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**LOW-TEMPERATURE, ANODE-SUPPORTED HIGH POWER
DENSITY SOLID OXIDE FUEL CELLS WITH NANOSTRUCTURED
ELECTRODES**

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ABSTRACT

This report summarizes the work done during the entire project period, between October 1, 1999 and March 31, 2003, which includes a six-month no-cost extension. During the project, eight research papers have, either been, published, accepted for publication, or submitted for publication. In addition, several presentations have been made in technical meetings and workshops. The titles of the papers that have been published based on this project are listed below.

- 1) "Synthesis of Nanosize Yttria-Stabilized Zirconia by a Molecular Decomposition Process", Y. Jiang, S. V. Bhide and A. V. Virkar, *J. of Solid State Chem.*, **157** 149-159 (2001).
- 2) "The Effect of Testing Geometry on the Measurement of Cell Performance in Anode-Supported Solid Oxide Fuel Cells", Y. Jiang, A. V. Virkar, and F. Zhao, *J. Electrochem. Soc.*, **148** [10] A1091-A1099 (2001).
- 3) "The Effect of Electrode Microstructure on Cathodic Polarization", F. Zhao, Y. Jiang, G-Y. Lin, and A. V. Virkar, in SOFC-VII, edited by S. C. Singhal and H. Yokokawa, The Electrochemical Society, Pennington, NJ (2001).
- 4) "A High Performance, Anode-Supported Solid Oxide Fuel Cell Operating on Direct Alcohol", Y. Jiang and A. V. Virkar, *J. Electrochem. Soc.*, **148** [7] A701-A709 (2001).
- 5) "Performance of Solid Oxide Fuel Cells with LSGM-LSM Composite Cathodes", T. J. Armstrong and A. V. Virkar, *J. Electrochem. Soc.*, **149** [12] A1565-A1571 (2002).
- 6) "Reduction and Re-Oxidation Kinetics of Nickel-Based Solid Oxide Fuel Cell (SOFC) Anodes", N. M. Tikekar, T. J. Armstrong, and A. V. Virkar, in SOFC-VIII, edited by S. C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ (2003).
- 7) "Measurement of O₂-N₂ Effective Diffusivity in Porous Media at High Temperatures using an Electrochemical Cell", F. Zhao, T. J. Armstrong, and A. V. Virkar, *J. Electrochem. Soc.*, **150** [3] A249-A256 (2003).
- 8) "Fuel Composition and Diluent Effect on Gas Transport and Performance of Anode-Supported SOFCs", Y. Jiang and A. V. Virkar, *J. Electrochem. Soc.*, **150** [7] (2003).

The project also has provided support for four graduate students working towards advanced degrees. The principal technical objective of the project was to analyze the role of electrode microstructure on solid oxide fuel cell performance. Prior theoretical work conducted in our laboratory demonstrated that the particle size of composite electrodes has a profound effect on cell performance; the finer the particle size, the lower the activation polarization, the better the performance. The composite cathodes examined consisted of electronically conducting perovskites such as Sr-doped LaMnO₃ (LSM) or Sr-doped LaCoO₃ (LSC), which is also a mixed conductor, as the electrocatalyst, and yttria-stabilized zirconia (YSZ) or rare earth oxide doped CeO₂ as the ionic conductor. The composite anodes examined were mixtures of Ni and YSZ. A procedure was developed for the synthesis of nanosize YSZ by molecular decomposition, in which unwanted species were removed by leaching, leaving behind nanosize YSZ. Anode-supported cells were made using the as-synthesized powders, or using commercially acquired powders. The electrolyte was usually a thin (~10 microns), dense layer of YSZ, supported on a thick (~1 mm), porous Ni + YSZ anode. The cathode was a porous mixture of electrocatalyst and an ionic conductor. Most of the cell testing was done at 800°C with hydrogen as fuel and air as the oxidant. Maximum power densities as high as 1.8 W/cm²

were demonstrated. Polarization behavior of the cells was theoretically analyzed. A limited amount of cell testing was done using liquid hydrocarbon fuels where reforming was achieved internally.

Significant polarization losses also occur at the anode, especially at high fuel utilizations. An analysis of polarization losses requires that various contributions are isolated, and their dependence on pertinent parameters is quantitatively described. An investigation of fuel composition on gas transport through porous anodes was investigated and the role of fuel diluents was explored. This work showed that the molecular weight of the diluent has a significant effect on anode concentration polarization. This further showed that the presence of some molecular hydrogen is necessary to minimize polarization losses.

Theoretical analysis has shown that the electrode microstructure has a profound effect on cell performance. In a series of experiments, cathode microstructural parameters were varied, without altering other parameters. Cathode microstructural parameters, especially three phase boundary (TPB) length, were estimated using techniques in quantitative stereology. Cell performance was quantitatively correlated with the relevant microstructural parameters, and charge transfer resistivity was explicitly evaluated. This is the first time that a fundamental parameter, which governs the activation polarization, has been quantitatively determined.

An important parameter, which governs the cathodic activation polarization, and thus cell performance, is the ionic conductivity of the composite cathode. The traditional composite cathode is a mixture of LSM and YSZ. It is well known that Sr and Mg-doped LaGaO_3 (LSGM), exhibits higher oxygen ion conductivity compared to YSZ. Cells were fabricated with composite cathodes comprising a mixture of LSM and LSGM. Studies demonstrated that LSGM-based composite cathodes exhibit excellent behavior.

Studies have shown that $\text{Ni} + \text{YSZ}$ is an excellent anode. In fact, in most cells, the principal polarization losses, at least at low fuel utilizations, are associated with the cathode. Theoretical analysis conducted in our group has also shown that anode-supported cells exhibit lower polarization losses compared to cathode-supported or electrolyte-supported cells. It is essential, however, that $\text{Ni} + \text{YSZ}$ anode be not subjected to a re-oxidation step, such as may occur accidentally, as this can cause anode disintegration. A theoretical model was developed for reduction and re-oxidation kinetics of Ni-based anodes. The model was experimentally verified. In addition, criteria for the development of redox tolerant, yet Ni-based, anodes were established.

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INTRODUCTION

Research over the past few years has shown that in thin-film, electrode-supported solid oxide fuel cells (SOFC), significant part of the polarization losses are associated with the cathode, where the reaction of oxygen reduction to oxygen ions occurs. Substantial losses can also occur at the anode. Theoretical work has shown that electrode polarization can be minimized provided the electrodes have adequate porosity to allow rapid transport of gaseous species, and the electrodes exhibit mixed ionic electronic conducting (MIEC) characteristics. In a typical SOFC, the anode is a porous cermet of Ni and yttria-stabilized zirconia (YSZ). In such an anode, MIEC characteristics arise due to electronic conduction through Ni and ionic conduction through YSZ. For several years, the material of choice for the cathode has been Sr-doped LaMnO_3 (LSM). While LSM is good electronic conductor, its ionic conductivity is poor. In order to improve its performance, it is necessary to impart MIEC characteristics. This can be achieved by mixing LSM with YSZ. There are other perovskites, which can exhibit MIEC characteristics in a single-phase material. An example is Sr-doped LaCoO_3 (LSC). Experience shows, however, that the addition of an ionic conductor, such as ceria, to LSC improves the performance further.

Theoretical work conducted in our laboratory has shown that electrode microstructure has a profound effect on polarization. Specifically, the finer the microstructure, the lower the polarization resistance. A natural extension of the concept leads to the conclusion that ideally the electrode microstructure should be on a nanometer scale. Thus, the first step is the synthesis of nanosize powders of the prospective electrode materials. During the course of this work, a method for the synthesis of nanosize powders of zirconia and ceria was developed. The approach led to the synthesis of powders of size between 5 and 10 nm. However, making well-dispersed, agglomerate-free composite electrodes is a major challenge. In addition, the nanosize powders invariably coarsen at the cell operating temperature. Despite this, significant benefit can still be gained as long as the electrode microstructure is on a submicron scale – if not at the nanometer scale. Experimental work conducted during the course of this project confirmed the validity of this hypothesis.

Characterization of the polarization behavior in thin-film, electrode-supported fuel cells is difficult for two reasons. (1) In small cells, one of the electrodes (the thinner one) is usually of an area smaller than that of the thicker, supporting electrode, necessitated by difficulties in testing procedures. Research done, both theoretical and experimental, showed that as long as the diameter of the smaller electrode is much greater than the electrolyte thickness, the error introduced is relatively modest – and can be easily corrected for. (2) The second factor concerns the placement of reference electrodes in thin film, electrode-supported cells. Some numerical work on the mapping of equipotential lines and flux lines through thin film cells has shown that substantial errors can be introduced in the measurement of overpotentials. These studies recommend that reference electrodes, as such, should not be used. Despite this recommendation, reference electrodes were used in the present work in selected cases, especially when only one of the parameters was varied. Work is currently underway to conduct additional numerical analysis for the geometries used in the present work.

Most of the work reported on cathode polarization measurements has been on porous cathode materials screen-printed on the surface of an electrolyte disc, and then using techniques such as complex impedance spectroscopy, or techniques involving the application of a DC bias. The measurements are rarely related to the microstructural parameters in order to isolate the fundamental, microstructure-independent parameter. Experimental approach was used to explicitly determine the charge transfer resistivity, assuming that the electrochemical reaction occurs at three-phase boundaries (TPB) between the electrocatalyst, electrolyte and the gas phase.

An important contribution to the total polarization arises due to the resistance associated with the transport of gases through porous electrodes, oxidant through the cathode and fuel through the anode. Often, impedance spectroscopy has been used. The approach involves the use of an equivalent circuit approach – such as the Warburg impedance. However, such an approach does not lend itself to relating polarization losses to fundamental transport parameters, such as binary and Knudsen diffusivities, and to microstructural parameters – such as porosity and tortuosity. An approach chosen here involves solving the relevant transport equations, and conducting out of cell (and in-cell) measurements to explicitly determine concentration polarization. Using such an approach, concentration polarization behavior was investigated at both the cathode and the anode.

EXECUTIVE SUMMARY

Nanosize yttria-stabilized zirconia (YSZ) was synthesized by a novel approach based on molecular decomposition. Precursors, yttria-doped BaZrO_3 (Y- BaZrO_3) and yttria-doped Na_2ZrO_3 (Y- Na_2ZrO_3), were boiled in dilute HNO_3 or water, respectively, to leach away the unwanted species, BaO or Na_2O , resulting in the formation of nanosize YSZ, of a particle size on the order of 5 nm. Even when the powder was heated to as high as 1000°C , the particle size was well in the nanosize range, indicating suitability for application as an electrolyte or electrodes.

A simple, approximate analysis of the effect of differing cathode and anode areas on the measurement of cell performance on anode-supported solid oxide fuel cells, wherein the cathode area is smaller than the anode area, was developed. It was shown that the effect of cathode area on cathode polarization, on electrolyte contribution, and on anode resistance, as normalized on the basis of the cathode area, is negligible. There is a small but measurable effect on anode polarization, which results from concentration polarization. Effectively, it is the result of a greater amount of fuel transported to the anode/electrolyte interface in cases wherein the anode area is larger than the cathode area. Experiments were performed on cells made with differing cathode areas and geometries. Cathodic and anodic overpotentials measured using reference electrodes, and the measured ohmic area specific resistances by current interruption, were in good agreement with expectations based on the analysis presented. At 800°C , the maximum power density measured with a cathode area of $\sim 1.1 \text{ cm}^2$ was $\sim 1.65 \text{ W/cm}^2$ compared to $\sim 1.45 \text{ W/cm}^2$ for cathode area of $\sim 2 \text{ cm}^2$, for anode thickness of $\sim 1.3 \text{ mm}$, with hydrogen as the fuel and air as the oxidant. At 750°C , the measured maximum power densities were $\sim 1.3 \text{ W/cm}^2$ for the cell with a cathode area $\sim 1.1 \text{ cm}^2$, and $\sim 1.25 \text{ W/cm}^2$ for the cell with a cathode area $\sim 2 \text{ cm}^2$.

Ni + yttria-stabilized zirconia (YSZ)-anode-supported cells with a thin YSZ electrolyte and Sr-doped LaMnO_3 (LSM) + YSZ composite cathode were fabricated. Volume fractions of LSM and YSZ in the composite cathode were varied over a wide range. Cell performance was measured at 800°C with hydrogen as fuel and air as oxidant. Cathode microstructures were characterized by quantitative stereology to estimate the three-phase boundary (TPB) length, porosity and the aggregate grain size of YSZ in the cathode. Measured polarization was correlated with microstructure. Experimental results are in good agreement with the previously published theoretical model. The intrinsic charge transfer resistivity, ρ_{ct} , at LSM/YSZ/air TPB was determined as $\sim 1.0 \times 10^5 \text{ } \Omega\text{cm}$ at 800°C .

Since LSGM is known to exhibit higher ionic conductivity compared to YSZ, it was chosen as a prospective material for composite cathodes. The relative proportions of LSGM and LSM were varied between 30 wt.% LSGM + 70 wt.% LSM and 70 wt.% LSGM + 30 wt.% LSM, while the firing temperature was varied between 1000 and 1200°C . The cathode interlayer composition had a profound effect on cathode performance at 800°C with overpotentials ranging between 60 and 425 mV at 1.0 A/cm^2 and exhibiting a minimum for 50 wt.% LSGM + 50 wt.% LSM. The cathodic overpotential decreased with increasing firing temperature of the composite interlayer in the range $1000 \leq T \leq 1150^\circ\text{C}$, and then increased dramatically for the interlayer fired at 1200°C . The cell with the optimized cathode interlayer of 50 wt.% LSM + 50

wt.% LSGM fired at 1150°C exhibited an area specific cell resistance of 0.18 Ωcm^2 and a maximum power density of 1.4 W/cm² at 800°C. Chemical analysis revealed that LSGM reacts with YSZ above 1000°C to form the pyrochlore phase, La₂Zr₂O₇. The formation of the pyrochlore phase at the interface between the LSGM/LSM composite cathode and the YSZ electrolyte limits the firing time and temperature of the cathode interlayer.

Anode-supported cells were operated directly on pure methanol and on an equi-volume mixture of ethanol and water over a range of temperatures. Power density achieved with methanol was between 0.6 W/cm² at 650°C and 1.3 W/cm² at 800°C, and with ethanol + water between 0.3 W/cm² at 650°C and 0.8 W/cm² at 800°C. Results were compared with tests on humidified hydrogen as a fuel. No carbon deposition on Ni-YSZ anode was observed with either methanol or an equi-volume solution of ethanol and water as fuels. Differences in performance with different fuels were attributed to differences in anode polarization.

Reduction and re-oxidation kinetics of Ni-based anodes were investigated over a range of temperatures between 650 and 800°C. The experimental part of the investigation consisted of first fabricating NiO + YSZ two-phase composites of essentially full density. The fully dense samples were subsequently reduced in a hydrogen-containing environment. The reduced layer thickness was measured as a function of time at temperature. Some of the samples were reduced for a time long enough to ensure that they were fully reduced. Subsequently, the reduced samples were re-oxidized in air at various temperatures, ranging between 650 and 800°C. In this set of experiments, the re-oxidized layer thickness was measured as a function of time at temperature. These two types of experiments were used for determining the kinetics of reduction as well as that of re-oxidation. It was observed that the reduction kinetics was linear (interface-controlled), while the re-oxidation kinetics was parabolic (diffusion-controlled). A simple theoretical analysis was conducted to describe the two processes. The interface control of the reduction process was attributed to the rapid gaseous transport through the pores formed upon reduction of NiO to Ni. By contrast, diffusion control for the re-oxidation process was attributed to the existence of a very small amount of porosity that forms when Ni re-oxidizes to NiO, which occurs due presumably to a slight shape change of Ni particles.

Anode-supported solid oxide fuel cells with Ni + yttria-stabilized zirconia (YSZ) anode, YSZ-samarium-doped ceria (SDC) bi-layer electrolyte and Sr-doped LaCoO₃ (LSC) + SDC cathode were fabricated. Fuel used consisted of H₂ diluted with He, N₂, H₂O or CO₂, mixtures of H₂ and CO, and mixtures of CO and CO₂. Cell performance was measured at 800°C with above-mentioned fuel gas mixtures and air as oxidant. For a given concentration of the diluent, the cell performance was higher with He as the diluent than with N₂ as the diluent. Mass transport through porous Ni-YSZ anode for H₂-H₂O, CO-CO₂ binary systems and H₂-H₂O-diluent gas ternary systems was analyzed using multi-component gas diffusion theory. At high concentrations of the diluent, the maximum achievable current density was limited by the anodic concentration polarization. From this measured limiting current density, the corresponding effective gas diffusivity was estimated. Highest effective diffusivity was estimated for fuel gas mixtures containing H₂-H₂O-He mixtures (~0.55 cm²/s), and the lowest for CO-CO₂ mixtures (~0.07 cm²/s). The lowest performance was observed with CO-CO₂ mixture as a fuel, which in part was attributed to the lowest effective diffusivity of the fuels tested, and higher activation polarization.

EXPERIMENTAL

Nanosize YSZ Powder Synthesis:

For the synthesis of nanosize yttria-stabilized zirconia by the present method, the precursor can be a suitable alkali or an alkaline earth zirconate. Two types of precursors, namely, yttria-doped barium zirconate, (Y-BaZrO₃), and yttria-doped sodium zirconate, (Y-Na₂ZrO₃), were synthesized by a conventional solid state reaction method. For preparing Y-BaZrO₃, the starting materials, namely, BaCO₃, ZrO₂ and Y₂O₃, or BaCO₃ and a commercial yttria-stabilized zirconia (YSZ) powder, were mixed in requisite proportions, wet ball-milled in alcohol for 24 h and then dried. For the synthesis of Y-Na₂ZrO₃, Na₂CO₃ and commercial YSZ powder were mixed in requisite proportion, wet ball-milled and then dried. The ball-milled and dried powder mixtures were calcined at various temperatures and the resulting powders were examined by x-ray diffraction (XRD) with CuK α radiation to identify calcination conditions which ensured the formation of completely converted, single phase, precursor powders; i.e., Y-BaZrO₃ or Y-Na₂ZrO₃.

Doped sodium zirconate was then boiled and washed in de-ionized water since the reaction between Na₂ZrO₃ and water is thermodynamically favored. In this way, Na₂O can be easily leached out. To ensure the complete removal of Na₂O, the powder was continuously washed until the pH of the solution was near neutral (~7). Then, the resulting powder was dried and later characterized. The Gibbs free energy change for the reaction of barium zirconate with water at or near room temperature is close to zero [1] indicating that BaZrO₃ is thermodynamically stable in the presence of water. Thus, water is not a suitable leaching agent for BaZrO₃. A dilute acid solution is necessary to facilitate the removal of BaO from barium zirconate. Y-doped barium zirconate was boiled in dilute HNO₃ acid (0.07M) repeatedly until no further change in pH of the solution occurred. Then, the powder was thoroughly washed with de-ionized water and dried. In both cases, the leaching solution as well as the as-synthesized powder, were chemically analyzed using Inductively Coupled Plasma (ICP) technique. For the analysis of the as-synthesized YSZ powder by ICP, samples were dissolved in concentrated HCl. The as-synthesized powders were also examined by XRD with CuK α radiation. The objective was to determine the crystal structure and to estimate the particle size by line broadening. Specific surface area was measured by Brunauer-Emmett-Teller (BET) adsorption isotherm using nitrogen gas.

Raman spectra were obtained to determine the crystallographic polymorph of the YSZ formed with an Ar plasma laser (Spectra-Physics, Model 2580) and a 0.6 m triple spectrometer (Spex. Industries, Inc., Model 1877). The spectrometer was calibrated using Ar laser plasma lines. A 488 nm laser was focused on the sample with a beam diameter of 1 mm. The plasma lines were removed from the laser beam using a 10 nm bandpass filter. The spectrometer slit width was adjusted to 20 nm.

One of the samples was also examined under a transmission electron microscope (TEM) to estimate the crystallite size of as-synthesized YSZ using JEOL 4000FX transmission electron microscope.

Differential Thermal Analysis (DTA) was conducted on the as-synthesized YSZ powders. In the DTA experiments, the samples were purged with purified air and heated up to 1200°C at a heating rate of 10°C/min. Based on the DTA information, several temperatures were identified for the calcination of the powders after the leaching treatments. The as-synthesized YSZ powders were subsequently calcined at various temperatures up to a maximum of 1000°C. The calcined powders were further examined by XRD.

Cathode Area Effect:

The following is a simple theoretical analysis of the testing of SOFC of different electrode areas. It is to be emphasized that the exact solution will require numerical analysis, as the actual problem is a three dimensional, mixed boundary value problem with rather complex boundary conditions, which result from the various processes that occur. Specifically, a rigorous solution will need to address: (a) A mixed boundary value problem of electrostatic potential distribution, with cathode/electrolyte interface as well as anode/electrolyte interface exhibiting interface resistances, thus precluding them from being equipotential surfaces. (b) A mixed boundary value problem of gaseous transport through porous electrodes, with similar issues concerning the boundary conditions at the electrode/electrolyte interfaces. (c) A coupling between these two. A rigorous analysis of this problem is a formidable task, even numerically. What is desirable is a simple analytical approach, albeit approximate, which will yield simple analytical expressions that can be succinctly used to describe cell behavior. The analytical results then can be readily verified experimentally to determine the accuracy and the applicability of analytical results. This is the approach followed in the present work.

Figure #1(a) shows a schematic of a cell wherein the cathode diameter is the same as the anode diameter, the preferred testing geometry, but difficult to achieve experimentally. Figure #1(b) is the one often used, and the one in question. Insofar as the anode is concerned, transport of two species through the anode must be examined; transport of electrons (electronic current) through the contiguous Ni, and the transport of gaseous species (e.g. H₂ and H₂O) through the porosity. Transport of electrons, or the electronic current, is determined by solving the Laplace equation in the anode subject to appropriate boundary conditions.

There appear to be three possible ways in which the asymmetry of the cathode and the anode (cathode/electrolyte interface area < anode/electrolyte interface area) may influence the measured cell performance characteristics: (a) Extended region of the electrolyte beyond the periphery of the cathode. (b) Lower electronic resistance of the anode due to the larger anode/fuel gas interface compared to the active anode/electrolyte interface. (c) Lower resistance to gas transport through the anode due to the larger anode/fuel gas interface compared to the active anode/electrolyte interface. These three aspects are discussed in what follows, and approximate analytical relations are developed.

