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## Abstract

An electrochemical cell [Au/yttria-stabilized zirconia (YSZ)/Au] serves as a model system to investigate the effect of O<sub>2</sub> and NO<sub>x</sub>. Possible mechanisms responsible for the response are presented. Two dense Au electrodes are co-located on the same side of a dense YSZ electrolyte and are separated from the electrolyte by a porous YSZ layer, present only under the electrodes. While not completely understood, the porous layer appears to result in enhanced NO<sub>x</sub> response. Impedance data were obtained over a range of frequencies 0.1 Hz to 1 MHz, temperatures 600–700°C, and oxygen 2–18.9% and NO<sub>x</sub> 10–100 ppm concentrations. Spectra were fit with an equivalent circuit, and values of the circuit elements were evaluated. In the absence of NO<sub>x</sub>, the effect of O<sub>2</sub> on the low-frequency arc resistance could be described by a power law, and the temperature dependence by a single apparent activation energy at all O<sub>2</sub> concentrations. When both O<sub>2</sub> and NO<sub>x</sub> were present, however, the power-law exponent varied as a function of both temperature and concentration, and the apparent activation energy also showed dual dependence. Adsorption mechanisms are discussed as possibilities for the rate-limiting steps. Implications for impedancemetric NO<sub>x</sub> sensing are also discussed.

## Comments

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## Impedance Characterization of a Model Au/Yttria-Stabilized Zirconia/Au Electrochemical Cell in Varying Oxygen and NO<sub>x</sub> Concentrations

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An electrochemical cell [Au/yttria-stabilized zirconia (YSZ)/Au] serves as a model system to investigate the effect of O<sub>2</sub> and NO<sub>x</sub>. Possible mechanisms responsible for the response are presented. Two dense Au electrodes are co-located on the same side of a dense YSZ electrolyte and are separated from the electrolyte by a porous YSZ layer, present only under the electrodes. While not completely understood, the porous layer appears to result in enhanced NO<sub>x</sub> response. Impedance data were obtained over a range of frequencies (0.1 Hz to 1 MHz), temperatures (600–700 °C), and oxygen (2–18.9%) and NO<sub>x</sub> (10–100 ppm) concentrations. Spectra were fit with an equivalent circuit, and values of the circuit elements were evaluated. In the absence of NO<sub>x</sub>, the effect of O<sub>2</sub> on the low-frequency arc resistance could be described by a power law, and the temperature dependence by a single apparent activation energy at all O<sub>2</sub> concentrations. When both O<sub>2</sub> and NO<sub>x</sub> were present, however, the power-law exponent varied as a function of both temperature and concentration, and the apparent activation energy also showed dual dependence. Adsorption mechanisms are discussed as possibilities for the rate-limiting steps. Implications for impedancemetric NO<sub>x</sub> sensing are also discussed.

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The development of NO<sub>x</sub> sensors has been motivated primarily by environmental concerns and the automotive industry's desire to monitor gases in the exhaust stream.<sup>1</sup> Fast, reliable sensors are needed in order to meet increasingly stringent governmental regulations for emission limits. Ceramic metal oxides are candidate materials for operation in harsh, high-temperature environments, especially the oxygen-ion conductor yttria-stabilized zirconia (YSZ). YSZ is currently used for automotive oxygen sensors and has shown good stability and operation at temperatures 700 °C and higher.<sup>1-3</sup>

NO<sub>x</sub> sensor development poses significant challenges due to a number of issues including cost, sensitivity, stability, and response time. In the past decade, development of YSZ-based NO<sub>x</sub> sensors has focused on amperometric and potentiometric operation.<sup>1-3</sup> Amperometric operation typically measures a diffusion-limited current and has been shown to be effective as an NO-selective or a total-NO<sub>x</sub> sensor. Typically, research focuses on various metal-oxide electrodes to optimize the response.<sup>4-7</sup> In order to isolate the NO<sub>x</sub> from the O<sub>2</sub> response, a separate pumping cell may be necessary to maintain a constant O<sub>2</sub> concentration at the sensing electrode, leading to complicated device structures.<sup>1-3</sup> Potentiometric sensors correlate the measured open circuit potential (OCP) to the gas composition. The OCP can be measured between an electrode in the test atmosphere and another electrode in reference gas, or between dissimilar electrodes in the same atmosphere. In potentiometric operation, the response to NO<sub>2</sub> is generally opposite in sign to that of NO, and generally larger, making total-NO<sub>x</sub> sensing difficult.<sup>8</sup>

More recently, a YSZ-based impedancemetric technique has been reported for sensing of NO<sub>x</sub> and CO.<sup>9-12</sup> In that technique, the modulus (or magnitude) of the measured complex impedance at ≤1 Hz serves as the sensing signal. NO and NO<sub>2</sub> were shown to produce similar responses, offering the potential for total-NO<sub>x</sub> sensing. Impedancemetric NO<sub>x</sub> sensors show promise for overcoming the problems associated with amperometric (complex device structures) and potentiometric (interference between NO and NO<sub>2</sub>) sensors; however, a better understanding of the sensing mechanisms is necessary to optimize sensor operation.

Previous work has demonstrated the effectiveness of an imped-

ancemetric NO<sub>x</sub> sensor using dense Au, porous YSZ/Cr<sub>2</sub>O<sub>3</sub> composite electrodes, and a YSZ electrolyte in an in-plane geometry (i.e., both electrodes are co-located on the same side of the electrolyte).<sup>12</sup>

In an effort to better understand the sensing mechanism, the present work uses a model electrochemical cell to isolate the role of the Au/porous YSZ interface. Using an in-plane geometry, the model system consists of a dense YSZ electrolyte and two planar Au plates, with a porous YSZ layer separating the Au and dense YSZ. Electrochemical characterization of the model cell involves impedance measurements that are then fit with an equivalent circuit. Data taken at different temperatures and concentrations are used to interpret the effect of O<sub>2</sub> and NO<sub>x</sub>.

Understanding the cross sensitivity to interfering gases (e.g., water vapor, hydrocarbons, etc.) is also crucial for sensor operation, but a comprehensive study is outside the scope of the current work. For automotive exhaust applications, interference from hydrocarbons and other gases may be mitigated using separate strategies. A cross-sensitivity study in conjunction with automotive dynamometer testing of a prototype impedancemetric YSZ-based sensor is being conducted and will be the subject of a separate study. The present analysis provides a base from which future work on the role of different oxides (e.g., Cr<sub>2</sub>O<sub>3</sub>), microstructures (e.g., porosity), and other material parameters can be examined.

