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Voltammetry using multiple cycles: Porous electrodes

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Abstract

Simulations are reported for the cyclic voltammetry of both electrochemically reversible and irreversible one-electron processes at porous electrodes where the potential cycle is applied for multiple cycles. It is shown that an ‘ultimate state’ is approached asymptotically and that the long time voltammogram can be very different in terms of the peak height from those recorded in the first scan though peak-to-peak potential separations are conserved. The implications for the experimental study of porous electrodes are considered.

Keywords

Multiple-cycle voltammetry, porous electrodes, ultimate state.

1 Introduction

Cyclic voltammetry^{1:2} is ubiquitously applied for the study of electrochemical processes and is familiar to all electrochemists as, at least, an initial starting point for their investigations. Ensuring that mass transport to and from the electrode occur exclusively via diffusion, the method involves the application of a triangular potential waveform to a working electrode as part of a conventional three electrode system^{3:4}. Current (I) is then measured as a function of the applied potential (E). The resulting voltammogram is characterised by the magnitude of the peak currents (I_p) and the peak-to-peak potential differences (ΔE_{pp}), see Figure 1. The expected behaviour for both fast (‘reversible’) and slow (‘irreversible’) electrode transfer kinetics is well known and described in terms of the peak currents by the Randles-Ševčík equations for a simple one electron process, $A + e \rightarrow B$:

$$I_p^{RS} = 0.446FAc_i^* \sqrt{\frac{FD_i v}{R_u T}} \quad (\text{reversible}) \quad (1)$$

$$I_p^{RS} = 0.496\sqrt{\alpha}FAc_i^* \sqrt{\frac{FD_i v}{R_u T}} \quad (\text{irreversible}) \quad (2)$$

where F is Faraday constant, A is the surface area of the electrode, c_i^* is the bulk concentration of species i , D_i is the diffusion constant of species i , v is the potential scan rate, R_u the universal gas constant, T is the temperature, and α ^{5:6} is the transfer coefficient.^{3:4} The peak-to-peak separation is given by:⁴

$$\Delta E_{pp} = 2.218 \frac{R_u T}{F} \quad (\text{reversible}) \quad (3)$$

$$\Delta E_{pp} = \frac{2R_u T}{F} \ln v + \text{const.} \quad \text{with} \quad \alpha = \frac{1}{2} \quad (\text{irreversible}) \quad (4)$$

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