The Effective Electrolyte Extension beyond the Cathode Periphery: One possible consequence of the asymmetry between the cathode and the anode is an extended region in the electrolyte through which ionic current may flow. This is shown schematically in Figure #2 wherein the diameter of the conical region at the electrolyte/anode interface is shown to be somewhat larger than the cathode radius, r_c . Let the radius of the active part of the electrolyte be given by r_o

where $r_o > r_c$. Figure #3 shows an exploded schematic in which the approximate nature of ionic flux distribution through the extended region is shown. Again, an order of magnitude calculation of the ionic resistance of this region (which is an in-plane contribution) can be given by

$$R_{ex} \approx \int_{r_c}^{r_o} \frac{\rho_e dr}{2\pi r l_e} = \frac{\rho_e}{2\pi l_e} \ln\left(\frac{r_o}{r_c}\right) \quad (1)$$

The above is only an order of magnitude estimate since it ignores the fact that the in-plane current through the electrolyte between r_o and r_c is distributed. The distributed nature of the current can be estimated, for example, by, a ladder network approach, which consists of constructing an equivalent circuit of resistive and other circuit elements to represent distributed current. Thus, the above equation overestimates the in-plane resistance. This resistance is for the current between the cathode and the anode, through the extended region of the electrolyte. Note that this resistance is in parallel with the usual electrolyte resistance for the current flowing between the cathode and the anode, through the flat and parallel surfaces. This is simply the electrolyte resistance given by

$$R_{el} = \frac{\rho_e l_e}{\pi r_c^2} \quad (2)$$

Since these resistances are in parallel, the currents flowing through these two are inversely proportional to the respective resistances. Let us estimate the magnitude of the extension assuming for R_{ex} to be about 100 times R_{el} , that is, $R_{ex} \approx 100R_{el}$ and estimate the radius r_o of the extended region; that is, for a correction of $\sim 1\%$. Thus,

$$\ln\left(\frac{r_o}{r_c}\right) \approx 200 \left(\frac{l_e}{r_c}\right)^2 \quad (3)$$

where l_e is the electrolyte thickness. Now $l_e \ll r_c$ for an anode-supported cell with a thin YSZ film as an electrolyte. Thus, the above reduces to

$$r_o - r_c \approx 200 \frac{l_e^2}{r_c} \quad (4)$$

For $r_c = 1$ cm and $l_e = 10$ μ m, it is seen that $(r_o - r_c) \sim 2$ μ m. That is, there is negligible extension of the region in the electrolyte through which an in-plane current can flow. Thus, this effect can be neglected.

Electronic Resistance of the Asymmetric Anode: Figure #4(a) shows a schematic of equipotential lines and flux (electrical) lines. The flux lines are orthogonal to the equipotential lines, within the anode, away from the anode/electrolyte interface. At the anode/electrolyte interface, the flux lines need not meet the interface orthogonally, if a significant interfacial resistance exists (as discussed by Tanner et al. [2]). It is clear, however, that the net current across the anode/external contact is the same as that across active anode/electrolyte interface. Solution to Laplace equation for this geometry will have to be obtained numerically, and is not available analytically. However, as a simplification, we will assume that the net current flows through the conical region shown in Figure #4(b). The net anode electronic resistance then can be determined as follows:

The radius $r(y)$ through which electronic current transports at a cross section at y is given by

$$r(y) = r_a + (r_c - r_a) \frac{y}{l_a} \quad (5)$$

where r_a , r_c and l_a denote the anode radius (in contact with the fuel), the cathode radius, and the anode thickness, respectively. If the anode electronic resistivity is ρ_a , the net anode electronic resistance is given by

$$R_a = \frac{\rho_a}{\pi} \int_0^{l_a} \frac{dy}{r^2(y)} = \frac{\rho_a l_a}{\pi r_a r_c} \quad (6)$$

The electronic resistivity of Ni at 800°C is about $\sim 15 \times 10^{-6} \Omega\text{cm}$ [3]. Assuming the volume fraction of Ni to be about 55%, ρ_a is about $\sim 27 \times 10^{-6} \Omega\text{cm}$. For an anode thickness of 1 mm, a cathode radius of 1 cm, and an anode radius of 2 cm, the anode resistance is estimated to be $\sim 4.3 \times 10^{-7} \Omega$. As the cathode area is π , the area specific resistance of the anode (normalized to the cathode area) is $\sim 1.35 \times 10^{-5} \Omega\text{cm}^2$. This is negligible in comparison to the electrolyte area specific resistance given by $\rho_e l_e \approx 4 \times 10^{-2} \Omega\text{cm}^2$, assuming $\rho_e \approx 40 \Omega\text{cm}$. That is, the overall contribution to the anode resistance due to the asymmetry of the cathode and anode (different diameters) is negligible. It would matter little whether the anode radius is the same as the cathode, or is different. This assumes that the anode radius is not too different from the cathode radius (a difference of within a factor of few, not orders of magnitude different), and the anode is relatively thick.

The preceding estimate assumes that the anode is relatively thick. If the anode is relatively thin, as shown in Figure #4(c), such that $(r_a - r_c) \gg l_a$, then not all of the anode/fuel gas area will be active. Thus, in this case, the active anode radius will not be the actual anode radius, but some effective anode radius, $r_{a(\text{eff})}$, which will be a function of the cathode radius, and the anode thickness, l_a , but not a function of anode radius, r_a . It is expected, based on the dimensional grounds, that

$$r_{a(\text{eff})} \approx r_c + \lambda l_a \quad (7)$$

where λ is a geometric factor. Then, the corresponding anode resistance is given by

$$R_a = \frac{\rho_a}{\pi} \int_0^{l_a} \frac{dy}{r^2(y)} = \frac{\rho_a l_a}{\pi r_{a(\text{eff})} r_c} \quad (8)$$

We will assume λ to be approximately unity in what follows. Experimentally, however, one should be able to estimate λ by fitting to experimental data.

Resistance to Gas Flow through an Asymmetric Anode: Concentration Polarization: Our recent work [4,5] has analyzed the role of both anodic and cathodic concentration polarizations on fuel cell performance. The analysis was based on the use of effective diffusivities and the assumption of negligible viscous flow [6,7]. Under these conditions, it can be shown that the fluxes of H_2 and H_2O through the anode are given by

$$J_{\text{H}_2} = -D_{\text{eff}(a)} \nabla n_{\text{H}_2} = -\frac{D_{\text{eff}(a)}}{k_B T} \nabla p_{\text{H}_2} \quad (9)$$

and

$$J_{H_2O} = -D_{eff(a)} \nabla n_{H_2O} = -\frac{D_{eff(a)}}{k_B T} \nabla p_{H_2O} \quad (10)$$

where n_{H_2} and n_{H_2O} denote the number of H_2 and H_2O molecules per unit volume, respectively, p_{H_2} and p_{H_2O} denote the partial pressures of H_2 and H_2O , respectively, k_B is the Boltzmann's constant, T is the temperature, and $D_{eff(a)}$ is the effective anode diffusivity, which, for hydrogen as a fuel, is given by [6]

$$D_{eff(a)} = \frac{V_v}{\tau} D_{H_2-H_2O} \quad (11)$$

in which V_v is the anode porosity, τ is the tortuosity factor, and $D_{H_2-H_2O}$ is the binary diffusivity.

Now, under steady state conditions,

$$|J_{H_2}| = |J_{H_2O}| = \frac{iN_A}{2F} \quad (12)$$

wherein the fluxes are measured at the anode/electrolyte interface, and so is the current density, which will be on the basis of r_o , which is $\approx r_c$. For the geometry shown in Figure #4(b), the local fluxes of H_2 or H_2O vary from position to position along the y-axis by virtue of the varying cross sectional area. Referring to Figure #4(b), it is readily seen that

$$J_{H_2}(y) \pi r^2(y) = J_{H_2}(0) \pi r_a^2 = J_{H_2}(l_a) \pi r_c^2 \quad (13)$$

where $J_{H_2}(y)$, $J_{H_2}(0)$, and $J_{H_2}(l_a)$ are local flux densities at $y = y$, $y = 0$, and $y = l_a$, respectively.

A simplified, pseudo one-dimensional flux equation leads to

$$\int_{p_{H_2(0)}}^{p_{H_2(l_a)}} dp_{H_2(y)} = -\frac{iN_A k_B T}{2D_{eff(a)} F} \int_0^{l_a} \frac{dy}{\left\{ \frac{r_a}{r_c} + \left(\frac{r_c - r_a}{r_c} \right) \frac{y}{l_a} \right\}^2} \quad (14)$$

which gives

$$p_{H_2(l_a)} = p_{H_2(0)} - \frac{RTl_a}{2FD_{eff(a)}} \left(\frac{r_c}{r_a} \right) i \quad (15)$$

and the anode limiting short circuit current density, i_{as} , is given by

$$i_{as} = \frac{2FD_{eff(a)} p_{H_2(0)}}{RTl_a} \left(\frac{r_a}{r_c} \right) \quad (16)$$

which is the current density at which $p_{H_2(l_a)} \approx 0$. This equation for i_{as} differs from the one given in our earlier work [4,5], which is for symmetric electrodes, by the factor $\left(\frac{r_a}{r_c} \right)$. That is, the anode limiting short circuit current density, as calculated on the basis of the cathode area, is

larger by the above factor. If the anode radius, r_a , is much greater than the cathode radius, r_c , in relation to thickness (Figure #4(c)), then r_a from equation (16) is to be replaced by $r_{a(eff)}$ from equation (7). In such a case, the i_{as} is given by

$$i_{as} = \frac{2FD_{eff(a)}p_{H_2(0)}}{RTl_a} \left(\frac{r_{a(eff)}}{r_c} \right) \quad (17)$$

Our prior work has shown that the anodic concentration polarization is given by [4,5]

$$\eta_{conc(a)} = -\frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}} \right) + \frac{RT}{2F} \ln \left(1 + \frac{p_{H_2(0)}}{p_{H_2O(0)}} \frac{i}{i_{as}} \right) \quad (18)$$

or, substituting for the i_{as}

$$\eta_{conc(a)} = -\frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}} \right) + \frac{RT}{2F} \ln \left(1 + \frac{RTl_a}{2FD_{eff(a)}} \left(\frac{r_c}{r_{a(eff)}} \right) \frac{i}{p_{H_2O(0)}} \right) \quad (19)$$

The preceding analysis shows that the source of potential differences in the reported power densities due to asymmetric electrodes (cathode area smaller than the anode area) lies principally in differences in the anodic concentration polarization. The magnitude of the difference will depend upon a number of factors such as the anode thickness, l_a , the effective diffusivity of the anode, $D_{eff(a)}$, and the factor $\left(\frac{r_a}{r_c} \right)$ or $\left(\frac{r_{a(eff)}}{r_c} \right)$.

Using the preceding analysis, and measurements reported in [4], an estimate of the difference in anodic overpotentials for two different cell geometries is given in what follows. The following values based on our prior work were used for the calculations:

$$D_{eff(a)} \approx 0.2 \text{ cm}^2/\text{sec at } 800^\circ\text{C}.$$

$$l_a \approx 1 \text{ mm}$$

$$p_{H_2(0)} \approx 0.97 \text{ atm}$$

$$p_{H_2O(0)} \approx 0.03 \text{ atm}.$$

$$r_a \approx 1.3 \text{ cm}$$

We will choose two values of r_c ; namely 0.5 cm and 1.0 cm. The corresponding anode-limiting short circuit current densities are $\sim 5.53 \text{ A/cm}^2$ for the larger cathode radius, and $\sim 11.06 \text{ A/cm}^2$ for the smaller cathode radius using equation (16). The estimated anodic concentration polarizations, $\eta_{conc(a)}$, for the two cases, are plotted vs. current density, i , in Figure #5(a). The figure shows that, for the numbers chosen, the difference in the overpotentials is modest. In the example chosen above, note that for $r_c \approx 0.5 \text{ cm}$, $(r_a - r_c) \gg l_a$, and for $r_c \approx 1 \text{ cm}$, $(r_a - r_c) > l_a$. Thus, one should use equation (17) instead of equation (16). Choosing $r_{a(eff)} \approx r_c + l_a$, the corresponding anode-limiting short circuit current densities, i_{as} , become 4.68 A/cm^2 for the larger cathode, and 5.1 A/cm^2 for the smaller cathode. Figure #5(b) shows the estimated anodic concentration polarizations, $\eta_{conc(a)}$, for the

two cases plotted vs. current density, *i*. Experiments were conducted to test the above analysis. This is described in what follows.

Cell Fabrication: Anode-supported cells with Ni + YSZ as the anode, YSZ electrolyte, a thin, dense layer of Sm₂O₃-doped CeO₂ (SDC) barrier layer which serves as a part of the electrolyte, Sr-doped LaCoO₃ (LSC) + SDC porous cathode, and a porous LSC layer as a current collector, were fabricated using the following procedure. Discs of NiO + YSZ powder mixture were die-pressed. A thin layer of YSZ was applied on one surface, and edges, by drop coating a YSZ slurry. After drying, a thin layer of SDC was also applied by drop coating. The disc was subsequently sintered in air at a temperature between 1400 and 1500°C.

Two types of cells were made. In one case, the cathode was applied in a circular area. A paste of LSC + SDC made in an organic liquid was applied on the electrolyte (dense SDC layer) in a circular area. Two discs were prepared; in one case the area covered was ~1.1 cm², while in the other case, the area covered was ~2 cm². After drying, a layer of LSC was applied over it. Reference electrodes on the cathode side, prepared similarly, were deposited in a similar manner. The cell was heated to a temperature between 1000 and 1200°C to ensure a good bond between the cathode and the electrolyte. In the second case, the two cathodes were applied on one cell, both semicircular in geometry, as shown in Figure #6. Care was taken to ensure that spacing between the two semicircular areas was made as small as possible. In this case also, reference electrodes were deposited on the cathode side. The rationale for placing two cathodes on the same cell was that this should eliminate any possible differences in the electrolyte thickness, or possible differences in cathode activity that may result in any inadvertent differences in cathode preparations between cells, or possible differences in the fuel composition; e.g. the amount of water content.

Cell Testing: Cells were mounted in a fixture using alumina tubes and flexible, glass-free, compression seals. Figure #7 shows a schematic of the cell testing setup. Silver wire meshes, in the same geometry as the electrode areas, were placed on the cathode. Silver wire leads were connected to the wire meshes. The cells were heated in a furnace. Hydrogen gas, bubbled through water, was circulated past the anode, and air was circulated past the cathode. The NiO from the anode was reduced to Ni, in-situ. Voltage vs. current traces, were measured using an external electronic load. Anode and cathode potentials were measured with respect to the reference electrodes. The ohmic contribution was measured by current interruption. The cathode and anode overpotentials were determined by subtracting the ohmic contribution. For cells with circular cathodes, cell performance measurements were made at two different temperatures; 750°C and 800°C. In all experiments, the temperature was measured very close to the cell.

For the cell with semicircular cathodes, three separate measurements were made; the two semicircular cathodes separately, and a third measurement wherein the two cathodes were shorted (externally) using a heavy gage silver wire.

Microstructural Characterization: The cells after testing were fractured and examined in a scanning electron microscope (SEM) to measure the electrolyte, the anode interlayer and the

cathode interlayer thicknesses; and to examine the microstructures of the cathode and anode interlayers.

Effect of Cathode Microstructure:

NiO + YSZ powders were mixed in requisite proportions. Discs of the powder were die-pressed. A thin interlayer of NiO + YSZ was applied on one surface by spray coating. Subsequently, a thin layer of YSZ was applied by spray coating on the NiO + YSZ interlayer. The disc was then sintered in air at 1400°C for 2 hours. The cathode interlayer was made of LSM + YSZ wherein the composition of LSM was $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{(3-\delta)}$. The interlayer composition, that is the relative proportion of LSM and YSZ, was varied between 25 wt.% LSM + 75 wt.% YSZ and 60 wt.% LSM + 40 wt.% YSZ. An organic liquid was added to the interlayer powder mixture to form a paste. The YSZ electrolyte layer on the surface of the sintered disc was coated with the cathode interlayer paste. Subsequently, a layer of LSM was applied over the cathode interlayer, again by mixing it in an organic liquid to form a paste. The cell was then heated in air to 1150°C to remove the organic liquid, and form a good bond between the cell and the cathode interlayer, and between the cathode interlayer and the LSM cathode current collector, while maintaining sufficient porosity. At all stages, care was taken to ensure that, within the accuracy and repeatability of the experimental procedure, the thickness of any given layer was essentially the same in all cells. The only differences from cell to cell were differences in cathode interlayer compositions, and any associated microstructural differences.

Each cell was mounted in a test fixture, which consists of an alumina tube and an alumina ring. Each cell was secured between the alumina tube and the alumina ring. Flexible gaskets were used to ensure good sealing. No glass was used. Silver wire gauzes were pressed against the two electrodes, to which silver wires were connected. Air was circulated past the cathode, and humidified hydrogen was circulated past the anode. The cell was then heated to 800°C. Reduction of NiO to Ni was achieved in-situ. Voltage vs. current polarization curves were recorded using an electronic load.

After testing, cells were removed from the fixture and fractured. One of the fractured pieces of each cell was impregnated with an epoxy. The epoxy used completely filled up the porosity of the cathode current collector, the cathode interlayer, the anode interlayer, and the anode support. Upon curing and hardening the epoxy, the sample was mounted in a plastic mount, and subsequently polished to a 1 micron finish. A thin layer of carbon was deposited on the sample, which was then examined under an electron microprobe (Cameca SX 50). Several color-coded micrographs of cathode interlayers were obtained.

Color-coded micrographs of the cathode interlayers were used for quantitative stereological measurements. The parameters of specific interest are: (a) Grain (actually grain aggregate) size of YSZ in the cathode interlayer, d , (b) Porosity of the cathode interlayer, V_v , and (c) Three phase boundary (TPB) line length in the cathode interlayer, l_{TPB} . The grain aggregate size, d , of the YSZ in the cathode interlayer can be related to the average intercept length determined by repeatedly applying a test line on the micrographs [8]. For the determination of the average intercept length, a test line of equivalent length $\sim 8 \mu\text{m}$ was applied on micrographs of each

cathode interlayer up to 50 times [8]. The V_v was measured by a systematic point count procedure wherein a 25 point grid was applied on each micrograph up to 50 times. Similarly, volume fractions of LSM and YSZ in the cathode interlayer were also estimated. The average TPB line length, l_{TPB} , was estimated by measuring number of three phase boundary (TPB) points per unit area of each micrograph, P_A [8]. The experimentally measured parameters are as follows.

$P_{p(V)}$ = Fraction of points falling on the porous regions of the cathode interlayer = V_v (volume fraction of porosity). $P_{p(LSM)}$ = Fraction of points falling on LSM in the cathode interlayer = V_{LSM} (volume fraction of LSM). $P_{p(YSZ)}$ = Fraction of points falling on YSZ in the cathode interlayer = V_{YSZ} (volume fraction of YSZ).

A test line was applied and the number of intersections with boundaries of YSZ grain aggregates were measured. This measurement is P_L in units of 1/length. The surface area of YSZ grains per unit volume is given by $S_V = 2P_L$ [8]. Finally, the grain aggregate diameter is given by $d = 3V_{YSZ} / P_L$.

For the measurement of three phase boundary (TPB) length, number of TPB points per unit area, P_A , was measured. The three phase boundary (TPB) length per unit area of the YSZ grains in the cathode interlayer is given by $l_{TPB} = L_V / S_V = P_A / P_L$.

Alcohol as a Fuel:

Cell Fabrication: A typical single cell consists of five layers; anode support, anode interlayer, thin YSZ electrolyte, cathode interlayer and cathode layer. NiO and YSZ powders from commercial sources were mixed in requisite proportion and ball-milled in alcohol, dried and screened through a 150-mesh sieve. A circular disc of ~1.25 mm thickness and of ~3 cm diameter was uniaxially die-pressed. The disk was pre-sintered at 1000°C for one hour. The disk was then coated with a slurry of an anode interlayer of NiO + YSZ. Subsequently, a thin layer of YSZ was applied using its slurry in a suitable liquid. The disk was then sintered at 1400°C for a couple of hours. The thickness of the disc after sintering was ~1 mm. The typical thicknesses of the anode interlayer and the YSZ film were, respectively, ~10-30 μm and ~10 μm . The cathode interlayer was a porous composite of Sr-doped LaMnO₃ (LSM) and YSZ, wherein the composition of LSM was La_{0.8}Sr_{0.2}MnO_{3- δ} . A paste of LSM + YSZ powder mixture in an organic liquid was applied on the YSZ surface of the disc, followed by a layer of a pure LSM paste prepared similarly. The disc was then heated to a temperature typically between ~1000 and ~1200°C for 1 h. The thicknesses of the cathode interlayer and the LSM layer were, respectively, ~10-30 μm , and ~100 μm . The effective electrode area was 1.1 cm². The single cell was mounted in a test fixture, which consists of an alumina tube and an alumina ring. A flexible gasket was used for sealing. Figure 1 shows a schematic of the cell-testing fixture. Silver and nickel meshes were used as current collectors on the cathode and the anode, respectively. A reference electrode of platinum was applied on the cathode side, a few millimeters away from the cathode, and heated in air to 800°C for 1 h to ensure a good bond.

Cell Testing: Prior to testing with alcohols as fuels, the anode was reduced, *in-situ*, by flowing hydrogen gas at 800°C over the anode for a few hours. Then, further cell testing was conducted using CH₃OH and C₂H₅OH + H₂O (equi-volume mixture) as fuels. The liquid fuel was injected by a microinjection device at a controlled flow rate of 0.2 ml/min, and vaporized before introducing into the anode compartment. On the cathode side, air was circulated over the cathode surface at a flow rate of 600 ml/min. Voltage between the anode and the cathode, as well as between the anode and the reference electrode, was measured as a function of current. The ohmic resistances of: (1) the cell, (2) that between the anode and the reference electrode, and (3) between the cathode and the reference electrode, were determined using a current interruption technique with a potentiostat/galvanostat (EG&G 263), in conjunction with an oscilloscope (HP54622A). Voltage drops were measured at several current densities. Voltage drops were linearly related to the current density. Electrode overpotentials were obtained by subtracting ohmic contributions. Cell performance was measured over a range of temperatures between 550 and 800°C using H₂, CH₃OH and C₂H₅OH + H₂O as fuels.

LSM-LSGM Cathodes:

The anode-supported solid oxide fuel cells of the present study are comprised of five component layers: a Ni/YSZ composite anode support, a Ni/YSZ anode interlayer, a thin film YSZ electrolyte, an LSGM/LSM composite cathode interlayer, and an LSM current collecting cathode layer. The Ni/YSZ anode is thick relative to the other four layers and provides the support and mechanical integrity to the fuel cell. The anode substrates were prepared by, tape casting a solvent-based slip consisting of 80 wt.% NiO and 20 wt.% YSZ, and an organic pore former. Multiple tapes were laminated together in order to achieve an anode thickness of approximately 1.0 mm. The anodes used in this work were taken from the same batch of tape in order to minimize possible differences in the anode from cell to cell. Circular cells with a diameter of approximately 3 cm were cut from the tape and were subsequently bisqued at 1000°C in air for one hour in order to remove the binders and pore formers and to partially sinter the green part. An anode interlayer of 60 wt.% NiO and 40 wt.% YSZ was deposited on the anode by suspending the powders in a solvent and spraying the mixture on the anode support. The anodes with the anode interlayers were fired a second time at 1000°C for one hour resulting in an anode interlayer of approximately 20 µm in thickness. Similarly, the YSZ electrolyte was deposited by spraying YSZ (TZ-8Y) powder suspended in a solvent onto the bisqued part. The cell was fired at 1400°C for 2 hours resulting in a dense YSZ film with a thickness of ~10 µm.

The composite cathode interlayer was prepared from La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_(3-λ) (LSGM) and La_{0.8}Sr_{0.2}MnO_(3-δ) (LSM) (Praxair) powders. The relative amounts of LSGM and LSM were varied between 30 and 70 wt.% LSGM and 70 and 30 wt.% LSM. The two powders were mixed with a solvent-binder system in order to form a paste that was subsequently applied to the YSZ electrolyte by a modified screen-printing method. The cells were masked before printing to produce a uniform area of cathode coverage of 1 cm² that was fixed for all cells. The composite cathode interlayer was fired at a temperature between 1000 and 1200°C for 2 hours in air. The composite cathode interlayers were between 20 and 25 µm thick after firing. The final LSM cathode current collecting layer was applied in a paste form by a similar

method. In addition, a platinum reference electrode was applied on the electrolyte in close proximity to the cathode. The LSM cathode current collector layer was fired at 1000°C for 2 hours and had a thickness of approximately 50 µm after firing.

