The oxygen reduction reaction (ORR) has been studied by using a rotating disk electrode (RDE) in acidic electrolytes such as sulfuric, perchloric, hydrochloric, and organic acid solutions. Several reaction pathways have been proposed for the ORR based on the RDE experimental data, of which the four-electron pathway is primarily used to characterize the behavior of this reaction at a platinum electrode or a glassy carbon electrode coated with platinum-supported catalyst. The overall ORR is given by

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$$

where a mechanism that consists of four separate single-electron-transfer steps is implicitly assumed.

A linear Tafel plot is expected for this four-electron reaction mechanism when the potential is lower than the standard electrode potential of 1.229 V vs the standard hydrogen electrode (SHE). Note that all the potentials mentioned in this work are with respect to the SHE. The potential region of 1.0–0.6 V is where the polymer electrolyte membrane fuel cell (PEMFC) is operated practically. Important kinetic information such as the exchange current density and the transfer coefficient can be extracted by studying this voltage window for the ORR occurring at metal electrodes or carbon-supported platinum nanoparticle catalyst-coated electrodes.

Transitions in the Tafel slopes for the ORR are observed when experimental data is analyzed. The Tafel slope is just about doubled in the higher current density (LCD) region (the potential region below about 0.8 V) compared to the lower current density (LCD) region (the potential region above 0.8 V). Table I presents a collection of examples from the literature which present changing Tafel slopes. When the temperature is around 298 K, the Tafel slope in the LCD region is around 60 mV/dec, which is close to 2.303RT/F, whereas this value is about 120 mV/dec or 2 × 2.303RT/F in the HCD region. The double Tafel slope phenomenon is observed at smooth surfaces such as electrodes made of polycrystalline Pt, Pt (111), Pt (100), or Pt alloy, etc., and at inert electrodes coated with nanosized carbon-supported Pt catalyst powder. Various explanations have been suggested to explain the change in the Tafel slope, and one of them is the oxygen adsorption mechanism, which relates the change in the Tafel slope to the change in the applied potential. The adsorption of oxygen on the platinum surface is further complicated by the presence of other competing species and intermediates. The adsorption of the anion HSO$_4^-$ can compete with the molecular oxygen adsorption for the Pt site. Reversible dissolution of water at the surface of the electrode can lead to PtOH formation in the potential region of 0.6–1.0 V vs SHE, and this process may interfere with the electrochemical reactions occurring at the surface of the electrode.

In this work, a generalized model is presented for the adsorption of multiple species $R_{\text{sur}}$. Each adsorbing species is assumed to be transported to the surface of the electrode and become adsorbed to the electrode surface to form $R_{\text{ads}}$

$$R_{\text{sur}} = R_{\text{ads}}$$

where the subscripts sur and ads represent the species in the solution phase adjacent to the surface of the electrode and the species adsorbed on the electrode surface, respectively. The adsorbed species subsequently participates in a charge-transfer reaction together with other species $P_\alpha$, which are involved in the reaction on the electrode directly without undergoing an adsorption step

$$R_{\text{ads}} + \sum_i s_i P_i^{\alpha} \equiv n_i \text{e}^-$$

For example, the oxygen reduction mechanism is modeled using an intermediate step involving oxygen adsorption, during which the reactant oxygen is transferred to the solution phase adjacent to the electrode surface; then the oxygen reaches the electrode surface via an adsorption step, and it is assumed that only the adsorbed oxygen on the electrode can proceed to the charge-transfer reaction as shown below

$$O_{\text{ads}} \equiv O_{\text{sur}}$$

$$O_{\text{ads}} + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$$

Models for Reactions 1-5 are presented below, with a detailed derivation of the kinetic equation for the adsorption mechanism. The models are compared by simulating the polarization curves for both the models and regression of transport and kinetic parameters for the ORR in 0.5 M H$_2$SO$_4$ solution at an RDE. The equations used for representing mass transfer are based on the Nernst–Planck equation, and the kinetic equations used for the boundary conditions are based on the Butler–Volmer equation. These equations were derived in detail for the RDE system by White et al. The effect of oxygen adsorption is included in the kinetic equation for the adsorption mechanism. The models presented here are coded in the Fortran language and solved with a subroutine named general nonlinear estimation technique. The effects of changes in some important kinetic parameters are demonstrated.
Table I. Literature showing double Tafel slopes for the ORR.