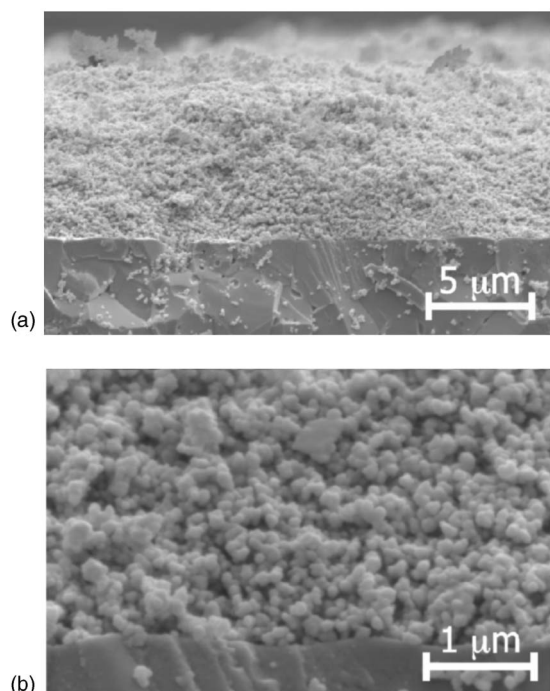
### Experimental

Yttria-stabilized zirconia (YSZ) powder (Tosoh 8-YS) was pressed in a uniaxial die and then sintered at 1450 °C for 2 h. The sintered pellet had a diameter of 12.2 mm with a nominal thickness of ~1.5 mm. Porous YSZ was then spray coated onto the surface of the pellet using YSZ powder dispersed in a 50% H<sub>2</sub>O/50% ethanol solution. The porous YSZ was deposited as two side-by-side rectangles (each with area ~28 mm<sup>2</sup>) with ~0.5 mm separation, and was then fired at 1000 °C for 1 h. The thickness of the porous YSZ layer was ~10 μm, as seen in the scanning electron microscopy (SEM) image in Fig. 1a. The SEM image in Fig. 1b shows an interconnected network of ~100 nm diam YSZ particles. Two thin Au plates were contacted to the porous YSZ layers using constant spring-loaded pressure.

Testing was performed in a quartz tube (i.d. of 16.8 mm) placed inside a tube furnace with both electrodes exposed to the same gas flow. The gas flow rate was maintained at 500 mL/min with composition controlled by mixing air, N<sub>2</sub>, and 1000 ppm NO or NO<sub>2</sub>

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**Figure 1.** SEM images showing (a) the thickness of the spray coat deposited porous YSZ and (b) the morphology of the interconnected ~100 nm diam YSZ particles in the porous layer.

using a standard gas handling system equipped with thermal mass flow controllers. Electrochemical measurements were performed using a Solartron Analytical SI 1260 Impedance/gain-phase analyzer with the Solartron Analytical SI 1287 electrochemical interface. Computer-controlled data acquisition used the commercially available Zplot software (Scribner Associates, Inc.). Impedance spectra were collected by scanning the frequency from 1 MHz to 0.1 Hz at 20 steps per decade with an excitation voltage of 50 mV. Impedance spectra were analyzed using Boukamp's Equevrt.com software.<sup>13</sup>

### Results and Discussion

**Impedance spectroscopy.**— The impedance of a material ( $Z$ ) describes the response to an alternating signal, and includes both magnitude ( $|Z|$ ) and phase angle ( $\theta$ ) information. The following relationships describe the complex impedance [ $Z(\omega) = \text{Re}(Z) + j \text{Im}(Z)$ ], where  $\text{Re}(Z)$  is the real component and  $\text{Im}(Z)$  is the imaginary component<sup>14</sup>

$$\text{Re}(Z) = |Z|\cos\theta \quad \text{and} \quad \text{Im}(Z) = |Z|\sin\theta \quad [1]$$

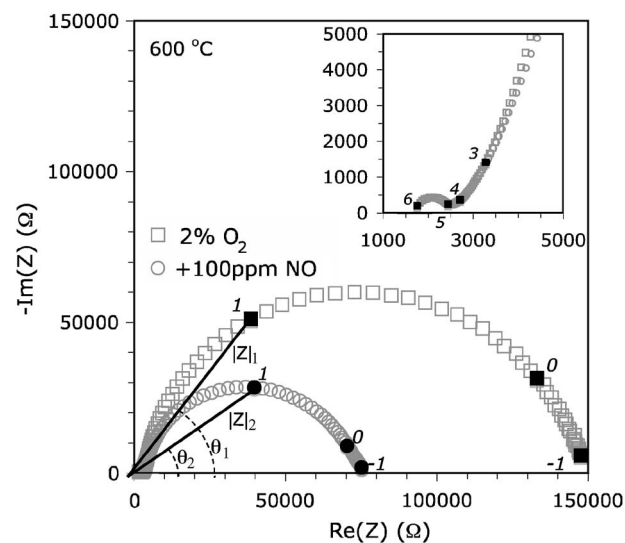
The relationship for phase angle is described by the following

$$\theta = \tan^{-1}\left(\frac{\text{Im}(Z)}{\text{Re}(Z)}\right) \quad [2]$$

and for the magnitude

$$|Z| = \sqrt{[\text{Re}(Z)]^2 + [\text{Im}(Z)]^2} \quad [3]$$

For impedancemetric sensor operation, either of the measured quantities (i.e., magnitude or phase angle) at a specified frequency can serve as the sensing signal.<sup>9,12</sup> Impedance spectroscopy entails using a frequency response analyzer to measure the response to (typically) small amplitude excitation over a range of frequencies (spectrum). The data can be presented in a so-called Nyquist plot, which is a complex plane representation [ $-\text{Im}(Z)$  vs  $\text{Re}(Z)$ ] that provides indirect information about both magnitude ( $|Z|$ ) and phase

