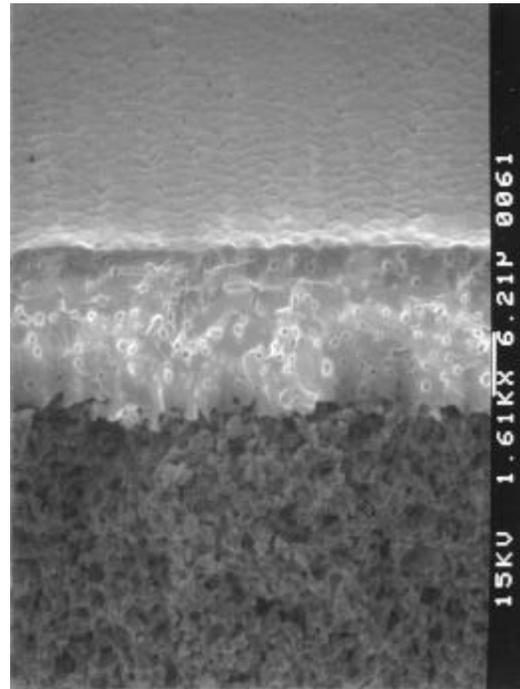


Figure 2. 15 μm CGO on Ni-Ceria Substrate

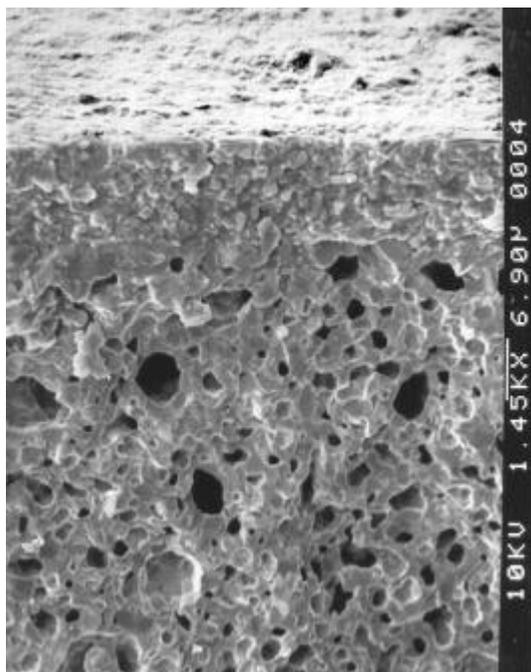


Figure 3. 10 μm SrZr_{0.95}Y_{0.05}O₃ on NiO-ceria.

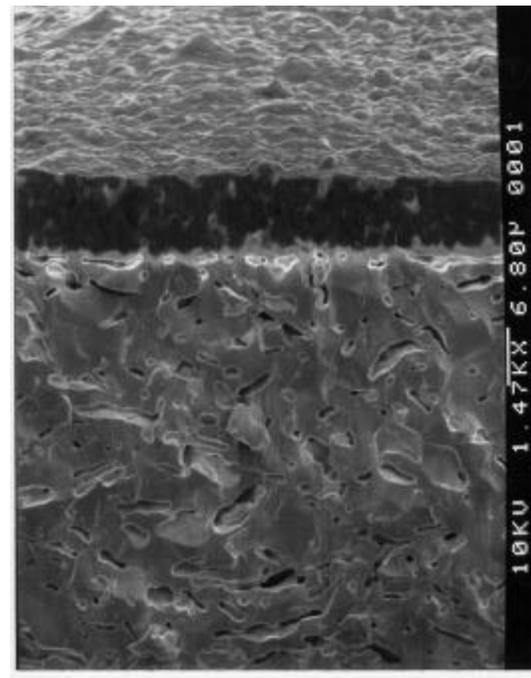


Figure 4. 8 μm La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-δ} on ceria.

