INVESTIGATION OF ELECTROLYTE STABILITY USING AMPEROMETRIC SENSORS: IMPLICATIONS CONCERNING ELECTRODE POLARIZATION MEASUREMENTS

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ABSTRACT

Amperometric sensors with yttria-stabilized zirconia (YSZ) discs and YSZ cylinders were made with platinum electrodes applied on the YSZ disc, which served as working (inside) and counter (outside) electrodes, and a platinum wire electrode positioned along the circumference of the disc. Two sets of platinum electrodes were applied on the YSZ cylinder, one inside and the other outside. The YSZ cylinder was attached to the YSZ disc using a sealing glass. A YSZ disc with a tiny diffusion hole was glass-sealed on the other end of the YSZ cylinder. The amperometric sensor was tested at 800°C in air over an applied DC voltage range from zero to 2.5 V. The measured current over a voltage range from ~0.4 to ~1.6 V exhibited a plateau. For applied voltage ≥1.7 V, the measured current increased, with a rapid increase for applied voltage ≥1.9 V. This rapid rise is consistent with the development of nonstoichiometry or the occurrence of YSZ electrolyte decomposition. The voltage between the reference and the working electrodes was measured. Based on this information, the cathodic activity of the platinum working electrode was estimated. Implications concerning the use of the three electrode system for the study of electrode polarization are discussed.

INTRODUCTION

The three electrode system comprising an electrolyte disc upon which working, counter and reference electrodes are applied in an axisymmetric arrangement, is routinely used for the investigation of electrode kinetics. The typical approach is to apply a DC voltage between the working and the counter electrodes, measure the current flowing, measure the voltage between the reference and the working electrodes, and determine the ohmic loss between the working and the reference electrodes by current interruption. It is generally recognized that the applied voltage must be low enough to avoid decomposition of the electrolyte. In many cases, however, the magnitude of the applied voltage above which decomposition of the electrolyte (or the development of oxygen deficiency) occurs cannot be readily determined, since it depends on transport properties of the electrolyte as well as of the electrode/electrolyte interfacial regions. In addition, one also often does not have sufficient information on concentration polarization at the working electrode for lack information on its porosity, tortuosity and thickness. In the extreme case if the working electrode is too thick, or not porous enough, or both, the net current due to the electrode reaction under investigation may become concentration polarization limited.
Yet, with increasing applied voltage, the current may continue to increase due either to the occurrence of oxygen deficiency or electrolyte decomposition. Thus, the net measured current will have two contributions: (a) Current due to the actual electrode reaction, which is the object of the investigation. For example, the cathodic current could be for the reaction \( \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \) under investigation. (b) Current due to decomposition or development of oxygen deficiency (nonstoichiometry). However, the experimenter would have no way of separating the two currents, and the entire current is inadvertently attributed to the cathodic current. This can lead to an overestimation of the electrocatalytic activity of the electrode, thus leading to an incorrect result. The degree to which overestimation can occur will depend upon a number of factors, such as: (a) The transport properties of the material and interfacial regions, (b) The range of stoichiometry of the material in question, and (c) The magnitude of the applied voltage.

The principal objective of the present work was to determine the relative magnitudes of the two currents. This required that at least over some range, the net cathodic current should be precisely known. A possible way of achieving this is to deliberately introduce a concentration polarization limit, which can be independently calculated and verified. A convenient method of achieving this is to construct an amperometric sensor around the three electrode system, wherein above a certain applied voltage, the net oxygen flux entering the sensor chamber is fixed by the geometry of the diffusion hole. This also automatically fixes the maximum possible cathodic current. Thus, any measured current beyond the limiting current can be unequivocally attributed to current due to decomposition/nonstoichiometry development. Implications of the present work concerning the often used three-electrode system, at a minimum, is that it may be necessary to thoroughly characterize the working electrode microstructure (porosity, pore size, etc.) and thickness, so that a possible concentration polarization limit can be a-priori calculated, which will set upper limit to the current, that should not be exceeded.