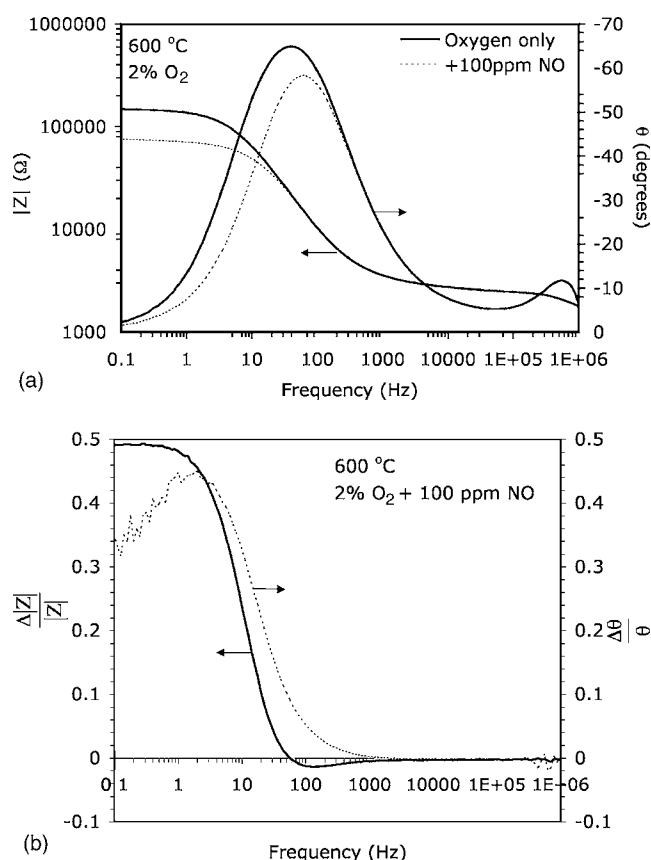


**Figure 2.** Nyquist plot of the model Au/YSZ/Au cell at 600°C in 2% O<sub>2</sub> and in 2% O<sub>2</sub> with 100 ppm NO.  $|Z|$  and  $\theta$  at 10 Hz are shown as solid and dotted lines, respectively, where  $|Z|_1$  and  $\theta_1$  refer to the response in 2% O<sub>2</sub> and  $|Z|_2$  and  $\theta_2$  refer to the response in 2% O<sub>2</sub> with 100 ppm of NO. Numbers corresponding to darkened points represent log of frequency in Hz.

angle ( $\theta$ ) over a range of frequencies. Alternatively, the data can be presented as a Bode plot, where either  $|Z|$  or  $\theta$  is plotted vs log frequency.

Figure 2 shows a Nyquist plot of the Au/YSZ/Au cell at 600°C in 2% O<sub>2</sub> and in 2% O<sub>2</sub> with 100 ppm of NO. Material behavior with both resistive and capacitive components produces characteristic arcs that appear in different frequency ranges in the Nyquist representation. In Fig. 2, a discernable high-frequency arc is shown in the inset, while a larger low-frequency arc dominates the spectra.  $|Z|$  and  $\theta$  at 10 Hz are graphically illustrated as solid and dotted lines, respectively, where  $|Z|_1$  and  $\theta_1$  refer to the response in 2% O<sub>2</sub>, and  $|Z|_2$  and  $\theta_2$  refer to the response in 2% O<sub>2</sub> with 100 ppm of NO. The cell behavior at higher frequencies, above ~10<sup>3</sup> Hz, does not change with NO (see inset of Fig. 2). However, the diameter of the large arc at the large arc decreases significantly with the introduction of NO. Corresponding decreases can be seen in both the magnitude (from  $|Z|_1$  to  $|Z|_2$ ) and phase angle (from  $\theta_1$  to  $\theta_2$ ) at 10 Hz. The response to NO<sub>2</sub> was qualitatively similar to that for NO, but slightly smaller under certain conditions. These differences are further discussed below.

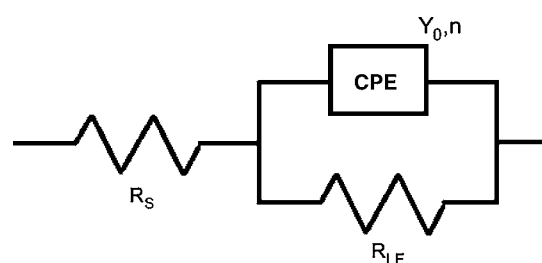
Miura et al.<sup>10</sup> and Wu et al.<sup>11</sup> have seen qualitatively similar impedance response using ZnCr<sub>2</sub>O<sub>4</sub> and Au-Ga<sub>2</sub>O<sub>3</sub> sensing electrodes to detect NO<sub>x</sub> and CO, respectively. In Ref. [10], the counter electrode was Pt exposed to atmospheric air, with only the ZnCr<sub>2</sub>O<sub>4</sub> sensing electrode exposed to the test atmosphere. In Ref. [11], the Au-Ga<sub>2</sub>O<sub>3</sub> sensing electrode and Pt reference electrode were both exposed to the same test atmosphere. Sensors using different electrodes and atmospheres may induce corresponding voltage changes (open circuit potentials) due to different reactions or kinetics at the electrodes, an effect usually explained with “mixed potential” or “differential electrode equilibria” theory. The mixed potential theory refers to differences in equilibria between electrochemical NO<sub>2</sub>/NO and O<sub>2</sub> reactions taking place at the electrodes.<sup>8,9,15</sup> Differential electrode equilibria theory is a more general term that includes nonequilibrium phenomena and changes in chemical adsorption behavior of the electrodes.<sup>16,17</sup> The measured impedance, however, only reflects the material phenomena, and not the induced electromotive force, as long as small-amplitude fields are applied to prevent the possibility of microstructural damage. In the current work, both electrodes of the model cell are identical and exposed to the same test atmosphere.



**Figure 3.** (a) Bode plot of magnitude ( $|Z|$ ) and phase angle ( $\theta$ ) for the model cell at 600°C in 2%  $O_2$  and in 2%  $O_2$  with 100 ppm NO. (b) The fractional change in  $|Z|$  and  $\theta$  over the range of frequencies between the cell in 2%  $O_2$  and in 2%  $O_2$  with 100 ppm NO.

Miura et al. and Wu et al. utilized the magnitude (or modulus)  $|Z|$  as the sensing signal at low frequencies, 1 and 0.42 Hz, respectively.<sup>10,11</sup> In the current work, the phase angle ( $\theta$ ) response is also investigated for use as a sensing signal.<sup>12</sup> Figure 3a shows Bode plots demonstrating the variation of  $|Z|$  and  $\theta$  with frequency for the model cell at 600°C in 2%  $O_2$  and 2%  $O_2$  with 100 ppm of NO. Figure 3a demonstrates that the  $\theta$  response persists to higher frequencies than the  $|Z|$  response. Neither parameter exhibits any significant difference in response in the presence of NO at frequencies  $\geq 1$  kHz. As a measure of the sensitivity, Fig. 3b shows the fractional change in  $|Z|$  and  $\theta$  with the addition of 100 ppm NO. As reported in Ref. 10 and 11, the  $|Z|$  sensitivity decreases with increasing frequency. However, it can be seen that the  $\theta$  sensitivity passes through a weak maximum at  $\sim 2$  Hz. A maximum is always present since  $\theta$  goes to zero as the frequency goes to zero and infinity. Furthermore, in Fig. 3b, it is shown that  $\theta$  is a more sensitive indicator of NO than  $|Z|$  for frequencies greater than  $\sim 3$  Hz. Higher frequency operation is desirable since it allows for reduced sampling times and potentially lower noise background.<sup>12</sup> Therefore, in terms of sensor operation, operating frequency may be selected as a compromise between sensitivity (lower frequencies) and reduced sampling time (higher frequencies). An analysis of the performance of a working sensor at 10 Hz is the subject of another publication.<sup>12</sup> The present work focuses on interpreting the response of the model electrochemical cell in the range of  $\sim 10$  Hz to varying  $O_2$  and  $NO_x$  concentrations.