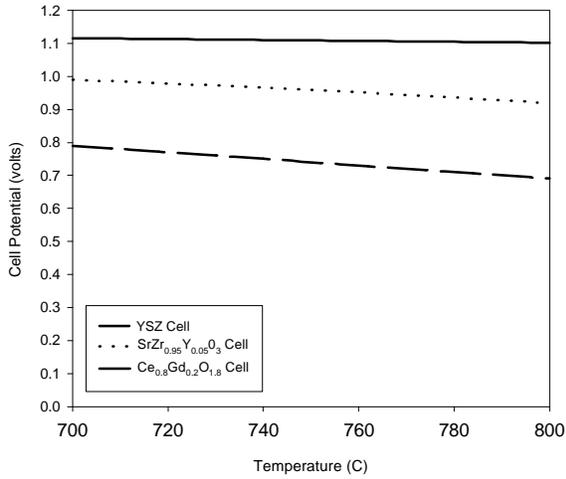


Figure 5. Open circuit potentials of three electrolyte cells in air/ $H_2 + 3 \text{ v/o } H_2O$.

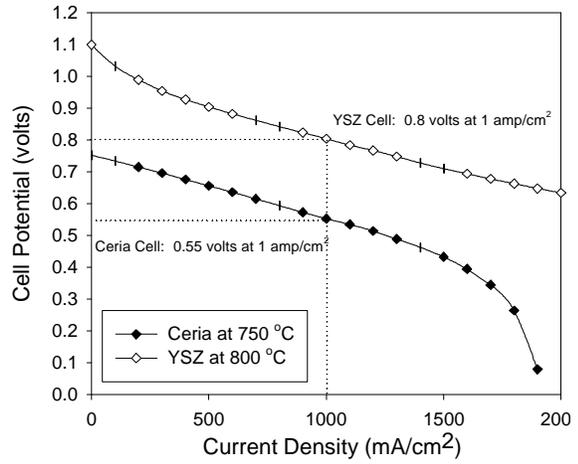


Figure 6. i - V characteristics of YSZ and CGO cells (air/cathode/electrolyte/anode/ $H_2 + 3 \text{ v/o } H_2O$).

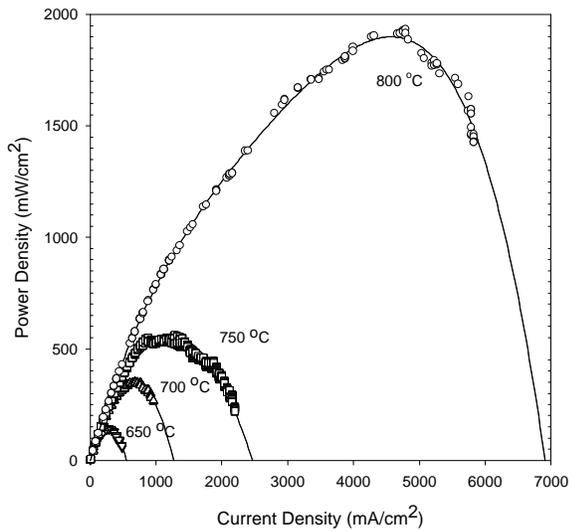


Figure 7. Performance of thin-film Ni-YSZ/YSZ/LSM-YSZ fuel cell as a function of cell temperature.

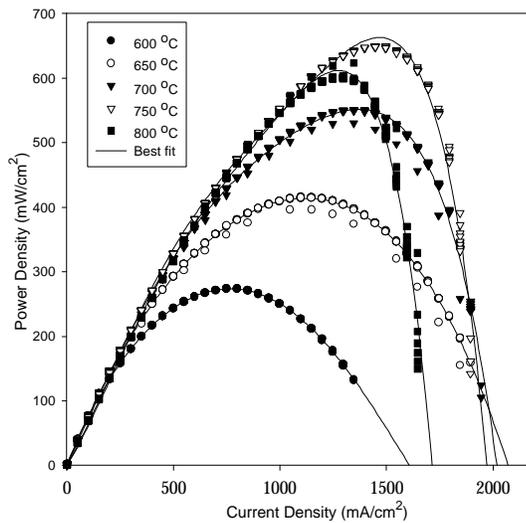


Figure 8. Performance of thin-film ceria cell as a function of temperature.

