SOLID OXIDE FUEL CELL PERFORMANCE STUDIES: ANODE DEVELOPMENT

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ABSTRACT

In this research the microstructure → property relations in solid oxide fuel cells (SOFC's) are being studied to better understand the mechanisms involved in cell performance. The overall aim is to fabricate SOFC's with controlled, stable, high performance microstructures. In this paper anodic studies are presented which exhibit the influence of starting powder characteristics, processing conditions and composition on the electrical conductivity and overpotential.

INTRODUCTION

The main functions of the porous anode are to provide electrochemical reaction sites for oxidation of the fuel, allow the fuel and byproducts to be delivered and removed from the surface sites, and to provide a path for electrons to be transported from the electrolyte/anode reaction sites to the interconnect. Along with these functions the anode must meet stringent requirements in a reducing environment including a high electronic conductivity, chemical compatibility with the interconnect and electrolyte, dimensional stability, and a compatible thermal expansion coefficient with other cell components. Because of the low oxygen activity of the fuel, metals can be used as the anode in SOFC's. Suitable metals must be non-oxidizable not only in the fuel inlet but also in the less reducing fuel outlet (1). At present, Ni is the common choice because of its low cost and high catalytic activity towards H₂ oxidation. Pure Ni has a melting point of 1453°C, a thermal expansion coefficient of 13.3 x 10⁻⁶ cm/cm K, and an electrical conductivity of ~2 x 10⁴ S/cm at 1000°C (2).

Because of the low melting temperature (resulting in the tendency to sinter at 1000°C) and high expansion coefficient of Ni, YSZ is usually added to the Ni to form a composite anode. The purpose of the YSZ additions are to maintain the porous structure of the anode for long periods of time at high temperatures, to support the Ni particles, to inhibit the sintering of the Ni particles, and to reduce the thermal expansion of pure Ni to values more compatible with other cell components (1). During fabrication, anode compositions are initially in the form of interconnected NiO and YSZ, and are then reduced in situ to form Ni-YSZ cermets. Processing in ambient atmospheres improves flexibility in fabrication techniques and reduces processing costs. During reduction of NiO to Ni in situ the porosity of the anode increases due to the loss of oxygen in conversion of NiO to Ni. The phase boundary where NiO converts to Ni occurs at an approximate pO₂ = 10⁻⁶ atm at 1000°C (3). Since typical oxygen pressures of the fuel in a SOFC operating at 1000°C are ~ 10⁻¹⁷ to 10⁻¹⁸ atm, NiO will be reduced to metallic Ni in fuel cell operating conditions. For a porous film of Ni-YSZ, ~50 μm thick, it takes only minutes for NiO to be reduced to Ni metal in H₂ at 1000°C (4).
The electrical conductivity of Ni-YSZ cermets is a strong function of Ni content as predicted by diphasic percolation theory (5). The electrical conductivity of porous Ni-YSZ composites exhibits a percolation threshold at approximately 30 vol% Ni, where the conductivity changes ~ 4 orders of magnitude. The dramatic change in conductivity in the narrow Ni vol% range is controlled by the YSZ at low Ni loadings and by the Ni at higher contents. Above the threshold value, the Ni forms a continuous path for electronic conduction throughout the sample with a maximum conductivity of ~ 1000 S/cm. Low surface area Ni powders provide better Ni coverage, resulting in improved Ni-Ni contact and a higher conductivity (4).

The Ni particle size also effects the percolation threshold (6). The threshold value is lowest for fine NiO powders, and shifts to higher Ni contents with increasing NiO particle size. Certainly the % porosity, pore size , and distribution, and the connectivity of all three phases should have an impact. The porous Ni-YSZ cermets should therefore be treated as a three phase composite, each phase three dimensionally interconnected with itself, 3-3-3 notation (7). The electrical behavior of Ni-YSZ composites therefore becomes more complex and more difficult to predict using percolation theory due to the variations in size, size distribution, volume fraction Ni, and possible structural changes in Ni at high temperatures.

