Infiltrated composite electrodes for solid oxide fuel cells

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INFILTRATED COMPOSITE ELECTRODES FOR SOLID OXIDE FUEL CELLS

by

ALIGUL BUYUKAKSOY

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The other two parts related to the present study, but not included in the body of this dissertation, are given in the appendix. The first part is entitled “Microstructure and Electrical Properties of Infiltrated Ni-YSZ Cermets” which provides additional information about the Ni-YSZ anodes prepared by infiltration. The second part is entitled “Redox Cycling of Electrolyte Supported SOFCs with Co-sintered Ni-YSZ Anodes” which provides an example of changes in the performance of SOFCs with co-sintered Ni-YS anodes for comparison.
ABSTRACT

Solid oxide fuel cells (SOFCs) are electrochemical devices which can convert chemical energy to electrical energy with efficiencies up to 60%. In order for SOFCs to be favorable energy conversion devices, the power obtained from a unit volume should be improved. This corresponds to minimized resistances from SOFC components (composite electrodes and electrolyte). Stability of the generated power is another important issue. Degradation of SOFCs with time due to microstructural processes or chemical reactions that occur at operating conditions; and due to reduction/oxidation cycles caused by the changes in the anode has been an important obstacle that has prevented the widespread commercial use of SOFCs.

In this dissertation, the electrochemical properties of SOFC electrodes prepared by an infiltration technique were investigated. The long-term behavior and redox stability of the electrodes were evaluated individually and in the form of complete SOFCs. Interpretation of impedance spectra was used extensively to gain some fundamental understanding of the electrochemical properties of the electrodes along with voltammetry. Microstructural characterization was performed by electron microscopy techniques.

LSM-YSZ cathodes prepared by polymeric LSM precursor infiltration resulted in cathode polarization resistance of 0.022 Ohm.cm² at 800 °C, which then increased to 0.035 Ohm.cm² and remained stable at this value for 100 hours. SOFCs with Ni-YSZ anodes and LSM-YSZ cathodes prepared by infiltration yielded total electrode polarizations of 0.080 Ohm.cm² at 800 °C. The electrode polarization resistances showed no degradation with time or upon redox cycling.
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1. INTRODUCTION

1.1. WHY SOLID OXIDE FUEL CELLS?

The advances in technology offers people progressively improving life standards. The widespread use of technological devices in the everyday life results in a high demand for energy. This demand has been met by the use of fossil fuels which are limited in resources. In addition, they produce CO$_2$ gas upon burning which contributes significantly to global warming. Figure 1.1. provides the change in total energy consumption and CO$_2$ emission from combustion with time. An approximate 1.5 fold increase is observed since 1990 for both parameters. The similarity of the increasing profiles is particularly worth noting.

Solid oxide fuel cells (SOFCs) are promising energy conversion devices which can convert chemical energy to electrical energy with extremely high efficiencies ($>60\%$)\footnote{1}.\footnote{2}. Their ability to operate with hydrogen as fuel makes them independent of the limited fossil fuel resources. In addition, since no carbon would be involved in the electrochemical reaction, there would be no CO$_2$ emissions during operation. The fact that they can operate with hydrogen or hydrocarbon gases as fuel, makes them attractive alternatives for energy conversion. In the case hydrocarbon fuels the high efficiency of the SOFCs would allow energy conversion with a much lower amount of fuel, which corresponds to lower CO$_2$ emissions.
Despite the aforementioned advantages of SOFCs, there are several important issues that need to be addressed for the SOFC technology to be viable. These include the reduction of cost per produced power, long-term stability and the ability to shut down – start up without degradation. All of these issues are mainly materials related issues and stimulating challenges for materials scientists.

1.2. OPERATING PRINCIPLE OF SOLID OXIDE FUEL CELLS

A typical SOFC consists of an oxygen ion conductor electrolyte, an air electrode (cathode) and a fuel electrode (anode). Air and fuel (typically hydrogen) is fed from cathode and anode sides respectively and are separated by the dense electrolyte layer. The

Figure 11.1. The changes in the energy consumption and CO₂ emissions with time.
difference in the oxygen partial pressures in anode and cathode sides create a chemical
potential difference across the electrolyte called the “open circuit voltage”. This voltage
is given by the Nernst equation which can be derived from the Gibbs free energy of the
reaction of water formation from oxygen and hydrogen as follows:

\[ \Delta G = \Delta G^\circ + RT\ln(K) \]  \hspace{1cm} (1)

\[ \Delta G = -\Delta W_{electrical} = -E \cdot Q = -nFE \]  \hspace{1cm} (2)

\[ -nFE = -nFE^\circ + RT\ln(K) \]  \hspace{1cm} (3)

Rearranging the terms;

\[ E = E^\circ + \frac{RT}{nF} \ln(K) \]  \hspace{1cm} (4)

where;

\[ K = \frac{pH_2O}{pO_2^{0.5}pH_2} \]  \hspace{1cm} (5)

Here; \( R \) is gas constant, \( T \) is temperature, \( K \) is reaction constant, \( \Delta W_{electrical} \) is
electrical work, \( E \) is Nernst potential \( Q \) is charge in Coulombs, \( F \) is Faraday constant and
\( E^\circ \) is standard electrode potential for the reaction of hydrogen and oxygen to produce
water.

The conversion of this chemical energy to the electrical energy is realized when
current is drawn from the cell. In this case, the oxygen molecules are reduced to oxygen
ions at the cathode and then delivered to the anode side through the ionically conductive
electrolyte. The oxygen ions delivered to the anode react with hydrogen to produce water and two electrons per oxygen ion (Figure 1.2.). The electrode reactions are given below:

Cathode: \( \frac{1}{2} O_2 + 2e^- \rightarrow O^{2-} \) \hspace{1cm} (6)

Anode: \( O^{2-} + H_2 \rightarrow H_2O + 2e^- \) \hspace{1cm} (7)

**Figure 1.2.** Schematic representation of a solid oxide fuel cell operation.

1.3. SOLID OXIDE FUEL CELL COMPONENTS AND MATERIALS

1.3.1. Electrolyte. Figure 1.3. provides the temperature dependence of electrical conductivities of some oxide ion conductors. Materials such as doped lanthanum gallate, doped bismuth oxide and doped ceria exhibit the highest electrical conductivities at the range of operating temperatures. However, these materials suffer from dimensional instability and high electronic conductivity which reduces the
maximum achievable open circuit voltage. Consequently, yttria stabilized zirconia (YSZ) with the fluorite structure remains the most widely preferred electrolyte material due to its relatively high electrical conductivity (0.02 S/cm at 800 °C), negligible electronic conductivity, chemical and dimensional stability. In the undoped form, ZrO$_2$ has a monoclinic crystal structure which exhibits quite low electrical conductivity (2.9×10$^{-5}$ S/cm at 800 °C in air). The monoclinic structure transforms into tetragonal at 1170 °C and then to the fluorite structure at 2370 °C. Additions of Y$_2$O$_3$ above 6 mol% stabilizes the fluorite structure, which is a rather open structure, suitable for ion transport, down to room temperature. Doping of ZrO$_2$ with Y$_2$O$_3$ creates extrinsic oxygen vacancies which provide the oxygen ion conduction. This is given below in Kroger-Vink notation:

$$Y_2O_3 \rightarrow 2Y'_Zr = 3O'_0 + V'_o$$  \hspace{1cm} (8)
According to Equation 8, there is a linear relationship between the yttria content and the vacancy concentration which is the charge carrier. However, although the ionic conductivity increases until 8-9 mol% yttria doping, a decrease in electrical conductivity is observed when yttria content is higher than this value. In this case, the attraction between the oxygen vacancies and yttria will result in the formation of complexes and decreases the mobility of the oxygen vacancies. 4

1.3.2. Cathode. Cathodes in SOFCs are required to possess several properties simultaneously. Firstly, it should be catalytically active for the oxygen reduction reaction (Equation 6). Secondly, it should possess electronic conductivity for the delivery of electrons from the circuit to the sites where the oxygen reduction reaction takes place. In
addition, the cathode must possess sufficient ionic conductivity so that the oxygen ions formed as a result of the oxygen reduction reaction (Equation 6) are delivered efficiently to the electrolyte which transports these ions to the anode. Besides these prerequisite electrochemical properties, the SOFC cathodes must also fulfill stringent requirements such as; chemical stability in oxidizing conditions, chemical compatibility with the electrolyte material, compatible thermal expansion coefficient with the electrolyte material and adequate porosity for facile oxygen gas delivery 6-8.

Perovskite materials have been found to be the most suitable class of materials for SOFC cathode applications. Strontium doped Lanthanum Manganite (La$_{0.8}$Sr$_{0.2}$MnO$_3$, LSM) is one of the most widely used cathode materials due to its relatively high electrical conductivity (120 S/cm at 800 °C), sufficient catalytic activity for the oxygen reduction reaction $^7$-$^9$ and a thermal expansion coefficient (TEC) somewhat close to 8 mol% Yttria stabilized zirconia (TEC$_{LSM}$: 12.4 $\times$10$^{-6}$ K$^{-1}$; TEC$_{YSZ}$: 10.5 $\times$10$^{-6}$ K$^{-1}$) $^{10}$. The electrical conductivity of LSM is predominantly of electronic nature rather than ionic (i.e. ionic conductivity of LSM is in the 5.9$\times$ 10$^{-8}$ S/cm in the pressure range 10$^{-1}$ –10$^{-3}$ atm oxygen at 800 °C $^{11}$). In general, LaMnO$_3$-based perovskites exhibit intrinsic p-type conductivity due to changes in the Mn valence. The electrical conductivity is further enhanced by replacing La$^{3+}$ with lower valence cations (e.g. Sr$^{2+}$), due to the generation of charged holes which act as the charge carrier upon the replacement of La$^{3+}$ ion by Sr$^{2+}$ ion to maintain electroneutrality. This can be represented as follows:

$$LaMnO_3 \xrightarrow{xSrO} La_{1-x}Sr_xMn_{3-x}^3+Mn_x^{4+}O_3$$ (9)
As mentioned earlier, the oxygen reduction reaction can only occur when the electrons, oxygen ions and oxygen gas are in contact (Equation 6). The fact that LSM is almost a purely electronic conductor necessitates that oxygen ions are delivered to the locations where the electrons and oxygen gas meet by another material which is ionically conductive. As a result, in the case of a single phase LSM cathode the reactions are confined to the boundary where oxygen gas, electrons and ions meet, called triple phase boundaries (TPBs). On the other hand, if a mixed ionic – electronic conductor is used instead of LSM (e.g., La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, LSCF) the oxygen reduction reaction is not limited to the TPBs but can also occur at the cathode surface. A schematic representation for both cases is given below (Figure 1.4).

![Figure 1.4. Schematic representation of a) a purely electronic conductor b) a mixed ionic-electronic conductor](image)

The straightforward way to obtain acceptable electrode performances using LSM as a cathode material is by adding an ionically conductive phase to compensate for the pure electronic conductive nature of LSM and maximize the TPB length. In the presence
of a YSZ electrolyte, it is reasonable to select YSZ as the ionically conductive component. The most conventional route for fabricating LSM-YSZ composites is deposition an ink containing a mixture of YSZ and LSM powders on the electrolyte and co-sintering at temperatures in the range of 1100-1250 °C, depending on the initial particle sizes of the corresponding powders. A significant amount of research has been carried out to determine the optimum process parameters to fabricate LSM-YSZ composites with maximized performance. However, this is a challenging task due to the different sintering rates of both phases along with the tendency of resistive La$_2$Zr$_2$O$_7$ phase formation at temperatures higher than 1200 °C.

1.3.3. Anode. In a similar way to the cathode, the anode must be catalytically active for its corresponding electrochemical reaction which is fuel oxidation (Equation 7). In order for collection of electrons generated during fuel oxidation, the anode should also possess sufficient electronic conductivity. Ni is widely used as the main anode material for SOFCs due to its catalytic activity for hydrogen oxidation and high electronic conductivity at operational temperatures. Conventionally, it is mixed in its oxide form (NiO) with YSZ, co-sintered at temperatures ranging from 1300-1450 °C and reduced to obtain a Ni-YSZ composite with enhanced TPB length in comparison with single phase Ni.

Certainly, the issues related with the processing of composites with different sintering rates and stringent microstructural requirements for sufficient electrode performances mentioned in the cathode section are also in effect in the anode case. Additionally, another important issue; redox instability of Ni-YSZ anodes has been an important challenge for materials scientists. It can be expected that the commercial SOFC
will go through several redox (reduction-oxidation) cycles due to intentional or erroneous interruption of fuel supply. For this reason, SOFCs have to be resistant to redox cycling. However, the Ni-YSZ cermets mechanically fail due to the expansion of the Ni phase upon oxidation (69 vol% \(^{18}\)) and the consequent cracks are generated in the anode layer. As a potential solution to the redox instability problem, several studies have focused on the development of new anode materials. Prospective ceramic materials which do not undergo reduction/oxidation with high electrical conductivity in anode conditions, such as; \(\text{Sr}_{0.86}\text{Y}_{0.08}\text{TiO}_{3-\delta}\) (82 S/cm at 800 °C and \(\text{pO}_2=10^{-9}\)) \(^{19}\) and \((\text{La}_{0.75}\text{Sr}_{0.25})_{1-x}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3\) (LSCM) \(^{20}\) were also proposed as alternatives to Ni.

1.4. RESEARCH SCOPE

Fabrication of composite electrodes for SOFCs by infiltration of the second phase into a previously sintered porous skeleton holds significant potential for the development of novel composites which could be applied in SOFC electrodes. The introduction of the second phase into scaffolds with percolating networks of pores allows the achievement of composites with both phases in percolation. This dissertation focused on the investigation of the electrochemical properties of SOFC electrodes prepared by infiltration and evaluation of their potential to solve fundamental problems in SOFCs. The infiltrated electrodes exhibited the potential to solve the fundamental materials problems in SOFCs. Furthermore, unique properties of the composite electrodes the infiltration technique allowed, such as redox stability on Ni-YSZ anodes, were demonstrated and their governing mechanisms were discussed. In Paper 1, electrochemical properties of infiltrated LSM-YSZ cathodes and their long-term stability was discussed. In Papers 2 and 3 the electrochemical properties of infiltrated Ni-YSZ anodes and their behavior
upon redox cycling was discussed. In Paper 4, the long term stability of SOFCs with infiltrated electrodes was the focus. Finally in Paper 5, microstructural stabilization and enhancement of electrochemical performance of Pt electrodes by YSZ infiltration was presented.

Additional appendix sections are presented at the end of the dissertation, focusing on microstructural and electrical properties of infiltrated Ni-YSZ cermets (Appendix A), and redox cycling of conventional anodes (Appendix B).
I. Efficient Cathodes for Solid Oxide Fuel Cells Prepared by Polymeric Precursor Infiltration

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Abstract

A novel technique based on polymeric precursor infiltration into porous layers was developed to process composite materials as highly efficient cathode/current collector structures for solid oxide fuel cells (SOFCs). Powder based Pt and YSZ inks were used to form porous cathode/current collector layers on electrolyte supported symmetrical structures that were infiltrated with polymeric LSM precursor. Electrochemical testing of the samples was performed by impedance spectroscopy techniques. Polarization resistance of the cathode was as low as 0.022 Ohm.cm² at 800°C demonstrating the potential of fabricating highly efficient cathodes. Infiltration process led to a stable composite of the cathode/current collector structures, ensuring a high current collection efficiency and long term stability at operational temperatures.
INTRODUCTION

La$_{1.8}$Sr$_3$MnO$_3$ (LSM) is a mixed ionic and electronic conductor widely used in high temperature solid oxide fuel cells (SOFCs) with yttria stabilized zirconia (YSZ) electrolytes. The relatively low ionic conductivity of LSM is generally compensated by mixing with YSZ. In this manner, the oxygen gas molecules that are reduced to oxygen ions by the catalytically active LSM sites are collected and transported to the electrolyte and finally to anode reaction sites.

