OXYGEN REDUCTION AT A STABILIZED ZIRCONIA INTERFACE WITH
$Y_{1-x}Ca_xMnO_3$ OR $La_{1-x}Sr_xMnO_3$ CATHODE MATERIALS

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ABSTRACT

Impedance spectroscopy, combined with an unbonded interface cell, has been used to assess oxygen reduction behavior at interfaces between an yttria-stabilized zirconia electrolyte and perovskite or platinum cathode materials. Intrinsic oxygen reduction specific activities of $Y_{1-x}Ca_xMnO_3$ ($x = 0.5, 0.6$ and $0.7$) and $La_{1-x}Sr_xMnO_3$ ($x = 0.1$ and $0.3$) were determined as a function of temperature and oxygen partial pressure, independent of the interface morphology. The overall cathodic interfacial polarization consists of two or more fundamental processes. In the temperature range of 900-1000°C and in air, the operating conditions for a solid oxide fuel cell, charge transfer and oxygen dissociation processes were approximately equivalent relative to the overall oxygen reduction kinetics.

1. INTRODUCTION

The performance of high-temperature solid oxide fuel cells (SOFC) is often dependent upon the kinetics of the electrochemical processes that occur at solid-gas interfaces between the cathode and electrolyte. The performance of a SOFC can be limited by low or deteriorating rates of oxygen reduction at this interface. Changes in these interfaces can alter both reaction mechanisms and kinetics.

Oxygen reduction rates at the cathode-electrolyte interface depend upon:
(1) the rate at which reacting constituents arrive at reaction sites, (2) the number of available reaction sites, (3) the temperature and activation energy for reaction, and (4) the oxygen activity at the reaction sites. The first depends on diffusion pathways through the cathode material (cathode morphology) and is critical in SOFC design and performance. The second also will initially depend upon morphology. This research is directed at understanding and optimizing the intrinsic electrochemical properties of the cathode-electrolyte interface independent of morphology effects. This paper examines the effects of temperature, oxygen partial pressure $p(O_2)$ and material composition on the oxygen reduction behavior.

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Choice of cathode materials can be of significant importance in minimizing the cathodic contribution to the overall polarization resistance in an SOFC, which can be as high as 75% of the overall value depending on SOFC design.\(^7\) Anodic performance, diffusional processes, and electrolyte conductivity also contribute to the overall polarization. It is desirable to reduce the cathodic polarization, thereby improving cell performance.

2. IMPEDANCE SPECTROSCOPY & UNBONDED INTERFACE CELL

An experimental method was developed to quantify the intrinsic cathodic performance of electrode materials. The method utilized ac impedance measurements in conjunction with an unbonded interface cell (UIC) design. In this cell design, a small pellet of electrode material with a flat, roughened surface was pressed against a similarly roughened electrolyte material. It is estimated that the rough mating surfaces made only a few electrical contact points per cross-sectional area. The surrounding gas atmosphere had sufficient access to the contact points to uniformly reach the physical boundary line between the solid and gas phases. This boundary line is called the triple phase boundary (tpb). The length of the tpb is proportional to a localized surface region at which oxygen reduction takes place.\(^2,3\) This reaction surface is referred to as the "effective reaction length" (ERL) and can be determined \textit{in situ} using impedance spectroscopy (IS). It also can be determined by direct measurement of the circumference of a single point contact electrode\(^4\) or by \textit{post mortem} examination by SEM.\(^5\)

Once the ERL has been determined for a particular interface, the electrochemical activity can be determined independently of the surface morphology. The normalized reaction rate, herein called the specific activity (Sp Act), is defined by:

\[
\text{Sp Act} = (\text{ERL} \times R_p)^{-1} \quad \text{(S/cm)}
\]

where \(R_p\) is a polarization resistance obtained from IS measurements. The specific activity, with units of electrical conductivity, is an intrinsic material property independent of morphology.