During reduction of NiO-YSZ composites at 1000°C, the conductivity shows a dramatic increase due to Ni formation, ~3-4 orders of magnitude, then falls off slowly until a steady state is reached (4). The decrease in conductivity can be attributed to loss of Ni-Ni particle contacts resulting in a reduction in the number of conduction paths. High surface area Ni particles will provide more surface sites for the oxidation of the fuel, but tend to coarsen more due to their high thermodynamic driving force at high temperatures. Various processing and deposition techniques have been employed to inhibit the coarsening of the Ni. The addition of MgO to NiO to form a solid solution (1-x)Ni - xMgO (x=0.1,0.2) has been proposed to inhibit the sintering of Ni particles (8). Upon exposure to the fuel, the (Ni,Mg)O particles reduce to Ni metal and MgO. The MgO, precipitates out of the solid solution and pins the Ni particles, thus helping the Ni maintain a high surface area.

In this research further microstructure ↔ property relations of the anode were studied to better understand the mechanisms involved in cell performance. The influence of starting powder characteristics, and resultant microstructures as a function of processing conditions (i.e. powder calcination temperature, and annealing temperature) and composition on the electrical conductivity and overpotential measurements are presented.

**EXPERIMENTAL PROCEDURE**

The YSZ electrolyte used in this investigation was self supporting (=200 µm thick) and the cathode and anode were applied via screen printing onto a pre-sintered dense electrolyte. A flowchart describing the techniques used to fabricate single cells is shown in Fig. 1. Commercially available Y stabilized ZrO₂ (YSZ - Zirconia Sales of America) powders were used in this study for the electrolyte and as a major constituent in the anode. It is a fully stabilized (8 mole % Y₂O₃), co-precipitated powder, with a primary particle size of approximately 250 nm and a corresponding BET surface area of ~ 8.0 m²/g. NiO, and Mg-doped NiO were synthesized using the glycine nitrate method with Ni(NO₃)₂·xH₂O, MgCO₃, glycine, and distilled water as the starting materials. Powder crystallinity, phase, and surface area were characterized using X-ray diffraction and BET techniques as a function of calcination temperature. A YSZ-NiO (45 vol % Ni) composition was also prepared in which both components were combusted simultaneously using the glycine nitrate process. Starting raw materials were Ni(NO₃)₂·xH₂O, Y(NO₃)₃·xH₂O, and a zirconium citrate complex.
A total of three different techniques were used to prepare powder mixtures with the goal of producing different resultant microstructures including: 1) mixing YSZ with \( \text{Ni}_{1-x}\text{Mg}_x\text{O} \) \( (x=0.0, 0.1, 0.2) \), 2) mixing YSZ with NiO followed by calcination at 1400°C for 4 h, and 3) simultaneous combustion of both components using the glycine nitrate technique.

Anode powders were mixed with a commercial resin solution, BX018-16, from Ferro Corp. The suspension was mixed using a three roll mill to prepare a well-dispersed paste for screen printing. In all instances the highest amount of powder was loaded into the binder such that the paste was still workable, typically 50 to 75 wt%. Anode compositions were screen printed onto dense YSZ electrolytes and sintered onto the electrolyte between 1300°C and 1500°C in 100°C increments for a 1 h hold, with a heating and cooling rates of 3°C/min. A goal of this investigation was to investigate the influence of grain size and porosity of the electrode on the cell performance, therefore powders were calcined and sintered at various temperatures. Anodes were porous, exhibited grain sizes on the order of 1 μm, and gave resultant dimensions of 0.635 cm x 0.635 cm and = 20 μm thick.

A porous Pt grid (0.2 mm line width and 0.2 mm spacing) was screen printed on the electrodes for cell performance experiments to act as a current collector, and allow gas diffusion to the electrode/electrolyte interface, Fig. 2. The rings were designed with pads which were coated with Pt paste to allow for electrical sensing. Pt wires of 10 mil diameter were bonded from the Pt grid to the Pt pads on the rings using Pt paste, this was done to both the anode and cathode side of the electrolyte. Pt paste was also used as the connection between the Pt voltage probe and a pad on the ring for voltage sensing. There are 2 pads on the cathode side: one for electrical connection to the cathode and one for sensing the voltage probe. Only one pad was active on the anode side. The cell was sintered at 1200°C for 1 h to densify the Pt and achieve a good bond between the YSZ rings and electrolyte.

