Diagnostic Criteria for Identifying an ECE Mechanism with Cyclic Square Wave Voltammetry

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Theory for cyclic square wave voltammetry of an irreversible first-order chemical reaction coupling two electron transfers, i.e. an ECE mechanism, is presented. Theoretical voltammograms were calculated following systematic variation of empirical parameters to assess their impact on the shape of the voltammogram. Note that the results presented herein are applicable only to ECE processes where $E^0$ for the second electron transfer step is negative of that for the first. Under this condition, disproportionation reactions do not occur. From the trends obtained, diagnostic criteria for this mechanism were deduced. When properly applied, these criteria will enable non-experts in voltammetry to assign the electrode reaction mechanism and accurately measure reaction kinetics over the range $-2 \leq \log k_r \leq 6$.

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Square wave voltammetry (SWV) has been shown to be particularly useful in identifying electrode reaction mechanisms especially those involving chemical reactions coupled to the electron transfer step.1–7 Although a strong theoretical basis exists,8 the use of SWV for identifying electrode reaction mechanisms has been limited to a small number of electrochemists. Our goal is to broaden the use of SWV for determining electrode reaction mechanisms especially by non-experts in electrochemistry who make occasional use of voltammetry in characterizing new compounds. Cyclic square wave voltammetry (CSWV) is a modified form of SWV that steps through the region of the formal potential of the electroactive species under study and back to the initial potential as shown in Fig. 1a. The empirical parameters that comprise the CSWV waveform are period ($\tau$), amplitude ($E_{SW}$), increment ($\delta E$), and the potential at which the direction of the sweep is reversed ($E_c$).

Our current effort is focused on identifying the specific mechanisms CSWV provides a straightforward means for determining the mechanism and associated kinetic parameters.9–14 In this work, we critically evaluate CSWV for the analysis of consecutive electron transfers coupled by a homogeneous irreversible chemical reaction, i.e. an ECE mechanism. The process used to evaluate CSWV is as follows. Theoretical voltammograms were computed by systematic variation of each empirical parameter. Figures of merit that describe the shape of the voltammogram as shown in Fig. 1b (peak potentials, peak currents, and peak widths) were compiled and correlated with the empirical parameter being varied. Trends characteristic of this mechanism were identified from these correlations and provide diagnostic criteria for assigning an electrode reaction as an ECE process. Application of these criteria will enable non-specialists to accurately assign the mechanism and, in many instances, quantify the rate constant of the chemical reaction.

The ECE mechanism has been the subject of considerable interest by electrochemists over the past five decades.2–4,15–24 The continuing interest reflects: (1) the challenge in mathematically modeling the complex electrode reaction sequence involving two sequential heterogeneous electron transfer reactions coupled by a homogeneous kinetically-controlled chemical reaction(s) that may or may not involve homogeneous electron transfer, and (2) the advent of new electrochemical techniques to identify short lived intermediates and quantify reaction rates.25–30 The primary motivation educes from the fact that this mechanism is quite common in organic electrochemistry.31–33

Figure 1. CSWV waveforms. Panel a presents the potential pulses applied to the working electrode as a function of time. The inset illustrates the empirical parameters used in configuring the potential-time trace. Panel b presents a typical voltammogram for an ECE process. The figures of merit are denoted on the voltammogram ($W_{1/2}$ are omitted for clarity).

Theory.—The generalized ECE electrode reaction sequence is:

$$\begin{align*}
{\text{Ox}_1} + n_1e^- &\leftrightarrow {\text{Red}_1} \\
{\text{Red}_1} &\rightarrow {\text{Ox}_2} \\
{\text{Ox}_2} + n_2e^- &\leftrightarrow {\text{Red}_2}
\end{align*}$$

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where $E_0^i$ is the formal potential for reduction of Ox$_1$, and $E_0^c$ is the formal potential for the reduction of Ox$_2$. For simplicity, we have arbitrarily set $E_0^i = 0$ and reference all other potential values to it. We consider herein only the situation where $E_0^i \leq E_0^c$ and denote the difference in formal potentials as $\Delta E_0 = E_0^c - E_0^i$. This restriction enables discussion of the mechanism without considering the complication of homogeneous electron transfer (disproportionation$^{38-21,25,34,35}$) reaction, i.e. Ox$_1 +$ Red$_2 \rightleftharpoons$ Red$_1 +$ Ox$_2$.