The most commonly used technique to fabricate LSM-YSZ composites is screen printing powder based inks and co-sintering at temperatures between 1100 °C and 1200 °C. However, both components have different sintering rates; therefore controlling microstructural development becomes more challenging. For instance, in order for YSZ to be ionically conductive, sintering temperatures of at least 1150 °C are necessary which results in a density about 50% of its theoretical density. On the other hand, at similar temperatures, LSM sinters typically up to 90% of its theoretical density. Consequently, YSZ particles stay disconnected at low co-sintering temperatures (less than 1100°C) and high co-sintering temperatures result in over densification of LSM, which, in turn, leads to reduced YSZ-LSM interfacial area. In addition, formation of the La$_2$Zr$_2$O$_7$ phase at YSZ-LSM interface at sintering temperatures above 1100°C has been reported to degrade the performance and stability of YSZ and LSM based composite cathodes. In previous studies, various attempts were made to determine the optimum process parameters including LSM – YSZ solids loading, particle size ratios, sintering temperatures and sintering additives. These investigations resulted in lower cathode polarization resistances of 0.1 Ohm.cm$^2$ at 800°C.
Attempts were made to fabricate SOFC electrodes by low temperature infiltration techniques which possess the potential to produce high surface area cathodes. Generally, infiltration of aqueous nitrate solutions into a porous YSZ backbone was employed. Despite the significant progress achieved, aqueous nitrate solutions into porous layers remain problematic in several ways: i) Random formation of aggregated and disconnected crystals, ii) Failure to obtain the desired phase in mixed oxides due to poor mixing, iii) High surface tension of water resulting in high resistance to infiltration. One approach reported in the literature to overcome the issues related with poor mixing was to use commercially available polymeric dispersants. Other techniques such as infiltration of molten salts or suspensions containing mixed oxide nanoparticles were employed successfully to ensure formation of the desired perovskite phase. In addition, mixtures of low surface tension solvents with water were used to facilitate more effective infiltration.

Infiltration of polymeric precursors into a porous matrix is a unique method which has shown promise for low temperature processing of SOFC electrodes and cermets. This paper reports preparation of YSZ-LSM cathodes by polymer precursor infiltration with a platinum current collector as a highly efficient composite structure that shows long term stability at operating temperatures of SOFCs.

**SAMPLE PREPARATION**

Symmetrical electrolyte-supported structures were used in this investigation. Dense, ~170 micron thick YSZ substrates stabilized with 8 mol% Y₂O₃ (NexTech Materials; Columbus, OH) were used as the electrolyte. Platinum paste (ElectroScience;
King of Prussia, PA) and YSZ powder (Tosoh, Japan) were used to form the cathode/current collector structure. La$_{0.8}$Sr$_{0.2}$MnO$_3$ polymeric precursor was used for infiltration.

La$_{0.8}$Sr$_{0.2}$MnO$_3$ polymeric precursor was prepared as described previously \cite{21}. Appropriate amounts of lanthanum(III) nitrate hexahydrate, anhydrous strontium nitrate, manganese(II) nitrate tetrahydrate salts (Alfa Aesar; Ward Hill, MA) were dissolved in deionized water. Ethylene glycol was added as chelating agent to achieve an ethylene glycol to cation mole ratio of 0.04 (which corresponds to ~52wt% LSM equivalent) and stirred at 100 °C until water completely evaporated. Finally, 2-butoxyethanol, equal to the weight of ethylene glycol, was added to improve the wetting behavior of the polymeric precursor. An infiltration cycle consisted of three steps: i) application of the polymeric precursor, ii) drying at 70 °C, iii) decomposition at 450 °C and for all samples 20 infiltration cycles were carried out.

Four different symmetrical structures with an electrode area of 0.5 cm$^2$ were prepared. Pt paste was applied on both sides of the YSZ substrate and sintered at 800 °C for 30 minutes (Pt800). Another sample was prepared by infiltrating the symmetrical Pt structure with LSM polymeric precursor (Pt800-LSM). For the third sample, porous YSZ layers (~10 µm thick) were deposited on both sides of the dense YSZ substrate by spin coating a YSZ ink and sintering at 1200 °C. Subsequently, Pt paste was applied on porous YSZ layers and sintered at 800 °C for 30 minutes. Polymeric LSM precursor was then infiltrated through the Pt layer into porous YSZ (Pt800-YSZ-LSM). The fourth sample was prepared similar to the third sample with a difference that infiltration of
polymeric LSM precursor was performed directly into the porous YSZ followed by deposition of the Pt current collecting layer (YSZ-LSM-Pt800).

A summary of sample preparation steps and sample codes are given in Table I. In order to confirm the accuracy of ohmic area specific resistance values, an additional sample was prepared by depositing Ag paste (ElectroScience; King of Prussia, PA) on both sides of dense YSZ substrate and sintered at 800 °C (Ag800).

RESULTS AND DISCUSSION

Analysis of symmetrical cells by impedance spectroscopy techniques is a common approach to investigate cathode/current collector structures of solid oxide fuel cells (SOFC) \(^{22-24}\). Use of symmetrical cells allows characterization of cathodes by impedance spectroscopy in a less complicated way as compared to complete fuel cell testing. DC current-voltage measurements were conducted to reveal that the composite structures can operate at high current densities. Four probe DC resistivity measurements of YSZ electrolytes were conducted for the interpretation of impedance spectra data. All electrical measurements were performed using a Solartron Analytical 1470 CellTest electrochemical interface. ZView software was used for fitting of the impedance spectra by the equivalent circuit model to obtain the corresponding parameters.

The fitting procedure is illustrated in Figure 1 for sample Pt800-YSZ-LSM which shows experimental data (open circles) as well as fitting results (solid curves) in the form of Cole-Cole curves (Figure 1a) and Bode plots (Figure 1b). Two area specific resistances, ASR1 and ASR2, were obtained from this fitting. ASR1 corresponds to the high frequency x-intercept in Figure 1a and summarizes all fast processes in the cell.
described as ohmic. ASR2 is related to the distance between the high and low frequency x-intercepts and describes the total polarization resistances of two cathode layers having a symmetrical structure, so that half of ASR2 corresponds to single cathode polarization resistance. This value will be referred to as the cathode polarization resistance hereafter.

The ohmic resistance (ASR1) consists of three components; electrode resistance, electrolyte resistance and current collection resistance. Four probe DC resistivity was measured using rectangular strips cut from YSZ substrates to analyze the electrolyte effect on ohmic resistance and to estimate current collection efficiency of the cathode and current collector. Figure 2 reveals a comparison of ASR1 values obtained from both four probe measurements of the electrolyte and the impedance spectra of Ag800 and Pt800-YSZ-LSM symmetrical structures. The data obtained from these three measurements are consistent with each other, i.e. current collection resistance is low (< 0.005 Ohm.cm²). Fitting with the Arrhenius function (solid line) gives an activation energy of 0.975 eV that is in good agreement with the values reported for YSZ with 8 mol% Yttria content.

Figure 3a shows the changes in ASR1, as a function of time. ASR1 of Pt800 was 0.27 Ohm.cm² initially and remained unchanged throughout the measurements for 80 hours. Introduction of LSM to the Pt layer by polymeric precursor infiltration (Pt800-LSM), reduced the initial ASR1 value to 0.25 Ohm.cm², and this value stabilized at 0.26 Ohm.cm². The sample prepared by infiltration of a porous YSZ/Pt double layer (Pt800-YSZ-LSM), had an initial ASR1 value of 0.25 Ohm.cm², and increased to 0.28 Ohm.cm² after 40 hours. No further changes of ASR1 were recorded in 140 hours of operation. YSZ-LSM-Pt800 revealed the highest initial ASR1 value at 0.28 Ohm.cm². In 40 hours,
this value increased to 0.32 Ohm.cm\(^2\) and remained unchanged after 80 hours of operation.

As shown in Figure 3b, the cathode polarization resistance of Pt800 was initially higher than 0.400 Ohm.cm\(^2\) and decreased to 0.165 Ohm.cm\(^2\) with time. Polymeric LSM precursor infiltration had a significant impact on the cathode polarization resistance and long time performance of Pt electrode (Pt800-LSM). Cathode polarization resistance of Pt800-LSM was 0.055 Ohm.cm\(^2\) initially. However, in contrast to Pt800, Pt800-LSM showed an increase in cathode polarization resistance with time. A. Babaei et. al also reported low polarization resistances in precious metal – LSM composite cathodes (0.018 Ohm.cm\(^2\))\(^{25}\). A significantly low cathode polarization resistance was obtained by infiltration of a porous YSZ-Pt bilayer with LSM polymeric precursor. Initial cathode polarization resistance for Pt800-YSZ-LSM was 0.022 Ohm.cm\(^2\) which then increased to 0.035 Ohm.cm\(^2\) and remained stable at this value. Infiltration of the porous YSZ layer first with LSM polymeric precursor followed by deposition of Pt layer (YSZ-LSM-Pt800) showed a similar long time behavior to Pt800-YSZ-LSM. Despite the similar long term behavior, the actual cathode polarization values of YSZ-LSM-Pt800 were twice as that of Pt800-YSZ-LSM.

Cole-Cole (Figure 4a) and Bode (Figure 4b) plots shows the performances of cells after they reached saturation. The samples containing porous YSZ layers revealed relatively smaller semicircles indicating high efficiency that is attributed to the increased triple phase boundary length where the electrochemically active and electronically conductive material (LSM) meet the ionic conductor (YSZ) and oxygen (air)\(^{26}\). Infiltration of polymeric LSM precursor into the Pt layer increases the efficiency to a
certain extent; however, the efficiency is limited by the ionic conductivity of LSM and the interfacial area between infiltrated LSM and the YSZ electrolyte. All samples showed a peak of the phase shift at frequencies around 1-5 kHz. This high frequency response is attributed to the transport of oxide ions or oxygen intermediates at phase boundaries \(^{23}\). The fact that the efficiency is enhanced when the interfacial contact area between YSZ and LSM is increased by introducing a porous YSZ layer confirms that the high frequency process is strongly dependent on the microstructural development \(^{23}\).

The temperature dependence of cathode polarization resistances for the two best performing cathodes (Pt800-YSZ-LSM and YSZ-LSM-Pt800) are shown in Figure 5a. The cathode polarization resistance of samples containing a porous YSZ interlayer followed an Arrhenius curve with activation energies of 1.35 eV and 1.31 eV for Pt800-YSZ-LSM and YSZ-LSM-Pt800, respectively. These values are within the range of reported activation energies for LSM-YSZ composites \(^{26}\). Previously, cathode polarization resistances of 0.5 Ohm.cm\(^2\) at 700 °C \(^{13}\) and 0.3 Ohm.cm\(^2\) at 800 °C \(^{27}\) were reported for LSM-YSZ composite cathodes prepared by infiltration. Thus, it can be suggested that the polymeric precursor infiltration has a significant advantage over other infiltration methods.

Figure 5b shows the current density-voltage characteristics of the samples. Samples without porous YSZ interlayers give hysteresis like curves indicating that these materials are not effective cathodes for fuel cells. On the other hand, samples with porous YSZ interlayers exhibit linear current-voltage characteristics with resistances close to ASR1+ASR2 values verifying that Pt800-YSZ-LSM and YSZ-LSM-Pt800 electrodes are promising cathodes for highly efficient solid oxide fuel cells.
The scanning electron microscopy image of the best performing sample, Pt800-YSZ-LSM, after measuring for 110 hours at 800 °C is given in Figure 6 to illustrate the general cathode/current collector structure and the microstructure of the LSM-YSZ composite. The thicknesses of the Pt-LSM current collecting layer and the YSZ-LSM layer are ~23 µm and ~10 µm, respectively. A well-developed connection between the current collecting Pt-LSM layer and the YSZ-LSM layer shown in Figure 6a is considered to have an effect on the aforementioned low current collection resistance (< 0.005 Ohm.cm²). A higher magnification image of the LSM-YSZ layer (Figure 6b) shows that the YSZ skeleton is composed of well-connected grains of average size 200 nm. The inserted image illustrates that the infiltration of the polymeric LSM precursor resulted in a nanostructured coating on the surface of YSZ grains, rather than isolated aggregates. The described microstructure is considered to have resulted in an increased length of triple phase boundaries yielding a significantly improved efficiency of the cathode/current collector structure.

CONCLUSIONS

Highly efficient cathode/current collector structures for SOFC applications were prepared by a polymeric precursor infiltration technique. An increase in the effective interface area between YSZ and LSM resulted in low polarization resistance ~ 0.030 Ohm.cm². Low current collection resistance (< 0.005 Ohm.cm²) and long term stability with nanostructured composite cathodes were achieved.
REFERENCES


### Table 1. Processing steps of the samples.

<table>
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<th>Pt800*</th>
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<td>YSZ substrate</td>
<td>YSZ substrate</td>
<td>YSZ substrate</td>
<td>YSZ substrate</td>
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<tr>
<td>Pt paste painted on both sides</td>
<td>Pt paste painted on both sides</td>
<td>Porous YSZ layer on both sides</td>
<td>Porous YSZ layer on both sides</td>
</tr>
<tr>
<td>Sintered at 800 °C</td>
<td>Sintered at 800 °C</td>
<td>Pt paste painted on both sides</td>
<td>Infiltrated with LSM polymer</td>
</tr>
<tr>
<td>-</td>
<td>Infiltrated with LSM polymer</td>
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<td>Infiltrated with LSM polymer</td>
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Figure 1. a) Cole-Cole b) Bode plots describing the equivalent circuit fitting procedure using the data obtained from the first measurements of Pt800-YSZ-LSM at 800 °C.
Figure 2. Temperature dependence of ASR1 obtained from four probe DC resistivity measurements of YSZ samples (squares) and impedance spectroscopy of Ag800 (triangles) and Pt800-YSZ-LSM (circles).
Figure 3. The change in a) area specific ohmic resistance b) cathode polarization resistance per electrode as a function of time at 800 °C.
Figure 4. a) Cole-Cole b) Bode plots measured after the ohmic and cathode polarization resistances stabilized at 800 °C. Symbols and lines represent the measured values the fittings according to the equivalent circuit respectively.
Figure 5. a) Temperature dependence of the cathode polarization resistance per electrode for the best performing samples, Pt800-YSZ-LSM and YSZ-LSM-Pt800 b) Current density-voltage characteristics of all samples measured at 800 °C.
Figure 6. a) Low magnification scanning electron micrograph of sample Pt800-YSZ-LSM showing the cathode/current collector structure b) High magnification scanning electron micrograph of sample Pt800-YSZ-LSM showing the microstructure of the YSZ-LSM composite layer.
II. Redox Stable Solid Oxide Fuel Cells with Ni-YSZ Cermet Anodes Prepared by Polymeric Precursor Infiltration

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Abstract

Redox stable SOFCs with Ni-YSZ cermet anodes were developed for electrolyte supported design (electrolyte thickness: 170µm). A redox stable Ni-YSZ anode was prepared by infiltrating polymeric NiO precursor into a pre-sintered porous YSZ layer (~10µm thick) followed by reduction, in situ. A polymeric precursor infiltration technique yielded a Ni-YSZ cermet microstructure with nanosized Ni particles coating the surface of porous YSZ. Low temperature processing of nanostructured Ni-YSZ cermets resulted in the reduction of internal stresses between the Ni/NiO coating and the YSZ skeleton during the redox cycling process. An electrolyte supported SOFC prepared with Ni-infiltrated anode had a power density of ~0.315 Watt.cm⁻² and a highly redox stable anode (reduction of power density less than 1% after 15 redox cycles) in humidified forming gas (10%H₂-90%Ar).
INTRODUCTION

Solid oxide fuel cells (SOFCs) are promising energy conversion devices due their high efficiency and fuel flexibility. Typical SOFCs use a Ni-YSZ cermet as the anode and a LSM-YSZ composite as cathode with YSZ (Yttria-Stabilized Zirconia) electrolyte. The Ni-YSZ cermet is an attractive anode material due to the fact that it provides low ohmic and polarization resistances at operational temperatures (600-1000 °C). Commonly, Ni-YSZ cermet is prepared by co-sintering a mixture of NiO and YSZ powders at high temperatures (1300-1450 °C), followed by in situ reduction in fuel (e.g. hydrogen) at 800 °C.

