



Diagnostic Criteria for the Characterization of Electrode Reactions with Chemical Reactions Following Electron Transfer by Cyclic Square Wave Voltammetry



John C. Helfrick Jr., Megan A. Mann, Lawrence A. Bottomley*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA

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ABSTRACT

Theory for cyclic square wave voltammetry of electrode reactions with coupled chemical reactions following the electron transfer is presented. Theoretical voltammograms were calculated following systematic variation of empirical parameters to assess their impact on the shape of the voltammogram. 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.

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1. Introduction

Electron transfer reactions that generate an unstable product are commonly referred to as an EC mechanism when the product of the chemical reaction following the electron transfer is electroinactive over the potential range examined. The chemical reaction may be reversible or irreversible; the electron transfer may be fast or kinetically-controlled. The EC mechanism can be identified with a variety of electrochemical techniques [1–8]. While theory to guide the experimentalist in identifying this electrode reaction using square wave voltammetry (SWV) has been reported [5,6,9–17], very few applications of this theory have been published [18–23].

Our current objective is to stimulate 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. Interestingly, the technique most often used by these workers is cyclic voltammetry (CV). Most workers assign the electrode mechanism from observing shifts in peak potentials and changes in peak current magnitudes with increasing potential sweep rate as directed by the classic work by Nicholson and Shain [2]. The theory described in this paper was

developed when analog instrumentation was commonplace. Now, digital instruments predominate. Cyclic voltammograms acquired with digital instruments are actually cyclic staircase voltammograms. The applicability of Nicholson and Shain theory depends upon when the current is sampled during the potential pulse [24–27]. The “correct” sampling point depends upon the electrode reaction mechanism [28–32].

This report focuses on the application of cyclic square wave voltammetry (CSWV) in characterizing an EC mechanism. CSWV is SWV in two directions; the potential is stepped through the region of the formal potential of the electroactive species under study and then back in an analogous fashion with CV. Readers unfamiliar with this waveform are directed to Table of Contents graphic. The immediate reverse potential sweep functions as a probe of the stability of the product generated on the forward potential sweep. The data display format is familiar to non-electrochemists who currently make extensive use of CV for compound characterization. Since the current is sampled at the end of each potential pulse, no correction factors are required to interpret shifts in peak potentials or changes in peak current magnitudes that occur following systematic adjustment of the waveform parameters. We assert that non-specialists in electrochemistry will appreciate the similarity in output of CSWV to CV and will use this technique to characterize electrode reactions if protocols for doing so are available. To this end, we have recently presented protocols for

* Corresponding author.

E-mail address: Bottomley@gatech.edu (L.A. Bottomley).

evaluating single and consecutive reversible electron transfer reactions [33], kinetically-controlled electron transfer reactions [34,35], and chemically-coupled reactions [36,37]. In these studies, signature trends resulting from systematic variation of the empirical parameters for CSWV, *i.e.* period, increment, switching potential, and amplitude, were identified and used to establish diagnostic criteria for identifying each mechanism. In this report, theory of CSWV for the EC mechanism is presented and the signature trends are identified. When properly applied, these trends enable the experimentalist to calculate both the equilibrium constant and rate of the following reaction.

Experts in electrochemistry will appreciate the complementary nature of CSWV to SWV. In conventional SWV, the immediate reverse potential step functions as a probe of the stability of the product generated on the forward potential sweep. A chemical reaction following the electron transfer will diminish the current on the reverse potential pulse by a magnitude dependent upon the potential of the step, the kinetics of the following homogeneous reaction, and the duration of the potential step. Consequently, the net current will decrease. To assign the process as an EC mechanism requires careful examination of the individual currents on each potential step [5,11,14,17]. While SWV is fully capable of identifying an EC process, the CSWV protocol presented herein enables a more straightforward characterization of this mechanism and makes use of all empirical parameters rather than just frequency or period [5,9,11,15,17]. The key CSWV features that provide this capability involve comparison of the net peak magnitudes and potentials on the forward and reverse sweeps as well as systematic variation of the potential at which the forward sweep is reversed. The diagnostic criteria presented herein are novel and educe from the widely used trends commonly used to assign electrode reaction mechanisms in CV.

2. Theory

The general reaction pathway for an electron transfer followed by a chemical reaction is:



where Ox is the reactant, Red is the initial product of the electron transfer, Z is the electroinactive product of the following chemical reaction, k_f is the rate constant for the conversion of Red to Z in s^{-1} , and k_b is the rate constant for conversion of Z to Red in s^{-1} . All chemical reactions are treated herein as first order. The derivation of an equation that enables calculation of current at each applied potential for this electrode reaction starts from Fick's laws of diffusion. Expressions for the concentrations of Ox and Red as a function of time and distance from the electrode are found using Laplace transformations following application of the boundary conditions. These expressions are related by the Nernst equation for a reversible electron transfer:

