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Ionic currents exceeding the diffusion limitation in planar nano-cavities

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ABSTRACT

Theory predicts that ionic currents through electrochemical cells at nanometer scale can exceed the diffusion limitation due to an expansion of the interfacial electrostatic double layer. Corresponding voltammetry experiments revealed a clear absence of a plateau for the current, which cannot be described by the classical Butler–Volmer approach using realistic values for the transfer coefficient. We show that extending the classical approach by considering the double layer structure using the Frumkin correction leads to an accurate description of the anomalous experimental data.

1. Introduction

The description of charge transfer at nanometer sized electrodes is among the most important and puzzling problems in electrochemistry [1–6]. For large-scale electrochemical cells one generally assumes a negligible space charge density in the bulk electrolyte (electro-neutrality) combined with the phenomenological Butler–Volmer equation for charge transfer [7–10]. However, this approach is inappropriate for cells where the electrode spacing is small relative to the thickness of the interfacial double layers (DLs) [7–11]. In this communication we study a planar electrochemical cell with nanometer electrode spacing where the DLs might significantly influence the shape of voltammograms [2,6–15]. Therefore we employ the Poisson–Nernst–Planck (PNP) theory for ion transport coupled to the generalized Frumkin–Butler–Volmer (gFBV) equation for charge transfer, which transparently account for any non-zero space charge density [7–11].

To support this theory we re-analyze the data for the electrochemical cells reported in Refs. [4,5]. Their cells consist of a planar cavity with 50–70 nm electrode spacing (Fig. 1a), which was filled with either (i) an aqueous solution containing ferrocenedimethanol, $Fc(MeOH)_2$, in an excess of KCl or (ii) $Fc(MeOH)_2$ dissolved in acetonitrile, ACN, with tetrabutylammonium hexafluorophosphate, $TBAPF_6$, as the supporting electrolyte. In both cases the ferrocene cations were reduced at the negatively biased electrode to a neutral species that shuttled to the opposite electrode where they were oxidized again. Voltammograms were obtained by keeping one electrode at the reducing potential while sweeping the potential of the opposite electrode. Here we show that the anomalous voltammograms for ACN can be due to DL-expansion at high electrode potentials.

2. Theory

A one-dimensional system with spatial coordinate X is used (i.e. the electrode area is assumed infinitely large compared to its spacing). Furthermore, we assume that the charge transfer proceeds at a predefined reaction plane adjacent to the electrodes (Fig. 1b). Therefore X runs from the bottom reaction plane at $X=0$ to the top plane at $X=L$. The system contains four species, namely; (i) monovalent oxidants with concentration C_{ox}, (ii) neutral reductants, C_{re}, (iii) inert cations, C_c, and (iv) inert anions, C_a, with initially all reactive species in the uncharged (reduced) state. Finally, we assume that all species have the same diffusion coefficient, D. Below we adopt the common dimensionless parameters [7–11]. First, we scale the coordinate to the electrode spacing, L, i.e. $x=X/L$. Next, we scale the electrical potential V in volts to the thermal voltage, $\phi=fV$, where $f=F/(RT)$, and T is the temperature. Furthermore, we scale all fluxes, J_i, to the flux of oxidants at the diffusion limitation, J_{lim}. To determine this limitation we consider an electroneutral bulk electrolyte where in the presence of an excess of inert electrolyte the electrical field, and thus ion migration, is completely suppressed [10,16]. This results in linear concentration profiles for the reactive species across the bulk, which due to mass conservation, i.e. $\int_L (C_{ox}+C_{re})dx = C^o_{re}L$, leads to $J_{lim}=D\partial C_i/\partial X=DC^o_{re}/L$, where o denotes the initial concentrations [17]. Finally, we scale all concentrations according to $c_i=C_i/C^o_{re}$.

