Multiple Charge-Transfer Reactions in Zirconia Electrolytic Cells: NO_x Reduction on Platinum

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ABSTRACT

This paper investigates the electrochemical activity of nitrogen, NO, and NO₂ on platinum paste electrodes in zirconia oxygen sensors. Open-circuit voltages and steady-state current-voltage characteristics were measured at 600° - 800° C as a function of the partial pressures of oxygen, nitrogen, and nitrogen oxides. The open-circuit voltage and the current density both increased monotonically with the NO and NO₂ pressures in the sensor feed stream; both were most sensitive to the NO₂ concentration. These data are well described by a reaction network in which two parallel charge-transfer reactions occur on platinum: oxygen reduction to oxygen dianions; and NO₂ reduction to NO and oxygen dianions. The electrochemical behavior is not consistent with a reaction network in which NO₂ and NO are reduced catalytically, nor is it consistent with networks in which the oxides are completely reduced to nitrogen and oxygen cannot always be assumed to be the dominant charge-transfer reaction in zirconia electrolytic cells.

Electrochemical oxygen sensors fabricated from ceramic oxide electrolytes find application in the automotive and steel making industries (1-3). The typical electrolyte in these devices is calcia- or yttria-stabilized zirconia. This oxygen dianion conductor has high chemical stability and a wide electrolytic domain which make zirconia oxygen sensors well suited for use in high temperature, reactive environments (4).

A sensor is formed by depositing two thin, porous, metallic films on opposite sides of a section of stabilized zirconia. When the two electrodes are exposed to gas mixtures with differing oxygen partial pressures, a potential difference develops between the electrodes. If the electrodes are reversible to oxygen exchange

$$O_2 + 4e^- \rightleftharpoons 2 O^{2-}$$
[1]

the potential difference varies logarithmically with the ratio of oxygen partial pressures at the two electrodes as described by the Nernst equation

$$\mathbf{E} = \frac{RT}{4\mathbf{F}} \ln \left(\frac{p_{\mathrm{O}_{2,1}}}{p_{\mathrm{O}_{2,2}}} \right)$$
[2]

in which *T* is the absolute temperature, *R* is the gas constant, and **F** is the Faraday constant. When used to measure oxygen concentrations in unreactive mixtures, zirconia oxygen sensors with noble metal electrodes typically produce "nernstian" voltages at temperatures between 600° and 1000°C. Replacement of the noble metal electrodes with an appropriate conductive metal oxide can produce nernstian response at temperatures as low as 400°C (5). However, sensor response to reactive mixtures, such as carbon monoxide-oxygen mixtures, can be highly non-nernstian (6); deviations from expected thermodynamic voltages greater than 1V are not unusual.

The source of this non-nernstian behavior has been a matter of debate in the literature for several years. At the heart of this discussion is uncertainty about the nature of charge-transfer reactions in solid oxide electrolytic cells. A common assumption is that the dominant charge-transfer reaction is oxygen exchange. In the context of this assumption, a non-nernstian response is produced when the oxygen surface coverage is perturbed by catalytic reaction with other reactive species. This reaction scheme is illusstrated in Fig. 1b. If it is also assumed that equilibrium exists between adsorbed oxygen and oxygen ions, the electrode potential is a measure of the oxygen surface activity, which in principal can be related to the oxygen surface coverage. These ideas form the basis of solid electrolyte potentiometry, a technique which has been used to study the mechanisms of a variety of catalytic oxidation reactions (7-9).

On the other hand, non-nernstian response can also be produced by simultaneous charge-transfer reactions at the electrode-electrolyte interface (3). This is illustrated in Fig. 1a. When two or more charge-transfer reactions occur in parallel, the partial currents of each reaction sum to produce the total current (10). This is shown schematically for the case of two reactions in Fig. 2. The current-voltage characteristic of the electrode, shown by the dashed line, is the sum of the current-voltage characteristics of the individual reactions. It is clear from this diagram that the open-circuit voltage, labeled E_m in the figure, lies between the thermodynamic potentials of the individual chargetransfer reactions. This potential, which is commonly called a mixed potential, can be considered a kinetic aver-



Fig. 1. Electrode reaction networks in zirconia cells: O^{2-} is an oxygen dianion in the electrolyte; O(a), an oxygen adatom on the electrode surface; $O_2(g)$, an oxygen molecule in the gas; R, a gas-phase reduced species; RO, a gas-phase oxidized species; e-, an electron. (a) R and O are oxidized in parallel charge-transfer reactions. (b) R oxidized catalytically by electrochemically generated oxygen.

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Fig. 2. Current-voltage characteristic of an electrode at which two parallel charge-transfer reactions occur. The solid and dashed lines show the partial current densities of the individual charge-transfer reactions. The dotted line shows the apparent (measured) current-voltage characteristic.

age of the thermodynamic potentials of the appropriate charge-transfer reactions; if the rate of one charge-transfer reaction dominates all others, E_m approaches the thermodynamic potential of that reaction. A parallel chargetransfer reaction mechanism has been suggested to explain non-nernstian response to mixtures of carbon monoxide and oxygen (6, 11, 12). Unfortunately, the results of this latter study do not unambiguously demonstrate the occurrence of parallel charge-transfer reactions (13). However, recent studies of sulfur dioxide oxidation suggest that SO₂ is oxidized directly by oxygen dianions in parallel with oxygen exchange on platinum electrodes (14).

