

# Supporting Information to "Cyclic voltammetry with non-triangular waveforms: Electrochemically reversible systems"

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The following sections contain a detailed explanation<sup>1</sup> of the finite difference method briefly described in the paper and full-scaled figures of the cosine square potential wave voltammograms with varying potential shifts.

## S1 Finite difference method

The mathematical expression for the Fick's second law is a continuous function which is often solved by numerical methods such as finite differences. First consider the function  $C(X)$  that shows the concentration across space, and its first and second derivatives. Using the finite difference method, the spacial grid  $X$  is discretized into  $n$  points,  $X_0, X_1, \dots, X_{n-1}$ , in such a way that  $\Delta X$  is constant for each grid point  $i$ .  $X_0$  is the electrode surface and  $X_{n-1}$  is the outer spatial boundary.

$$X_{i+1} - X_i = X_i - X_{i-1} = \Delta X \quad (\text{S1})$$

and

$$n = \frac{X_{max} - X_0}{\Delta X} \quad (S2)$$

If we now look at the change in concentration with respect to change in space:

$$\left(\frac{dC}{dX}\right)_{X_i} = \lim_{\Delta X \rightarrow 0} \frac{C(X_{i+1}) - C(X_i)}{\Delta X} \quad (S3)$$

which gives the forward approximation of the first derivative.

$$\left(\frac{dC}{dX}\right)_{X_i} \approx \frac{C_{i+1} - C_i}{\Delta X} \quad (S4)$$

Using the same method, the backward difference approximation can be obtained as well. The difference between the forward and backward approximation divided by  $\Delta X$  gives the second derivative.

$$\left(\frac{d^2C}{dX^2}\right)_{X_i} \approx \frac{C_{i-1} - 2C_i + C_{i+1}}{(\Delta X)^2} \quad (S5)$$

Just like we did with space, we can also discretize time with equal intervals of  $\Delta \tau$  where the total number of time steps,  $m$ , is given by:

$$m = \frac{\tau_{max} - \tau_0}{\Delta \tau} \quad (S6)$$

Since we cannot know the concentration of the forward time step, we must use the backward approximation difference to calculate the derivative of concentration with respect to time, where  $k$  indicates the time step.

$$\frac{\partial C_i}{\partial \tau} \approx \frac{C_i^k - C_i^{k-1}}{\Delta \tau} \quad (S7)$$

The discretized form of the Fick's second law is:

$$\frac{C_i^k - C_i^{k-1}}{\Delta \tau} = \frac{C_{i-1} - 2C_i + C_{i+1}}{(\Delta X)^2} \quad (S8)$$

The concentration on the right hand side can either be taken from the previous time step,  $\tau^{k-1}$ , or the current time step,  $\tau^k$ . The former is known as the explicit method and can easily be solved by rearranging the equation but the results may not be very accurate. The latter implicit method, on the other hand, has greater accuracy but contains only one known value as shown below.

$$\frac{C_i^k - C_i^{k-1}}{\Delta \tau} = \frac{C_{i-1}^k - 2C_i^k + C_{i+1}^k}{(\Delta X)^2} \quad (\text{S9})$$

Equation (S9) considers a case where the spatial grid is equally divided into  $n$  points with equal  $\Delta X$  values. However, because we are interested in the reaction at the electrode surface and the changes in analyte concentration near it, we used an exponentially expanding grid based on Gavaghan's expanding mesh<sup>2</sup> in which the spatial grid contains more points near the electrode surface and less near the outer surface. The grid expands as follows:<sup>1</sup>

$$h_i = X_{i+1} - X_i = h_0 \omega_X^i \quad (\text{S10})$$

where  $h_0 = X_1 - X_0$  and  $\omega_X^i$  is the expansion factor. Since the value of  $\Delta X$  differs between each point, the discretized, backward implicit Fick's second law now becomes:

$$\frac{C_i^k - C_i^{k-1}}{\Delta \tau} = \frac{\frac{C_{i+1}^k - C_i^k}{\Delta X_+} - \frac{C_i^k - C_{i-1}^k}{\Delta X_-}}{\frac{1}{2}[\Delta X_+ + \Delta X_-]} \quad (\text{S11})$$