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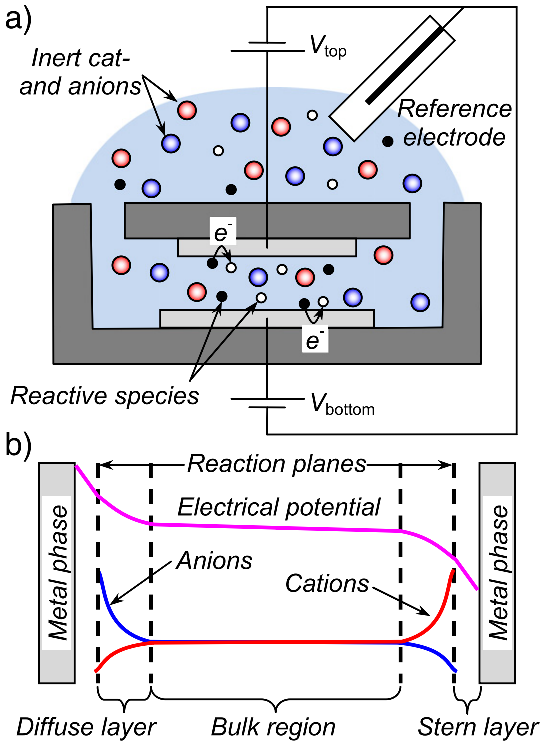

Fig. 1. Schematics of (a) the experimental setup of Refs. [4,5], and (b) a two-electrode system where we can distinguish a bulk region that is sandwiched between the double layers (i.e. diffuse plus Stern layer), which are found adjacent to the metal phases.

Using these dimensionless parameters the steady-state fluxes of the inert cat- and anions according to the PNP theory become,

$$\partial_x c_i + z_i c_i \partial_x \phi = 0, \tag{1}$$

where z_i is the valence of the ions. In addition, the flux of oxidants and reductants become,

$$\partial_x c_{ox} + c_{ox} \partial_x \phi = -j_f \tag{2a}$$

$$\partial_x c_{re} = j_f, \tag{2b}$$

with j_f as the charge transfer rate at the electrodes according to the dimensionless gFBV equation [7–11],

$$\pm j_f = k_R c_{ox} \exp[-\alpha \Delta\phi_S] - k_O c_{re} \exp[(1-\alpha)\Delta\phi_S], \tag{3}$$

where the ± -sign refers to the positive value for $x=1$ and the negative value for $x=0$, k_i are the rate constants, α is the transfer coefficient, and $\Delta\phi_S$ is the potential drop across the charge free Stern layer (Fig. 1b), which follows from Poisson's law, $\varepsilon \partial_X^2 V = -e\sum z_i C_i$, where ε is the permittivity of the electrolyte. To rewrite Poisson's law into dimensionless parameters we use the Debye length, $\lambda_D = \sqrt{\varepsilon RT/2F^2 C_\infty}$, where $C_\infty = \frac{1}{2}\sum {z_i}^2 C_i^o$, which is the ionic strength of the electrolyte, and equals $\epsilon = \lambda_D/L$ in dimensionless units. Hence;

$$-2\gamma\epsilon^2 \partial_x^2 \phi = \rho = \sum_i z_i c_i, \tag{4}$$

where $\gamma = C_c^o / C_{re}^o$, ρ is the dimensionless space charge density, and *i* runs over all ionic species. Consequently, $\Delta\phi_s = \pm\epsilon\delta\, \partial_x \phi$, with $\delta = \lambda_S/\lambda_D$, which is the Stern layer thickness scaled to λ_D. In Eq. (3) α theoretically equals 1/2, as assumed in this work, when the reorganization energy of the reaction is infinite [18–22], which we estimate for the outer-sphere electron transfer of $Fc(MeOH)_2$ by $\lambda_{os} = e^2(8\pi r)^{-1}(\varepsilon_{op}^{-1} - \varepsilon_s^{-1})$, where ε_{op} and ε_s are the optical and static permittivity, and *r* is the radius of the reactant [22], while deviations can be determined from $\alpha = \frac{1}{2}[1 + \Delta\phi_S\, k_B T/\lambda_{os}]$ [18–21].

