THE EFFECT OF ANODE THICKNESS ON THE PERFORMANCE OF ANODE-SUPPORTED SOLID OXIDE FUEL CELLS

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ABSTRACT

Anode-supported cells comprising a three layer structure of a porous composite cathode of Sr-doped LaMnO₃ (LSM) + yttria-stabilized zirconia (YSZ); a thin, dense YSZ electrolyte; and a porous Ni + YSZ anode were fabricated. The anode thickness was varied between ~1.04 and ~3.86 mm. The YSZ electrolyte thickness was ~10 µm and the LSM + YSZ cathode thickness was ~50 µm. The cells were tested at 800°C with humidified hydrogen as the fuel and air as the oxidant. The voltage (V) vs. current density (i) traces were nonlinear; concave-up \( \frac{d^2 V}{di^2} > 0 \) at low current densities and convex-up \( \frac{d^2 V}{di^2} < 0 \) at high current densities. The maximum power density for a cell with an anode thickness of ~1.04 mm was ~1.9 W/cm² and that for a cell with an anode thickness of ~3.86 mm was ~1.1 W/cm². The measured short circuit current densities were ~6.35 A/cm² for a cell with an anode thickness of ~1.04 mm and ~3.56 A/cm² for a cell with an anode thickness of ~3.86 mm. The V vs. i traces were fitted to a previously developed theoretical model. The present work shows that anode-supported cells can be made with a relatively thick and rugged anode while still exhibiting an excellent power density at a temperature of 800°C.

INTRODUCTION

Three designs of solid oxide fuel cells (SOFCs) are currently under development; (1) electrolyte-supported, (2) cathode-supported, and (3) anode-supported, where the distinction refers to the thickest or the structurally supporting member of the cell [1-4]. In electrolyte-supported cells with yttria-stabilized zirconia (YSZ) as the electrolyte, the electrolyte thickness is typically ≥ 150 µm. A relatively high resistivity of YSZ at
temperatures below about 900°C requires that these cells be operated at a relatively high
temperature, typically 900°C and above. In electrode-supported cells, the YSZ electrolyte
thickness is typically between 5 to 30 μm and these cells can be operated at a reasonable
power density at temperatures as low as 700 to 800°C due to a substantially lower ohmic
resistance.

In electrode-supported cells, the thickest component is the supporting electrode. In the
Westinghouse cathode-supported cells, for example, the cathode support tube thickness is
on the order of 2 mm. In electrode-supported cells, significant voltage losses may arise due
to concentration polarization related to the transport of gaseous species through porous
electrodes. Clearly, parameters such as the electrode porosity, the pore size, and the pore
morphology (which affects the tortuosity factor) are expected to influence the transport of
gaseous species and thus the accompanying concentration polarization. In addition to these
electrode microstructure-related parameters, the electrode thickness is also expected to
affect concentration polarization; the thicker is the support electrode, the greater is the
concentration polarization. From the standpoint of ruggedness and mechanical integrity, the
electrode should be of a sufficient thickness. From the standpoint of concentration
polarization losses, the thinner is the electrode, the lower are the losses. It is thus necessary
to know how thick the supporting electrode can be without significantly increasing
concentration polarization losses.

The principal objective of the present work was to experimentally study the effect of anode
thickness on cell performance and compare the results with a previously developed
theoretical model [5]. The model relates the voltage across the load, V, to the current
density, i, by taking into account (a) ohmic polarization, (b) concentration polarization
based on the assumption of binary diffusion of gaseous species through porous electrodes,
and (c) activation polarization in composite electrodes comprising a mixture of an
electrocatalyst (LSM for the cathode or Ni for the anode) and the electrolyte material, YSZ.
Anode-supported cells with an anode thickness over a wide range were made and tested at
800°C with humidified hydrogen as the fuel and air as the oxidant. The V vs. i traces were
fitted to the theoretical model and relevant parameters such as the area specific ohmic
resistance, $R_o$, the effective binary diffusivity through the anode, $D_{eff(a)}$, and the effective
exchange current density, $i_o$, were deduced.