Derivation of an equation for predicting current as a function of potential and time began by solving Fick’s laws of diffusion using Laplace transformations following application of appropriate boundary conditions for each case. Expressions for the concentrations of Ox$_1$, Red$_1$, Ox$_2$, and Red$_2$ are related by the Nernst equation for a formal potential for the reduction of Ox$_2$. For simplicity, we have arbitrarily set $E_0^i = 0$ and $E_0$, peak currents scale linearly with the number of electrons in both electron transfer steps equal one. The predicted difference current, $\Delta \Psi$, is computed from $\Psi_{\text{forward pulse}} - \Psi_{\text{reverse pulse}}$. The corresponding potential for $\Delta \Psi$ is the average of the corresponding forward and reverse potential pulses. The forward difference current, $\Delta \Psi^+$ denotes the difference currents acquired over the interval $E_{\text{final}}$ to the switching potential $E_i$, and the difference current, $\Delta \Psi^-$, denotes difference currents acquired over the reverse potential sweep from $E_i$ to the final potential, $E_{\text{final}}$. To capture the effect of period as it relates to current, $\Delta \Psi^+$ is used throughout this work where

$$\Delta \Psi^+ = \Delta \Psi/\sqrt{\tau}$$

The physical meaning of $\Delta \Psi^+$ is the normalized faradic current emanating from the electron transfer. The plotting convention used herein treats reduction currents as positive and oxidative currents as negative values. Figures of merit that describe the shape of the voltammogram are: $\Delta \Psi^+$, $\Delta \Psi^+$, the net peak currents on the forward and reverse sweep, peak ratio $\Delta \Psi^+/\Delta \Psi^-$, $E_{p,f}$ and $E_{p,r}$, the peak potentials on the forward and reverse sweep, $\Delta E_p$ the peak separation defined as $E_{p,r} - E_{p,f}$, and $W_{1/2,f}$ and $W_{1/2,r}$, the peak widths measured at half peak maximum (see Fig. 1b).

**Results and Discussion**

Previously, we have shown that determination of an electrode reaction is made possible from an in-depth analysis of the shape of the voltammogram following changes in the empirical parameters of period, increment, switching potential and amplitude.$^{5-14}$ In the following sections, we present the results of our simulations in a similar fashion, first considering the impact of the chemical reaction rate on the shape of the voltammogram and then individually examining the impact of the each empirical parameter. We conclude with a set of instructions on how to identify an electrode reaction as an ECE mechanism and determining $k_f$ from empirical data. Where appropriate, we include comparison of the diagnostic trends for the ECE mechanism to other mechanisms.

The impact of chemical reactions on voltammetric features depends upon the extent of the reaction within the time window of the measurement. The overall effect is usually evaluated using a dimensionless kinetic parameter. In cyclic voltammetry (CV) this parameter is $k_f/\tau$ where $\tau$ is the potential sweep rate. In CSWV, the effective sweep rate is the increment $+\tau$ period; the dimensionless kinetic parameter is $k_f \tau$. We have chosen to separate $k_f$ from $\tau$ to enable consideration of the empirical parameters. In doing so, we present theoretical trends that directly match what experimentalists observe from systematic variation in period.

**Effect of $k_f$—**At the onset, an ECE mechanism can be readily distinguished from case where the analyte undergoes two sequential electron transfers, i.e. the EE mechanism. Two separate reversible processes are observed in the voltammogram for the EE mechanism so long at the $\Delta E_p^i \geq 150$ mV. The peak potentials for each process remain at $E^i$, peak currents scale linearly with $\tau^{-1/2}$, and peak ratios for both processes are unity.$^9$ In cyclic voltammetry and CSWV, the number and magnitude of peaks observed for the ECE mechanism is a function of the rate of the chemical reaction interposed between the two electron transfers, the difference in formal potentials, and the effective potential sweep rate.$^{17}$ Fig. 2 presents the impact of log $k_f$ and $\Delta E_p^i$ on the voltammogram. For very slow rates of reaction, the voltammogram is comprised of a single peak on each sweep direction.
whose shape and magnitude resembles that found for a reversible electron transfer reaction. At intermediate rates (e.g. $-2 < \log k_f < 4$), the number of peaks observed on each sweep depends on $E_0^2$ relative to $E_1^2$. Two peaks are observed on each sweep direction when $E_0^2 = -300$ mV. At $E_0^2 = -100$ mV, on the forward sweep the first peak broadens and splits into two peaks while only one peak is observed on the reverse sweep with increasing $k_f$. When $E_0^2 = E_1^2$, only one peak is observed on each sweep. At fast rates (e.g. $\log k_f > 4$), two peaks are observed on the forward sweep and only one peak on the reverse sweep when $E_0^2 < E_1^2$.