The performance and electrochemical properties of the fuel cells were measured in a spring loaded testing fixture shown in Figure #7. The spring-loaded fixture ensures good electrical contact and good sealing, thus preventing leakages. Nickel mesh and silver mesh were used for current collection on the anode and cathode sides, respectively. A high temperature gasket was used for sealing. The cathode side of the cell was exposed to flowing air at a rate of 0.9 l/min. The anode side was exposed to a flowing stream of hydrogen gas saturated with water vapor at 25°C ($p_{H_2O} \sim 0.032$ atm) at a rate of 0.1 l/min. The NiO/YSZ composite anodes were reduced, *in situ*, at 800°C for 24 h before electrochemical measurements were conducted at 800°C. During testing, the voltage differences between the anode and the reference electrode, and the cathode and the reference electrode were measured. The ohmic resistance of the cells was measured by current interruption. The DC current was cycled with a potentiostat/galvanostat (EG&G 263A) and the voltages between the cathode, the anode, and the reference electrode were recorded by a digital oscilloscope (Agilent 54662A). The overpotentials were determined by correcting for the requisite ohmic contributions.

In order to investigate the possibility of chemical interactions between LSGM and YSZ, powders of LSGM and YSZ were mixed, milled, and fired at a temperature between 1000 and 1200°C for 2 hours. In addition, to study the possible reaction at the interface between LSGM and YSZ, a thin layer of LSGM was applied on sintered YSZ pellets by a modified screen-printing method and fired at a temperature between 1000 and 1200°C for 2 hours. The samples were then characterized using X-ray powder diffraction (XRD) to identify any secondary phases that may form at the interface. In order to determine the chemical composition of the resulting phases, sintered samples of LSGM and YSZ were prepared. LSGM and YSZ powders were mixed, milled, pelletized, and sintered at temperatures between 1000 and 1200°C. The pellets were polished and evaluated with electron dispersive spectroscopy (EDAX).

Anode Reduction-Re-Oxidation Kinetics:

In what follows, a brief description of the kinetic model is given along with relevant equations, for both reduction and reoxidation. Figure #8 shows a schematic of the reduction process for a dense NiO + YSZ two-phase composite into a porous Ni + YSZ cermet. The reduced layer thickness is X . A simple model, which takes into account gas transport through the porous cermet, and the occurrence of reduction at the interface, shows that the kinetics can be described by an equation of the form

$$X^2 + \frac{D_{eff}^r}{RTk_r} X = \frac{2D_{eff}^r}{RT} \frac{V_{NiO}^M}{V_{NiO}^f} (p_{H_2O}^{eq} - p_{H_2O}^o) t \quad (20)$$

where

X = Thickness of the reduced layer.

V_{NiO}^M = Molar volume of NiO, V_{NiO}^f = Volume fraction of NiO.

$p_{H_2O}^o$ = Partial pressure of water vapor in the H₂-H₂O mixture, used as the reducing environment.

$p_{H_2O}^{eq}$ = Equilibrium partial pressure of water vapor corresponding to the reaction.

NiO (s) + H₂(g) → Ni(s) + H₂O (g), under the condition that

$$p_{H_2}^o + p_{H_2O}^o = p_{H_2}^{eq} + p_{H_2O}^{eq}$$

D_{eff}^r = Effective binary gaseous diffusivity (of H₂-H₂O) through the porous Ni-YSZ. cermet formed. (If an inert gas is also present, e.g. nitrogen, its effect may also have to be taken into account).

k_r = Rate constant which defines the kinetics of reduction of NiO to Ni.

t = Time of reduction, R = Ideal gas constant, and T = Temperature.

The two limiting forms of equation (20) are:

a. k_r very large relative to D_{eff}^r :

In this case, the rate of reduction at the reaction interface is sufficiently fast such that equation (20) reduces to

$$X^2 \approx \frac{2D_{eff}^r}{RT} \frac{V_{NiO}^M}{V_{NiO}^f} (p_{H_2O}^{eq} - p_{H_2O}^o)t \quad (21)$$

That is, the reduction reaction is diffusion-controlled and a plot of the square of the reduced layer thickness as a function of time should be linear, consistent with the parabolic law of reduction kinetics. The above equation may also be written as

$$X^2 \approx D_{red}t \quad (22)$$

where a phenomenological diffusion coefficient is defined by

$$D_{red} \approx \frac{2D_{eff}^r}{RT} \frac{V_{NiO}^M}{V_{NiO}^f} (p_{H_2O}^{eq} - p_{H_2O}^o) \quad (23)$$

b. k_r very small relative to D_{eff}^r :

In this case, equation (20) becomes

$$X \approx 2k_r \frac{V_{NiO}^M}{V_{NiO}^f} (p_{H_2O}^{eq} - p_{H_2O}^o)t \quad (24)$$

In such a case, the reduction reaction is interface-controlled and a plot of reduced layer thickness, as a function of time should be linear. The above equation may be written as

$$X \approx k_{red}t \quad (25)$$

where a phenomenological interface parameter is defined as

$$k_{red} \approx 2k_r \frac{V_{NiO}^M}{V_{NiO}^f} (p_{H_2O}^{eq} - p_{H_2O}^o) \quad (26)$$

Thus, based on this model, the dependence of reduced layer thickness on reduction time at a given temperature should give insight into the nature of the reduction process.

Figure #9 shows a schematic of the re-oxidation process. If the original NiO + YSZ is fully dense, it is expected that after re-oxidation, Ni + YSZ should re-oxidize to a fully dense body. However, in the reduced state, if particle shape change of Ni occurs, which is likely due to faster diffusional creep in Ni as compared to NiO, upon re-oxidation the newly formed NiO may have a different shape than the available cavity corresponding to the original NiO particle (in the as-sintered state). In such a case, the re-oxidized composite will not be fully dense, and there will be some porosity. Assuming molecular (or atomic) oxygen transport through the solid part (either NiO or YSZ or both) is negligible, during the re-oxidation stage, the required oxygen must be transported to the reaction front by gaseous diffusion through the porous interstices. Under this assumption, the kinetics of re-oxidation may be given by an equation of the form

$$X^2 + \frac{D_{eff}^o}{RTk_o} X = \frac{4D_{eff}^o}{RT} \frac{V_{Ni}^M}{V_{Ni}^f} (p_{O_2}^o - p_{O_2}^{eq})t \quad (27)$$

where

X = Thickness of the re-oxidized layer.

V_{Ni}^M = Molar volume of Ni, V_{Ni}^f = Volume fraction of Ni.

$p_{O_2}^o$ = Partial pressure of oxygen in the oxidant (air).

$p_{O_2}^{eq}$ = Equilibrium partial pressure of oxygen corresponding to the reaction

D_{eff}^o = Effective binary diffusivity (O_2 - N_2) through pores of the re-oxidized NiO + YSZ layer.

and

k_o = Rate constant which governs the oxidation of Ni to NiO.

The remaining terms have the same meanings as before. Two limiting cases of this equation are as follows:

a. k_o very large relative to D_{eff}^o :

In this case, the rate of re-oxidation at the reaction interface is sufficiently fast such that equation (27) reduces to

$$X^2 \approx \frac{4D_{eff}^o}{RT} \frac{V_{Ni}^M}{V_{Ni}^f} (p_{O_2}^o - p_{O_2}^{eq})t \quad (29)$$

That is, the re-oxidation reaction is diffusion-controlled and a plot of the square of the re-oxidized layer thickness as a function of time should be linear, consistent with the parabolic law of re-oxidation kinetics. The above equation may be written as

$$X^2 \approx D_{ox}t \quad (30)$$

where a phenomenological diffusion coefficient is defined by

$$D_{ox} \approx \frac{4D_{eff}^o}{RT} \frac{V_{NiO}^M}{V_{NiO}^f} (p_{O_2}^o - p_{O_2}^{eq}) \quad (31)$$

b. k_o very small relative to D_{eff}^o :

In this case, equation (27) becomes

$$X \approx 4k_o \frac{V_{Ni}^M}{V_{Ni}^f} (p_{O_2}^o - p_{O_2}^{eq})t \quad (32)$$

In such a case, the re-oxidation reaction is interface-controlled and a plot of re-oxidized layer thickness as a function of time should be linear. The above equation may be written as

$$X \approx k_{ox}t \quad (33)$$

where a phenomenological interface parameter is defined by

$$k_{ox} \approx 4k_o \frac{V_{Ni}^M}{V_{Ni}^f} (p_{O_2}^o - p_{O_2}^{eq}) \quad (34)$$

Thus, based on this model, the dependence of re-oxidized layer thickness on re-oxidation time at a given temperature should give insight into the nature of the re-oxidation process.

Powder mixtures consisting of 60 vol.% NiO and 40 vol.% YSZ were made and attrition milled for 24 h. The powders were dried, screened and uniaxially pressed into rectangular bars. The samples were sintered at 1400°C for 2 h. The sintered samples were then cut to a final dimension of approximately 15 mm x 4 mm x 4 mm. The bulk density of the samples was determined by the Archimedes technique in accordance with ASTM C20-00. The samples were then reduced in a tube furnace under a flowing gas mixture of 10% hydrogen and 90% nitrogen in the temperature range 600 to 800°C. Reduction experiments were conducted in 50-degree intervals in the range 600 to 800°C for various periods of time. Some of the samples were reduced for a time long enough to ensure that they were fully reduced. These samples were subsequently re-oxidized in air over a range of temperatures between 600 and 800°C, and the re-oxidized layer thickness was measured as a function of time at temperature. Reduced and re-oxidized layer thicknesses were measured using optical and scanning electron microscopy (SEM).

Fuel Composition Effects on Anode Polarization:

Cell Fabrication: While only measurements on one cell are reported, a number of cells were fabricated. Single cells consisted of a Ni + YSZ anode substrate, a Ni + YSZ anode interlayer, a YSZ–SDC bi-layer thin film electrolyte, a LSC + SDC cathode interlayer, and a LSC cathode current collector layer. The procedure for preparing an anode substrate and an anode interlayer was described elsewhere in detail [9], and is briefly described here. NiO and YSZ powders from commercial sources were mixed in requisite proportions and ball-milled in alcohol, dried and screened through a 150-mesh sieve. A circular disc of ~1.2 mm thickness and ~3 cm diameter was uniaxially die-pressed, and pre-sintered at 1000°C for one hour. The disc was then coated with a slurry of NiO + YSZ anode interlayer and fired again at the same temperature for one hour to form a NiO + YSZ interlayer of ~20 μm thickness. YSZ and SDC

layers were applied on the anode interlayer surface sequentially using YSZ and SDC suspensions made from YSZ and 20 mol.% samarium-doped CeO₂ powders, dispersed ultrasonically in appropriate amounts of suitable liquids. Then, the bi-layer electrolyte - anode substrate assembly was sintered in air at a temperature between 1400 and 1500°C to form a dense, well-bonded YSZ-SDC bi-layer electrolyte – anode structure. The thickness of the SDC layer was around 3 μm and the total thickness of the YSZ-SDC bi-layer electrolyte thin film was ~10 μm. The thin SDC layer, as part of the electrolyte, served as a barrier, which prevented a direct contact between YSZ and LSC. In this manner, the possible chemical reaction between YSZ and LSC, which can form insulating La₂Zr₂O₇ during a high-temperature firing step, could be prevented.

The porous cathode interlayer was a composite of 50 wt.% strontium-doped lanthanum cobaltite (La_{1-x}Sr_xCoO_{3-δ} (LSC), x = 0.3~0.7) and 50 wt.% SDC. The cathode interlayer was applied by screen-printing, followed by firing at a temperature between 1050 and 1300°C for 2 hours to form a good bond between the SDC layer and the cathode interlayer. The thickness of the interlayer after firing was ~20 μm. On top of the interlayer, a porous layer of LSC was applied, followed by firing at a temperature between 1050 and 1300°C for 1 hour in air. The final anode thickness and the disk diameter were respectively 1.1 mm and 27.7 mm. The cathode area was 1.1 cm².

The Measurement of Cell Performance: The cell was mounted in a test fixture, which consisted of an alumina tube and an alumina ring. The cell was secured between the alumina tube and the alumina ring and spring-loaded to ensure good sealing between the cell and the alumina tube using a flexible gasket. A silver mesh and a Ni mesh, used as current collectors at the cathode and the anode, respectively, were spring-loaded against, respectively, the cathode and the anode. Measurements were carried out at 800°C, at one atmosphere total pressure (both fuel and air), and at predetermined, constant total flow rates of fuel or fuel mixture, and of air. The cell was reduced *in situ* at 800°C in a 10% H₂ + 90% N₂ mixture for several hours prior to measurements. The fuel flow-rate was maintained at 140 ml/min, and the air flow-rate was maintained at 550 ml/min, in all experiments. Open circuit potentials were measured under constant fuel flow over the anode and the airflow over the cathode.

Cell performance was measured using various fuel gas mixtures, which included as-received H₂ (straight from the as-received cylinders – 99.99% pure H₂), as-received CO (straight from the as-received cylinders – 99.99% pure CO), H₂ + CO mixtures, H₂ diluted with He, N₂, CO₂, H₂O and CO diluted with CO₂. I-V curves were measured at various diluent concentrations, i.e. at various partial pressures of the diluent while the total flow rate of fuel mixture was kept constant. Current densities were calculated based on the cathode area. The fact that cathode area is different from the anode surface exposed to fuel introduces a small error (typically <10%) in the power density. This issue has been addressed in detail elsewhere [9]. Cell tests with as-received hydrogen were conducted without bubbling through a water bubbler.

Cell Characterization: Porosity of the Ni-YSZ anode was measured using the Archimedes method. The tested cell was broken into several small pieces. Dry weight, W_{dry} , wet weight, W_{wet} , and weight in water, W_{water} , were measured using a high accuracy balance. Wet weight

was measured (in air) soon after the surface of the sample was wiped dry, after boiling in water for two hours. Porosity was calculated according to the equation:

$$Porosity = \frac{W_{wet} - W_{dry}}{W_{wet} - W_{water}} \quad (35)$$

One of the fractured pieces was evacuated (to remove air from the pores) and impregnated with an epoxy. After hardening the epoxy, the sample was polished down to 1 μm finish. The microstructure of the cell was examined using scanning electron microscopy (SEM) and the mean pore radius was determined by quantitative stereology [8].

RESULTS AND DISCUSSION

Nanosize YSZ Powder Synthesis:

Figures #10(a) and #10(b) show XRD patterns of Y-BaZrO₃ powders made by calcining mixtures of BaCO₃, ZrO₂ and Y₂O₃, and mixtures of BaCO₃ and YSZ, respectively, at 1250°C for 2h. The patterns are almost identical and match the standard pattern for the cubic structure of perovskite, BaZrO₃. Figure #10(b) shows the presence of a single phase, perovskite structure. In Figure #10(a), small peaks, indicating the existence of a small amount of a second phase, can be seen. Overlap of peaks prevents an unequivocal determination of the second phase. However, the peak positions of the second phase are consistent with cubic or tetragonal zirconia. Presumably, the precursor was not fully homogenized under the chosen calcination conditions. The results nevertheless show that yttria-doped BaZrO₃ can be synthesized with either of the starting materials at a temperature of 1250°C or above. Figure #11 is an XRD pattern of a mixture of Na₂CO₃ and YSZ after calcining at 1250°C for 2 h, which corresponds to monoclinic sodium zirconate, Na₂ZrO₃. Since YSZ was used instead of ZrO₂, it is expected that Na₂ZrO₃ formed should be yttria-doped, i.e., Y-Na₂ZrO₃. Again, XRD revealed that the reaction was complete and resulted in the formation of a single phase, within the accuracy of the XRD technique. A calcination temperature lower than 1050°C was not high enough to ensure the completion of the reaction, as evidenced by the lack of formation of a single phase material.

Chemical leaching of BaO from yttria-doped BaZrO₃ (Y-BaZrO₃) precursor was achieved in a dilute HNO₃ solution in water. The precursor was boiled in a dilute HNO₃ acid solution, filtered and washed repeatedly until the solution pH was unchanged. Then, it was thoroughly washed using de-ionized water to completely remove Ba as Ba(NO₃)₂. The solution containing leachable ions was chemically analyzed to determine the concentrations of Ba, Y, and Zr. The results showed (Table 1) a significant concentration of Ba²⁺ but only trace concentrations of Zr⁴⁺ and Y³⁺, confirming that Ba²⁺ was selectively dissolved and led to the formation Y₂O₃-ZrO₂, which is essentially insoluble in dilute HNO₃, by a reaction such as

For the yttria-doped Na₂ZrO₃ (Y-Na₂ZrO₃) precursor, since Na₂ZrO₃ readily reacts with water by a reaction such as

repeated boiling in de-ionized water, filtering and washing was adequate to completely remove Na₂O as NaOH. In this case also, the chemical analysis showed that the solution contained

predominantly Na, but only trace amounts of Y and Zr (Table 2). In order to determine the purity of the as-washed powders, chemical analysis was performed using Inductively Coupled Plasma (ICP) technique by dissolving YSZ powders synthesized using both precursors in concentrated HCl. Table 3 gives the results of this analysis. It is seen that for the case of YSZ made with Y-Na₂ZrO₃, the concentrations of Zr⁺⁴ and Y⁺³ in the solution are in accord with expected concentrations of Zr and Y in YSZ. However, in the case of YSZ made using Y-BaZrO₃, the concentration of Y⁺³ is lower than expected on the basis of the starting powder. This suggests that some of the yttrium was leached out in dilute HNO₃. In both cases, the concentrations of Na⁺ and Ba⁺² are in the ppm level, indicating that the concentrations of these impurities in the powders are small (on the order of ~0.5 wt.% or less in the respective YSZ powders). Some of this may, in part, be related to the possible incomplete washing of the powders, and not necessarily an indication of impurities dissolved in the YSZ powders.

XRD patterns of leached and washed powders synthesized from the two precursors are given in Figure #12(a). In both cases, the XRD patterns of leached and washed powders were quite different from those of the corresponding precursors (Y-Na₂ZrO₃ and Y-BaZrO₃). At the same time, the XRD patterns of the leached and washed powders were nearly identical, regardless of the precursor used, Y-Na₂ZrO₃ or Y-BaZrO₃. Figure #12(b) shows an XRD pattern of commercial YSZ. It is readily seen that the XRD patterns of leached and washed powders are similar to the commercial YSZ, insofar as peak positions are concerned. This shows that during leaching of the respective precursors, only BaO or Na₂O are leached away resulting in a residue containing Y, Zr, and O such that the Zr-Y-O skeleton has either a cubic or a tetragonal symmetry. Large peak broadening observed in XRD patterns makes it impossible to determine whether the phase formed is cubic or tetragonal, since there is only a small difference in XRD patterns of the two phases. The XRD peaks in the patterns of leached powders are very broad indicative of a very fine particle size. This shows that very fine (nanosize) particles of YSZ can be formed starting with precursors (Y-BaZrO₃ or Y-Na₂ZrO₃), whose particle size is several microns.

The formation of nanosize powders, starting with coarse precursor powders, can be illustrated via the following example. Let us consider the reaction of Y-BaZrO₃ with dilute HNO₃. The precursor, Y-BaZrO₃, is essentially insoluble in dilute HNO₃. However, it can react with HNO₃, as given by equation (36). Although the following illustration assumes that the formed structure of YSZ is cubic, the general conclusions concerning the accompanying volume change, leading to the formation of nanosize powders, are independent of the structure formed. The volume of a Y-BaZrO₃ unit cell is about 73.72 Å³. One unit cell of cubic zirconia contains four formula units, i.e. 4 'ZrO₂' or 4 'Y-ZrO₂', with a volume of ~135.72 Å³. Thus, per one formula unit, such as is created per one Y-BaZrO₃ unit cell, the volume is 135.72/4 or 33.93 Å³. That is, as Y-BaZrO₃ reacts with HNO₃ to form Y-ZrO₂, there is a net change in volume from 73.72 Å³ to 33.93 Å³. This is equivalent to $\frac{(73.72 - 33.93)}{73.72} \times 100 \approx 54\%$ decrease in volume. In terms of a linear change, this corresponds to $\frac{\sqrt[3]{73.72} - \sqrt[3]{33.93}}{\sqrt[3]{73.72}} \times 100 \approx 25\%$ decrease in a linear dimension. As the surface of the precursor particle reacts with HNO₃ to form soluble Ba(NO₃)₂, there is a substantial volume change and a linear change (a decrease), which should lead to cracks and fissures at the unit cell (Å) level.

This should thus lead to the formation of tiny fragments at the angstrom or nanometer level. As the product, Y-ZrO₂, is insoluble (or has a very low solubility) in the liquid used, Ostwald ripening, which requires dissolution, transport and reprecipitation, should not occur. Figure #13 shows a schematic of the leaching process of Y-BaZrO₃ in dilute HNO₃. The outer layer of the particle becomes porous since BaO (as Ba(NO₃)₂) is leached out of Y-BaZrO₃. Further reaction occurs by the transport of HNO₃ to the porous YSZ/dense Y-BaZrO₃ interface, reaction to form Ba(NO₃)₂ and YSZ, and the transport of dissolved Ba(NO₃)₂ away from the interface, through the porous YSZ, into the acid bath. The porous YSZ is easily fragmented into a very fine powder. Thus, even though the original Y-BaZrO₃ powder is coarse, the resulting YSZ powder should be nanosize. A similar mechanism is expected to be operative during the synthesis of nanosize YSZ starting with Y-Na₂ZrO₃. This is the origin of the molecular decomposition process for the synthesis of nanosize powders. The preceding also suggests that the initial precursor particle size should have no bearing on the final size of nanoparticles. Indeed, nanosize powder can be synthesized using precursors that are considerably coarse; for example several microns in size.

The Scherrer formula relates the average particle size, d , to X-ray peak broadening, B , by

$$d = \frac{0.9\lambda}{B \cos \theta} \quad (38)$$

In order to determine the peak broadening attributable only to the particle size effect, a commercial YSZ powder was sintered at 1500°C for a few hours to obtain a strain-free, coarse-grained (grain size on the order of a few microns) sample. An XRD pattern of the sample was obtained. Peak width (at half the peak height) from this sample for a given (hkl), in the present case (111), was subtracted from the corresponding peak width of the leached and washed powders. In this manner, line broadening attributable to the instrument as well as the presence of both $K\alpha_1$ and $K\alpha_2$, could be corrected for. The corrected peak width was measured to be approximately 4° (~0.07 radians) for the case of the as-washed powders, which is equivalent to an average crystallite size of about a few nanometers (~2 to ~3 nm) for both of the as-washed powders (Table 4).

