Calculation of cyclic voltammic responses for the reductive formation of catalyst–substrate adducts on electrode surfaces

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Electrocatalysts based on monolayers of transition-metal complexes attached to electrode surfaces frequently follow mechanisms in which a chemical step is interposed between the first and subsequent electron-transfer steps. The cyclic voltammetric responses to be anticipated for such systems were calculated using finite difference procedures to solve the relevant differential equation. The calculated variation of the peak currents and peak potentials with the kinetic parameters governing the three steps in the mechanistic scheme are presented in graphical form. Application of the results to a specific experimental system, the catalysis of the electroreduction of O₂ by a macrocyclic complex of Co(Il) adsorbed on graphite electrodes, produced reasonable agreement between calculated and observed cyclic voltammograms.

The catalysis of electrode reactions that involve the transfer of multiple electrons, e.g. the reduction of O₂ to H₂O₂ or H₂O, may proceed by a variety of conceivable mechanisms. One way to examine possible mechanistic schemes is to compare experimental current–potential responses with those calculated on the basis of feasible mechanisms. We have employed this approach in three recent studies in which the current-potential responses to be expected were calculated for single monolayers of molecules adsorbed on electrode surfaces where they acted as catalysts in simple outer-sphere, inner-sphere or intramolecular electron-transfer mechanisms. In the present study we extend the approach to a somewhat more complex mechanism in which a chemical reaction is interposed between the first and subsequent electron-transfer steps and a separate response appears from an intermediate in the catalytic cycle. Such ECE† mechanisms have been treated previously by Laviron and only for cases where the electrode reactions were assumed to be Nernstian and the chemical reaction was assumed to be totally irreversible. We were interested in cases where these restrictive assumptions were not made, in order to compare the calculated results with those obtained in an experimental system in which the catalysed reduction of O₂ to H₂O₂ by a complex of Co(Il) adsorbed on the surface of graphite electrodes appeared to proceed by such an ECE mechanism. In our previous reports the calculation procedures employed were based primarily on the original treatments of Andrieux and Saveant and Aoki et al., as elaborated and extended to encompass the mechanistic schemes of interest. In the present case it was possible to carry out all of the necessary calculations using finite difference procedures. Because of the availability of previous descriptions of the details of the calculations they are only outlined in the present report.

The mechanism we wish to consider is depicted in Scheme 1:

\[ \text{(O)}_{\text{ads}} + 2\text{e} \rightarrow \text{(R)}_{\text{ads}}; \quad E_{1}^{o}, k_{1}, \alpha_{1} \quad (1) \]

\[ \text{(R)}_{\text{ads}} + Z \rightarrow \text{(RZ)}_{\text{ads}}; \quad k_{2}, k_{-2}, K_{2} \quad (2) \]

\[ \text{(RZ)}_{\text{ads}} + 2\text{e} \rightarrow \text{(R-Z)}_{\text{ads}}; \quad E_{3}^{o}, k_{3}, \alpha_{3} \quad (3) \]

The catalyst, consisting of the O/R couple, is confined in a monolayer on the electrode surface. The substrate, Z, can be reduced only after it is bound by the reduced form of the catalyst to form the adduct, (R-Z)ads. This reaction is governed by equilibrium and rate constants, K₂, k₂, and k⁻₂. The adduct, (R-Z)ads, is reduced in half-reaction (3) which is characterized by the formal potential E₃, standard rate constant k₃ and transfer coefficient α₃. If the reduced adduct, (R-Z)ads, is stable, the reduction of Z ceases as soon as all of the O/R catalyst present on the electrode surface is converted to (R-Z)ads. In cases where (R-Z)ads can be further reduced to produce an unbound product with the reformation of (R)ads, a catalytic reduction of Z ensues. The combination where R is a macrocyclic complex of cobalt(II) and Z is O₂ represents one specific example of such a catalytic system to which we will return. However, the voltammetric responses to be expected from systems which adhere to the simpler, non-catalytic mechanism given in Scheme I will be considered first.