**EXPERIMENTAL PROCEDURE**

A mixture of NiO + 8 mol.% yttria-stabilized zirconia (YSZ) powders was ball-milled in
ethanol. After drying the powder mixture, disks of ~3.2 cm in diameter and various
thicknesses were die-pressed in a uniaxial press. One surface of each disk was coated with
a YSZ slurry in a liquid. After drying, the disks were isostatically pressed and were
sintered in air at a temperature between 1400 and 1500°C for 1 hour. This procedure
resulted in a thin (~10 μm), dense layer of YSZ on an essentially dense NiO + YSZ disk.
Subsequently, a cathode powder containing a mixture of Sr-doped LaMnO$_3$ (LSM) and
YSZ was mixed in an organic liquid and the resulting paste was applied on the YSZ-coated
side of the sintered disks. The typical area over which the cathode was applied was about 2
cm$^2$. The disks were later heated to 1200°C to bond the cathode onto the YSZ electrolyte.
This completed the cell fabrication procedure.
The single cell test stand consists of two alumina tubes in between which a cell can be secured. Silver wire meshes were used as current collectors which were pressed against the cathode and the anode with a thin layer of platinum resinate in between to ensure a good bond between the silver meshes and the electrodes. The cell was secured between two inconel bushings with mica gaskets. Silver current leads were affixed to the two silver meshes. The cell was placed inside a furnace. The test stand was designed to maintain the seals (gaskets) under a spring loading with springs outside the furnace. Hydrogen as a fuel was bubbled through water maintained at ~33°C and circulated past the anode, and ambient air was circulated past the cathode. The cells were tested at 800°C. The reduction of NiO into Ni was accomplished in-situ. The cell performance was measured using an electronic load.

RESULTS AND DISCUSSION

Figure #1 shows a typical scanning electron micrograph of a fractured cell. The cathode and the electrolyte thicknesses were typically ~50 µm and ~10 µm, respectively. The anode thickness was varied between ~1.04 mm and ~3.86 mm. Figure #2 shows the experimentally measured $V$ vs. $i$ traces for seven different cells with varying anode thicknesses. As evident in these traces, the $V$ vs. $i$ traces are nonlinear; concave up ($d^2V/di^2 > 0$) at low current densities and convex up ($d^2V/di^2 < 0$) at high current densities. The short circuit current density varies between ~3.56 A/cm$^2$ for a cell with an anode thickness of 3.86 mm and ~6.35 A/cm$^2$ for a cell with an anode thickness of 1.04 mm. Figure #3 shows the corresponding power density vs. $i$. The maximum power density varies between ~1.1 W/cm$^2$ for the thickest cell and ~1.9 W/cm$^2$ for the thinnest.

Recent work has shown that the $V$ vs. $i$ traces can be adequately described by [5]

$$V(i) = E_o - iR_i - a - b\ln i + \frac{RT}{4F}\ln\left(1 - \frac{i}{i_{cs}}\right) + \frac{RT}{2F}\ln\left(1 - \frac{i}{i_{as}}\right) - \frac{RT}{2F}\ln\left(1 + \frac{p_H^0}{p_H^0\delta_{as}}\right)$$  \hspace{1cm} (1)

for $i >> i_o$ where $i_o$ is the effective exchange current density. In equation (1), $E_o$ is the open circuit voltage, $R_i$ is the area specific resistance of the cell (which is predominantly that of the electrolyte), $a$ & $b$ are the Tafel parameters wherein it is assumed that the activation polarization can be adequately described by the Tafel equation, $i_{cs}$ is the cathode-limiting current density which results when the partial pressure of oxygen at the cathode/electrolyte interface is nearly zero, $i_{as}$ is the anode-limiting current density which occurs when the partial pressure of hydrogen at the anode/electrolyte interface is nearly zero, $p_H^o$ is the partial pressure of hydrogen in the fuel (outside of the anode), $p_H^{o,0}$ is partial pressure of water vapor in the fuel (outside of the anode), $R$ is the gas constant, $F$ is the Faraday constant, and $T$ is the temperature. The $i_{cs}$ and $i_{as}$ are related to the effective binary diffusion coefficients, $D_{eff(c)}$ for the cathode (between O$_2$ and N$_2$) and $D_{eff(a)}$ for the anode (between H$_2$ and H$_2$O), respectively, by

$$i_{cs} = \frac{4Fp_H^oD_{eff(c)}}{p - p_H^o}\left(\frac{RT_i}{p}\right)$$  \hspace{1cm} (2)
Figure 1. A scanning electron micrograph of a typical anode-supported cell.