In the present work amperometric sensors were fabricated using YSZ electrolyte discs upon which platinum working and counter electrodes were applied. A platinum wire reference electrode was positioned along the circumference of the disc. Two sets of platinum electrodes were applied on the YSZ cylinder, one outside and the other inside. The sensors were tested at 800°C under an applied DC voltage, varied between zero and ~2.5 V. From these measurements, area specific ionic charge transfer resistance, \( r'_i \), for the working electrode was estimated as a function of oxygen partial pressure, \( P_{O_2} \).

**EXPERIMENTAL PROCEDURE**

Cylinders of YSZ (8 mol% \( Y_2O_3 \)-stabilized zirconia) of approximate dimensions: \( \sim 2 \text{ cm} \times 2.2 \text{ cm} \times 0.2 \text{ cm} \) thickness were fabricated by a conventional process comprising pressing of YSZ powder followed by sintering in air at 1450°C for 2 hours. Discs of YSZ of approximate dimensions, \( 2.5 \text{ cm} \times 0.1 \text{ cm} \) thickness were fabricated. In few of the discs, a hole of \( \sim 250 \mu \text{m} \) diameter was drilled in the center. On the other YSZ discs, platinum electrodes of \( 2 \text{ cm}^2 \) area were applied on both sides, and fired at 1000°C in air. A platinum wire reference electrode was positioned along the disc circumference. Two platinum leads were attached to the two electrodes. On the YSZ cylinder, two sets of platinum electrodes were applied near the two ends of the
cylinder, one near the diffusion hole (4 mm from the disc with the diffusion hole), and the other near the YSZ disc with platinum electrodes (4 mm from the YSZ disc with electrodes). Platinum wires were attached to these electrodes also. These served as potentiometric sensors, S1 and S2. The distance between the two potentiometric sensors (S1 and S2) was 14 mm. The two discs were glass-bonded to the cylinder, making sure that the platinum leads were taken out through the glass seals, and the seals were hermetic. This completes amperometric sensor fabrication with two sets of potentiometric sensors on the YSZ cylinder. Figure 1 shows a schematic.

A typical sensor was heated in air to 800°C and a DC voltage was applied across the two platinum electrodes on the YSZ disc with positive lead connected to the outside electrode. The corresponding current was measured. Under the applied voltage, oxygen from the sensor chamber was pumped out, lowering the $p_{O_2}$ in the chamber. The Nernst potentials across the two potentiometric sensors give magnitudes of the local $p_{O_2}$, one near the diffusion hole, $p_{O_2}^S$, and the other near the inner electrode (cathode) on the YSZ disc, $p_{O_2}^E$. Measurements were conducted over a voltage range from 0 to -2.5 V, which covers the initial region, the plateau region, and the post-plateau region of rapidly rising current.

**RESULTS**

Figure 2 shows the measured current (logarithmic scale) as a function of time on one of the sensors tested. The voltage was increased in steps of 0.1 V, and each voltage was maintained for 300 sec. Note that at low voltages (~0.2 V), there is a hump in the current, which is the result of non-steady conditions. Beyond a voltage of 0.4 V, the current is independent of voltage up to ~1.6 V. The plateau current is ~3 mA, which is in good agreement with the amperometric sensor model [1]. Beyond ~1.6 V, the current sharply increases, due to decomposition or the development of nonstoichiometry. At a voltage of 2.5 V the maximum current is ~800 mA, while the cathodic current due to the reaction $\frac{1}{2}O_2 + 2e^- \rightarrow O^-$ occurring at electrode I is only ~3 mA. Thus, a very large part of the current is due to decomposition or development of nonstoichiometry. Beyond 2 V, the current continuously increases due to nonstoichiometry or decomposition zone spreading into the YSZ electrolyte disc.

Figure 3 shows the measured current (logarithmic scale) on another sensor as a function of the applied voltage, varied between zero and 2.4 V in increments of 0.1 V. The hump in current at 0.2 V of applied voltage is again due to non-steady conditions, similar to that in amperometric sensor 1, which existed during the initial stage, as the YSZ chamber had not been completely pumped out. Thereafter, the current was ~3.4 mA and was essentially independent of voltage for up to ~1.6 V. Beyond this voltage, the current rapidly increased with increasing voltage to ~400 mA at a voltage of 2.4 V. This means at a voltage of 2.4 V, (400 - 3.4) mA or ~397 mA of the current was due to decomposition/nonstoichiometry development, and very little of the current was due to the cathodic reaction. Beyond 1.9 V, the measured current was not steady, and continued to increase with hold time. Thus, beyond 1.9 V, the current is not a unique function of applied voltage.