Comparison of the voltamograms when $E_0^2 < E_1^2$ reveals that the peak potentials for the first electron transfer step shift positively as $\log k_f$ is increased from $-3$ to 6 whereas the peak potentials for the second process (both first and second cycle) are invariant with increasing $\log k_f$. When $E_0^2 = E_1^2$, only one peak is observed on each sweep. At fast rates (e.g. $\log k_f > 4$), two peaks are observed on the forward sweep and only one peak on the reverse sweep when $E_0^2 < E_1^2$.

A qualitative tool for identifying an ECE process with cyclic voltammetry involves performing multiple scans over the potential range. The same holds true for CSWV. For a reversible mechanism, there is no difference in the shape of the voltammogram on the first and second cycle. However, in the presence of coupled chemical reactions, the difference in peak currents between the first and second scans is a function of $\log k_f$ and $E_0^2$. This is illustrated in Fig. S-2. When $E_0^2 \leq -100$ mV, measurable differences in $\Delta \Psi_{p,f1}$ for the second relative to the first scan at $\log k_f \geq -1$; at $E_0^2 = 0$, measurable differences are observed at $\log k_f \geq 3$.

**Effect of period ($\tau$).—**The effect of period on the shape of the voltammogram is a complex function of the separation between $E_0^2$ and $E_1^2$ and $\log k_f$. Figure 3 presents the impact of varying period on the shape of the voltammogram as a function of $E_0^2$ for $\log k_f = 3$. On both the forward and reverse sweeps, the peak potential for the first process shifts positively with increasing period while the second process (at $E_0^2$) is invariant for $E_0^2 = -300$ and $-100$ mV. In contrast, when $E_0^2 = 0$, the peak potentials on both the forward and reverse sweeps are invariant with period at this particular value of $\log k_f$.

Figure 4 presents a detailed description of the relationships between peak potentials and currents on period and $\log k_f$ when $E_0^2 = -300$ mV. Both $E_{p,f1}$ and $E_{p,f2}$ shift positively by 30 mV per decade with increasing period (for $\log k_f \geq 0$) whereas $E_{p,f1}$ and $E_{p,f2}$ remain essentially constant at $E_0^2$. Peak currents are proportional to the $\tau^{-1/2}$ over a wide range in $\log k_f$. The $\Delta \Psi_{f2}/\tau^{1/2}$ trace is linear at $k_f \leq 1$, curvilinear over the range $2 \leq \log k_f \leq 3$, and again linear at log $k_f \geq 4$. The slopes of the linear traces decrease with increasing log $k_f$. The ratio of $\Delta \Psi_{p,f1}/\Delta \Psi_{p,f2}$ ranges from 0.1 to 1 depending upon $k_f$ and period. This is shown in the upper right panel of Fig. 4 and is comparable to the trend for an EC mechanism. Similarly, the ratio of $\Delta \Psi_{p,f1}/\Delta \Psi_{p,f2}$ ranges from 1 to 2 depending upon $k_f$ and period. At log $k_f \leq 0$, this ratio increases to a value of two and then decreases to a value of one. At $< \log k_f \leq 2$, the peak ratio decreases to a value of one over the range in period investigated herein. For log $k_f > 2$, the ratio is invariant at unity. The trend shown in $\Delta \Psi_{p,f1}/\Delta \Psi_{p,f2}$ is comparable to the trend for a CE mechanism where peak ratios > 1 reflect the amount of conversion of Red1 to Ox2 and subsequent reduction to Red2 over the period of the potential pulse. Finally, the ratio of $\Delta \Psi_{p,f2}/\Delta \Psi_{p,f1}$ ranges from 0 to 1.8 depending upon $k_f$ and

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Effect of $k_f$ and $E_0^2$ on the shape of the voltammogram when $E_0^2$ is $-300$ mV relative to $E_1^2$ (top panel), $-100$ mV (middle panel), and equal to $E_1^2$ (bottom panel) and log $k_f$ is $-3$ (red), $-2$ (orange), $-1$ (yellow), 0 (green), 1 (cyan), 2 (blue), 3 (purple), 4 (magenta), 5 (light gray) and 6 (dark gray). Parameter values are: period (green), 1 (cyan), 2 (blue), 50 ms (blue), 100 ms (magenta), 200 ms (magenta), 500 ms (dark gray), 1 s (dark gray), 2 s (black), and 5 s (brown).