The calculations were carried out using the following assumptions or conditions: The quantity of the O/R catalyst present on the electrode surface, I, was assumed to remain unchanged:

\[ I = I_{0} + I_{k} + I_{k-Z} + I_{k-Z} \quad (I) \]

For cases where the two electrode reactions adhere to the Nernst equation one has

\[ I_{0} = \exp \left[ \frac{F}{RT} (E - E_{1}^{o}) \right] \quad (II) \]

and

\[ I_{k-Z} = \exp \left[ \frac{F}{RT} (E - E_{3}^{o}) \right] \quad (III) \]

For cases where the electrode reactions are not Nernstian, the concentrations of the reactants present on the electrode surface are calculated from eqns. (IV) and (V)

\[ \frac{dI_{0}}{dt} = -k_{1} \Gamma_{0} \exp \left[ -\frac{E_{1}^{o}F}{RT} (E - E_{1}^{o}) \right] \quad - k_{2} \Gamma_{k-Z} \exp \left[ \frac{1 - \alpha_{2}E_{2}^{o}F}{RT} (E - E_{2}^{o}) \right] \quad (IV) \]

\[ \frac{dI_{k-Z}}{dt} = k_{o} \Gamma_{k-Z} \exp \left[ -\frac{E_{3}^{o}F}{RT} (E - E_{3}^{o}) \right] \quad - k_{3} \Gamma_{k-Z} \exp \left[ \frac{1 - \alpha_{3}E_{3}^{o}F}{RT} (E - E_{3}^{o}) \right] \quad (V) \]
For cases where reaction (2) remains at equilibrium

\[
\frac{\Gamma_k - \Gamma_k}{\Gamma_k} = K_z C_z(0, t)
\]

where \(C_z(0, t)\) is the concentration of \(Z\) at the electrode surface. If reaction (2) does not remain at equilibrium, eqn. (VII) is used in place of eqn. (VI)

\[
k_z C_z(0, t) \Gamma_k - k_{-z} \Gamma_k - \frac{d(\Gamma_0 + \Gamma_k)}{dt} = \frac{d(\Gamma_k + \Gamma_{k-z})}{dt}
\]

As the consumption of \(Z\) at the electrode surface is limited by the quantity of \(R_{ads}\) present on the electrode surface, the value of \(C_z(0, t)\) may remain essentially constant if the concentration of \(Z\) in the bulk of the solution, \(C_z^2\), is large enough. For cases where \(C_z(0, t)\) does not remain constant, its value can be calculated using finite difference methods as applied to eqn. (VIII) and (IX)

\[
\frac{\partial C_z(x, t)}{\partial t} = \frac{\partial J_z(x, t)}{\partial x}
\]

where \(J_z(x, t)\) is the flux of \(Z\) at and, at the electrode surface,

\[
J_z(0, t) = -D_z \left[ \frac{\partial C_z(x, t)}{\partial x} \right]_{x=0} + \frac{d(\Gamma_k + \Gamma_{k-z})}{dt}
\]

or, in dimensionless form,

\[
\psi_1 = I_1 \left[ \frac{F^2}{RT} \left( \frac{E_F}{v} \right) \right]^{-1}
\]

\[
\psi_3 = I_3 \left[ \frac{F^2}{RT} \left( \frac{E_F}{v} \right) \right]^{-1}
\]

\[
\psi_1 = \psi_1 + \psi_3
\]

where \(S\) is the electrode area and \(v\) is the rate at which the electrode potential is scanned from its initial value, \(E_1\)

\[
E = E_1 - vt
\]

**Results and Discussion**

It will be convenient to divide the analysis into two broad categories: Situations in which \(C_z(0, t)\) can be assumed to remain constant at \(C_z^2\) comprise the first category. The second involves situations where \(C_z(0, t)\) changes as the voltammogram is recorded. Within each category several cases will be examined. The cases are differentiated on the basis of the rates of reactions (1)–(3).

**Category I; \(C_z(0, t) = C_z^2\)**

Case (i). Half-reactions (1) and (3) are Nernstian; reaction (2) remains at equilibrium \((k_0^2, k_0^2, k_2, k_{-2} \to \infty)\).