During long term operation, it is expected that the SOFC will go through several redox (reduction-oxidation) cycles due to intentional or erroneous interruption of the fuel supply. Therefore, it is of great importance that the Ni-YSZ cermet withstands several redox cycles in order for SOFCs to be viable for long term operation. However, the initial performance of the fuel cell is generally not recovered after redox cycling due to the mechanical failure of the Ni-YSZ cermet. The internal stresses caused by the expansion of Ni upon oxidation crack the YSZ in the cermet structure. This causes a severe degradation in performance and even destruction of the electrolyte in configurations with thin electrolytes.

One of the approaches to obtain redox stable anodes is replacing Ni with ceramic materials that are redox stable by nature and electronically conductive in reducing atmospheres. On the other hand, a significant effort has been focused on understanding the redox behavior of Ni/NiO and modification of the standard Ni-YSZ cermet. These modifications include the variation of Ni content and grain size, introduction of a
buffering interlayer, using 3 mol% YSZ for improved mechanical strength and addition of dopants to the structure\textsuperscript{4,5,12,13,14}.

Considering the fact that the degradation of Ni-YSZ cermets processed at temperatures above 1300 °C is caused by mechanical stresses associated with the Ni phase, lower temperature processing techniques, such as infiltration into a pre-sintered porous YSZ skeleton has been proposed\textsuperscript{15,16}. It was reported that the conductivity of the Ni-YSZ anode prepared by a polymeric precursor infiltration method remained nearly unchanged\textsuperscript{15}. However, redox stable SOFCs with Ni-YSZ cermets prepared by polymeric precursor infiltration have not been reported up to date.

The objective of this study is to achieve redox stable SOFCs with Ni-YSZ cermet anodes. SOFCs with Ni-YSZ cermets were fabricated by polymeric precursor infiltration technique and their microstructural development was characterized by scanning electron microscopy techniques. Influence of redox cycles on the impedance spectra, power and short circuit current density is reported.

**EXPERIMENTAL**

Dense YSZ substrates (170 μm thick, 8 mol% Y\textsubscript{2}O\textsubscript{3} content) from NexTech Materials; Columbus, OH were used to prepare electrolyte supported SOFCs. Composite LSM-YSZ and Ni-YSZ cermet were used as cathode and anode respectively. Pt paste was applied on anode and cathode sides as current collector. Ni-YSZ cermet anode was prepared in two stages. First, porous YSZ layer (~10μm) was formed on the anode side of the electrolyte by spin coating YSZ (Tosoh, Japan) slurry followed by sintering at 1150°C. Second, a polymeric NiO precursor solution was infiltrated into porous YSZ layer by spin coating at a rotation speed of 3000 rpm to form Ni-YSZ cermet. Repeated
infiltration and decomposition of polymeric precursor at 400 °C (20 cycles) was carried out to obtain adequate Ni loading in the cermet. The NiO polymeric precursor was prepared by mixing an aqueous solution of Ni(NO₃)₆H₂O (Alfa Aesar; Ward Hill, MA) with ethylene glycol (molar ratio of Ni/ethylene glycol: 0.4). The resultant solution was heated to 100 °C and stirred until water evaporated and Ni was incorporated into polymer complex. 2-butoxyethanol was added to equal amount of polymeric precursor (1:1 weight ratio) to promote wetting. The resultant Ni-YSZ cermet is estimated to contain 15vol% Ni in comparison to the bulk volume of the Ni-YSZ.

Electrochemical testing of the cell was conducted at 800°C using Solartron Analytical 1470 CellTest. Air and humidified forming gas (10%H₂-90%Ar) were supplied to the cathode and anode of the cell, respectively. AC impedance and current to voltage characteristics were measured to characterize the performance of the SOFC. Redox stability was investigated by cycling air and humidified forming gas at the anode side of SOFC and measuring current density in short circuit conditions.

RESULTS AND DISCUSSION

The microstructure of a SOFC sample after testing at 800°C for 26 hours followed by 15 redox cycles is shown in Figure 1a. No visible defects, such as cracks, were observed. Figure 1b shows the microstructure of the Ni-YSZ cermet anode at a higher magnification. A porous microstructure with well-connected YSZ grains (average grain size of ~200 nm) was obtained. Figure 1c reveals that the microstructure of the Ni-YSZ cermet prepared by infiltration was quite different from powder based cermets reported in the literature⁵. Instead of sintered, large Ni-grains obtained after heat treatment at
elevated temperatures (>1300 °C), nickel formed a uniform nanocrystalline coating on the surface of YSZ grains.

During redox cycles, measuring the current density in short circuit conditions is a useful way to evaluate redox stability of a fuel cell. In Figure 2, the influence of redox cycling on short circuit current density at 800 °C is depicted. Initially, under diluted hydrogen, the short circuit current density was around 0.8 A.cm\(^{-2}\). When the fuel flow was interrupted the current density dropped to negligible values immediately. When fuel flow was turned on again, the current density reached 1.5 A.cm\(^{-2}\) and did not change significantly after redox cycling. Some minor reversible fluctuations were observed when short circuit operation was interrupted for current density – voltage and/or impedance measurements in continuous fuel flow conditions. An example of the reversible fluctuations is given in the insert of Figure 2. During redox cycles, the potentiostatic measurement of short circuit current density at 800 °C revealed an initial peak in current density when the atmosphere is switched from air to fuel. Equilibrium current densities were reached at a relatively fast rate and remained stable within the time intervals. No significant degradation was observed over the time the measurements were conducted (26 hours).

Figure 3 shows current density – voltage characteristics of the fuel cell after redox cycles. Current density – voltage curve was linear in all measurements, except for a slight bending in the initial measurement which disappeared after 5 redox cycles. The slopes of the current density – voltage curves were close to each other. The initial power density was 0.313 Watt. cm\(^{-2}\) which remained at 0.311 Watt. cm\(^{-2}\) after 15 redox cycles. These
power density values are comparable to that reported in the literature. Power density of ~0.2 Watt.cm$^{-2}$ at 800 °C was obtained for an electrolyte supported fuel cell with an electrolyte thickness of 350 µm$^{17}$.

Figure 4 shows the impedance spectra of the fuel cell measured before and after several redox cycles. The total cell resistance consisted of three parts: i) Ohmic part related with the electrolyte resistance and current collection from the electrodes ii) anode polarization resistance iii) cathode polarization resistance. The Cole-Cole plot consisted of one semicircle associated with the sum of anode and cathode polarization resistances. The lower x-intercept of the plot corresponded to the ohmic resistance while the distance between the lower and the higher x-intercept corresponded to the sum of anode and cathode polarization resistances. Initially, total cell resistance of the fuel cell was 0.63 Ohm.cm$^2$. It is evident that in 15 oxidation cycles the total cell resistance remained nearly unchanged. The insert graph in figure 4 shows the change in frequency at maximum phase shift angle with redox cycles. A significant shift towards high frequency was observed when the cell was subjected to redox cycles. After 10 redox cycles, this shift stopped and the frequency remained at ~ 10kHz. Low temperature incorporation of Ni into the porous YSZ skeleton resulted in a structure where Ni is mobile and upon oxidation-reduction, Ni was allowed to expand and shrink without forming cracks in the porous YSZ matrix. During redox cycles, Ni particles were redistributed on the porous YSZ that might have affected the shape of the impedance arc and shifted the frequency until equilibrium was reached.

Influence of redox cycling on the total fuel cell resistance, measured by impedance spectroscopy and calculated from the slope of the J-V plot, are shown in
figure 5 along with the polarization resistance and power density of the fuel cell. Previously, it was reported that the polarization resistance of a fuel cell with a Ni-YSZ cermet anode increased from 0.18 Ohm.cm$^2$ to 0.40 Ohm.cm$^2$ after 8 redox cycles at 850 °C $^{13}$. In another study, a typical electrolyte supported fuel cell with a Ni-YSZ cermet anode showed an 18% increase in the polarization resistance of the cell after the third cycle at 950 °C $^{18}$. In the present study, the polarization resistance extracted from the impedance spectra was ~0.2 Ohm.cm$^2$ and remained unchanged after 15 redox cycles. The fact that the polarization resistance was ~ 30% of the total fuel cell resistance suggests that the performance of the fuel cell can be improved significantly by reducing the electrolyte thickness. Further experiments are underway to optimize the polymeric precursor infiltration technique for higher performance as well as to characterize the redox stability in more detail over a broader range of redox cycles.

CONCLUSIONS

Preparation and performance of a redox stable solid oxide fuel cell with Ni-YSZ cermet anodes were presented. Ni-YSZ cermets were fabricated by polymer precursor infiltration of Ni into a porous YSZ skeleton. The lower temperature processing method allowed for formation of a nanostructured coating of Ni particles on the porous YSZ. Mechanical stresses caused during oxidation and reduction of Ni were reduced so that anodes remained free of cracks and stable during redox cycling. Low polarization resistance (~0.2 Ohm.cm$^2$) and acceptable power densities (~310 Watt.cm$^2$) were obtained for electrolyte supported SOFCs. No significant changes in the power density or the polarization resistance were recorded after 15 redox cycles.
REFERENCES


**Figure 1.** Scanning electron micrographs of the fuel cells after 15 redox cycles at 800 °C.

a) Low magnification image showing the general structure of the fuel cell  
b) Higher magnification image showing the general microstructure of the anode  
c) High magnification image showing the Ni coating on YSZ grains
Figure 2. Influence of redox cycles on the current density at short circuit conditions at 800 °C. The insert graph shows the change in short circuit current density in time between 7th and 10th redox cycles at 800 °C.
Figure 3. Influence of redox cycles on current density –voltage curve and the associated power density at 800 °C.
Figure 4. Influence of redox cycles on the impedance spectra under 0.5 V at 800 °C. a) Cole-Cole b) Bode plots.
Figure 5. Summary of the influence of redox cycles on the area specific resistance of the cell obtained from the current density-voltage curve (up triangles), area specific resistance of the cell obtained from the impedance spectra (down triangles), polarization resistance of the cell (filled circles) and the power density (hollow circles).
III. Optimization of Redox Stable Ni-YSZ Anodes for SOFCs by Two-Step Infiltration

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Abstract

Infiltration of a polymeric nickel oxide precursor into a sintered porous ytrria – stabilized zirconia (YSZ) skeleton is a promising approach to achieve redox stable solid oxide fuel cells. In order to ensure that the porous YSZ skeleton was mechanically strong enough to withstand the stresses caused by the volumetric expansion of the Ni phase upon oxidation, even at relatively high loadings, a polymeric YSZ precursor was infiltrated into the porous YSZ skeleton, prior to NiO infiltration. It was shown that infiltration of YSZ precursor strengthened the porous YSZ skeleton without compromising the porosity or initial YSZ particle size significantly. The amount of infiltrated YSZ and the subsequent heat treatment temperature were determined to be important processing parameters in achieving redox stable Ni-YSZ anodes. An electrolyte supported SOFC (electrolyte thickness ~ 180 µm) with a redox stable anode, prepared by YSZ and NiO infiltrations, showed a power density of ~0.41 Watt/cm² at 800 °C. Further, the power density did not change significantly after 20 redox cycles in 10%H₂ – 90% Ar fuel. Impedance spectroscopy measurements at 800 °C showed significantly low electrode polarization resistances (anode + cathode ~0.07 Ohm.cm² at 800 °C) which remained stable upon redox cycling.
INTRODUCTION

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert chemical energy to electrical energy with high efficiency. A relatively high operation temperature (600-1000 °C) makes the SOFCs suitable for operation using a variety of fuels (i.e. hydrogen, hydrocarbons). Conventional SOFCs use Ni as the anode material due to its high catalytic activity for fuel oxidation and high electronic conductivity. It is most frequently used in the form of a composite with yttria stabilized zirconia (YSZ) in order to increase the Ni-YSZ contact area for higher anode efficiency and to obtain a good connection with the electrolyte. These composites are generally fabricated by mixing YSZ and NiO powders and co-sintering at elevated temperatures (1300 – 1450 °C) followed by in situ reduction \(^1,^2\). Relatively high power densities were achieved in SOFCs fabricated by this route (>1 Watt/cm\(^2\) at 800 °C) \(^3-^5\).

A viable SOFC is expected to be able to operate for >40,000 hours \(^6\). It is quite likely that during this time of operation there will be interruptions in fuel flow and consequently go through reduction – oxidation (redox) cycles. However, Ni-YSZ cerments cannot withstand redox cycling, mainly due to the large dimensional changes that occur in the Ni phase upon oxidation and the consequent cracks in the YSZ phase \(^7-^10\). Two main approaches have been taken in order to overcome this problem. The first approach involved the replacement of Ni with electronically conductive ceramics which do not undergo significant dimensional change when the atmosphere is switched from reducing to oxidizing \(^11-^14\). However, despite the significant progress, ceramic based anodes have not reached the efficiencies of Ni based anodes. The second approach to achieve redox stable anodes was through microstructural optimization of the Ni-YSZ composites. It has
been reported that the strength of the zirconia phase, the amount of Ni, Ni particle size and porosity were important parameters that affected the redox tolerance of the Ni-YSZ composites\textsuperscript{15, 16}. Although important understanding of the redox behavior of Ni-YSZ cerments was developed, redox stability in conventional Ni-YSZ cerments have not been reported to date.

Infiltration of the catalytically active phase into a porous YSZ skeleton has been reported as a prospective way to fabricate SOFC electrodes with high surface areas\textsuperscript{17-19}. This technique has been suggested as a promising route to fabricate redox stable Ni-YSZ anodes\textsuperscript{20-22}. In this paper, redox stable SOFCs with Ni-YSZ anodes prepared by polymeric precursor infiltration were reported. Additional treatments involving infiltration processes to obtain redox stable anodes exhibiting high electrode efficiencies are described.

**BACKGROUND AND APPROACH**

Relatively high sintering temperatures (1300 – 1450 °C), used for fabrication of conventional Ni-YSZ anodes, result in strongly connected Ni and YSZ networks with comparable Ni and YSZ grain sizes (0.5 µm - 2 µm) after reduction\textsuperscript{5, 16}. Although respectable power densities have been achieved with this type of conventional anode\textsuperscript{3-5}, they are vulnerable to redox cycling. When the fuel flow is interrupted during the operation of the fuel cell, the conditions become highly oxidizing and Ni readily oxidizes into NiO which is accompanied by a ~69 % increase in volume\textsuperscript{10}. The stresses caused by this expansion create cracks in the YSZ network which disrupts the collection of oxygen ions from the electrolyte, resulting in severe degradation of the anode performance (Figure 1a)\textsuperscript{7, 23}. In anode supported designs, complete destruction of the fuel
cell is observed. The scanning electron microscopy image provided next to the schematic (Figure 1a) shows the microstructure of a standard Ni-YSZ cermet prepared by conventional routes after 5 redox cycles at 800 °C, as an example. The cracks in the microstructure are circled.

