THE EFFECT OF ELECTRODE MICROSTRUCTURE ON CATHODIC POLARIZATION

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ABSTRACT

Ni + yttria-stabilized zirconia (YSZ)-anode-supported cells with a thin YSZ electrolyte and Sr-doped LaMnO₃ (LSM) + YSZ composite cathode were fabricated. Volume fractions of LSM and YSZ in the composite cathode were varied over a wide range. Cell performance was measured at 800°C with hydrogen as fuel and air as oxidant. Cathode microstructures were characterized by quantitative stereology to estimate the three phase boundary (TPB) length, porosity and the aggregate grain size of YSZ in the cathode. Measured polarization was correlated with microstructure. Experimental results are in reasonable agreement with the previously published theoretical model. The intrinsic charge transfer resistivity, $\rho_{ct}$, at LSM/YSZ/air TPB was determined as $\sim 1.0 \times 10^5 \Omega \text{cm}$ at 800°C.

INTRODUCTION

Recent work has demonstrated high performance, intermediate temperature (800°C), anode-supported solid oxide fuel cells (SOFC). For example, maximum power densities approaching 2 W/cm² in single cells operating at 800°C with humidified hydrogen as fuel and air as oxidant have been demonstrated by two research groups, and power densities exceeding 1 W/cm² have been achieved by several research groups (1,2). Common to all of these reported studies are the following features: (a) Electrolyte is a thin (~10 μm) film of yttria-stabilized zirconia (YSZ) supported on a porous Ni + YSZ anode of a thickness between ~200 μm and ~1-2 mm. (b) Cathode is a porous mixture of strontium-doped lanthanum manganite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, or LSM, and YSZ. A composite cathode of LSM + YSZ has been shown to exhibit much lower overpotential than single phase LSM, both experimentally as well as theoretically. Analysis of electrode polarization shows that composite electrodes comprising mixtures of an electronically conducting electrocatalyst and an oxygen ion conducting material are expected to exhibit much lower polarization as compared to single phase electrodes made of the electrocatalyst alone by virtue of the parallel paths for both ionic and electronic currents that exist in composite electrodes (3-6). Excellent performance of Ni + YSZ anode is in part due to the existence of parallel paths for electrons through Ni, and oxygen ions through YSZ. A logical extension of this concept leads to LSM + YSZ as the composite cathode. Indeed, excellent performance with LSM as the electrocatalyst can only be achieved provided an oxygen ion conductor, such as YSZ or ceria, is mixed with LSM.
While excellent performance has been demonstrated at 800°C using LSM + YSZ cathode and Ni + YSZ anode, it is known that the principal contribution to the total polarization is still from the cathode, which increases rapidly with a lowering of temperature. It is imperative that further improvements in cathode performance are necessary if the goal of achieving good performance at a temperature ~600°C or lower is to be realized. One possible approach is to search for a better electrocatalyst, and several efforts are currently underway to achieve this. In addition to this approach, however, it is clear that electrode microstructure has a profound effect on polarization. That is, in addition to searching for a better electrocatalyst, it is also necessary to understand the role of microstructure in electrode polarization. The ultimate goal is to develop a composite electrode wherein the electrocatalyst has an intrinsically high electrocatalytic activity, and the electrode microstructure has the desired morphology. While several studies have been reported on the use of composite electrodes, and their role in lowering polarization losses has been recognized in a qualitative manner, what is still lacking is an experimental verification of a quantitative relation between electrode polarization and electrode microstructure.

The present work was undertaken with the objective of relating electrode polarization to microstructure. The overall approach consisted of fabricating a number of cells, each with five layers; namely, (a) supporting anode, (b) anode interlayer, (c) electrolyte, (d) cathode interlayer, and (e) cathode current collector. The cells were made such that all cells had nearly identical supporting anodes, anode interlayers, electrolytes, and cathode current collectors. The cells differed in the compositions of cathode interlayers. Cell performance was measured at 800°C with hydrogen as fuel and air as oxidant. Differences in cell performance thus could be unequivocally attributed to differences in cathode interlayers. In order to correlate the observed performance differences to differences in interlayers, it was necessary to characterize the interlayers. This was done using techniques in quantitative stereology (7). Microstructural parameters estimated using stereological techniques were then used in combination with the theoretical model developed earlier, to estimate the fundamental electrocatalytic parameter governing the electrocatalytic activity of LSM on YSZ for the electrochemical reduction of oxygen into oxygen ions (4).