where  $\Delta X_+ = X_{i+1} - X_i$  and  $\Delta X_- = X_i - X_{i-1}$ . This can be rearranged and written in a more general form with the following coefficients:

$$\alpha_i C_{i-1}^k + \beta_i C_i^k + \gamma_i C_{i+1}^k = \delta_i \quad (\text{S12})$$

$$\alpha_i = -\frac{2\Delta \tau}{\Delta X_-^2 + \Delta X_+ \Delta X_-} \quad (\text{S13})$$

$$\beta_i = \frac{2\Delta \tau}{\Delta X_+^2 + \Delta X_+ \Delta X_-} + \frac{2\Delta \tau}{\Delta X_-^2 + \Delta X_+ \Delta X_-} + 1 \quad (\text{S14})$$

$$\gamma_i = -\frac{2\Delta \tau}{\Delta X_+^2 + \Delta X_+ \Delta X_-} \quad (\text{S15})$$

At each time step  $k$ , Equation (S12) must be solved for all spatial points,  $i$ , simultaneously. The equations can be represented as a tridiagonal matrix in the form of  $\mathbf{Ax} = \mathbf{b}$ , which is solved using the Thomas algorithm with the boundary conditions listed below where Equation (S16) refers to the electrode surface boundary condition and Equation (S17) is the outer surface boundary condition.

$$\alpha_0 = 0, \beta_0 = 1, \gamma_0 = 0, \delta_0 = \frac{1}{1 + e^{-\theta}} \quad (\text{S16})$$

$$\alpha_{n-1} = 0, \beta_{n-1} = 1, \gamma_{n-1} = 0, \delta_{n-1} = 1 \quad (\text{S17})$$

The electrode surface boundary condition is obtained by rearranging Equation (4) in the paper, and the outer surface boundary condition is set in a way that the concentration always equals to the bulk concentration, which, in this case, is 1.

## S2 Cosine square graphs

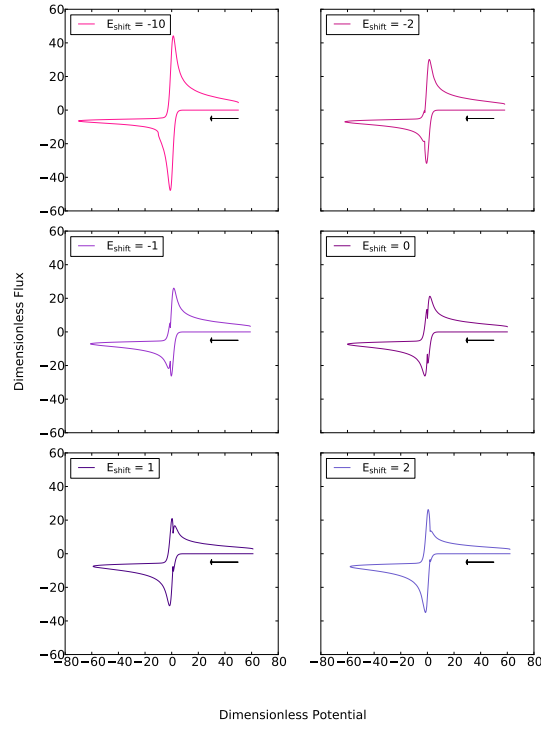


Figure S1: Cosine graphs for  $n = 2$  with different potential shifts.

Figure S1 is the full-scale view of Figure 6 in the paper. The arrows indicate the sweep direction, and the difference in peak currents can be observed.

## References

- [1] R. G. Compton, E. Laborda, and K. R. Ward. *Understanding Voltammetry: Simulation of Electrode Processes*. Imperial College Press, 2013.

- [2] D. J. Gavaghan. An exponentially expanding mesh ideally suited to the fast and efficient simulation of diffusion processes at microdisc electrodes. 1. derivation of the mesh. *Journal of Electroanalytical Chemistry*, 456(1-2):1–12, 1998.