For electrode-electrolyte surfaces with multiple point contacts separated by distances that are large in comparison to the radii \(r_i\) of the point contacts, the net contact resistance for \(i\) parallel point contact resistances is given by the expression:\(^6\)

\[
R_c = (4\sigma \sum r_i)^{-1}
\]

where \(\sigma\) is the ionic conductivity of the electrolyte. Taking the ERL as the total length of tpb between surfaces with multiple point contacts as \(2\pi \sum r_i\), the ERL can be expressed as:

\[
\text{ERL} = \pi/(2\sigma R_c)
\]
When using the UIC design, $R_c$, $R_p$, ERL and Sp Act can be determined \textit{in situ} from a single IS scan as a function of temperature, oxygen partial pressure $p(O_2)$, applied dc potential, time and material composition.

Specification of a maximum cathodic polarization resistance, $R_p^c$, also defines the minimum specific activity for cathode materials, following Equation (1). For a thin, porous oxide cathode material sintered onto a dense zirconia electrolyte, a typical value of the specific ERL, i.e., the ERL divided by the sample cross-sectional area, is $10^3 \text{ cm/cm}^2$, although this value can vary considerably.\textsuperscript{1,5} For $R_p^c$ limited to 0.2 $\Omega\text{-cm}^2$ and using a value of specific ERL = $10^3 \text{ cm/cm}^2$, the limit on the cathodic specific activity is given by:

$$\text{Sp Act} \geq \frac{1}{0.2 \text{ cm}^2}(10^3 \text{ cm/cm}^2) = 0.005 \text{ S/cm}$$

(4).

This minimum value for specific activity, an intrinsic material property, provides a useful benchmark by which suitability of cathode compositions may be assessed. Clearly, a low and stable cathodic polarization resistance, acceptable for SOFC cathode-electrolyte interfaces, requires both a high and stable specific activity and ERL.

Several kinetic studies of the oxygen reduction process on perovskite cathode materials have been reported with some disagreement on how the electrode reaction proceeds and/or what process is rate limiting, i.e., charge transfer, oxygen dissociation or oxygen diffusion.\textsuperscript{8,9} Experimental evidence obtained in the operating range of a SOFC cathode (900-1000°C and $p(O_2)$ = 0.2 atm) indicates that these processes are about equivalent in limiting the overall oxygen reduction kinetics.

3. EXPERIMENTAL

The cathode materials tested were $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5$, 0.6 and 0.7), $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.1$ and 0.3) and platinum. Starting powders were prepared by the Pechini process,\textsuperscript{10} the glycine-nitrate process\textsuperscript{11} or conventional oxide mixing. The cathode and electrolyte materials are identified in Table 1. Discs were pressed from these powders and sintered to at least 90% of full density. XRD and microstructural examination by SEM of the sintered materials indicated the presence of a single crystalline phase. Small pellets ($\approx 5$ mm dia. x 1 mm thick), core-drilled from the discs, were mounted in the UIC configuration, which is depicted in Figure 1. For reference, a platinum bead cathode material also was tested.

In the UIC design, the sample pellet is pressed against an yttria-stabilized zirconia electrolyte disc (8YSZ). Mating surfaces were roughened by grinding with a 15 $\mu$m diamond wheel. Typical roughened surfaces, as examined by SEM, are shown in Figure 2 for a cathode material and the 8YSZ electrolyte. Only about 10 to 20 actual electrical contacts occur between such surfaces. The counter and reference electrodes, on the backside of the 8YSZ electrolyte disc, were made from sintered platinum paste and mesh.
The cell, in the three electrode configuration, was mounted inside an alumina tube in a furnace and heated in an appropriate flowing gas mixture (argon and air or oxygen). Complex impedance spectra (IS) were collected over a frequency range 0.6 Hz to 60 kHz. To match SOFC operating conditions as closely as possible, the p(O_2) was varied from 1.0 to 10^-4 atm and the temperature was varied from 700 to 950°C. Since the interface was unbonded, the cathode sample could be exchanged at the conclusion of each run without changing the 8YSZ electrolyte.

