Cyclic voltammetry with non-triangular waveforms: Electrochemically reversible systems

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ABSTRACT

Cyclic voltammetry is typically performed using triangular waveforms, however, complications inevitably arise from the discontinuous nature of the differentiated triangular wave: As the capacitive current contributions are proportional to the derivative of the applied electrode potential, the measured current is (at least theoretically) discontinuous, which experimentally manifests in perturbed voltammetric data following minima and maxima in the applied triangular wave that is mostly due to unavoidable parasitic capacitances. We herein investigate voltammetry using alternative waveforms which on the one hand circumvent such difficulties and on the other exhibit unique features in the voltammetric response. We show that these features immediately reveal the formal potential of an investigated reaction that is readily available without any need for further data processing, and enable a new and easy-to-use route to determine formal potentials.

1. Introduction

For decades cyclic voltammetry [1–4] has been the key technique in electrochemistry and still today remains an integral part of most electrochemical and electro-analytical studies published. In a typical cyclic voltammetry experiment, an electrode is set in contact with an electrolyte solution containing an analyte of interest. The surface is then biased with respect to the solution, while a triangular potential wave $E(t)$ is applied to the electrode relative to a reference electrode:

$$E(t) = \begin{cases} \pm \sigma t + E(t{=}0) & \text{for} \quad t < t_{1/2} \\ \mp \sigma(t - t_{1/2}) + E(t{=}t_{1/2}) & \text{for} \quad t \geq t_{1/2} \end{cases} \quad (1)$$

where σ is the scan rate and $t_{1/2}$ is half of the duration of one cycle. During the potential scan, the electrode current, the current through the solid–liquid interface, is monitored and enables diverse insights into the nature of the reaction at the electrode surface. As a vast amount of accessible and easy-to-use theory exists [5], numerous physical quantities can be readily extracted from voltammetric data including analyte concentrations, diffusion constants, and rate constants to just name a few.

Aside from the great opportunities offered by cyclic voltammetry using the triangular wave (Eq. (1)), experimental challenges inevitably result from the discontinuity of the potential's first derivative with respect to time. As capacitive contributions I_c to the measured current ($I = I_c + I_F$) are proportional to the first derivative of the applied electrode potential $E(t)$ with respect to time:

$$I_c \propto d_t E(t). \quad (2)$$

I_c is discontinuous, which entails perturbed voltammetric data following turning points at $t = n \cdot t_{1/2}$, $n \in \mathbb{N}^0$. The perturbations are mostly due to parasitic capacitances present in the measurement set-up, which may in a complex fashion depend on parameters such as the scan rate, potential, and current magnitude, and hence can typically not be distinguished from actual voltammetric data. A more detailed discussion on capacitive effects can be found in recent literature [6]. While such perturbations are of course present at any time of the experiment and generally affect all data, their influence may however be much larger at discontinuities in the current where they pose a much greater challenge to the acquisition and quantitative analysis of experimental results and which should therefore desirably be avoided.

In this work, we present an alternative approach to cyclic voltammetry using a slightly different waveform to the above triangular wave to prevent discontinuities in the measured electrode current. Related voltammetry is investigated in much detail and an expression for the height of the first peak is established akin to the well-known Randles-Ševčík equation [7,8]. Our analysis further reveals that the proposed method gives rise to unique voltammetric features that can be exploited to determine the formal potential of a reaction at an ease and clarity far beyond means offered by triangular wave cyclic voltammetry.

2. Theory

In the following section, the proposed method of an alternative non-triangular waveform is explained and a theoretical model introduced. We further introduce practical dimensionless coordinates and two different computational approaches, finite difference simulation and computation based on fractional calculus, which complement each other.

2.1. Theoretical model

We investigate a simple one-electron electrochemically-reversible reduction reaction of A to B at a planar macroelectrode under diffusion-only conditions, where both species have equal diffusion coefficients:

$$A + e^- \rightleftharpoons B. \tag{3}$$

The system is assumed to be fully-reversible in which the electrode kinetics are much faster in comparison to the mass transport resulting in a Nernstian equilibrium at the electrode surface: [2,9,10]

$$E = E_f^0 + \frac{RT}{F} ln \frac{c_A(x=0)}{c_B(x=0)} \tag{4}$$

where E is again the applied potential, E_f^0 is the formal potential of the A/B couple, and $c_A(x=0)$ and $c_B(x=0)$ are the surface concentrations of species A and B, respectively. In this system, only diffusion is considered as means of mass transport of the analytes to the electrode surface with no convection and the presence of a sufficiently high concentration of supporting electrolyte is assumed so that migration can be neglected [11–14]. It is, however, important to note that with sufficiently long scan duration times, convection may affect experimental results [2,3,15-17]. The transport of analytes is hence described via the one-dimensional diffusion equation given by Fick's second law, which relates the change in concentration, c, over space, x, with time, t: [18,19]