<table>
<thead>
<tr>
<th>Catalyst/electrode</th>
<th>Tafel slopes LCD/HCd (mV/dec)</th>
<th>Other conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(100) smooth surface</td>
<td>65/120</td>
<td>0.05 M H₂SO₄ solution, 900 rpm, 50 mV/s, room temperature 1 atm O₂</td>
</tr>
<tr>
<td>Pt(110) smooth surface</td>
<td>80/120</td>
<td>0.05 M H₂SO₄ solution, 900 rpm, 50 mV/s, room temperature 1 atm O₂</td>
</tr>
<tr>
<td>Pt(111) smooth surface</td>
<td>61–66/118–162</td>
<td>1 M H₂SO₄ mixed with 0.5, or 1 M K₂SO₄, 2000 rpm, 10 mV/s, 298.15 K, 1 atm O₂</td>
</tr>
<tr>
<td>Pt(100) smooth surface</td>
<td>61–64/162–165</td>
<td>1 M H₂SO₄ mixed with 0.5, or 1 M K₂SO₄, 2000 rpm, 10 mV/s, 298.15 K, 1 atm O₂</td>
</tr>
<tr>
<td>Pt polycrystalline, smooth surface</td>
<td>67–69/120–163</td>
<td>1 M H₂SO₄, mixed with 0.5, or 1 M K₂SO₄, 2000 rpm, 10 mV/s, 298.15 K, 1 atm O₂</td>
</tr>
<tr>
<td>Pt(100), Pt(111), smooth surface</td>
<td>70/120</td>
<td>0.05 M H₂SO₄ solution, 900 rpm, 50 mV/s, 298 K, 313 K, 333 K, 1 atm O₂</td>
</tr>
<tr>
<td>Pt polycrystalline, PtNi-sputtered, or PtCo-sputtered, or PtCo-annealed, smooth surface²</td>
<td>74–86/105–113</td>
<td>0.1 M HClO₄ solution, 1600 rpm, 20 mV/s, 293 K, 1 atm O₂</td>
</tr>
<tr>
<td>Pt²⁰% Pd/Vulcan XC72 carbon coated on carbon glass surface³</td>
<td>80/110–123</td>
<td>Catalyst loading: 14 µg/cm² 0.5 M H₂SO₄ solution, 1600 rpm, 5 mV/s 293 K, 303 K, 313 K, 333 K, 1 atm O₂</td>
</tr>
<tr>
<td>Pt plug, smooth surface</td>
<td>59/112</td>
<td>1 M trifluoromethane sulfuric acid (TFMSA) solution, 1000 rpm, 25 mV/s room temperature, 1 atm O₂</td>
</tr>
<tr>
<td>Platinum microelectrode, 100 µm in diameter⁴</td>
<td>65–76/110–123</td>
<td>Nafion/water, vapor in a pressure vessel, no rotation, 1 mV/s, temperature 303–353 K, 5 atmO₂</td>
</tr>
<tr>
<td>Pt Pt₃Co, Pt₃Ni polycrystalline, Pt/C⁵</td>
<td>59–65/107–126</td>
<td>0.1 M HClO₄, 1600 rpm, 5 mV/s 293 K, 1 atm O₂</td>
</tr>
<tr>
<td>Pt, PtCo, Pt₃Ni polycrystalline, Pt/C⁶</td>
<td>46–53/92–124</td>
<td>0.1 M HClO₄, 1600 rpm, 5 mV/s 333 K, 1 atm O₂</td>
</tr>
</tbody>
</table>

Model Equations

Mass-transfer equations.—The material balance for each species within the boundary layer near the surface of an RDE, in terms of dimensionless spatial coordinates (ξ), is of the following form²⁰,²²,²⁵

$$\frac{D_i}{D_R} \frac{d^2c_i}{d\xi^2} + 3\xi \frac{dc_i}{d\xi} + \frac{z_iF}{D_R RT} \left[ \frac{dc_i}{d\xi} + \frac{dc_i}{d\xi} \right] = 0 \quad [6]$$

where $D_i$ is the diffusion coefficient of species $i$ in cm²/s, $D_R$ is the diffusivity of the limit reactant in cm²/s, $F$ is the Faraday constant with a value of 96,487 C/mol, $R$ is the universal gas constant with a value of 8.3143 J/mol K, $T$ is the absolute temperature in K, $c_i$ is the concentration of species $i$ in mol/cm³, $\Phi$ is the potential in the solution within the diffusion layer in V, and the subscript $i$ is the index of species. When Reaction 1 or Reactions 4 and 5 are under consideration, $i = 1, 2$, and 3 corresponding to O₂, H₂, and HSO₄⁻, respectively. The homogeneous reaction term is omitted in Eq. 6. Also, the equations are solved in one spatial dimension. Following the estimation method in the book by Bard and Faulkner,²⁶ the thickness of the hydrodynamic boundary layer near the surface of the electrode is of the order of $1 \times 10^{-3}$ cm in magnitude, at rotating speeds ranging from several hundred to several thousand revolutions per minute (rpm), whereas the radius of the disk is normally of the order of several millimeters. Hence the choice of a one-dimensional model is justified. The electroneutrality condition given by

$$\sum_i z_i \xi = 0 \quad [7]$$

completes the set of equations needed to solve for the unknowns of concentration $c_i$ and liquid potential $\Phi$. All changes in the solution are assumed to be limited to a distance of $\xi < 2$ and hence the bulk conditions in the solution are assumed to prevail at $\xi \gg 2$. The boundary conditions in the bulk solution and at the electrode surface are given by²⁰,²²,²⁵

$$c_i = c_i, \quad \Phi = \Phi_{RE} \quad \text{at} \quad \xi = 2 \quad [8]$$

and

$$\sum_i s_j \gamma_i \rightarrow \gamma_j \quad [10]$$

where $s_j$ is the stoichiometric coefficient of species in reaction $j$, and $n_j$ is the number of electrons transferred in reaction $j$ when written using the reduction convention

$$\sum_i s_i \Delta M_{ij} = n_j e^- \quad [10]$$

Kinetic equation for the four-electron-transfer model.—The current densities ($i_j$) in Eq. 10 can be obtained from the Butler–Volmer expression²⁰,²²,²⁵

$$i_j = i_{0,j} \left[ \exp \left( \frac{\alpha_j F}{RT} \eta_j \right) - \exp \left( - \frac{\alpha_j F}{RT} \eta_j \right) \right] \quad [11]$$

where

$$i_{0,j} = i_{0,j} \prod_{i} \left( \frac{C_{i,0}}{C_{i,red}} \right)^{\gamma_{ij}} \quad [12]$$

and the open-circuit potential of reaction $j$ at the reference concentrations relative to a standard reference electrode of a given kind is expressed as²⁰,²²,²⁵

$$U_{j,ref} = U^0_j - \frac{RT}{n_j F} \sum_i s_i \ln \left( \frac{C_{i,red}}{C_{i,0}} \right) - U^0_{RE} \quad [13]$$