EXPERIMENTAL PROCEDURE

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

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

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

Color-coded micrographs of the cathode interlayers were used for quantitative stereological measurements. The parameters of specific interest are: (a) Grain (actually grain aggregate) size of YSZ in the cathode interlayer, \( d \), (b) Porosity of the cathode interlayer, \( V_v \), and (c) Three phase boundary (TPB) line length in the cathode interlayer, \( l_{TPB} \). The grain aggregate size, \( d \), of the YSZ in the cathode interlayer can be related to the average intercept length determined by repeatedly applying a test line on the micrographs (7). For the determination of the average intercept length, a test line of equivalent length ~8 \( \mu m \) was applied on micrographs of each cathode interlayer up to 50 times (7). The \( V_v \) was measured by a systematic point count procedure wherein a 25 point grid was applied on each micrograph up to 50 times. Similarly, volume fractions of LSM and YSZ in the cathode interlayer were also estimated. The average TPB line length, \( l_{TPB} \), was estimated by measuring number of three phase boundary (TPB) points per unit area of each micrograph, \( P_A \) (7). The experimentally measured parameters are as follows.

\[
P_p(V_v) = \text{Fraction of points falling on the porous regions of the cathode interlayer} = V_v \quad \text{(volume fraction of porosity)}.
\]
\[
P_p(\text{LSM}) = \text{Fraction of points falling on LSM in the cathode interlayer} = V_{\text{LSM}} \quad \text{(volume fraction of LSM)}.
\]
\[
P_p(\text{YSZ}) = \text{Fraction of points falling on YSZ in the cathode interlayer} = V_{\text{YSZ}} \quad \text{(volume fraction of YSZ)}.
\]

A test line was applied and the number of intersections with boundaries of YSZ grain aggregates were measured. This measurement is \( P_L \) in units of 1/length. The surface area
of YSZ grains per unit volume is given by \( S_Y = 2P_L \) (7). Finally, the grain aggregate diameter is given by \( d = 3V_{YSZ} / P_L \).

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

**RESULTS**

Figure 1 shows typical voltage vs. current density traces for two cells tested at 800°C with humidified hydrogen and air. Note that cell performance is dependent on cathode interlayer composition, with the maximum power density ranging between \(-0.35\) W/cm\(^2\) and \(-1.1\) W/cm\(^2\), depending upon the cathode interlayer composition. Figure 2 shows a plot of the maximum power density measured as a function of wt.% LSM in the cathode interlayer.

Figure 3 is a photomicrograph of the cathode interlayer of composition 35 wt.% LSM and 65 wt.% YSZ, obtained on Cameca SX 50 electron microprobe. The length and width of the micrograph are \(\sim 18.3\) \(\mu\)m and \(\sim 13.6\) \(\mu\)m, respectively. White areas are YSZ, gray areas are LSM, and black regions represent porosity. Table I lists results of the microstructural measurements made on the cells tested.

**DISCUSSION**

Figure 2 shows that the maximum power density depends on the composition of the cathode interlayer, all other factors remaining the same. Table I shows that there is a significant variation in the microstructural parameters as a function of cathode interlayer composition, the most notable being the three phase boundary length, \( l_{TPB} \), which varies between \(\sim 1780\) and \(\sim 6550\) cm\(^{-1}\). Also of interest to note is that the YSZ aggregate grain size, \( d \), of the sample with the least amount of LSM was one and a half to three times that of the other samples. The cathode interlayer compositions were chosen such that all three