**Equivalent circuit analysis.**— The Nyquist representation of impedance spectra for material phenomena exhibiting both resistive and capacitive components (e.g., grain boundaries, interfaces, etc.)



**Figure 4.** Simplified equivalent circuit used to fit the low-frequency behavior of the model cell where R is resistor, S is series, CPE is constant phase element (defined by two parameters  $Y_0$  and  $n$ , see text), and LF is low frequency.

often produces the characteristic semicircular arcs seen in Fig. 2. The discrete arcs represent processes with distinguishably separate characteristic time constants ( $\tau$ ). For a perfect resistor and capacitor in parallel, the diameter of the arc corresponds to the magnitude of the resistance ( $R$ ). The angular frequency at the top of the arc ( $\omega_{top}$ ) is related to the value of the capacitor ( $C$ ) through the time constant  $\tau$  ( $\tau = R \times C$ ) using the following relationship

$$\omega_{top} = \frac{1}{\tau} = \frac{1}{RC} \quad [4]$$

At least two orders of magnitude difference between time constants are necessary to produce clearly separated arcs. Unfortunately, in real material systems, it is often the case that multiple phenomena have similar time constants (less than two orders of magnitude difference). This causes the arcs to be overlapped and convoluted. In addition, for real nonideal systems, heterogeneity in the behavior, especially at interfaces, may lead to distributions of time constants. This typically causes “depressed” arcs, where the center of the arc lies below the real axis of the Nyquist plot. One way to simulate the nonideal behavior is to replace the capacitor with a constant phase element (CPE) in the equivalent circuit. The CPE has the following impedance relationship<sup>14</sup>

$$Z(\omega) = \frac{1}{Y_0(j\omega)^{-n}} \quad [5]$$

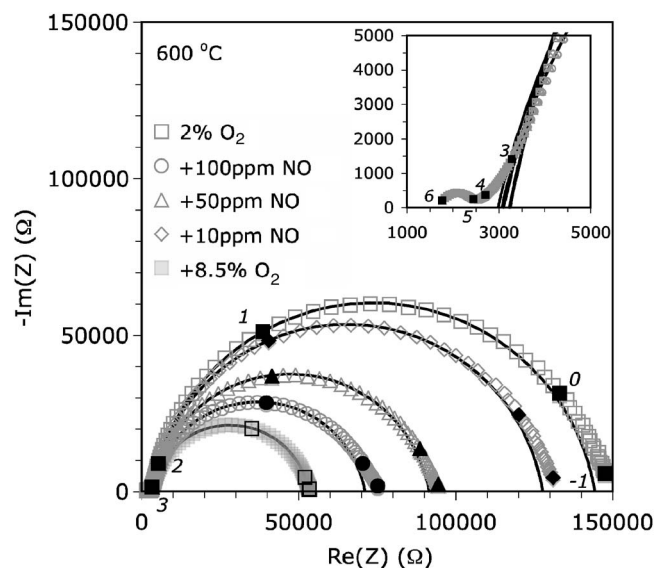
where  $Y_0$  is a constant,  $\omega$  is angular frequency, and  $n$  is a measure of arc depression

$$n = 1 - \frac{2\phi}{\pi} \quad [6]$$

The angle of the arc depression below the real axis of the Nyquist plot is given by  $\phi$ . For  $n = 0$ , the impedance reduces to a resistor with a value of  $Y_0^{-1}$ , and for  $n = 1$ , the impedance reduces to a capacitor with a value of  $Y_0$ . For values of  $n$  approaching 1, it is common practice to use the  $Y_0$  value as an approximation for capacitance.

It should be noted that interpretation of the Nyquist plot is not always straightforward. For instance, while changes in resistive behavior are clearly evidenced by decreasing arc diameters, for example with the addition of  $NO_x$ , changes in capacitive behavior are not as easily quantified. For this reason, equivalent circuit analysis is commonly used to quantify the response of electrochemical cells in terms of various circuit elements (i.e., resistors, capacitors, inductors, etc.). In the present work using the model electrochemical cell, the addition of  $NO_x$  induces changes primarily in the low-frequency behavior, which can be approximated with a single arc and is considered separately from the remaining higher-frequency response.

Figure 4 shows the equivalent circuit used to fit the low-frequency arc where a resistor ( $R_S$ ) is in series with a subcircuit that consists of a resistor ( $R_{LF}$ ) in parallel with a constant phase element (CPE). The subscripts “S” and “LF” stand for series and low fre-



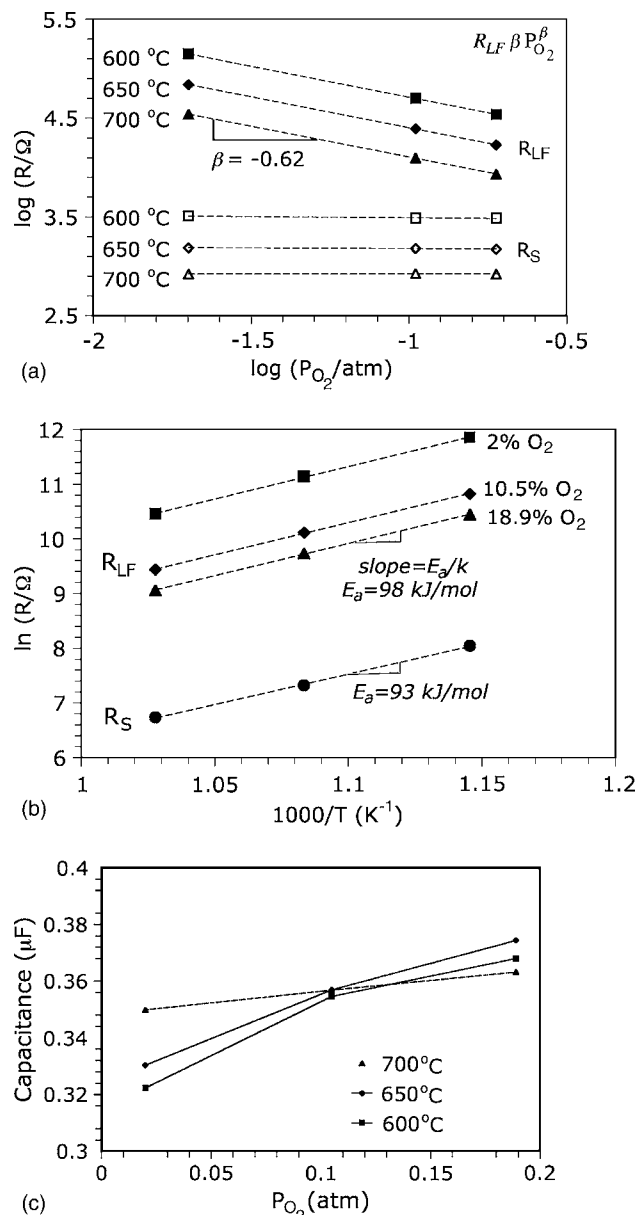
**Figure 5.** Nyquist plot of model cell at 600°C and 2% O<sub>2</sub> with the addition of 10, 50, and 100 ppm NO or 8.5% O<sub>2</sub>. The best fit to the equivalent circuit in Fig. 4 is shown as solid lines. Numbers corresponding to darkened points represent log of frequency in Hz.