4. RESULTS AND DISCUSSION

In Figure 3, a typical IS scan is shown as a Bode plot when using the UIC design. The phase angle variation with frequency suggests at least three peaks centered at about 1, 500 and 20,000 Hz. The IS data were analyzed using the non-linear least squares (NLLS) fitting program EQUIVCRT\textsuperscript{12} with either an LR(RQ)(RQ)(RQ) or an LR(RQ)\textsuperscript{4} equivalent circuit model as shown in Figure 4. For the data shown in Figure 3, the latter model was used. It revealed that the broad lower frequency peak actually was made up of two overlapping peaks centered at about 0.3 and 7 Hz. In these models, the L component is a system inductance in series with the UIC and not connected with the oxygen reduction reaction. The first R, in series with L, represents the contact resistance R_c used to calculate the ERL via Equation (3). The remaining R's and Q's, within the parentheses, represent the resistive-like and capacitive-like oxygen reduction characteristics. The specific activity values for oxygen reduction were calculated by Equation (2) from the calculated ERL values and the overall polarization resistance R_p where R_p = \Sigma R_i from the model-fits.

The specific ERL values fell within a range 0.89 to 2.48 cm/cm\textsuperscript{2}, as listed in Table 2. Values of R_c were independent of p(O_2), but its temperature dependence was essentially that of the zirconia electrolyte. According to Equation (3), the ERL should be temperature independent, as observed and as expected for a physical tpb. The platinum bead ERL calculated from the IS data (0.15 cm) agreed within 20% of the circumference of the bead tip directly measured by SEM. These observations indicate that Equation (3) produces reliable estimates of the ERL for the UIC design.

To present an overview of the specific activity temperature dependence, only the values at 900 and 1000°C in air are presented in Table 2. The 1000°C values were projected from measured values of the specific activity, which gave a straight line when plotted as a function of 1000/T over the 700 to 950°C range. In the SOFC operating range, all of the tested perovskites have intrinsic specific activity values that exceed the 0.005 S/cm benchmark. Also, the specific activity values for the perovskite materials exceeded those for platinum by at least an order of magnitude. The LS3M specific activity values, the highest measured, were about a factor of four higher than those for LS1M. Although the LS1M specific activity value just exceeded the 0.005 S/cm benchmark at 900°C, the LS3M specific activity exceeded this limit down to 800°C. The specific activity values for the three YCxM compositions fell between those for LS3M and LS1M and showed little difference between each other.
in the 900-1000°C temperature range, although their temperature dependencies were slightly different.

Figures 5(a-c) and 6 are isothermal or isobaric Nyquist plots of the IS data for the YC6M and LS3M cathode materials. In general, the overall shapes of the IS curves for these materials were similar with changes in temperature and p(O₂). It was also apparent that the overall polarization was composed of at least a higher and a lower frequency process. In Figure 5a at 900°C with p(O₂)=1.0 atm, it is observed that the high (HF) and low (LF) frequency peaks have similar sizes; while in Figure 5b, with p(O₂)=0.01 atm, the LF peak dominates the overall polarization more and more as the temperature is lowered from 900 to 700°C.

It was observed that the resistance values R₁ and R₂ obtained from the NLLS model-fits, could be added together to give an effective HF process polarization and via Equation (1) to give an individual process specific activity. Likewise, R₃ and R₄ could be added to give an effective LF process polarization and individual process specific activity. In Figure 5c for the YC6M material at 900°C, typical deconvolution arcs are indicated by dashed lines, which explicitly show that the HF process arcs were p(O₂) independent while the LF process arcs depended upon p(O₂). The model-fits indicate similar behavior for the other materials, as can be visualized in the Nyquist plot for the LS3M material at 900°C shown in Figure 6. In these figures, the p(O₂) independence of Rᵥ discussed earlier, also is demonstrated.

For the YCxM and LS3M materials, the p(O₂) dependencies at 900°C of the separated HF and LF process specific activity values are shown in Figure 7. In the p(O₂) range of 1.0 to 0.01 atm, the HF specific activity values were constant, while the LF specific activities decreased as p(O₂) was decreased. If the LF process specific activity values are assumed to vary as p(O₂)ⁿ, the n-values range from 0.4 to 0.9 with the slopes gradually decreasing as p(O₂) decreases. An n-value of 0.5 indicates that atomic oxygen concentration limited the reaction, while an n-value of 1.0 indicates that molecular-O₂ concentration limited the reaction. Thus, it appears that the rate limiting step for the LF process gradually shifts from control by atomic oxygen when p(O₂)=0.2 atm (air) to control by molecular-O₂ when p(O₂)≤10⁻² atm.