Several studies focused on altering the microstructure of the Ni-YSZ cermets to endure the volumetric changes in the Ni phase without causing any damage to the YSZ backbone. It was reported that a Ni phase consisting of coarser particles resulted in smaller changes in the dimensions upon redox cycling, but the use of coarser particles would result in a decreased triple phase boundary length. In another study, increased porosity in the microstructure was shown to improve redox tolerance due to increased space to accommodate the expansion of Ni upon oxidation. Improving the mechanical properties of the YSZ network by replacing 8 mol% Y₂O₃ doped ZrO₂ with 3 mol% Y₂O₃ doped ZrO₂ was also reported to result in Ni-YSZ cermets with higher redox tolerance. The Ni content was reported to be another important parameter in the redox behavior of the Ni-YSZ cermet. Cermets with lower contents were shown to be more redox tolerant.

Another approach to the redox instability problem was introducing the Ni phase into a previously sintered porous YSZ skeleton by a lower temperature infiltration route. In this manner, it was aimed that a much weaker Ni phase is obtained due to the low temperature processing and that sufficient electrical conductivity is achieved with much lower Ni content. In addition, the possibility to obtain composites where Ni is in the form of a thin coating on the YSZ grains, rather than a random mixture of particles, can be considered as a prospective advantage for fabricating Ni-YSZ cermet less susceptible to
redox cycling (Figure 1b). The SEM image of this composite structure looks quite similar to the microstructure of the YSZ skeleton used, which suggests that the Ni phase forms a continuous thin coating on the YSZ surface instead of as discrete particles. Energy dispersive x-ray spectroscopy (EDX) mapping allowed the identification of the distribution of the Ni phase within the cermet (below the SEM image). Evidently, the Ni phase was distributed uniformly throughout the microstructure, rather than as separated particles (signals from Ni are depicted in green color). It was first demonstrated that the electrical conductivity of Ni-YSZ cermets prepared by this route did not change upon redox cycling \(^{20}\). Another study reported that these cermets showed no change in dimensions when oxidized \(^{21}\). Certainly, the changes in the electrical conductivity upon redox cycling provide valuable information on the redox stability of the samples. However, along with the electrical conductivity, the actual anode performance of the Ni-YSZ cermet depends on several other parameters such as the quality and the effective area of contact between the Ni and YSZ phases, Ni particle size, porosity, the connection between the anode and the electrolyte layers \(^{2}\). Therefore, in order to make a sound assessment of the redox stability of the Ni-YSZ cermets prepared by infiltration routes, it is necessary to evaluate the changes in the SOFC performance upon redox cycling.

Redox stable SOFCs with Ni-YSZ cermet anodes prepared by infiltration were reported in an earlier publication \(^{22}\). It was shown that no change in power density was observed after 15 redox cycles. Although a decent power density for an electrolyte supported SOFC was achieved (~0.31 Watt/cm\(^2\)), a detailed analysis of the impedance spectra showed that the ohmic contribution was significantly higher than what was expected for the given electrolyte thickness (0.4 Ohm.cm\(^2\) obtained while the expected
value was 0.28 Ohm.cm² for a ~180 µm thick electrolyte). It is possible that the infiltrated Ni content in the anode (estimated NiO/YSZ ratio ~ 30 vol%) was not sufficient to provide the required electrical conductivity and that the power density could be enhanced significantly at the given electrolyte thickness. In another study, it was demonstrated that increased Ni content (estimated NiO/YSZ ratio ~ 40 vol%) in infiltrated Ni-YSZ cermet anodes resulted in significantly reduced ohmic and electrode polarization resistances with long term stability. However the redox stability of the cell with increased Ni loading was not investigated.

The key question that needs to be addressed is whether it is possible to achieve high electrode efficiencies in Ni-YSZ anodes while maintaining redox stability. In order for the cermet to be redox stable, the aforementioned properties of the infiltrated structures should be retained (mechanically stronger YSZ skeleton – weaker Ni phase, lower Ni content when compared to conventional cermets and the coating type structure). On the other hand, the infiltrated Ni amount should be kept higher than a certain level (NiO/YSZ ~ 40%) to ensure good coverage and sufficient conductivity. Although redox stability was observed with Ni-YSZ cermets having NiO/YSZ of ~ 30 vol%, it is possible that increased Ni content would cause an increase in the stresses exerted on the YSZ skeleton and create cracks. Therefore, in order to achieve redox stable Ni-YSZ cermets with relatively high Ni content, porous YSZ skeletons should be reinforced. Since partial sintering of YSZ powders at relatively low temperatures (1150 °C) was used to obtain the porous YSZ skeleton (~50% porosity) in the previous work, increasing the sintering temperature seems to be the straight forward way to obtain a stronger YSZ skeleton. Nevertheless, higher sintering temperatures would result in a
significant loss in the amount and the interconnectivity of porosity which would hinder effective infiltration of the Ni phase. Although it is possible to use pyrolyzable pore formers to generate large pores \(^{30, 31}\), the grain growth and the accompanying surface area loss associated with the high temperature sintering of the YSZ skeleton would result in a lower anode performance. Therefore, it is suggested that the porous YSZ skeleton is reinforced without increasing the sintering temperature and causing a dramatic change in the porous YSZ skeleton microstructure. In a previous publication, it was reported that polymeric YSZ precursor infiltration into a layer consisting of unsintered YSZ powders provided a strong connection between the YSZ particles, which was evidenced by significantly high electrical conductivity of the obtained layer \(^{32}\). Therefore, in order to reinforce the porous YSZ skeleton without sacrificing significantly porosity or surface area, infiltration of a YSZ precursor prior to Ni infiltration is proposed. It is reasonable to assume that most cracking originates from the weak contact areas (necks between the particles) in the porous YSZ due to lower temperature sintering. Another source of crack formation may be attributed to constrained sintering between the porous YSZ layer and the dense electrolyte (Figure 2a). Polymeric YSZ precursor infiltration would potentially cover the defected or weak points and reinforce the structure after heat treatment (Figure 2b). The amount of YSZ infiltration should be well controlled in order to avoid clogging of the pores and closing up porosity, which was the case in the previously reported study \(^{32}\). SEM images in Figure 2c-e shows the effect of YSZ infiltration into the porous YSZ skeleton. Porous YSZ skeletons obtained by sintering YSZ powder at 1150 °C for 2 hours is shown in Figure 2c. The size of grains and pores are comparable and in the range of ~200 nm. Figure 2d shows the porous YSZ skeleton after 30 cycles of YSZ infiltration
while Figure 2e reveals the microstructure after YSZ infiltration followed by heat treatment at 1000 °C for 45 minutes. Although a change in the surface morphology of the grains is observed, the grain and pore sizes remain nearly unchanged which is in agreement with the suggested microstructural development (Figure 2e).

The microstructures of two samples with increased Ni content (NiO/YSZ ~ 40%) after redox cycling at 800 °C are given in Figure 3. Figure 3a shows the sample without prior YSZ infiltration while Figure 3b shows the sample with prior YSZ infiltration. It is evident that both structures consisted of ~200 nm size particles and pores, similar to the porous YSZ structure. The fact that no obvious difference between the two microstructures were observed suggests that the Ni phase is uniformly distributed and that prior YSZ infiltration does not markedly influence the microstructure of the infiltrated Ni phase drastically.

**EXPERIMENTAL**

Preparation of NiO and La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) polymeric precursors were described in detail in previous studies $^{22, 28, 29}$. For the preparation of each precursor; nitrate salts of the desired composition were dissolved in water and ethylene glycol was added as a chelating agent. The resultant mixture was stirred on a hot plate at 100 °C until water was evaporated. The resultant solutions were diluted with 2-butoxyethanol for better wetting properties. For YSZ polymeric precursor preparation, yttrium nitrate hexahydrate and zirconium oxychloride (Alfa Aesar; Ward Hill, MA) were used as starting materials.
In order to assess the redox stability of Ni-YSZ cermets, a set of samples were prepared for electrical conductivity measurements. It was aimed that redox stable Ni-YSZ cermets with the highest possible Ni loading would be achieved. Dense YSZ substrates (500 µm thick, 8 mol% Y₂O₃ content) from NexTech Materials; Columbus, OH were used as substrates. Porous YSZ layers (~15 µm) were formed on the substrate by spin coating of a YSZ (Tosoh TZ-8Y, Japan) slurry followed by sintering at 1150°C for 2 hours to achieve 50% porosity. Infiltration cycles were carried out by using spin – on deposition at 3000 rpm followed by decomposition at 450 °C. Utilization of the spin – on deposition technique allowed uniformity and good control of the amount of infiltrated components. In order to obtain the maximum possible Ni loading, the porous YSZ layer was infiltrated with polymeric NiO precursor for 35 cycles (YSZ(1150)-35Ni). This resulted in a significant increase in the Ni loading (NiO/YSZ ~ 40 vol%) as compared to the previous work with a lower Ni loading (NiO/YSZ ~ 30 vol%) ²². Other samples were prepared by introducing an additional YSZ infiltration step prior to Ni infiltration. The YSZ infiltration amount, and the subsequent heat treatment temperature, were changed to obtain redox stable Ni-YSZ cermets. Sample preparation steps and the sample codes are given in Table I. As a general observation, increased prior YSZ infiltration did not significantly change the amount of Ni that can be infiltrated (less than ~2 %).

For solid oxide fuel cell preparation, dense YSZ substrates (170 µm thick, 8 mol% Y₂O₃ content; NexTech Materials; Columbus, OH) were used as the electrolyte. Porous YSZ layers (~15 µm) were deposited on both sides of the electrolyte as described above. Infiltration of polymeric YSZ precursor from the anode side was carried out for 15 cycles and heat treated at 1000 °C for 45 minutes. Then polymeric NiO precursor
solution was infiltrated to form the final Ni-YSZ cermet anode structure. Infiltration – decomposition cycles were carried out for 35 cycles to obtain adequate Ni loading. The cathode was prepared in a similar way. First, Pt paste was deposited on the porous YSZ layer and heat treated at 800°C. Polymeric LSM precursor was infiltrated through the Pt layer into porous YSZ. 20 cycles of infiltration/decomposition were carried out to obtain a sufficiently high LSM content (~20 vol%). Pt paste was also applied also on the anode side as a current collector.

The redox stability of the cermets were assessed by monitoring the changes in the two probe DC conductivity of the samples upon changing the gas flow between humidified diluted hydrogen (10% H₂-90% Ar) and air at 600 °C, 700 °C and 800 °C. For SOFC measurements; air and humidified diluted hydrogen (10%H₂–90%Ar) were supplied to the cathode and anode of the cell, respectively. The electrochemical performance of the cell was tested by impedance spectroscopy and current density – voltage measurements (Solartron Analytical 1470 CellTest). The cell was kept under short circuit conditions at 800 °C and the effect of redox cycles on the electrochemical performance was monitored. The impedance spectroscopy measurements were performed at 0.5 V. Microstructural characterization of the porous YSZ skeleton before and after YSZ infiltration was carried out by scanning electron microscopy (Hitachi S-4700) techniques.

RESULTS AND DISCUSSION

In order to obtain high performance from the infiltrated redox stable Ni-YSZ anodes, it was aimed that the Ni amount in the cermet is increased from a NiO/YSZ ratio
of ~ 30% to a NiO/YSZ ratio of ~ 40%. Useful information about the redox stability of the cermet can be obtained by measuring the changes in the electrical conductivity upon redox cycling. Figure 4 shows the changes in the electrical conductivity of the sample upon changing the gas flow from fuel (10% H₂-90% Ar) to air at 600 °C and 700 °C for the sample prepared by the infiltration of polymeric NiO precursors (YSZ(1150)-35 Ni). The higher conductivity values indicate the electrical conductivities under fuel flow while the lower values indicate the electrical conductivities when the sample is oxidized. The two data points at each interval indicate the first and the last values obtained before the fuel flow is changed. Initial electrical conductivity was 700 S/cm at 600 °C which increased to 1000 S/cm after the first redox cycle. The conductivity then dropped to 590 S/cm after 16 redox cycles at 600 °C. The measurements of the same sample were resumed at 700 °C to determine the effect of temperature. The electrical conductivity decreased from 550 S/cm to 75 S/cm after 16 redox cycles at 700 °C. It is evident that the electrical conductivity remained relatively stable at 600 °C while a consistent degradation trend upon redox cycling at 700 °C was observed. The decrease in the electrical conductivity is related with the cracks generated in the YSZ skeleton upon the oxidation of Ni where the Ni phase could penetrate when reduced and eventually disconnect. Faster oxidation kinetics of Ni at 700 °C is considered as the origin of less tolerance towards redox cycling.

Figure 5 shows the change in the electrical conductivity of the samples prepared by YSZ infiltration prior to Ni infiltration. The samples that were heat treated at 900 °C for 45 minutes after YSZ infiltration are given in Figure 5a and 5b. The sample with 10 cycles of YSZ infiltration (YSZ(1150) – 10YSZ(900)-35Ni) was relatively stable upon
redox cycling at 600 °C at ~450 S/cm. When the operation temperature was raised to 700 °C, a significant decrease in the electrical conductivity upon redox cycling was observed (decrease from 400 S/cm to 80 S/cm after 12 redox cycles) as shown in Figure 5a. Figure 5b depicts the changes in the electrical conductivity of the sample with an increased amount of infiltrated YSZ (YSZ(1150)-20YSZ(900)-35Ni) upon redox cycling. The sample was relatively stable at 600 °C at ~450 S/cm and the electrical conductivity dropped from 400 S/cm to 250 S/cm after 15 redox cycles at 700 °C. Evidently, the increase in the infiltrated YSZ amount improved the redox stability of the cermet significantly. It was also observed that YSZ infiltration prior to Ni infiltration resulted in some decrease in the electrical conductivity of the cermet (when compared to the sample without prior YSZ infiltration (YSZ(1150)-35 Ni). It is suggested that although pore and grain sizes were kept at the same level, some connectivity between the pores was compromised. Although infiltrated Ni amount did not change significantly, the connectivity of the Ni phase was, to some extent, compromised.

In order to determine the effect of heat treatment temperature after polymeric YSZ precursor infiltration on the redox stability of the cermets, the porous YSZ skeleton was infiltrated with polymeric YSZ precursor for 20 and 30 cycles and heat treated at 1000 °C for 45 minutes prior to Ni infiltration (YSZ(1150)-20YSZ(1000)-35Ni and YSZ(1150)-30YSZ(1000)-35Ni. Both samples were stable after 32 redox cycles at 600 °C and 700 °C. YSZ(1150)-20YSZ(1000)-35Ni remained in the 600 S/cm and 500 S/cm range at the operational temperatures of 600 °C and 700 °C, respectively (Figure 5c). The sample with increased amount of infiltrated YSZ (YSZ(1150)-30YSZ(1000)-35Ni) was stable at 400 S/cm for 16 redox cycles at 600 °C and further redox cycling at
700 °C did not show a significant decrease from the initial conductivity at this temperature (350 S/cm) (Figure 5d).

