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The Marcus-Hush model of electrode kinetics at a single nanoparticle

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ABSTRACT

We examine the effect of the Marcus-Hush model of electrode kinetics on electron transfer at the surface of a single nanoparticle impacting an electode. Using numerical simulation we demonstrate the possibility of observing a kinetically limited steady state current which is smaller than the mass transport limiting current for such a system.

1. Introduction

The differences between the Marcus-Hush model and the ubiquitous Butler–Volmer model were first highlighted for surface-bound redox couples by Chidsey [1]. Where the Butler–Volmer model gives rate constants which increase *ad infinitum*, the Marcus-Hush model gives rate constants which level off at large overpotentials.

Later, Feldberg examined the conditions that would be necessary to observe this difference in behaviour between the two models for solution-phase systems using steady state voltammetry at a microdisc electrode [2]. Notably, this work demonstrated that the Marcus-Hush model could, in principle, lead to a kinetically limited steady state current which is *smaller* than the mass transport limit provided that the limiting electron transfer rate is sufficiently slow.

Since then several studies have been undertaken comparing the two kinetic models in the fitting of both cyclic and pulse voltammetry for several redox systems both under diffusion-only conditions at a hemispherical microelectrode [3,4] and under convective mass transport conditions at the channel flow electrode [5]. These studies showed that the so-called symmetric Marcus-Hush model, which assumes the potential energy curves of reactant and product to be parabolae of equal curvature, was generally unable to fit practical experimental voltammetry while the Butler–Volmer model was consistently able to produce accurate fitting.

Further work then introduced the asymmetric Marcus-Hush model [6], which removes the assumption that the parabolic potential energy curves are of equal curvature, which was seen to be equal to the Butler–Volmer model in its ability to accurately fit both cyclic and pulse voltammetry.

While the limiting behaviour of the Marcus-Hush model has been reported many times for surface-bound redox systems, it has thus far not been possible to observe such behaviour for solution-phase systems. The conditions which Feldberg identified as necessary to distinguish the models have not been realised experimentally [2], and another study using the channel flow electrode found that the two models would likely be indistinguishable for 'real' redox systems [7].

Nevertheless, the chances of observing a kinetically limited steady state current are increased by decreasing the size of the electrode. Mass transport to the electrode surface then becomes more efficient and thus the rate of electron transfer can be higher than at a larger electrode and yet still be current limiting.

One possible route to achieving such conditions is to study the rate of electron transfer at nanoparticles impacting on an electrode whereby electron transfer to and from the solution occurs only at the surface of the impacting nanoparticle. Recent work has demonstrated the possibility of extracting quantitative kinetic data from such systems [8]. Such nanoparticle impacts can be modelled as an isolated sphere supported on a planar, non-conducting surface [9]. Using such a model, we aim to demonstrate the possibility of experimentally observing a steady state current which is limited by the rate of electron transfer, rather than mass transport, for a solution-phase redox system.

2. Theory

2.1. Sphere on a plate

We model the impacting nanoparticle as a single conductive sphere of radius r_e conductively supported on a surface which is infinite in extent. Electrolysis is confined to the surface of the nanoparticle, the plate simply provides an electrical connection.

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Such a system can be described using cylindrical polar coordinates (r, z, ω) with the origin at the point of contact between the sphere and the surface. This system is axisymmetric (*i.e.* all properties of the system are invariant with respect to angle ω) and so we need consider only a 2-dimensional (r, z) 'slice' through the axis.

We assume the presence of a sufficiently high concentration of supporting electrolyte such that the effects of migrative mass transport may be neglected. The mass transport in this system is thus purely diffusional and may be described by Fick's 2nd law, which takes the following form in this coordinate system:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{\partial^2 c}{\partial z^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \tag{1}$$

where c is the concentration of the species in question, D is its diffusion coefficient and t is time.

Throughout this study, we consider a one-electron reduction of the form:

$$A + e^- \rightleftharpoons B \tag{2}$$

for which the diffusion coefficients of both species are equal, and only species A is initially present in bulk solution. In a linear sweep voltammetry (LSV) experiment, the potential, E, is swept at a constant rate, v, from some initial potential, E_i, to some final potential such that at any time, $t > 0$:

$$E = E_i - vt \tag{3}$$

The flux of species A normal to the electrode surface at a given value of E is described by:

$$D_{\mathrm{A}}\frac{\partial c_{\mathrm{A}}}{\partial n} = k_0(k_{\mathrm{red}}c_{\mathrm{A},0} - k_{\mathrm{ox}}c_{\mathrm{B},0}) \tag{4}$$

where n is some coordinate normal to the electrode surface, $c_{\mathrm{A},0}$ and $c_{\mathrm{B},0}$ are the concentrations of species A and B respectively at the electrode surface, k_0 is the standard heterogeneous rate constant and k_{red} and k_{ox} are the rate constants for reduction and oxidation respectively.