The overpotential for electrochemical reaction $j$, $\eta_j$ in Eq. 11, is given as²⁰,²²,²⁵

$$\eta_j = \Phi_{met} - \Phi_{RE} - (\Phi_j - \Phi_{RE}) - U_{j,ref} + \frac{RT}{n_j F} \sum_i s_i \ln \left( \frac{C_{i,0}}{C_{i,red}} \right) \quad [14]$$

Also, $\gamma_{ij}$ is assumed to be related to $s_{ij}$ in the following way
where

\[ \gamma_i = p_i - \frac{\alpha_i \eta_i^a}{n} \text{ for anodic reactions} \]

\[ \gamma_i = q_i + \frac{\alpha_i \eta_i^c}{n} \text{ for cathodic reactions} \]  \[\text{[15]}\]

and the reaction order constants \( p_i \) and \( q_i \) are related to \( s_i \) by

\[ \begin{cases} p_i = s_i - q_i = 0 \quad \text{if } s_i > 0 \\ p_i = 0 \quad q_i = -s_i \quad \text{if } s_i < 0 \end{cases} \]  \[\text{[16]}\]

The apparent transfer coefficients for a reaction sum up to the number of electrons transferred in that reaction, that is

\[ \alpha_{a,j} + \alpha_{c,j} = n_j \]  \[\text{[17]}\]

**Kinetic equation for the adsorption model.**—The following assumptions are made in this derivation: there are no double-layer effects and the adsorption process is fast; the Langmuir isotherm is applicable; the adsorbed species at the electrode surface \( R_{ads} \) occupies only one monolayer on the electrode surface and their concentration \( c_{ads} \) is proportional to their corresponding fractional coverage \( \theta_i \) at the electrode. Interactions among the adsorbed species are ignored for simplicity.

The following derivations are based on the adsorption mechanism that consists of an adsorption step and a charge-transfer step, as shown in Reaction mechanisms 2 and 3. The adsorption step shown in Reaction 2 is a chemical reaction rather than an electrochemical reaction; however, in order to derive the kinetic expression for Reactions 2 and 3, it is convenient to express the rate equation in a form similar to that of an electrochemical reaction

\[ i_{a,l} = -k_c R_{R,0} \left( 1 - \sum_{k=1}^{\infty} \theta_k - \theta_i \right) - k_l \theta_i \]  \[\text{[18]}\]

where \( i_{a,l} \) is the current density of the adsorption step at the electrode surface, and \( \theta_i \) is the fraction of the electrode surface covered by the adsorbed species. The corresponding expression for Eq. 4 is

\[ i_{a,c} = -k_c R_{R,0} \left( 1 - \sum_{k=1}^{\infty} \theta_k - \theta_i \right) - k_l \theta_i \]  \[\text{[19]}\]

where \( i_{a,c} \) is the current density of the oxygen adsorption step at the electrode surface. \( \theta_c \) is the fraction of the electrode surface covered by the adsorbed oxygen. The surface coverage \( \theta_i \) in Eq. 18 is not an equilibrium value and hence cannot be obtained from the adsorption isotherms. In order to obtain an expression for the current density for the mechanism proposed in Reactions 2 and 3, it is necessary to eliminate the variable \( \theta_i \) in the rate expressions for the individual steps as shown below.

The first step is to relate the rate of adsorption to the surface coverage at equilibrium. When the adsorption process is in equilibrium with the solution immediately adjacent to the electrode surface, the adsorption rate \( i_{a,l} \) should be 0 because the rate of adsorption equals the rate of desorption, the net change in \( c_{ads} \) is zero

\[ 0 = k_c R_{R,0} \left( 1 - \sum_{k=1}^{\infty} \theta_k - \theta_i \right) - k_l \theta_i \]  \[\text{[20]}\]

Substituting Eq. 21 into Eq. 18, we have

\[ i_{a,l} = -k_c R_{R,0} \left( \theta_i \left( 1 - \sum_{k=1}^{\infty} \theta_k \right) - \theta_i \left( 1 - \sum_{k=1}^{\infty} \theta_k \right) \right) \]  \[\text{[22]}\]

If we define the rate constant for the adsorption reaction \( (i_{a,ads}) \) as follows

\[ i'_{a,ads} = -k_c R_{R,0} \]  \[\text{[23]}\]

we have

\[ i_{a,l} = -i'_{a,ads} \left( \theta_i \left( 1 - \sum_{k=1}^{\infty} \theta_k \right) - \theta_i \left( 1 - \sum_{k=1}^{\infty} \theta_k \right) \right) \]  \[\text{[24]}\]

For a charge-transfer step occurring at the surface of the electrode, as shown in Reaction 3, the current density can be expressed according to the Butler–Volmer equation. The adsorbed species is assumed to be reduced in the following derivation. However, the equations for the case of the adsorbed species being oxidized can be derived likewise. The Butler–Volmer equation for the charge-transfer step is of the following form

\[ i_l = k_c \left( \prod_i c_{i,F}^0 \exp \left( \frac{\alpha_i F}{RT} V \right) - k_i R_{ads} \left( \prod_i c_{i,F}^0 \exp \left( -\frac{\alpha_i F}{RT} V \right) \right) \right) \]  \[\text{[25]}\]