The electrical conductivity measurements at 600°C and 700 °C provided valuable information about the important parameters of the infiltration process to obtain redox stable cerments. However, especially for electrolyte supported SOFC configurations, these temperatures are not sufficient to obtain low resistances. Hence, electrical conductivity measurements of the selected samples were carried out at 800 °C. Figure 6 provides a comparison of changes of electrical conductivities of samples YSZ(1150)-35Ni, YSZ(1150)-20YSZ(1000)-35Ni and YSZ(1150)-30YSZ(1000)-35Ni after redox cycling at 800 °C. An initial conductivity of 600 S/cm dropped to 60 S/cm after 15 redox cycles for the sample with only Ni infiltration (YSZ(1150)-35Ni). This sample showed a continuing trend of degradation. On the other hand, YSZ(1150)-20YSZ(1000)-35Ni had an initial electrical conductivity of 300 S/cm which dropped to the level of 200 S/cm after 10 redox cycles and was stable at this value for the next five redox cycles. The sample with higher amount of infiltrated YSZ showed an initial conductivity of 120 S/cm which increased to 250 S/cm after first redox cycle. The conductivity dropped to the 200 S/cm range after five redox cycles and remained at this level after 15 redox cycles. Evidently, YSZ infiltration reinforces the YSZ skeleton and improves the redox stability of the Ni-YSZ cerments prepared by polymeric precursor infiltration. Another study reported that Ni-YSZ cerments became more tolerant to redox cycling when Al₂O₃ powders were added to the starting powder mixture or when 3 mol% Y₂O₃ doped ZrO₂ was used instead of 8 mol% Y₂O₃ doped ZrO₂.² The improvement was interpreted as a result of improved mechanical strength of the ceramic phase, which is in good agreement with the results.
obtained in the present work. YSZ infiltration serves as a pre-treatment to reinforce the porous YSZ matrix in this study.

SOFCs were prepared to assess the changes in the anode performance upon redox cycling of the Ni-YSZ anodes prepared by YSZ and Ni infiltration. A LSM-YSZ composite cathode prepared by LSM polymeric precursor infiltration was used as the cathode. An impedance spectroscopy measurement of the fuel cell was carried out at 800 °C under 0.5 V (Figure 7a). The higher frequency intercept corresponds to the ohmic contribution to the cell resistance which is dominated by the electrolyte resistance and current collection resistance while the interval between the higher and the lower frequency intercepts corresponds to the total electrode polarization resistances (anode + cathode). Initially, the ohmic resistance of the cell was 0.32 Ohm.cm² which is significantly lower than what was achieved previously in cells with less Ni content (~0.4 Ohm.cm²) 22. The improvement in the cell performance with increased Ni content was also apparent in the polarization resistance values. The polarization resistance of the cell was ~0.12 Ohm.cm² while the cell with the lower Ni content reported earlier showed a polarization resistance of ~0.2 Ohm.cm² 22. In another paper, it was reported that LSM-YSZ cathodes prepared by polymeric precursor infiltration showed cathode polarization resistances of ~ 0.030 Ohm.cm² at 800 °C and was stable for >100 hours 28. When it is taken into account that the same cathode configuration was used in the fabrication of the fuel cell, it can be roughly estimated that the anode polarization resistance is ~0.090 Ohm.cm². Although there were some variations, the total cell resistance decreased to below 0.40 Ohm.cm² and remained unchanged after 20 redox cycles. The drop in the total cell resistance was mainly due to the decrease in the total electrode polarization
resistance which remained under 0.1 Ohm.cm\(^2\) and showed no degradation after 20 redox cycles. This drop in the electrode polarization resistances may be attributed to microstructural changes in the Ni phase of low temperature processed cells upon re-reduction. Figure 7b shows the current density – voltage characteristics of the cell at 800 °C. The current density – voltage curves were linear and the initial power density remained stable above 0.4 Watt.cm\(^2\) after 20 redox cycles which is a significant improvement from the value reported for the lower Ni content anode with the same electrolyte thickness in the earlier study (0.31 Watt.cm\(^2\))\(^{22}\). Since the technological aim for a fuel cell was reported to be 5-20 redox cycles per year during the lifetime of a viable fuel cell \(^{15, 33}\), the redox stability reported in this work can be considered as a realistic assessment.

Figure 8 summarizes the influence of redox cycling on several important parameters of the fuel cell. Significantly low electrode polarization resistances remained stable after redox cycling. It is evident that the total fuel cell resistance is dominated by the ohmic resistance which could be further decreased by reducing the electrolyte thickness. Figure 9 shows a comparison of the impedance spectra of the redox stable fuel cell with lower Ni content \(^{22}\) and the redox stable fuel cell with increased Ni content which was reinforced by prior YSZ infiltration. The impedance spectra for both cells correspond to the values obtained after redox cycling. Increased Ni content resulted in a decrease in the ohmic resistance from 0.4 Ohm.cm\(^2\) to 0.33 Ohm.cm\(^2\) and from 0.2 Ohm.cm\(^2\) to ~ 0.07 Ohm.cm\(^2\) in the total electrode polarization resistance at 800 °C.
SUMMARY

Redox stable Ni-YSZ cermet anodes by low temperature infiltration methods were reported in a previous study. Redox stability of the cell was attributed to Ni phase that is mechanically weaker than the porous skeleton and the amount of infiltrated Ni was much lower than what is required for conventional Ni-YSZ cermets (NiO/YSZ ratio ~ 30%). In order to increase the anode performance, the Ni content should be increased. However, it was shown that the redox stability was not retained when the Ni content was maximized. In the present study, YSZ infiltration prior to Ni infiltration was suggested as a route to obtain a mechanically stronger porous YSZ skeleton without a significant loss in the surface area and porosity. Electrical conductivity measurements revealed that the amount of prior YSZ infiltration and the subsequent heat treatment temperature are important parameters to achieve redox stable cermets. Reinforcement of the porous YSZ skeleton by YSZ infiltration allowed processing of redox stable SOFCs with increased Ni content (NiO/YSZ ratio ~ 40%) which showed a significantly improved performance. The ohmic resistance decreased from 0.4 Ohm.cm$^2$ to 0.33 Ohm.cm$^2$ while the electrode polarization resistance decreased from 0.2 Ohm.cm$^2$ to ~ 0.07 Ohm.cm$^2$ at 800 °C. The fuel cell showed a power density over 0.4 Watt/cm$^2$ that remained stable after 20 redox cycles.

ACKNOWLEDGEMENTS

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REFERENCES


Table 1. Summary of preparation steps for each sample.

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<th>Sample</th>
<th>YSZ(1150)-35Ni</th>
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<th>YSZ(1150)-20YSZ(900)-35Ni</th>
<th>YSZ(1150)-20YSZ(1000)-35Ni</th>
<th>YSZ(1150)-20YSZ(1000)-35Ni</th>
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<td>YSZ infiltration (20 cycles)</td>
<td>YSZ infiltration (20 cycles)</td>
<td>YSZ infiltration (30 cycles)</td>
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<tr>
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Figure 1. a) Schematic representation of the changes occurring in conventional Ni-YSZ cermets prepared by high temperature co-sintering and a scanning electron microscopy image showing the actual microstructure of such a cermet after redox cycling b) Schematic representation of the changes occurring in a Ni-YSZ structure obtained by polymeric precursor infiltration, and scanning electron microscopy images showing the general microstructure of such a cermet (upper) and the energy dispersive X-ray spectroscopy mapping showing the distribution of the Ni phase (lower).
Figure 2. Schematic representation of the YSZ skeleton showing that; a) the grain boundaries (due to relatively low temperature sintering) and the contact points between the porous YSZ layer and the electrolyte (due to constrained sintering) are the possible weak points in the porous YSZ skeleton b) polymeric YSZ precursor infiltration could cover these areas and reinforce the skeleton after heat treatment. Scanning electron microscopy images of c) initial porous YSZ obtained by sintering at 1150 °C d) after 30 cycles of polymeric YSZ precursor infiltration e) after 30 cycles of polymeric YSZ precursor infiltration followed by sintering at 1000 °C for 45 minutes
Figure 3. Scanning electron microscopy images showing the microstructures of Ni-YSZ cermets without YSZ(1150)-35Ni and with (YSZ(1150)-30YSZ(1000)-35Ni) prior YSZ infiltration.
Figure 4. The changes in the electrical conductivity of the sample prepared by Ni infiltration into pre-sintered YSZ (YSZ(1150)-35Ni) upon redox cycling at 600 °C and 700 °C.
Figure 5. The changes in the electrical conductivity of the samples with different YSZ infiltration amounts and heat treatment temperatures; a) YSZ(1150)-10YSZ(900)-35Ni b) YSZ(1150)-20YSZ(900)-35Ni c) YSZ(1150)-20YSZ(1000)-35Ni d) YSZ(1150)-30YSZ(1000)-35Ni upon redox cycling at 600 °C and 700 °C.
Figure 6. The changes in the electrical conductivity of the samples YSZ(1150)-35Ni, YSZ(1150)-20YSZ(1000)-35Ni and YSZ(1150)-30YSZ(1000)-35Ni upon redox cycling at 800 °C.
Figure 7. Influence of redox cycles; a) on the impedance spectra of the fuel cell under 0.5 V at 800 °C b) on current density –voltage curve and the associated power density at 800 °C.
Figure 8. Summary of the influence of redox cycles on the area specific ohmic resistance of the cell obtained from the impedance spectra (up triangles), electrode polarization resistance of the cell (down triangles) and the power density (hollow circles).
Figure 9. Comparison of the impedance spectra of the fuel cells at 800 °C under 0.5 V with NiO/YSZ ratio ~ 30% after 15 redox cycles and NiO/YSZ ratio ~ 40% after 20 redox cycles.
IV. Stability and Performance of Solid Oxide Fuel Cells with Nanocomposite Electrodes

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Abstract

The long term performance of a SOFC with a nanocomposite Ni-YSZ anode and a LSM-YSZ cathode was reported. The SOFC was prepared by infiltrating polymeric precursors of NiO and LSM from the anode and cathode sides respectively. The fuel cell showed a relatively high initial performance (0.49 Watt/cm² at 800 °C) for the given electrolyte thickness (~170 µm). Long term stability tests showed that the power density dropped to 0.41 Watt/cm² in the first 60 hours of operation in short circuit conditions and no further change in the power density was observed after that. A low electrode polarization resistance was obtained (~ 0.080 Ohm.cm²) for the combined anode and cathode at 800 °C, and there was no significant change with time. The slight drop in power density was related to the change in ohmic resistance which was attributed to the increase in current collection resistance. The fact that the majority of the resistance was due to the electrolyte resistance (~80%) suggests that stable SOFCs with high power densities could be achieved with thinner electrolytes. After >100 hours of operation at 800 °C, in short circuit conditions, the fuel cell was measured at higher temperatures.
Power densities were 0.71 Watt/cm$^2$ and 1.0 Watt/cm$^2$ at 900 °C and 1000 °C, respectively.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are promising energy conversion devices owing to their high efficiency and fuel flexibility. Conventional SOFCs consist of a Ni-YSZ cermet anode, YSZ electrolyte and LSM-YSZ composite cathode. The most widely used electrode fabrication technique is mixing the constituent powders followed by consolidation and sintering at relatively high temperatures (1300-1400 °C for Ni-YSZ cermet anodes and 1100-1200 °C for LSM-YSZ cathodes)\textsuperscript{1-2}. SOFCs fabricated by co-sintering of powders with relatively high power densities (>1 Watt/cm$^2$ at 800 °C) have been reported up to date\textsuperscript{3-4}.

The fact that both cathode and anode consist of two components with different sintering temperatures makes it challenging to determine the optimum processing parameters for electrode fabrication. In both cases, the sintering temperature should be high enough to ensure well sintered YSZ phase for sufficient ionic conductivity, while exaggerated sintering temperatures should be avoided to prevent the coarsening of the catalytically active phase with the lower sintering temperature (Ni for anode, and LSM for cathode). Several studies focused on the optimization of the processing parameters to obtain efficient electrodes for SOFCs\textsuperscript{5-8}.

Another approach to achieve efficient electrodes is infiltration of aqueous solutions containing the nitrate salts of the catalytically active materials into pre-sintered porous YSZ skeletons. This method allows low temperature fabrication of the
catalytically active component which leads to a high surface area\textsuperscript{9-13}. Despite the fact that infiltration has shown significant potential to overcome the surface area limitation in the electrodes prepared by high temperature co-sintering processes, some challenges such as long-term stability of the electrodes remain an issue. It has been reported that the Ni-YSZ cermets prepared by infiltration shows a drastic degradation due to the tendency of the nanostructured Ni phase to sinter and consequently disconnect\textsuperscript{14-16}. Infiltration of other compounds to inhibit the sintering of Ni has been proposed in order to overcome this problem \textsuperscript{14-15}. Degradation in the performance of Ni-YSZ anodes prepared by high temperature co-sintering processes has also been reported \textsuperscript{17-18}. In that case, the degradation mechanism was the coarsening and the consequent decrease in the surface area of the Ni phase.

Polymeric precursor infiltration is a promising technique for the fabrication of composite electrodes for SOFCs \textsuperscript{19-20}. Previously, very low polarization resistances with high stability was reported for LSM-YSZ cathodes prepared by polymeric precursor infiltration (~0.030 Ohm.cm\textsuperscript{2}, at 800 C for >100 hours) \textsuperscript{21}. In addition, redox stable SOFC with Ni-YSZ cermet was achieved by this method \textsuperscript{22}. In this study, performance and stability of SOFC with nanocomposite Ni-YSZ anode and LSM-YSZ cathode prepared by polymeric precursor infiltration is presented.

**EXPERIMENTAL**

NiO polymeric precursor was prepared by mixing of an aqueous solution of Ni(NO\textsubscript{3})\textsubscript{6}H\textsubscript{2}O (Alfa Aesar; Ward Hill, MA) with ethylene glycol (molar ratio of Ni/ethylene glycol: 0.4). The resultant solution was heated to 100 °C and stirred until
water was removed and Ni was incorporated into polymer complex. 2-butoxyethanol was added to promote wetting (1:2 weight ratio of polymeric precursor and 2-butoxyethanol). La$_{0.8}$Sr$_{0.2}$MnO$_3$ polymeric precursor was prepared in a similar fashion. Appropriate amounts of Lanthanum(III) nitrate hexahydrate, anhydrous Strontium nitrate, Manganese(II) nitrate tetrahydrate salts (Alfa Aesar; Ward Hill, MA) were dissolved in deionized water. Ethylene glycol was added as chelating agent to achieve an ethylene glycol to cation mole ratio of 0.04, which corresponds to ~52wt% LSM equivalent, and stirred at 100 °C until water completely evaporated. Finally, 2-butoxyethanol equal to the weight of ethylene glycol was added to improve the wetting behavior of the polymeric precursor.

Dense YSZ substrates (170 µm thick, 8 mol% Y$_2$O$_3$ content) from NexTech Materials; Columbus, OH were used as electrolyte. Porous YSZ layers (~15µm) were formed on both sides of the electrolyte by spin coating YSZ (Tosoh, Japan) slurry followed by sintering at 1150°C for 2 hours. Polymeric NiO precursor solution was infiltrated into porous YSZ layer to form Ni-YSZ cermet. After the solution was completely infiltrated inside the porous layer, the sample was heated gradually to 400 °C and kept at this temperature for ~10 minutes for full decomposition. Infiltration–decomposition cycles were carried out for 35 cycles to obtain adequate Ni loading. Although it is difficult to measure the exact NiO content within the relatively thin porous YSZ layer (~15µm), considering the concentration of the polymeric precursor and the number of infiltration cycles, it was roughly estimated that the ratio of NiO/YSZ was ~40 vol%. The cathode was prepared in a similar way. First, Pt paste was deposited on the porous YSZ layer and heat treated at 800 °C. Polymeric LSM precursor was infiltrated
through the Pt layer into porous YSZ. 20 cycles of infiltration/decomposition steps were carried out to obtain a sufficiently high LSM content (~20 vol%). Pt paste was applied also on the anode side as current collector.