As an independent confirmation of the nanosize of the powders formed, specific surface area measurements were conducted using the BET adsorption isotherm method. The surface area measurements were made on both of the precursors (Y-Na₂ZrO₃ and Y-BaZrO₃) and the synthesized powders. The specific surface area of the precursors was typically only ~3 m²/g (Table 5), consistent with the large particle size of the precursors. The specific surface area of the nanosize powder made from the Na₂ZrO₃ precursor, however, was measured to be around 67 m²/g. Assuming particles to be spherical for simplicity, the diameter of the particle can be estimated from the relation

$$d = \frac{6}{S\rho} \quad (39)$$

where ρ is the density of YSZ and S is the specific surface area. Assuming $\rho = 5.9$ g/cm³ for YSZ and 67 m²/g for S (measured by BET), the diameter is estimated to be ~15 nm. Thus, specific surface area measurement also shows that the synthesized powder is indeed nanosize. However, the estimated particle size from surface area measurements is about 5 to 6 times greater than that estimated from XRD peak broadening. A possible reason for this may be the formation of agglomerates. In order to explore this possibility, samples were examined by

transmission electron microscopy (TEM) on JEOL 4000FX TEM. For TEM examination, a sample of YSZ powder synthesized using Y-BaZrO₃ was suspended in alcohol, and vibrated ultrasonically. Figure #14(a) shows a bright field image of the sample at 25,000 X. It is seen that the observed particles, which are agglomerates, are in the range of 50 to 200 nm in size. A higher magnification image (1,000,000 X) in Figure #14(b) shows lattice fringes of individual particles in the agglomerates. As evident from this micrograph, the individual crystallite size is about 5 nm, in reasonably good agreement with an estimate based on XRD peak broadening. The lattice image also shows that the as-synthesized powder is crystalline and not amorphous.

The above results conclusively demonstrate that nanosize YSZ powder can be effectively prepared by the molecular decomposition approach using alkali or alkaline earth metal oxide precursors. XRD patterns of the YSZ obtained from the two precursors are consistent with the formation of cubic zirconia. However, it is known that XRD peaks of cubic and tetragonal zirconia are very similar and thus difficult to delineate, especially when the peaks are rather broad. Thus, XRD is not a very good technique for distinguishing between cubic and tetragonal zirconia, especially if the crystallite size is in the nanometer range. However, Raman spectra of cubic, tetragonal and monoclinic zirconia are quite different. For this reason, selected samples were examined by Raman spectroscopy, the results of which are discussed below.

Figures #15(a) and #15(b) are Raman spectra of monoclinic ZrO₂ and cubic (8 mol.% Y₂O₃-doped) zirconia obtained commercial vendors, respectively. It is seen that the spectra of these two materials are quite different. The cubic structure of zirconia is characterized by, a broad peak between 600 and 650 cm⁻¹, while the monoclinic spectrum contains several sharp lines. These results are similar to the ones reported in the literature. A spectrum of the tetragonal phase is known to exhibit characteristic lines at 260 cm⁻¹, 500 cm⁻¹, and 640 cm⁻¹. Figure #15(c) shows a spectrum of the as-synthesized nanosize powder made using Y-BaZrO₃. Note that, this pattern is also characterized by the existence of rather broad peaks. The pattern shows no evidence of either the monoclinic or the tetragonal phases, and is similar to the cubic spectrum. Figure #15(d) is a spectrum of the synthesized powder after a thermal treatment at 1000°C for 5 h. This spectrum is also characterized by the presence of broad peaks. Peaks representative of monoclinic phase are absent. However, the presence of humps at ~260 cm⁻¹ and ~640 cm⁻¹ may indicate the possible existence of a mixture of cubic and tetragonal phases. Note, however, that the same peaks are present in commercial YSZ as well.

In order to examine possible changes in the crystal structure of the synthesized nanosize YSZ powders, Differential Thermal Analysis (DTA) on the as-washed powders was conducted. In addition, XRD patterns were obtained on powders after heat-treating the as-washed powders at various temperatures. Figure #15 shows the DTA traces of YSZ nanopowders synthesized from both precursors. The peaks centered at ~235°C in the two traces are attributed to endothermic desorption of adsorbed water. The traces also show broad exothermic peaks in the temperature range from ~300 to ~600°C. An exothermic peak is usually attributed to the crystallization process, provided the as-formed powders are amorphous. In the present case, the as-synthesized powder is crystalline and not amorphous, as seen in the TEM micrograph given in Figure #15(b), unlike some other YSZ powders prepared by sol-gel or chemical co-precipitation. In such cases, the exothermic peak due to the crystallization, is generally well defined and sharp. In the present work, by contrast, the exothermic peak is very broad for

powders made using either of the precursors, but more so in the case of nanosize YSZ powder made from Y-BaZrO₃ precursor, indicating that there is neither the occurrence of a distinct crystallization, nor the occurrence of a phase transition over the temperature range investigated. The broad exothermic peak may be attributed to the possible removal of point defects, and/or the occurrence of particle growth during the thermal treatment. The occurrence of particle growth during thermal treatment can be readily verified by XRD examination of nano YSZ powders heat-treated at various temperatures.

Figure #17 shows the XRD spectra of nanosize YSZ powders, synthesized from Y-BaZrO₃, thermally treated at various temperatures. It is seen that the crystal structure of the YSZ powder is essentially unaffected by the thermal treatment, all the way up to 1000°C, the maximum temperature to which the synthesized powders were heated. The structure of YSZ appears to be cubic, although the presence of a small amount of tetragonal phase cannot be ruled out. The possible presence of tetragonal phase will cause splitting of (200) and (220) peaks from the original peaks into (200)/(002) and (220)/(202) doublets. The approximate peak positions for these two sets of peaks (with CuK α radiation) are $\sim 30.95^\circ$ and $\sim 50.27^\circ$, respectively. XRD pattern of the powder after 5 h at 1000°C given in Figure 8 shows that there is no evidence of peak splitting indicating that even after 5 h at 1000°C, the powder remains cubic. Very small peaks observed in these patterns at $\sim 43.3^\circ$ and $\sim 54.05^\circ$ are due to the incomplete removal of the original precursor, Y-BaZrO₃. As the temperature of heat treatment is increased, the peak height increases at the expense of peak width, consistent with the occurrence of particle growth. The estimated particle size of the powders after heat treatment at 1000°C is about 37 nm, showing that the nanosize particles are relatively stable against significant growth at temperatures as high as 1000°C.

Nanosize YSZ obtained from Y-Na₂ZrO₃ precursor was similarly subjected to various thermal treatments. The corresponding XRD patterns are given in Figure #18, and the dependence of the particle size on the temperature of heat treatment is given in Table 4. It is seen that in this case also, even after heat treating at 1000°C for 5 h, the average particle size is only about 31 nm. This shows that nanosize powder derived from Y-Na₂ZrO₃ is also stable against significant particle growth, up to 1000°C for 5 h. However, the XRD pattern of the powder heat treated at 1000°C shows the presence of a small amount of monoclinic phase (characterized by two small peaks on either side of the (111) peak at $\sim 30.05^\circ$). It is not clear if this is the result of possible low-level sodium as an impurity. The other possibility is that in the original precursor formulation, not all of the Na₂ZrO₃ was doped with Y₂O₃. That is, there may have been some Na₂ZrO₃ present with little or no Y₂O₃ dissolved in it. The presence of some undoped Na₂ZrO₃ cannot be ruled out on the basis of XRD results. If some undoped Na₂ZrO₃ is present, it is expected to form nanosize, undoped ZrO₂ upon boiling in water. The as-synthesized, undoped zirconia is expected to be cubic rather than monoclinic by virtue of the lower surface energy of the cubic phase compared to the monoclinic phase. When heated to a high temperature where growth of particles occurs, the monoclinic phase will become the stable phase. The formation of some monoclinic phase when heated to 1000°C, as evidenced in Figure #18, may be related to the possible existence of some undoped Na₂ZrO₃ in the precursors. Table 4 gives the average particle size of YSZ powders, treated at various temperatures after synthesis, calculated from the Scherrer formula using the half peak widths from the XRD patterns given in Figures #17 and #18. The particle sizes of YSZ from both

precursors are similar, which are in the range from a few nanometers to tens of nanometers after thermal treatment at a temperature as high as 1000°C. An investigation of the sinterability of YSZ powders made by the present process, and the measurement of ionic conductivity of sintered samples is underway. The results of these studies will be reported in a separate communication.

Cathode Area Effect:

Cell Microstructure and Dimensions: Figures #19(a) and #19(b) show scanning electron micrographs of the two cells with different cathode areas; $\sim 1.1 \text{ cm}^2$ and $\sim 2 \text{ cm}^2$. Note that the electrolyte thicknesses are essentially identical, and so are the thicknesses of cathodic and anodic interlayers. It is also seen that electrode microstructures are similar.

Cell Performance with Circular Cathodes: Figures #20 and #21 show voltage, V , vs. current density, i , (as-determined on the basis of cathode area) traces, as well as power density (as determined on the basis of the cathode area) vs. i , for cells with cathode areas of $\sim 1.1 \text{ cm}^2$ and $\sim 2 \text{ cm}^2$, tested at 800 and 750°C, respectively. Note that the maximum power density measured for the cell with the smaller cathode is $\sim 1.65 \text{ W/cm}^2$, while that for the larger cathode is $\sim 1.45 \text{ W/cm}^2$ at 800°C. At 750°C, the maximum power density for the cell with the smaller cathode is $\sim 1.3 \text{ W/cm}^2$, while that for the cell with the larger cathode is $\sim 1.25 \text{ W/cm}^2$. The preceding shows that the difference at 800°C is about $\sim 0.2 \text{ W/cm}^2$ and at 750°C, it is about $\sim 0.05 \text{ W/cm}^2$. That is, the difference in power densities is rather modest, even when the cathode area in the cell with the larger cathode is almost twice as large as the cell with the smaller cathode area. A preliminary conclusion is that there is a small difference, which decreases with decreasing temperature.

Figure #22 shows the plots of ohmic contribution (IR drop) as a function of current density, i , (on the basis of the cathode area) at 800°C for the two cells with cathodes of circular areas. As can be seen, the two plots overlap showing that there is virtually no discernible difference. This is consistent with the analysis presented here. The results of tests at 750°C were similar.

Figure #23 shows the plots of measured cathodic overpotential as a function of current density, i , at 800°C for the two cells with circular cathodes of different areas. In this case also, it is readily seen that the two plots are virtually identical, which essentially overlap. The results of the tests at 750°C were similar.

Figure #24 shows the plots of measured anodic overpotential vs. current density at 800°C, for cells with circular cathodes of two different areas, namely, $\sim 1.1 \text{ cm}^2$ and $\sim 2 \text{ cm}^2$. The figure shows that the anodic overpotential is larger for the cell with the larger cathode area, in qualitative agreement with the analysis presented here, and the plots given in Figure #5. The results of the tests at 750°C were similar, with the exception that the difference in overpotentials was even smaller.

Figure #25 shows plots of voltage, V , vs. current density, i , and power density vs. i , for cell with semicircular cathodes individually, and shorted with an external wire. Note that the V vs. i as well as power density vs. i traces with the two semicircular cathodes are identical, while for

the one shorted are slightly lower. Figure #26 shows the measured anodic overpotentials vs. i . Note that the plots for the two semicircular cathodes are identical, with the one for the two cathodes shorted being slightly higher, again consistent with the analysis. A quantitative comparison with the analytical results is difficult, however, due to the complicated nature of the cathode geometries. Nevertheless, the effect of asymmetric cathode on anodic polarization, principally anodic concentration polarization, is quite clear. By contrast, the ohmic contribution (Figure #27) and cathodic overpotentials (Figure #28) were virtually identical for the individual semicircular cathodes, as well as for shorted cathodes.

Figures #22 and #23 show that the cathodic overpotentials as well as the ohmic drops are virtually the same for two circular cathodes of differing areas. Similar conclusions are arrived at for cells with semicircular cathodes (Figures #27, and #28). This is in accord with expectations.

Figure #5 shows the plots of calculated anodic concentration polarization, $\eta_{conc(a)}$, vs. current density, i , calculated for two values of cathode radii; 0.5 cm and 1 cm, with an anode radius of 1.3 cm. It is readily seen that the dependence of the calculated $\eta_{conc(a)}$ on i plots is qualitatively similar to that observed experimentally. For the experimental data shown in Figure #24, not all of the relevant parameters were known; for example, i_{as} , $p_{H_2(0)}$ and $p_{H_2O(0)}$, were not known. As is evident from equation (18), an accurate knowledge of $p_{H_2(0)} / p_{H_2O(0)}$ is especially important since this ratio can vary over a wide range; from say ~ 33 , for 3% water vapor in the fuel to say ~ 9 , for 10% water in the fuel. Alternatively, from equation (19), it is clear that the partial pressure of H_2O in the fuel has a significant effect on concentration polarization. In the absence of this information, $\eta_{conc(a)}$ vs. i curve cannot be calculated for comparison with the experimental results. However, a comparison between the two plots in Figure #24 for different cathode areas (radii) may be made as follows.

For the cell with cathode area of $\sim 2 \text{ cm}^2$ ($r_c \approx 0.8 \text{ cm}$), the open circuit voltage (OCV) was 1.018 V. At 800°C , this corresponds to a $p_{H_2(0)} / p_{H_2O(0)} \approx 5.91$. A lower value of $p_{H_2(0)} / p_{H_2O(0)}$ than a typical practical fuel cell may be the result of some air leakage into the fuel stream. A value of i_{as} estimated for the best fit to the experimental data given in Figure #24 is $\sim 5.6 \text{ A/cm}^2$. The OCV for the cell with a cathode area of $\sim 1.1 \text{ cm}^2$ ($r_c \approx 0.6 \text{ cm}$) was $\sim 1.021 \text{ V}$. The corresponding value of $p_{H_2(0)} / p_{H_2O(0)}$ is 6.296. From these results, and equation (18), the estimated value of i_{as} is 7.62 A/cm^2 . Using this value of i_{as} , and $p_{H_2(0)} / p_{H_2O(0)} \approx 6.296$, $\eta_{conc(a)}$ was calculated at various values of current density. The calculated values of $\eta_{conc(a)}$ are compared with the experimental results in Figure #29. Note that there is qualitative agreement between the experimental results and prediction, insofar as the general trends are concerned. An exact agreement is not to be expected as the calculations only give $\eta_{conc(a)}$, while the experimental measurements also include anodic activation polarization. Also, the assumptions made in developing simple analytical relations are not

sufficiently rigorous to expect an exact agreement. In addition, the neglect of viscous flow in the derivation of anodic concentration polarization, and the assumption of fixed $D_{eff(a)}$, probably are other sources of uncertainty. Finally, there are critical issues concerning the placement of reference electrodes, which imply that there also are uncertainties in the exact measurement of anodic and cathodic overpotentials.

The value of i_{as} corresponding to the best fit in Figure #24 is about 5.6 A/cm². From this value and equation (16), the effective anode diffusivity, $D_{eff(a)}$, can be estimated. This value turns out to be ~0.31 cm²/sec. Indeed, this value is close to that deduced by curve fitting a previously developed theoretical model to voltage, V , vs. current density, i , traces [4,5]. An important point to note is that the estimated i_{as} is not necessarily the short-circuit current density measured experimentally. An examination of Figures #22, #23, and #24 shows that at any current density, anodic overpotential is lower than either the ohmic overpotential or the cathodic overpotential. That is, the experimental short circuit current density is largely due to these two overpotentials instead of the anode-limiting short circuit current density, i_{as} .

The preceding discussion suggests that in the case of cathode-supported cells with a smaller anode compared to the cathode, qualitatively similar effects would be observed; i.e., in this case the cathodic concentration polarization will be smaller, the smaller is the anode area relative to the cathode area. In general, however, cathodic concentration polarization is expected to be greater due to the lower binary diffusivity of O₂-N₂ compared to that of H₂-H₂O. As a consequence, it is expected that the effect of asymmetric electrodes would be more pronounced in the case of cathode-supported cells than in the case of anode-supported cells.

Effect of Cathode Microstructure:

Figure #30 shows typical voltage vs. current density traces for two cells tested at 800°C with humidified hydrogen and air. Note that cell performance is dependent on cathode interlayer composition, with the maximum power density ranging between ~0.35 W/cm² and ~1.1 W/cm², depending upon the cathode interlayer composition. Figure #31 shows a plot of the maximum power density measured as a function of wt.% LSM in the cathode interlayer.

Figure #32 is a photomicrograph of the cathode interlayer of composition 35 wt.% LSM and 65 wt.% YSZ, obtained on Cameca SX 50 electron microprobe. The length and width of the micrograph are ~18.3 μm and ~13.6 μm, respectively. White areas are YSZ, gray areas are LSM, and black regions represent porosity. Table 6 lists results of the microstructural measurements made on the cells tested.

Figure #31 shows that the maximum power density depends on the composition of the cathode interlayer, all other factors remaining the same. Table 6 shows that there is a significant variation in the microstructural parameters as a function of cathode interlayer composition, the most notable being the three phase boundary length, l_{TPB} , which varies between ~1780 and ~6550 cm⁻¹. Also of interest to note is that the YSZ aggregate grain size, d , of the sample with the least amount of LSM was one and a half to three times that of the other samples. The

cathode interlayer compositions were chosen such that all three phases are contiguous. The contiguity of LSM was confirmed by measuring the in-plane resistance of the cathode interlayer. Specifically, it was ensured that the layer was not insulating at room temperature, which would have been the case had LSM not been contiguous. The V_{YSZ} was above 0.34 in all samples, and thus is expected to be contiguous. The V_v was between ~ 0.14 and ~ 0.19 . For a random distribution of near spherical particles, the usual guideline for contiguity is that the volume fraction of a given phase be in excess of ~ 0.3 (the percolation threshold). This condition is not satisfied. However, it is to be noted that in a typical sintered compact, porosity is usually along three-grain junctions of a three dimensional, polyhedral packing, which is in the form of cylindrical, not spherical, pores. It is well known that porosity in a sintered compact becomes isolated (noncontiguous) below about 6% (0.06 on a volume fraction basis). As the porosity in the cathode interlayer is well in excess of the minimum (~ 0.06), the porosity was indeed contiguous. The porosity in the rest of the cathode current collector layer, anode interlayer,

and the supporting anode structure was well in excess of 20%, and thus was contiguous.

It is readily seen that the weight fraction of LSM, namely, W_{LSM} , is given by

$$W_{LSM} = \frac{\lambda_{LSM} V_{LSM}}{\lambda_{LSM} V_{LSM} + \lambda_{YSZ} V_{YSZ}} \quad (40)$$

or

$$\frac{1}{W_{LSM}} = 1 + \frac{\lambda_{YSZ}}{\lambda_{LSM}} \frac{V_{YSZ}}{V_{LSM}} \quad (41)$$

where λ 's are the respective densities. Thus, a plot of $1/W_{LSM}$ vs. V_{YSZ}/V_{LSM} should be a straight line with slope = $\lambda_{YSZ}/\lambda_{LSM}$, and intercept = 1.0. Figure #33 shows that a plot of $1/W_{LSM}$ from the as-formulated cathode interlayer, vs. V_{YSZ}/V_{LSM} obtained from microstructural measurements, is indeed a straight line. The slope of the line is ~ 1.02 . It is known that the densities of YSZ and LSM, are respectively, ~ 5.9 and ~ 6.5 g/ml., the ratio of which is ~ 0.91 , in reasonable agreement with expectations. Also note that the intercept is ~ 0.986 , which is very close to the expected value of unity.

The effect of electrode microstructure on charge transfer at three phase boundaries in composite electrodes was theoretically analyzed by Tanner et. al. who showed that the effective charge transfer resistance, R_{ct}^{eff} , of a composite electrode is given by [2]

$$R_{ct}^{eff} \approx \sqrt{\frac{R_{ct} \rho_{YSZ} d}{(1 - V_v)}} \quad (42)$$

where ρ_{YSZ} is the ionic resistivity of YSZ, a constituent in the cathode, and R_{ct} is the intrinsic charge transfer resistance, which depends on the electrocatalyst-electrolyte pair, here LSM and YSZ, the particle size of LSM and the number density per unit area, the latter two parameters effectively defining the three phase boundary (TPB) length, l_{TPB} . In terms of the charge

transfer resistivity, ρ'_{ct} , width, ε , and thickness, δ , through which charge transfer occurs, and l_{TPB} , the intrinsic charge transfer resistance, R_{ct} , is given by

$$R_{ct} = \frac{\rho'_{ct} \delta}{\varepsilon l_{TPB}} \quad (43)$$

The parameters δ and ε are on the order of a few angstroms, dimensions over which the actual charge transfer reaction occurs. Parameters, ρ'_{ct} , δ and ε are not separable from each other. Thus, one can define an intrinsic charge transfer resistivity, ρ_{ct} , by

$$\rho_{ct} = \frac{\rho'_{ct} \delta}{\varepsilon} \quad (44)$$

and the intrinsic charge transfer resistance is then given by

$$R_{ct} = \frac{\rho_{ct}}{l_{TPB}} \quad (45)$$

Substitution of R_{ct} in equation (42) gives

$$R_{ct}^{eff} \approx \sqrt{\rho_{YSZ} \rho_{ct}} \sqrt{\frac{d}{(1-V_v)l_{TPB}}} \quad (46)$$

The measured area specific resistance includes contributions from the electrolyte resistance, the anode interlayer, the anode support, and the cathode current collector. However, these other contributions are the same for all of the cells tested in the present study. Let us denote these other contributions by R_{other} such that the area specific resistance of each cell tested is given by

$$R_{cell} = R_{other} + R_{ct}^{eff} = R_{other} + \sqrt{\rho_{YSZ} \rho_{ct}} \sqrt{\frac{d}{(1-V_v)l_{TPB}}} \quad (47)$$

Microstructural measurements and analysis allows one to determine the parameter $\sqrt{d/((1-V_v)l_{TPB})}$, while R_{cell} is determined from experimentally measured voltage, V , vs. current density, i , traces. Thus, a plot of R_{cell} vs. $\sqrt{d/((1-V_v)l_{TPB})}$ gives R_{other} as the intercept, and $\sqrt{\rho_{YSZ} \rho_{ct}}$ as the slope. Since the ρ_{YSZ} is known from independent measurements, from the slope one can determine ρ_{ct} , the fundamental parameter which determines the charge transfer resistivity at LSM/YSZ/air three phase boundary, exclusive of any microstructural effects. This parameter is the most fundamental one, which may be used to compare various electrocatalyst/electrolyte pairs.

Table 7 lists the measured R_{cell} and the microstructural parameter $\sqrt{d/((1-V_v)l_{TPB})}$. Figure #34 is a plot of R_{cell} vs. $\sqrt{d/((1-V_v)l_{TPB})}$. The slope of the plot is $\sim 2110 \text{ } \Omega\text{cm}$ with a regression coefficient of ~ 0.98 . The ionic resistivity of YSZ at 800°C is about $40 \text{ } \Omega\text{cm}$. Thus, the estimated value of the charge transfer resistivity, ρ_{ct} is $\sim 1.11 \times 10^5 \text{ } \Omega\text{cm}$. This is an interesting result in that it has been possible to estimate the fundamental parameter, which determines charge transfer characteristics at a LSM/YSZ/air three phase boundary. This suggests that a correct comparison between two electrocatalysts can only be made on the basis

of ρ_{ct} , which is free from any microstructural effects. The other interesting point is that the present results clearly and quantitatively emphasize the importance of electrode microstructure, and the role of composite electrodes. It shows, for example, that through appropriate electrode microstructures, it is possible to achieve very low overall electrode polarization even if the intrinsic charge transfer characteristics, as expressed through ρ_{ct} , are not particularly good. The intercept in Figure #34 should yield R_{other} , the expected value of which is $\sim 0.1 \Omega\text{cm}^2$, based on prior work [10]. However, intercept in Figure #34 is $\sim -0.11 \Omega\text{cm}^2$, which of course cannot be true. A possible reason is the scatter in data and the fact that cathodic polarization is the dominant factor. That is, since R_{other} is expected to be rather small, a negative intercept is believed to be merely due to scatter, and insufficient data. Thus, the slope appears to be reasonable, but the intercept is not. Although without any basis, one may plot R_{cell} vs. $1/l_{TPB}$, a typical procedure used in plotting data when the electrode is not a composite one (that is LSM on YSZ, rather than LSM + YSZ on YSZ), as done in Figure #35. Even though the intercept is reasonable, the corresponding regression coefficient is only ~ 0.84 , indicating a poorer fit. If the last data point is ignored, the fit will be considerably better, although then the intercept is not reasonable. In any event, there is no basis to ignore this point. It is thus concluded that the composite model offers a better fit to the data, although considerably more data are needed for an unequivocal assertion.