Figure 4 shows the measured current (linear scale) and the measured Nernst voltages across potentiometric sensors S1 and S2 as a function of the applied voltage. Over the plateau, the
Nernst voltages slightly decrease with increasing voltage. Thus, over this range, the $p_{O_2}$ in the chamber is not constant either. From the Nernst potentials, $p_{O_2}^{S_1}$ and $p_{O_2}^{S_2}$ were estimated. Over the plateau (~0.4 to ~1.6 V), the $p_{O_2}^{S_1}$ varies between ~0.022 and ~0.005 atm, while $p_{O_2}^{S_2}$ varies between ~0.0125 and ~0.0016 atm. Table I lists values of $p_{O_2}^{S_1}$ and $p_{O_2}^{S_2}$ at various applied voltages. For an applied voltage $\geq$1.7 V, the magnitudes of Nernst voltages increase rapidly. At S2 (near the YSZ disc), the lowest Nernst voltage was ~ -520 mV (highest magnitude), and that at S1 (near diffusion hole) was ~ - 350 mV.

Figure 5 shows plots of the applied voltage, and the measured voltage between the cathode and the reference electrode (linear scale, on the y-axis), vs. the measured current (logarithmic scale, on the x-axis). Note that for the entire pre-plateau, plateau, and initial parts of the post-plateau regions, the applied voltage (between the cathode and the anode) is only slightly greater than that measured between the cathode and the reference electrode. However, once past the plateau, even with further increase in applied voltage, the measured voltage between the cathode and the reference electrode actually decreases. For the highest applied voltage of 2.5 V, the measured voltage between the cathode and the reference electrode is only ~0.25 V. This implies that cathode/electrolyte interface became electrocatalytically more active – which is known for black zirconia.

**DISCUSSION**

Figures 2 through 5 show that the current deviates from the plateau above a voltage of ~1.6 V, and rapidly rises above ~1.9 V. Figure 3, for example, shows that at a voltage of ~2.2 V, the total current is ~90 mA. Of this, only ~3.4 mA is due to the cathodic reaction ($\frac{1}{2}O_2 + 2e^- \rightarrow O_2^-$) at electrode I. The remaining ~86.6 mA is due to decomposition or development of nonstoichiometry in YSZ. This is consistent with a sharp increase in the magnitude of Nernst potential (Figure 4), indicating a rapid decrease in chamber $p_{O_2}$. The lowest chamber $p_{O_2}$ was ~ $5 \times 10^{-11}$ atm. This signifies that YSZ near electrode I has either undergone decomposition, or has developed a significant oxygen deficiency.

Figure 5 shows plots of the applied voltage between the counter and the working electrodes, and the measured voltage between the working and the reference electrode, both on the y-axis (linear scale), and the measured current on the x-axis (logarithmic scale). Figure 6 shows the geometry of the YSZ disc with the locations of working, counter and reference electrodes. The working electrode is exposed to oxygen partial pressure $p_{O_2}^I$, while the counter and reference electrodes are exposed to oxygen partial pressure $p_{O_2}^{II}$, which is ~0.21 atm. Reduced (negative) electrochemical potentials of electrons at the working, the reference and counter electrodes are, respectively, $\mu^I$, $\mu(X)$, and $\mu^{II}$ (where $\mu = -\tilde{\mu}_e / e$ with $\tilde{\mu}_e$ as the electrochemical potential of electrons and $e$ is the electronic charge). The electrochemical potentials of oxygen ions similarly are $\tilde{\mu}_{O^{2-}}^I$,
Now, inside the YSZ disc, the flux of O\(^{2-}\) ions from I to II is essentially unidirectional. At position X from electrode I inside the YSZ disc, which is directly under the reference electrode, the various potentials are \(\mu^X_{O^2}, \phi^X\), and \(\tilde{\mu}^X_{O^2}\).