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Effect of period and $E_0^2$ on the shape of the voltammogram when $E_0^2$ is $-300$ mV relative to $E_1^2$ (top panel), $-100$ mV (middle panel), and equal to $E_1^2$ (bottom panel) and log $k_f$ = 3. Parameter values are: amplitude = 50 mV, increment = 10 mV, switching potential is 200 mV negative of $E_2^2$, and period is varied from 1 ms (red), 2 ms (orange), 5 ms (yellow), 10 ms (green), 20 ms (cyan), 50 ms (blue), 100 ms (purple), 200 ms (magenta), 500 ms (dark gray), 1 s (dark gray), 2 s (black), and 5 s (brown).
period as shown in Fig. 4. The slope of the linear portions of the traces depicted in this panel of the figure are consistently 0.778. Note that peak ratios presented in Fig. 4 are specific to the increment, amplitude and switching potential values given in the caption. At switching potentials further negative of \(E_0^2\), each trace shifts to the left.

Figure 5 presents the relationships between peak potentials and currents on period and \(\log k_f\) when \(E_0^2 = -100\) mV, \(E_{p,1}\) shifts positively by 30 mV per decade increase in period (for \(\log k_f \geq 0\)). \(E_{p,2}\) emerges when \(\log k_f \geq 0\), and remains essentially constant at \(E_0^2\). This trend is not observed for \(E_{p,r}\). At \(\log k_f \geq 3\), the peak is located at \(E_0^2\) over all periods. At \(\log k_f < 3\), the peak moves from \(E_0^2\) to \(E_0^1\) as period increases. Peak currents are linearly or curvilinearly related to \(\tau^{-1/2}\) depending upon \(\log k_f\). The \(\Delta \Psi_{p,1}/\Delta \Psi_{p,1}\) and \(\Delta \Psi_{p,r}/\tau^{-1/2}\) traces are linear at \(\log k_f \leq 1\), curvilinear over the range \(2 \leq \log k_f \leq 3\), and again linear at \(\log k_f \geq 4\). At \(\log k_f \leq 0\), the ratio of \(\Delta \Psi_{p,r}/\Delta \Psi_{p,1}\) diminishes from 1 to \(\sim 0.7\) with increasing period until the \(E_{p,r}\) shifts to \(E_0^2\) whereupon

![Figure 4](image1.png)

**Figure 4.** Plots of peak current versus \(\tau^{-1/2}\) and peak potentials and peak ratios versus log period for \(E_0^2 = -300\) mV as a function of \(\log k_f\) ranging from \(-3\) (red) to 6 (dark gray) using the color scheme described in the caption of Fig. 2. Parameter values are: amplitude = 50 mV, increment = 10 mV, and switching potential is 200 mV negative of \(E_0^2\). Open circles denote the specific parameter levels for simulated data.

![Figure 5](image2.png)

**Figure 5.** Plots of peak current versus \(\tau^{-1/2}\) and peak potentials and peak ratios versus log period for \(E_0^2 = -100\) mV as a function of \(\log k_f\) ranging from \(-3\) (red) to 6 (dark gray) using the color scheme described in the caption of Fig. 2. Parameter values are: amplitude = 50 mV, increment = 10 mV, and switching potential is 200 mV negative of \(E_0^2\). Open circles denote the specific parameter levels for simulated data.
the ratio begins to increase to $\sim 1.15$. At $\log k_f > 0$, the shift in $E_{p2}$ to $-100$ mV occurs at shorter periods and the forward peak separates into two. When this occurs, the ratio $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p2}^{+}$ increases from 1.15 to 1.8 whereas the ratio $\Delta \Psi_{p1}^{-}/\Delta \Psi_{p2}^{-}$ decreases from 1.15 to unity with increasing period. Thus, the transition in the shape of the voltammogram from one to two peaks on the forward sweep occurs for all $\log k_f$ values but at different periods; the higher the $\log k_f$ value, the shorter the period at which the transition occurs. Figure 6 provides insight into this transition by presenting the individual and difference currents (i.e. $\Psi$ and $\Delta \Psi$) as a function of period for $\log k_f = 1$.