In the preceding, it was assumed that activation polarization, η_{act} , is linearly dependent on i , and can be expressed in terms of R_{ct}^{eff} . At high current densities, it is expected that η_{act} may be linearly related to $\ln i$ through the Tafel equation. If such is the case, the mathematical relationship between η_{act} and microstructure will be different from the one implied in equation (47). Nevertheless, it is clear that the role of electrode microstructure will be equally profound, regardless of the details of relationship between η_{act} and i .

Alcohol as a Fuel:

Figure #36 is a scanning electron micrograph (SEM) of a cell, fractured after testing. Five distinct layers are visible in the micrograph. The anode substrate was optimized to facilitate rapid transport of large fuel molecules, such as CH_3OH and $\text{C}_2\text{H}_5\text{OH}$. Microstructures of the anode and cathode interlayers, which are electrochemically active regions for the occurrence of the anode and cathode reactions, respectively, are relatively fine as can be seen in the inset. Recent theoretical modeling by Tanner, et al. [2] emphasizes the importance of electrode microstructure on the effective charge transfer resistance, a measure of electrode electrochemical activity. The effective charge transfer resistance was shown to be proportional to the square root of a microstructural feature of an electrode, e.g. the grain size [2]. Thus, the finer the electrode microstructure, the smaller is the effective charge transfer resistance, and the higher is the effective exchange current density. The microstructures of the anode and the cathode in the present study were optimized to enhance the overall electrode reaction rate.

Figure #37 shows performance characteristics of such a cell with hydrogen, methanol and ethanol + water (1:1 in volume) as fuels. Open circuit voltages (OCV) with H_2 , methanol and

ethanol + water as fuels, were, respectively, 1.005 V, 0.978 V and 0.95 V. A slightly lower OCV with H₂ than the theoretical value (~1.04 V) was probably due to some leakage of air through the seal. Lower values of OCV with methanol, and ethanol + water, as fuels, may also be due to possible non-equilibrium conditions. At 800°C, the maximum power density was measured to be 1.7 W/cm² with hydrogen, 1.3 W/cm² with CH₃OH and 0.8 W/cm² with C₂H₅OH + H₂O (1:1 in volume). The actual power densities could be between 5 and 10% lower due to differences in cathode and anode diameters. These data demonstrate that the cells made in the present work can be successfully operated on alcohols while yielding high power densities. With C₂H₅OH + H₂O as the fuel, although a fairly high power density of 0.8 W/cm² at 800°C was achieved, the cell performance was still much lower than with either CH₃OH or H₂. The possible reasons include: (1) Higher concentration polarization due to the larger molecular weight of C₂H₅OH. (2) Higher activation polarization. Further optimization of electrode microstructures may be necessary to improve performance with C₂H₅OH as a fuel. To the authors' knowledge, power densities measured here with CH₃OH and C₂H₅OH as fuels, are by far among the highest values reported on SOFC directly using CH₃OH and C₂H₅OH as fuels, and significantly higher than polymer electrolyte based direct methanol fuel cells (DMFC).

Figure #38 shows cell performance with CH₃OH at lower temperatures. The maximum power densities measured were 0.6 W/cm² at 650°C and 0.2 W/cm² at 550°C. These results show that although there is a significant decrease in cell performance at lower temperatures, power densities of practical interest can be realized at temperatures as low as 550°C. With C₂H₅OH + H₂O as a fuel, the maximum power density measured was 0.3 W/cm² at 650°C. As discussed in what follows, lower cell performance at low temperatures is largely attributed to the decrease in the cathodic activity of LSM-YSZ electrode at low temperatures.

The performance of a fuel cell is governed by, anode and cathode polarizations as well as the cell ohmic resistance. The ohmic resistance is due to the resistances of the electrolyte and of the electrodes. The total cell ohmic resistance measured by the current interruption technique was 0.08, 0.12 and 0.3 Ωcm² at 800, 650 and 550°C, respectively. Although it increases by greater than a factor of three from 800°C to 550°C, it is still low enough to yield power densities of practical interest at temperatures as low as 550°C.

Figures #39 and #40 show cathode and anode polarizations as functions of current density. Cathode polarization is due to the resistance to electrochemical reduction of O₂, including charge transfer and mass transport processes. The cathode polarization (overpotential) was small, about 0.1 V at a current density of 3 A/cm² at 800°C, and comparable to the anode polarization with hydrogen and methanol as fuels. However, it increases rapidly with decreasing temperature and is responsible for the observed low performance at lower temperatures. As shown in Figure #39, the cathode overpotential reaches as high as 0.5 V at 2 A/cm² at 650°C, and 0.7 V at only 0.75 A/cm² at 550°C, which is much higher than the anode overpotential under similar conditions (Figure #40). These results indicate that Ni-YSZ based anode is sufficiently active for methanol. However, LSM + YSZ is not a very good cathode material for operation at low temperatures.

Anode polarization is principally related to the resistance to mass transport of fuel and/or to its electrochemical oxidation. The cathodic polarization and the ohmic resistance, both are expected to be independent of the fuel used. Thus, the observed differences in cell performance with different fuels are attributed to differences in anodic polarization. The results of anodic overpotential measurements with methanol as a fuel at various temperatures, as well as with hydrogen and ethanol + water as fuels at 800°C, are shown in Figure #40. The open symbols in Figure #40 denote anodic overpotential for methanol at 800, 650 and 550°C. As can be seen from Figure #40, the anodic polarization with CH₃OH is quite small at 800°C, and is close to that for H₂ at a current density up to about 2 A/cm². At higher current densities, the anodic overpotential with CH₃OH exhibits a faster increase. The relatively weak temperature dependence of the anodic polarization suggests that the principal contribution may be related to mass transport.

At 650°C, the anodic polarization with CH₃OH as a fuel is only slightly higher than at 800°C. By contrast, it is considerably greater at 550°C. This difference may be related to concentration polarization and the effects of anode gas composition. The possible mechanism for the electrochemical oxidation of CH₃OH could be either a direct oxidation into CO₂ + H₂O, or first a decomposition of CH₃OH into CO + H₂, followed by electrochemical oxidation of CO + H₂ into CO₂ + H₂O. If decomposition into CO + H₂ occurs prior to electrochemical oxidation, concentration polarization in the anode will be related to the transport of H₂ in addition to the transport of other gas species such as H₂O, CO and CO₂. The important binary diffusivities which govern transport are D_{H_2-CO} , $D_{H_2-H_2O}$ and $D_{H_2-CO_2}$. If, on the other hand, a direct electrochemical oxidation of CH₃OH occurs, the anode gas will contain CH₃OH, CO₂, H₂O, and possibly CO; but little or no H₂. In such a case, the pertinent binary diffusivities are $D_{CH_3OH-H_2O}$, $D_{CO_2-H_2O}$, $D_{CH_3OH-CO_2}$, D_{CH_3OH-CO} , D_{CO-H_2O} , etc. The calculated value of the binary diffusivity of H₂-CO, that is D_{H_2-CO} using the Chapman-Enskog theory, is ~6.4 cm²/s at 800°C, and that of H₂-H₂O, $D_{H_2-H_2O}$, is ~7.7 cm²/s. By contrast, the corresponding binary diffusivity of CH₃OH-H₂O, $D_{CH_3OH-H_2O}$ is ~1.7 cm²/s., and that of CH₃OH-CO₂, $D_{CH_3OH-CO_2}$, is ~1.16 cm²/s. This suggests that if methanol is not converted into CO + H₂ prior to its electrochemical oxidation, there could be significant losses associated with concentration polarization. It is possible that at a temperature as low as 550°C, methanol does not readily decompose into a mixture of CO + H₂, but at 800°C it does. With ethanol as a fuel, concentration polarization will similarly be high if C₂H₅OH + H₂O does not reform to form a gaseous mixture containing H₂. Indeed, with ethanol as a fuel, even at 800°C, anodic polarization was much higher than with either H₂ or CH₃OH as fuels, and that the power density was considerably lower than with either hydrogen or methanol as fuels. Presumably, the in-situ reformation reaction with ethanol did not readily occur at 800°C. In order to verify the validity of this hypothesis, the following experiments were conducted.

Methanol was circulated through the anode chamber of a cell at 800°C without operating the cell. The exhaust was condensed to determine how much of the methanol remained un-reacted. It was observed that ~25% of the methanol remained un-reacted; that is ~75% was converted into CO + H₂. A similar experiment was conducted wherein an equi-volume mixture of C₂H₅OH + H₂O was passed through the anode compartment of the cell. Analysis of the

condensate showed that ~50% of the C_2H_5OH remained un-reacted. These results are preliminary. Nevertheless, they suggest that with ethanol as a fuel, the amount of H_2 formed must have been less, and the resulting concentration polarization must have been rather high. This may explain, in part, the observed lower performance with ethanol as a fuel. These results have important implications with regard to direct electrochemical oxidation of hydrocarbon fuels. On one hand, direct electrochemical oxidation of hydrocarbon fuels is desired since it simplifies system design, as no reformer is necessary, and the introduction of water may not be required, provided carbon deposition can be suppressed. On the other hand, however, a lack of H_2 in the fuel may substantially increase concentration polarization thus limiting performance.

After testing, the cells were examined visually as well as under an SEM. No noticeable carbon deposition on Ni-YSZ anode was observed with methanol as a fuel. A thermodynamic calculation shows lower tendency for carbon formation with CH_3OH compared to that with C_2H_5OH . Carbon deposition on the Ni-YSZ anode was observed when pure ethanol was used as a fuel. Carbon deposition, however, was successfully suppressed when the fuel used was an equi-volume solution of ethanol and water.

The present study demonstrates the feasibility of operating SOFC directly on alcohols at relatively low temperatures, while yielding fairly high power densities. Direct alcohol SOFC may significantly simplify the fuel cell system and improve the overall efficiency. The abundance and the ease of handling liquid fuels such as alcohols may lead to widespread applications of the SOFC. Also, since ethanol is a renewable fuel derived from agricultural byproducts, it is not dependent on fossil energy and may be more viable in the long run. Considerable work remains to be done to further improve the fuel cell performance with C_2H_5OH as a fuel. Improvements in cathode material and further optimization of the microstructures of both electrodes may lead to better performance at lower temperatures.

LSM-LSGM Cathodes:

A scanning electron micrograph (SEM) of a typical anode-supported cell is shown in Figure #41. The micrograph shows the porous LSGM/LSM composite cathode (top), the dense YSZ electrolyte film, and the porous Ni/YSZ anode interlayer (bottom). The composite cathode of this particular cell contained 50 wt.% LSGM and 50 wt.% LSM, which was fired at 1150°C for 2 hours.

The effect of cathode composition on cell performance was studied by varying the relative composition of the composite cathode interlayer between 30 and 70 wt.% LSGM and 70 and 30 wt.% LSM. For this study, the composite cathode interlayers were fired at the same temperature of 1150°C for two hours. The other components of the cells, including the anode, anode interlayer, electrolyte film, and cathode current collecting layer, were fabricated in batch processes under standard conditions in order to minimize differences from cell to cell. SEM analysis confirmed that the composite cathode interlayers partially sintered to form a contiguous two-phase structure while still containing a substantial amount of open porosity necessary for adequate gas flow. In addition, the composite cathode interlayers appeared firmly bonded to the dense YSZ electrolyte and no signs of delamination were observed before or after testing of the cells. The performance curves for cells with composite cathode interlayers

of various compositions fired at 1150°C are shown in Figure #42. The cell testing was conducted at 800°C. The maximum power density increased with increasing LSGM content in the composition range 30 to 50 wt.% LSGM and then decreased for LSGM compositions greater than 50 wt.%. The overall area specific resistance (ASR) of the cell decreased with increasing LSGM content up to 50 wt.% and then increased again for LSGM contents greater than 50 wt.%. The cell with the 50 wt.% LSGM + 50 wt.% LSM composite cathode interlayer exhibited the best performance with a maximum power density of 1.4 W/cm² at 2.6 A/cm² and an overall cell ASR of 0.18 Ωcm².

The overpotentials at the anode and the cathode, as well as the ohmic overpotential (IR drop) of the cells, were measured with a reference electrode located next to the cathode. Calculations of Winkler *et. al.* have shown that the measured overpotentials depend upon the relative position of the reference electrode [11]. The implied recommendation is that on anode-supported cells, one should not use a reference electrode. However, it is the experience in our laboratory that while some errors in the absolute values of overpotentials measured may well exist, reference electrode is still a valuable tool in evaluating relative differences in electrochemical performance of cells, especially when all other parameters are fixed, and only one parameter is varied. In an attempt to minimize measurement errors and variations from cell to cell, all cells from this work were made from a single anode support tape. In addition, care was taken to ensure that the thickness and the morphology of the anode interlayer, the thickness of the electrolyte layer, the morphology and the thickness of the cathode current collector layer, and the thickness of the cathode interlayer, were essentially the same for all cells. The only variability was in the composition of the cathode interlayer (and any associated morphological differences that arise due to differences in the cathode interlayer composition), or the firing temperature (and any associated morphological changes that arise due to differences in firing temperatures). In this manner, differences in the measured cathode overpotentials could be attributed to differences in the cathode interlayer.

The anode overpotential as a function of current density for cells with cathode interlayer compositions between 30 and 70 wt.% LSGM and 70 and 30 wt.% LSM are shown in Figure #43. Note that the anode overpotential at 1.0 A/cm² varies between ~30 mV and ~50 mV. The total ohmic overpotentials (IR drops) as a function of current density for the same cells are shown in Figure #44. At a current density of 1.0 A/cm², the ohmic overpotential varies between ~100 and ~125 mV. The corresponding area specific ohmic resistances of the cells with cathode interlayer compositions of 30/70, 60/40, and 70/30 were approximately 0.125 Ωcm², while that for the cells with cathode interlayer compositions of 40/60 and 50/50 were lower with a value of approximately 0.1 Ωcm². The total ohmic overpotential (IR drop) measured includes contributions from the anode, electrolyte, and cathode. The estimated ohmic resistance of a 10 μm YSZ electrolyte layer is 0.05 Ωcm² at 800°C. Thus, over half of the ohmic resistance of the cell is due to the anode and the cathode. Furthermore, since the anodes were prepared from the same tape, the higher ohmic resistances of the cells with cathode interlayer compositions of 30/70, 60/40, and 70/30 as compared to the cells with cathode interlayer compositions of 40/60 and 50/50 must be due to differences in the cathode interlayer. Because of the higher electronic conductivity of LSM as compared to YSZ, it is expected that the ohmic resistances of the cathode interlayers would decrease with increasing LSM content. The lower ohmic resistances of the cells with cathode interlayers containing 50 and 60 wt.%

LSM as compared to those with only 30 and 40 wt.% LSM is consistent with this notion. However, the high ohmic resistance of the cell with LSM rich 30/70 cathode interlayer indicates that other factors, such as sinterability and bonding between cathode interlayer and electrolyte, are likely factors, which determine the ohmic resistance.

The overpotentials at the cathode as a function of current density are shown in Figure #45. As seen in the figure, the cathode interlayer composition has a profound effect on the overpotential at the cathode with the worst performing cell (70/30) exhibiting an overpotential of approximately 425 mV at 1.0 A/cm² while the best performing cell (50/50) with an overpotential of only 60 mV at 1.0 A/cm², which is a difference of 365 mV. Note that this difference is much greater than even the absolute values of anodic and ohmic overpotentials. As the differences in the anodic overpotentials and ohmic overpotentials were less than 25 mV, it is clear that errors due to surface mounting of a reference electrode must be small (for < 1 A/cm²). For this reason, it can be concluded that measurements made with respect to a reference electrode are valuable in assessing the performance of the cathode.

Since the cathode interlayers are comprised of the same materials, LSGM and LSM, the differences in performance with variation in relative amounts of LSGM and LSM are likely due to microstructural and compositional differences. Firstly, in order for composite electrodes to be effective, the two phases must be contiguous throughout the electrode. Typically a minimum of 30 vol.% of a phase must be present to ensure contiguity, with this value being higher depending on the amount and the morphology of porosity. The theoretical densities of LSGM and LSM are approximately 6.2 g/cm³ and 6.5 g/cm³, respectively. Thus, approximate volume % of the two phases must be in proportion to their wt.%. Therefore, for the 30/70 and 70/30 cathode interlayer compositions, it is possible that one of the two phases has low contiguity in the electrode. In cases where the two phases are indeed contiguous, it has been shown that the performance of composite electrodes is dependent on porosity and three-phase boundary length (TPB). The porosity in the electrode must be adequate to allow for the transport of gases in and out of the electrode. In cases where the porosity is low and/or the current densities are high, the effects of concentration polarization can be large and may adversely affect the performance of a cell. SEM analysis, however, shows that the LSGM/LSM composite cathodes are highly porous. Although some differences in porosity may occur with differing compositions of the composite cathode interlayer, the effects of concentration polarization are small at low current densities. Thus, the large differences in cathode overpotentials at current densities below 0.5 A/cm² (Figure #45) are likely due to changes in the three-phase boundary length (TPB) and thus dominated by activation polarization. The effects of TPB on the activation polarization of composite electrodes have been analyzed by, several groups including Kenjo et al. [12] and Tanner et al. [2]. In the model proposed by Tanner et. al., the effective charge transfer resistance (R_{ct}^{eff}) depends on the intrinsic charge transfer resistance (R_{ct}) and the electrode microstructure such that

$$R_{ct}^{eff} = \sqrt{\frac{R_{ct}d\rho_i}{(1-V_V)}} \quad (48)$$

where, ρ_i is the ionic resistivity of the solid electrolyte (LSGM) in the cathode, V_V is the volume percent of porosity, and d is a microstructural parameter related to the particle size of solid electrolyte in the cathode. The intrinsic charge transfer resistance (R_{ct}) is given as

$$R_{ct} = \frac{\rho_{ct}}{l_{TPB}} \quad (49)$$

where ρ_{ct} is the charge transfer resistivity and l_{TPB} is the three phase boundary length. The ionic resistivity ρ_i , a property of solid electrolyte part of the composite cathode, and the charge transfer resistivity ρ_{ct} , a property of the electrocatalyst, solid electrolyte, and gas phase system, are dependent on material properties. The volume percent of porosity V_V , particle size d , and three-phase boundary length l_{TPB} , by contrast, are microstructural parameters. The effective charge transfer resistance can be rewritten as

$$R_{ct}^{eff} = \sqrt{\rho_{ct}\rho_i} \sqrt{\frac{d}{l_{TPB}(1-V_V)}} \quad (50)$$

in order to separate and emphasize the effects of the fundamental material properties from the microstructural properties. For the LSGM/LSM composite cathodes studied, the ionic resistivity of LSGM and the intrinsic charge transfer resistivity of the LSGM/LSM system are constant and should not vary from cell to cell¹. Furthermore, the different compositions of composite cathodes were prepared from the same starting LSGM and LSM powders. For a given firing temperature, the particle size of the electrolyte d should not vary to a large degree, since the maximum cathode firing temperature was only 1200°C, while the typical sintering temperature of LSGM is above 1500°C. Thus, changes in the effective charge transfer resistance for various compositions of composite cathode should primarily be due to varying TPB length. At low current densities, the charge transfer resistance of the cathode can be estimated from the linear portions of the overpotential versus current density plots. Also, the effective exchange current density can be determined using the low current density approximation of the Butler-Volmer equation, since it is inversely proportional to the effective charge transfer resistance, R_{ct}^{eff} . The area specific charge transfer resistance and the exchange current density for composite cathodes of various compositions are given in Table 8. The area specific charge transfer resistance varies from 0.557 Ωcm^2 for the cathode of 30/70 composition to 0.242 Ωcm^2 for the cathode of 50/50 composition. The cell with the 50/50 cathode interlayer exhibited the lowest charge transfer resistance, which is consistent with its low cathode overpotential (Figure #45) and a high power density (Figure #42). The anodic and the cathodic overpotentials, and the total ohmic overpotential (IR drop) for the cell with the 50/50 cathode interlayer fired at 1150°C are shown in Figure #46. For this cell, the anodic and cathodic overpotential contributions to the total overpotential losses are similar and lower than that due to the total ohmic resistance.

In addition to the cathode interlayer composition, the firing temperature of the cathode interlayer was varied and the resulting effects on cell performance were investigated. The cathode interlayer composition was fixed at 50 wt.% LSGM and 50 wt.% LSM, and fired at a temperature between 1000 and 1200°C for two hours. The voltage and the power density curves as a function of current density for these cells measured at 800°C are shown in Figure #47. The total area specific resistance decreases from 0.20 Ωcm^2 to 0.16 Ωcm^2 with increasing firing temperature from 1000°C to 1150°C, but then increases dramatically to 0.24 Ωcm^2 for a firing temperature of 1200°C. Thus, as expected, the power density increases from

¹ This is strictly not true, as the ionic conductivity of LSGM is expected to be a function of the grain size.

approximately 1.0 W/cm^2 to 1.4 W/cm^2 with an increasing firing temperature between 1000 to 1150°C , and then decreases to $\sim 0.6 \text{ W/cm}^2$ for the interlayer fired at 1200°C . The anode overpotential, as a function of current density for the cells tested at 800°C , is shown in Figure #48. Similar to the cells previously tested (Figure #43), the anode overpotential at 1.0 A/cm^2 varies over a range of about 20 mV . The ohmic overpotentials (IR drop) of the cells as a function of current density are shown in Figure #49. The ohmic resistances for the cells with cathode interlayers fired at 1000 , 1050 , and 1100°C are approximately the same with a value of $0.125 \text{ }\Omega\text{cm}^2$. The ohmic resistance of the cell whose cathode interlayer was fired at 1150°C is lower with a value of $0.1 \text{ }\Omega\text{cm}^2$, while that for the interlayer fired at 1200°C is higher with a value of approximately $0.175 \text{ }\Omega\text{cm}^2$. The lower area specific resistance of the sample with cathode interlayer fired at 1150°C may be due to better bonding between the cathode to the electrolyte thus reducing the contact resistance at the interface. The high resistance of the cell with the cathode interlayer fired at 1200°C may be due to the formation of an intermediate phase at the interface between the cathode and the electrolyte. This possibility will be discussed later.