The combination of eqn (I)–(III), (VI) and (XVI) leads to expressions for \(I_1\) and \(I_{k-z}\) whose time derivatives \([using (dI_1/dt) = -v(dI_1/dE)]\) give eqn. (XVII) and (XVIII)

\[
\begin{align*}
\frac{dI_0}{dt} &= \frac{vF^2}{RT} \frac{\theta_1 \theta_3}{\theta_z} \\
\frac{dI_k}{dt} &= \frac{vF^2}{RT} \left[ \frac{2K_z C_z^2 + (1 + K_z C_z^2) \theta_3}{[K_z C_z^2 + (1 + K_z C_z^2) \theta_3 + \theta_1 \theta_3]^2} \right] \\
\frac{dI_{k-z}}{dt} &= \frac{vF^2}{RT} \left[ \frac{K_z C_z^2 + (1 + K_z C_z^2) \theta_3}{[K_z C_z^2 + (1 + K_z C_z^2) \theta_3 + \theta_1 \theta_3]^2} \right]
\end{align*}
\]

The dimensionless current–potential curves can then be calculated directly from eqn. (X)–(XV). The results of such calculations are shown in Fig. 1 for various values of \(K_z C_z^2\) and \((E_i^2 - E_f^2)\). In Fig. 1A the formal potentials of half-reactions (1) and (3) are assumed to be equal and the value of \(K_z C_z^2\) is varied between \(10^{-4}\) and \(10^{2}\) corresponding, respectively, to little or extensive equilibrium formation of the reducible adduct \((R-Z)_{ads}\). Because the two electrode reactions are taken to be Nernstian, the cathodic and anodic peak potentials are identical. When \(K_z C_z^2\) is much less than unity (curves a and b in Fig. 1A) two separated current peaks appear in the voltammogram despite the fact that \(E_i^2\) and \(E_f^2\) were taken as equal. The first peak appears near \(E_i^2\) but the second appears at potentials notably more negative than \(E_f^2\). The two peaks move together as \(K_z C_z^2\) is increased and merge into a single larger peak when \(K_z C_z^2\) is unity (curve d in Fig. 1A). At larger values of \(K_z C_z^2\), separate, smaller peaks develop again with one centred near \(E_i^2\) (= \(E_f^2\)) and the other at much more positive potentials (curves c, d) and when \(K_z C_z^2\) is small (\(10^{-2}\)) the response contains two separated peaks (curves a and b in Fig. 1B). The separation between the two peaks diminishes as \(E_i^2\) approaches \(E_f^2\) (curves c, d) and when \(E_i^2\) is much more positive than \(E_f^2\), a single peak results at a potential between \(E_i^2\) and \(E_f^2\) and with a dimensionless peak current \(\psi_1\) (Fig. 1B) the width at half-height of each is \(3.53RT/F = 90.4\) mV and the dimensionless peak current of each is 0.25.

In Fig. 1B–D are shown the responses calculated for cases where \(E_i^2\) and \(E_f^2\) are unequal and \(K_z C_z^2\) is \(10^{-2}\), 1 or \(10^{2}\). When \(E_i^2\) is much more negative than \(E_f^2\) and \(K_z C_z^2\) is small (\(10^{-2}\)) the response contains two separated peaks (curves a and b in Fig. 1B). The separation between the two peaks diminishes as \(E_i^2\) approaches \(E_f^2\) (curves c, d) and when \(E_i^2\) is much more positive than \(E_f^2\), a single peak results at a potential between \(E_i^2\) and \(E_f^2\) and with a dimensionless peak current of 1.0 (curve h in Fig. 1B). The width of curve h is 1.76RT/F = 45.1 mV and it has all the characteristics of a single, two-electron reaction. The behaviour is qualitatively similar with larger values of \(K_z C_z^2\) (Fig. 1C and D).

Under circumstances where two peaks are present in the voltammogram and \(K_z\) is known, the value of \(E_i^2\) may be calculated from the combination of eqn. (XIX) and (XX)

\[
\begin{align*}
\theta_1 &= 1 + K_z C_z^2 + \frac{K_z C_z^2}{\theta_3} \\
\theta_3 &= \frac{K_z C_z^2 + (1 + K_z C_z^2) \theta_3}{(1 + K_z C_z^2 + 4K_z C_z^2 \theta_1)}
\end{align*}
\]

where

\[
\begin{align*}
\theta_1 &= \exp \left[ \frac{F}{RT} (E_{p1} - E_i^2) \right] \\
\theta_3 &= \exp \left[ \frac{F}{RT} (E_{p3} - E_f^2) \right] \\
\theta_1 &= \exp \left[ \frac{F}{RT} (E_{p2} - E_i^2) \right]
\end{align*}
\]
Cyclic voltammetric responses calculated for case (i) of Scheme I (see text) with $C_i(0, t) = C_i^0$. A, $E'_1 = E'_2$; $K_2 C_i^0 = a$, $10^{-3}$; b, $10^{-2}$; c, $10^{-1}$; d, 1; e, 10; f, $10^2$; g, $10^3$. B-D, $F/RT(E'_1 - E'_2) = a$, $-4$; b, $-2$; c, 0; d, 2; e, 4; f, 6; g, 8; h, 14 and $K_2 C_i^0 = B$, $10^{-2}$; C, 1, D, $10^2$.