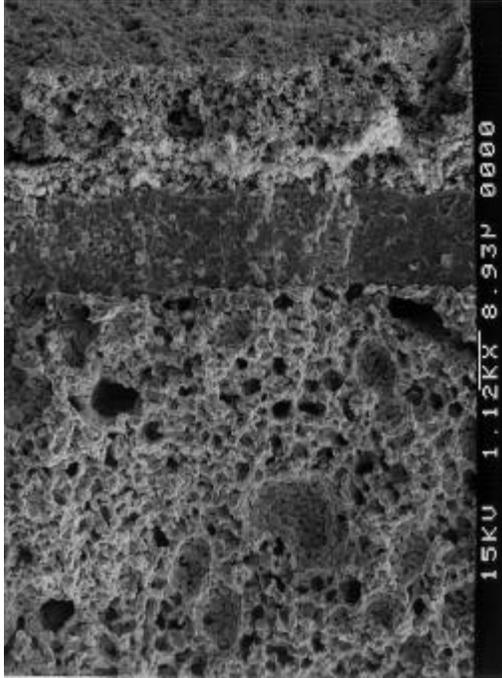


Figure 9. $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_3$ fuel cell with LSCN cathode after testing.

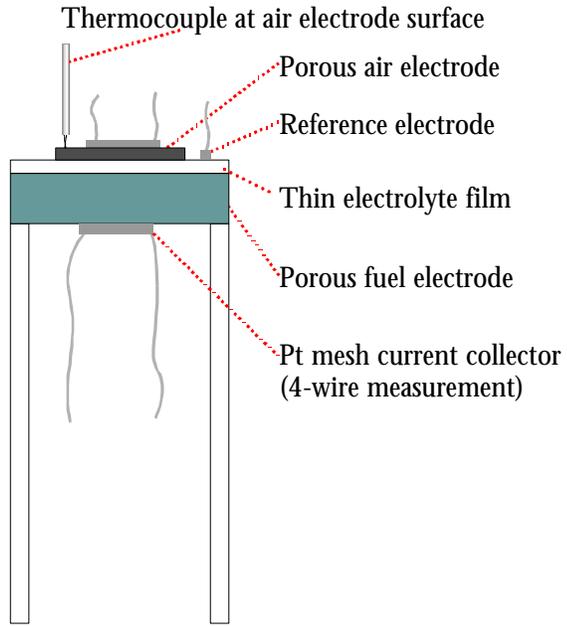


Figure 10. Location of reference electrode in cell geometry

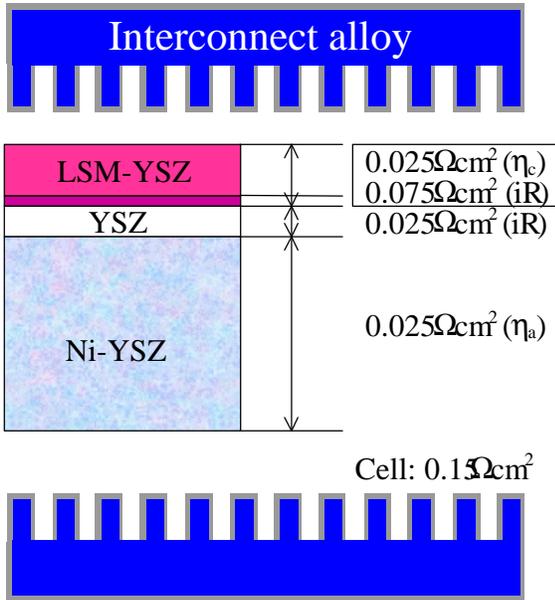


Figure 11. Importance of low resistance interconnect for thin-film SOFC

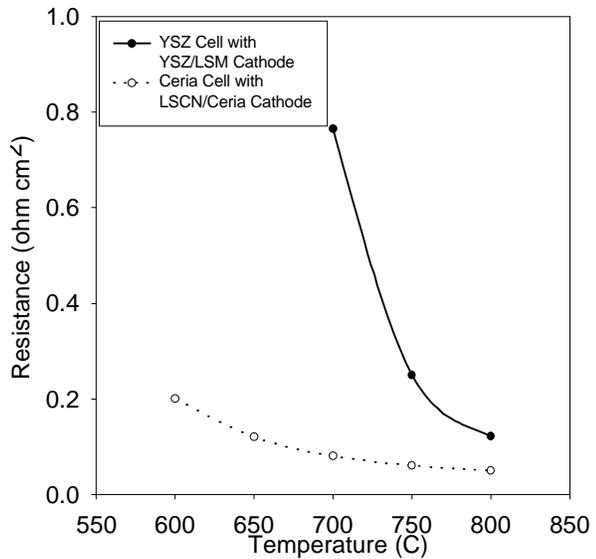


Figure 12. Total ohmic drop (iR) of YSZ cell with LSM/YSZ cathode and of CGO cell with LSCN/CGO cathode.