

Analytical Relation Between the Concentration of Species at the Electrode Surface and Current for Quasi-Reversible Reactions

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Abstract: Cyclic voltammetry take into account the mass transport of species and the kinetics at the electrode surface. Analytical solutions of these models are not well-known due to the complexity of the boundary conditions. In this study we present analytical relation between the concentration at the electrode surface and the current for quasi-reversible reaction. A new semi analytic description of quasi-reversible cyclic voltammetry at a electrode is obtained, assuming equal diffusion coefficients. It provides rigorous and complete expression for the voltametric current, in the form of the integral or the integral equation. This solution method can be extended to cases that are more general and may be useful for benchmarking purposes.

Keywords: Mathematical Modeling, Boundary Value Problems, Non Linear Equations, Quasi-Reversible

1. Introduction

Cyclic voltammetry is one of the main tools used to characterize electrochemical systems and has a broad range of applications. This method is frequently used for analyzing electroactive species and surfaces and for the determination of reaction mechanisms and rate constants. Investigators over the years have sought analytical expressions and relationships to enable a theoretical interpretation and understanding of experimentally recorded cyclic voltammograms and other electrochemical characterization techniques [1–6]. Bortels et al. [7] found analytical solutions for the one dimensional steady state transport of ions in an electrolyte between two planar electrodes. Molina et al. [8] derived analytical expressions for the current or potential response and concentration profiles for the reversible ion transfer at the interface between two immiscible electrolyte solutions.

Berzins and Delahay [9] derived an equation for oscillographic polarographic waves corresponding to the reversible deposition of an insoluble substance and compared their results with experimental data. White and Lawson [4]

presented a solutions for the voltammetric deposition and dissolution of a metal from an electrode accounting for spherical effects as well as kinetics, uncompensated cell resistance, and submonolayer metal deposition. Lantelme and Cherrat [3] explored the analytical solutions to the cyclic voltammetry process. Oldham and Myland [10] derived mathematical solutions for the cyclic voltammetry of strong adsorption such that the redox pair is confined to the surface. In addition, Oldham and Myland [11], developed a semi-analytical method for describing the current in cyclic voltammetry.

Eswari and Rajendran [12] reported the closed-form analytical expressions for the concentration in an EC reaction for limiting cases of small and large reaction rates at the electrode and small and large time intervals. In that investigation, the authors employed the equation in planar geometry to describe the mass transport and the Butler-Volmer equation at the electrode surface to account for the kinetics. The asymptotic expressions for the normalized current were derived by using the Laplace transformation.

Furthermore, Eswari and Rajendran [13] explored analytical solutions for the EC₂ cyclic voltammetry model

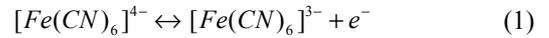
[13] using He’s homotopy perturbation method. Samin, and Jinsuo Zhang [14] derive analytical solutions to the planar cyclic voltammetry model which describes mass transport of species through the equations and the kinetics at the electrode surface through the Nernst and Butler-Volmer equations. In this study we have obtained the relation between the concentration ferrocyanide at the electrode surface and the current for quasi-reversible reaction.

Table 1. Nomenclature.

Symbols	Definitions
c_{red}	The concentration of redox species
c_{ox}	The concentration of oxidised species
D_{red}	Diffusion coefficient of redox species
D_{ox}	Diffusion coefficient of oxidised species
k^e	EC rate constant
$c_{red}(0,t), c_{ox}(0,t)$	The concentrations of the reacting species at the electrode surface
$c_{red,\infty}, c_{ox,\infty}$	The concentrations of the reacting species in the bulk of the solution
E	Electrode potential
E_r	The equilibrium electrode potential
β	symmetry factor
F	Faraday constant
R	The universal gas constant
T	The thermodynamic temperature
$a = C_{red} / C_{red}^*$	Dimensionless concentration of redox species
$b = C_{ox} / C_{red}^*$	Dimensionless concentration of oxidised species
$\tau = tFv / RT$	Dimensionless time
$X = Z\sqrt{FV / RTD_{red}}$	Dimensionless distance
$\xi = \frac{Ke}{D_{red}}\sqrt{RTD_{red} / FV}$	Dimensionless parameter