Electrochemical (I-V) measurements were carried out using a five electrode configuration which allowed for separation of anode and cathode overpotentials during operation. I-V behavior was performed on both half cells and complete cells using an Anatronics I/V Control Fuel Cell Testing Module, a Keithley Model 196 μV Meter, and a Fluke 27/FM Multimeter. The Fuel Cell Testing Module was placed in the voltage control mode thus enabling the desired cell voltage and corresponding current to be measured.

Measurements were carried out from small voltages to larger ones in increments of 25mV; in all cases steady state voltages and currents were measured. Stabilization times were typically 2-3 min. The current, total cell voltage \( V_{\text{cell}} \), voltage drop from the Pt probe to the cathode \( V_C \) and the anode \( V_A \) were all simultaneously measured. At open circuit and at any given voltage under load \( V_{\text{cell}} \) was equal to the two half cell voltages, i.e.

\[
V_{\text{cell}} (I) = V_C (I) + V_A (I) \tag{1}
\]
Anode overpotentials were calculated by subtracting the voltage drop under load from the corresponding voltage drop at open circuit:

$$\eta_{\text{anode}}(I) = V_{c@O.C.} - V_c(I) - IR_{\text{electrolyte}} - IR_{\text{anode}}$$  \[2\]

where

- $\eta_{\text{anode}}(I)$ = anodic overpotential
- $V_{c@O.C.}$ = voltage drop between cathode and Pt probe at open circuit
- $V_c(I)$ = voltage drop between cathode and Pt probe under load
- $IR_{\text{electrolyte}}$ = voltage drop associated with the electrolyte (100 μm thick)
- $IR_{\text{anode}}$ = voltage drop associated with the anode

RESULTS AND DISCUSSION

The primary focus of this research was to reduce the sintering of the Ni particles, increasing the number of reaction sites, which would result in a lower overpotential. Electrical conductivity and $\eta$-$j$ plots were monitored for a 24 h period to better understand the coarsening between Ni particles. Conductivity experiments were used to reveal how the Ni particles were distributed throughout the cermet. Since the conductivity is controlled by the Ni, these experiments help to determine if the YSZ support structure was sufficient in reducing the tendency of the Ni particles to sinter. Electrochemical measurements, $\eta$-$j$, were not only used to determine resultant overpotentials, but also how the Ni-YSZ particle contacts were distributed in the composite.

Resistive (IR) Contribution from the Anode

Four point DC conductivity experiments were performed on anode compositions to determine the resistive loss associated with the anode during cell operation. Anode conductivities ranged from ≈3 - 800 S/cm which depended on the starting raw materials, fabrication technique, and the sintering temperature. Figure 3 is a typical V-I plot of an anode demonstrating ohmic behavior. From the dimensions of a screen-printed anode
then, for a current density of 1000 mA/cm² the voltage drop in the anode would be at most 0.7 mV. Hence the measured voltage as a function of current density between the anode and the Pt voltage probe can be attributed solely to the resistive loss of the electrolyte and the overpotential of the anode.

**Effect of Vol % Ni**

Compositions studied for this experiment ranged from 40-55 vol % Ni in increments of 5 vol %. Oxide powder mixtures were calcined at 900°C, sintered on the YSZ electrolyte at 1400°C, and then reduced in situ. After the fuel was introduced to the anode, the cell was allowed to stabilize for ~ 1-3 h before electrochemical measurements were performed. Conductivity experiments were monitored in air, during reduction of NiO to Ni, and under reducing conditions for 24 h.