Resolution of the question about the number and nature of charge-transfer reactions in solid oxide electrolytic cells is vital for the development of quantitative relationships between composition and sensor response. Furthermore, this question is of primary importance in evaluation of the performance of these devices as electrosynthetic reactors. Ideally, if one suspects that a species is electrochemically active, one could study its activity by measuring currentvoltage characteristics in the absence of interfering electroactive substances. Unfortunately, this is not possible in solid oxide electrolyte systems, because oxygen dianions cannot be excluded from the system. For this reason, oxygen exchange unavoidably contributes to the total currentvoltage characteristic, and it is impossible to study alternate charge-transfer reactions independently.

The purpose of this work is to begin to address the question of the dominance of oxygen exchange on noble metal electrodes in solid oxide electrolytic cells. We set out with two primary goals. The first is to demonstrate that multiple charge-transfer reactions do occur on these electrodes. The second is to develop experimental methods for discriminating between different charge-transfer and catalytic reactions and quantifying their kinetics.

To this end, we have studied the steady-state electrochemical behavior of a platinum paste electrode exposed to mixtures of oxygen, nitrogen, and nitrogen oxides at 600°-800°C. This system was chosen because of its relevance to automotive oxygen sensors and electrochemical reduction of nitrogen oxides. At the elevated temperatures of this study, NO and NO2 should be the only kinetically stable oxides of nitrogen (15, 16). Thus, there are three possible charge-transfer reactions which may occur in parallel with oxygen exchange: complete reduction of NO and NO₂ to nitrogen and oxygen ions

$$NO + 2e^{-} \rightleftharpoons 1/2 N_2 + O^{2^{-}}$$
[3]

$$NO_2 + 4e^- \rightleftharpoons 1/2 N_2 + 2 O^{2-}$$
 [4]

and partial reduction of NO2 to NO and oxygen ions

$$NO_2 + 2e^- \rightleftharpoons NO + O^{2-}$$

Our results indicate that reaction [5] occurs in parallel with oxygen exchange at rates large enough to produce significantly non-nernstian open-circuit voltages. Reactions [3] and [4] do not occur at measurable rates.

Theory

General considerations.-Charge-transfer reactions in zirconia electrolytic cells generally involve three basic steps: adsorption of gas-phase species onto the electrode surface; transport of electroactive species to electrochemical reaction sites in the vicinity of the electrode-electrolyte interface; and charge-transfer reaction at these active sites (16). For example, oxygen exchange on platinum is believed to occur by dissociative adsorption of oxygen, diffusion of adsorbed oxygen atoms into the interfacial region between the electrode and the electrolyte, and exchange between oxygen atoms and lattice oxygen ions (18, 19). The current, therefore, depends directly on the electrode potential and the surface concentration of oxygen adatoms in the reaction zone.

Addition of a second reactive compound can effect the open and closed-circuit behavior of an electrode in two ways. First, if the compound is electroactive, it will participate in a charge-transfer reaction which will increase or decrease the net current produced at the electrode. When no current flows, a mixed potential will be measured. Second, if the additional component reacts or adsorbs competitively with oxygen, its presence will alter the surface concentration of oxygen, thereby altering the current. The open-circuit voltage will adjust to reflect this change in the oxygen concentration. In the most general situation, both mechanisms occur simultaneously.

Because NO oxidation is a facile and reversible gasphase reaction at and above room temperature, NO and NO₂ will coexist in a zirconia electrolytic cell under normal operating conditions. For this reason, reduction of the oxides may occur in parallel with oxygen exchange on a platinum electrode. These reactions may be purely catalytic, purely electrochemical, or both. Unfortunately, information does not exist which rules out any of these possibilities a priori.

There appears to be no direct method for determining which reactions occur at significant rates and which occur electrochemically or catalytically. For this reason, we have prepared four models which represent idealizations of the reaction network. Three of these models are parallel charge-transfer models which assume that oxygen exchange occurs in parallel with one of reactions [3]-[5]. These models assume further that the surface concentration of oxygen is unaffected by the presence of the nitrogen oxides. The fourth model is a catalytic model which assumes that neither NO nor NO2 is electroactive; all reactions involving these species are purely catalytic. In this model, it is assumed that the oxygen surface coverage is perturbed by NO and/or NO₂. We compare measured electrode kinetics to model predictions and reject those models which fail to correlate the data. In this way, we can reduce the number of consistent electrode reaction networks and ascertain the most important electrochemical reactions.

Parallel charge-transfer models.—If NO and NO₂ are electroactive on platinum, they may participate in any or all of reactions [3]-[5]. For simplicity, we assume that only one of these reactions occurs at a significant rate. Since we do not know which reaction is dominant, we develop three models for the current-voltage characteristic of the electrode, one for each reaction. The model for reaction [5] is described here; the remaining models are outlined in the Appendix. We also assume that all species are in adsorption equilibrium and at low coverage. This decouples the surface coverages of all adsorbed species, making each coverage a function of a single species partial pressure.

If reaction [5] occurs in parallel with oxygen exchange, the total current density produced at the electrode is the sum of the partial current density from oxygen exchange, i_{O_2} , and the partial current density from partial reduction of NO₂, $i_{\text{NO}_2/\text{NO}}$. We develop below expressions for i_{O_2} and

[5] Downloaded on 2016-07-06 to IP 132.77.150.148 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract). $i_{\rm NO_2/NO}$ in terms of electrode potential and gas-phase composition.