2. Mathematical Formulation of the Problem

Consider the EC reaction



The concentration profiles of the red and ox forms can be obtained by solving the diffusion equation, which can be simplified in the case of a rotating disk electrode (RDE) to the following one dimensional form.

$$\frac{\partial c_{red}(z,t)}{\partial t} = D_{red} \frac{\partial^2 c_{red}(z,t)}{\partial z^2} \tag{2}$$

$$\frac{\partial c_{ox}(z,t)}{\partial t} = D_{red} \frac{\partial^2 c_{ox}(z,t)}{\partial z^2} \tag{3}$$

Where c_{red}, c_{ox} are the concentration of redox and oxidised species. D_{red} and D_{ox} are the corresponding diffusion coefficient. The initial and boundary conditions for the above equations are given by [15].

$$c_{red}(z,0) = c_{red}^*, \quad c_{ox}(z,0) = c_{ox}^*, \quad \text{when } t = 0 \tag{4}$$

$$D_i \left. \frac{\partial c_i(z,t)}{\partial z} \right|_{z=0} = \frac{i(t)}{nFA} = \pm r(t) \quad \text{where } + \text{ or } - \text{ sign stands for } i = red \text{ or } ox \tag{5}$$

$$c_i(\delta_{D,i}, t) = c_\infty \quad \text{where } \delta_{D,i} = 1.61 D_i^{1/3} \nu^{1/6} \omega_r^{-1/2} \tag{6}$$

In the case of Butler-Volmer kinetics reaction rate $r(t)$ is given by

$$r(t) = k^e \left\{ \frac{c_{red}(0,t)}{c_{red,\infty}} \exp(\beta F(E(t) - E_r) / RT) - \frac{c_{ox}(0,t)}{c_{ox,\infty}} \exp(-(1-\beta)F(E(t) - E_r) / RT) \right\} \tag{7}$$

Where k^e is the EC rate constant, $c_{red}(0,t), c_{ox}(0,t), c_{red,\infty}, c_{ox,\infty}$ are the concentrations of the reacting species at the electrode surface and in the bulk of the solution, respectively. E is the electrode potential, E_r is the equilibrium electrode potential, and β is a symmetry factor, whereas $f = F/RT$, where F is the Faraday constant, R is the universal gas constant, and T is the thermodynamic temperature. The EC constant k^e is defined as follows:

$$K^e = K_{red}^* c_{red,\infty}^* \exp(\beta f(E_r)) = K_{ox}^* c_{ox,\infty}^* \exp(-(1-\beta)f(E_r)) \tag{8}$$

We introduce the following set of dimensionless variables:

$$a = \frac{C_{red}}{C_{red}^*}, \quad b = \frac{C_{ox}}{C_{red}^*}, \quad \tau = \frac{tFv}{RT}, \tag{9}$$

$$X = Z\sqrt{\frac{FV}{RTD_{red}}}, \quad \xi = \frac{Ke}{D_{red}}\sqrt{\frac{RTD_{red}}{FV}}$$

Using the above dimensionless variables the diffusion equations (1) and (2) are expressed in the following dimensionless form:

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial X^2} \tag{10}$$

$$\frac{\partial b}{\partial \tau} = \xi \frac{\partial^2 b}{\partial X^2} \tag{11}$$

The dimensionless initial and boundary conditions are

$$a = 1, \quad b = 0 \quad \text{when } \tau = 0; \tag{12}$$

$$a = \frac{C_\infty}{C_{red}^*}, \quad b = \frac{C_\infty}{C_{red}^*} \quad \text{when } X = \delta_{D,i} \sqrt{\frac{FV}{RT}} = \gamma \tag{13}$$

$$\left. \frac{da}{dX} \right|_{X=0} = K_1 \exp[l_1 + \beta\tau]a(0, \tau) - K_2 \exp[l_2 + \alpha\tau]b(0, \tau) \quad (14)$$

$$\left. \frac{db}{dX} \right|_{X=0} = -K_3 \exp[l_1 + \beta\tau]a(0, \tau) - K_4 \exp[l_2 + \alpha\tau]b(0, \tau) \quad (15)$$