Because the adsorption reaction occurs only at the fraction of the electrode surface occupied by the active sites \( (\theta_i) \) and the reverse reaction occurs only at the surface not covered by any adsorbed species, it is necessary to multiply the anodic part by the term \( (1 - \sum_{k=1}^{\infty} \theta_k - \theta_i) \) and the cathodic part by \( \theta_i \) in Eq. 25

\[ i_l = k_c \left( \prod_i c_{i,F}^0 \exp \left( \frac{\alpha_i F}{RT} V \right) - k_i R_{ads} \left( \prod_i c_{i,F}^0 \exp \left( -\frac{\alpha_i F}{RT} V \right) \right) \right) \]  \[\text{[26]}\]

where \( c_{i,F}^0 \) is the concentration of anodic species \( i \) in the charge-transfer reaction in mol/cm\(^3\), and \( R_{ads} \) is the transient concentration of species \( l \) adsorbed on the electrode surface in mol/cm\(^3\). The electrode potential \( V \) is given by

\[ V = \Phi_{net} - \Phi_0 \]  \[\text{[27]}\]

where both \( \Phi_{net} \) and \( \Phi_0 \) are measured with respect to the same reference electrode. The concentration of the adsorbed species \( c_{ads} \) can be expressed in terms of the fractional coverage \( \theta_i \). Because it is assumed that the adsorbed species occupies a monolayer at the surface of the electrode, \( c_{ads} \) is linearly related to the fractional coverage \( \theta_i \), i.e., \( c_{ads} \) is related to the surface coverage \( \theta_i \) by the following expression

\[ c_{ads} = k_{j,ads} \theta_j \]  \[\text{[28]}\]

where \( k_{j,ads} \) is a proportionally constant for the adsorption Reaction 1. The rate expression Eq. 26 can be rewritten in terms of the surface coverage \( \theta_i \) as follows
where \( k'_{i,j} \) and \( k_{i,j} \) are the new rate constants given by

\[
k'_{i,j} = k'_{i,j} \prod_{i} c_{i,j}^0, \quad k_{i,j} = k_{i,j} \prod_{i} c_{i,j}^0
\]

Rewriting Eq. 32 in terms of \( i_j \), we have

\[
i_j = k'_{i,j} \left( 1 - \sum_{k,l} \theta_{k,j} - \theta_{i,j} \right) \exp \left( \frac{\alpha_j F}{RT} V \right) - k_{i,j} \theta_{i,j}^2 \exp \left( - \frac{\alpha_j F}{RT} V \right) \]

where \( \theta_{j,0} \) is the surface coverage at equilibrium, and \( V_{0,j} \) is the corresponding equilibrium electrode potential. Using Eq. 32 to define the equilibrium exchange current density \( i'_{0,j} \), we have

\[
i'_{0,j} = k'_{i,j} \left( 1 - \sum_{k,l} \theta_{k,j} - \theta_{i,j} \right) \exp \left( \frac{\alpha_j F}{RT} V_{0,j} \right)
\]

\[
i'_{0,j} = k_{i,j} \theta_{i,j} \exp \left( - \frac{\alpha_j F}{RT} V_{0,j} \right)
\]

Rewriting Eq. 32 in terms of \( i'_{0,j} \), we have

\[
i_j = i'_{0,j} \left( \frac{1 - \sum_{k,l} \theta_{k,j} - \theta_{i,j}}{1 - \sum_{k,l} \theta_{k,j} - \theta_{i,j}} \exp \left( \frac{\alpha_j F}{RT} \eta_j \right) \right)
\]

\[
i_j = \frac{\theta_j}{\theta_{j,0}} \exp \left( - \frac{\alpha_j F}{RT} \eta_j \right)
\]

where

\[\eta_j = V - V_{0,j}\]

\[
i'_{0,j} = k_{i,j} \theta_{i,j} \prod_{i} c_{i,j}^0 (1 - \theta_{j,0})^{n_j} / \theta_{i,j} \prod_{i} c_{i,j}^0
\]

\[
V_{0,j} = \frac{RT}{n_j F} \left( \frac{\theta_j}{\theta_{j,0}} \prod_{i} c_{i,j}^0 \right) \left[ 1 - \sum_{k,l} \theta_{k,j} - \theta_{i,j} \right]
\]

Because we have assumed that there are no double-layer effects and that the adsorption step is fast, at steady state, the rate of the adsorption step should be the same as the charge-transfer step

\[i_j = i_{0,j}\]

This relationship can be used to eliminate the surface coverage (\( \theta_j \)) between Eq. 24 and 33. The equilibrium surface coverage values (\( \theta_{j,0} \)) are usually obtained by holding a potential value for a particular time interval and integrating the charge passed in desorbing the adsorbed layer formed during a cathodic potential sweep.}

**Limiting case of a single reaction.**— The system of equations described above is complicated because of the simultaneous occurrence of several reactions at the electrode surface. However, when a simplifying assumption that the ORR is the only reaction occurring at the electrode surface can be made, a closed form solution for the surface coverage as well as the current at the surface of the electrode as functions of the electrode potential can be obtained. Such a limiting case analysis provides options to obtain kinetic parameters as described in the next section.

At the limiting case of ORR being the only reaction at the electrode surface, the following additional assumptions are made: surface the concentration of the solvent (water) is constant and the protons do not undergo an adsorption process. The surface coverage (\( \theta \)) is assumed to be independent of the potential at the electrode surface. This assumption can readily be relaxed by introducing a function obtained from experimental data to relate the surface coverage to the surface potential; however, the derivation of such a function has been subject to criticism. As indicated in Eq. 38, for the case of fast adsorption, the rate of the adsorption process and Reaction 5 is the only charge-transfer reaction, the subscripts \( j \) and \( j \) are omitted. Equations 24 and 34 become

\[i_k = i'_{0,j} \left( \frac{\theta_j}{\theta_{j,0}} \right) \exp \left( - \frac{\alpha_j F}{RT} \eta_j \right)
\]

and Eq. 23, 28, and 35-37 become

\[i'_{0,j} = k_{i,j} \theta_{i,j} \prod_{i} c_{i,j}^0 (1 - \theta_{j,0})^{n_j} \theta_j^{n_j}/(1 - \theta_{j,0})^{n_j} \theta_j^{n_j}/2
\]

\[\eta_j = V - V_j
\]

\[V_j = \frac{RT}{4F} \left( \frac{\theta_j}{\theta_{j,0}} \prod_{i} c_{i,j}^0 \right) + \frac{RT}{4F} \ln \left( \frac{\theta_j^{n_j} \prod_{i} c_{i,j}^0}{\theta_{j,0}^{n_j} \prod_{i} c_{i,j}^0} \right)
\]