quency, respectively. Note that the value of  $R_S$  approximates the high-frequency contribution to the total cell resistance. The value of  $R_{LF}$  corresponds to the diameter of the low-frequency arc, where the CPE (defined by  $Y_0$  and  $n$ , see Eq. 5) is related to the frequency at the top of the low-frequency arc and the amount of arc depression. The experimental impedance data were fit by using the partial non-linear least squares fitting routine in the Boukamp Equivcrt.com software.<sup>13</sup> The  $n$  values derived from the fitting procedure vary from  $\sim 0.88$  to  $\sim 0.90$  and show no temperature or concentration dependence. Since these values of  $n$  approach one, the best-fit values of  $Y_0$  in the CPE are used to approximate capacitance. Typical results from the fitting procedure using the equivalent circuit are shown as solid lines in Fig. 5 and are discussed in detail below.

**Modeled behavior: Low-frequency arc.**— Figure 5 shows typical behavior of the model electrochemical cell at 600°C in 2% O<sub>2</sub> and with 10, 50, and 100 ppm additions of NO. Discrete points represent the experimentally measured data, and the solid lines are the best fit using the equivalent circuit in Fig. 4. Although the behavior predicted by the equivalent circuit deviates from the experimental data in the frequency extremes  $< 1$  Hz and  $> 1$  kHz (as seen in Fig. 5), there is excellent agreement over most of the frequency range. More importantly, the equivalent circuit accurately describes the behavior of the model electrochemical cell in the frequency range around 10 Hz, which is the desired frequency range for sensor operation.<sup>12</sup>

Figure 5 also shows the impedance behavior of the model electrochemical cell with the addition of 8.5% O<sub>2</sub> (for a total of 10.5% O<sub>2</sub>), as represented by the shaded squares. The Nyquist behavior shows comparable decreases in the low-frequency arc diameters when either 8.5% O<sub>2</sub> or 100 ppm NO (open circles) is introduced. This corresponds to decreases in  $R_{LF}$  of  $\sim 64\%$  with the addition of 8.5% O<sub>2</sub> and  $\sim 52\%$  with the addition of 100 ppm NO. Therefore, the impedance response to O<sub>2</sub> and NO<sub>x</sub> are similar when the NO<sub>x</sub> concentration is about three orders of magnitude smaller than the O<sub>2</sub> concentration (i.e., 8.5% = 85,000 ppm). The implication is that although both O<sub>2</sub> and NO<sub>x</sub> reduce the low-frequency arc diameter ( $R_{LF}$ ), NO<sub>x</sub> causes significantly more pronounced changes in the electrical response.

To develop a better understanding of the effects of O<sub>2</sub> and NO<sub>x</sub> with the model electrochemical cell, the impedance behavior is interpreted using the equivalent circuit to evaluate possible rate-



**Figure 6.** In the absence of NO<sub>x</sub>, the behavior of the model cell is shown by (a) the P<sub>O<sub>2</sub></sub> dependence of  $R_S$  and  $R_{LF}$ , (b) the temperature dependence of  $R_S$  and  $R_{LF}$ , and (c) the P<sub>O<sub>2</sub></sub> dependence of capacitance at different temperatures.

limiting mechanisms. The approach involves comparing the calculated values of the circuit elements (i.e., the best fit of the equivalent circuit to the experimentally measured data) as a function of both gas concentration and temperature. Analysis of the effect of O<sub>2</sub> is presented first, followed by the analysis of the behavior when NO<sub>x</sub> is introduced.

**Oxygen behavior.**— The effect of oxygen partial pressure, P<sub>O<sub>2</sub></sub>, on the values of the resistances ( $R_S$  and  $R_{LF}$ ) is shown in Fig. 6a.  $R_S$  is insensitive to P<sub>O<sub>2</sub></sub> and is likely dominated by the ohmic contributions from the leads and contacts and the ionic contribution from the dense YSZ electrolyte.  $R_{LF}$  shows identical P<sub>O<sub>2</sub></sub> dependences at all temperatures, with  $R_{LF} \propto P_{O_2}^{-0.62}$ . A P<sub>O<sub>2</sub></sub> dependence of  $R_{LF} \propto P_{O_2}^{-0.5}$  has been suggested when dissociative adsorption of oxygen is the rate-limiting step.<sup>18-20</sup> It is also possible that a surface diffusion process could produce a similar dependence on P<sub>O<sub>2</sub></sub>; however, in that case diffusion-limited current behavior would be expected, and

that was not observed in the present cell. The deviation of the measured power-law exponent ( $-0.62$ ) from  $-0.5$  could result from some additional contribution from processes other than dissociative adsorption. Possibilities include gas-phase diffusion or molecular adsorption, both of which produce a power-law exponent of  $-1$ .<sup>18</sup> Therefore, dissociative adsorption probably dominates the response with some contribution from other processes.

Investigation of the temperature dependence yielded an apparent activation energy for  $R_{LF}$  of 98 kJ/mol for all  $O_2$  concentrations, as shown in Fig. 6b. Since  $R_S$  does not show any  $P_{O_2}$  dependence, the average values at all  $O_2$  concentrations investigated (2–18.9%) are shown and used to calculate an apparent activation energy of 93 kJ/mol. This activation energy for  $R_S$  is consistent with ionic diffusion in the dense YSZ. The similarity between the apparent activation energies of  $R_S$  and  $R_{LF}$  may indicate that a diffusion mechanism is also responsible for  $R_{LF}$ ; however, no diffusion-limited current behavior was observed. The discrepancy could indicate a complex rate-limiting mechanism involving both diffusion and adsorption or similar activation energies for diffusion and adsorption.