Figure S-3 presents the relationships between peak potentials and currents on period and $\log k_f$ when $E_0^p = 0$ mV. $E_{p1}$ remains at $E_0^f$ until $\log k_f \geq 3$ when both $E_{p1}$ and $E_{p2}$ are resolved. At this point, $E_{p1}$ shifts positively by $30$ mV per decade with increasing period. $E_{p1}$ remains at $E_0^f$. $E_{p2}$ remains essentially constant at $0$ mV over the entire range in $\log k_f$. $\Delta \Psi_{p1}^{+}$ vs. $\tau^{1/2}$ is linear for all $\log k_f$ values. However, the slopes of the traces marginally vary with $\log k_f$. The ratio of $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p2}^{+}$ ranges from 0.9 to 1.0 depending upon $\log k_f$ and period until $E_{p1}$ and $E_{p2}$ are resolved. At this point, the ratio jumps to a value between 1.7 and 1.8 and the ratio of $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p2}^{+}$ is unity. At $-3 \leq \log k_f \leq -1$, the peak width is invariant with period and equivalent to that for a reversible process. At all other values of $\log k_f$, the $W_{p2}$ increases with period with a magnitude dependent on $k_f$ until two processes are resolved along the potential axis (see Fig. S-4).

Thus, key indicators of an ECE mechanism are the differential dependences of peak potentials, currents, and current ratios with period. The shift in peak potential with period is diagnostic for the presence of a chemical reaction following the first reduction process. A plot of peak current versus $\tau^{1/2}$ confirms that the electrode reaction is differential rather than surface-confined and identifies the presence of a chemical reaction following the first reduction process. Peak ratios deviate from unity and are indicative of both a following and preceding chemical reaction. It is interesting to note that the trends for the first process mirror those for an EC mechanism; however, the trends for the second process are unlike the trends for a CE mechanism. Taken collectively, systematic variation of period provides a diagnostic trend characteristic of the ECE mechanism from which the magnitude of $k_f$ can be determined.

**Effect of increment ($\Delta E$)**—The effect of increment on the shape of the voltammogram depends on the separation between $E_0^f$ and $E_0^p$ and $\log k_f$. Figure 7 presents the impact of varying increment on the shape of the voltammogram as a function of $E_0^f$ for $\log k_f = 3$ and 1. On the forward scan, $E_{p1}$ shifts negatively and $\Delta \Psi_{p1}^{+}$ increases with increment while $E_{p1}^{p2}$ and $\Delta \Psi_{p2}^{p2}$ are invariant at $E_0^f = -300$ and $-100$ mV and $\log k_f = 3$ and 1. When $E_0^f = 0$ mV at $\log k_f = 3$, $E_{p1}$ and $E_{p2}$ are essentially unchanged, $\Delta \Psi_{p1}^{+}$ increases slightly, and the apparent peak width increases with increment. At $\log k_f = 1$, $E_{p1} = E_{p2}$ and the peak currents are independent of increment. The effective scan rate is increment divided by period. Thus, increasing increment versus increasing period shifts $E_{p1}$ in opposite directions (see Figs. 3 and 7).

Figure 8 presents the dependence of peak potentials, currents, and current ratios on increment as a function of $\log k_f$ when $E_0^f = -300$ mV. $E_{p1}$ and $E_{p2}$ shifts negatively $\sim 28$ mV per decade in increment whereas $E_{p1}^{p2}$ and $E_{p2}^{p2}$ remain constant at $E_0^f$. As $\log k_f \leq -2$, $\Delta \Psi_{p1}^{+}$ and $\Delta \Psi_{p1}^{-}$ are independent of increment. At higher $k_f$ values, $\Delta \Psi_{p1}^{+}$ and $\Delta \Psi_{p1}^{-}$ increase curvilinearly with increment whereas $\Delta \Psi_{p2}^{+}$ and $\Delta \Psi_{p2}^{-}$ decrease with increment at low values of $k_f$ but become independent of increment at $\log k_f \geq 2$. The ratio of $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p1}^{-}$ ranges from 0.1 to 1 whereas the ratio of $\Delta \Psi_{p2}^{+}/\Delta \Psi_{p2}^{-}$ ranges between 1 and 2.2 depending upon $\log k_f$ and increment. Finally, the ratio $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p1}^{-}$ decreases with increment for $\log k_f \geq -1$. This trend is comparable to that observed in cyclic voltammetry where increasing the potential sweep rate shortens the time window for the conversion of $\text{Red}_2$ to $\text{Ox}_2$.