The electrochemical response of the four compositions is shown in Figure 4. The 40 and 45 vol % Ni samples show similar behavior, ~220 mV and 200 mV at 1000 mA/cm², but the 50 and 55 vol % compositions showed much higher overpotentials, ~280 and 370 mV at 1000 mA/cm². After 24 h, the overpotentials of all compositions increased, Figure 5. The 40 and 45 vol % Ni samples still show similar behavior, ~270 mV at 1000 mA/cm², and the 50 and 55 vol % Ni compositions had overpotentials of ~370 and 470 mV at 1000 mA/cm². The low vol % Ni samples, 40 and 45, have the lowest overpotentials due to the larger YSZ content in the cermet to support the Ni particles. This would effectively reduce the amount of sintering between Ni particles. For compositions with larger vol % Ni (i.e. 55 vol % Ni), less YSZ is available to support the Ni and larger Ni particles would be expected. The resultant microstructures for the four compositions after 24 h of operation are shown in

![Figure 3](image_url)  
**Figure 3.** Voltage - current behavior for a typical Ni-YSZ cermet.

![Figure 4](image_url)  
**Figure 4.** Initial \(\eta\)-\(j\) relations of Ni-YSZ cerments sintered at 1400°C.

![Figure 5](image_url)  
**Figure 5.** \(\eta\)-\(j\) results, initially and after 24 h, for Ni-YSZ cerments sintered at 1400°C.
Figure 6. Microstructures of the 40, 45, 50 and 55 vol% Ni compositions.

Figure 6. It is difficult to see any distinguishable difference for the three lowest Ni contents, 40, 45, and 50 %, although, the 55 % composition does show a dissimilarity. The Ni particles are larger and more easily distinguishable from the YSZ support.

Electrical conductivity measurements were also performed on all four compositions for 24 h, Figure 7. Since the samples contain various vol % Ni, a direct comparison cannot be made as to how the Ni particles are distributed within the cermet, although, similar trends were observed. All compositions had similar conductivities in the oxide form, ≈ 3.5 S/cm. Upon exposure to the fuel, a large increase in the conductivity occurred, within 5 min, then rapidly decreased within ≈ 3 h to a steady state value. The large increase in the conductivity is caused by the reduction of NiO to Ni metal. The very sharp decrease in conductivity is due to the rapid sintering between Ni particles, and the continued slow decrease in the conductivity can be attributed to further sintering of the Ni particles.

Effect of NiO Starting Raw Materials

Three different NiO sources were used in this study to examine the effect of Ni particle size and preparation conditions on the anodic overpotential. All anodes contained 45 vol % Ni, and were fired onto the YSZ electrolyte at 1400°C. The first NiO powder was synthesized by the glycine nitrate process and calcined at 900°C as described previously. The remaining two sources were commercially available powders with different primary particle sizes. The first powder had a reported particle size of -325 mesh ( < 45 μm) and the second powder was spray dried with a primary particle size less than 10 μm.

The η-j plots for the three different particle sizes initially and after 24 h are shown in Figure 8. The results of the powder prepared by the glycine nitrate process are the same as reported previously. The -325 mesh powder initially has an overpotential of ≈ 250 mV at 600 mA/cm² but increases to ≈ 370 mV after 24 h. The spray dried powder has a relatively stable overpotential but it is extremely high, ≈ 450 mV at 600 mA/cm². Examination of the microstructures after 24 h of operation revealed large, distinguishable Ni particles for both
commercial powders. This can explain the large overpotentials in that the number of
reaction sites (Ni-YSZ contacts) has drastically decreased due to the large Ni particle size.
The microstructure of the spray dried powder resembles spray dried granules which
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The conductivity for the three powders also correlates well with the electrochemical
results (Figure 9). The conductivity of the spray dried powder was relatively stable upon
reduction but was extremely low, comparable to the NiO-YSZ composite (=3 S/cm). This
suggests that the Ni particles have rapidly become large and separated from one another,
dercreasing the number of Ni-Ni contacts. The -325 mesh powder initially had a higher
conductivity (=200 S/cm) but quickly decreased to values comparable to the spray dried
powder. This also suggests that the Ni particles have coarsened and reduced the number of
Ni-Ni contacts throughout the cermet. For both commercial powders, the Ni-Ni and Ni-
YSZ particle contacts has decreased causing the conductivity to be extremely low and the
overpotential to be high.