Oxygen exchange kinetics have been well studied on platinum (18-21). The cathodic current is first order in dissociatively adsorbed oxygen, and the anodic current is first order in oxygen dianion concentration and vacant adsorption sites. Anodic and cathodic transfer coefficients are unity. At low and moderate current densities at which mass-transfer effects are expected to be unimportant, the current-voltage characteristic is well described by (18, 22)

$$i = k_{\rm a} C_{\rm O} \theta_{\rm S} \exp\left(\frac{(V - V_{\rm O_2})\mathbf{F}}{RT}\right) - k_{\rm c} \theta_{\rm O} \exp\left(-\frac{(V - V_{\rm O_2}^{\circ})\mathbf{F}}{RT}\right)$$
[6]

in which θ_S and θ_0 are the surface coverages of free sites and oxygen adatoms, respectively, k_a and k_c are anodic and cathodic rate constants, Co is the concentration of oxygen ions in the electrolyte, and $V_{0_2}^{\circ}$ is the standard equilibrium potential at unit oxygen fugacity. We assume that oxygen is in dissociative-adsorption equilibrium and at low coverage. Under these conditions, θ_S is unity and

$$\theta_0 = (K_0 p_{0_2})^{1/2}$$
[7]

where K₀ is the oxygen desorption equilibrium constant. Equations [6] and [7] can be combined to yield (22)

$$i_{O_2} = k^{\circ}_{O_2} \left\{ \exp\left(\frac{(V - V^{\circ}_{O_2})\mathbf{F}}{RT}\right) - p_{O_2}^{1/2} \exp\left(-\frac{(V - V^{\circ}_{O_2})\mathbf{F}}{RT}\right) \right\}$$
[8]

in which $k_{O_2}^{\circ} = (k_a k_c K_O^{1/2} C_O)^{1/2}$. When measured relative to a reversible oxygen electrode at 1 atm oxygen partial pressure, $V_{0_2}^{\circ} = 0$.

The mechanism of electrochemical reduction of NO₂ to NO is unknown. Both species adsorb associatively and dissociatively on platinum (23, 24), and NO decomposition is inhibited by oxygen (25). We assume, therefore, that both species exist on the electrode surface and that the elementary charge-transfer reaction is a two-electron transfer in which adsorbed NO₂ is reduced to adsorbed NO. We can write this reaction scheme as

$$NO + S \rightleftharpoons NO(a)$$
 [9]

$$NO_2 + S \rightleftharpoons NO_2(a)$$
 [10]

$$NO_2(\alpha) + 2e^- \rightleftharpoons NO(\alpha) + O^{2-}$$
 [11]

where S is a vacant adsorption site and (a) designates an adsorbed species. The charge-transfer rate should be well described by a Butler-Volmer type expression

$$i_{\rm NO_2/NO} = k'_a \theta_{\rm NO} C_{\rm O} \exp\left(\frac{\alpha_a (V - V^{\circ}_{\rm NO_2/NO})\mathbf{F}}{RT}\right) - k'_c \theta_{\rm NO_2} \exp\left(-\frac{\alpha_c (V - V^{\circ}_{\rm NO_2/NO})\mathbf{F}}{RT}\right)$$
[12]

where k'_{a} and k'_{c} are anodic and cathodic rate constants for reaction [11], and θ_{NO} and θ_{NO_2} are the surface concentrations of NO and NO2, respectively. V°NO2/NO is the standard equilibrium potential for reaction [5] when NO and NO₂ are at unit fugacity. Values of this potential, measured relative to a reversible oxygen electrode on the same electrolyte and at 1 atm oxygen partial pressure, can be calculated from the standard free energy of reaction [5]. Representative values are listed in Table I. The anodic and cathodic transfer coefficients of reaction [11], α_a and α_c , are unity, assuming symmetry coefficients of one-half (26). We also assume that NO and NO₂ are in adsorption equilibrium at low coverage

$$\theta_{\rm NO} = K_{\rm NO} p_{\rm NO} \qquad [13]$$

$$\theta_{\rm NO_2} = K_{\rm NO_2} p_{\rm NO_2}$$

Table I. Standard equilibrium potentials for reactions [3]-[5]

Standard potentials (V)1

T (°C)	V° _{NO/NO2}	V° _{NO/N2}	$V^{\circ}_{ m NO_2/N_2}$
600	0.046	0.411	0.229
700	0.086	0.404	0.245
800	0.124	0.394	0.264

¹ Expressed relative to a reversible oxygen electrode at 1 atm.

where $K_{\rm NO}$ and $K_{\rm NO_2}$ are the NO and NO₂ adsorption equilibrium constants, respectively. Combination of Eq. [12]-[14] yields (22)

$$i_{\text{NO}_2/\text{NO}} = k^{\circ}_{\text{NO}_2/\text{NO}} \left\{ p_{\text{NO}} \exp\left(\frac{(V - V^{\circ}_{\text{NO}_2/\text{NO}})\mathbf{F}}{RT}\right) - p_{\text{NO}_2} \exp\left(-\frac{(V - V^{\circ}_{\text{NO}_2/\text{NO}})\mathbf{F}}{RT}\right) \right\}$$
[15]

in which $k^{\circ}_{NO_2/NO} = (k'_a k'_c C_0 K_{NO} K_{NO_2})^{1/2}$ Addition of Eq. [8] and [15] yields an expression for the total current density in terms of experimentally controllable variables (p_{NO_2} , p_{NO_2} , p_{O_2} , V), thermodynamic quantities $(V^{\circ}_{O_2}, V^{\circ}_{NO_2(NO)})$, and two unknown rate parameters $(k^{\circ}_{O_2}, V^{\circ}_{O_2})$ $k^{\circ}_{NO_{2}/NO}$). To test this model, one must first measure the oxygen exchange rate constant from the current-voltage behavior of the electrode when it is exposed to mixtures of oxygen in an inert gas. A plot of the current density against the dimensionless oxygen exchange partial current density