The cathode overpotentials as function of current density for the cells with 50/50 interlayers fired at temperatures between 1000 and 1200°C are shown in Figure #50. The overpotential at the cathode decreases with increasing firing temperature in the range 1000 to 1150°C , then dramatically increases for the interlayer fired at 1200°C . At 1.0 A/cm^2 , the cathode overpotential varies between a low of 65 mV for the interlayer fired at 1150°C to a high of 250 mV for the interlayer fired at 1200°C . The effective charge transfer resistances and the effective exchange current densities for cathodes with interlayers fired at various temperatures are summarized in Table 9. The effective charge transfer resistance decreases with increasing firing temperature in the range 1000 to 1150°C , and then increases again above 1150°C . The decrease in charge transfer resistance at the cathode with increasing firing temperature of the interlayer ($1000^\circ\text{C} \leq T \leq 1150^\circ\text{C}$) is likely due to more complete sintering (better particle-to-particle contact). The effective charge transfer resistance is dependent on particle size d , three-phase boundary length l_{TPB} , and volume percent porosity V_V as modeled by equation (50). At higher firing temperatures (1200°C), it is possible that either a reaction between the electrocatalyst and the ionic conductor occurs wherein the intrinsic charge transfer resistivity is adversely affected, or that the microstructure is adversely affected, or both. Unless detailed microstructural analysis is conducted, it would be difficult to decipher the exact reason(s).

An examination of Figures #45 and #50 shows that cathodic overpotential exhibits a complex dependence on current density. Specifically, it is seen that in many cases, over some current density range, the overpotential is almost independent of current density ($d\eta_{cathode}/di \approx 0$). It is not known if this is a real effect, or a possible artifact of uncertainties related to the placement of reference electrodes.

In order to determine whether chemical reactions at the cathode played a role in the poor performance of the cell whose cathode was fired at 1200°C , possible chemical interactions between LSGM and LSM and LSGM and YSZ were investigated. Chemical interactions between LSM and YSZ at elevated temperatures have been reported [13,14]. LSM and YSZ react to form the secondary phase $\text{La}_2\text{Zr}_2\text{O}_7$ at temperatures above 1200°C . In the present

study, the phase $\text{La}_2\text{Zr}_2\text{O}_7$ was not detected by XRD in milled mixtures of LSM and YSZ powder fired at temperatures between 1000 and 1200°C for two hours. Since the maximum cathode firing temperature was 1200°C, it may be concluded that reaction between LSM and YSZ is not responsible for the poor performance of the cathode fired at 1200°C. Similarly, no secondary phases were detected by XRD for milled mixtures of LSGM and LSM powder fired for two hours at a temperature as high as 1200°C. This is in agreement with previous work by Huang et al., which reported inter-diffusion of La, Sr, Mn, and Ga between LSM and LSGM with no phase transformations [15]. Possible reactions between LSGM and YSZ were investigated by milling and firing mixtures of LSGM and YSZ powders at temperatures between 1000 and 1200°C for two hours. X-ray powder diffraction patterns of the powders after firing are shown in Figure #51. In the temperature range 1000 to 1200°C, LSGM reacts with YSZ to form a secondary phase with a cubic crystal structure, which was indexed as the pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ (JCPDS 17-0450). The relative amount of the pyrochlore phase increases with increasing temperature in the range, $1000 \leq T \leq 1200^\circ\text{C}$. For the powder mixture fired at 1200°C for two hours, no LSGM was detectable by XRD and appears to have completely reacted with YSZ. Other than the pyrochlore, no other phases were found in any of the patterns. In order to determine if Ga dissolved into $\text{La}_2\text{Zr}_2\text{O}_7$ or YSZ, energy dispersive spectroscopic (EDS) analysis was performed on dense samples fabricated from LSGM and YSZ powders fired at 1000, 1100, and 1200°C. The presence of Ga was detected in the pyrochlore phase but not in YSZ. This shows that LSGM reacts with YSZ to form Ga doped cubic $\text{La}_2\text{Zr}_2\text{O}_7$. It was not determined whether Ga substitutes on La or Zr sites of the $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore phase. The six-coordinated Ga^{3+} ion is closer in size to the Zr^{4+} ion than the larger La^{3+} ion [16]. Thus, it is the expectation that Ga^{3+} ion may substitute for the Zr^{4+} ion resulting in an oxygen deficient pyrochlore, $\text{La}_2\text{Zr}_{2-x}\text{Ga}_x\text{O}_{7-\delta}$.

In all fuel cells tested, a mixture of LSGM and LSM powder was screen-printed onto an already sintered dense layer of YSZ. In order to investigate a possible reaction at this interface, LSGM powder in the form of a paste was screen-printed onto dense YSZ pellets and then fired at 1000, 1100, and 1200°C for two hours. After firing, the LSGM side of the pellets was analyzed with XRD and the samples were sectioned and analyzed with EDS. The presence of a pyrochlore phase was not detected with XRD indicating that the reaction was limited to the interface. EDS analysis of the cross section of the cell, whose cathode was fired at 1200°C, revealed a thin reaction layer of approximately 4 μm in thickness between the LSGM and YSZ regions. The thickness of the reaction zone for the sample fired at 1100°C was less than 0.5 μm , while that for the 1000°C sample was not detectable. The formation of a thin layer of the resistive, Ga-containing $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore phase between the cathode interlayer and YSZ electrolyte, when fired at 1200°C for two hours, appears to increase the ohmic resistance of the cell and the cathodic overpotential and is thus detrimental to the performance of the cell.

Anode Reduction-Re-Oxidation Kinetics:

SEM micrographs of NiO-YSZ samples sintered showed that the samples were essentially fully dense, with no detectable open porosity. The grain sizes of NiO and YSZ were on the order of 1 to 2 microns. Figure #52 shows plots of the reduced layer thickness as a function of time at various temperatures, ranging between 600 and 800°C. It is seen that the plots are linear, indicating that the kinetics of reduction is interface-controlled. The slopes of lines in

Figure #52 give the phenomenological rate constant for the interface-controlled reduction, namely k_{red} . Typical porosity in the porous Ni + YSZ layer formed is ~25%. Prior work has shown that the estimated D_{eff}^r is on the order of ~0.1 cm²/s (at ~800°C). As seen in Figure #52, the maximum reduction thickness was on the order of 800 microns for the length of time the samples were reduced. A crude estimate of the characteristic time required to equilibrate gaseous compositions in a porous body is given by

$$\tau \sim \frac{l_r^2}{D_{eff}^r} \quad (51)$$

where l_r = reduced layer thickness. For the above values, τ is estimated to be ~0.1 second, which is orders of magnitude smaller than the time required to achieve a reduced layer thickness of 800 microns, which is on the order of 3 h or greater than 10,000 seconds. This shows that the kinetics of reduction must be interface-controlled, as observed. The kinetics of reduction is also thermally activated with activation energy on the order of 94 kJ/mol. This observation is also reasonable, since it is well known that reaction rates are usually thermally activated.

Figure #53 shows a plot of the square of the re-oxidized layer thickness as a function of time at 700°C. As seen in the figure, the plot is linear, consistent with diffusion-controlled kinetics, unlike reduction kinetics, which is interface-controlled. From the slope, an estimate of the phenomenological diffusion coefficient, D_{ox} , can be made. For the data shown in Figure #53, the estimated D_{ox} is ~1.1 x 10⁻⁷ cm²/s. It was observed that this was nearly the same for all temperatures between 650 and 800°C. Such a low value of D_{ox} suggests that either the re-oxidized layer has no open porosity and transport of oxygen must be occurring through the solid part (for example, oxygen ions through YSZ and electrons or holes through either NiO and/or YSZ); or that the re-oxidized layer has open porosity and oxygen transport must be occurring through the pores. If it is the former, it is expected that oxygen transport would be thermally activated. However, experiments showed that the measured D_{ox} was virtually independent of temperature. This is consistent with the occurrence of gaseous diffusion through pores. It is to be noted that for diffusion through pores, the expected temperature dependence of D_{ox} is approximately $T^{0.5}$, since through the Chapman-Enskog model, $D_{eff}^o \propto T^{3/2}$ (note that $D_{ox} \propto D_{eff}^o / T$). That is, the dependence of D_{ox} on temperature is rather weak. In order to determine if indeed porosity is formed upon re-oxidation, samples were examined in SEM in the as-sintered state as well as after re-oxidation of reduced samples. Figure #54 shows an SEM micrograph of an as-sintered sample. The light phase is NiO, the gray phase is YSZ, and black spots are pores. Note that the sample has very small amount of porosity. Figure #55 shows an SEM micrograph a re-oxidized sample. Note that the amount of porosity is much greater in the re-oxidized sample as compared to that in the as-sintered sample. Table 10 lists the densities and porosities of as-sintered and re-oxidized samples. The kinetics of re-oxidation appear to be governed by diffusion of oxygen through the pores formed.

Fuel Composition Effects on Anode Polarization:

An SEM micrograph of a polished section of the Ni-YSZ anode is shown in Figure #56. Figures #57, #58 and #59 show cell voltage vs. current density, and power density vs. current density traces with as-received H₂, and H₂ diluted with various concentrations of He, N₂ and CO₂. For as-received H₂ as the fuel, the open circuit potential was around 1.05 V, the maximum power density was about 1.7 W/cm², and there was no obvious limiting current density even at the highest current density of 4.5 A/cm² at which measurements were made. When H₂ was diluted with various diluents, the general trend was similar for each diluent, namely that: (1) with increasing dilution, the open circuit voltage decreased, and (2) the maximum power density as well as the maximum current density decreased. At high diluent concentrations, substantial concentration polarization was present as evidenced by the observation of a limiting current density. Since the cathode conditions were kept the same, the observed changes in performance with different diluents and their concentrations could be solely attributed to changes made in anodic conditions.

A comparison of Figures #57 (H₂-He), #58 (H₂-N₂), #59 (H₂-CO₂), and #60 (H₂-H₂O) shows that the maximum power density achieved at the highest concentration of the diluent (~78-81%) was the highest for H₂-He mixtures (~0.75 W/cm²) and the lowest for H₂-CO₂ mixtures (~0.3 W/cm²). Also, the corresponding short circuit current density was the highest for H₂-He mixture (~1.55 A/cm²) and the lowest for H₂-CO₂ mixture (~0.7 A/cm²). The highest power density measured was ~1.7 W/cm² for this cell with as-received H₂ as the fuel. A comparison of H₂-He and H₂-N₂ mixtures, wherein the diluent is inert, shows that the maximum power density at the highest diluent concentration is ~0.75 W/cm² for H₂-He and ~0.5 W/cm² for H₂-N₂ mixtures. Also, the corresponding anode-limiting current densities were ~1.5 A/cm² for H₂-He mixture and ~0.85 A/cm² for H₂-N₂ mixture of similar diluent concentrations.

As seen in Figures #61 and #62, the open circuit voltage (OCV) exhibited a stronger dependence on the diluent concentration when the diluent was either CO₂ or H₂O, consistent with expectations, as the diluents in these cases are not inert, and enter into chemical reactions of the following type:

In H₂-H₂O mixtures,

and, in H₂-CO₂ mixtures,

until the respective reaction equilibria are established.

Figure #61 shows cell performance curves for gas mixtures containing CO and CO₂ as the fuel. The maximum power density measured with as-received CO as the fuel was ~0.7 W/cm², which is considerably lower than that with as-received H₂ as the fuel (Figures #57 through #60). For the gas mixture containing 18% CO + 82% CO₂, the maximum power density was only ~0.1 W/cm², and the corresponding limiting current density was only ~0.2 A/cm². An examination of Figures #57 through #61 shows that a limiting current behavior is observed in all cases at higher diluent concentrations. The limiting current density, i_{as} , for each case is

plotted vs. the partial pressure of the fuel gas (either H₂ or CO) in Figure #62. It is seen that the dependence of i_{as} on the respective partial pressure (p_{H_2} or p_{CO}) is close to linear, with H₂-He fuel (or H₂-H₂O-He mixtures) exhibiting the highest i_{as} , and the highest slope; and the CO-CO₂ mixtures exhibiting the lowest i_{as} , and the lowest slope.

Figure #63 shows the performance curves with H₂ + CO gas mixtures as the fuel, where the composition was varied between ~100% (as-received) H₂ and ~100% (as-received) CO. The OCV is essentially independent of the relative proportions of H₂ and CO. The maximum power density varied between ~1.7 W/cm² for 100% H₂, to ~0.7 W/cm² for 100% CO. Note that the maximum power density for CO concentrations less than ~55% ranges between ~1.5 and ~1.7 W/cm²; and for CO concentrations between 68% and 100%, the maximum power density ranges between ~1.2 W/cm² and ~0.7 W/cm².

Thermodynamic Calculation of Open Circuit Voltages: The thermodynamic open circuit voltage (OCV) of a fuel cell, which is the Nernst potential, is given by

$$E = \frac{RT}{4F} \ln \left(\frac{p_{O_2(cathode)}}{p_{O_2(anode)}} \right) \quad (52)$$

where $p_{O_2(cathode)}$ is the partial pressure of oxygen at the cathode (under open circuit conditions), which is 0.21 atm when air is used as the oxidant; $p_{O_2(anode)}$ is the partial pressure of oxygen in fuel at the anode (under open circuit conditions). For example, when H₂ is the fuel,

at equilibrium, the partial pressure of oxygen at the anode, $p_{O_2(anode)}$ is given as

$$\ln p_{O_2(anode)} = \frac{2\Delta G_3^o}{RT} + 2 \ln \left(\frac{p_{H_2O}}{p_{H_2}} \right) \quad (54)$$

where ΔG_3^o is the standard free energy of reaction (53). The ΔG_3^o is -188.165 kJ/mol at 800°C [17]. At various partial pressures of H₂ and H₂O, $p_{O_2(anode)}$ can be calculated from Equation (54), and the OCV can be determined using Equation (52).

Figure #64 shows the calculated $p_{O_2(anode)}$ (except for as-received H₂, whose water content was not known), the calculated OCV and the experimentally measured OCV as a function of p_{H_2O} . The partial pressure of oxygen at the anode increases from 10⁻²⁰ atm to 10⁻¹⁷ atm, and the calculated OCV decreases from 1.021 V to 0.877 V, when the p_{H_2O} increases from 0.15 atm to 0.8 atm. The measured OCV, in general, exhibits the same trend as the calculated one, although it is about 50 mV lower than the calculated.

For the reaction

the standard free energy, ΔG_5^o is -189.65 kJ/mol [1]. At p_{CO} lower than 0.8 atm, the disproportionation reaction,

for which the standard free energy change is $\Delta G_6^o = 17.63$ kJ/mol [17], should not occur at 800°C and 1 atm pressure, based on a thermodynamic calculation. For values of p_{CO} less than 0.8 atm, the partial pressures of CO and CO_2 in the initial gas mixture were used to estimate the equilibrium partial pressure of oxygen at the anode, namely $p_{O_2(anode)}$, using the following equation

$$\ln p_{O_2(anode)} = \frac{2\Delta G_5^o}{RT} + 2 \ln \left(\frac{p_{CO_2}}{p_{CO}} \right) \quad (57)$$

For values of p_{CO} greater than 0.8 atm, first the partial pressures of CO and CO_2 according to the disproportionation reaction (56) were estimated. Then, $p_{O_2(anode)}$ was estimated using the corresponding values of the partial pressures of CO and CO_2 and Equation (57). Finally, the OCV was calculated as a function of the partial pressure of CO_2 in the initial mixture, $p_{CO_2}^o$. The calculated $p_{O_2(anode)}$, the calculated OCV, and the measured OCV, are plotted as a function of $p_{CO_2}^o$ in Figure #65. The trends in the measured OCV and the calculated OCV are similar, although the measured OCV is between 50 and 75 mV lower than the theoretical values.

For calculating $p_{O_2(anode)}$ and OCV for $H_2 + CO_2$ gas mixtures as the fuel, the reverse gas shift reaction, namely,

for which the standard free energy is $\Delta G_8^o = 0.385$ kJ/mol. at 800°C , was considered. The corresponding equilibrium p_{CO} , p_{CO_2} , p_{H_2} and p_{H_2O} were calculated. Then, the corresponding $p_{O_2(anode)}$ was calculated using either the H_2 - H_2O equilibrium, or the CO - CO_2 equilibrium. Using the calculated $p_{O_2(anode)}$, the OCV was estimated by equation (52). The calculated $p_{O_2(anode)}$, the calculated OCV and the measured OCV are plotted as a function of the partial pressure of CO_2 in the initial gas mixture, $p_{CO_2}^o$, in Figure #66. As seen in the figure, the calculated and the measured OCV are in good agreement, especially for higher values of $p_{CO_2}^o$.

The above thermodynamic calculations and comparison with experimental results show, in general, reasonable agreement between the calculated and experimental OCV values, insofar as the trends are concerned. However, the experimental values of the OCV are typically about 50 mV lower, and in some cases as much as 100 mV lower. There are a couple of possibilities for

this discrepancy. (1) There may have been a few pinholes in the YSZ film. (2) The sealing may not have been perfect. A lower OCV thus would imply a higher H₂O or CO₂ pressure, and a correspondingly higher partial pressure of oxygen at the anode, $p_{O_2(anode)}$. Leakage is also the possible reason that OCV in H₂-He and H₂-N₂ mixtures is dependent upon the relative proportions of H₂ and inert gas. If there had been no leakage, ideally, it would be expected that the OCV would be essentially independent of the concentration of inert diluent, He or N₂. In principle, using the measured OCV, this $p_{O_2(anode)}$ can be calculated, and thus the relative amount of water (or CO₂) present in the fuel can be estimated. However, as the general trend in measured OCV is consistent with calculations (and expectations) and significant uncertainties may exist in such calculations, no corrections for leakage were made, and the data reported are as measured.

Gas Transport in Porous Anodes: Gas transport through porous electrodes and correlation with electrochemical performance for binary gases, H₂-H₂O in the anode, and O₂-N₂ in the cathode, has been addressed in detail. There are two main fluxes contributing to mass transport in a porous electrode: (1) A diffusive flux and, (2) a viscous flux. In general, the viscous flow, which is driven by a pressure gradient, is negligible compared to the diffusive flow in porous electrodes. Therefore, gas transport in porous electrodes is mainly due to diffusion, which includes free molecular or Knudsen flow, and a continuum flow.

The general diffusion process for a multi-component gas system is described by Stefan-Maxwell equation [18]

$$\frac{N_i}{D_{K,i}} + \sum_{\substack{j=1 \\ j \neq i}} \frac{X_j N_i - X_i N_j}{D_{ij}} = - \frac{p}{RT} \frac{dX_i}{dx} \quad (59)$$

where N_i and N_j are molar fluxes of components i and j (# mols/cm²sec), respectively, $D_{K,i}$ and D_{ij} are the Knudsen diffusion coefficient for component i and the binary diffusion coefficient for components i and j , respectively, X_i and X_j are the mole fractions of components i and j , respectively, p is the total pressure, R is the gas constant, T is the absolute temperature, and x is the coordinate along the diffusion direction. Knudsen diffusion is due to molecule to wall collision, which predominates over molecule-to-molecule collision when the pore size is smaller than the mean free path [20]. The Knudsen diffusion coefficient can be computed according to the kinetic theory of gases, using the following formula [18]

$$D_{K,i} = \frac{2}{3} \left(\frac{8RT}{\pi M_i} \right)^{\frac{1}{2}} \bar{r} \quad (60)$$

where $\bar{r}$ is the mean pore radius, and M_i is the molecular weight of the diffusing gas. Binary diffusion coefficient, D_{ij} , is generally experimentally measured or calculated using the Chapman-Enskog equation [6], if it is not available experimentally. According to the Chapman-Enskog model, the binary diffusion coefficient in cm²/sec is given by [6]

$$D_{ij} = \frac{1.86 \times 10^{-3} T^{\frac{3}{2}} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{\frac{1}{2}}}{p \Omega \sigma_{ij}^2} \quad (61)$$

where Ω is the collision integral (dimensionless), σ_{ij} is the average collision diameter (in angstroms), M_i and M_j are respectively molecular weights of component i and j , and p is the total pressure (in atmospheres). Using Ω and σ_{ij} data from Cussler¹⁶, the calculated D_{ij} for various gaseous species and at several temperatures are listed in Table 11, along with some experimental values from the literature for comparison [17,19,20]. Slight difference, usually less than 10%, is often observed between the calculated values and the experimental values over a range of temperatures between room temperature and 473 K. Little data are available at higher temperatures. Hence, D_{ij} at 800°C were estimated using the Chapman-Enskog model.

In the present experiments, the mean pore radius of the Ni-YSZ electrode was estimated from SEM micrographs (Figure 54) to be $\sim 0.5 \mu\text{m}$. The calculated Knudsen diffusion coefficients at 800°C for H_2 and CO through the Ni-YSZ porous electrode are respectively $11.3 \text{ cm}^2/\text{s}$ and $3 \text{ cm}^2/\text{s}$. These values are comparable to the respective binary diffusion coefficients of $\text{H}_2\text{-He}$, which is $13.3 \text{ cm}^2/\text{s}$, and CO-CO_2 , which is $1.41 \text{ cm}^2/\text{s}$ at the same temperature (Table 11). This indicates that Knudsen diffusion is an important process in the present porous anodes with $0.5 \mu\text{m}$ mean pore radius, and should be taken into account.

For a ternary system such as $\text{H}_2\text{-He-H}_2\text{O}$, the H_2 molar flux from Equation (59) is given by

$$\frac{N_{\text{H}_2}}{D_{K,\text{H}_2}} + \frac{X_{\text{He}}N_{\text{H}_2} - X_{\text{H}_2}N_{\text{He}}}{D_{\text{H}_2,\text{He}}} + \frac{X_{\text{H}_2\text{O}}N_{\text{H}_2} - X_{\text{H}_2}N_{\text{H}_2\text{O}}}{D_{\text{H}_2,\text{H}_2\text{O}}} = -\frac{p}{RT} \frac{dX_{\text{H}_2}}{dx} \quad (62)$$

Under steady state conditions, $N_{\text{H}_2\text{O}} = -N_{\text{H}_2}$ and $N_{\text{He}} = 0$. Thus,

$$N_{\text{H}_2} \left(\frac{1}{D_{K,\text{H}_2}} + \frac{X_{\text{He}}}{D_{\text{H}_2,\text{He}}} + \frac{1 - X_{\text{He}}}{D_{\text{H}_2,\text{H}_2\text{O}}} \right) = -\frac{p}{RT} \frac{dX_{\text{H}_2}}{dx} \quad (63)$$

From Equation (63), H_2 flux can be written in a similar form as Fick's equation by

$$N_{\text{H}_2} = -\frac{pD_{\text{H}_2}}{RT} \frac{dX_{\text{H}_2}}{dx} \quad (64)$$

where D_{H_2} is defined as the H_2 diffusion coefficient in the $\text{H}_2\text{-H}_2\text{O-He}$ ternary system, and is given by

$$D_{\text{H}_2} = \left(\frac{1}{D_{K,\text{H}_2}} + \frac{X_{\text{He}}}{D_{\text{H}_2,\text{He}}} + \frac{1 - X_{\text{He}}}{D_{\text{H}_2,\text{H}_2\text{O}}} \right)^{-1} \quad (65)$$

When $X_{\text{He}} = 0$, i.e. for $\text{H}_2\text{-H}_2\text{O}$ binary system, the H_2 diffusion coefficient becomes

$$D_{\text{H}_2} = \left(\frac{1}{D_{K,\text{H}_2}} + \frac{1}{D_{\text{H}_2,\text{H}_2\text{O}}} \right)^{-1} \quad (66)$$

Similarly, for the CO-CO₂ binary system, the CO diffusion coefficient is given by

$$D_{CO} = \left(\frac{1}{D_{K,CO}} + \frac{1}{D_{CO,CO_2}} \right)^{-1} \quad (67)$$

where $D_{K,CO}$ and D_{CO,CO_2} are respectively the Knudsen diffusion coefficient of CO and the binary diffusion coefficient of CO-CO₂.