$$\theta'_3 = \exp \left[ \frac{F}{RT} (E_{p2} - E'_2) \right]$$

(XXIV)

and $E_{p1}$ and $E_{p2}$ are the two observed peak potentials (cathodic or anodic since they are the same). Eqn. (XIX) and (XX) were obtained by setting the derivatives of the right-hand sides of eqn. (XVII) and (XVIII) equal to zero at the two peak potentials.

In cases where $C_i^0$ cannot be increased or decreased sufficiently to cause two peaks to appear in the voltammogram, $E'_2$ may still be estimated if it is much more positive than $E'_1$ and $K_2 C_i^0$ is not extremely small or large. Under these conditions, and if the peak potential of the single observed peak, $E'_p$, satisfies the condition $E'_p < E'_1 < E'_2$, it follows that $\theta'_1 \sim K_2 C_i^0/\theta'_3$ and leads to eqn. (XXV)

$$E'_p = 0.5(E'_1 + E'_3) + \frac{RT}{2F} \ln(K_2 C_i^0)$$

(XXV)

Thus, $E'_2$ can be calculated from the observed value of $E'_p$ if $K_2$ is known.

Case (ii). Half-reactions (1) and (3) are Nernstian; reaction (2) is not at equilibrium ($k^0_1$, $k^0_3 \to \infty$; $k_2$, $k_{-2} < \infty$).

When the formation of $(R-Z)_{ads}$ is not instantaneous, the voltammetric responses are calculated from eqn. (I)-(III) and (VII). It is convenient to characterize the kinetics of reaction (2) by a dimensionless kinetic parameter, $r_2$,

$$r_2 = \frac{k_2 C_i^0 RT}{vF}$$

(XXVI)

Shown in Fig. 2A is a set of voltammetric responses for various values of $r_2$ and fixed values of $K_2$ and $E'_3 - E'_1$. When $r_2$ is sufficiently large, case (ii) becomes case (i) and symmetrical responses like that in curve a of Fig. 2A are obtained with identical cathodic and anodic peak potentials. As $r_2$ decreases, the cathodic peak current diminishes and the peak potential shifts toward $E'_1$ while the anodic peak diminishes and shifts towards $E'_2$ as shown in curves b-g in Fig. 2A. The increase in the dimensionless peak currents as the scan rate decreases means that the actual peak currents are not proportional to the scan rate, which is a diagnostically useful property (vide infra). For some combinations of $r_2$ and the range

Fig. 1 Cyclic voltammetric responses calculated for case (i) of Scheme I (see text) with $C_i(0, t) = C_i^0$. A, $E'_1 = E'_2$; $K_2 C_i^0 = a$, $10^{-3}$; b, $10^{-2}$; c, $10^{-1}$; d, 1; e, 10; f, $10^2$; g, $10^3$. B-D, $F/RT(E'_1 - E'_2) = a$, $-4$; b, $-2$; c, 0; d, 2; e, 4; f, 6; g, 8; h, 14 and $K_2 C_i^0 = B$, $10^{-2}$; C, 1, D, $10^2$.

Fig. 2 Cyclic voltammetric responses calculated for case (ii) of Scheme I (see text) with $C_i(0, t) = C_i^0$. $K_2 C_i^0 = 1$ and $F/RT(E'_1 - E'_3) = 10$. A, $r_2 = a$, $10^{-3}$; b, $10^{-2}$; c, $30$; d, 10; e, 3; f, 1; g, 0.3, B, as in A with an expanded (dimensionless) current scale and $r_2 = h$, $3 \times 10^{-3}$; i, $10^{-2}$; j, $3 \times 10^{-3}$; k, $10^{-3}$.
over which the potential is scanned, a pair of responses can be obtained with matching anodic and cathodic peak potentials as shown in Fig. 2B. If this circumstance can be realized, the value of $E_p^*$ can be read directly from the position of the single anodic peak. In cases where a response like those in Fig. 2B cannot be obtained (because impractical scan rates would be necessary) it is still possible to obtain estimates of $E_p^*$ from the anodic and cathodic peak potentials of responses like those shown in Fig. 2A. By carrying out calculations for a variety of conditions we observed that both peak potentials are linearly related to $\ln(r_2)$ (i.e. $\ln v$) over a reasonable range of scan rates. This linearity is demonstrated in the plots shown in Fig. 3A.