$$i'_{0_2} = \exp\left(\frac{V\mathbf{F}}{RT}\right) - p_{0_2}^{1/2} \exp\left(-\frac{V\mathbf{F}}{RT}\right)$$
 [16]

should be linear with slope $k^{\circ}_{O_2}$. Predetermination of $k^{\circ}_{O_2}$ allows calculation of i_{O_2} by Eq. [8] when the electrode is exposed to mixtures of NO, NO₂, and oxygen. This can be subtracted from the measured total current to yield the NO₂ reduction partial current. Therefore, if this model is consistent with the data, a plot of $(i - i_{O_2})$ against the dimensionless NO₂ reduction current density

$$i'_{\text{NO}_2/\text{NO}} = p_{\text{NO}} \exp\left(\frac{(V - V^{\circ}_{\text{NO}_2/\text{NO}})\mathbf{F}}{RT}\right) - p_{\text{NO}_2} \exp\left(-\frac{(V - V^{\circ}_{\text{NO}_2/\text{NO}})\mathbf{F}}{RT}\right)$$
[17]

should be linear with slope $k^{\circ}_{NO_2/NO}$. If the model is incorrect, such a plot should fail to correlate the data.

The two remaining parallel charge-transfer models are developed and tested in a similar fashion. Expressions for the partial current densities and dimensionless current densities of reactions [3] and [4] are derived in the Appendix.

Catalytic model.—If NO and NO₂ are not electroactive, oxygen exchange should be the sole charge-transfer reaction, and the total current density should be well described by Eq. [8]. However, if the surface reactions of NO and NO₂ perturb the oxygen coverage from its equilibrium value, Eq. [7] and [8] are not valid. Following the development of Saltsburg and Vayenas (7), if it is assumed that adsorbed oxygen and lattice oxygen ions are in local equilibrium, the open-circuit potential of the working electrode measured relative to a reversible oxygen reference electrode at 1 atm should be described by modified form of the Nernst equation

$$V^{\rm oc} = \frac{RT}{2\mathbf{F}} \ln\left(\frac{a_{\rm O}}{K_{\rm O}^{1/2}}\right)$$
[18]

where a_0 is the activity of oxygen adatoms on the working electrode. If adsorbed oxygen behaves as an ideal two-

[14]

Oxygen/Helium

dimensional lattice gas, the surface oxygen activity is related to the surface coverage by (27)

$$a_{\rm O} = \frac{\theta_{\rm O}}{(1 - \theta_{\rm O})}$$
[19]

Equation [19] should be valid whether or not oxygen is in adsorption equilibrium. When mass transfer of oxygen atoms on the electrode surface is fast compared to their rate of consumption or production, θ_0 is independent of current density. If we assume θ_0 is small, Eq. [6], [18], and [19] can be combined to yield the following expression for the total current density

$$i = k^{\circ}_{O_2} \left\{ \exp\left(\frac{V\mathbf{F}}{RT}\right) - K_{O}^{1/2} \exp\left(\frac{(2V^{oc} - V)\mathbf{F}}{RT}\right) \right\} \quad [20]$$

This model is easily tested by first measuring current-voltage characteristics at constant gas-phase composition. If the model is consistent, a plot of $(k^{\circ}_{O_2} \exp(\mathbf{F}V/RT) - i)$ against $k^{\circ}_{O_2} \exp((2V^{\circ c} - V)\mathbf{F}/RT)$ should be linear with slope $K_0^{1/2}$.

Experimental

The zirconia cell was fabricated from a 30.5 cm long, 3.8 cm od, 3.2 cm id 9 mole percent (m/o) yttria-stabilized zirconia tube (Zircoa Corporation) with one open and one closed end. The outside surface of the closed end was machined flat, polished, degreased with acetone, and rinsed several times with distilled water.

Unfluxed platinum paste electrodes (Engelhard 6926) were deposited using standard methods. Each electrode was split into a working electrode and a smaller reference electrode. Figure 3 is a schematic diagram of the cell showing the placement of the electrodes.

The cell was inserted into a gas manifold fashioned out of MACOR machinable ceramic (Corning Glass Company)



Top View



Bottom View



Fig. 3. Electrode placement in zirconia cell



Fig. 4. Zirconia cell and housing

as shown in Fig. 4. A gas-tight seal was produced by compression of an 0.051 cm diam gold O-ring between the tube and the manifold. The manifold was constructed to provide a 5 cm³ reaction volume at the working electrode. Three 0.32 cm od, 0.16 cm. id alumina tubes which were inserted through the bottom of the manifold and sealed into place with high-temperature ceramic cement (Sauereisen no. 29) acted as feed-throughs for gases, a thermocouple, and electrical connections to the working electrode. The tube-and-housing assembly was held together by two stainless steel plates and four stainless steel draw bolts. A combination of nuts and spring washers provided the compression necessary for a leak-tight seal at elevated temperatures. Stainless steel feed-throughs for oxygen flow and electrical connections to the reference and counterelectrodes were welded into the top plate.

The reactor assembly was placed in a tubular furnace and connected to a flow system of standard design. Oxygen, nitrogen, helium, and NO or NO_2 flow rates were controlled and monitored with needle valves and rotameters. Feed and product streams were analyzed with on-line Fourier transform infrared spectroscopy; either stream could be analyzed without flow interruption by adjustment of a six-port valve.

Helium (99.995%), 20.4% oxygen, 10.0% nitrogen, 4.85% NO, and 4.93% NO₂ certified standard mixtures in helium (Liquid Carbonic Company) were used without additional purification. The 20% oxygen-in-helium mixture was also metered to the reference electrode compartment.