| Cathode Interlayer Composition | \( V_Y \) | \( V_{LSM} \) | \( V_{YSZ} \) | \( d = 3V_{YSZ} / P_L \) (cm) | \( l_{TPB} = P_A / P_L \) (cm\(^{-1}\)) |
|---|---|---|---|---|---|
| 25wt.%LSM, 75wt.%YSZ | \(-0.185\) | \(-0.206\) | \(-0.609\) | \(-2.13 \times 10^4\) | \(-1782\) |
| 35wt.%LSM, 65wt.% YSZ | \(-0.185\) | \(-0.287\) | \(-0.528\) | \(-1.57 \times 10^4\) | \(-5173\) |
| 40wt.%LSM, 60wt.% YSZ | \(-0.192\) | \(-0.323\) | \(-0.485\) | \(-1.41 \times 10^4\) | \(-6547\) |
| 50wt.%LSM, 50wt.% YSZ | \(-0.194\) | \(-0.406\) | \(-0.4\) | \(-9.3 \times 10^5\) | \(-3115\) |
| 60wt.%LSM, 40wt.% YSZ | \(-0.144\) | \(-0.514\) | \(-0.342\) | \(-6.54 \times 10^5\) | \(-1945\) |
phases are contiguous. The contiguity of LSM was confirmed by measuring the in-plane resistance of the cathode interlayer. Specifically, it was ensured that the layer was not insulating at room temperature, which would have been the case had LSM not been contiguous. The $V_{VSSZ}$ was above 0.34 in all samples, and thus is expected to be contiguous. The $V_Y$ was between $-0.14$ and $-0.19$. For a random distribution of near spherical particles, the usual guideline for contiguity is that the volume fraction of a given phase be in excess of $-0.3$ (the percolation threshold). This condition is not satisfied. However, it is to be noted that in a typical sintered compact, porosity is usually along three grain junctions of a three dimensional, polyhedral packing, which is in the form of cylindrical, not spherical, pores. It is well known that porosity in a sintered compact becomes isolated (noncontiguous) below about 6% (0.06 on a volume fraction basis). As the porosity in the cathode interlayer is well in excess of the minimum (~0.06), the porosity was indeed contiguous. The porosity in the rest of the cathode current collector layer, anode interlayer, and the supporting anode structure was well in excess of 20%, and thus was contiguous.
Figure 3: An electron probe micrograph of the cathode interlayer from one of the cells.

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

$$W_{LSM} = \frac{\lambda_{LSM} V_{LSM}}{\lambda_{LSM} V_{LSM} + \lambda_{YSZ} V_{YSZ}}$$  \[1\]

or

$$\frac{1}{W_{LSM}} = 1 + \frac{\lambda_{YSZ}}{\lambda_{LSM}} \frac{V_{YSZ}}{V_{LSM}}$$  \[2\]

where $\lambda$'s are the respective densities. Thus, a plot of $1/W_{LSM}$ vs. $V_{YSZ}/V_{LSM}$ should be a straight line with slope $= \lambda_{YSZ}/\lambda_{LSM}$, and intercept $= 1.0$. Figure 4 shows that a plot of $1/W_{LSM}$ from the as-formulated cathode interlayer, vs. $V_{YSZ}/V_{LSM}$ obtained from microstructural measurements, is indeed a straight line. The slope of the line is $\sim 1.02$. It is known that the densities of YSZ and LSM, are respectively, $\sim 5.9$ and $\sim 6.5$ g/ml., the ratio of which is $\sim 0.91$, in reasonable agreement with expectations. Also note that the intercept is $\sim 0.986$, which is very close to the expected value of unity.

The effect of electrode microstructure on charge transfer at three phase boundaries in composite electrodes was theoretically analyzed by Tanner et. al. who showed that the effective charge transfer resistance, $R_{ct}^{eff}$, of a composite electrode is given by (4)

$$R_{ct}^{eff} = \frac{R_{ct} \rho_{YSZ} d}{(1 - V_{\ell})}$$  \[3\]

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

$$R_{ct} = \frac{\rho_{ct}' \delta}{\varepsilon l_{TPB}} \quad [4]$$

The parameters $\delta$ and $\varepsilon$ are on the order of a few angstroms, dimensions over which the actual charge transfer reaction occurs. Parameters, $\rho_{ct}'$, $\delta$ and $\varepsilon$ are not separable from each other. Thus, one can define an intrinsic charge transfer resistivity, $\rho_{ct}$, by

$$\rho_{ct} = \frac{\rho_{ct}' \delta}{\varepsilon} \quad [5]$$

and the intrinsic charge transfer resistance is then given by

$$R_{ct} = \frac{\rho_{ct}}{l_{TPB}} \quad [6]$$

Substitution of $R_{ct}$ in equation [3] gives

$$R_{ct}^{\text{eff}} = \sqrt{\rho_{YSZ} \rho_{ct}} \sqrt{\frac{d}{(1-V_v)_{TPB}}} \quad [7]$$

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

$$R_{cell} = R_{other} + R_{ct}^{\text{eff}} = R_{other} + \sqrt{\rho_{YSZ} \rho_{ct}} \sqrt{\frac{d}{(1-V_v)_{TPB}}} \quad [8]$$