The peak potentials were taken from calculated responses like those in Fig. 2A. The range of linearity of plots like those in Fig. 3A depends upon the difference between $E_p^*$ as shown in Fig. 3B. The intersections of the two linear plots of the anodic and cathodic peak potentials vs. $\ln(r_2)$ occur at $E_p^*$ so that plots like those in Fig. 3A and 3B can be used to evaluate $E_p^*$. The common anodic and cathodic peak potential that would be observed if reaction (2) remained at equilibrium. The intersection point occurs at larger values of $r_2$ as $F/RT(E_p^1 - E_f)$ becomes more positive (Fig. 3B) which reflects the fact that larger values of $k_2$ and $k_{-2}$ are required to keep reaction (2) at equilibrium as $E_p^1$ becomes more positive. The reason is that less and less ($R-Z$)$_{ads}$ is present on the electrode as $E_p^*$ becomes more positive (because $E_p^1$ is more positive) so that larger rate constants are needed to compensate for the smaller effective concentration of the reactant participating in reaction (2).

The behaviour shown in Fig. 3A and B can be exhibited in the more 'universal' format shown in Fig. 3C which provides a means for estimating $r_2$ (i.e. $k_2$). Once $E_p^*$ is obtained from the intersections of plots like those in Fig. 3A or B, the corresponding value of $(E_p^1 - E_p^2)$ at any scan rate leads, via Fig. 3C, to a value of $\ln r_2 - F/RT(E_p^1 - E_f)$ in which the only unknown is $r_2$ so that $k_2$ can be calculated. In carrying out this analysis, scan rates that correspond to the inclined portions of the curves in Fig. 3C would need to be employed to obtain the most reliable estimates of $r_2$.

Case (iii). Half-reaction (1) is Nernstian, half-reaction (3) is not; reaction (2) is at equilibrium $k_0^0$, $k_2$, $k_{-2} \to \infty$; $k_0^0 < \infty$.

When the second electron-transfer step is slow, the voltammetric responses to be expected can be calculated from Eqs. (I), (II), (V) and (VI). It is convenient to introduce a dimensionless parameter to characterize the kinetics of half-reaction (3)

$$m_3 = \frac{k_0^0 RT}{vF}$$

(XXVII)

Calculated voltammetric responses are shown in Fig. 4A for various values of $m_3$ with $E_p^1$ taken to be much more positive than $E_f^1$. A notable feature is the nearly constant dimensionless anodic peak current when the separation between anodic and cathodic peaks reaches ca. $5F/RT$. Under these conditions the actual anodic peak currents increase linearly with the scan rate, a property which allows discrimination between cases (ii) and (iii).

When $m_3$ is large, the anodic and cathodic peak potentials are close together (curve h in Fig. 4A). As $m_3$ decreases the anodic and cathodic peaks shift apart, the anodic peak shifting more rapidly than the cathodic peak (Fig. 4A). Plots of the two peak potentials vs. $\ln m_3$ for several values of the transfer coefficient for half-reaction (3) are shown in Fig. 4B. The plots are linear over a reasonable range of $m_3$ (i.e. scan rates) and the intersections of the extrapolated lines all occur at the same potential which turns out to be ca. 15 mV more negative than $E_f^1$ for any combination of the values of $K_j C_j^0$, $a_3$ and $E_p^1$. Thus, the intersection point provides a rough estimate of $E_p^1$.

The slopes of the lines of Fig. 4B are quite different for the anodic and cathodic peak potentials. This behaviour differs from that in the corresponding plots for case (ii) (Fig. 3A) and provides another means for distinguishing between cases (ii) and (iii).

