



# Cyclic voltammetry with non-triangular waveforms: Electrochemically irreversible and quasi-reversible systems

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## ABSTRACT

The voltammetry of electrochemically-irreversible and quasi-reversible reactions are investigated theoretically at a macroelectrode for the case of an applied cosine square-based potential waveform. The results reveal distinct features in the voltammograms which can be exploited to determine the electrochemical transfer coefficient,  $\alpha$ , and the standard electrochemical rate constant,  $k_0$ , of a reaction with high sensitivity.

## 1. Introduction

Cyclic voltammetry is used in electrochemistry for the study of electrode kinetics and the mechanisms of electrode reactions [1–4], providing physical quantities such as the analyte concentrations, diffusion constants, and rate constants through the analysis of voltammograms [5]. A conventional cyclic voltammetry experiment is conducted by applying a potential to the working electrode which is immersed in an electrolyte solution containing the analyte(s) under study and the current response is recorded [1,5,6]. The potential is applied in a linear fashion in the forward and reverse direction with a window large enough to encompass the desired redox reaction known as the triangular potential wave, which is given by the following expression [5]

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

where  $\sigma$  is the scan rate given by the slope of the wave, which has the same value for the forward and reverse sweep but opposite in magnitude, resulting in a discontinuity in its first derivative with respect to time at  $t_{1/2}$ , the point at which the scan is reversed. Since the capacitive current is proportional to the derivative, this discontinuity results in the discontinuity of the capacitive current. In a real experiment, there are, however, a number of different parasitic capacitances and Ohmic resistances in various parts of the analogue measurement set-up, which compensate for the discontinuity in a complex, partial, and usually unknown fashion.<sup>1</sup> This effect disrupts the voltammetric data and much

complicates the quantitative analysis of experimental results. In a previous paper, we proposed a novel method for cyclic voltammetry using cosine-based potential waveforms, which do not feature any discontinuities in their first derivative and hence avoid the complication [5].

Here, we apply the same cosine-based potential waveform to an electrochemically irreversible and quasi-reversible system to theoretically investigate the voltammetry for varying transfer coefficients [7,8],  $\alpha$ , and standard electrochemical rate constants,  $k_0$ . Our analysis reveals that both parameters of an investigated reaction can be determined through the voltammograms resulting from certain cosine-based potential waveforms applied at varying potential offsets with good sensitivity and precision.

## 2. Theory

In the following, the employed theoretical model is introduced, the method of the cosine-based potential waveform is explained, the dimensionless coordinates used are defined, and the simulation approach is described.

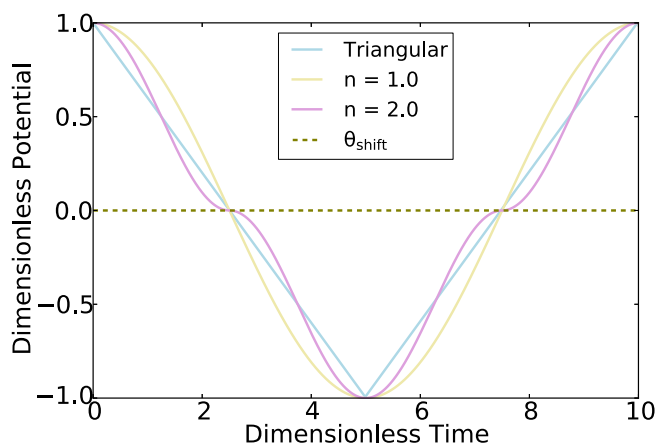
### 2.1. Theoretical model

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

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<sup>1</sup> A more detailed discussion of the capacitive current in a triangular sweep cyclic voltammogram can for instance be found in the first chapter of the textbook by Bard and Faulkner [3]. The book illustrates the capacitive current for an interface modelled as a series of an ideal Ohmic resistor and an ideal capacitor element. Under experimental conditions as well as in more complex interface models both, the resistance and particularly the capacity of the interface, may however be dependent on the applied potential.



**Fig. 1.** Triangular, cosine, and cosine squared potential waves centred at 0 with an amplitude of 1. Light blue represents triangular wave, yellow represents cosine function wave with  $n = 1$ , and light purple represents cosine function wave with  $n = 2$ . Figure has been adapted from [5]. The dotted line shows the dimensionless potential shift. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