For p(O₂) values between 1.0 to 0.01 atm. and temperatures of 700 to 950°C, an Arrhenius plot of the separated HF and LF process specific activity values provided estimated activation energies for each cathode material, which are listed in Table 3. The HF (LF) process was characterized by an activation energy that fell within the 0.4 to 0.9 eV (1.4 to 1.8 eV) range. No dependence of the individual process activation energies on p(O₂) could be detected within the limits of the fairly large activation energy ranges.

The similar IS curve shapes and their similar temperature and p(O₂) dependence behavior suggests that both the HF and LF processes are the same for all the perovskite materials tested. Unfortunately, the HF and LF processes could not be resolved for the platinum IS data since the specific activity values were too low for reliable deconvolution. As the units of specific activity suggest, the HF and
LF specific activity values add together reciprocally to give the overall polarization specific activity. For instance from the LS3M specific activity values shown in Figure 7, HF Sp Act = 0.05 S/cm and LF Sp Act = 0.04 S/cm when p(O2) = 0.21 atm. When added reciprocally, these values give an overall specific activity of 0.022 S/cm, which is the value listed in Table 2 for LS3M at 900°C.

The component resistance values R1, R2, R3 and R4 obtained from NLLS modelling of the IS curves, had a rather high variance, especially for the higher temperature and/or p(O2) curves. Therefore, the HF and LF estimated activation energy values listed in Table 3 are subject to a large uncertainty, perhaps as large as ±20%. Nevertheless, the demarcation of the overall polarization into at least two or more fundamental processes with major differences in temperature and p(O2) dependence was clearly evident in all the perovskite IS data analyzed in this work.

Others have attempted to analyze the oxygen reduction reaction in terms of a single rate determining step (rds). For a porous La0.6Ca0.4MnO3/YSZ interface in air at 1000°C, Mizusaki, et al, indicated that monatomic oxygen surface diffusion with an activation energy 1.85 eV was the rds, not charge transfer. Also, by SEM examination and a geometrical model, they determined an “electrode conductivity” σE = 3.4 x 10^-4 S/cm, which is nearly two orders of magnitude smaller than the intrinsic specific activity values reported herein for YCxM’s and LSxM’s. We believe that either a reaction layer or possibly a perturbation of the interface by a dc potential was responsible for such a low specific activity value, but not a material composition effect.

Takeda, et al, using dc polarization measurements at 800°C in air to assess oxygen reduction for porous electrodes, reported that charge transfer was the rds for La(Sr)CoO3 while dissociation of O2 molecules was the rds for La(Sr)MnO3. They based their conclusions on analysis of the p(O2) dependence of the reciprocal polarization resistance, assuming a single dominant rds for each material. This is in disagreement with our findings that the overall polarization process generally consists of at least two somewhat equivalent processes as rate limiting in the SOFC operating temperature and p(O2) ranges.

Recently, others have concluded that the oxygen reduction process is more complex. Inoue et al, showed that the exchange current density (proportional to the reciprocal polarization resistance) dependence on p(O2) could shift from n=+1/4 to n=-1/4 for a transition from O2 dissociation to charge transfer as the rds. They observed such a transition for La(Sr)CoO3 at 600°C. Since the O2 dissociation process has a relatively large activation energy, it should dominate the overall reaction at higher temperatures, which they also observed.

Ostergard and Mogensen used IS to analyze oxygen reduction mechanisms for a porous La0.85Sr0.15MnO3/ZrO2-Y2O3 interface at 1000°C and obtained separation into three time constants similar to our results. Based on p(O2) and dc bias potential effects, they assigned the HF process to charge transfer, the medium frequency process to O2 dissociation, and the LF process to diffusion. Unlike their results,
however, we found the HF process to be $p(O_2)$ independent for all perovskite materials.

We tentatively assign the HF process to charge transfer, since its specific activity had a relatively low activation energy and no $p(O_2)$ dependence. We then assign the LF process to $O_2$ dissociation on the cathode material, since its specific activity had a relatively high activation energy and tended toward a linear dependence on $p(O_2)$ as the $p(O_2)$ was lowered. Continuing work will examine the effects of electrical current and potential to further elucidate the oxygen reduction reaction.