and

\[ i_{as} = \frac{2FP_{H_2}D_{eff(a)}}{RTl_a} \]  

where \( l_c \) is the cathode thickness, \( l_a \) is the anode thickness, \( p_{O_2}^0 \) is the partial pressure of oxygen in the oxidant (outside of the cathode), and \( p \) is the total pressure of the oxidant (air). The effective binary diffusivities are related to electrode microstructural parameters by

\[ D_{eff(c)} = \frac{V_v(c)D_{O_2-N_2}}{\tau_c} \]  

and

\[ D_{eff(a)} = \frac{V_v(a)D_{H_2-H_2O}}{\tau_a} \]

where \( D_{O_2-N_2} \) and \( D_{H_2-H_2O} \) respectively are the binary diffusivities of \( O_2-N_2 \) and \( H_2-H_2O \), \( V_v(c) \) and \( V_v(a) \) respectively are the porosities of the cathode and anode, and \( \tau_c \) and \( \tau_a \) are respectively the tortuosity factors for the cathode and anode. Equation (1) is similar to the one given by McDougall [6] with the exception of the last term, namely

\[-\frac{RT}{2F}\ln\left(1 + \frac{p_{H_2}^0i}{p_{H_2O}^0i_{as}}\right)\]

which describes concentration polarization related to the out diffusion of water vapor through the anode.
Figure 2. Voltage, $V$, vs. current density, $i$, traces for anode-supported cells at 800°C with humidified hydrogen as the fuel and air as the oxidant. The anode thickness ranged between 1.04 and 3.86 mm.

The effective exchange current density, $i_o$, takes into account electrode kinetics for both electrodes, the cathode and the anode. In terms of the exchange current densities at the cathode, $i_c$, and at the anode, $i_a$, the effective exchange current density, $i_o$, is given by

$$i_o = \frac{i_c + i_a}{1 + \frac{i_c}{i_a}}$$

Clearly, if $i_c << i_a$, the estimated $i_o$ will be representative of the electrode kinetics at the cathode.

In the present case, $i_c << i_a$, thus, $i_c >> i_as$. As a result, equation (1) is not very sensitive to the choice of $i_c$. Thus, for $i >> i_o$, equation (1) can be given as

$$V(i) = E_o - iR_t - a - b \ln i + \frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}}\right) \frac{RT}{2F} \ln \left(1 + \frac{p_{H_2}^o i}{p_{H_2O}^o i_{as}}\right)$$

Alternatively, for $i << i_o$, the $V$ vs. $i$ is given by

$$V(i) = E_o - iR_t - \frac{RT}{4Ft_o} i + \frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}}\right) \frac{RT}{2F} \ln \left(1 + \frac{p_{H_2}^o i}{p_{H_2O}^o i_{as}}\right)$$
Figure 3. Power density vs. current density traces corresponding to the data in Figure 2.

The experimentally measured $V$ vs. $i$ traces were fitted to equation (7) and the corresponding parameters, namely, $a$, $b$, $R_i$ and $i_{as}$ were estimated. These parameters are listed in Table 1.

Table 1 shows that the ohmic area specific resistance of the cells, $R_i$, for five of the cells is about 0.074 $\Omega$cm$^2$, for one cell it is about 0.085 $\Omega$cm$^2$ and for one of them it is 0.046 $\Omega$cm$^2$. As the electrolyte thickness is about the same ($\sim$10 $\mu$m) in all cells, the $R_i$ is expected to be about the same for all cells. Thus, with the exception of one value of $R_i$, all other six are nearly the same, consistent with expectations.

For $i \gg i_o$, the activation overpotential, $\eta_{act}$, is related to the parameters $a$ and $b$ through the Tafel equation given by

$$\eta_{act} = a + b \ln i$$

where the $a$ and $b$ are of the form

$$a = -\frac{RT}{4\alpha F} \ln i_o \quad \text{and} \quad b = \frac{RT}{4\alpha F}$$

where $i_o$ is the effective exchange current density and $\alpha$ is the transfer coefficient. Thus, the exchange current density, $i_o$, can be estimated using the fitted parameters $a$ and $b$. It is to be noted that as given, the parameter $a$ has the factor $\ln i_o$ in it. Thus, the magnitude of $a$ depends on the choice of units for the current density. Table 1 also lists the estimated $i_o$ from curve-fitting of the experimental set of data.
Table 1 shows that the estimated $i_0$ is about 100 to 110 mA/cm$^2$, regardless of the thickness of the anode. This is not surprising since both the cathode and the anode are composite mixtures of respectively LSM + YSZ and Ni + YSZ with very fine microstructures. The theory of porous, mixed ionic electronically conducting (MIEC), single phase or composite, electrodes shows that above a certain threshold electrode thickness, the activation overpotential (or the polarization resistance) achieves a limiting value [7-10]. For electrode microstructural features (grain size and pore diameter) on the order of 1 μm, theoretical work has shown that the threshold value of electrode thickness is on the order of 20 to 25 μm [10]. In all of the cells tested, the cathode thickness was ~50 μm which is higher than the threshold value. The anode in each case was much thicker than the threshold value. Thus, the observation that the estimated effective exchange current density, $i_0$, was about the same for cells of different anode thicknesses is consistent with expectations. It is known that activation polarization on the cathode (LSM + YSZ) side is usually larger than that on the anode side (Ni + YSZ). Thus, the estimated $i_0$ is representative of charge transfer processes at the cathode. That is, the exchange current density on the anode side would be greater than the experimentally estimated one. Also, consistent with expectations, the transfer coefficient, $\alpha$, is also about the same for all cells. The estimated value of $i_0$ on the order of 100 mA/cm$^2$ is indeed very high and is a result of the highly efficient electrode design consisting of a mixture of LSM and YSZ [5,10].