Shown in Fig. 4C is a 'universal' plot which may be used to estimate $k_0^0$ and $a_3$ from the anodic peak potentials, $E_p^1$, measured at various scan rates (i.e. values of $m_3$). As long as $F/RT(E_p^1 - E_f^1)$ is large enough, a single line is obtained for various values of $K_j C_j^0$ and $a_3$. Approximate values of $F/RT(E_p^1 - E_f^1)$ are accessible at various scan rates from the measured values of $E_p^1$ and the intersection potential of plots like those in Fig. 4B. The corresponding values of $\ln m_3 - a_3 F/RT(E_p^1 - E_f^1)$ read from the line in Fig. 4C can then be used to calculate both $a_3$ and $K_j^0$ (from $m_3$).

For smaller values of $F/RT(E_p^1 - E_f^1)$, deviations from linearity develop in the plot of Fig. 4C as $m_3$ increases. A few examples are shown in Fig. 4D.

Case (iv). Half-reaction (1) is Nernstian; half-reaction (3) is not; reaction (2) is not at equilibrium $k_{0,1}^0$ (i.e. $k_0^0 < \infty$; $k_0^0$, $k_2$, $k_{-2} < \infty$).

For this case the voltammetric responses are influenced by both of the previously defined kinetic parameters, $r_2$ and $m_3$. Calculations were carried out using eqn. (I) (II), (V) and (VI) and some of the results are compared with those for cases (ii) and (iii) in Fig. 5A. Curve a corresponds to case (ii) with $r_2 \to \infty$ and $m_3 = 1$ while curve b corresponds to case (ii) with...
electrode surface, the effects of the diffusion of concentrations high enough to prevent its depletion at the electrode surface have to be taken into account by means of finite difference calculations using eqn. (VIII) and (IX). The results of some selected calculations for cases (i), (ii) and (iii) are summarized in Fig. 6. In Fig. 6A are shown voltammograms calculated for case (i) where the small changes in the peak positions and shapes are caused by changes in the total quantity of catalyst present on the electrode surface. The outermost dotted curve corresponds to curve d in Fig. 1A where \( C_d(0, t) \) is constant.

The responses expected for case (ii) are shown in Fig. 6B. The dotted curves are for constant \( C_d(0, t) \) and the solid curves are those calculated when \( C_d(0, t) \) changes. As \( C_d^2 \) is decreased (curves a–e), the cathodic peak currents decrease because of the diminished rate at which \( Z \) diffuses to the electrode surface to react with all of the catalyst generated there. However, the anodic peak current remains unchanged as long as the conditions (scan rate, range of the potential scan, value of \( r_2 \)) are not changed because the diminished rate at which \( Z \) is generated on the electrode surface is slow relative to the rate of half-reaction (3).

For case (iii) (Fig. 6C) the cathodic peaks are not as sensitive to changes in \( C_d^2 \) as for case (ii). The anodic peak is decreased (curves a–e) because of the diminished rate at which \( Z \) diffuses to the electrode surface to react with all of the catalyst generated there. However, the anodic peak remains unchanged as long as the conditions (scan rate, range of the potential scan, value of \( r_2 \)) are not changed because the diminished rate at which \( Z \) is generated on the electrode surface is slow relative to the rate of half-reaction (3).
1.2
0.8
0.4
wt
0.0
-0.4
A
-0.8
15.0 10.0 5.0
2.0 0.0
-2.0
-4.0
-6.0
Fig 5 A, Cyclic voltammetric responses calculated for case (iv) of Scheme I (see text) with $C_d(0, t) = C_d^2$, $K_3C_2^2 = 0.1$, $F/RT(E'_1 - E'_1) = 10$, $x_2 = 0.5$ and $m_1$, $r_1 = a$, 1, $\infty$, b, $\infty$, 1; c, 10, 1; d, 1, 1; e, 1, 10. B, Anodic (upper lines) and cathodic (lower lines) peak potentials vs. scan rate for the parameters in A except $K_3C_2^2$, $k_2^2(s^{-1}) = (\Delta) 10^5$, 1; (O) 10, 10; (C) 10, 1.