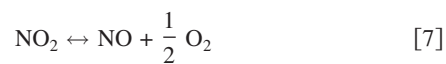
Alternatively, an apparent activation energy of 89 kJ/mol has been reported for the electrode behavior of an Au,  $O_2(g)/YSZ$  system.<sup>21</sup> In another study, Hertz et al. found that the electrode behavior of lithographically patterned electrodes on thin film YSZ electrolytes depends on the electrode material, exhibiting activation energies of 0.91 eV (88 kJ/mol) for gold electrodes and 0.77 eV (74 kJ/mol) for platinum electrodes.<sup>22</sup> The similarity between these reported values and the measured apparent activation energies in the present work may indicate that the mechanism(s) responsible for the oxygen response are related to the Au/YSZ interface.

The  $P_{O_2}$  dependence of the capacitance calculated from the equivalent circuit is shown in Fig. 6c. Recall that for values of  $n$  approaching one, the best-fit values of  $Y_0$  in the CPE approximate capacitance. As seen in Fig. 6c, the calculated capacitances exhibit only slight dependence on temperature or  $P_{O_2}$ , in all cases within the range of 0.32–0.37  $\mu F$ . However, general trends in the data indicate that capacitance increases with  $P_{O_2}$ . For example, the capacitance increases similarly with  $P_{O_2}$  at 600 and 650°C,  $\sim 9\%$ , when  $P_{O_2}$  increases from 2 to 10.5%, and  $\sim 14\%$  when  $P_{O_2}$  increases from 2 to 18.9%. This increase in capacitance with  $P_{O_2}$  may be related to an increase in the fraction of adsorbed  $O_2$  species at the Au/YSZ interface.<sup>21,23</sup> At 700°C, the capacitance increases only  $\sim 2\%$  when  $P_{O_2}$  increases from 2 to 10.5% and  $\sim 4\%$  when  $P_{O_2}$  increases from 2 to 18.9%. The amount of capacitance change at 700°C is not significant. Since the measured capacitance changes are small, care should be taken in making concrete conclusions. Nevertheless, the trends, especially at lower temperatures, indicate that adsorbed  $O_2$  species at the Au/YSZ interface may be important in determining the measured capacitance values.

**$NO_x$  behavior.**—The response of the electrochemical cell to either NO or  $NO_2$  is similar under all test conditions. The symmetric electrode configuration with both electrodes exposed to the same atmosphere seems a likely explanation for the similar response to NO and  $NO_2$ . The similar response may also be due to thermodynamic equilibration of the NO/ $NO_2$  ratio, which will result in identical gas compositions regardless of whether NO or  $NO_2$  is introduced initially. NO is more stable than  $NO_2$  at temperatures  $> 600^\circ C$ , and thermodynamic calculations predict  $\sim 90\%$  NO, balance  $NO_2$ .<sup>24</sup> However, the calculated values of  $R_{LF}$  are slightly larger with the addition of  $NO_2$  relative to NO, ranging from  $\sim 0.1\%$  to  $\sim 11\%$ . Experimental error associated with the accuracy of the mass flow controller may account for some of the difference, but there are consistent trends with temperature and composition. General trends include larger differences between NO and  $NO_2$  with increasing concentration and at lower temperature.

Yoo et al. performed temperature-programmed reaction experi-

ments using NO/ $NO_2$  and  $O_2$  gas mixtures as the reactant gas over a YSZ-8Y substrate. They demonstrated that only gas-phase  $NO_2$  decomposition occurs<sup>24</sup>



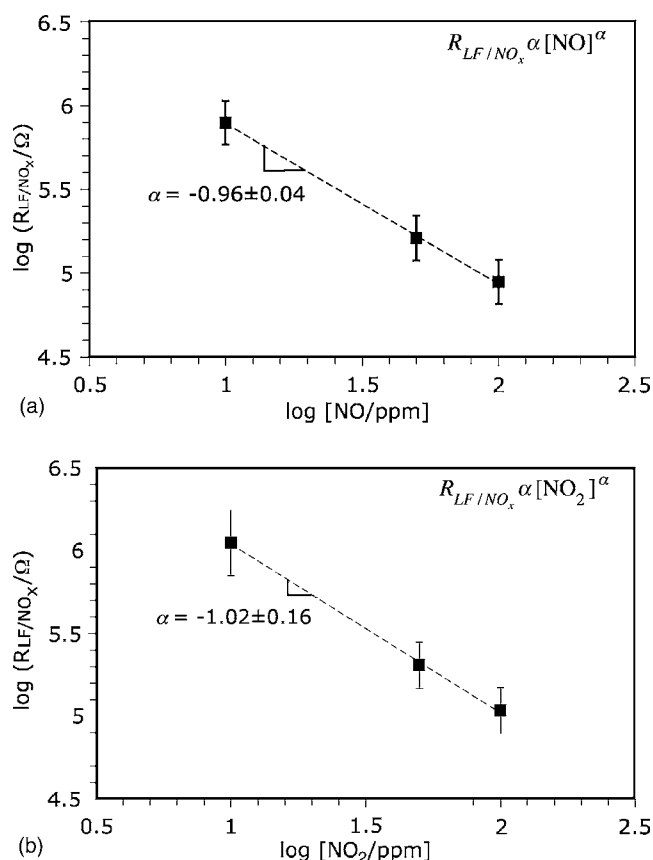
Yoo, Van Assche, and Wachsmann also showed that when  $NO_2$  is introduced, the reaction remains incomplete at temperatures  $< 700^\circ C$  without an appropriate catalyst, and leads to nonequilibrium gas compositions.<sup>24</sup> The addition of NO causes little change in overall gas composition since only  $\sim 10\%$  reacts to form  $NO_2$ , and the kinetics have been shown to be relatively fast.<sup>24</sup> In the present study, the minimal catalytic ability of the Au/YSZ system probably does not allow complete equilibrium decomposition of  $NO_2$ , especially at the lower temperatures. Larger amounts of  $NO_2$  would also be expected to remain unreacted for larger concentrations of  $NO_2$ . Therefore, larger deviations from the equilibrated NO/ $NO_2$  ratio are expected at lower temperatures and larger concentrations. The deviations result in smaller amounts of NO and larger amounts of  $NO_2$  than predicted by thermodynamic equilibrium. If adsorption is the prevailing mechanism,  $NO_2$  may not have as many sites available for adsorption due to its relatively larger size.<sup>8</sup> If this were the case, the amount of NO determines the impedance response and decrease in  $R_{LF}$ . It is possible that the larger values of  $R_{LF}$  calculated for  $NO_2$  are due to a reduction in the amount of NO from nonequilibrium conditions. This effect would then be expected to be more pronounced at lower temperatures and higher concentrations, as seen in the current study. The data collected in the current study only provide a preliminary investigation into mechanistic details leading to response differences between NO and  $NO_2$ . Further studies are required to explain the exact mechanism.