The experimentally measured short circuit current density, $i_s$, given in Table 1, decreases with increasing anode thickness as expected. In general, the $i_s$ may or may not be limited by either of the electrodes. However, in the present case with relatively thick anodes, it is expected that the $i_s$ may be close to $i_{as}$. In general, it is expected that $i_s \leq i_{as}$, consistent with observations. The parameter which should depend upon the anode thickness is of course the anode limiting current density, $i_{as}$, which varies between 3.59 A/cm$^2$ for an anode thickness of 3.86 mm and 6.35 A/cm$^2$ for an anode thickness of 1.04 mm. Equation (3) gives a relation between the anode thickness and the $i_{as}$. If the effective binary diffusivity on the anode side, $D_{eff(a)}$, is a constant, it is expected that $i_{as}$ will vary inversely with $l_a$. From the $i_{as}$ from the curve fit of the data to equation (3), the $D_{eff(a)}$ was determined. As seen in Table 1, the $D_{eff(a)}$ varies between 0.31 cm$^2$/sec for the thinnest anode and 0.65 cm$^2$/sec for the thickest. If the only variation from cell to cell is the thickness of the anode, it would be expected that $D_{eff(a)}$ should be the same. However, the $D_{eff(a)}$ is seen to monotonically increase with the anode thickness by a factor of two over the range of anode thicknesses tested. There are a number of possible reasons responsible for this behavior. Firstly, it is possible that the morphology of the pore structure was not uniform through the thickness of the anode and varies as a function of position. Microstructural examination failed to reveal detectable differences from cell to cell. However, independent measurements of transport properties of porous anodes show that there can be significant differences in transport properties of porous bodies with small changes in microstructure. Thus, it is possible that there are differences in anode structures of different cells but are not readily discernible through microstructural examination. Secondly, the transport of gaseous species through porous bodies is a rather complex phenomena involving binary diffusion, Knudsen diffusion, surface diffusion, and viscous
Table I

| Anode Thickness | 1.04 mm | 1.44 mm | 1.90 mm | 2.48 mm | 2.95 mm | 3.46 mm | 3.86 mm |
|-----------------|---------|---------|---------|---------|---------|---------|---------|
| a (V)           | 0.115   | 0.0906  | 0.116   | 0.122   | 0.108   | 0.128   | 0.116   |
| b (V)           | 0.052   | 0.041   | 0.051   | 0.053   | 0.047   | 0.055   | 0.050   |
| \(\alpha\)      | 0.445   | 0.563   | 0.453   | 0.436   | 0.492   | 0.42    | 0.462   |
| \(i_o\) (mA/cm²)| 110     | 109     | 103     | 100     | 98      | 98      |         |
| \(R_t\) (Ωcm²)  | 0.046   | 0.074   | 0.085   | 0.075   | 0.075   | 0.073   | 0.073   |
| \(i_s\) (A/cm²) | 6.35    | 5.9     | 4.69    | 4.38    | 4.05    | 3.75    | 3.56    |
| \(i_as\) (A/cm²)| 6.35    | 6.25    | 4.7     | 4.4     | 4.1     | 3.78    | 3.59    |
| \(D_{eff(a)}\) (cm²/sec) | 0.31 | 0.42 | 0.42 | 0.53 | 0.56 | 0.61 | 0.65 |
| \(-A\) (Ωcm²)   | 0.404   | 0.399   | 0.557   | 0.522   | 0.536   | 0.581   | 0.518   |
| \(R_t + \frac{RT}{4F_i_o}\)  | 0.402   | 0.434   | 0.506   | 0.516   | 0.532   | 0.554   | 0.566   |
| \(\frac{RT}{2F_{as}}\) \left\{1 + \frac{p_{H_2}}{p_{H_2O}}\right\} |         |         |         |         |         |         |         |
| Maximum Power Density (W/cm²) | 1.90 | 1.56 | 1.31 | 1.28 | 1.25 | 1.18 | 1.11 |

flow. The analysis upon which equations (1) through (3) are based assumes binary diffusion as the only mode of gas transport through porous anodes. This may be an oversimplification and that the observed (apparent) dependence of \(D_{eff(a)}\) on the anode thickness may be related to the neglect of other modes of transport. Nevertheless, the estimated values of \(D_{eff(a)}\) are consistent with expectations based on the binary diffusivity \(D_{H_2-H_2O}\), the porosity, and the tortuosity factor [5].