As indicated in Eq. 38, for the case of fast adsorption, the rate of the adsorption process should be the same as that of the charge-transfer step, and because in the limiting case there are no other reactions, the rates of adsorption and charge-transfer reaction are also the same as the total current density across the cell

\[i = i_k
\]

This relationship can be used to eliminate the surface coverage (\( \theta_j \)) in Eq. 40 and 41. The derivation of the relationship between the current density (\( i \)) to the cell potential (\( V \)) in terms of the equilibrium surface coverage (\( \theta_j \)) and the concentration of oxygen at the surface of the electrode (\( c_{O_2,j} \)) is shown in the Appendix. A closed form solution and a limiting case are presented below. From Eq. 41, solving for \( \theta \) we have
and the concentration of oxygen at the surface of the electrode deriving Eq. 48-51 be much smaller than one, the following approximation was made in Because the surface coverage of oxygen at all times was assumed to

Substituting Eq. 47 and the expression for $\theta$ (i.e., Eq. 48) into the rate expression for the adsorption step (i.e., Eq. 40) we have

Solving for the current density across the cell ($i$) from the above equation gives

where

Because the surface coverage of oxygen at all times was assumed to be much smaller than one, the following approximation was made in deriving Eq. 48-51

In Eq. 50 and 51, $\eta$ is given by Eq. 44, $i_{0,a}'$ is given by Eq. 42, and $i_0'$ is given by Eq. 45.

Thus we have an expression relating the current density ($i$) to the cell potential ($V$) in terms of the equilibrium surface coverage ($\theta_0$) and the concentration of oxygen at the surface of the electrode ($c_{O_2,0}$). To complete the derivation, the Langmuir’s isotherm for chemisorption is introduced to relate the equilibrium surface coverage to the concentration of the adsorbed species.26,29,30

where $\Delta G^0$ is the Gibbs free energy change for the adsorption process. Because we have assumed that $\theta \ll 1$ under all conditions, this

implies that the surface adsorption is not energetically favorable or in other words, the $\Delta G^0$ value for this reaction is a large positive value. Hence, we have

Equations 42 and 45 are used to calculate $i_{0,a}'$ and $i_0'$, containing terms that are dependent on the concentration at the surface of the electrode. It is convenient to define these quantities in terms of the exchange current densities defined at reference conditions

Here, $\theta_{0,ref}$ is the fractional coverage of oxygen with respect to a reference solution, which is practically chosen to be 0.5 M $\text{H}_2\text{SO}_4$ solution saturated with oxygen. Because the exponent in Eq. 54 is constant at a given temperature, we have

Therefore, Eqs. 42 and 45 become

Once again, in obtaining Eq. 59, the approximation shown in Eq. 52 is used. Note that this approximation assumes that the surface coverage of oxygen is negligible, independent of the potential at the electrode surface. This is not strictly valid at all values of the surface potential. A more rigorous derivation can be obtained using the equations shown in the Appendix. However, closed-form solutions similar to those presented in Eqs. 49, 50, and 59 may not be possible. A detailed comparison of the limiting case solution to the rigorous solution will be published elsewhere.

The expression for overpotential in terms of the reference concentrations is given by the following equation20,22,25

Substituting Eq. 27 into Eq. 60 we have

where $U_{ref}$ is defined by Eq. 13.

Thus, the final expression relating the current density ($i$) to the cell voltage ($V$) is given by

Equations 62 and 63 are more convenient to use because the exchange current densities and the overpotential are evaluated at the reference concentrations as opposed to the surface concentrations.
Consequently, the exchange current density values can be obtained experimentally at a particular reference condition and the values at other conditions can be calculated readily using Eq. 58 and 59. The exchange current density of the adsorption step \( i_{0,a} \), is linearly proportional to the concentration of oxygen adjacent to the surface of the electrode \( c_{O_2,0} \).

### Results and Discussion

The governing equations (Eq. 6 and 7) subject to the given boundary conditions (Eq. 8 and 9) are solved numerically by an iterative procedure using both Fortran and Comsol Multiphysics as previously mentioned. The applied potential \( E_{pple} = E_{met} - E_R \) is varied in the range of 1.0–0.0 V and the distribution of \( c_i \) and \( \Phi \) in the electrolyte solution, and the current density \( i \) at each specified applied potential \( E_{pple} \) are obtained. The plots of \( i \) vs \( E_{pple} \) are the polarization curves. The parameters used to simulate the ORR in a 0.5 M H\textsubscript{2}SO\textsubscript{4} solution at 25°C are shown in Table II. Diffusion coefficients for all species in dilute water were used because literature values for this acidic solution are not readily available.