When the electrode kinetics are fast compared to the mass transport, the system is termed electrochemically reversible and the concentration of the electroactive species at the electrode surface can be described using the Nernstian equation [1,5,9,10]. The system of interest, on the other hand, is assumed to be irreversible in which the electrode kinetics are slow compared to the mass transport and hence the electrode kinetics described using the Butler-Volmer equation [2,4] drive the reaction:

$$j = k_0 \exp \left[ \frac{-\alpha F(E - E_f^0)}{RT} \right] c_{A_0} - k_0 \exp \left[ \frac{(1 - \alpha)F(E - E_f^0)}{RT} \right] c_{B_0} \quad (3)$$

where  $j$  is the flux of the reactant to the electrode surface,  $c_{A_0}$  and  $c_{B_0}$  are the concentrations of species  $A$  and  $B$  at the electrode surface respectively, and  $k_0$  is the standard electrochemical rate constant. This system considers diffusion as the exclusive 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 [11–15]. Note, however, that convection needs to be taken into consideration when using long scan duration times [1,3,5,16–18]. The transport of analytes is thus described by the one-dimensional diffusion equation given by Fick's second law [19,20]:

$$\frac{\partial c_j}{\partial t} = D \frac{\partial^2 c_j}{\partial x^2} \quad (4)$$

where  $j$  is the species under study and  $D$  is its diffusion coefficient. Boundary conditions are established under the assumption that initially only species  $A$  is present in the bulk solution [1,19] and prior to applying potential, the concentrations of both  $A$  and  $B$  are uniform in space [5]:

$$t \leq 0, \quad \text{all } x, \quad c_A = c_A^*, \quad c_B = 0 \quad (5)$$

With increasing  $t$ , the values of  $c_A$  and  $c_B$  change near the electrode surface but no change is observed at the outer boundary surface set sufficiently far from the electrode to give the condition:

$$t > 0, \quad x \rightarrow \infty, \quad c_A = c_A^*, \quad c_B = 0 \quad (6)$$

From conservation of mass, the amount of  $A$  consumed at the electrode surface must equal the amount of  $B$  produced:

$$t > 0, \quad x = 0, \quad -\frac{\partial c_A}{\partial x} = \frac{\partial c_B}{\partial x} \quad (7)$$

**Table 1**  
Dimensionless parameters [19].

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	$J = \frac{i}{\pi \epsilon F D_A c_A^*}$
Rate constant	$K_0 = \frac{k_0 \epsilon}{D}$

assuming  $D_A = D_B$ , and hence for equal diffusion coefficients the following condition holds true for all space and time.

$$c_A + c_B = c_A^* \quad (8)$$

## 2.2. Voltammetric scan

As described earlier, the conventional triangular potential wave results in the perturbation of the voltammetric data due to the discontinuity in the capacitive current. However, the complexity of the aforementioned capacitive current can be reduced through the application of a cosine-based function wave, which is given as [5]:

$$E(i) = A \cdot |\cos(2\pi \cdot a \cdot i \Delta t)|^n \cdot \frac{\cos(2\pi \cdot a \cdot i \Delta t)}{|\cos(2\pi \cdot a \cdot i \Delta t)|} + E_{shift} \quad (9)$$

where  $A$  is the amplitude of the wave in Volts,  $a$  is an auxiliary coefficient defined as  $\nu_{avg} \cdot \frac{1}{4A}^2$  with  $\epsilon$  representing the radius of the electrode,  $\nu_{avg}$  is the average scan rate in Volts per second,  $i$  is the time step,  $\Delta t$  is the difference between each time step,  $n$  is the power of the function, and  $E_{shift}$ , defined as  $E_{avg} - E_f^0$ , is the offset of the wave which is the vital information when analyzing results.

Fig. 1 shows the conventional triangular potential wave and cosine potential waves when  $n = 1$  and  $n = 2$ . As can be seen, the duration time remains constant between the triangular and cosine function potential waves but the instantaneous scan rate at each applied potential differs depending on the wave used for non-linear waveforms [5].

## 2.3. Dimensionless coordinates

For practicality, all results are presented using a dimensionless unit system. The conversion factors between dimensional and dimensionless units are listed in Table 1. By using these expressions, Eq. (9) can be written in dimensionless form where  $A$  is now the amplitude of the dimensionless potential,  $a = \frac{\sigma_{avg}}{4A}$  where  $\sigma_{avg}$  is the dimensionless average scan rate, and  $\theta_{shift} = \theta_{avg} - \theta_f^0$  for which  $\theta_f^0$  is set to equal 0 for simplicity.

## 2.4. Simulation via finite difference methods

The theoretical model introduced above was simulated via a finite

<sup>2</sup> We note that in our previous work [5]  $a$  was erroneously given as  $\frac{\epsilon^2}{D} \cdot \frac{F}{RT} \cdot \nu_{avg} \cdot \frac{1}{4A}$ .

$$E_{avg} = \frac{1}{t_{max}} \int_0^{t_{max}} E(t) dt \quad (10)$$

where  $t_{max}$  is the maximum scan duration time.[5]

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