The electrochemical cell was controlled with a Princeton Applied Research Model 173 potentiostat equipped with a Model 276 plug-in current follower. The potential of the working electrode was measured and controlled relative to the reference electrode on the counter side of the cell. Open-circuit voltages were monitored with a digital multimeter (Fluke Model 8050A, input resistance 10 M Ω).

The on-line infrared spectrometer allowed rapid analysis of the NO and NO₂ concentrations in the product stream. Unfortunately, the measured composition differed significantly from that in the reactor due to the rapid homogeneous reaction between NO and oxygen in the IR gas cell and lines of the flow system. Correction for this reaction

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was accomplished in one of two ways, depending on the composition of the feed stream. When the feed mixture contained NO, we assumed that equilibrium between NO and NO₂ was attained in the reactor. This should be a reasonable assumption because NO is the thermodynamically favored oxide at the elevated temperatures of this study, therefore the feed mixture was near equilibrium when it entered the hot reactor. The NO and NO₂ concentrations in the reactor, therefore, were calculated from the measured concentrations in the product stream and the equilibrium constant for NO oxidation at the reactor temperature. When the feed mixture contained NO₂, the residence time in the reactor was too short for equilibrium to be attained. For these experiments, the kinetics of NO oxidation at room temperature in the gas cell and lines of the flow system were measured by diverting flow around the reactor and measuring the difference between the feed composition calculated from the rotameter settings and the product composition measured with the FTIR. The kinetics were fit to a power-law expression which was subsequently used to calculate the NO and NO₂ concentrations in the reactor from the measured concentrations in the product stream. The oxygen and nitrogen concentrations in the product streams were determined by mass balance. We believe that these estimates of the reactant partial pressures are accurate to within $\pm 10\%$.

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In all experiments, NO or NO₂ were mixed with oxygen, nitrogen, and helium to produce a feed stream flowing at 100 cm³ (STP)/min. At this flow rate, decomposition of the nitrogen oxides was typically less than 10%, and the reactor was therefore assumed to behave as a differential reactor. In most experiments, the steady-state current was measured as a function of gas-phase composition at a fixed working electrode potential. Steady-state currents or open-circuit voltages were typically attained within 30 min of changing the potential or feed composition.

Results

Open-circuit measurements.—The reversibility of the working electrode to oxygen exchange was investigated by measuring its open-circuit potential in the absence of NO and NO₂. As shown by the filled symbols and solid line in Fig. 5, the measured potential agreed with the thermodynamic potential for oxygen exchange, calculated with Eq. [2], over the range of temperature and composition studied. In general, the measured potential was within 5 mV of the calculated potential.

Addition of NO or NO₂ to the feed initially had no effect on the open-circuit potential. However, after intermittent exposure to both species over several days, the potential deviated significantly and consistently from the oxygenexchange potential. This is illustrated by the open symbols in Fig. 5 which show the open-circuit potential of an electrode which was in service for several weeks. The circles show the variation of the potential with oxygen partial pressure when 0.01 atm (1 atm = 0.101 MPa) of NO was in the feed; the squares show the same measurements when 0.01 atm of NO₂ was in the feed. Similar results were ob-



Fig. 6. Oxygen-exchange kinetics. Lines are best fits of Eq. [9]

served when a second source of NO was used, indicating that the deviation in the potential was produced by NO and NO_2 and not by an unidentified impurity.

The measured potential always was more positive than the thermodynamic potential for oxygen exchange and less negative than that for NO_2 reduction to NO. This behavior would be expected if both charge-transfer reactions occurred in parallel, as described by the first parallel charge-transfer model. However, the thermodynamic potentials for reduction of NO_2 and NO to nitrogen were more positive than that for partial reduction of NO_2 , therefore the open-circuit measurements are not sufficient to rule out the other parallel charge-transfer models.

Closed-circuit measurements.—The rate constant for oxygen exchange was determined by measuring the current-voltage behavior of the electrode in the absence of NO and NO₂. These measurements were conducted at overpotentials between $\pm 60 \text{ mV}$ to minimize variations in oxygen surface coverage due to slow mass transfer. The measurements are summarized in Fig. 6, which shows plots of the current density against the dimensionless oxygenexchange current density, i'_{O_2} . The linearity of the plots at all temperatures indicates that Eq. [8] accurately represents oxygen exchange kinetics in the absence of other catalytically or electrochemically active species.

The slopes of the lines in Fig. 6 equal the overall oxygen exchange rate constant, $k^{\circ}_{O_2}$. An Arrhenius plot of $\ln (k^{\circ}_{O_2})$ vs. inverse temperature is shown by the open circles in Fig. 7. Clearly, the plot is nonlinear at high temperatures. The reason for this nonlinearity is not clear. However, we did observe that the activity of the electrode for oxygen exchange varied with time, particularly at higher temperatures. The curvature of this plot may reflect these changes in electrode activity. The lower temperature rate constants are reasonably collinear; their slope yields an apparent activation energy of 126 kJ/mol. This compares favorably with the value of 128 kJ/mol measured by Mason and coworkers (28).



Fig. 5. Dependence of open-circuit potential of working electrode at 800°C on oxygen partial pressure in the cell. Filled circles: no nitrogen oxides in feed. Open circles: 0.01 atm NO in feed. Open squares: 0.01 atm NO₂ in feed.





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Fig. 8. Dependence of current-density on NO partial pressure in feed at 800°C. Lines are drawn to guide the eye.