2.2. Electrode kinetics

Within the Butler–Volmer model of electrode kinetics, k_{red} and k_{ox} are defined as:'

$$k_{\mathrm{red}} = \exp\left[-\frac{\alpha F}{RT}(E - E_{\mathrm{f}}^{\ominus})\right] \tag{5}$$

$$k_{\mathrm{ox}} = \exp\left[+\frac{(1-\alpha)F}{RT}(E - E_{\mathrm{f}}^{\ominus})\right] \tag{6}$$

where $E_{\mathrm{f}}^{\ominus}$ is the formal potential of the A/B couple, α is the so-called transfer coefficient, F, R and T have their usual meanings.

Within the Marcus-Hush model of electrode kinetics, k_{red} and k_{ox} are given by:

$$k_{\mathrm{red}} = k_0\frac{S_{\mathrm{red}}(\theta, \Lambda)}{S_{\mathrm{red}}(0, \Lambda)} \tag{7}$$

$$k_{\mathrm{ox}} = k_0\frac{S_{\mathrm{ox}}(\theta, \Lambda)}{S_{\mathrm{ox}}(0, \Lambda)} \tag{8}$$

where θ is dimensionless potential and Λ is the dimensionless analogue of the reorganisation energy (assuming units of eV):

$$\theta = \frac{F}{RT}(E - E_{\mathrm{f}}^{\ominus}) \tag{9}$$

$$\Lambda = \frac{F}{RT}\lambda \tag{10}$$

and $S_{\mathrm{red/ox}}(\theta, \Lambda)$ is an integral of the form:

$$S_{\mathrm{red/ox}}(\theta, \Lambda) = \int_{-\infty}^{\infty}\frac{\exp\left[-\Delta G^{\ddagger}_{\mathrm{sym,red/ox}}(x)/RT\right]}{1 + \exp\left[\mp x\right]}\,dx \tag{11}$$

where

$$\frac{\Delta G^{\ddagger}_{\mathrm{asym,red/ox}}(x)}{RT} = \frac{\Lambda}{4}\left(1 \pm \frac{\theta + x}{\Lambda}\right)^2 + \gamma\left(\frac{\theta + x}{4}\right)\left\{1 - \left(\frac{\theta + x}{\Lambda}\right)^2\right\} + \gamma^2\frac{\Lambda}{16} \tag{12}$$

x is a dimensionless integration variable:

$$x = \frac{F}{RT}(\epsilon - E) \tag{13}$$

and the parameter γ accounts for the differences between the inner-shell force constants of oxidised and reduced species [10]. Note that when $\gamma = 0$ the asymmetric Marcus-Hush model is reduced to its symmetric counterpart.

2.3. Simulation procedure

The simulation model is normalised according to the set of dimensionless parameters shown in Table 1. Under this system, Fick's second law becomes:

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial R^2} + \frac{\partial^2 C}{\partial Z^2} + \frac{1}{R}\frac{\partial C}{\partial R} \tag{14}$$

and the flux equation becomes:

$$\frac{\partial C_{\mathrm{A}}}{\partial N} = \kappa(k_{\mathrm{red}}C_{\mathrm{A}} - k_{\mathrm{ox}}C_{\mathrm{B}}) \tag{15}$$

where $N = n/r_{\mathrm{e}}$ is some dimensionless coordinate normal to the particle surface.

The outer boundary of the simulation space is placed such that it is sufficiently far from that nanoparticle surface that the diffusion layer will be entirely contained within the simulation space for the duration of the experiment. This condition is satisfied when the boundary is placed a distance of $6\sqrt{\tau_{\mathrm{max}}}$ from the particle surface in both the R and Z directions where τ_{max} is the dimensionless experiment duration [11]. At this outer boundary we may therefore fix the concentrations of both species A and B as their respective bulk value throughout the simulation.

The 2-dimensional simulation space is discretized by dividing it up into a finite grid of spatial points. In the dimensionless (R, Z) coordinate system, the surface of the spherical nanoparticle is described by:

$$R^2 = (Z - 1)^2 = 1 \tag{16}$$

where the dimensionless radius of the nanoparticle is (by definition) 1. The distribution of spatial points in the vicinity of the nanoparticle is determined by specifying an angular increment $\Delta\phi$, and calculating the values of R and Z at each successive value of ϕ, where ϕ is the angle shown in Fig. 1. This allows grid points to fit precisely to the curved surface of the spherical particle. A similar

Table 1
Dimensionless parameters.

Parameter	Normalization
Radial coordinate	$R = r/r_{\mathrm{e}}$
Axial coordinate	$Z = z/r_{\mathrm{e}}$
Time	$\tau = Dt/r_{\mathrm{e}}^2$
Potential	$\theta = (F/RT)(E - E_{\mathrm{f}}^{\ominus})$
Concentration	$C_i = c_i/c_{\mathrm{A}}^*$
Heterogeneous rate constant	$\kappa = k_0 r_{\mathrm{e}}/D$