The preceding equations for diffusion coefficients are for transport in a multi-component gas system and do not account for the volume fraction of porosity, and the tortuous nature of path through porous bodies. When the transport occurs through a porous body, the interaction of gaseous species with the porous matrix must be included. The simplest approach for taking this into account is to modify the diffusion coefficients by the volume fraction porosity, V_v , and the tortuous nature of the actual transport, characterized by the so-called tortuosity factor, τ [6]. The resulting diffusion coefficients or diffusivities are termed effective diffusion coefficients or effective diffusivities. For H₂ and CO, the corresponding effective diffusivities are given by [6]

$$D_{H_2,eff} = \frac{V_v}{\tau} D_{H_2} \quad (68)$$

and

$$D_{CO,eff} = \frac{V_v}{\tau} D_{CO} \quad (69)$$

where D_{H_2} and D_{CO} are given respectively by equations (65 or 66) and (67).

As shown on the right side of Equation (15), for a ternary system, D_{H_2} is not only a function of diffusion coefficients, D_{K,H_2} , $D_{H_2,He}$ and D_{H_2,H_2O} , but is also a function of the mole fraction of the diluent gas, X_{He} . If X_{He} varies from position to position along the diffusion direction, D_{H_2} will be a function of position. The variation of X_{He} as a function of the position, x , can be determined by solving Equation (59) for the He flux, N_{He} , given by

$$\frac{N_{He}}{D_{K,He}} + \frac{X_{H_2}N_{He} - X_{He}N_{H_2}}{D_{He,H_2}} + \frac{X_{H_2O}N_{He} - X_{He}N_{H_2O}}{D_{He,H_2O}} = -\frac{p}{RT} \frac{dX_{He}}{dx} \quad (70)$$

Since the net flow of He, N_{He} , is zero and $N_{H_2} = -N_{H_2O}$ in steady state, Equation (70) becomes

$$N_{H_2} \left(\frac{1}{D_{He,H_2O}} - \frac{1}{D_{He,H_2}} \right) X_{He} = -\frac{p}{RT} \frac{dX_{He}}{dx} \quad (71)$$

Integration of Equation (71) gives

$$X_{He}^{l_a} = X_{He}^o \exp \left[\frac{RTN_{H_2}l_a}{p} \left(\frac{1}{D_{He,H_2}} - \frac{1}{D_{He,H_2O}} \right) \right] \quad (72)$$

where l_a is the anode thickness, X_{He}^o is the mole fraction of He at $x = 0$, and $X_{He}^{l_a}$ is the mole fraction of He at $x = l_a$. The case of interest is that of a porous anode. Thus, the diffusivities must be those corrected for porosity and tortuosity factor. Thus, the applicable equation is actually

$$X_{He}^{l_a} = X_{He}^o \exp \left[\frac{RTN_{H_2}l_a}{p} \left(\frac{1}{D_{He,H_2,eff}} - \frac{1}{D_{He,H_2O,eff}} \right) \right] \quad (73)$$

Equations (72) and (73) show that, X_{He} , varies exponentially as a function of position. For the case of transport through space, in the absence of a porous body, the calculated variation of X_{He} along the electrode is very small. Using the estimated diffusion coefficients from the Chapman-Enskog model, $D_{He,H_2} = 13.29 \text{ cm}^2/\text{s}$ and $D_{He,H_2O} = 4.07 \text{ cm}^2/\text{s}$, the X_{He} at the electrode /electrolyte interface ($l_a = 0.1 \text{ cm}$) is about 0.8% lower than the bulk molar value of He, X_{He}^o , at a current density of $1 \text{ A}/\text{cm}^2$, i.e. for a molar flux of $5.18 \times 10^{-6} \text{ mol}/\text{cm}^2\text{s}$. Even at a current density close to the anode limiting current density, $3 \text{ A}/\text{cm}^2$, X_{He} is only 3% lower than X_{He}^o . Such, however, will not be the case for a porous body. For transport through porous anodes, equation (73) must be used. The corresponding variation in X_{He} is $\sim 10\%$ at a current density of $1 \text{ A}/\text{cm}^2$ and $\sim 20\%$ at a current density of $3 \text{ A}/\text{cm}^2$. Though this variation is not insignificant, for simplicity, we will neglect this aspect, and assume that the diffusion coefficient of H_2 is independent of position.

If the electrode microstructure is not a function of position, i.e. V_v and τ are constant, integration of Equation (64), using effective diffusivities, gives a simple equation for H_2 flux in a ternary system, similar to that for a binary system, namely

$$N_{H_2} = -\frac{pD_{H_2,eff}}{RTl_a} (X_{H_2} - X'_{H_2}) \quad (74)$$

where X'_{H_2} and X_{H_2} are the mole fractions of H_2 over the anode surface ($x = 0$) and at the anode/electrolyte interface ($x = l_a$), and $D_{H_2,eff}$ is the effective ternary diffusion coefficient as defined by Equations (65) and (68). Replacing mole fractions with partial pressures, Equation (74) becomes

$$N_{H_2} = -\frac{D_{H_2,eff}}{RTl_a} (p_{H_2} - p'_{H_2}) \quad (75)$$

where, p'_{H_2} and p_{H_2} are respectively the partial pressure of H_2 over the anode surface ($x = 0$) and the partial pressure of H_2 at the anode/electrolyte interface ($x = l_a$). Assuming gases are well-mixed above the anode, similar to the situation in a continuously stirred tank reactor (CSTR), p'_{H_2} is given by

$$p'_{H_2} = p_{H_2}^o - \frac{N_{H_2}A}{m_T} p \quad (76)$$

where $p_{H_2}^o$ is the initial (incoming fuel) partial pressure of H_2 , A is the electrode area (1.1 cm^2), m_T is the total molar flow rate of fuel and diluent, and p is the total pressure. Substituting for p_{H_2}' from equation (76), into equation (75) gives

$$N_{H_2} = -\frac{D_{H_2,eff}}{RTl_a} \left(p_{H_2} - p_{H_2}^o + \frac{N_{H_2} A}{m_T} p \right) \quad (77)$$

Rearranging equation (77), H_2 molar flux is given by,

$$N_{H_2} = -\frac{\frac{D_{H_2,eff} (p_{H_2} - p_{H_2}^o)}{RTl_a}}{1 + \frac{D_{H_2,eff} A p}{RTl_a m_T}} \quad (78)$$

A maximum in H_2 flux occurs when p_{H_2} at the interface approaches zero. This maximum flux is given by

$$N_{H_2,max} = \frac{\frac{D_{H_2,eff} p_{H_2}^o}{RTl_a}}{1 + \frac{D_{H_2,eff} A p}{RTl_a m_T}} \quad (79)$$

The net current density passing through the cell is related to the net hydrogen flux arriving at the anode/electrolyte interface, and is given by

$$i = 2FN_{H_2} = -\frac{\frac{2FD_{H_2,eff} (p_{H_2} - p_{H_2}^o)}{RTl_a}}{1 + \frac{D_{H_2,eff} A p}{RTl_a m_T}} \quad (80)$$

For the maximum possible hydrogen flux given by Equation (79), there will be a corresponding maximum in current density, which is, the anode limiting current density given by

$$i_{as} = \frac{\frac{2FD_{H_2,eff} p_{H_2}^o}{RTl_a}}{1 + \frac{D_{H_2,eff} A p}{RTl_a m_T}} \quad (81)$$

In all experiments, when the mole percent of the diluent was more than 40%, a limiting current density was observed. From the experimentally measured anode limiting current density, one can estimate the effective diffusion coefficients for H_2 for several diluents and at various concentrations by rearranging Equation (81) as follows

$$D_{H_2,eff} = \frac{i_{as}}{\frac{2Fp_{H_2}^o}{RTl_a} - \frac{i_{as} A p}{RTl_a m_T}} \quad (82)$$

Also, for CO-CO₂ mixtures, Equation (82) can be used with $p_{H_2}^o$ replaced by p_{CO}^o , and $D_{H_2,eff}$ replaced by $D_{CO,eff}$. Table 12 lists the calculated diffusion coefficients from Equations (65) through (67), and the estimated effective H₂ (and CO) diffusion coefficients from Equation (82) and the experimentally measured i_{as} values from the voltage-current density polarization curves.

From Table 12, it is seen that the H₂ diffusion coefficient, D_{H_2} , for H₂-H₂O is about five times larger than that for CO-CO₂, D_{CO} . For H₂-H₂O, the effective diffusion coefficient, estimated using equation (82), ranges from 0.470 to 0.506 cm²/s, almost independent of gas composition, consistent with Equation (66). For CO-CO₂ mixtures, it varies from 0.063 to 0.090 cm²/s over the range of p_{CO} investigated. This suggests that mass transport of H₂ in H₂-H₂O mixtures should be about five to six times faster than that of CO in CO-CO₂ mixtures. If CO is used as a fuel, the cell performance is expected to be lower than with H₂ as a fuel due to slow diffusion rate, regardless of other effects, such as the intrinsically low electrochemical activity of CO.

Prior work has shown that anodic concentration polarization for H₂-H₂O gas mixtures is given by [4]

$$\eta_{conc} = -\frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}} \right) + \frac{RT}{2F} \ln \left(1 + \frac{p_{H_2}^o i}{p_{H_2O}^o i_{as}} \right) \quad (83)$$

It is readily seen that the corresponding equation for CO-CO₂ gas mixtures as a fuel is given by

$$\eta_{conc} = -\frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}} \right) + \frac{RT}{2F} \ln \left(1 + \frac{p_{CO}^o i}{p_{CO_2}^o i_{as}} \right) \quad (84)$$

Using equations (83) and (84)², η_{conc} was calculated as a function of current density for a H₂-H₂O mixture of composition 34% H₂ – 66% H₂O, and for a CO-CO₂ mixture of composition 32% CO – 68% CO₂, for which the corresponding anode limiting current densities were, respectively, ~2 A/cm² and ~0.5 A/cm². The calculated concentration polarization is compared with the measured total polarization (by subtracting the ohmic contribution) in Figure #67. It is readily seen that anodic concentration polarization is much greater in CO-CO₂ mixtures as compared to H₂-H₂O mixtures. The difference between the measured total (excluding the ohmic) and the calculated anodic concentration polarization is attributed to anodic and cathodic activation polarizations, and cathodic concentration polarization. The cathodic polarization (activation + concentration) is the same for the two curves. For the test with H₂-H₂O as the fuel, at 0.25 A/cm², the difference between the measured and the calculated polarization (equation (83)) is ~0.017 V, which includes: (a) cathodic concentration polarization, (b) cathodic activation polarization, and (c) anodic activation polarization. At the same current

² Since the partial pressure of H₂ or CO at the anode/fuel interface is a function of the current density (using equation 76), one must strictly use $p_{H_2}^i$ instead of $p_{H_2}^o$ (or p_{CO}^i instead of p_{CO}^o) in estimating the concentration polarization, and attribute the remainder of the terms to polarization associated with the depletion of fuel. Here, the two terms are combined into a single equation describing concentration polarization, namely equation 33 for H₂ as a fuel (or equation 84 for CO as a fuel).

density, the difference between the measured and calculated polarization (equation (84)) is ~ 0.19 V for CO-CO₂ as the fuel. This again includes: (a) cathodic concentration polarization, (b) cathodic activation polarization, and (c) anodic activation polarization. However, the cathodic polarizations, for (a) and (b) are identical for the two tests. Clearly, greater polarization with the CO-CO₂ mixture, beyond what can be attributed to anodic concentration polarization, is attributed to anodic activation polarization. That is, anodic activation polarization with CO-CO₂ gaseous mixture of the chosen composition at 0.25 A/cm² is ~ 0.151 V higher than that with H₂-H₂O gaseous mixture. This also suggests that Ni + YSZ is not a very good anode for CO as the fuel. Indeed, it has been reported in the literature that the electrochemical reaction rate of CO is slower than that of H₂ by at least a factor of two [21]. Comparison of performance curves for H₂-H₂O mixtures with CO-CO₂ mixtures from Figures 5 and 6 shows that the lower performance with CO-CO₂ mixtures cannot be attributed entirely to concentration polarization. Thus, although CO does not poison SOFC anodes unlike proton exchange membrane (PEM) fuel cells, its low electrochemical activity, at least with nickel-based anodes, and high concentration polarization, suggests that it is not an ideal fuel for SOFC, if a high power density is a requirement.

The estimated D_{H_2} using the Chapman-Enskog model, and the analysis of multi-component transport, as a function of diluent type and concentration, is given in Table 12. The experimentally determined $D_{H_2,eff}$ from the anode-limiting current behavior via Equation (82), which includes the effects of porosity and tortuosity, are also given in Table 12. Note that for He as a diluent, the estimated D_{H_2} is higher than with N₂ as the diluent. Table 12 also shows that estimated $D_{H_2,eff}$ is also similarly higher for He as a diluent compared to N₂ as a diluent. Similar trends are observed for CO₂ as a diluent. Finally, for CO-CO₂ mixtures, the estimated D_{CO} is much lower, and so is the $D_{CO,eff}$. In the case of either N₂ or CO₂ as a diluent, it is also seen that the trends in D_{H_2} and $D_{H_2,eff}$ as a function of composition are similar. That is, the results indicate that, except for He, H₂ diluted with either N₂ or CO₂ not only lowers the partial pressure of H₂ but also reduces the effective H₂ diffusion coefficient. Thus, the diluent can lower cell performance in two ways; reduced p_{H_2} and reduced transport kinetics. From the experimental results (Figure #58), at 32% N₂ dilution, the maximum power density was reduced by more than 30%. It was even worse for CO₂ dilution with almost 40% reduction of the maximum power density (Figure #59) at the same diluent concentration. This suggests when either partial oxidation or auto-thermal reforming is used for processing fuel, nitrogen introduced into fuel will lead to a lowering of diffusive transport, in addition to fuel dilution. The present work also shows that if in a reforming stage most of the CO is converted to CO₂ via a gas shift reaction, in addition to fuel dilution, there will also be an adverse effect on diffusive transport.

Using D_{H_2} , $D_{H_2,eff}$, D_{CO} , and $D_{CO,eff}$ and the measured porosity of 54% for the Ni-YSZ anode, the tortuosity factor of the anode, τ , was calculated from equations (68) and (69). All of the tortuosity factors fall between 5.0 to 7.0 from H₂-H₂O and CO-CO₂ binary system measurements (with the exception of one value which is over 8.0) and from H₂-H₂O with He, N₂ and CO₂ dilution (with the exception of one value which is 9). The observation that

tortuosity factor is on the order of ~5 to ~7 justifies the use of effective diffusivities. At the same time, the observation that the estimated tortuosity factor does exhibit some variability suggests that it may include effects in addition to purely geometric factors (such as, possibly adsorption and surface diffusion). A value of 5 measured by a different method for a Ni-YSZ anode has been reported in the literature [22]. This suggests that the possible effects of adsorption/desorption and surface diffusion must be small in anodes of the present study.

Cell Performance with $H_2 + CO$ Mixture as the Fuel: The cell performance with as-received CO as fuel was poor because of slow diffusion and slow electrochemical reaction rate, as discussed earlier. However, the cell performance on $H_2 + CO$, even when CO concentration was as high as 55%, was very high, close to that with as-received H_2 (Figure #63), and quite high with CO content as high as 80%. The diffusion coefficient of H_2 in H_2 - H_2O -CO ternary mixtures (ignoring the effects of CO_2) may be given by

$$D_{H_2} = \left(\frac{1}{D_{K,H_2}} + \frac{X_{CO}}{D_{H_2,CO}} + \frac{1-X_{CO}}{D_{H_2,H_2O}} \right)^{-1} \quad (85)$$

The calculated D_{H_2} ranges between 4.17 and 4.31 cm^2/s for CO mole fraction between 0.8 and 0.5, which is similar to that for H_2 - H_2O - N_2 . However, the observed performance with H_2 -CO is much superior to that with H_2 - H_2O - N_2 mixtures as the fuel. This, of course, is consistent with expectations, since a shift reaction is expected in H_2 -CO gas mixtures during cell operation. At 800°C, the standard Gibbs free energy for the gas shift reaction

is only -0.368 kJ/mol [17]. However, the reaction rate constant is very high as reported in the literature and thus it may be assumed that the shift reaction at the anode/electrolyte interface is at equilibrium [22]. Thus, for a fuel gas composition containing greater than 50% H_2 (and balance CO), it can be argued that H_2O produced by the electrochemical oxidation of H_2 is more than sufficient to react with CO present to form H_2 and CO_2 . In such a case, there should be little difference in performance when compared to pure H_2 as fuel (with the exception of a small difference related to differences in concentration polarization). Indeed, it is seen that there is very little difference in performance with fuels ranging in composition from ~100% H_2 and ~45% $H_2 + \sim 55\%$ CO, as seen in Figure #63. For compositions of fuel containing substantially greater than 50% CO, the H_2O produced by the electrochemical oxidation of H_2 will not be sufficient to shift most of CO to CO_2 . The remaining CO will have to be oxidized electrochemically to CO_2 , for which polarization is observed to be much greater (Figure #61). Indeed, Figure #63 shows that the performance is much worse with fuels containing ~68% CO + ~32% H_2 and ~80% CO + ~20% H_2 .

CONCLUSIONS

Nanosize YSZ powder was prepared by a novel approach, in which yttria-doped $BaZrO_3$ or yttria-doped Na_2ZrO_3 precursors were first synthesized by a solid-state reaction. Then, the unwanted species, BaO or Na_2O , was leached away by washing the precursors in a dilute HNO_3 solution or in water. This led to the formation of very fine, nanosize yttria-stabilized zirconia (YSZ). The particle size of the as-synthesized YSZ powders was a few nanometers and increased to tens of nanometers after thermal treatment at a temperature as high as 1000°C.

The effect of asymmetric testing geometry was examined, both theoretically and experimentally, in this work. The present work developed simple analytical relationships, which elucidate the role of different cathode and anode areas, the so-called asymmetric electrodes, on the measured performance of anode-supported solid oxide fuel cells. The analytical relations show that there should be negligible effect of anode electronic resistance and the possible enhanced electrolyte region on the measured cell performance when testing cells with a different cathode area compared to anode area, wherein the cathode area is smaller than the anode area. The analysis shows that the principal source of the difference lies in differences in anodic concentration polarizations. Specifically, a cell with a smaller cathode, in relation to the anode, will exhibit a lower anodic concentration polarization by virtue of the larger area of the anode through which fuel gas transport occurs. This will effectively lead to a higher value of power density in a cell with a smaller cathode. The degree to which the power density will be overestimated will depend upon transport properties of the anode, the thickness of the anode, and the relative size of the cathode. For a cell with a relatively thin anode, for example 500 μm or less, there would be virtually no detectable difference in the measured power density due to the so-called asymmetry of the cathode, as long as $r_c \gg l_a$. That is, as long as the anode is sufficiently thin, there should be virtually no effect of the cathode asymmetry on the measured cell performance. Indeed, experimental results in our laboratory and those of other researchers are in accord with this expectation. The results of experimental work of the present study are in general good agreement with the analysis presented here. Measurements demonstrated that cells with a smaller cathode exhibited a somewhat smaller overall anodic overpotential, while the ohmic and cathodic overpotentials were independent of the cathode area.

The effect of electrode microstructure on polarization was examined. The present work shows that electrode microstructure has a profound effect on polarization, and thus on cell performance. Anode-supported single cells were made with varying amounts of LSM and YSZ in cathode interlayers. Cell performance was strongly dependent on the cathode interlayer composition. Cathode interlayer microstructure was quantitatively analyzed by quantitative stereology, which was used to estimate volume fraction porosity, V_v , aggregate grain size of YSZ, d , and three phase boundary (TPB) line length, l_{TPB} , in the cathode interlayer. The previously developed theoretical model affords the definition of an effective charge transfer resistance, R_{ct}^{eff} , a measure of electrode activation polarization, which depends linearly on the microstructural parameter, $\sqrt{d / ((1 - V_v) l_{TPB})}$. From a plot of R_{cell} vs. $\sqrt{d / ((1 - V_v) l_{TPB})}$, the fundamental charge transfer parameter, ρ_{ct} , which defines the nature of charge transfer at LSM/YSZ/air TPB, was determined to be $\sim 1.0 \times 10^5 \Omega\text{cm}$ at 800°C. A realistic comparison between various electrocatalyst/electrolyte pairs would require the measurement of ρ_{ct} .

Anode-supported solid oxide fuel cells were fabricated with a thin film YSZ electrolyte and a composite cathode, consisting of a mixture of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{(3-\lambda)}$ (LSGM) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{(3-\delta)}$ (LSM). The relative compositions and firing temperatures of the composite cathode interlayers were varied and the resulting effects on cell performance were investigated. Variations in the composition of the cathode interlayer had a profound effect on the overpotential at the cathode and the performance of the cells. In the composition range 30 to 70

wt.% LSGM and 70 to 30 wt.% LSM, the cathodic overpotential varied between 65 mV and 400 mV at 1.0 A/cm^2 at 800°C and exhibited a minimum for the 50/50 composition. The large change in cathodic performance with composition is reflected in the maximum power densities of the cells, which varied between 0.4 and 1.4 W/cm^2 . In addition to compositional changes, the cathode interlayer firing temperature was varied between 1000 and 1200°C while the composition was fixed at 50 wt.% LSGM + 50 wt.% LSM. The overpotentials at the cathode decreased with increasing firing temperature in the range $1000 \leq T \leq 1150^\circ\text{C}$, and then increased again for the interlayer fired at 1200°C . The effects of cathode interlayer firing temperature on cell performance are dramatic, with maximum power densities ranging between 0.6 and 1.4 W/cm^2 for firing temperatures of $1000 \leq T \leq 1200^\circ\text{C}$. The dramatic decrease in performance between the cell with the cathode interlayer fired at 1150°C and the one fired at 1200°C is attributed to a phase reaction between LSGM and YSZ. Chemical analysis and powder X-ray diffraction revealed that LSGM reacts with YSZ above 1000°C to form the pyrochlore phase $\text{La}_2\text{Zr}_2\text{O}_7$. The formation of this resistive pyrochlore phase at the interface between the LSGM/LSM composite cathode and the YSZ electrolyte may limit the firing time and temperature of the cathode interlayer. The cathode interlayer was optimized with a composition of 50 wt.% LSGM and 50 wt.% LSM and a firing temperature of 1150°C , resulting in a cell exhibiting an area specific resistance of $0.18 \text{ }\Omega\text{cm}^2$ and a maximum power density of 1.4 W/cm^2 at 800°C .

The effects of temperature on the reduction of NiO-YSZ based two-phase composites, and re-oxidation kinetics of porous Ni-YSZ anodes were investigated. In the temperature range of 600 - 800°C for thickness up to 1 mm , the reduction kinetics was interface-controlled and was thermally activated with an activation energy of $\sim 94 \text{ kJ/mol}$. By contrast, the re-oxidation kinetics was diffusion-controlled with an apparent diffusion coefficient on the order of $\sim 10^{-7} \text{ cm}^2/\text{s}$, which was essentially independent of temperature over the range investigated. An examination of the re-oxidized layers showed that some porosity was created during the process. The re-oxidation process is believed to be governed by the occurrence of gaseous diffusion through the pores formed during the reduction/reoxidation process.