Electrochemical testing of the cell was conducted at 800°C using Solartron Analytical 1470 CellTest. Air and humidified forming gas (10%H₂-90%Ar) were supplied to the cathode and anode of the cell, respectively. The cell was tested under short circuit conditions for >100 hours. AC impedance and current to voltage characteristics were measured intermittently to characterize the performance of the SOFC. Microstructural characterization of the fuel cell was carried out after electrochemical measurements by scanning electron microscopy (Helios Nanolab 600 FIB).

RESULTS AND DISCUSSION

Previous studies on the stability and electrochemical performance of the LSM-YSZ cathode prepared by polymeric precursor infiltration showed that the infiltrated LSM phase remained as a uniform thin coating on YSZ grains (200-300 nm grain size). No significant change in the microstructure of the cathode after >100 hours of measurement which was the case for the LSM-YSZ cathode reported here ²¹.

Microstructural characterization of the Ni-YSZ cermet anode prepared by polymeric precursor infiltration was carried out after >100 hours of operation along with a porous YSZ skeleton by scanning electron microscopy (Figure 1). The general structure of the anode-electrolyte interface is depicted in Figure 1a. It is shown that the porous layer (~15 µm thick) is well connected to the dense electrolyte layer. The microstructures of porous YSZ skeleton and Ni-YSZ cermet were compared (Figure 1b and 1c). The
images showed that both microstructures consist of well-connected YSZ grains with the size of 200-300 nm. The porosity remained uniformly distributed and open in both cases. It was also observed that no precipitates or particles with different features which could be distinguished as Ni phase. Energy dispersive x-ray spectroscopy (EDS) mapping was utilized in order to identify the distribution of the Ni phase (Figure 2). The EDS data was collected from the fracture surface shown in Figure 2a. It is evident that Ni phase was continuous and consistent with the morphology of the cermet (Figure 2b). Considering the similarity between the microstructures of the porous YSZ and the Ni-YSZ cermet in conjunction with the EDS results, it is suggested that the polymeric precursor infiltration results in a thin uniform coating of Ni on the YSZ grains.

Figure 3 shows current density-voltage characteristics of the fuel cell measured initially, after operating at 800 °C under short circuit conditions for 10, 78 and 105 hours. Initial power density at 800 °C was 0.49 Watt/cm$^2$, which is higher than what was obtained in a similar configuration $^{22}$. The improvement in power density from 0.31 Watt/cm$^2$ to 0.49 Watt/cm$^2$ can be attributed to increased Ni loading and a higher surface coverage of the YSZ grains by Ni as a result of increased 2-butoxyethanol content which decreases the surface tension of the used precursor. After operation in short circuit conditions for 10 hours the performance dropped to 0.45 Watt/cm$^2$. Further measurements revealed that the maximum power density measured after 78 hours of operation was 0.41 Watt/cm$^2$ at 800 °C and was stable at the same value after 105 hours of operation.

Impedance spectra of the fuel cell measured intermittently over 105 hours at 0.5 V is depicted in Figure 4. The total cell resistance consisted of three parts: i) Ohmic part
related with the electrolyte resistance and current collection from the electrodes ii) anode polarization resistance iii) cathode polarization resistance. The Cole-Cole plot consisted of one semicircle associated with the sum of anode and cathode polarization resistances. The lower x-intercept of the plot corresponds to the ohmic resistance while the distance between the lower and the higher x-intercept corresponds to the sum of anode and cathode polarization resistances. Initially, ohmic and total cell resistances were 0.25 Ohm.cm$^2$ and 0.4 Ohm.cm$^2$ respectively. Previously, four probe resistivity measurements of the identical YSZ substrate was reported$^{21}$. The insert in Figure 4 contains the temperature dependence of the resistivity of the YSZ substrate along with the initial and final ohmic resistances of the fuel cell extracted from the impedance spectra. The temperature dependence of the ohmic resistance and the ohmic resistance obtained initially, agrees well with the resistance of the YSZ electrolyte substrate obtained by four probe resistivity. This agreement points out that the extracted ohmic and polarization resistance values are reasonable. After 10 hours of measurement, the impedance arc shifted to higher resistance without significant change in the shape, resulting in a total cell resistance of 0.43 Ohm.cm$^2$. Impedance spectra measured after 78 hours and 105 hours were fairly identical, and showed ohmic resistances of 0.41 Ohm.cm$^2$. Evidently, the size of the impedance arcs decreased. Polarization resistances (total polarization resistance of anode and cathode) for both measurements were $\sim$0.080 Ohm.cm$^2$. It has been reported that the symmetrical cell measurements of the cathode prepared by infiltration method resulted in a polarization resistance of $\sim$0.030 Ohm.cm$^2$. It can be roughly estimated that the polarization resistance of the anode prepared by this method is $\sim$ 0.050 Ohm.cm$^2$. It is known that current collector layers with high catalytic activities
(i.e. Pt) can play some role in the performance of the electrodes. However, this occurs when the pore size of the electrodes are comparable to the particle size of the current collector which makes it possible for the current collector particle to penetrate into the pores generating triple phase boundaries. In the present case, as evidenced by Figure 1a, the particle size of the Pt current collector layer is in the range of several microns, while the pore size of the electrodes are ~ 200 nm. Therefore, it is reasonable to assume that the polarization resistance obtained here is not influenced by the Pt current collector. In another study, it was reported that the polarization resistance of the Ni-YSZ cermet prepared by infiltration of molten Ni nitrate salt degraded from 0.25 Ohm.cm\(^2\) to ~2.5 Ohm.cm\(^2\) at 650 °C in 24 hours. The composite structure of the Ni-YSZ anode obtained by polymeric precursor infiltration allows a significantly low polarization resistance and good stability. The porous layer obtained by partial sintering consisted of a uniform structure with relatively small grains and pores, which allowed for uniform distribution of the infiltrated Ni, is considered to play an important role in the observed performance and stability.

Figure 5 shows a summary of the changes in the ohmic resistance, polarization resistance and the maximum power density with short circuit operation time. It is evident that the power density decreases from 0.49 Watt/cm\(^2\) to 0.41 Watt/cm\(^2\) during the first 60 hours and no further changes occur in the following 40 hours of the measurement. The polarization resistance decreases from 0.150 Ohm.cm\(^2\) to 0.080 Ohm.cm\(^2\) after 20 hours and remains stable at this value for the rest of the duration of the measurement. On the other hand, the initial ohmic resistance of 0.25 Ohm.cm\(^2\) increases to 0.4 Ohm.cm\(^2\) after 60 hours and remains stable at this value for the rest of the measurement. It is evident that
the majority of the total cell resistance originates from the ohmic resistance (~80% of the total cell resistance after long term operation). Therefore, it can be suggested that the drop in the cell performance is mostly related with the increase in the ohmic resistance. In the previous study, the symmetrical cell with the same electrolyte substrate and cathodes prepared by the same technique, showed an increase in the ohmic resistance from 0.25 Ohm.cm$^2$ to 0.30 Ohm.cm$^2$. Therefore, in order to determine whether the origin of degradation of the ohmic resistance is related with the conductivity of the anode, a Ni-YSZ cermet was prepared by the same technique and the change in the two probe DC conductivity with time was measured. A relatively high conductivity (~600 S/cm) was achieved while the degradation of the conductivity was minor (<10%) after measurements for 100 hours (not shown). It can be concluded that the degradation of the ohmic resistance, therefore the power density, was mainly connected with changes in the Pt current collecting layer. In order to achieve better stability in the fuel cell performance, the microstructural stability of the Pt current collecting layer should be investigated in more detail, and improved.

In order to obtain higher power densities of the electrolyte supported structure, a decrease in the electrolyte thickness and/or an increase in the operation temperature is necessary. Figure 6a shows the results of current density-voltage measurements taken at 900 °C and 1000 °C with power densities of 0.71 Watt/cm$^2$ and 1.0 Watt/cm$^2$, respectively. The impedance plots show that the polarization resistances were 0.065 Ohm.cm$^2$ and 0.050 Ohm.cm$^2$ at 900 °C and 1000 °C, respectively (Figure 6b). The fact that with increased temperature, the ohmic resistances did not decrease to the levels
theoretically expected, is a result of the aforementioned additional series resistance of the current collector observed upon prolonged operation at 800 °C.

**SUMMARY**

Stability and performance of a solid oxide fuel cell with nanocomposite Ni-YSZ cermet anode and LSM-YSZ cathode were presented. The electrodes were fabricated by infiltration of the polymeric precursors of the catalytic components. The fuel cell was operated under short circuit conditions for >100 hours. The initial power density at 800 °C was 0.49 Watt/cm² and decreased to 0.41 Watt/cm² in the first 60 hours and showed no further degradation. The impedance spectroscopy measurements revealed that the main source of power loss was the increase in current collection resistance with prolonged time. Significantly low polarization resistances (combined anode and cathode) were achieved which showed no degradation for the duration of the measurement (~0.080 Ohm.cm²). Power densities of 0.7 Watt/cm² and 1.0 Watt/cm² were achieved at temperatures 900 °C and 1000 °C, respectively. The fact that the polarization resistance was 0.050 Ohm.cm² at 1000 °C, suggests that the power density could be significantly improved when the current collection resistances are reduced.

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Figure 1. Scanning electron microscopy images of the porous YSZ skeleton and Ni-YSZ cermet after > 100 hours of operation. a) Overall structure of the anode layer, b) porous YSZ skeleton, c) Ni-YSZ cermet
**Figure 2.** a) The fracture surface where the EDS mapping data was collected, b) EDS map showing the Ni distribution in the Ni-YSZ cermet (Ni signals are in green).
Figure 3. Influence of time on current density—voltage curve and the associated power density at 800 °C.
Figure 4. Influence of time on the impedance spectra under 0.5 V at 800 °C. The insert shows the temperature dependence of the resistivity of the YSZ substrate, the initial and final ohmic resistances of the fuel cell extracted from the impedance spectra.
Figure 5. Summary of the influence of short circuit operation time on the ohmic resistance, polarization resistance, total resistance and power density.
Figure 6. a) Current density –voltage curves and the associated power densities b) Impedance spectra at 900 °C and 1000 °C measured after >100 hours of operation at 800 °C. The insert contains the Bode plots of the associated impedance spectra
V. Solid Oxide Fuel Cells with Symmetrical Pt-YSZ Electrodes Prepared by YSZ Infiltration

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Abstract

Platinum electrodes for high temperature electrochemical devices (solid oxide fuel cells, solid oxide electrolyzer cells and sensors) generally show limited performances due to confinement of triple phase boundaries (TPBs) to the Platinum-electrolyte interface. Performance degradation as a result of TPB length loss due to the microstructural instability of the Platinum electrodes at operational temperatures is the other major problem. Infiltration of yttrium stabilized zirconia (YSZ) into porous Platinum electrodes using polymeric metal-oxide precursor was utilized as a prospective solution to these problems. It was shown that this process formed a YSZ coating on the Platinum particle surface which led to significantly increased effective contact area between Platinum electrodes and the electrolyte, and prevented the coarsening of Platinum. Symmetrical cells with YSZ infiltrated Platinum electrodes showed polarization resistance of 0.045 Ohm.cm$^2$ per cathode at 800 °C, in air. In fuel cell operation mode, the total electrode polarization resistance (anode+cathode) was 0.35 Ohm.cm$^2$ at 800 °C and 0.130 Ohm.cm$^2$ at 900 °C. Power densities of 0.45 Watt/cm$^2$ and
0.9 Watt/cm² at 800 °C and 900 °C were obtained respectively. No degradation of the cell was observed for the duration of measurement (248 hours).

**INTRODUCTION**

Platinum is an attractive electrode material for a variety of electrochemical devices due to its high catalytic activity and high electronic conductivity. The high melting temperature (1768 °C) and chemical stability of Pt at elevated temperatures (i.e. it does not readily transform into metal oxide) makes it especially attractive for electrochemical devices with solid oxide electrolytes operating at elevated temperatures such as solid oxide fuel cells (SOFCs); solid oxide electrolyzers (SOECs), gas sensors, etc.¹,²

Various techniques are used for the deposition of Pt electrodes including sputtering, chemical and electrochemical deposition. RF sputtering was applied to form Pt anode and cathode layers in micro solid oxide fuel cells (µ-SOFC)³⁻⁵. However, printing of Pt powder based inks on the electrolyte substrates is a common method to deposit Pt electrodes for high-temperature electrochemical devices. Powder based techniques allow a better control of the microstructure of porous electrodes. Well-connected conductive layers and relatively high porosity can be obtained depending on the characteristics of the initial powders. Despite the possibility of good control over the Pt electrode microstructure by adjusting the processing parameters (such as initial particle size and sintering temperature), microstructural changes of porous electrodes could proceed during the operation of high-temperature electrochemical devices. Pt electrodes could go through either sintering which results in elimination of porosity and densification; or coarsening which results in increased Pt particle and pore size without
significant increase in density. The process that dominates during cell operation is determined by several factors such as particle size distribution of Pt powder, operating temperature and operating atmosphere. In the case of sintering, the porous electrode begins to densify, resulting in a decreased TPB. This could be avoided to some extent by using Pt powders with relatively large particle size (of the order of several microns) to reduce the driving force for sintering at operational conditions. However, this approach results in limited TPB length and high electrode polarization resistance. In the case of coarsening process, the pores are not eliminated but the particle and pore sizes increase drastically. The increase in the particle size results in decreased TPB length and consequently increased polarization resistance $^{6-9}$.

One of possible ways to address these problems is the use of Pt-YSZ composite electrodes prepared by co-sintering a mixture of Pt and YSZ powders, instead of single phase Pt electrodes $^{6-11}$. Several papers reported a significant decrease in the polarization resistance of the Pt-YSZ electrodes prepared by the co-sintering route when compared to single phase Pt electrodes $^{7-9}$. In addition, it has also been shown that the introduction of the YSZ phase stabilizes the electrode microstructure and consequently improves long-term stability $^{6,11}$. Despite the significant progress shown in this direction, electrode polarization resistances of Pt-YSZ composites prepared by mixed powder method are still relatively high (0.4 Ohm.cm$^2$ per cathode at 900 °C) and strongly composition dependent $^{8,9}$. Moreover, YSZ addition leads to substitution of some Pt particles by YSZ particles so that the stabilization of the Pt electrode is achieved at the expense of electrical conductivity of the electrode.
Fabrication of composite electrodes for SOFCs by infiltration of catalytically active components into porous YSZ matrix has been previously suggested as an alternative to the conventional co-sintering route. Efficient electrodes with relatively good stability were fabricated by this method. However, the electrical conductivity of these electrodes is relatively poor because of the relatively high percentage of YSZ phase in electrode composition. The objective of this study is to reverse the composite configuration, i.e. to prepare electrodes by infiltration of YSZ phase into pre-sintered porous Pt skeleton. It is expected that such electrodes would exhibit an increased TPB length and result in improved cell performance. Infiltration of YSZ could also stabilize the microstructure of the initial Pt skeleton at operational conditions to improve the long-term stability of the cells.