Addition of NO and NO₂ to the feed also effected the closed-circuit performance of aged platinum electrodes significantly. To characterize this effect, the current density at fixed potential was measured at 800°C as a function of gas-phase composition. These measurements were made at NO₂ partial pressures (in the reactor) between 1.1 \times 10⁻⁵ and 2.1 \times 10⁻³ atm and NO partial pressures between 9.1 \times 10⁻⁴ and 4.5 \times 10⁻² atm. Once again, the electrode was polarized to no more than \pm 60 mV to minimize the effects of mass transfer on the electrode kinetics. Representative results are shown in Fig. 8, which shows the variation of the current with feed NO concentration at two different potentials. The plot shows that the current increases monotonically with NO₂ concentration.

All of the closed-circuit data collected at 800°C were plotted according to the kinetic models developed earlier in an effort to better understand how the nitrogen oxides participate in the electrode reaction network. In Fig. 9A, for example, the closed-circuit results are plotted according to the first parallel charge-transfer model which assumes that NO₂ is reduced electrochemically to NO. Using the value of $k^{\circ}_{O_2}$ measured at 800°C, the oxygen-exchange current density, i_{O_2} , was calculated from the electrode potential and oxygen partial pressure with Eq. [8]. This partial current density was subtracted from the measured current density, and the difference was plotted against the dimensionless current density for NO₂ reduction to NO, calculated with Eq. [17]. Within experimental scatter, the data fall onto a single curve which is linear at low and moderate values of i'_{NO_2/NO_2}

In Fig. 9B and 9C, the same data are plotted according to the remaining two parallel charge-transfer models. Clearly, no correlation is apparent in either plot. Thus, these kinetic models fail to describe the observed currentvoltage behavior, indicating that electrochemical reduction of NO_2 and NO to nitrogen does not occur at significant rates.

The data are also plotted according to the catalytic model in Fig. 10. Plots of $(k^{\circ}_{O_2} \exp (\mathbf{F}V/RT) - i) vs. k^{\circ}_{O_2} \exp ((2V^{\circ c} - V)\mathbf{F}/RT)$ were prepared from current-voltage characteristics measured at the same gas-phase composition. Once again, no correlation is apparent, indicating that the catalytic model is also inconsistent with the observed electrode behavior.

Similar behavior was observed at lower temperatures. Accordingly, the closed-circuit data was reduced according to the first parallel charge-transfer model, and the results are plotted in Fig. 11. At the lower temperatures, the plots are linear, in agreement with the prediction of this kinetic model; the slopes of these lines should equal the rate constant for reduction of NO₂ to NO, $k^{\circ}_{\text{NO/NO_2}}$. Values of these rate constants estimated from the low $-i'_{\text{NO/NO_2}}$ slopes are plotted as open squares in Arrhenius fashion in Fig. 7. The rate constants are collinear within experimental uncertainty and yield an apparent activation energy of 71 kJ/mol.

Discussion

Of the four kinetic models developed in this study, only one describes the observed current-voltage behavior of a



Fig. 9. Tests of parallel charge-transfer models. (A) partial reduction of NO₂ to NO; (B) reduction of NO; (C) complete reduction of NO₂.

platinum electrode exposed to mixtures of nitrogen oxides and oxygen in an acceptable fashion. The remaining models are clearly inconsistent with experimental measurements. These results strongly suggest that NO_2 is reduced electrochemically at the platinum-zirconia interface to NO and oxygen dianions. This reaction occurs in parallel with oxygen exchange, and the two charge-transfer reactions occur at comparable rates. Complete reduction of either oxide to nitrogen and oxygen ions apparently does not occur at a measurable rate. While it is likely that NO and NO₂ also decompose catalytically on platinum, this reaction does not occur at a large enough rate to perturb the open-circuit potential or current-voltage characteristic of the electrode. This is consistent with the observation that oxygen reversibly poisons the platinum surface toward NO decomposition (24).

Further support for these conclusions is found in the variation of the open-circuit potential with gas-phase composition. If partial reduction of NO_2 and oxygen exchange are the dominant charge-transfer reactions on platinum, one can calculate the mixed potential at open circuit by



equating the oxygen exchange and NO₂ reduction partial currents, Eq. [8] and [15], and solving for the potential. We compare measured open-circuit potentials to mixed potentials calculated at the same conditions in Fig. 12. Over the entire range of gas-phase composition and temperature studied, the calculated potential agrees with the measured potential within experimental uncertainty.

These conclusions are also consistent with a model proposed for the decomposition of nitric oxide in a zirconia electrolytic cell (29, 30). At low cathodic overpotentials, NO was assumed to decompose catalytically to nitrogen and oxygen adatoms; this rate was enhanced by electrochemically "pumping" chemisorbed oxygen from the catalytic surface. Our work indicates that NO reduction does not occur at a significant rate via a charge-transfer reaction; therefore its decomposition must occur primarily by a catalytic mechanism. This implies that NO decomposition should not be strongly potential dependent in this low overpotential regime, as the reaction becomes limited by a potential-independent catalytic surface reaction. This behavior was observed experimentally by Huggins et al. (29).

Our work also indicates that nitrogen is not electroactive on platinum. This is not particularly surprising, as nitrogen is not dissociatively adsorbed on platinum, and the coverage of associatively adsorbed nitrogen should be extremely small at the temperatures and pressures investigated (31). Nitrogen, therefore, should not interfere with zirconia oxygen sensor response. This also implies that nitrogen cannot be oxidized electrochemically on platinum. It is interesting to speculate whether this conclusion would change if the electrode were capable of dissociatively adsorbing nitrogen. We are currently studying electrode materials with demonstrated ability to adsorb nitrogen dissociatively.