Figure S-5 presents the dependence of peak potentials, currents, and current ratios on increment as a function of $\log k_f$ when $E_0^f = -100$ mV. $E_{p1}$ shifts negatively $\sim 28$ mV per decade in increment whereas $E_{p2}$, when it emerges, remains constant at $E_0^f$. At $\log k_f < 1$, $E_{p2}$ moves from $E_0^f$ to $E_{p2}$ as increment increases whereas at $\log k_f \geq 1$, $E_{p2}$ is located at $E_0^f$ over all increments. At $\log k_f \leq -2$, $\Delta \Psi_{p1}^{+}$ and $\Delta \Psi_{p1}^{-}$ are independent of increment. At higher $k_f$ values, $\Delta \Psi_{p1}^{+}$ and $\Delta \Psi_{p1}^{-}$ increase curvilinearly with increment whereas $\Delta \Psi_{p1}^{+}$ decreases with increment at low values of $k_f$ but become independent of increment at $\log k_f \geq 2$. The ratio of $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p1}^{-}$ ranges from 0.75 to 4 whereas the ratio of $\Delta \Psi_{p2}^{+}/\Delta \Psi_{p2}^{-}$ ranges between 1 and 1.5 depending upon $\log k_f$ and increment.

Figure S-6 presents the dependence of peak potentials, currents, and current ratios on increment as a function of $\log k_f$ when $E_0^f = 0$ mV. $E_{p1}$ remains constant (within the value of the increment) until it becomes resolved from $E_{p2}$. Then, $E_{p1}$ shifts negatively by $\sim 28$ mV per decade in increment whereas $E_{p2}$, remains constant at $E_0^f$, $E_{p2}$ remains constant at $E_0^f$ (within the value of the increment) over all increments. $\Delta \Psi_{p1}^{+}$ and $\Delta \Psi_{p1}^{-}$ increase with increment whereas $\Delta \Psi_{p2}^{+}$ remains constant when present. The ratios $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p1}^{-}$ and $\Delta \Psi_{p2}^{+}/\Delta \Psi_{p2}^{-}$ are equal to unity except when $E_{p2}$ is resolved from $E_{p1}$. Then $\Delta \Psi_{p1}^{+}/\Delta \Psi_{p1}^{-}$ drops curvilinearly from 4.5 to 1.5 with increment.

The differential dependences of peak potentials and current ratios with increment are also indicators of an ECE mechanism. When the two processes are sufficient separated along the potential axis, $E_{p1}$ and $E_{p2}$ shift negatively towards $E_0^f$ with increment similar to an EC mechanism. In contrast to the CE mechanism, $E_{p1}$ and $E_{p2}$ shift negatively towards $E_0^f$ and $E_{p2}^{p2}$.
$E_{p,r2}$ are independent of increment.$^{12}$ Peak ratios for the first process are $\leq 1$ (similar to an EC mechanism) and for the second process $\geq 1$ (similar to a CE process).$^{12,13}$ Peak potential dependence on increment can provide a measure of $k_f$ if $E^0_1$ is known. When the two processes are not resolved along the potential axis, trends in peak potentials and peak current ratios distinguish this mechanism from a reversible, quasireversible, EC, and CE mechanism (vide supra).

Figure 7. Effect of increment and $E^0_2$ on the shape of the voltammogram when $E^0_2$ is $-300$ mV relative to $E^0_1$ (top panel), $-100$ mV (middle panel), and equal to $E^0_1$ (bottom panel) and log $k_f = 3$ (left column) and log $k_f = 1$ (right column). Parameter values are: period $= 50$ ms, amplitude $= 50$ mV, switching potential is $200$ mV negative of $E^0_2$, and increment is varied from 1 mV (red), 5 mV (orange), 10 mV (yellow), 15 mV (green), and 20 mV (cyan).

$E_{p,f2}$ are independent of increment.$^{12}$ Peak ratios for the first process are $\leq 1$ (similar to an EC mechanism) and for the second process $\geq 1$ (similar to a CE process).$^{12,13}$ Peak potential dependence on increment can provide a measure of $k_f$ if $E^0_1$ is known. When the two processes are not resolved along the potential axis, trends in peak potentials and peak current ratios distinguish this mechanism from a reversible, quasireversible, EC, and CE mechanism (vide supra).

Effect of amplitude ($E_{SW}$).—The effect of amplitude on the shape of the voltammogram also depends on the separation between $E^0_2$ and $E^0_1$ and log $k_f$. Figure 9 presents the impact of varying amplitude on the shape of the voltammogram as a function of $E^0_2$ for log $k_f = 3$. On both the forward and reverse sweeps, the peak potentials for the first process shift positively with amplitude while the peak potentials for second process (at $E^0_2$) are invariant for all three $E^0_2$ values investigated herein.