Where

$$\alpha = 1 - \beta, \quad l_1 = \frac{\beta F(E_1 - E_r)}{RT},$$

$$l_{21} = \frac{(\beta - 1)F(E_1 - E_r)}{RT}, \quad K_1 = \frac{k_e RT}{C_{red, \infty} D_{red} FV}$$

$$K_2 = \frac{k_e RT}{C_{ox, \infty} D_{red} FV} \quad K_3 = \frac{k_e RT}{C_{red, \infty} D_{ox} FV}$$

$$K_4 = \frac{k_e RT}{C_{ox, \infty} D_{ox} FV} \quad (16)$$

We get the following relation between the surface concentration and current (Appendix A)

$$a(0, \tau) = 1 - \frac{1}{m\sqrt{\pi}} \left[\int_0^\tau \frac{i(\tau)}{\sqrt{t-\tau}} [1 - 2 \exp(-\gamma^2 / 4(t-\tau))] d\tau \right] \quad (17)$$

Similarly we get

$$C_{red}(0, \tau) = C_{red}^* - \left\{ [1 / (\sqrt{D_{red}} nFRA \sqrt{FV / RT})] \left\{ \int_0^\tau \frac{i(\tau)}{\sqrt{t-\tau}} [1 - 2 \exp(-\gamma^2 / 4(t-\tau))] d\tau \right\} \right\} \quad (22)$$

$$C_{ox}(0, \tau) = [1 / (\sqrt{D_{red}} nFRA \sqrt{FV / RT})] \left[\int_0^\tau \frac{i(\tau)}{\sqrt{t-\tau}} [1 - 2 \exp(-\gamma^2 / 4(t-\tau))] d\tau \right] \quad (23)$$

The above equation can be rewritten as

$$C_{red}(0, \tau) = C_{red}^* - \frac{I(\tau)}{\sqrt{D_{red}} nFRA \sqrt{FV / RT}} \quad (24)$$

$$C_{ox}(0, \tau) = \frac{I(\tau)}{\sqrt{D_{ox}} nFRA \sqrt{FV / RT}} \quad (25)$$

Under few diffusion control condition $C_{red}(0, \tau) = 0$ and therefore $I(t)$ reaches the limit value I_L

$$C_{red}(0, \tau) = \frac{I_L - I(\tau)}{\sqrt{D_{red}} nFRA \sqrt{FV / RT}} \quad (26)$$

Where

$$I(\tau) = \left\{ \int_0^\tau \frac{i(\tau)}{\sqrt{t-\tau}} (1 - 2e^{-\gamma^2/4(t-\tau)}) d\tau \right\} \text{ and}$$

$$I_L = C_{red}^* \sqrt{D_{red}} nFRA \sqrt{FV / RT} \quad (27)$$

3. Conclusions

We have derived the analytical relation between the

$$b(0, \tau) = \frac{1}{m\sqrt{\pi}} \left[\int_0^\tau \frac{i(\tau)}{\sqrt{t-\tau}} [1 - 2 \exp(-\gamma^2 / 4(t-\tau))] d\tau \right] \quad (18)$$

Where

$$m = \frac{1}{D_{red} C_{red, \infty} nFA \sqrt{\frac{FV}{RT D_{red}}}} \quad (19)$$

This is the new analytical expression of surface concentration in terms of current. When $\gamma = 0$ from Eqn. (17) and (18) we get

$$a(0, \tau) = 1 + \frac{1}{m\sqrt{\pi}} \left[\int_0^\tau \frac{i(\tau)}{\sqrt{t-\tau}} d\tau \right] \quad (20)$$

$$b(0, \tau) = \frac{1}{m\sqrt{\pi}} \left[\int_0^\tau \frac{i(\tau)}{\sqrt{t-\tau}} d\tau \right] \quad (21)$$

Which is the well known analytical expression of surface concentration which is obtained from convolution transformation[16].

In the case of dimension variable the above Eqn. (20) and (21) becomes

concentration of the species at the electrode surface and current for quasi-reversible reactions. From this result we can also obtain the concentration of the species at the electrode surface and current for reversible reactions. The extension of the procedure to other convection diffusion process in rotating disc, rotating ring-disc electrodes, etc apart from the study of nonlinear convection diffusion process in all hydronamic electrodes seems possible.