Neither \(\mu^X_{O^2}\) nor \(\phi^X\) are known. However, assuming symmetry,

\[
\tilde{\mu}^X_{O^2} = \frac{1}{2} \mu^X_{O^2} - 2e\phi^X \approx \tilde{\mu}^X_{O^2} = \frac{1}{2} \mu_{O^2}(X) - 2e\phi(X) \quad (1)
\]

Also, note that \(\mu_{O^2}(X) = \mu_{O^2}^H\), which is known (that corresponding to air in this case), and \(\phi(X)\) is also known (measured relative to electrode I). Now, the flux of O\(^{2-}\) ions occurs from I to II. This is proportional to the difference in electrochemical potentials of oxygen, that is, proportional to

\[
\tilde{\mu}^I_{O^2} - \tilde{\mu}^I_{O^2} \approx \tilde{\mu}^I_{O^2} - \tilde{\mu}^I_{O^2}(X) = \frac{1}{2} (\mu_{O^2}^H - \mu_{O^2}^I) - 2e\phi^I + 2e\phi(X) \quad (2)
\]

or

\[
(\phi(X) - \phi^I) = \frac{\left(\tilde{\mu}^I_{O^2} - \tilde{\mu}^I_{O^2}(X)\right)}{2e} + \frac{\left(\mu_{O^2}^H - \mu_{O^2}^I\right)}{2e} = \frac{\left(\tilde{\mu}^I_{O^2} - \tilde{\mu}^I_{O^2}(X)\right)}{2e} + \frac{k_BT}{4e} \ln \frac{p_{O^2}^H}{p_{O^2}^I} \quad (3)
\]

Equation (3) is applicable only over the plateau (and pre-plateau), since it only accounts for the current attributable to the net cathodic reaction. Now, \((\phi(X) - \phi^I)\) is the voltage measured between the reference electrode and electrode I (cathode). The \(p_{O^2}^I\) can be approximately estimated by extrapolating the line joining \(p_{O^2}^{S_1}, x_1\) and \(p_{O^2}^{S_2}, x_2\) to electrode I/YSZ interface. It is assumed here that electrode I is thin and highly porous. The first term in equation (3) is related to the net ionic current density flowing through the YSZ disc. It is easily seen that

\[
|I_i| = \frac{\left(\tilde{\mu}^I_{O^2} - \tilde{\mu}^X_{O^2}\right)}{2e(X\rho_i + r_i')} \approx \frac{\left(\tilde{\mu}^I_{O^2} - \tilde{\mu}^I_{O^2}(X)\right)}{2e(X\rho_i + r_i')} \quad (4)
\]

where \(I_i\) is the ionic current density, \(r_i'\) is the ionic area specific charge transfer resistance at electrode I and \(\rho_i\) is the electrolyte ionic resistivity. Thus, equation (3) can be rearranged as

\[
\frac{(\phi(X) - \phi^I)}{|I_i|} = \frac{k_BT}{4e} \ln \frac{p_{O^2}^H}{p_{O^2}^I} - X\rho_i \quad (5)
\]

With YSZ as the electrolyte, which has negligible electronic conductivity, the ionic current is essentially the same as the measured current. All parameters are known in equation (6),
and thus one can estimate the ionic charge transfer resistance at electrode I/electrolyte interface, \( r_i' \). The \( \rho_1 \) of YSZ at 800°C is \(~30 \Omega \text{cm}\). The \( X \) was \(~1 \text{ mm}\). Thus, \( X \rho_1 \approx 3 \Omega \text{cm}^2 \). The net current over the plateau was 3.4 mA, and the corresponding \( I_i \approx 1.7 \times 10^{-3} \text{ A/cm}^2 \). As sensor S2 was quite close to electrode I, it is assumed that \( p_{O_2}^I \sim p_{O_2}^{S2} \). Table I lists the applied voltage, the measured voltage between the cathode and reference electrodes, \( \phi(X) - \phi^I \), \( p_{O_2}^{S1} \), \( p_{O_2}^{S2} \), and the estimated \( r_i' \) using equation (5).