Anode-supported solid oxide fuel cells exhibit substantial effect of an inert gas diluent in the fuel on concentration polarization, consistent with expectations based on multi-component gas diffusion in porous bodies. Specifically, anodic concentration polarization is lower with an inert gas diluent of a low molecular weight (such as He), than an inert gas diluent of a higher molecular weight (such as N_2). For a sufficiently high concentration of the diluent, the voltage vs. current density traces exhibits anode limiting current density behavior, characterizing a rapid drop of voltage at a critical current density. This current density was used to estimate the corresponding effective diffusivities. Electrochemical performance with $\text{CO} + \text{CO}_2$ gas mixtures is much worse than fuel gas mixtures containing H_2 . This is rationalized in part on higher anodic concentration polarization, and slower electrochemical oxidation of CO. The results show that Ni + YSZ is an excellent anode for hydrogen gas (H_2)-containing fuel, but not for CO. Studies on cell performance with $\text{CO} + \text{H}_2$ gas mixtures as fuel show that water gas shift reaction plays a major role. Effectively, as long as the H_2 content is greater than $\sim 50\%$, high performance is maintained by producing additional H_2 through the shift reaction. As a result, the cell performance with essentially pure H_2 is about the same as that with a $\text{H}_2 + \text{CO}$ gaseous mixture as fuel, as long as the CO concentration is not too high.

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TABLES

Table 1: Chemical analysis of the leaching solution (dilute HNO₃) after boiling Y-BaZrO₃ in it.

Powder	Solution	Barium (mol/l)	Yttrium (mol/l)	Zirconium (mol/l)
Y:BaZrO ₃	0.3 M HNO ₃	0.104	7.11×10^{-4}	$< 2.0 \times 10^{-5}$
Y:BaZrO ₃	0.07 M HNO ₃	0.062	3.0×10^{-5}	$< 2.0 \times 10^{-5}$

Table 2: Chemical analysis of the leaching solution (water) after boiling Y-Na₂ZrO₃ in it.

Powder	Sodium (mol/l)	Yttrium (mol/l)	Zirconium (mol/l)
Y:Na ₂ ZrO ₃	0.713	$< 5 \times 10^{-5}$	$< 5 \times 10^{-5}$

Table 3: Chemical analysis of the synthesized YSZ nanosize powders

Sample	Zr ⁴⁺	Y ³⁺	Ba ²⁺	Na ⁺
YSZ made using Y-Na ₂ ZrO ₃	0.095 wt. %	0.017 wt. %	-----	7 ppm
YSZ made using Y-BaZrO ₃	0.21 wt. %	0.01 wt. %	12 ppm	-----

Table 4: Particle size (nm) of as-synthesized nanosize YSZ powder and after heating in air at various temperatures.

Thermal treatment conditions	YSZ from Y-BaZrO ₃ <i>d</i> in nm	Thermal treatment conditions	YSZ from Y-Na ₂ ZrO ₃ <i>d</i> in nm
as washed	2.4	As-washed	2.4
350°C/1.5 h	8.0	300°C/1.5 h	4.8
450°C/1.5 h	10	350°C/1.5 h	17
650°C/1.5 h	23	650°C/1.5 h	18
1000°C/5 h	37	1000°C/5 h	31

Table 5: Surface areas of as-calcined precursors, as-synthesized nanosize YSZ, and after heating the nanosize YSZ to 1000°C for 5 hrs.

Sample	Y-BaZrO ₃	Y-Na ₂ ZrO ₃	As-synthesized Nanosize YSZ from Y-Na ₂ ZrO ₃ precursor	Nanosize YSZ after 5 hrs. at 1000°C
Surface Area (m ² /g)	3.5	2.7	66.6	13.6

Table 6: Measured Microstructural Parameters by Quantitative Stereology

Cathode Interlayer Composition	V_v	V_{LSM}	V_{YSZ}	$d = 3V_{YSZ} / P_L$ (cm)	$l_{TPB} = P_A / P_L$ (cm ⁻¹)
25wt.%LSM, 75wt.%YSZ	~0.185	~0.206	~0.609	~2.13 x 10 ⁻⁴	~1782
35wt.%LSM, 65wt.% YSZ	~0.185	~0.287	~0.528	~1.57 x 10 ⁻⁴	~5173
40wt.%LSM, 60wt.% YSZ	~0.192	~0.323	~0.485	~1.41 x 10 ⁻⁴	~6547
50wt.%LSM, 50wt.% YSZ	~0.194	~0.406	~0.4	~9.3 x 10 ⁻⁵	~3115
60wt.%LSM, 40wt.% YSZ	~0.144	~0.514	~0.342	~6.54 x 10 ⁻⁵	~1945

Table 7: Estimated Microstructural Parameter using Data from Table I and Measured Area Specific Resistance.

Cathode Interlayer Composition	Microstructural Parameter $\sqrt{d / ((1 - V_v) l_{TPB})}$ (cm)	R_{cell} (Ωcm^2)
25 wt.% LSM, 75 wt.% YSZ	3.8296 x 10 ⁻⁴	0.694
35 wt.% LSM, 65 wt.% YSZ	1.9297 x 10 ⁻⁴	0.243
40 wt.% LSM, 60 wt.% YSZ	1.6326 x 10 ⁻⁴	0.229
50 wt.% LSM, 50 wt.% YSZ	1.9246 x 10 ⁻⁴	0.288
60 wt.% LSM, 40 wt.% YSZ	1.9819 x 10 ⁻⁴	0.371

Table 8: Charge transfer resistance and exchange current density for composite cathodes with various compositions fired at 1150°C.

Cathode Composition	30% LSGM 70% LSM	40% LSGM 60% LSM	50% LSGM 50% LSM	60% LSGM 40% LSM	70% LSGM 30% LSM
Charge transfer resistance (Ωcm^2)	0.557	0.277	0.242	0.431	0.417
i_0 exchange current density (mA/cm^2)	41.5	83.4	95.4	53.6	55.4

Table 9: Charge transfer resistance and exchange current density for the 50 wt.% LSGM/50 wt% LSM composite cathode fired at various temperatures.

Cathode Firing Temperature	1000°C	1050°C	1100°C	1150°C	1200°C
Charge transfer resistance (Ωcm^2)	0.348	0.323	0.282	0.242	0.405
i_0 exchange current density (mA/cm^2)	66.4	71.5	81.9	95.4	57.0

Table 10: Density and porosities of as-sintered, reduced, and re-oxidized samples.

Porosity	Reduced and re-oxidized At 800°C	Reduced and re-oxidized At 700°C
As-sintered density (% theoretical)	99.5%	99.5%
Porosity of reduced Samples (%) (by water immersion)	25.8%	26%
Porosity after Re-oxidation (by SEM)	9.9%	8.7%

Table 11: Calculated binary diffusion coefficients from the Chapman-Enskog equation and comparison with some experimental data from the literature.

D_{ij} cm ² /s	H ₂ -He	H ₂ -N ₂	H ₂ -CO ₂	H ₂ -H ₂ O	H ₂ -CO	CO-CO ₂
293 K	1.535 1.53 ^a 1.49 ^c	0.722 0.728 ^a 0.772 ^c	0.604 0.651 ^b	0.738 0.834 ^b	0.726 0.735 ^a 0.772 ^c	0.149 0.162 ^c
473K	3.417 3.45 ^a 3.39 ^c	1.626 1.631 ^a 1.743 ^c	1.395 1.513 ^b 1.473 ^c	1.819 1.996 ^b	1.642 1.651 ^a 1.743 ^c	0.349 0.384 ^c
1073K	13.29	6.303	5.56	7.704	6.373	1.408

- a. From reference [19].
b. From reference [20].
c. From reference [17].

Table 12: Partial Pressure of Dilute Gas, Anode Limiting Current Density, H₂ and CO Diffusion Coefficient, Porosity and Tortuosity

H₂- H₂O Binary System

p_{H_2}	i_{as} (A/cm ²)	D_{H_2} , cm ² /s (cal.)	$D_{H_2,eff}$, cm ² /s (exp.)	Porosity, % (exp.)	Tortuosity
0.2	1.3	4.58	0.506	54	4.89
0.34	2.1	4.58	0.470	54	5.26
0.5	3.25	4.58	0.506	54	4.89

CO-CO₂ Binary System

p_{CO}	i_{as} (A/cm ²)	D_{CO} , cm ² /s (cal.)	$D_{CO,eff}$, cm ² /s (exp.)	Porosity, % (exp.)	Tortuosity
0.18	0.21	0.958	0.063	54	8.27
0.23	0.31	0.958	0.073	54	7.08
0.32	0.49	0.958	0.084	54	6.17
0.44	0.73	0.958	0.091	54	5.65

H₂-He-H₂O Ternary System

p_{He}	i_{as} (A/cm ²)	D_{H_2} , cm ² /s (cal.)	$D_{H_2,eff}$, cm ² /s (exp.)	Porosity, % (exp.)	Tortuosity
0.78	1.5	5.677	0.545	54	5.62
0.65	2.4	5.458	0.550	54	5.35
0.53	3.25	5.269	0.558	54	5.10
0.42	4	5.108	0.556	54	4.96

H₂-N₂-H₂O Ternary System

p_{N_2}	i_{as} (A/cm ²)	D_{H_2} , cm ² /s (cal.)	$D_{H_2,eff}$, cm ² /s (exp.)	Porosity, % (exp.)	Tortuosity
0.8	0.89	4.135	0.295	54	7.56
0.67	1.56	4.2	0.320	54	7.09
0.57	2.3	4.252	0.379	54	6.05
0.5	2.65	4.289	0.375	54	6.18

H₂-CO₂-H₂O Ternary System

p_{CO_2}	i_{as} (A/cm ²)	D_{H_2} , cm ² /s (cal.)	$D_{H_2,eff}$, cm ² /s (exp.)	Porosity, % (exp.)	Tortuosity
0.81	0.7	3.858	0.230	54	9.00
0.68	1.43	3.957	0.296	54	7.20
0.6	1.88	4.021	0.317	54	6.84
0.5	2.4	4.103	0.327	54	6.77

FIGURES

Figure #1(a)

Figure #1(b)

Figure #1(a): A schematic showing the preferred geometry of an anode-supported cell.

Figure #1(b): A schematic showing the geometry often used in the actual testing, and the subject of the present study.

Figure #2: A schematic showing a possible extension of the active region of the electrolyte.

Figure #3: A schematic showing the exploded view of the extended region from Figure #2, used for the analysis.

Figure #4(a): A schematic showing the equipotential lines and the flux lines.

Figure #4(b): A schematic showing the active region of the anode used in the calculations.

Figure #4(c): A schematic showing the active region of the anode when the cathode radius is much larger than the anode thickness.

Figure #5(a): Calculated anodic concentration polarization as a function of current density for two different cathode radii using equation (16) for the anode-limiting short circuit current density, i_{as} .

Figure #5(b): Calculated anodic concentration polarization as a function of current density for two different cathode radii using equation (17) for the anode-limiting short circuit current density, i_{as} .

Figure #6: A schematic of a cell with two, semicircular cathodes.

Figure #7: A schematic of the test fixture for testing of single cells.

Figure #8: A schematic of the reduction process. X denotes the reduced layer thickness. $p_{H_2}^o$, $p_{H_2}^i$, and $p_{H_2}^{eq}$ are respectively hydrogen partial pressures in the atmosphere, at the reduced/pristine interface, and that corresponding to Ni/NiO equilibrium. Similarly, $p_{H_2O}^o$, $p_{H_2O}^i$, and $p_{H_2O}^{eq}$ are the corresponding H_2O partial pressures.

Figure #9: A schematic of the re-oxidation process. X denotes the re-oxidized layer thickness. $p_{O_2}^o$, $p_{O_2}^i$, and $p_{O_2}^{eq}$ are respectively the partial pressures of oxygen in the atmosphere, at the re-oxidized/reduced interface, and that corresponding to Ni/NiO equilibrium.

Figure #10: (a) An XRD pattern of yttria-doped BaZrO_3 powder synthesized by calcining a mixture of BaCO_3 , ZrO_2 and Y_2O_3 at 1250°C for 2h. (b) An XRD pattern of yttria-doped BaZrO_3 powder synthesized by calcining a mixture of BaCO_3 and YSZ at 1250°C for 2 h.

Figure #11: An XRD pattern of yttria-doped Na_2ZrO_3 powder synthesized by calcining a mixture of Na_2CO_3 and YSZ at 1250°C for 2h.

Figure #12: (a) XRD patterns of the residue after boiling Y-BaZrO₃ in dilute HNO₃ (after leaching Ba), and washing in water, and of the residue after boiling Y-Na₂ZrO₃ in de-ionized water (after leaching Na), and washing in water. (b) An XRD pattern of a commercial YSZ powder.

Figure #13: A schematic showing a particle of Y-BaZrO₃ reacting with HNO₃. The porous outer layer is of YSZ. The dense inner region is of the original Y-BaZrO₃. The reaction involves the following steps. (i) Transport of HNO₃ through the porous YSZ layer to the porous YSZ/dense Y-BaZrO₃ interface. (ii) Reaction between Y-BaZrO₃ and HNO₃ to form soluble Ba(NO₃)₂ and insoluble, porous YSZ. (iii) Transport of Ba(NO₃)₂ through the porous YSZ layer into the acid bath.

Figure #14(a): A bright field TEM image of nanosize YSZ, synthesized using Y-BaZrO₃, at 25,000 X showing agglomerates of ~50 to 200 nm in size.

Figure #14(b): A bright field TEM image of the same sample at 1,000,000 X, showing lattice fringes consistent with the formation of crystalline YSZ. The individual crystallite size is about 5 nm.

Figure #15: Raman spectra of (a) Cubic YSZ, (b) Monoclinic ZrO_2 , (c) As-washed YSZ powder (synthesized using Y-BaZrO_3), (d) The same sample as in (c) after 5 h at 1000°C.

Figure #16: DTA traces obtained at 10°C/min. in air, of nanosize YSZ powders synthesized from (a) Y-BaZrO₃ and (b) Y-Na₂ZrO₃ powders.

Figure #17: XRD patterns of nanosize YSZ powders obtained from Y-BaZrO₃ subjected to subsequent thermal treatments at various temperatures.

Figure #18: XRD patterns of nanosize YSZ powders obtained from $\text{Y-Na}_2\text{ZrO}_3$ subjected to subsequent thermal treatments at various temperatures.

Figure #19(a)

Figure #19(b)

Figure #19: Scanning electron micrographs of fractured cells showing the electrolyte, the cathode and anode interlayers, and parts of the cathode current collector and the anode support: (a) Cell with cathode area $\sim 1.1 \text{ cm}^2$, (b) Cell with cathode area $\sim 2.0 \text{ cm}^2$.

Figure #20: Voltage and power density vs. current density for two cells tested at 800°C with hydrogen as fuel and air as oxidant with different cathode areas; ~1.1 cm² and ~2 cm².

Figure #21: Voltage and power density vs. current density for the same two cells as in Figure #20 at 750°C with hydrogen as fuel and air as oxidant.

Figure #22: Ohmic contribution (IR drop) vs. current density at 800°C obtained by current interruption on the two cells, corresponding to Figure #20.

Figure #23: Cathodic overpotential vs. current density measured at 800°C on the two cells, corresponding to Figure #20.

Figure #24: Anodic overpotential vs. current density measured at 800°C on the two cells, corresponding to Figure #20.

Figure #25: Voltage and power density vs. current density for the cell with semicircular cathodes, measured at 800°C with hydrogen as fuel and air as oxidant. The figure shows data for the two cathodes individually, as well as after shorting the cathodes with a thick silver wire.

Figure #26: Anodic overpotential vs. current density measured for the cell with semicircular cathodes, corresponding to Figure #25.

Figure #27: Ohmic contribution (IR drop) vs. current density measured for the cell with semicircular cathodes, corresponding to Figure #25.

Figure #28: Cathodic overpotential vs. current density measured for the cell with semicircular cathodes, corresponding to Figure #25.

Figure #29: Experimentally measured anodic overpotentials (the same as Figure #24) along with fits to equation (18). The i_{as} for the best fit to the experimental data for the cell with cathode area $\sim 2.0 \text{ cm}^2$ was made by matching at $i = 2 \text{ A/cm}^2$. Using this value of i_{as} , the i_{as} for the cell with cathode area of $\sim 1.1 \text{ cm}^2$ was estimated using equations (16 or 17). The dotted curve for the cell with $\sim 1.1 \text{ cm}^2$ of cathode area, was calculated using equation (18).

Figure #30: Voltage vs. current density traces at 800°C for two cells with different cathode interlayers.

Figure #31: A plot of maximum power density vs. the LSM content in the cathode interlayers.

Figure #32: An electron probe micrograph of the cathode interlayer from one of the cells.

Figure #33: A plot of $1/W_{LSM}$ vs. V_{YSZ}/V_{LSM} .

Figure #34: A plot of the experimentally measured R_{cell} vs. $\sqrt{d / ((1 - V_v) l_{TPB})}$.

Figure #35: A plot of the experimentally measured R_{cell} vs. $1/l_{TPB}$.

Figure #36: An SEM micrograph of a fractured cell showing five layers: (a) The top layer is the Ni-YSZ anode support of ~ 1 mm thickness. (b) The adjacent layer, sandwiched between the dense YSZ electrolyte layer and the Ni-YSZ anode support, is the anode interlayer of ~ 20 μm thickness. (c) Dense YSZ layer of ~ 10 μm in thickness. (d) Cathode interlayer of ~ 20 μm thickness adjacent to the YSZ electrolyte layer. (e) Cathode layer of ~ 80 μm thickness. The bar (3 μm) is for the inset.

Figure #37: Cell performance at 800°C with methanol, ethanol and hydrogen as fuels. Flow rate for hydrogen was 100 ml/min. Methanol used was undiluted. Ethanol used was an equi-volume solution of ethanol and water. The flow rates for liquid fuels were 0.2 ml/min for both.

Figure #38: Cell performance with methanol as a fuel at various temperatures. The flow rate was 0.2 ml/min.

Figure #39: Cathode overpotentials vs. current density at 800°C, 650°C and 550°C for an air flow rate of 600 ml/min.

Figure #40: Anode overpotentials vs. current density. Overpotentials were measured at 800°C, 650°C and 550°C for methanol (open symbols) and for hydrogen and ethanol + water (solid symbols) as fuels at 800°C. The liquid flow rate was 0.2 ml/min. Hydrogen flow rate was 100 ml/min.

Figure #41: A scanning electron micrograph of a fractured single cell.

Figure #42: Voltage and power density as a function of current density for cells with varying cathode interlayer compositions. The cells were tested at 800°C with air and humidified hydrogen.

Figure #43: Anode overpotential as a function of current density for cells with varying cathode interlayer compositions. The cells were tested at 800°C with air and humidified hydrogen.

Figure #44: Ohmic overpotential (IR drop) as a function of current density for cells with varying cathode interlayer compositions. The cells were tested at 800°C with air and humidified hydrogen.

Figure #45: Cathode overpotential as a function of current density for cells with varying cathode interlayer compositions. The cells were tested at 800°C with air and humidified hydrogen.

Figure #46: Anodic, cathodic, and ohmic overpotentials at 800°C for the cell with the 50 wt.% LSGM and 50 wt.% LSM composite cathode fired at 1150°C.

Figure #47: The effect of cathode interlayer firing temperature on performance at 800°C as shown with voltage and power density as a function of current density. The cathode interlayer consisted of 50 wt.% LSGM and 50 wt.% LSM.

Figure #48: Anode overpotential as a function of current density at 800°C for cells with a 50 wt.% LSGM and 50 wt.% LSM composite cathode fired at various temperatures.

Figure #49: Ohmic overpotential (IR drop) as a function of current density for cells with 50 wt.% LSGM and 50 wt.% LSM composite cathodes fired at various temperatures.

Figure #50: Cathode overpotential as a function of current density for cells with 50 wt.% LSGM and 50 wt.% LSM composite cathodes fired at various temperatures.

Figure #51: Powder X-ray diffraction patterns for LSGM and YSZ powders mixed and fired at temperatures between 1000 and 1200°C for two hours.

Figure #52: Plots of the experimentally measured reduced layer thickness as a function of reduction time at various temperatures.

Figure #53: Experimentally measured plot of the square of the re-oxidized layer thickness vs. time at 700°C. A straight-line behavior of the re-oxidized layer thickness vs. time suggests that the kinetics of re-oxidation is diffusion controlled.

Figure #54: An SEM micrograph of an as-sintered sample. Light regions are NiO, dark gray regions are YSZ, and black are pores. Note that the amount of porosity is very small in the as-sintered samples. That is, the original, as-sintered sample was essentially, fully dense.

Figure #55: An SEM micrograph of a sample that was reduced, and then re-oxidized. Note that a considerable amount of porosity was created during the reduction/reoxidation process.

Figure #56: An SEM micrograph of a polished section of the Ni + YSZ anode (after impregnating with an epoxy).

Figure #57: Voltage and power density vs. current density at 800°C with as-received H_2 and H_2 diluted with He as fuel.

Figure #58: Voltage and power density vs. current density at 800°C at with as-received H_2 and H_2 diluted with N_2 as fuel.

Figure #59: Voltage and power density vs. current density at 800°C with as-received H_2 and H_2 diluted with CO_2 as fuel.

Figure #60: Voltage and power density vs. current density at 800°C for H₂-H₂O binary system with various concentrations of H₂O.

Figure #61: Voltage and power density vs. current density at 800°C for CO-CO₂ binary system with various concentrations of CO₂.

Figure #62: Anode limiting current density vs. partial pressure of H_2 or CO at 800°C .

Figure #63: Voltage and power density vs. current density at 800°C for H₂-CO mixtures as fuel with various concentrations of CO.

Figure #64: Partial pressure of oxygen at the anode and open circuit voltage (OCV) as a function of p_{H_2O} for H_2 - H_2O at $800^\circ C$.

Figure #65: Partial pressure of oxygen at the anode and open circuit voltage (OCV) as a function of p_{CO_2} for CO-CO₂ at 800°C.

Figure #66: Partial pressure of oxygen at the anode and open circuit voltage (OCV) as a function of p_{H_2} for H_2 - CO_2 at $800^\circ C$.

Figure #67: Comparison of the measured total polarization (less the ohmic contribution) as a function of current density vs. calculated concentration polarization for: (a) ~34% H₂ + ~66% H₂O, and (b) ~32% CO + ~68% CO₂.

LIST OF ACRONYMS AND ABBREVIATIONS

BET:	Brunauer-Emmett-Teller
DMFC:	Direct methanol fuel cell
DTA:	Differential thermal analysis
EDS:	Energy dispersive spectra
ICP:	Inductively coupled plasma
LSC:	Sr-doped LaCoO_3
LSGM:	Sr- and Mg-doped LaGaO_3
LSM:	Sr-doped LaMnO_3
MIEC:	Mixed ionic electronic conduction
OCV:	Open circuit voltage
SDC:	Sm_2O_3 -doped CeO_2
SEM:	Scanning electron microscopy
SOFC:	Solid oxide fuel cells
TEM:	Transmission electron microscopy
TPB:	Three-phase boundary
XRD:	X-ray diffraction
YSZ:	Yttria-stabilized zirconia