The electroactivity of NO and NO₂ seriously complicates the use of zirconia oxygen sensors to monitor the composition of combustion gases and related gas mixtures. Because the open-circuit voltage is a mixed potential, the sensor signal is not a simple function of oxygen concentra-



Fig. 11. NO₂ reduction kinetics. Lines are best fits of Eq. [17]



Fig. 12. Comparison of measured and predicted open-circuit electrode potentials, expressed relative to a reversible oxygen electrode at 1 atm.

tion. Indeed, any given voltage does not necessarily correspond to a unique gas-phase composition, but rather to a variety of mixtures of NO, NO₂, and oxygen. Furthermore, the absolute sensor response is likely to be a strong function of the composition and morphology of the working electrode, both of which effect the relative activity of the electrode for the two charge-transfer reactions. Evidence is building in the literature of other species which are electroactive on platinum in zirconia electrolytic cells (11, 14), and this suggests that these devices will be of limited utility for quantitative measurement of oxygen concentrations in all but the simplest gas mixtures.

Finally, this work demonstrates the importance of studying the closed-circuit behavior of an electrode in identifying the dominant charge-transfer and catalytic processes in an electrode reaction network. Open-circuit measurements are not generally sufficient to discriminate between different networks. Rather, one must vary the electrode potential over a large enough range to change the rates of the various charge-transfer reaction significantly. For example, under the conditions of this study, the cathodic terms of Eq. [15], [A5], and [A11] dominate the partial current densities at potentials near the open-circuit potential. For this reason, the partial currents for NO₂ reduction to NO and N_2 are both proportional to p_{NO_2} at open circuit, and one cannot distinguish between the two reactions. One must polarize the cell to potentials at which the anodic terms in these partial currents become significant in order to discriminate between them. The observations of this work suggest that these simple steady-state measurements are a useful probe of the dominant chargetransfer processes occurring in solid oxide electrochemical systems.

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LIST OF SYMBOLS

- activity
- oxygen dianion concentration
- $\ddot{C}_{\rm O} \\ E_{\rm m} \\ \mathbf{F}$ mixed potential
- Faraday constant
- $\substack{\substack{\theta\\i'\\i}}$ surface coverage
 - dimensionless rate constant
 - current density
- k° standard overall electrochemical rate constant
- k, K rate constant
- adsorption-equilibrium constant p R T V
 - partial pressure (atm)
 - gas constant
 - absolute temperature
- working electrode potential \dot{V}°
 - standard equilibrium potential

a

- V^{oc} open-circuit potential
- transfer coefficient α

Subscripts

anodic а cathodic Ν atomic nitrogen molecular nitrogen N_2 NO_2 nitrogen dioxide NO nitric oxide O_2 molecular oxygen or oxygen exchange 0 atomic oxygen Ś free sites NO/N₂ reaction [3]

 NO_2/N_2 reaction [4] NO₂/NO reaction [5]

APPENDIX

NO reduction to nitrogen and oxygen ions.—We assume that NO is reduced to nitrogen and oxygen dianions by the following reaction network

$$NO + S \rightleftharpoons NO(a)$$
 [A1]

$$N_2 + 2S \rightleftharpoons 2N(a)$$
 [A2]

$$NO(a) + 2e^{-} \rightleftharpoons N(a) + O^{2^{-}}$$
 [A3]

The rate of the charge-transfer reaction should be well described by a Butler-Volmer equation which is first order in adsorbed NO and nitrogen atoms

$$i_{\rm NO/N_2} = k'_{\rm a} C_0 \theta_{\rm N} \exp\left(\frac{(V - V^{\circ}_{\rm NO/N_2})\mathbf{F}}{RT}\right) - k'_{\rm c} \theta_{\rm NO} \exp\left(-\frac{(V - V^{\circ}_{\rm NO/N_2})\mathbf{F}}{RT}\right)$$
[A4]

It is assumed in this expression that the symmetry coefficient is 1/2, therefore the anodic and cathodic transfer coefficients are both unity. We assume that nitrogen and NO are in adsorption equilibrium and at low coverage and follow the same procedure used to derive Eq. [8] to yield the following expression for the rate of reaction NO reduction in terms of measurable quantities

$$i_{\text{NO/NO}_2} = k_{\text{NO/N}_2}^{\circ} \left\{ p_{\text{N}_2}^{1/2} \exp\left(\frac{(V - V_{\text{NO/N}_2}^{\circ})\mathbf{F}}{RT}\right) - p_{\text{NO}} \exp\left(-\frac{(V - V_{\text{NO/N}_2}^{\circ})\mathbf{F}}{RT}\right) \right\}$$
[A5]

where V°_{NO/N_2} is the standard potential and k°_{NO/N_2} is the overall rate constant for NO reduction to nitrogen. The corresponding dimensionless current density is expressed by

$$i'_{\text{NO/N}_2} = p_{\text{N}_2}^{1/2} \exp\left(\frac{(V - V^{\circ}_{\text{NO/N}_2})\mathbf{F}}{RT}\right) - p_{\text{NO}} \exp\left(-\frac{(V - V^{\circ}_{\text{NO/N}_2})\mathbf{F}}{RT}\right)$$
[A6]

NO2 reduction to nitrogen and oxygen ions.-In an analogous fashion, we assume that NO₂ is reduced to nitrogen and oxygen dianions by the following mechanism

$$NO_2 + S \rightleftharpoons NO_2(a)$$
 [A7]

$$N_2 + 2S \rightleftharpoons 2N(a)$$
 [A8]

$$NO_2(a) + 4e^- \rightleftharpoons N(a) + 2 O^{2-}$$
 [A9]