### Table II. Parameter values for simulating the polarization curves for the ORR.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Reaction 1</th>
<th>Reaction 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_c )</td>
<td>0.5–1.5</td>
<td>0.5–1.5</td>
</tr>
<tr>
<td>( i_{0,a} ) (A/cm\textsuperscript{2})</td>
<td>( 1 \times 10^{-6} )–( 1 \times 10^{-14} )</td>
<td>( 1 \times 10^{-6} )–( 1 \times 10^{-14} )</td>
</tr>
<tr>
<td>( E_{pple} ) (V)</td>
<td>1.229</td>
<td>1.229</td>
</tr>
<tr>
<td>( n )</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Solution properties ( c_i ) (mol/cm\textsuperscript{3})</td>
<td>( 1.13 \times 10^{-6} )</td>
<td>( 5 \times 10^{-4} ) or ( 5 \times 10^{-5} )</td>
</tr>
<tr>
<td>( D_i ) (cm\textsuperscript{2}/s)</td>
<td>( 1.79 \times 10^{-5} )</td>
<td>( 9.312 \times 10^{-5} )</td>
</tr>
<tr>
<td>( F = 96.487 ) C/mol</td>
<td></td>
<td>( \rho = 0.001 ) kg/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>( R = 8.314 ) J/K mol</td>
<td></td>
<td>( v = 0.01187 ) cm\textsuperscript{2}/s</td>
</tr>
<tr>
<td>Reaction properties</td>
<td></td>
<td>( \Omega = 900 ) rpm</td>
</tr>
<tr>
<td>( s_i )</td>
<td>(-1)</td>
<td>(-4)</td>
</tr>
<tr>
<td>( z_i )</td>
<td>0</td>
<td>+1</td>
</tr>
<tr>
<td>( p_i )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( q_i )</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>( \gamma_{i,k} )</td>
<td>( 1 - \alpha_c /4 )</td>
<td>( 4 - \alpha_c )</td>
</tr>
</tbody>
</table>

Parameter estimation and comparison of models.— The utility of the limiting case analysis is significant in obtaining the kinetic parameters from experimental data. No quantitative result distinguishing the surface coverage of individual species on an electrode surface involving multiple reactions is reported in the literature. Hence, we used the limiting case results to obtain the parameters from experimental data using both models for reaction mechanisms 1, 4, and 5 in this work. For the regression scheme, the Gauss–Newton nonlinear parameter estimation method is employed.\textsuperscript{31,32} The exchange current density for the charge-transfer step \( i_{0,ref} \), the cathodic transfer coefficient \( \alpha_c \), and the diffusion coefficient of oxygen \( D_{O_2} \) in the electrolyte are regressed simultaneously and the 95% confidence intervals are also calculated.\textsuperscript{31} The parameter \( i_{a,ref} \) is assigned a value of 10 A/cm\textsuperscript{2}, which is a relatively large value so that the adsorption process is fast enough so as not to affect the limiting current densities. One set of regression results with the data digitized from a polarization curve published by Paulus et al.\textsuperscript{3} is shown in Fig. 1. The regressed parameter values, 95% confidence intervals, and the experimental and fitting lines are shown in the figure.
The model shows the change in the Tafel slope similar to the experimental observations. Reaction 1 predicts a constant slope, the adsorption model indicates that the adsorption process introduces an increase in the resistance to the charge-transfer process, which is counteracted by the increase in the transfer coefficient. The same trend is observed in the other three sets of regression results (see Table III). The higher values for the transfer coefficients estimated from the adsorption model indicate that the adsorption process introduces an increase in the resistance to the charge-transfer process, which is counteracted by the increase in the transfer coefficient. In other words, if the ion were to undergo adsorption at the surface of the electrode before the charge-transfer reaction can take place, the gradient in the field that the ion has to traverse across the interface is increased. The validity of the parameters obtained by nonlinear regression is further supported by the calculation of the 95% confidence intervals, which is shown alongside the values of the parameters. The small values for the confidence intervals indicate that the use of the corresponding models is appropriate for the set of data considered. The comparison of the experimental Tafel slope with those obtained from the two models is shown in the inset of Fig. 1 in the form of Levich–Koutecky plots made with data corrected for mass transfer following the procedure outlined by Bard et al. As observed, while Reaction 1 predicts a constant slope, the adsorption model shows the change in the Tafel slope similar to the experimental curve. It should be reinforced again that the model equations used in the simulation above assume that the surface coverage is independent of the potential and the influence of the potential dependence of the surface coverage parameter (θ) on the values reported in Table III has not been considered. We did not consider a detailed mechanism for the adsorption process either. However, a mechanistic investigation of the adsorption process often results in a more complicated isotherm. Hence, the set of equations describing the new system can readily be obtained by using such an expression in the place of Eq. 53 presented here.

In obtaining Fig. 1 the regressed values for the diffusion and transfer coefficients were used. To compare the adsorption model and the four-electron-transfer model for the same set of parameters, a pair of simulations with both models is shown in Fig. 2. The parameters used are \( i_{\text{ref}} = 1.0 \times 10^{-7} \text{ A/cm}^2 \), \( \alpha_s = 1.0 \), and \( D_{\text{O}_2} = 1.557 \times 10^{-5} \text{ cm}^2/\text{s} \) for the four-electron-transfer model. In addition to these, \( i_{\text{ref}} = 10 \text{ A/cm}^2 \) is used for the adsorption model. Note that the value of \( i_{\text{ref}} \) is relatively big so that the adsorption rate is fast and will not affect the limiting current density. The respective Tafel slopes are shown in the Levich–Koutecky plots inserted in this figure. From this figure, we can see that the model with the adsorption mechanism can predict the change in the Tafel slope. The Tafel slope is roughly doubled in the region where the exchange current density and a larger transfer coefficient.