4. CONCLUSIONS

A method was developed to assess the intrinsic specific activity for oxygen reduction at a cathode-electrolyte interface independent of morphology. A benchmark specific activity value was defined. The intrinsic specific activity values of all the perovskite materials tested exceeded the benchmark value in the operating temperature and $p(O_2)$ range of a SOFC. The overall oxygen reduction process is composed of at least two or more fundamental processes. The rds can shift with change in temperature and/or $p(O_2)$, but in the SOFC operating range, it is likely that both charge transfer and oxygen dissociation are about equivalent in limiting the overall oxygen reduction reaction kinetics.

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TABLE 1  Cathode and Electrolyte Materials Identification

| Code | Composition                                      |
|------|--------------------------------------------------|
| 8YSZ | 8 mole% yttria-stabilized zirconia (Tosoh TZ8Y)  |
| YC5M | 50 mole% calcia-doped yttria manganite           |
| YC6M | 60 mole% calcia-doped yttria manganite           |
| YC7M | 70 mole% calcia-doped yttria manganite           |
| LS3M | 30 mole% strontium-doped lanthanum manganite     |
| LS1M | 10 mole% strontium-doped lanthanum manganite     |

TABLE 2  ERL, Specific ERL and Specific Activity Values for Tested Cathode Materials and Platinum

| Material | ERL(cm) | sp ERL (cm/cm²) | Sp Act* (at 900°C) | Sp Act* (at 1000°C) |
|----------|---------|----------------|--------------------|---------------------|
| YC5M     | 0.41    | 1.69           | 0.0097             | 0.027               |
| YC6M     | 0.23    | 0.89           | 0.0098             | 0.020               |
| YC7M     | 0.37    | 1.43           | 0.0105             | 0.023               |
| LS3M     | 0.32    | 2.48           | 0.022              | 0.058               |
| LS1M     | 0.39    | 1.22           | 0.0057             | 0.017               |
| Platinum | 0.15    | -              | 0.00054            | 0.0020              |

*with p(O₂) = 0.21 atm. (air)

TABLE 3  Temperature and p(O₂) Dependence of the Specific Activity Values for the Component HF and LF Polarization Processes

| Material | HF Eₚₑₓₑ (eV) | n | LF Eₚₑₓₑ (eV) | n |
|----------|---------------|---|---------------|---|
| YC5M     | 0.9           | 0 | 1.5           | 0.5 - 0.9 |
| YC6M     | 0.4           | 0 | 1.4           | 0.4 - 0.8 |
| YC7M     | 0.5           | 0 | 1.5           | 0.6 - 0.8 |
| LS3M     | 0.8           | 0 | 1.5           | 0.4 - 0.8 |
| LS1M     | 0.6           | - | 1.8           | - |
Figure 1. Unbonded Interface Cell (UIC) schematic.

Figure 2. Typical appearance of "mating roughened" surfaces (ground with 15 μm diamond) from a UIC. An 8YSZ electrolyte (LS3M cathode) surface is shown in the lefthand (righthand) SEM micrograph.
Figure 3. Typical IS scan shown as a Bode plot when using a UIC. The cathode sample was LS3M at 750°C with $p(O_2) = 0.01$ atm. Deconvolution of the polarization resistance spectra by NLLS model-fitting indicated four components with peaks centered at 0.3, 7, 500 and 20,000 Hz, as shown.

Figure 4. "Equivalent Circuit" model used for NLLS-fitting of IS data.
Figure 5. Temperature and $p(O_2)$ dependence of IS shapes for a YC6M cathode sample in a UIC. (a) 700, 800 and 900°C when $p(O_2) = 1.0$ atm.; (b) 700, 800 and 900°C when $p(O_2) = 0.01$ atm.; and (c) $p(O_2) = 1.0, 0.1$ and 0.01 atm. at 900°C. The frequency range 60 kHz (▲) to 1 Hz (●) is indicated. The high (low) frequency real axis intercept yields $R_c$ ($R_p$).
Figure 6. IS shapes for a LS3M cathode sample in a UIC at 900°C when p(O_2) = 1.0, 0.21 (air), 0.1 and 0.01 atm. The frequency range 60 kHz (△) to 1 Hz (○) is indicated.

Figure 7. The specific activity p(O_2) dependence of the high (HF) and low (LF) frequency processes for the YCXM (x = 0.5, 0.6 and 0.7 Ca) and the LS3M (x = 0.3 Sr) cathode materials at 900°C.