Reaction [A9] represents the overall charge-transfer reaction; we assume that this four-electron transfer occurs by a series of steps whose overall rate can be characterized by a Butler-Volmer type expression which is first order in adsorbed nitrogen, NO2, and oxygen ions with transfer coefficients of unity

$$i_{\text{NO/N}_2} = k'_{a} C_0 \theta_{\text{N}} \exp\left(\frac{(V - V^{\circ}_{\text{NO}_2/\text{N}_2})\mathbf{F}}{RT}\right)$$
$$- k'_{c} \theta_{\text{NO}_2} \exp\left(-\frac{(V - V^{\circ}_{\text{NO}_2/\text{N}_2})\mathbf{F}}{RT}\right) \qquad [A10]$$

Again, we assume that all gas-phase species are in adsorption equilibrium and at low coverages. Following the procedure used to derive Eq. [11], we can express this partial current in terms of measurable quantities

$$i_{\text{NO}_2/\text{N}_2} = k^{\circ}_{\text{NO}_2/\text{N}_2} \left\{ p_{\text{N}_2}^{1/2} \exp\left(\frac{(V - V^{\circ}_{\text{NO}_2/\text{N}_2})\mathbf{F}}{RT}\right) - p_{\text{NO}_2} \exp\left(-\frac{(V - V^{\circ}_{\text{NO}_2/\text{N}_2})\mathbf{F}}{RT}\right)$$
[A11]

where $V^{\circ}_{NO_2/N_2}$ is the standard equilibrium potential and $k^{\circ}_{NO_2/N_2}$ is the overall rate constant for NO₂ reduction to nitrogen. The corresponding dimensionless current density is

$$i'_{NO_{2}/N_{2}} = p_{N_{2}}^{1/2} \exp\left(\frac{(V - V_{NO_{2}/N_{2}}^{\circ})\mathbf{F}}{RT}\right) - p_{NO_{2}} \exp\left(-\frac{(V - V_{NO_{2}/N_{2}}^{\circ})\mathbf{F}}{RT}\right)$$
[A12]

REFERENCES

- 1. W. C. Maskell and B. C. H. Steele, J. Appl. Electrochem., 16, 475 (1986).
- 2. K. Nagata and K. S. Goto, Solid-State Ionics, 9&10, 1249 (1983).
- 3. H. Dietz, W. Haecker, and H. Jahnke, in "Advances in Electrochemistry and Electrochemical Engineer-ing," H. Gerischer and C. W. Tobias, Editors, Wiley Interscience, New York (1977).
- W. L. Worell, Top. Appl. Phys., 21, 143 (1977).
 S. P. S. Badwal, J. Electroanal. Chem., 202, 93 (1986).
 H. Okamoto, H. Obayashi, and T. Kudo, Solid-State
- Ionics, 3/4, 453 (1981).
- 7. C. G. Vayenas and H. M. Saltsburg, J. Catal., 57, 299 (1979).
- 8. C. G. Vayenas, B. Lee, and J. N. Michaels, ibid., 66, 36 (1980).
- S. Seimanides and M. Stoukides, *ibid.*, **88**, 490 (1984).
 K. Vetter, "Electrochemical Kinetics: Theoretical and Experimental Aspects," Academic Press, New York $(19\bar{6}7).$
- 11. H. Okamoto, G. Kawamura, and T. Kudo, J. Catal., 86, 437 (1984); ibid., 82, 322 (1983); ibid., 82, 332 (1983).
- H. Okamoto, K. Go, and T. Kudo, J. Catal., 87, 1 (1984).
 C. G. Vayenas, *ibid.*, 90, 371 (1984).

- 14. H. M. Saltsburg, Personal communication. 15. C. A. Streuli and P. R. Averell, "The Analytical Chemistry of Nitrogen and Its Compounds," pp. 86-98, J.
- Wiley and Sons, New York (1975).
 16. W. L. Jolly, "The Inorganic Chemistry of Nitrogen," pp. 71-75, W. A. Benjamin Inc., New York (1964).
 17. S. Pizzini, in "Fast-Ion Transport in Solids," W. Van Gool, Editor, pp. 461-476, North Holland Publ. Co., Amatondom (1072). Amsterdam (1973).
- 18. D. Braunstein, D. S. Tannhauser, and I. Riess, Solid-State Ionics, 3/4, 509 (1981); This Journal, 128, 82 (1984).
- 19. Da. Yu. Wang and A. S. Nowick, This Journal, 128, 55 (1981)
- 20. Da. Yu. Wang and A. S. Nowick, ibid., 126, 1155 (1979); ibid., 126, 1166 (1979).
- 21. R. J. Brook, W. L. Pelzmann, and F. A. Kroger, ibid., 118, 185 (1971).
- 22. A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications," J. Wiley and Sons, New York (1980).
- 23. B. E. Nieuwenhuys, Surf. Sci., 126, 307 (1983).
- 24. U. Schwalke, H. Niehus, and G. Comsa, ibid., 152-153, 596 (1985)
- 25. A. Amirnazmi, J. E. Benson, and M. Boudart, J. Catal., 30, 55 (1973).
- J. O'M. Bockris and A. K. N. Reddy, "Modern Electro-chemistry," Plenum Press, New York (1970).
 T. L. Hill, "An Introduction to Statistical Thermody-namics," Chap. 7, Addison-Wesley, Menlo Park, CA (1962).
- B. C. Nguyen, T. A. Lin, and D. M. Mason, *This Journal*, **133**, 1807 (1986).
- 29. S. Pancharatnam, R. A. Huggins, and D. M. Mason, ibid., 122, 869 (1975).
- T. M. Gur and R. A. Huggins, *ibid.*, **126**, 1067 (1979).
 M. Wilf and P. T. Dawson, *Surf. Sci.*, **60**, 561 (1976).