Table III. Regression results with 95% confidence intervals for the parameter values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Adsorption model</th>
<th>Diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy carbon coated with Pt/C</td>
<td>( \alpha_s ), s</td>
<td>(1.21 ± 0.22) ( \times 10^{-7} )</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>( \alpha_s ), s</td>
<td>(2.28 ± 0.049) ( \times 10^{-5} )</td>
</tr>
<tr>
<td>Our data, bare platinum electrode</td>
<td>( \alpha_s ), s</td>
<td>(8.5385 ± 0.0005) ( \times 10^{-5} )</td>
</tr>
<tr>
<td>Our data, glassy carbon coated with Pt/C</td>
<td>( \alpha_s ), s</td>
<td>(0.5528 ± 0.0068) ( \times 10^{-5} )</td>
</tr>
</tbody>
</table>

\(^a\) Mean squares of errors.
\(^b\) The data was obtained using a bare Pt RDE (Pine Instruments) at 900 rpm in a 0.5 M \( \text{H}_2\text{SO}_4 \) solution.
\(^c\) The data was obtained using an RDE coated with 30 wt % Pt/C catalyst (provided by E-TEK) at a rotating speed of 900 rpm in a 0.5 M \( \text{H}_2\text{SO}_4 \) solution.
The electrochemical reaction accelerates exponentially as the $E_{\text{app}}$ is decreased linearly, but the adsorption process slows down quickly with the decrease of the oxygen concentration adjacent to the surface of the electrode. Thus, the overall reaction rate is controlled by adsorption once the reaction proceeds into the so-called ohmic region where the polarization curves descend quickly. With the decrease in the applied potential, the overall reaction rate is limited by the supply of oxygen instead of the charge-transfer reaction. Limitation in the supply of oxygen may arise from either the adsorption process being slow or from mass-transfer effects. Figure 2 shows the case that oxygen supply is limited by mass transport because the adsorption process is relatively fast with the assigned value $i_{a,\text{ref}}$ = 10 A/cm$^2$. For this case, the apparent limiting current density is the same as that predicted by the four-electron-transfer model or the Levich equation. The case of relatively slower adsorption rate (i.e., with smaller values of $i_{a,\text{ref}}$) which can change the limiting current density is discussed in the next section.

*Studies of the effect of parameters.*— Figure 3 shows the effect of the cathodic transfer coefficient and the exchange current density of the four-electron-transfer model (Reaction 1) on the polarization curves. Again the inserted figure shows the respective Levich–Koutecky plots with mass-transfer-corrected data, while the values of the corresponding Tafel slopes can be found in Table IV. When the transfer coefficient is held constant at 1.0, a change in the exchange current density makes the polarization curve shift horizontally without changing the shape of the curve. But the transfer coefficient affects both the curvature and the position of the curve.
when the exchange current density is held at $1 \times 10^{-10}$ A/cm². Calculated Tafel slopes coincide with the slopes predicted using the Tafel equation given by $2.303 \frac{RT}{F c}$. However, this model predicts only one Tafel slope, and subsequently, the fit to experimental data is not satisfactory.

Figure 4 shows the effect of the transfer coefficient in the adsorption model. The inset figure shows the Levich–Koutecky plots. Table IV contains the respective values of the Tafel slopes. For this case, the transfer coefficient shows about the same effect on the polarization curves as in the four-electron-transfer model, but the Tafel slope changes as shown in the Levich–Koutecky plots. When the exchange current density is held at $1 \times 10^{-10}$ A/cm², the Tafel slope changes at higher potentials for the cases where the transfer coefficient is larger. The Tafel slopes at the LCD region coincide with the predictions from the Tafel equation, while the Tafel slopes in the HCD region are roughly doubled compared to the slopes in the LCD region.

![Figure 4. Effect of $\alpha_c$ in the adsorption model. Parameters used in the plot: $i_{a,ref} = 1 \times 10^{-8}$ A/cm², $D_O2 = 1.557 \times 10^{-5}$ cm²/s, and $i_{ref} = 1 \times 10^5$ A/cm².](image)

### Table IV. Apparent Tafel slopes in Fig. 1-6.

<table>
<thead>
<tr>
<th>Line description</th>
<th>Voltage at which the slope changes (V)</th>
<th>LCD Tafel slope (mV/dec)</th>
<th>HCD Tafel slope (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In Fig. 1</td>
<td>Experimental data*</td>
<td>0.85</td>
<td>58</td>
</tr>
<tr>
<td>$i_{a,ref} = 1.21 \times 10^{-7}$ A/cm², $\alpha_c = 0.776^b$</td>
<td>N/A</td>
<td>58</td>
<td>76</td>
</tr>
<tr>
<td>$i_{a,ref} = 2.06 \times 10^{-9}$ A/cm², $\alpha_c = 1.14^b$</td>
<td>N/A</td>
<td>58</td>
<td>105</td>
</tr>
<tr>
<td>In Fig. 2</td>
<td>$i_{a,ref} = 1 \times 10^{-9}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>0.8</td>
<td>62</td>
</tr>
<tr>
<td>$i_{a,ref} = 1 \times 10^{-10}$ A/cm², $\alpha_c = 0.8^b$</td>
<td>N/A</td>
<td>59</td>
<td>74</td>
</tr>
<tr>
<td>$i_{a,ref} = 1 \times 10^{-10}$ A/cm², $\alpha_c = 1.2^b$</td>
<td>N/A</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>In Fig. 3</td>
<td>$i_{a,ref} = 1 \times 10^{-10}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>0.8</td>
<td>62</td>
</tr>
<tr>
<td>$i_{a,ref} = 1 \times 10^{-10}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>0.75</td>
<td>76</td>
<td>142</td>
</tr>
<tr>
<td>In Fig. 4</td>
<td>$i_{a,ref} = 1 \times 10^{-10}$ A/cm², $\alpha_c = 0.6^b$</td>
<td>0.65</td>
<td>101</td>
</tr>
<tr>
<td>$i_{a,ref} = 1 \times 10^{-9}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>0.85</td>
<td>60</td>
<td>109</td>
</tr>
<tr>
<td>$i_{a,ref} = 1 \times 10^{-10}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>0.70</td>
<td>60</td>
<td>110</td>
</tr>
<tr>
<td>$i_{a,ref} = 1 \times 10^{-12}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>0.60</td>
<td>60</td>
<td>113</td>
</tr>
<tr>
<td>In Fig. 5</td>
<td>$i_{a,ref} = 1 \times 10^{-14}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>0.50</td>
<td>60</td>
</tr>
<tr>
<td>$i_{a,ref} = 1 \times 10^{-9}$ A/cm², $\alpha_c = 1.0^b$</td>
<td>N/A</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>In Fig. 6</td>
<td>Polarization curves with various $i_{a,ref}$</td>
<td>0.80</td>
<td>77</td>
</tr>
</tbody>
</table>

*a Experimental data obtained from Ref. 3.