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

Table II lists the measured \( R_{cell} \) and the microstructural parameter \( \sqrt{d / \left( (1 - V_v) \right)} \). Figure 5 is a plot of \( R_{cell} \) vs. \( \sqrt{d / \left( (1 - V_v) \right)} \). The slope of the plot is \( \sim2110 \ \Omega \text{cm} \) with a regression coefficient of \( \sim0.98 \). The ionic resistivity of YSZ at 800°C is about 40 \( \Omega \text{cm} \). Thus, the estimated value of the charge transfer resistivity, \( \rho_{ct} \) is \( \sim1.11 \times 10^5 \ \Omega \text{cm} \).

This is an interesting result in that it has been possible to estimate the fundamental parameter, which determines charge transfer characteristics at a LSM/YSZ/air three phase boundary. This suggests that a correct comparison between two electrocatalysts can only be made on the basis of \( \rho_{ct} \), which is free from any microstructural effects. The other interesting point is that the present results clearly and quantitatively emphasize the importance of electrode microstructure, and the role of composite electrodes. It shows, for example, that through appropriate electrode microstructures, it is possible to achieve very low overall electrode polarization even if the intrinsic charge transfer characteristics, as expressed through \( \rho_{ct} \), are not particularly good. The intercept in Figure 5 should yield \( R_{other} \), the expected value of which is \( \sim0.1 \ \Omega \text{cm}^2 \), based on prior work (1). However, intercept in Figure 5 is \( \sim0.11 \ \Omega \text{cm}^2 \), which of course cannot be true. A possible reason is the scatter in data and the fact that cathodic polarization is the dominant factor. That is, since \( R_{other} \) is expected to be rather small, a negative intercept is believed to be merely due to scatter, and insufficient data. Thus, the slope appears to be reasonable, but the intercept is not. Although without any basis, one may plot \( R_{cell} \) vs. \( 1/l_{TPB} \), a typical procedure used in plotting data when the electrode is not a composite one (that is LSM on YSZ, rather than LSM + YSZ on YSZ), as done in Figure 6.
Figure 5: A plot of the experimentally measured $R_{cell}$ vs. $\sqrt{d/(1-V_v)}_{TPB}$.

Even though the intercept is reasonable, the corresponding regression coefficient is only $-0.84$, indicating a poorer fit. If the last data point is ignored, the fit will be considerably better, although then the intercept is not reasonable. In any event, there is no basis to ignore this point. It is thus concluded that the composite model offers a better fit to the data, although considerably more data are needed for an unequivocal assertion.

In the preceding, it was assumed that activation polarization, $\eta_{act}$, is linearly dependent on $i$, and can be expressed in terms of $R_{cell}^{eff}$. At high current densities, it is expected that
\( \eta_{act} \) may be linearly related to \( \ln i \) through the Tafel equation. If such is the case, the mathematical relationship between \( \eta_{act} \) and microstructure will be different from the one implied in equation [8]. Nevertheless, it is clear that the role of electrode microstructure will be equally profound, regardless of the details of relationship between \( \eta_{act} \) and \( i \).

**SUMMARY**

The present work shows that electrode microstructure has a profound effect on polarization, and thus on cell performance. Anode-supported single cells were made with varying amounts of LSM and YSZ in cathode interlayers. Cell performance was strongly dependent on the cathode interlayer composition. Cathode interlayer microstructure was quantitatively analyzed by quantitative stereology, which was used to estimate volume fraction porosity, \( V_v \), aggregate grain size of YSZ, \( d \), and three phase boundary (TPB) line length, \( l_{TPB} \), in the cathode interlayer. The previously developed theoretical model affords the definition of an effective charge transfer resistance, \( R_{ct}^{eff} \), a measure of electrode activation polarization, which depends linearly on the microstructural parameter, \( \sqrt{d/(1-V_v)l_{TPB}} \) (1,4). From a plot of \( R_{cell} \) vs. \( \sqrt{d/(1-V_v)l_{TPB}} \), the fundamental charge transfer parameter, \( \rho_{ct} \), which defines the nature of charge transfer at LSM/YSZ/air TPB, was determined to be \( \sim 1.0 \times 10^5 \Omega \text{cm} \) at 800°C. A realistic comparison between various electrocatalyst/electrolyte pairs would require the measurement of \( \rho_{ct} \).

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