Effect of Pre-calcination of Powders

The influence of calcining NiO and YSZ together at high temperatures (1400°C)
before depositing the composition onto the YSZ was investigated. This approach was
examined to provide a more stable anode structure by allowing the YSZ and NiO powders
to further densify during calcination. The composition studied was 50 vol % Ni; the η-j
results are shown in Figure 10. For comparison, a 50 vol % Ni composition prepared by
the conventional technique (described previously with no pre-calcination of NiO and YSZ)
is also illustrated. Both the precalcined and conventionally prepared samples have the same
starting raw materials, commercial YSZ and NiO prepared by the glycine nitrate process.

The pre-calcined powders resulted in a lower and more stable overpotential (=240 mV
at 1000 mA/cm²) than the conventionally prepared composition (=380 mV at 1000
mA/cm²) after 24 h. The lower and more stable overpotential is believed to be caused by a
more rigid and stronger YSZ structure due to the high temperature calcination of the YSZ
and NiO. The pre-calcination treatment allows more densification to occur between YSZ
particles because the anode is normally constrained to sinter by the YSZ electrolyte during
annealing. Therefore, the pre-calcination treatment is more effective than the conventional
Effect of Annealing Temperature on the Anodic Overpotential

The temperature at which the anode was sintering on the YSZ electrolyte was investigated to increase the stability of the anode over a 24 h period. Two compositions prepared by two different techniques were examined. The first composition contained 50 vol % Ni and the powders were pre-calcined at 1400°C. The second anode was a 45 vol % Ni composition prepared by the conventional technique. Both composition were fired on the electrolyte at 1300, 1400, and 1500°C.

Pre-calcined Powders (50 vol % Ni) The electrochemical behavior of the pre-calcined 50 vol % Ni composition fired on the electrolyte at 1300, 1400, and 1500°C is shown in Figure 12. Both the initial results and those after 24 h of operation are illustrated. The 1500°C firing shows the best stability and lowest overpotential after 24 h (~ 220 mV at 1000 mA/cm²). The anode densified at 1400°C also showed a low overpotential but
slightly increased with time (~ 240 mV at 1000 mA/cm^2). The sample sintered at 1300°C had the highest overpotential and was unstable within the 24 h period (~ 400 mV at 400 mA/cm^2 after 24 h). The improved electrochemical response with higher sintering temperatures is due to the improved sintering of YSZ particles, a more rigid YSZ support will further inhibit the Ni particles from coarsening. The densification of the YSZ support at high temperatures (1300-1500°C) should provide a stable backbone and is not expected to change under fuel cell conditions (pO2 ~ 10^{-17}, 1000°C).

The conductivity and microstructures after 24 h of operation are shown in Figures 13 and 14. The conductivity results correlate well with the electrochemical response, both suggesting that the sintering between Ni particles has been reduced with higher annealing temperatures. For a higher sintering temperature, better Ni-Ni particle contact results in more paths for conduction to occur. The microstructures also suggest that the lower firing temperature has a less rigid structure (the grains appear to be smaller and not as well bonded to one another) than the progressively higher annealing temperatures.

![Figure 12](image1.png)  
**Figure 12.** \(\eta\)-j relations of 50 vol % Ni compositions pre-calcined at 1400°C and sintered at various temperatures.

![Figure 13](image2.png)  
**Figure 13.** Conductivity versus time for 50 vol % Ni compositions pre-calcined at 1400°C and sintered at various temperatures.

![Figure 14](image3.png)  
**Figure 14.** Microstructures of 50 vol % Ni compositions pre-calcined at 1400°C and sintered on the YSZ electrolyte at various temperatures.
SUMMARY AND CONCLUSIONS

♦ YSZ anodes prepared with lower Ni volume fractions (40 & 45%) resulted in lower overpotentials and improved stability.

♦ Higher sintering temperatures effectively lowered the overpotential and increased the in-plane conductivity. Due to constrained sintering between the anode and the YSZ electrolyte, higher sintering temperatures allowed more densification in the z-direction, resulting in a rigid YSZ structure to support Ni particles.

♦ By decreasing the densification between Ni grains, there are more paths for conduction (more Ni-Ni contacts throughout the structure and higher conductivities) and a larger number of Ni-YSZ contacts (lower overpotentials).

♦ The 45 vol% Ni composition co-fired with the electrolyte had the lowest initial overpotential of any cermet with a similar composition.

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