*b Simulated results using the four-electron-transfer model.

*c Simulated results using the adsorption model.
A certain value, 1.0 in this case. But the Tafel slopes do not change significantly, as shown in Table IV. The LCD Tafel slopes follow the prediction of the Tafel equation for this case also.

The only adsorption-related parameter which has an effect on the polarization curves is the exchange current density $i_{\text{a,ref}}$ according to Eq. 62 and 63. Figure 6 shows a set of polarization curves with different values for $i_{\text{a,ref}}$, and Fig. 7 is a plot of $i_{\text{a,ref}}$ vs the limiting current densities. The adsorption affects the apparent limiting current density only if the value of $i_{\text{a,ref}}$ is less than a critical value, which is about 1 A/cm$^2$ in this calculation. The adsorption process limits the overall reaction rate before the mass-transfer limit is reached, and the apparent limiting current density does not follow the Levich equation for this case. Figure 7 shows how the parameter $i_{\text{a,ref}}$ affects the limiting current density and reinstates the observations made above. The Tafel slopes do not change with the rate of adsorption, as shown in the inset in Fig. 6.

Conclusion

An adsorption model for the ORR at an RDE was developed based on the oxygen adsorption mechanism. The conventional four-electron-transfer model was also simulated for comparison. The fit to experimental data using both these models was carried out by
Solving Eq. A-2 through A-4 for $H9258$

where costs of this article.

which the adsorption process limits the overall reaction rate is observed. The existence of a critical adsorption rate below which the adsorption process limits the overall reaction rate is observed.

Acknowledgments

The authors are grateful for the financial support provided by the U.S. Department of Energy under cooperative agreement no. DE-FC36-04GO14232.

The University of South Carolina assisted in meeting the publication costs of this article.

Appendix

From Eq. 40 and 41 above, we have

$$i = i_0 - \frac{\theta - \theta_0}{\theta_0}$$  \[A-1\]

$$i = i_0 \left[ 1 - \theta \right] - \frac{\theta}{\theta_0} \frac{\left( \theta - \theta_0 \right)^2}{B}$$  \[A-2\]

where

$$A = \exp\left( \frac{\alpha_i F}{RT} \eta \right)$$  \[A-3\]

$$B = \exp\left( - \frac{\alpha_i F}{RT} \eta \right)$$  \[A-4\]

Solving Eq. A-2 through A-4 for $\theta$ we have

$$\theta = \frac{\theta_0}{2\theta_0 - 1} \left( A_i \theta_{0i} - \sqrt{A_i \theta_{0i}^2 - 4\theta_0 \theta_{0i}} \right)$$  \[A-5\]

Substituting the expression for $\theta$ in A-1 and solving for $i$ we have

Equations A-6 and 61 can now be used to relate the current and potential in terms of the concentration of oxygen at the surface and the equilibrium surface coverage. The equilibrium coverage can be obtained from Eq. 53 or other expressions for the isotherm, which involve interaction parameters to account for the presence of other species and/or the dependence on potential. However, note that these equations have to be solved numerically now, because a closed-form solution does not exist for this case.

List of Symbols

- $c_j$: concentration of species $i$, mol/cm$^3$
- $c_{j,RE}$: concentration of species $i$ at reference electrode, mol/cm$^3$
- $c_{j,eq}$: concentration of species $i$ at equilibrium with the solution adjacent to the electrode surface, in Reactions 2-5, mol/cm$^3$
- $c_{j,ads}$: transient concentration of species $i$ adsorbed on the electrode surface, mol/cm$^3$
- $D_i$: diffusion coefficient of species $i$, cm$^2$/s
- $D_{O2}$: diffusion coefficient of the limit reactant, cm$^2$/s
- $E_{app}$: applied potential between working electrode and reference electrode, V
- $F$: Faraday’s constant, 96,487 C/mol
- $\Delta G^0$: free energy change for adsorption process, J/mol
- $i$: current density across the cell, A/cm$^2$
- $i_a$: current density of adsorption step of process $i$ as Reaction 2, A/cm$^2$
- $i_j$: current density of reaction $j$, A/cm$^2$
- $i_{adj}$: exchange current density of the charge transfer reaction $j$ at equilibrium with the solution adjacent to the electrode surface, A/cm$^2$
- $i_{adj}$: exchange current density of the charge transfer reaction $j$ at reference concentrations, A/cm$^2$
Greek

$\alpha_{an,cath}$  anodic and cathodic transfer coefficient for the charge-transfer reaction $j$

$\gamma_j$ exponent in the composition dependence of the exchange current density $i_{0,j}$

$b_0$ diffusion layer thickness, cm

$v$ kinematic viscosity, cm$^2$/s

$l$ dimensionless distance from electrode surface into electrolyte, $y/b_0$

$\rho_0$ density of the pure solvent, kg/cm$^3$

$\Phi$ potential in the solution within the diffusion layer, V

$\Phi_0$ potential in the solution adjacent to the electrode surface, V

$\Phi_{ex}$ potential of the reference electrode, V

$v$ rotating speed of electrode, rads

References

30. S. E. Lorimer, M.Sc. Thesis, Department of Chemical Engineering, Texas A&M University, College Station, TX (1982).