The effect of  $NO_x$  concentration on the resistances ( $R_S$  and  $R_{LF}$ ) was qualitatively similar to the effect of  $O_2$ , where  $R_S$  was insensitive to  $NO_x$  concentrations. The  $NO_x$  dependence of the low-frequency resistance ( $R_{LF}$ ) was determined by accounting for the effect of oxygen

$$\frac{1}{R_{LF/NO_x}} = \frac{1}{R_{LF/O_2+NO_x}} - \frac{1}{R_{LF/O_2}} \quad [8]$$

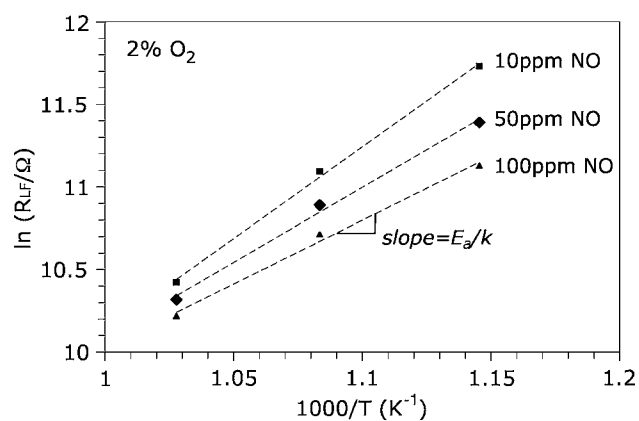
where  $R_{LF/NO_x}$  is the resistance contribution for  $NO_x$ ,  $R_{LF/O_2+NO_x}$  is the  $R_{LF}$  measured when both  $O_2$  and  $NO_x$  are present, and  $R_{LF/O_2}$  is the  $R_{LF}$  measured when only  $O_2$  is present. In the range 10–100 ppm of  $NO_x$ , the  $R_{LF/NO_x} \propto [NO_x]^\alpha$ , with  $\alpha = -0.96 \pm 0.04$  and  $\alpha = -1.02 \pm 0.16$  for NO and  $NO_2$ , respectively, as shown in Fig. 7.  $R_{LF/NO_x}$  was effectively insensitive to temperature and  $P_{O_2}$ , so the average values are shown in Fig. 7 with error bars indicating the standard deviation.

A possible explanation for the dependence of  $R_{LF/NO_x}$  on the  $NO_x$  concentration is a rate-limiting step controlled by the molecular adsorption of NO (nondissociative adsorption). This is analogous to the case of molecular adsorption of  $O_2$  which, when acting as the rate-limiting step, results in a power-law exponent of  $-1$ .<sup>18</sup> In the current cell, dissociative adsorption of NO is not expected based on prior reports that the process requires either an appropriate catalyst (e.g., Pt, Rh, and Pd)<sup>25</sup> or high electric fields.<sup>26-28</sup> In addition, the absence of limiting current behavior suggests that gas phase diffusion is not responsible for the  $NO_x$  behavior. Thus, the  $NO_x$  dependence of  $R_{LF/NO_x}$  appears to be consistent with the nondissociative adsorption of  $NO_x$ . Furthermore, since the calculated  $R_{LF/NO_x}$  from Eq. 8 is independent of  $O_2$ , it appears that the impedance behaviors of  $O_2$  and  $NO_x$  have parallel contributions to the overall measured impedance. Therefore, the parallel behavior of  $O_2$  and  $NO_x$ , which have different concentration dependences,  $R_{LF} \propto P_{O_2}^{-0.62}$  and  $R_{LF/NO_x} \propto [NO_x]^{-1}$ , results in larger changes in impedance for  $NO_x$  compared to  $O_2$ .



**Figure 7.**  $\text{NO}_x$  concentration dependence of  $R_{\text{LF}/\text{NO}_x}$  for (a) NO and (b)  $\text{NO}_2$ . Since  $R_{\text{LF}/\text{NO}_x}$  was insensitive to temperature and  $P_{\text{O}_2}$ , average values are shown with error bars indicating the standard deviation.

In general, the temperature dependence of  $R_{\text{LF}/\text{NO}_x}$  results in negative apparent activation energies, which indicates an increase in  $R_{\text{LF}/\text{NO}_x}$  with temperature. This is in contrast to the response of the cell in the absence of  $\text{NO}_x$ , where  $R_{\text{LF}}$  decreases with temperature (see Fig. 6b). Increasing resistance with temperature has been attributed to adsorption processes, where the magnitude of the apparent activation energy is related to the surface coverage.<sup>29,30</sup> The magnitudes of the apparent activation energies for NO range from 0.3 to 6 kJ/mol for varying relative concentrations of NO (10–100 ppm) and  $\text{O}_2$  (2–18.9%), indicating little temperature sensitivity. The exception is a mixture of 18.9%  $\text{O}_2$  (high oxygen) and 10 ppm NO gas mixture, which produces a slightly larger magnitude of 12 kJ/mol for the apparent activation energy. The magnitude of the apparent activation energies in  $\text{O}_2$  mixtures for  $\text{NO}_2$  is larger than those for NO. For 50 and 100 ppm  $\text{NO}_2$ , apparent activation energies range from 1 to 14 kJ/mol. For 10 ppm  $\text{NO}_2$ , apparent activation energies range from 37 to 54 kJ/mol. In general, the magnitude of the apparent activation energy appears to decrease as  $\text{NO}_x$  concentration increases and  $\text{O}_2$  concentration decreases. However, there is considerable scatter in the data. If surface coverage is the dominant factor, the results may indicate larger surface coverage for either larger concentrations of  $\text{NO}_x$  or smaller concentrations of  $\text{O}_2$ , with NO



**Figure 8.** Temperature dependence of the low-frequency resistance,  $R_{\text{LF}}$ , for 10, 50, and 100 ppm NO in 2%  $\text{O}_2$ . The apparent activation energy ( $E_a$ ) changes with respect to both NO and  $\text{O}_2$  concentration (see Table II).

showing more pronounced adsorption than  $\text{NO}_2$ , as discussed above. Although further studies are needed to explain the temperature dependence of  $R_{\text{LF}/\text{NO}_x}$ , the data seem to support a rate-limiting adsorption mechanism being responsible for the sensing behavior.

The capacitance values for any combination of  $\text{O}_2$  (2, 10.5, and 18.9%) and  $\text{NO}_x$  (10, 50, and 100 ppm) concentrations and temperatures (600, 650, and 700°C) were similar, with values ranging from 0.31 to 0.39  $\mu\text{F}$ . At 650 and 700°C,  $\text{NO}_x$  had no effect, within experimental error, on the measured capacitance calculated from the low-frequency arc. Larger changes in capacitance were measured at 600°C; however, the differences are <9%. The small changes in capacitance (<9%) at all temperatures do not allow any definitive mechanistic conclusions, regarding the effect of either  $\text{O}_2$  or  $\text{NO}_x$ , be made in the concentration ranges investigated.