Table I shows that the estimated \( r_i' \) at electrode I ranges between \(~157 \Omega \text{cm}^2 \) for \( p_{O_2}^I \sim 0.0125 \text{ atm} \) and \(~893 \Omega \text{cm}^2 \) for \( p_{O_2}^I \sim 0.00158 \text{ atm} \). The \( r_i' \) is expected to be a function of oxygen surface coverage, which in turn is expected to follow one of the adsorption isotherms. If a dissociative adsorption is assumed, it is expected that a plot of \( r_i' \) vs. \( 1/\sqrt{p_{O_2}^{S2}} \) should be a straight line. Figure 7 shows a plot of \( r_i' \) vs. \( 1/\sqrt{p_{O_2}^{S2}} \). The agreement is reasonable. An important conclusion is that \( r_i' \) is a function of \( p_{O_2}^I \), and over the range investigated, the \( r_i' \) is much greater than the ohmic contribution. Figure 7 shows that the last data point, corresponding to an applied voltage of 1.7 V deviates from the plot which implies that the effects of nonstoichiometry development/decomposition are already present. For higher applied voltages, however, the \( \phi(X) - \phi^I \) decreased, even when the applied voltage was increased. This indicates improved electrocatalysis at electrode I. However, the current measured now contains two contributions; the cathodic current and that due to the occurrence of nonstoichiometry or decomposition.

Returning to the three-electrode system under an applied voltage, a technique often used for the investigation of electrode kinetics, e.g. evaluation of a prospective cathode for a fuel cell, the present results have significant implications. Depending upon the nature of electrode (I), that is porosity, tortuosity, and thickness, the net current may become diffusion-limited (concentration polarization limited) — even in the absence of a diffusion hole and without the experimenter being aware of it. In such cases, the diffusion limit may occur due to low porosity and/or large thickness of the porous electrode. Suppose a three-electrode system is used for the investigation of electrode kinetics of a prospective cathode. Let us assume for simplicity that the counter electrode is highly porous and has a small thickness, so that concentration polarization at the counter electrode (II) can be ignored. The testing is conducted in air wherein the oxygen partial pressure is \( p_{O_2}^H \). Under the action of externally applied voltage, \( E_A \), a net current is established. A flux of molecular oxygen is established through the porous cathode such that at the interface between the cathode (electrode I) and the electrolyte, the local oxygen partial pressure is \( p_{O_2}^I \). Figure 8 shows a schematic variation of \( \mu_{O_2} \) through the electrode and the membrane. The figure only shows a schematic variation, and the actual variation need not be linear.

The preceding shows that, depending on the charge transfer characteristics, the porosity and the thickness of the electrode, and the magnitude of the applied DC voltage, a
A significant portion of the measured current may be due to electrolyte decomposition and/or the development of nonstoichiometry, and not attributable to the cathodic reaction. A significant contribution to the total current may also arise due to the development of nonstoichiometry at applied voltages significantly lower than the decomposition potential. As such, there will be situations in which the three-electrode system will lead to an overestimation of the electrode activity. For this reason, the only conditions under which the three-electrode system can be used without ambiguity, is under no applied DC bias. That is, the three-electrode system for solid-state electrochemical studies is ideally suited only for the determination of the exchange current density under no applied DC bias – and its application for the generation of the entire current – overpotential relationship may not be reliable. The greater the degree of nonstoichiometry that can develop, the greater will be the error. In this context, the use of the three-electrode system under an applied DC bias may be particularly problematic with ceria as the electrolyte.

SUMMARY

Amperometric oxygen sensors were fabricated with a reference electrode wound on the circumference of the YSZ disc. Platinum working and counter electrodes were applied on the YSZ disc, and platinum potentiometric sensors were applied on the YSZ cylinder of the chamber. The sensors were tested at 800°C under an applied DC voltage ranging between zero and 2.5 V. Over the applied voltage range from ~0.4 V to ~1.6 V, the current exhibited a plateau, consistent with the expectations of an amperometric sensor. Beyond a voltage of ~1.6 V, the current rapidly increased, indicating either decomposition of the electrolyte or the occurrence of nonstoichiometry. Based on the measured current over the plateau region and the voltage measured between the reference and the working electrodes, the ionic charge transfer resistance, $r'_i$, at the cathode was estimated. Measurements made using the potentiometric sensors showed that over the plateau region, the $p_{O_2}$ in the chamber varied by a factor of eight. From these measurements, it was noted that the $r'_i$ varied by a factor ~5.6 over the same range, such that the $r'_i$ increased with decreasing $p_{O_2}$. Past the plateau, the measured current increased sharply. Since the maximum possible cathodic current was limited by the diffusion hole (to ~3 mA), all excess current could be unequivocally attributed to nonstoichiometry/decomposition. In a typical three-electrode system, if the electrode is too thick or too dense (low porosity), it is possible that the actual cathodic current may become concentration polarization limited. Yet, under the application of a DC bias, the measured current may continue to increase with increasing voltage. However, in such a case, a large part of the current may be due to the occurrence of decomposition or the development of nonstoichiometry. In many situations, the experimenter may be unaware of the existence of two currents, with the entire current being attributed to the electrode reaction, and thus leading to an overestimation of the electrode activity.