It proved possible to characterize the behaviour of a variety of systems from both category I and category II in terms of a single dimensionless parameter, $Y$, defined in eqn. (XXVIII)

$$Y \equiv \frac{C_d^2}{\Gamma} \left( \frac{RTD_2}{Fv} \right)^{1/2} \tag{XXVIII}$$

Plotted in Fig. 6D are ‘universal’ curves giving the calculated values of the dimensionless cathodic peak current as a function of $\ln Y$ for cases (i), (ii) and (iii). The peak current is quite sensitive to the experimental parameters between $\ln Y = -2$ and $\ln Y = +2$. When $\ln Y$ is smaller than ca. $-2$ the dimensionless peak current remains close to 0.25 and there is essentially no contribution to the current from half reaction (3). For values of $\ln Y$ greater than ca. 2, $C_d(0, t)$ remains essentially constant and the analyses presented for category I apply.

**Application to a specific system**

An experimental example of a system that adheres to the reaction mechanism depicted in Scheme I is provided by the complex of cobalt(III) with the macrocyclic ligand hmc.
(hmc = C₆mexo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclocotetradecane) irreversibly adsorbed on the surface of a graphite electrode where it catalyses the reduction of O₂. The first three steps in the catalytic mechanism are shown in reactions (4)–(6).

\[
\begin{align*}
((hmC)Co^3)_{ads}^{2+} + e & \rightarrow [(hmC)Co^2]_{ads}^{2+} ; \\
((hmC)Co^2)_{ads}^{2+} + O_2 & \rightarrow [(hmC)CoO_2]_{ads}^{2+} ; \\
((hmC)CoO_2)_{ads}^{2+} + e + H^+ & \rightarrow [(hmC)CoO_2H]_{ads}^{2+} ; \\
E_1', k_0', x_1 & \quad \text{(4)} \\
E_2', k_2, x_2 & \quad \text{(5)} \\
E_3', k_3, x_3 & \quad \text{(6)}
\end{align*}
\]

The values of \( x_1, k_0', E_1' \), and \( K_2 \) were available from a previous study. A value of 0.66 V was estimated for \( E_2' \) from the intersection of the plots shown in Fig. 7A using Eqn. (XXV). Estimates of \( K_2, x_3 \) and \( k_0'^{0} \) were obtained by fitting calculated current-potential curves to the experimental curves. For example, the dotted line in Fig. 7B was calculated to fit the experimental currents shown by the open circles. The agreement between the calculated and experimental currents is reasonably good except at the point where the scan direction is reversed and at the anodic peak. The better agreement shown by the solid line in Fig. 7B resulted when account was taken of the further reduction of the [((hmC)CoO₂H)]ₜ⁻ complex [half-reaction (7)].

\[
((hmC)CoO₂H)_{ads}^{2+} + e + H^+ \rightarrow [(hmC)Co]_{ads}^{2+} + H_2O_2 ; \\
E_4'^{0}, x_4, k_4'^{0} & \quad \text{(7)}
\]

The peak current for the reduction of [((hmC)CoO₂H)]ₜ⁻ occurs at a considerably less positive potential (0.06 V, ref. 7) than the cathodic peak in Fig. 7B, but sufficient reduction proceeds during the recording of the cathodic peak in Fig. 7B to diminish slightly the quantity of [((hmC)CoO₂H)]ₜ⁻ that controls the magnitude of the anodic current in Fig. 7B. When this small correction was included in the calculations the solid curve in Fig. 7B was obtained. The experimental conditions corresponded to case (ii) of category II with \( F/RT(E_1' - E_4') > 20 \). The comparison of the calculated and observed responses in Fig. 7B provided a reasonable basis for assigning the mechanism depicted in reactions (4)–(6) to the (hmC)Co^3+/-2-O₂ system with the kinetic parameters indicated in the caption of Fig. 7B.

**Conclusions**

The primary purpose of this study was the application of the finite difference calculation procedure to systems that follow the ECE mechanism depicted in Scheme I. The results show that a variety of cyclic voltammetric responses can be encountered depending on the values of the kinetic parameters governing the electrode and chemical reactions. Comparison of the representative calculated responses shown in the figures with experimental responses should allow the presence of an ECE mechanism to be established in favourable cases. Procedures for estimating the relevant kinetic parameters were also described. ECE mechanisms are likely to be involved when electrocatalysts must be generated by reduction or oxidation of catalytically inactive precursors that contain redox-active metal centers. The reduction of O₂ at catalyst-coated electrodes as discussed in this report is one example of such a system. Others include the catalysis of the electroreductions of CO₂ by adsorbed Ni(cyclam)^(2-)^11 and of NO by adsorbed heteropolytungstate anions, respectively.

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**References**


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