Next we define the boundary conditions. First consider the conservation of charge in the metal phase of the electrodes, $a_e(\sigma_0 + \sigma_1) + A_{ref}\sigma_{ref,av} = 0$, where a_e is the electrode area, σ_0 and σ_1 are the surface charge densities of the electrodes at $x=0$ and $x=1$, and A_{ref} and $\sigma_{ref,av}$ are the area and average surface charge density of the reference electrode, respectively (for dimensional units multiply σ_i with $C_{re}^o FL$). The potential of the bottom electrode is kept constant with respect to the reference electrode, so that $\sigma_{ref,av} - \sigma_0 = q$, where *q* is a constant, and $\sigma_0 = -(a_e\sigma_1 + A_{ref}q)/(a_e + A_{ref})$. For $A_{ref} = 0$ we now retain the two electrode case where $\sigma_0 = -\sigma_1$, while for our situation ($A_{ref} \gg a_e$), we have $\sigma_0 \approx -q$ and $\sigma_{ref,av} \approx 0$, so that any variation in charge of the top electrode is almost completely countered by the reference electrode, which retains a negligible surface charge density due to its vast area. Consequently, the mixed boundary condition for the bottom electrode becomes, $\partial_x \phi = -q/(2\epsilon^2\gamma)$, and $\phi = -q\,\delta/(2\epsilon\gamma)$, where the latter equation represents a zero electrical potential in the metal phase. At the reaction plane of the top electrode we assign, $\partial_x \phi = -\sigma_1/(2\epsilon^2\gamma)$. Consequently, the cell potential becomes $\phi_{cell} = \phi_1 - \sigma_1\,\delta/(2\epsilon\gamma)$.

In addition to the boundary conditions we require relations for the conservation of species, i.e. $a_e\int_0^L C_i dX + V_{res}C_{i,res} + A_{ref}\Gamma_i = (a_e L + V_{res})C_i^0$, where Γ_i is the amount of adsorbed ions at the reference electrode, V_{res} is the volume of the reservoir surrounding the nano-cavity indicated by subscript res. Here V_{res} is much larger than that of the nano-cavity, so that $C_{i,res} \approx C_i^0$, while for Γ_i we can use the linear Debye–Hückel approximation, in which the charge density is composed of an equal surplus and deficit of counter- and co-ions, since $\sigma_{ref,av}$ remains small. Relating $\Gamma_i = \frac{1}{2} z_i \sigma_{ref,av} C_{re}^o L$ to the electrode area and using $a_e(\sigma_0 + \sigma_1) = -A_{ref}\sigma_{ref,av}$ gives,

$$\begin{aligned} &\int_0^1 c_a dx = \gamma + \frac{1}{2}\left(\int_0^1 c_{ox} dx - \sigma_1 + q\right), \\ &\int_0^1 c_c dx = \gamma - \frac{1}{2}\left(\int_0^1 c_{ox} dx - \sigma_1 + q\right), \\ &\int_0^1 (c_{ox} + c_{re}) dx = 1, \end{aligned} \tag{5}$$

for conservation of species in the system, where the inert cat- and anions equally counter any increase in charged species due to the transfer of C_{re} into C_{ox}.

Finally we derive an equation for voltammograms in case of (i) linear concentration profiles, (ii) a large excess of inert electrolyte, and (iii) infinitesimally thin DLs ($\epsilon \to 0$), so that here the Poisson–Boltzmann distribution is valid, and we can distinguish an electro-neutral bulk electrolyte [7–11]. For these assumptions we find from Eqs. (1)–(5) that

$$j = \frac{k_O k_R (B_0 A_1 - B_1 A_0)}{k_R A_0 + k_R B_0 + (k_R A_1 + k_O B_1)(k_R A_0 + k_O B_0 + 1)}, \tag{6}$$

where $A_i = \exp\left(-\frac{1}{2}\Delta\phi_S - \Delta\phi_{DL}\right)$, and $B_i = \exp\left(\frac{1}{2}\Delta\phi_S\right)$, with $\Delta\phi_{DL}$ the potential across the DL, and subscript 0 and 1 indicate the electrode at $x=0$ and $x=1$, respectively. Note that for $\epsilon \to 0$ $\Delta\phi_S = \delta \sinh\left(\frac{1}{2}\Delta\phi_{DL}\right)$ [7–11]. Additionally we can obtain analytical relations for two cases, namely (i) the Helmholtz limit where the potential drop from the metal phase of the electrode to the point of zero charge in the electrolyte is completely across the Stern layer, i.e. $\delta = \infty$, and