ACKNOWLEDGEMENT

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REFERENCE

1. W. Gopei, T. A. Jones, M. Kleitz, J. Lundstrom and T. Seiyama, ‘Sensors’, 2, VCH Publication, Weinheim, Germany, (1991).

Table I. Partial pressures of oxygen at the two potentiometric sensors, namely $P_{O_2}^{S_1}$ and $P_{O_2}^{S_2}$, and the measured voltage across the reference electrode and electrode I (cathode), namely, $(\varphi(X) - \varphi^I)$, as a function of applied voltage.

| Applied Voltage (V) | $P_{O_2}^{S_1}$ (atm) | $P_{O_2}^{S_2}$ (atm) | $(\varphi(X) - \varphi^I)$ (V) | $1/\sqrt{P_{O_2}^{S_2}}$ | $r_i$ (Ωcm$^2$) |
|---------------------|-----------------------|-----------------------|-------------------------------|--------------------------|------------------|
| 0.4                | 0.02216               | 0.0125                | 0.3368                        | 8.944                    | 156.8            |
| 0.6                | 0.01159               | 0.00586               | 0.5394                        | 13.063                   | 265.6            |
| 0.8                | 0.00852               | 0.00414               | 0.741                         | 15.542                   | 379.5            |
| 1.0                | 0.00701               | 0.0032                | 0.942                         | 17.678                   | 494.2            |
| 1.2                | 0.00605               | 0.0025                | 1.148                         | 20.00                    | 612.1            |
| 1.4                | 0.00573               | 0.0022                | 1.34                          | 21.32                    | 723.2            |
| 1.6                | 0.00573               | 0.00196               | 1.537                         | 22.588                   | 837.6            |
| 1.7                | 0.00543               | 0.00158               | 1.636                         | 25.158                   | 892.9            |

Figure 1. A schematic of the amperometric sensor fabricated and tested. S1 and S2 are potentiometric sensors used for the measurement of $P_{O_2}$ in the sensor chamber.
Figure 2. Measured current as a function of time. The voltage was increased in steps of 0.1 V, and maintained at a given voltage for 300 sec. At small applied voltages (~0.2 V), there is a hump in the current, which is due to non-steady state conditions. At intermediate voltage, note the existence of a plateau in current (~3 mA). Beyond a voltage of ~1.6 V, the current increases. The maximum current at 2.5 V is ~800 mA. Of this, only ~3 mA is due to the cathodic reaction. The rest is due to decomposition/nonstoichiometry development.

Figure 3. Measured current (mA) as a function of applied voltage. Higher current than the plateau at low applied voltages is due to non-steady state conditions. The plateau current is ~3.4 mA. Note the increasing current with increasing voltage past the plateau region.
Figure 4. The measured Nernst voltages on sensors $S_1$ (close to the diffusion hole) and $S_2$ (close to the YSZ disc with electrodes – away from the diffusion hole) as a function of applied voltage.

Figure 5. A plot of the applied voltage, and the measured voltage across the cathode and the reference electrode, vs. the current.

Figure 6. A schematic of the test set-up and the position of the reference electrode.
Figure 7. A plot of the $r'_l$ vs. $1/\sqrt{P_{O_2}^{S2}}$.

Figure 8. A schematic variation of $\mu_{O_2}$ through the electrode (cathode) and the electrolyte of a three-electrode system often used for the study of electrode kinetics. If $\mu_{O_2}$ is low enough, either a nonstoichiometry will be developed or electrolyte decomposition may occur. In either case, this will be reflected as additional current, not attributable to the cathodic reaction. This effectively leads to an overestimation of electrocatalytic activity.