Figure 8. Plots of peak currents, potentials, and ratios versus increment for $E^0_2 = -300$ mV as a function of log $k_f$ ranging from $-3$ (red) to 6 (dark gray) using the color scheme described in the caption of Fig. 2. Parameter values are: period $= 50$ ms, amplitude $= 50$ mV, and switching potential is $-500$ mV. Open circles denote the specific parameter levels for simulated data.
The dependence of peak potentials, currents, and current ratios on amplitude is also indicative of log $k_f$. When $E_0^2 = -300$ mV, $E_{p,f1}$ and $E_{p,r1}$ shift positively whereas $E_{p,f2}$ and $E_{p,r2}$ remain constant with increasing amplitude (see Fig. 10). The peak current magnitudes increase curvilinearly with amplitude; the degree of curvature depends upon log $k_f$. In contrast, peak ratios are almost always independent of amplitude but the value changes with log $k_f$.

When $E_0^2 = -100$ mV, $E_{p,f1}$ shifts positively when log $k_f \geq 2$ whereas $E_{p,f2}$ remains essentially constant with increasing amplitude (see Fig. S-7) Note that at log $k_f \leq -2$, $E_{p,r}$ remains at $E_0^2$ and at log $k_f \geq 2$, $E_{p,r}$ remains at $E_0^2$. In between these limits in log $k_f$, $E_{p,r}$ shifts with amplitude (see Fig. S-7). The peak current magnitudes increase curvilinearly with amplitude; the degree of curvature depends somewhat upon log $k_f$. In contrast to when $E_0^2 = -300$ mV, the peak ratio $\Delta \Psi_{p,f2}/\Delta \Psi_{p,f1}$ depends upon both amplitude and log $k_f$. At log $k_f \leq -2$, $\Delta \Psi_{p,f2}/\Delta \Psi_{p,f1}$ equals unity at all amplitudes. At $-2 < \log k_f \leq 0$, $\Delta \Psi_{p,f2}/\Delta \Psi_{p,f1}$ is less than unity and increases towards unity with amplitude. At $\log k_f = 1$, two forward peaks are resolved along the potential axis at amplitudes $\leq 50$ mV. At $\log k_f \geq 2$, $\Delta \Psi_{p,f2}/\Delta \Psi_{p,f1}$ increases from 1.4 to 2.2 with amplitude. When $E_{p,f2}$ is resolved from $E_{p,r1}$, the ratio $\Delta \Psi_{p,f2}/\Delta \Psi_{p,f1}$ is measureable and equal to unity except with log $k_f = 1$ (see Fig. S-7).

Figure S-8 presents the dependence of peak potentials, currents, and current ratios on amplitude as a function of log $k_f$ when $E_0^2 = 0$ mV, $E_{p,f1}$ remains essentially constant with increasing amplitude up to log $k_f \leq 3$. When log $k_f = 4$, $E_{p,f2}$ becomes resolved from $E_{p,r1}$ at low amplitudes. At log $k_f > 4$, $E_{p,f1}$ is resolved from $E_{p,r1}$ at all amplitudes and both shift positively with increasing amplitude but with differing slopes. In contrast, $E_{p,r}$ remains essentially constant at $E_0^2$ regardless of $k_f$ and amplitude. The peak current magnitudes increase curvilinearly with amplitude; the degree of curvature depends somewhat upon log $k_f$ and whether the two processes are resolved. The dependence of peak ratios on amplitude mirrors that presented above for $E_0^2 = -100$ mV (see Fig. S-8). Thus, the shift in peak potentials and the magnitude of peak ratios as a function of amplitude can be used to identify the value of $k_f$.

**Figure 9.** Effect of amplitude and $E_0^2$ on the shape of the voltamogram when $E_0^2$ is $-300$ mV relative to $E_1^0$ (top panel), $-100$ mV (middle panel), and equal to $E_0^2$ (bottom panel) and log $k_f = 3$. Parameter values are: period = 50 ms, increment = 10 mV, switching potential is 200 mV negative of $E_1^0$, and amplitude is varied from 10 mV (red) to 90 mV (light gray) in steps of 10 mV.

**Figure 10.** Plots of peak currents, potentials, and ratios versus amplitude for $E_0^2 = -300$ mV as a function of log $k_f$ ranging from $-3$ (red) to $6$ (dark gray) using the color scheme described in the caption of Fig. 2. Parameter values are: period = 50 ms, increment = 10 mV, and switching potential is $-500$ mV. Open circles denote the specific parameter levels for simulated data.
the experimenter should consult other publications in this series9–14. In this paper, theory for an ECE mechanism has been developed and applications via CSWV will be forthcoming.