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Appendix A: Analytical relation between the surface concentration and the current.

The dimensionless form of one dimensional planar diffusion are described by the following equations:

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial X^2} \quad (\text{A1})$$

$$\frac{\partial b}{\partial \tau} = \xi \frac{\partial^2 b}{\partial X^2} \quad (\text{A2})$$

The initial and boundary conditions are

$$a = 1, \quad b = 0 \quad \text{when } \tau = 0 \quad (\text{A3})$$

$$a = \frac{C_{\infty}}{C_{red^*}}, \quad b = \frac{C_{\infty}}{C_{red^*}} \quad \text{when } X = \delta_D \sqrt{\frac{FV}{RT}} \quad (\text{A4})$$

$$\left. \frac{da}{dX} \right|_{X=0} = K_1 \exp[l_1 + \beta\tau]a(0, \tau) - K_2 \exp[l_2 + \alpha\tau]b(0, \tau) \quad (\text{A5})$$

$$\left. \frac{db}{dX} \right|_{X=0} = -K_3 \exp[l_1 + \beta\tau]a(0, \tau) - K_4 \exp[l_2 + \alpha\tau]b(0, \tau) \quad (\text{A6})$$

Taking the Laplace transform of Eqn. (A1), we get

$$\bar{a}(X, s) = c_1 e^{\sqrt{s}X} + c_2 e^{-\sqrt{s}X} + \frac{1}{s} \quad (\text{A7})$$

Using the boundary condition Eqns. (A3)-(A6) we get

$$\bar{a}(0, s) = c_1 [2 - e^{\sqrt{s}\gamma}] + \frac{1}{s} \quad (\text{A8})$$

Now current becomes

$$\frac{i(\tau)}{nFA} = D_{red} C_{red^*} \sqrt{\frac{FV}{RTD_{red}}} \left. \frac{da(X, s)}{dX} \right|_{X=0} \quad (\text{A9})$$

Taking Laplace on both sides

$$\frac{i(s)}{nFA} = D_{red} C_{red^*} \sqrt{\frac{FV}{RTD_{red}}} \left. \frac{d\bar{a}(X, s)}{dX} \right|_{X=0} \quad (\text{A10})$$

From Eqn. (A8), we get

$$\left. \frac{\partial \bar{a}(X, s)}{\partial X} \right|_{X=0} = c_1 \sqrt{s} e^{\sqrt{s}\gamma} \quad (\text{A11})$$

Using Eqns. (A10) and (A11)

$$\frac{i(s)}{D_{red} C_{red^*} nFA \sqrt{\frac{FV}{RTD_{red}}}} = \left. \frac{d\bar{a}(X, s)}{dX} \right|_{X=0} = c_1 \sqrt{s} e^{\sqrt{s}\gamma} \quad (\text{A12})$$

The above equation can be written as

$$\frac{i(s)}{m} = \left. \frac{d\bar{a}(x, s)}{dX} \right|_{X=0} = c_1 \sqrt{s} e^{\sqrt{s}\gamma} \quad (\text{A13})$$

Where

$$m = \frac{1}{D_{red} C_{red^*} nFA \sqrt{\frac{FV}{RTD_{red}}}} \quad (\text{A14})$$

Now the constant c_1 becomes

$$c_1 = \frac{i(s)}{m \sqrt{s} e^{\sqrt{s}\gamma}} \quad (\text{A15})$$

Using this constant the Eqn. (A8) becomes

$$\bar{a}(0, s) = \frac{i(s)}{m \sqrt{s}} [2e^{-\sqrt{s}\gamma} - 1] + \frac{1}{s} = \frac{2i(s)}{m} e^{-\sqrt{s}\gamma} - \frac{i(s)}{m \sqrt{s}} + \frac{1}{s} \quad (\text{A16})$$

Taking laplace inverse on both sides we get

$$a(0, \tau) = 1 - \frac{1}{m \sqrt{\pi}} \left\{ \int_0^{\tau} \frac{i(t)}{\sqrt{t-\tau}} [1 - 2 \exp(-\gamma^2 / 4(t-\tau))] dt \right\} \quad (\text{A17})$$

Which is the equation (17) in the text.

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