BACKGROUND AND APPROACH

As a noble metal, Pt exhibits high electronic conductivity and practically no bulk ionic conductivity. Hence, in Pt electrodes, the charge transfer reaction is confined to the TPBs where the electronic conductor (Pt), ionic conductor (YSZ electrolyte) and the gas phase meet. This makes the electrochemical performance of Pt electrodes strongly dependent on the TPB length, hence on the microstructure of the electrode material. A dense Pt electrode which covers entire YSZ electrolyte surface would perform poorly due to the limited gas delivery and complete loss of TPB. Therefore, porous Pt electrode attached to the YSZ electrolyte in the form of finely separated parts will perform better. Limitations in TPB will be controlled by the size of Pt particles and the possibility of stabilizing such a fine microstructure at operational
temperatures. Achieving of the long-term stability of the single phase Pt electrodes under operating conditions is a significant issue. In practical applications, although a desirable porous Pt microstructure may be obtained to some extent in as-deposited electrodes, this initial form cannot be retained during long term operation. Pt particles have been reported to coarsen at high operational temperatures leading to a decrease in the TPB length and consequently, an increase in electrode polarization resistance \(^6, 19\). The increase in polarization resistance corresponds to power density loss in SOFCs, efficiency loss in SOECs and sensitivity loss in sensors. This phenomenon is depicted schematically in Figure 1a along with the scanning electron microscopy (SEM) images of a Pt electrode before and after long term operation at 800 °C. The SEM images clearly show that the Pt grain size and the pore size increased significantly without densification (i.e. the porous structure is maintained). It is also worth noting that the interfacial area between the Pt layer and the YSZ electrolyte decreased as a result of the coarsening. Initially, there was higher number of Pt-YSZ electrolyte contact points with relatively small separation distances. However; coarsening of the Pt phase led to a decreased number of connections, increased the separation distance between the connection points.

Further improvements of the electrode performance can be achieved using Pt based composites \(^6, 8-10\). It was suggested that incorporation of a second phase which is microstructurally stable at the operational temperatures (such as YSZ) would act as barriers to the growth of Pt particles and prevent the coarsening of the Pt phase \([6, 10]\). A similar approach was also used successfully to stabilize the Ag current collector microstructures which otherwise would densify and seal the SOFC cathode surface at the operational temperatures, preventing gas penetration \(^20, 21\).
The use of Pt-YSZ composites may appear a straightforward method to improve the performance and long term stability of the electrodes. However, in order for Pt-YSZ composite electrodes to yield desired electrochemical performance and stability, it is required that all three phases (electronically conductive metal phase, ionically conductive ceramic phase and gas phase (i.e. pores)) percolate. It is challenging to achieve such a microstructure by co-sintering of Pt and YSZ powder mixtures. Porosity, electronic conductivity and overall electrochemical performance of the Pt-YSZ composite electrodes depend strongly on the composition, particle size ratio, and sintering conditions, therefore obtaining of the optimum electrode characteristics simultaneously is problematic.

A prospective solution for these problems is the infiltration of a polymeric YSZ precursor into a previously sintered porous Pt skeleton. This technique allows the formation of a thin uniform YSZ coating on the Pt particles resulting in a continuous ionically conductive phase and extends the TPB length from the Pt-YSZ electrolyte interface to the interface of Pt-YSZ coating. The YSZ coating is considered to have the potential to encapsulate Pt particles, consequently inhibit their coarsening and ensure microstructural stability. A schematic representation of the proposed microstructure and the representative SEM images of the microstructure before and after long term operation are shown in Figure 1b. It clearly shows that no change in the general microstructure of the YSZ infiltrated Pt electrode was present, as opposed to the single phase Pt electrode. A comparison of the microstructures of the YSZ infiltrated and single phase Pt electrodes after long term operation at elevated temperatures (800 °C) reveals that for the single phase Pt electrodes TPB contact was confined only to the surface of the electrolyte and
degraded significantly due to coarsening of Pt grains, while TPB contact for YSZ infiltrated electrodes remained stable on the electrolyte surface as well as between Pt and YSZ coating due to the encapsulation effect (Figure 1). However, it should also be noted that the points where the YSZ particles are placed would decrease the number of Pt surface sites for adsorption processes.

**EXPERIMENTAL**

Two types of electrolyte supported symmetrical cells were used in this investigation. Dense, ~80 micron thick YSZ electrolytes were prepared by tape casting using YSZ powders (Tosoh, Japan) and sintering at 1400 °C for two hours. First type of cell was processed by depositing platinum paste (ElectroScience; King of Prussia, PA) on both sides of the YSZ electrolyte and sintering at 800 °C for 20 minutes (Cell name: Pt800). For preparation of the second type of cell, Pt paste was deposited on both sides of the electrolyte and sintered at 600 °C for 20 minutes. The reason for selecting a lower sintering temperature was to obtain a conductive Pt skeleton with the smallest particle size possible. The cell was then infiltrated by a polymeric YSZ precursor for 40 cycles. Each cycle consisted of infiltration, drying (70 °C) and decomposition (450 °C) steps (Cell name: Pt600-YSZ). For polymeric YSZ precursor preparation, yttrium nitrate hexahydrate and zirconium oxychloride (Alfa Aesar; Ward Hill, MA) were dissolved in deionized water to obtain a Y/Zr molar ratio of 0.16/0.84. The solution was then mixed with ethylene glycol (ethylene glycol/cation molar ratio: 0.04) and stirred on a hot plate at 100 °C until the water content was removed by evaporation. 2-butoxyethanol was added to the resulting polymeric precursor to improve the wetting properties. A
polymeric precursor with 2-butoxyethanol to ethyleneglycol volume ratio of 1:2 was achieved. Although it was not possible to accurately determine the YSZ and Pt ratios by measuring changes in weight due to the relatively thin electrodes (~10 micron), it was estimated that YSZ to Pt volume ratio was ~0.3 by considering the concentration of the precursor, porosity of the electrode layer and the number of infiltration cycles.

All electrical measurements were performed using Solartron Analytical 1470 CellTest electrochemical interface. Symmetrical cells in symmetrical air conditions were analyzed by impedance spectroscopy techniques under open circuit voltage at 800 °C. The changes of the impedance spectra as a function of time were monitored for both samples. After long term measurements in air, the cell conditions were switched to fuel cell conditions. Humidified diluted hydrogen (10% H₂-90% Ar) from one side and air from the other side were introduced to test the electrochemical performance of the electrodes under the fuel cell conditions. The changes in the impedance spectra (at 0.5 V) and current – voltage characteristics were monitored during long term operation under short circuit current at 800 °C. For Pt600-YSZ, the temperature was later increased to 900 °C and fuel cell performance and stability was tested at this temperature. Microstructural characterization of both samples was carried out after long-term operation (248 hours) by scanning electron microscopy (SEM, Hitachi-S4700). In addition, samples identical to those used for electrochemical analysis were prepared and characterized by SEM to compare the effect of long-term operation on the microstructural features. For all samples, the fracture surfaces of the electrodes were analyzed.
RESULTS AND DISCUSSION

Cathode performance of the sample Pt800 was tested by impedance spectroscopy at 800 °C, under open circuit conditions in air (Figure 2a). The distance from the origin to the high frequency intercept is attributed to the ohmic resistance which is dominated by the resistance of the electrolyte and includes the ohmic resistance of the electrodes. The distance from the high frequency intercept to the low frequency intercept refers to the polarization resistance of the cathodes (i.e. the total polarization resistance should be divided by two to obtain polarization resistance per cathode). The ohmic resistances of both samples remained at a stable value of ~0.1 Ohm.cm$^2$ at 800 °C which roughly corresponds to the area specific resistance of 80 µm thick YSZ electrolyte at this temperature. Initial cathode polarization resistance of Pt800 per cathode was ~ 0.1 Ohm.cm$^2$ which increased to 0.35 Ohm.cm$^2$ after 20 hours and to 0.39 Ohm.cm$^2$ after 29 hours. This degradation in the electrode performance was attributed to the microstructural coarsening and the accompanied reduction in the TPB length.

After long term measurements in air at 800 °C, the test conditions were switched to fuel cell mode at the same temperature for both cells (i.e. humidified 10%H$_2$-90%Ar was fed from one side of the identical electrodes). The cell was kept at short circuit conditions and electrochemical performance measurements were conducted intermittently. The change in the impedance spectra for Pt800 with time is given in Figure 2b. Shortly after switching to fuel cell mode, Pt800 showed the same ohmic resistance (~0.1 Ohm.cm$^2$), while the total electrode polarization resistance increased to 3.88 Ohm.cm$^2$. The fact that the electrode polarization resistance of the symmetrical cell increased significantly upon switching to fuel cell mode suggests that Pt is catalytically
more active for oxygen reduction reaction than hydrogen oxidation reaction. After operation at short circuit conditions for 5 hours the ohmic resistance and the electrode polarization resistances increased to 0.23 Ohm.cm² and 6.57 Ohm.cm², respectively. The cell performance continued to degrade for the next 10 hours which is attributed to further coarsening of Pt and decrease in the electrolyte/electrode interfacial area. Figure 2c shows the current-voltage characteristics of Pt800 at 800 °C measured shortly after switching to fuel cell mode for 5 and 10 hours of operation. The considerably low power density achieved initially (0.020 Watt/cm²) decreased further after 15 hours of operation. It was also noted that the current density-voltage characteristics were non-linear.

The impedance spectra of the Pt600-YSZ sample measured in air is shown in Figure 3a. The polarization resistance of Pt600-YSZ per cathode was initially ~0.050 Ohm.cm² at 800 °C and slightly decreased to 0.045 Ohm.cm² after 55 hours. This rather minor decrease in the polarization resistance can be attributed to the crystallization of the YSZ coating resulting in an increase of the ionic conductivity. The cathode polarization resistance remained stable after a measurement time of 110 hours. Previous publications reported an improvement in the cathode performance of Pt when used as a composite with YSZ due to the increased TPB length. In a similar case, infiltration of gadolinia doped ceria (GDC) into porous Pt skeleton to enhance electrode performance has recently been reported. It was shown that GDC infiltration improved the electrode performance significantly (from 3.9 Ohm.cm² to 0.7 Ohm.cm² per electrode at 700 °C). However, the mixed conductivity of GDC and the fact that it exhibits some catalytic activity for the oxygen reduction reaction needs to be considered for a comparison with the present work.
YSZ infiltrated sample (Pt600-YSZ) also showed an initial increase in the total polarization resistance upon switching to the fuel cell mode, which confirms that Pt is catalytically more active for oxygen reduction than for hydrogen oxidation. The initial electrode polarization resistance of 0.85 Ohm.cm$^2$ dropped to ~0.35 Ohm.cm$^2$ after 49 hours and remained stable for the next 44 hours. Unlike Pt800, the ohmic resistance was also stable at 0.1 Ohm.cm$^2$ for the duration of the measurement. This suggests that the encapsulation of the Pt skeleton by the YSZ coating prevents the coarsening of Pt and the accompanying reduction of the contact area between the Pt phase and the YSZ electrolyte. Figure 3c provides the current density – voltage characteristics of the sample Pt600-YSZ. Initial performance of Pt600-YSZ was ~0.25 Watt/cm$^2$ which increased to ~0.45 Watt/cm$^2$ after 49 hours of operation and was stable for the next 44 hours. It should also be noted that the current-voltage characteristics were linear.

It is common practice that the electrolyte supported SOFCs are operated at relatively high temperatures to compensate for the ohmic losses due relatively thicker electrolytes when compared to the electrode supported designs \(^{23}\). Since the activation energy for the cathode polarization resistance of Pt electrodes is also known to be relatively high (~1.5 eV) \(^{8}\), the operating temperature of the Pt600-YSZ fuel cell was increased to 900 °C. Figure 4a shows the change in the impedance spectra of the cell with time at 900 °C operating under short circuit conditions. The decrease in the ohmic resistance upon increasing the operating temperature from 800 °C to 900 °C is in accordance with the expected increase in the ionic conductivity of the YSZ electrolyte \(^{24}\) without noticeable change with time. The initial total electrode polarization resistance was ~0.180 Ohm.cm$^2$ which dropped to 0.130 Ohm.cm$^2$ after 24 hours and was stable at
this value for the remaining 24 hours. The change in the current density – voltage curve with time is given in Figure 4b. The maximum power density improved from 0.78 Watt/cm$^2$ to 0.9 Watt/cm$^2$ after 24 hours and remained at this value. The decrease in the electrode polarization resistance and the associated improvement in the power density were attributed to the further crystallization and the related increase in the ionic conductivity of the infiltrated YSZ phase.

Microstructural characterization of the samples was carried out by scanning electron microscopy (SEM) after long term measurements. Figure 5a-b shows the changes in the microstructure of the bare Pt electrode (Pt800) after measurements for 45 hours at 800 °C. An increase in the particle and pore size after long term exposure to 800 °C is evident (increase of particle and pore size from 2 µm to ~4 µm). The coarsening of Pt and the accompanied loss of TPB length during long term operation at elevated temperatures (>600 °C) have been reported in the literature and was identified as the main source of performance degradation of Pt electrodes $^6, 11, 19$. The changes in the microstructure of YSZ infiltrated Pt electrode (Pt600-YSZ) after 200 hours of the measurement at 800 °C followed by another 48 hours of the measurement at 900 °C is given in Figure 5c-d. Before the measurement, finely divided Pt particles are covered with an amorphous YSZ coating while a long term operation results in a slight growth of Pt particles and a crystallized YSZ coating. In both cases YSZ covers the Pt surface very efficiently, and the uncovered spots are the connection points of Pt as depicted on the fracture surface of the cells (Figure 5). Evidently, a lower sintering temperature (600 °C) resulted in a smaller initial Pt particle size (<1 µm particle and pore size) which remained stable after long term exposure to relatively high temperatures (800-900 °C). However, it
should be noted that the extent of YSZ coverage on Pt particles and the initial Pt particle size are considered to be important parameters affecting the microstructural stability. It is reasonable to assume that the smaller initial Pt particle size will result in an increased surface area that will allow the higher coverage of Pt surface by YSZ upon infiltration.

Figure 6 provides a summary of the change in the performance of YSZ infiltrated Pt electrodes (Pt600-YSZ) under different conditions with time. Generally, it is evident that no degradation in the electrode performance was observed under the investigated conditions after 248 hours of operation. The ohmic resistance at 800 °C did not change when the operating conditions were switched to fuel cell mode. The increase in the total electrode polarization resistance is due to the different catalytic behavior of Pt in anode and cathode conditions. The following decrease of the polarization resistance (until saturation at 0.35 Ohm.cm$^2$) is attributed to changes of the Pt surface in the reducing environment. When the temperature was increased to 900 °C, the ohmic resistance dropped according to the ~1 eV activation energy of the YSZ electrolyte. The total electrode polarization resistance first showed a sharp decrease due to the enhanced reaction kinetics as a result of the temperature increase. Further gradual decrease in the electrode polarization resistance was attributed to the enhanced ionic conductivity of the infiltrated YSZ phase as a result of proceeding improvement in crystallinity.

**SUMMARY**

Infiltration of YSZ phase into porous Pt skeletons was applied to enhance the performance and the microstructural stability of Pt based electrodes for solid state electrochemical devices. It was shown that the infiltrated YSZ formed a coating on the Pt
particles and prevented their coarsening. The electrochemical performance and the long-term stability of SOFC with symmetrical Pt-YSZ electrodes were evaluated. The cathode polarization resistance of the YSZ infiltrated Pt was 0.045 Ohm.cm$^2$ at 800 °C while the bare Pt electrode was 0.39 Ohm.cm$^2$ at the same temperature after long term operation. Power densities of ~0.45 Watt/cm$^2$ at 800 °C and 0.9 Watt/cm$^2$ at 900 °C were obtained from the symmetrical Pt-YSZ composites in the fuel cell mode. In general, no degradation in the electrochemical performance of the electrodes was observed throughout the 248 hours of operation at two different temperatures (800 °C and 900 °C) and operation modes (in air and fuel cell mode). This was in agreement with the microstructural stability observed in the SEM images taken before and after measurements.