Conclusions

In this work, theory for an ECE mechanism has been developed for CSWV. The peak currents, potentials, and shapes of cyclic square wave voltammograms for the ECE mechanism have been shown to be a complex function \( k_f \), increment, period, and amplitude. The effects of these empirical parameters on the voltammograms for this mechanism are summarized in Table I. It is anticipated that experimenters will prepare the diagnostic plots listed in this table. If the mechanism is properly assigned, the \( k_f \) value obtained from the trend in peak potentials will be consistent with that obtained from peak current and peak ratio data. Note that the range in measureable log \( k_f \) values is a function of \( \Delta E^0 \) and whether an independent measure of \( E^0 \) is available (i.e. at low temperatures or fast scan rates). If \( \Delta E^0 \geq 100 \text{ mV} \), the range in log \( k_f \) extends from \(-2\) to \(6\) if \( E^0 \) is known and from \(-2\) to \(2\) if it isn’t. When \( \Delta E^0 < 100 \text{ mV} \), only fast rates of reaction can be determined (i.e. log \( k_f > 4 \)).

Table I. Diagnostic Plots and Protocol for Assessing an ECE Reaction by CSWV.

| Waveform parameters | Period, \( \tau \) | Increment, \( \Delta E \) | Amplitude, \( E_{SW} \) |
|---------------------|-----------------|------------------|-----------------|
| **Peak currents**   | \( \Delta I_p \) vs. \( \tau^{-1/2} \) | All peak currents decrease linearly or curvilinearly with increasing period regardless of separation between \( E^0_1 \) and \( E^0_2 \) (see Figs. 4, 5, and S-3) | \( \Delta I_p \) vs. \( E_{SW} \) | All peak currents increase with \( E_{SW} \) with magnitude and curvature dependent on log \( k_f \) and \( E^0_2 \) relative to \( E^0_1 \) (see Figs. 10, 8, 7, and S-8) |
| **Peak potentials** | \( E_{p,f} \) vs. \( \log \tau \) | Complex behavior that depends on log \( k_f \) and \( E^0_2 \) relative to \( E^0_1 \) (see Figs. 4, 5, and S-3) | \( E_{p,r} \) vs. \( E_{SW} \) | Trend depends upon log \( k_f \) and \( E^0_2 \) relative to \( E^0_1 \) (see Figs. 10, 8, 7, and S-8) |
| **Peak widths**     | \( W_{1/2} \) vs. \( \log \tau \) | General increase when \( E^0_2 = E^0_1 \) (see Figs. S-4) | \( W_{1/2} \) vs. \( \delta E \) | Small increase in \( W_{1/2} \) with \( \delta E \) |

*Diagnostic criteria applies only to when \( E^0_1 \leq E^0_2 \) where no disproportionation takes place.

Conclusions

In this work, theory for an ECE mechanism has been developed for CSWV. The peak currents, potentials, and shapes of cyclic square wave voltammograms for the ECE mechanism have been shown to be a complex function \( k_f \), increment, period, and amplitude. The effects of these empirical parameters on the voltammograms for this mechanism are summarized in Table I. It is anticipated that experimenters will prepare the diagnostic plots listed in this table. If the trends observed match those listed in Table I, then assignment of the electrode reaction as an ECE mechanism is appropriate. If not, then the experimenter should consult other publications in this series9–14 or the text by Mirčeski15 to identify the electrode reaction pathway. The magnitude of \( k_f \) can then be determined by comparison of the observed trends in the diagnostic plots with those presented in figures both in this paper and in Supplementary Material. If the mechanism is properly assigned, the \( k_f \) value obtained from the trend in peak potentials will be consistent with that obtained from peak current and peak ratio data. Note that the range in measureable log \( k_f \) values is a function of \( \Delta E^0 \) and whether an independent measure of \( E^0 \) is available (i.e. at low temperatures or fast scan rates). If \( \Delta E^0 \geq 100 \text{ mV} \), the range in log \( k_f \) extends from \(-2\) to \(6\) if \( E^0 \) is known and from \(-2\) to \(2\) if it isn’t. When \( \Delta E^0 < 100 \text{ mV} \), only fast rates of reaction can be determined (i.e. log \( k_f > 4 \)). Reports of diagnostic criteria for the ECEq vs. and ECEq vs.C mechanisms and the means to evaluate reaction rates via CSWV will be forthcoming.

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