*$\text{O}_2$  and  $\text{NO}_x$  interaction.*— The  $P_{\text{O}_2}$  dependence of the cell was calculated at each  $\text{NO}_x$  concentration and temperature. The behavior is similar to that when only oxygen is present with  $R_{\text{LF}} \propto P_{\text{O}_2}^\beta$ , but with variations in the power-law exponent depending on the  $\text{NO}_x$  concentration and temperature, as seen in Table I. The absolute value of  $\beta$  decreases with additions of  $\text{NO}_x$ , an effect that becomes more pronounced at lower temperatures. The values of  $\beta$  range from  $-0.62$  to  $-0.49$ , where the smallest absolute value of  $\beta$  occurs for 100 ppm NO at 600°C.

The overall apparent activation energy of  $R_{\text{LF}}$  when both  $\text{O}_2$  and  $\text{NO}_x$  are present varies as a function of gas compositions. Figure 8 shows the temperature dependence for the three levels of NO concentration in 2%  $\text{O}_2$ , where the activation energy decreases for larger amounts of NO. Quantitatively, similar results were observed for  $\text{NO}_2$ . Measured apparent activation energies for  $R_{\text{LF}}$  are higher for the larger  $\text{O}_2$  concentrations and always decrease with the addition of  $\text{NO}_x$ . Table II lists the apparent activation energy values for the various  $\text{O}_2$  and  $\text{NO}_x$  concentrations. The lowest activation energy occurs for 2%  $\text{O}_2$  and 100 ppm NO gas composition, with a value of 64 kJ/mol.

The trends, as seen in Tables I and II, result from the parallel contributions of  $\text{O}_2$  and  $\text{NO}_x$ , each having different concentration and temperature behavior, and seem to indicate a competition be-

**Table I.** Power-law exponent ( $R_{\text{LF}} \propto P_{\text{O}_2}^\beta$ ) for various  $\text{NO}_x$  concentrations and temperatures.

	$\text{O}_2$ only	10 ppm NO	10 ppm $\text{NO}_2$	50 ppm NO	50 ppm $\text{NO}_2$	100 ppm NO	100 ppm $\text{NO}_2$
600°C	-0.63	-0.60	-0.61	-0.53	-0.55	-0.49	-0.51
650°C	-0.63	-0.62	-0.62	-0.57	-0.58	-0.54	-0.55
700°C	-0.62	-0.61	-0.62	-0.59	-0.60	-0.57	-0.58



**Table II. Apparent activation energy (kJ/mol) of  $R_{LF}$  for various  $O_2$  and  $NO_x$  concentrations.**

	O <sub>2</sub> only	10 ppm NO	10 ppm NO <sub>2</sub>	50 ppm NO	50 ppm NO <sub>2</sub>	100 ppm NO	100 ppm NO <sub>2</sub>
2% O <sub>2</sub>	99	92	93	76	78	64	68
10.5% O <sub>2</sub>	98	94	94	82	84	74	76
18.9% O <sub>2</sub>	98	95	95	85	86	77	79

tween the mechanisms responsible for the O<sub>2</sub> and NO<sub>x</sub> responses. The behavior also implies a greater effect from NO<sub>x</sub> at lower temperatures. While it is not completely clear at present, the behavior may result from competition for available adsorption sites. Previous work suggests that oxygen adsorption sites on Au are related to surface impurities, and no adsorption is anticipated on Au that is free of impurities.<sup>31</sup> The dense Au used in this study probably contains impurities, and some oxygen adsorption on the Au may be expected. Also, due to the low surface area of the dense Au, reduced catalytic activity is anticipated. Adsorption of oxygen on YSZ has been studied by Yamawaki et al.<sup>32</sup> In their work, a high-temperature Kelvin probe was used to monitor the in situ oxygen chemisorption on YSZ surfaces. Singly ionized atomic oxygen species were proposed to be the dominant species with a maximum surface coverage of ~62% at 700°C.<sup>32</sup> The coverage decreases linearly with temperature to ~20% at 600°C. If O<sub>2</sub> and NO<sub>x</sub> are competing for available sites, possibly more sites are available for NO<sub>x</sub> adsorption at lower temperatures leading to a more significant effect on the O<sub>2</sub> partial pressure dependence.

Since adsorption processes appear to dominate the response, the decrease in apparent activation energies with the introduction of NO<sub>x</sub> may indicate changes in the adsorption energy and heat of adsorption. The amount of equilibrium adsorbed oxygen may affect the interaction between NO<sub>x</sub> and the surface and leads to changes that depend on both O<sub>2</sub> and NO<sub>x</sub> concentration.<sup>33</sup>

### Conclusions

Electrochemical characterization of an Au/yttria-stabilized zirconia (YSZ)/Au cell demonstrates that increases in either O<sub>2</sub> or NO<sub>x</sub> concentrations decrease the low-frequency arc diameter ( $R_{LF}$ ), while high-frequency behavior remains unaffected. An equivalent circuit consisting of a resistor in series with a subcircuit containing a resistor and constant phase element in parallel was used to fit the experimental data, where the resistor in the subcircuit ( $R_{LF}$ ) corresponded to behavior associated with impedancemetric NO<sub>x</sub> sensing. Examination of the concentration and temperature dependences of  $R_{LF}$  provided mechanistic information. In the absence of NO<sub>x</sub>, a single power-law exponent (-0.62) describes the  $P_{O_2}$  dependence (2–18.9%) of  $R_{LF}$  at all temperatures (600–700°C). Dissociative adsorption of oxygen is suggested as a possibility for the rate-limiting step. Also, when only O<sub>2</sub> is present, a single apparent activation energy of 98 kJ/mol describes the temperature dependence for all concentrations, which may indicate the possible role of the Au/YSZ interface.

The dependence of  $R_{LF/NO_x}$  on NO<sub>x</sub> concentration (10–100 ppm) yields a power-law exponent of -1, and the molecular adsorption of NO is proposed as the rate-limiting step. When both O<sub>2</sub> and NO<sub>x</sub> are present, the resulting apparent activation energies and  $P_{O_2}$  dependence vary with gas compositions and temperature, which may indicate competition between the two species. One possible explanation could be changes in the available adsorption sites for O<sub>2</sub> and NO<sub>x</sub>, which vary with temperature and gas concentrations.

If adsorption processes are primarily responsible for the cell response, surface treatments of the YSZ could help to increase sensitivity and sensor signal. Also, other contributions to the impedance response, e.g., diffusion, should be minimized. Further studies to elucidate the mechanisms are currently in progress.

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