$$\frac{\partial c_j}{\partial t} = D_j \frac{\partial^2 c_j}{\partial x^2} \tag{5}$$

where j is the species of interest and D is the diffusion coefficient of the said species. In order to solve the diffusion equation, boundary conditions are established for the case where only species A is present in the bulk solution [2,18], and the concentration of both A and B is uniform in space:

$$t \leq 0, \text{ all } x, \quad c_A = c_A^*, \quad c_B = 0. \tag{6}$$

As t increases, both c_A and c_B change, however, at a distant significantly far from the electrode, no reaction is observed and the solution remains the same as the initial condition:

$$t > 0, \quad x \to \infty, \quad c_A = c_A^*, \quad c_B = 0. \tag{7}$$

Since both species have the same diffusion coefficient and by conservation of mass, the amount of A consumed at the electrode equals the amount of B gained:

$$t > 0, \quad x = 0, \quad -\frac{\partial c_A}{\partial x} = \frac{\partial c_B}{\partial x} \tag{8}$$

and, due to the symmetry of all boundary conditions with respect to the exchange of A and B, the following condition holds at any point in space:

$$c_A(x, t) + c_B(x, t) - c_A^* = 0. \tag{9}$$

2.2. Proposed method

In contrast to a triangular wave, the here-introduced method uses a cosine potential wave with varying powers, while the scanned potential window is shifted between different experiments. The cosine potential
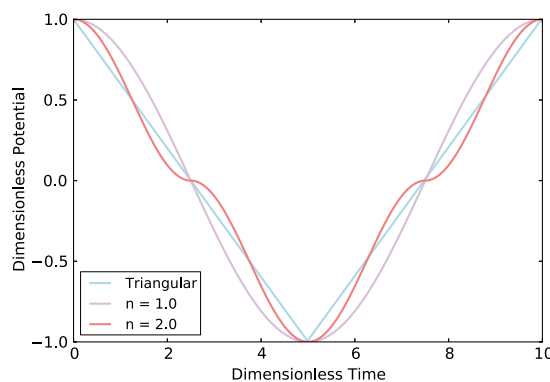

Fig. 1. Triangular, cosine, and cosine square potential waves centred at 0 with an amplitude of 1.

wave equation is given as:

$$E(i) = A \cdot |\cos(2\pi \cdot a \cdot i \Delta t)|^n \cdot \frac{\cos(2\pi \cdot a \cdot i \Delta t)}{|\cos(2\pi \cdot a \cdot i \Delta t)|} + E_{shift} \tag{10}$$

where A is the amplitude of the wave in volts, a is an auxiliary coefficient defined as $\frac{\epsilon^2}{D} \cdot \frac{F}{RT} \cdot \nu_{avg} \cdot \frac{1}{4A}$ in which ϵ is the radius of the electrode, D is the diffusion coefficient of the species of interest, F is the Faraday constant, R is the gas constant, T is the temperature, and ν_{avg} is the average scan rate measured in volts per second. The other parameters, i, is the time step, Δt is the difference between each time step, n is the power of the function, and E_{shift} is the offset of the wave. It is herein noted that although sine and cosine waves are used in AC voltammetry, this paper focuses on the use of cosine waves in cyclic voltammetry.

As can be seen in Fig. 1, the duration time is kept the same between the triangular and non-triangular potential waves but the instantaneous scan rate at any potential differs depending on the applied potential for non-triangular waveforms. In addition, the figure reveals that there are no discontinuities in the first temporal derivative of the potential and the above-bespoken perturbations arising from parasitic capacitances will not be observed in experimental data. We further note that a plateau is observed for the cosine square wave at the midpoint of the applied potential range, which moves up or down depending on the potential window shift, E_{shift}.

2.3. Dimensionless coordinates

For simplicity and both easier and general application of our results to various experimental conditions, dimensionless parameters [18] are used in the following manuscript, while conversion factors are shown in Table 1. Given these expressions, the cosine equation can now be expressed in terms of dimensionless parameters where A is the amplitude

Table 1
Dimensionless parameters [18].

Parameter	Normalization
Concentration	$C_j = \frac{c_j}{c_A^*}$
Diffusion coefficient	$d_j = \frac{D_j}{D_A}$
Spatial coordinate	$X = \frac{x}{\epsilon}$
Time	$\tau = \frac{D_A t}{\epsilon^2}$
Potential	$\theta = \left(\frac{F}{RT}\right)(E - E_f^0)$
Scan rate	$\sigma = \left(\frac{\epsilon^2}{D_A}\right)\left(\frac{F}{RT}\right)\nu$
Current	$J = \frac{I}{\pi \epsilon F D_A c_A^*}$