$$E_{\text{applied}} = E^0 + \left(\frac{RT}{nF}\right) \ln\left(\frac{C_{\text{Ox}}(0, t)}{C_{\text{Red}}(0, t)}\right) \quad (2)$$

where n = number of electrons transferred, F = Faraday constant, A = area of the electrode, R = gas constant, T = temperature in Kelvin, E = applied potential, E^0 = formal potential for the electron transfer reaction, D_{Ox} = diffusion coefficient of Ox (cm^2/sec), D_{Red} = diffusion coefficient of Red (cm^2/sec), $C_{\text{Ox}}(0, t)$ = concentration of Ox at the electrode surface at any time t , and $C_{\text{Red}}(0, t)$ = concentration of Red at the electrode surface at any time t . Numerical approximation of the resultant integral equations were performed in the same manner put forth by Nicholson and

Olmstead [38]. The final equation used to compute theoretical voltammograms for the $E_{\text{rev}}C$ mechanism is

$$\Psi_m = \frac{\frac{(k\tau\pi)^{1/2}}{\varepsilon} - \left(\frac{1}{K+1} + \frac{1}{\varepsilon}\right) \left(\frac{2k\tau}{L\pi}\right)^{1/2} \sum_{j=1}^{i=m-1} \Psi_j S_j - \left(\frac{K}{K+1}\right) \sum_{j=1}^{i=m-1} \Psi_j R_j}{\left(\frac{1}{K+1} + \frac{1}{\varepsilon}\right) \left(\frac{2k\tau}{L\pi}\right)^{1/2} + \left(\frac{K}{K+1}\right) R_1} \quad (3)$$

where L = number of subintervals on each potential, K = the equilibrium constant for the following chemical reaction and equal to k_f/k_b , Ψ_m = dimensionless current for each time increment with the serial number m , τ = period, k = the sum of the forward and reverse rate constants for the chemical reaction following the electron transfer, *i.e.* $k_f + k_b$, and

$$\varepsilon = \exp\left[\frac{nF}{RT}(E_{\text{applied}} - E^0)\right] \quad (4)$$

assuming $D_{\text{Ox}} = D_{\text{Red}}$.

To compute theoretical voltammograms for CSWV, we employed the cyclic waveform available with current commercial electrochemical instrumentation. The recursive calculation of current on each step for every step in the voltammogram was performed by systematic variation of period (τ), increment (δE), switching potential (E_λ), and amplitude (E_{SW}), over the following intervals: $1 \text{ ms} \leq \tau \leq 5 \text{ s}$, $1 \text{ mV} \leq \delta E \leq 25 \text{ mV}$, $-100 \leq E_\lambda \leq -1000 \text{ mV}$ (relative to E^0), $10 \text{ mV} \leq E_{\text{SW}} \leq 90 \text{ mV}$, and $L = 20$ over each period. Period limits were set in consideration of typical potentiostat rise times, commonly encountered solution resistances and electrode double layer capacitances as well as the time duration required per scan. Amplitude limits were set in accordance with the range typically used in SWV. Increment limits were set in consideration of the number of points to define the peak. Specific parameter levels for simulated data are denoted by open circles and listed in the captions of figures contained in this report and Supplementary Data.

Cyclic square wave voltammograms were calculated to examine the impact of the empirical parameters period, increment, switching potential, and amplitude on the characteristic features of the voltammogram for the singular case where the number of electrons transferred equals one. The predicted difference current, $\Delta\Psi$ is determined by subtracting $\Psi_{\text{reverse pulse}}$ from $\Psi_{\text{forward pulse}}$ and is plotted versus the average of the potentials (E_{step}) at which both currents were calculated. Throughout this work, the forward difference current, $\Delta\Psi_f$ will denote the difference currents acquired over the interval E_{initial} to the switching potential E_λ , and the difference current, $\Delta\Psi_r$, will denote difference currents acquired over the reverse potential sweep from E_λ to the final potential, E_{final} . To capture the effect of period as it relates to current, $\Delta\Psi^+$ is used throughout this work where

$$\Delta\Psi^+ = \Delta\Psi / \sqrt{\tau} \quad (5)$$

The physical meaning of $\Delta\Psi^+$ is the normalized faradaic current emanating from the electron transfer. The plotting convention used herein treats reduction currents as positive and oxidative currents as negative values. Net peak currents on the forward and reverse sweeps are designated as $\Delta\Psi_{p,f}^+$ and $\Delta\Psi_{p,r}^+$, respectively. Peak ratio is denoted as $\Delta\Psi_{p,r}^+ / \Delta\Psi_{p,f}^+$. Similarly, $E_{p,f}$ and $E_{p,r}$ are used to represent peak potentials with peak separation $\Delta E_p = E_{p,r} - E_{p,f}$. Peak widths ($W_{1/2,f}$ and $W_{1/2,r}$) are measured at half peak currents.

3. Results and Discussion

In our previous reports [33–37], we showed that mechanistic identification of an electrode reaction is made possible from an in-

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