The current density-dependent area specific cell resistance for \(i \ll i_o\) is given by

\[
R(i) = -\frac{dV(i)}{di} = R_t + \frac{RT}{4F_{i_o}} + \frac{RT}{4F} \left\{ \frac{2}{(i_{as} - i)} + \frac{2}{\left(\frac{p_{H_2O}}{p_{H_2}} - \frac{i_{as}}{i_{as} + i}\right)} \right\}
\]

(11)

which is obtained by differentiating equation (8) with respect to \(i\). As \(i \to 0\), equation (11) reduces to

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\[ R(i \rightarrow 0) = R_i + \frac{RT}{4F_i} + \frac{RT}{2F_{i_{as}}} \left( 1 + \frac{p_{H_2}^0}{p_{H_2O}^0} \right) \] (12)

Equation (12) essentially is the magnitude of the slope of \( V \) vs. \( i \) as \( i \rightarrow 0 \). The third term on the right hand side of equation (12) is the concentration polarization term and arises due to the resistance to the transport of water vapor away from the anode/electrolyte interface. This equation shows that the lower the \( p_{H_2O}^0 \), that is the drier the fuel, the greater is this concentration polarization at low current densities. In the current tests, the water content was ~5%. That is, the ratio \( p_{H_2}^0 / p_{H_2O}^0 = 95/5 = 19 \).

The \( V \) vs. \( i \) traces given in Figure #2 were also fitted to a polynomial
\[ V(i) = E_o + \sum_{n=1} A_n i^n \] (13)

Then, the area specific resistance at zero current density is the negative of the coefficient \( A_1 \). This must be equal to
\[ -A_1 = R(i \rightarrow 0) = R_i + \frac{RT}{4F_i} + \frac{RT}{2F_{i_{as}}} \left( 1 + \frac{p_{H_2}^0}{p_{H_2O}^0} \right) \] (14)

Table 1 lists the \(-A_1\) from the polynomial fit to the \( V \) vs. \( i \) traces as well as the estimated \( R(i \rightarrow 0) \) from the curve fit to the \( V \) vs. \( i \) traces in accordance with equation (7). It is seen that the agreement is quite good between two different types of curve fit to the data; one based on the theoretical model with four parameters, and the other a polynomial fit.

The curve fitting of the experimental data to equation (7) has four parameters. However, of these, only two \((a\) and \(b\)) need be adjustable parameters since there is an independent check for the other two \((i_{as}\) and \(R_i\)). For very thick anodes, it is expected that \(i_{as}\) will be close to the experimentally measured short circuit current density, \(i_s\). The electrolyte thickness was about 10 \(\mu m\). The ionic resistivity of YSZ at 800°C is about 70 \(\Omega cm\). Thus, the estimated value of \(R_i\) is ~0.07 \(\Omega cm^2\), in good agreement with the curve fit to the experimental set of data.

Figure #3 and Table 1 show that the maximum power density measured was in excess of 1 W/cm² even for an anode of 3.86 mm thickness. For the thinnest anode (1.04 mm), the maximum power density was about 1.9 W/cm². This shows that very high power densities can be realized in anode supported cells with relatively thick and rugged anodes.

**SUMMARY**

Anode-supported single cells with anode thickness approaching 4 mm were fabricated and tested at 800°C. Maximum power density in excess of 1 W/cm² was measured at 800°C with humidified hydrogen as the fuel and air as the oxidant for a cell with an anode thickness of 3.86 mm. Although the actual anode thickness in prospective SOFCs is considerably smaller, the present work shows that it is possible to fabricate a high power...
density, rugged anode-supported cells. The anode thickness of the thinnest cell was 1.04 mm which exhibited a maximum power density of 1.9 W/cm². The \( V \) vs. \( i \) traces were fitted to a previously developed model. From the curve-fit to the experimental data, the ohmic area specific resistance, \( R_h \), the effective exchange current density, \( i_o \), and the effective binary diffusivity (for \( \text{H}_2-\text{H}_2\text{O} \)) on through the porous anode, \( D_{\text{eff}(\alpha)} \), were estimated.

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