ACKNOWLEDGEMENTS

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REFERENCES


Figure 1. Schematic representations with representative scanning electron microscopy images of the initial microstructure and the microstructure after long term operation at 800 °C of samples a) Single phase Pt electrode b) YSZ infiltrated Pt electrode.
Figure 2. The changes in the impedance spectra of the sample with symmetrical single phase Pt electrodes (Pt800) with time at 800 °C a) in air, at open circuit voltage b) in fuel cell mode under 0.5 V (10% Hydrogen-90% Argon from anode side, air from cathode side). c) The changes in the current density – voltage curve of the sample in fuel cell mode.
Figure 3. The changes in the impedance spectra of the sample with symmetrical YSZ infiltrated Pt electrodes (Pt600-YSZ) with time at 800 °C a) in air, at open circuit voltage b) in fuel cell mode under 0.5 V (10%Hydrogen-90%Argon from anode side, air from cathode side). c) The changes in the current density – voltage curve of the sample in fuel cell mode.
Figure 4. The changes in the a) impedance spectra in fuel cell mode under 0.5 V (10% Hydrogen-90% Argon from anode side, air from cathode side) b) the current density–voltage curve of the sample with symmetrical YSZ infiltrated Pt electrodes (Pt600-YSZ) with time at 900 °C.
Figure 5. SEM images of the sample with single phase Pt electrodes (Pt800) a) before measurement b) after 44 hours of operation at 800 °C. SEM images with YSZ infiltrated Pt electrodes (Pt600-YSZ) c) before measurement d) after 200 hours of measurement at 800 °C followed by 48 hours of measurement at 900 °C.
Figure 6. A summary of the performance of the sample with YSZ infiltrated Pt electrodes (Pt600-YSZ) involving the different operating modes (symmetrical air and fuel cell) and temperatures (800 °C and 900 °C).
SECTION

2. CONCLUSIONS

Performance and stability of the composite electrodes are the major challenges in the development of SOFCs for practical use. In this dissertation, it was shown that processing of the SOFC electrodes by low temperature infiltration techniques has the potential to overcome both performance and stability related issues.

Infiltration of LSM into a previously sintered porous YSZ skeleton allowed cathode polarization resistances as low as 0.030 Ohm.cm$^2$ at 800 °C which was stable for over 100 hours. SOFCs with total electrode polarization resistances of 0.070 Ohm.cm$^2$ at the same operating temperature were obtained by infiltrating Ni and LSM phases into porous YSZ skeletons from anode and cathode sides respectively. The stability of the total electrode polarization resistance for over 100 hours pointed out that it was also possible to obtain Ni-YSZ anodes with similar electrochemical performance and stability.

Processing of the anodes by the infiltration technique was shown to address the redox instability problem of conventionally processed Ni-YSZ anodes. It was proposed that the different type of composite, relatively low processing temperatures (i.e. decomposition temperature after infiltration is 400 °C) and lower Ni amount in comparison with the conventional Ni-YSZ cermet were important parameters in achieving this redox stability.

The case of ionically conductive oxide (YSZ) infiltration into a microstructurally unstable metal skeleton (Pt) was also investigated. The infiltrated YSZ formed a coating on the Pt particles and prevented their coarsening. The electrochemical performance in symmetrical and fuel cell modes was also enhanced.
3. FUTURE WORK

This dissertation aimed to understand the electrochemical properties of infiltrated SOFC electrodes and evaluate the potential of this technique to solve the known issues in SOFCs. The information gained as a result of this investigation can be further extended in several aspects:

1. Mechanical Properties of Ni-YSZ anodes prepared by infiltration:
   Electrical/electrochemical characterizations revealed that the processing of SOFC anodes by Ni infiltration into porous YSZ skeletons. In addition, prior YSZ infiltration was also shown to improve the redox stability at higher Ni loadings. Evaluation of the mechanical properties of the Ni-YSZ layers at different Ni loadings before and after redox cycling would provide useful information.

2. Optimization of LSM-YSZ cathodes: Investigations of the LSM-YSZ cathodes prepared by infiltration techniques revealed that it was possible to obtain polarization resistances of 0.030 Ohm.cm$^2$ at 800 °C. Optimization of processing parameters and microstructure (e.g. optimization of polymeric precursor concentration, YSZ skeleton microstructure) holds the potential to obtain even lower electrode polarization resistances. This could result in enhanced power densities in SOFCs.

3. Evaluation of infiltrated cathodes with different cathode materials: This study was based on understanding the properties of SOFC electrodes prepared by infiltration techniques. For the sake of clear interpretation of results, most common materials were selected (e.g. Ni for anode, YSZ for electrolyte, LSM for cathode). As a result, cathode materials that exhibit both electronic and ionic conductivity has the
potential to show much lower electrode polarizations than what was reported in the study.

4. Detailed microstructural analysis of electrodes in different conditions: The nanostructured nature of the composite necessitates the use of a higher resolution technique than SEM. The preliminary results shown in this dissertation suggest that TEM studies using ion milling/lift-out technique has the potential to provide useful information. The changes in the structure of Ni-YSZ anodes upon redox cycling can be monitored by TEM, as well as time dependent changes in LSM-YSZ and Ni-YSZ electrodes.
APPENDIX A

MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF INFILTRATED Ni-YSZ CERMETS
Introduction

Sections 3, 4 and 5 of this dissertation concentrated on the electrochemical properties of Ni-YSZ anodes prepared by low temperature infiltration techniques. It was shown that processing of Ni-YSZ anodes by introducing the Ni phase into the porous YSZ skeleton resulted in a microstructure which consisted of YSZ grains with continuous, uniform Ni coatings. However, this was mostly based on the similarity between the microstructures of infiltrated and non-infiltrated YSZ skeletons and the uniformity of the EDX signal obtained for Ni from the composite layer. Although the focus of this dissertation was the electrochemical properties of infiltrated electrodes, preliminary TEM investigations were carried out to gain a clear understanding of the formed microstructure.

Electrical conductivity measurements provide useful information about the structure and stability of Ni-YSZ cermets. In section 4, the changes in the electrical conductivity upon switching the gas flow from diluted hydrogen to air was used as a preliminary test for the redox stability of the cermet. The level and long-term stability of the electrical conductivity can also give important information about the reasons for dominating losses and the long-term degradation mechanism of a fuel cell.

In this appendix section, more detailed information on the microstructural and electrical properties of Ni-YSZ cermets prepared by infiltration is provided. TEM characterization and 2-probe electrical conductivity measurements were used.
Experimental

All experiments were conducted on the Ni-YSZ layer prepared by infiltration of polymeric NiO precursor into ~15µm thick porous YSZ skeleton with ~50% porosity. Dense YSZ substrates (500 µm thick, 8 mol% Y2O3 content) from NexTech Materials; Columbus, OH were used as substrates. Infiltration cycles were carried out by using spin – on deposition at 3000 rpm, for uniformity and good control of the amount of infiltrated components, followed by decomposition at 450 °C. Porous YSZ layer was infiltrated with polymeric NiO precursor for 35 cycles (YSZ(1150)-35Ni in Section 4).

Two probe DC conductivity of the samples current density – voltage measurements were performed by Solatron Analytical 1470 CellTest. TEM analysis was performed by Technai F20 TEM.

Results and Discussion

The polymeric precursor that is used in this study in conjunction with the nanoscale scaffold allowed the formation of thin continuous film on YSZ surfaces. The transmission electron microscopy (TEM) image of the cross –section of the NiO-YSZ composite after NiO infiltration is given together with the EDX maps (Figure 1). It is evident that NiO is uniformly distributed on YSZ particles as a thin coating. The NiO phase located in the middle of the pore is the top view of the NiO layer covering another YSZ particle that has not been sliced by ion milling.
Figure 2 shows the change in the electrical conductivity of Ni-YSZ cermet with time at 800 °C. Initially, the electrical conductivity is at 610 S/cm which drops to 590 S/cm in 20 hours and remains stable at this level for the following 40 hours. Unlike this case, it has been reported that the Ni-YSZ cermets prepared by infiltration shows a drastic degradation due to the tendency of the nanostructured Ni phase to sinter and consequently disconnect. The porous layer obtained by consisting of a uniform structure with relatively small grains and pores (~200nm pore and grain size), uniform and continuous distribution of the infiltrated Ni phase, is considered to play an important role in the observed stability.

Figure 3 provides the temperature dependence of the electrical conductivity of Ni-YSZ cermet. The electrical conductivity dropped approximately linearly from 820 S/cm to 610 S/cm when the temperature was increased from 550 °C to 800 °C. The typical metallic behavior of the temperature dependence of the electrical conductivity confirms that electronic conduction through Ni is the dominating electrical conduction mechanism in the Ni-YSZ cermet.

Conclusions

The TEM analysis of the cross-section of the as infiltrated NiO-YSZ provided detailed information about the NiO distribution in the composite prepared by infiltration. A uniform coating of NiO covers the surface of YSZ grains. It was shown that, unlike what has been reported in the literature for the infiltrated Ni-YSZ cermets, the electrical conductivity was stable with time. The temperature dependence of the electrical...
conductivity of the Ni-YSZ cermets confirmed metallic characteristic of electrical conductivity.

References


Figure 1. Transmission electron microscopy images of the cross-section of the NiO-YSZ composite prepared by infiltration of the polymeric NiO precursor into the YSZ scaffold (a-c). (EDX) maps of Zr and Ni elements are shown in (b) and (c), respectively.
Figure 2. Changes in the electrical conductivity of Ni-YSZ cermet prepared by infiltration at 800 °C under 10%H₂-90%Ar flow.
Figure 3. Temperature dependence of electrical conductivity of Ni-YSZ cermet prepared by infiltration.
APPENDIX B

REDOX CYCLING OF ELECTROLYTE SUPPORTED SOFCs WITH CO-SINTERED Ni-YSZ ANODES
Introduction

One of the highlights of this dissertation is overcoming the fundamental problem of redox instability of Ni-YSZ anodes. Upon an interruption of the fuel flow, Ni oxidizes to form NiO which causes a ~69% increase in the Ni volume. As a result of this expansion create cracks in the YSZ network.

In this dissertation the redox instability problem addressed by introducing the Ni phase into a previously sintered porous YSZ skeleton by low temperature infiltration route. It was aimed that a weaker Ni phase is obtained due to the low temperature processing. In addition, it was possible to obtain sufficient electrical conductivity with much lower Ni content when compared to conventionally fabricated Ni-YSZ cermets (600 S/cm at 800 °C with NiO/YSZ: 0.4). Another advantage of this technique was the possibility to obtain composites where Ni is in the form of a thin coating on the YSZ grains rather than a random mixture of particles.

In sections 3 and 4 it was shown that SOFCs with Ni-YSZ anodes processed by low-temperature infiltration techniques showed polarization resistance of 0.170 Ohm.cm² and 0.040 Ohm.cm² after optimization at 800 °C. However, for a sound assessment of the redox cycling properties of the infiltrated Ni-YSZ anodes prepared by infiltration, it is necessary to evaluate the changes in the performance of SOFCs with co-sintered Ni-YSZ anodes having similar designs. In this appendix, the changes in the electrochemical properties of electrolyte supported (180 µm thick) SOFCs with similar electrode thicknesses (Ni-YSZ anode thickness: 10 µm) were evaluated. The identical LSM-YSZ cathode as the redox stable SOFCs was used for the sake of clear comparison.
**Experimental**

The anode of the SOFC was formed by depositing a slurry prepared by dispersing NiO (Alfa Aesar 12359) and YSZ (Tosoh-8YSZ) powders in a mixture of polyvinyl butyral (PVB, binder), dioctyl phthalate (DOP, plasticizer), ethanol and toluene. The deposited layer (~10 µm thickness) was sintered at 1300 °C for 2 hours. The cathode part was prepared by infiltrating an LSM polymeric precursor into a previously sintered porous YSZ as described in previous sections.

Electrochemical testing of the cell was performed using Solartron Analytical 1470 CellTest. Air and diluted hydrogen (10%H$_2$-90%Ar) were fed to the cathode and anode of the cell, respectively. Impedance spectra and current to voltage characteristics were measured to characterize the performance of the SOFC. Redox stability was investigated by cycling air and humidified forming gas at the anode side of SOFC and measuring current density in short circuit conditions.

**Results and Discussion**

The change in the impedance spectra of the SOFC upon redox cycling at 800 °C is given in Figure 1. Initially the ohmic resistance was 0.25 Ohm.cm$^2$ which corresponds to the resistance of the YSZ electrolyte at this temperature. The total electrode polarization resistance is 0.38 Ohm.cm$^2$. Since the SOFC has the identical cathode described in section 2, it can be estimated that the anode polarization resistance is ~0.35 Ohm.cm$^2$. Certainly, it can be assumed that with optimization much lower electrode
polarization resistances can be achieved. After 5 redox cycles the ohmic resistance increases to 1 Ohm.cm$^2$ which points to contact losses between the anode and the electrolyte. After 5 redox cycles another semi-circle appears and the total non-ohmic polarization resistance increases to 0.6 Ohm.cm$^2$. Further redox cycling increases the non-ohmic part of the impedance and the total cell resistance increases up to 2.2 Ohm.cm$^2$

Figure 2 shows the changes in the current-voltage characteristics and power density of the cell upon redox cycling at 800 °C. Initially the current – voltage curve is linear and a maximum current density of 1 Ampere/cm$^2$ is achieved. The maximum power density was 0.215 Watt/cm$^2$ at this temperature prior to redox cycling. After 5 redox cycles the slope of the current-voltage curve increased noticeably and the maximum power density obtained was 0.1 Watt/cm$^2$. Further redox cycling decreases the maximum power density to 0.080 Watt/cm$^2$.

It can be estimated that the loss in the power density would be much more pronounced if an anode supported SOFC was the case. However in the present case, the ohmic resistance which originates from the 180 µm electrolyte dominates the total cell resistance which, in turn, suppresses the drop in cell performance. Even when this phenomenon is considered the difference between the electrochemical response of the SOFC with conventional and infiltrated Ni-YSZ anodes is clear.

Figure 3 shows the microstructure of the Ni-YSZ anode after measurements. YSZ grains in the range of 1 µm and Ni grains in the range of 2 µm are evident. In addition, several intergranular cracks are visible which has been reported to be the reason for the performance loss $^{1,2}$. 
Conclusions

Electrolyte supported SOFC with co-sintered Ni-YSZ anodes were fabricated and the changes in their electrochemical properties upon redox cycling was tested. The SOFC had a similar geometrical configuration to the redox stable SOFCs reported in sections 3 and 4. In addition to the similar geometries, use of the identical cathode allowed a clear comparison between the redox stability of Ni-YSZ anodes prepared by infiltration and Ni-YSZ anode prepared by co-sintering. It was shown that the electrode polarization resistance of the cell increased from 0.38 Ohm.cm$^2$ to ~1 Ohm.cm$^2$ after 15 redox cycles. When this is considered in conjunction with the zero decrease in electrode polarization resistance obtained in Ni-YSZ anodes prepared by infiltration, it can be concluded that the redox stability obtained in infiltrated Ni-YSZ anodes cannot be explained solely by the geometrical configuration.

References

Figure 1. Influence of redox cycles; a) on the impedance spectra of the fuel cell under 0.5 V at 800 °C
Figure 2. Influence of redox cycles on current density –voltage curve and the associated power density at 800 °C.
**Figure 3.** Scanning electron microscopy image showing the microstructure of Ni-YSZ cermets after redox cycling at 800 °C.
BIBLIOGRAPHY


VITA

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