

## SHORT COMMUNICATION

**Effects of diffusion-limited mass transfer on metal underpotential deposition voltammograms**

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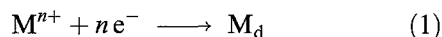
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**1. Introduction**

Underpotential deposition (UPD) of metals is frequently studied by analysing the shapes of voltammograms (current–voltage data) obtained with linear sweep voltammetry (LSV) [1, 2]. The actual adsorption isotherm contained in such a voltammogram can be obscured by diffusion-limited mass transfer (DLMT) effects [1]. Previous authors have discussed DLMT processes in multistep (adsorption–desorption) oxidation reactions involving soluble adsorbates [3, 4]. In the following calculations we demonstrate how DLMT can affect UPD where an insoluble deposit is formed in a single charge transfer (reduction) step. We also present a method of resolving these effects from an adsorption isotherm, explicitly in terms of the experimental variables of LSV.

**2. Background**

We consider the UPD of a metal cation  $M^{n+}$  on a plane electrode of another metal, occurring in a negative going voltage scan:



where  $M_d$  is the deposited species. We also consider a system where Equation 1 represents the only faradaic process in a chosen voltage range. By denoting the time ( $t$ ) dependent applied voltage in LSV as  $E(t)$ , we have [5, 6]

$$E(t) = E_i - vt \quad (2)$$

$$\theta(E) = \frac{Q(E)}{nQ_0} = \frac{1}{nQ_0} \int_0^t i(E) d\tau \quad (3)$$

where  $E_i$  is the initial, offset voltage of LSV, and  $v$  is the voltage scan rate. The ‘apparent’ coverage, that does not include the electroadsorption valency of  $M_d$ , is denoted by  $\theta$  [7, 8].  $Q$  is the charge obtained by integrating the current  $i$  of the voltammogram.  $Q_0$  is the total faradaic charge corresponding to a full coverage of a monovalent cation [5]. Traditionally, the UPD voltammograms are analysed by comparing the experimentally obtained  $\theta(E)$  (Equation 3) with a modified Nernst equation [9, 10]:

$$\theta(E) = (C_b f_b / f) \exp [-(E - E_0)B] \quad (4)$$

where  $B = nF/RT$ ;  $F$ ,  $R$ , and  $T$  being the Faraday constant, the gas constant, and the ambient tempera-

ture, respectively.  $E_0$  is the standard reaction potential,  $C_b$  is the bulk concentration of  $M^{n+}$ , and  $f_b$  and  $f$  are the activity coefficients of  $M^{n+}$  and  $M_d$ , respectively. Typically,  $f_b$  is taken as unity, and the adsorption isotherm is described by a specific choice of  $f$  [9, 11, 12]. Since DLMT is not included in Equation 4, any diffusion related feature of the voltammogram cannot be easily separated in this formalism. Consequently, the DLMT effects can influence the choice of  $f$ . On the other hand,  $f$  is strictly a ‘surface’ parameter, and should represent only the adsorbate–adsorbate and adsorbate–substrate interactions;  $f$  should not explicitly include any events (such as DLMT) on the ‘solution’ side of the interface. As a result of this complication, a single choice of  $f$  may sometimes be insufficient to characterize an UPD voltammogram. The following calculations provide a relatively straightforward method for separating the DLMT features from such voltammograms.

**3. Diffusion-limited deposition**

To focus specifically on the DLMT effects, we ignore the roles of surface crystallographic structure and anion co-adsorption [13, 14]. We also consider a typical situation, involving a three electrode cell and low concentrations of  $M^{n+}$  in a relatively passive supporting electrolyte [3, 5, 15].

When diffusion of  $M^{n+}$  is the rate determining step in UPD,  $C_b$  of Equation 4 should be replaced by  $C(0, t)$ . Here we denote the spatially varying concentration of  $M^{n+}$  with  $C(x, t)$ , and the coordinates perpendicular to the UPD substrate with  $x$ . The electrode surface, and the bulk electrolyte are represented by the limits  $x \rightarrow 0$  and  $x \rightarrow \infty$ , respectively. Thus we incorporate the role of DLMT in UPD by writing

$$\theta(E) = [C(0, t) f_b / f] \exp [-(E - E_0)B] \quad (5)$$

with the assumption that  $f_b$  is independent of  $x$ . The UPD current is given by Fick’s law of diffusion [1, 2]

$$i(t) = -nFD [\partial C(x, t) / \partial x]_{x=0} \quad (6)$$

Where  $D$  is the diffusion coefficient of  $M^{n+}$ . The diffusion equation and the boundary conditions (involving  $C_b$ ) are as follows:

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} \quad (7)$$

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$$C(x, 0) = C_b \quad (8a)$$

$$\lim_{x \rightarrow \infty} C(x, t) = C_b \quad (8b)$$

Equations 6–8 lead to the commonly known integral equation [1]

$$C(0, t) = C_b - (\pi D)^{-1/2} \int [G(\tau)/(t - \tau)] d\tau \quad (9)$$

where

$$G(\tau) = D \left[ \frac{\partial C(x, t)}{\partial x} \right]_{x=0} = \frac{i(t)}{nF} \quad (10)$$

In the present formalism  $C(0, t)$  (boundary condition on the interfacial reactant) is voltage (time) dependent. We obtain this  $C(0, t)$  by combining Equations 2, 3 and 5:

$$\begin{aligned} C(0, t) &= \left[ \frac{\theta(t)f}{f_b} \right] \exp(-Bvt + a) \\ &= - \left( \frac{f}{nf_b Q_0} \right) \int_0^t \exp(-Bvt + a) i(\tau) d\tau \quad (11) \end{aligned}$$

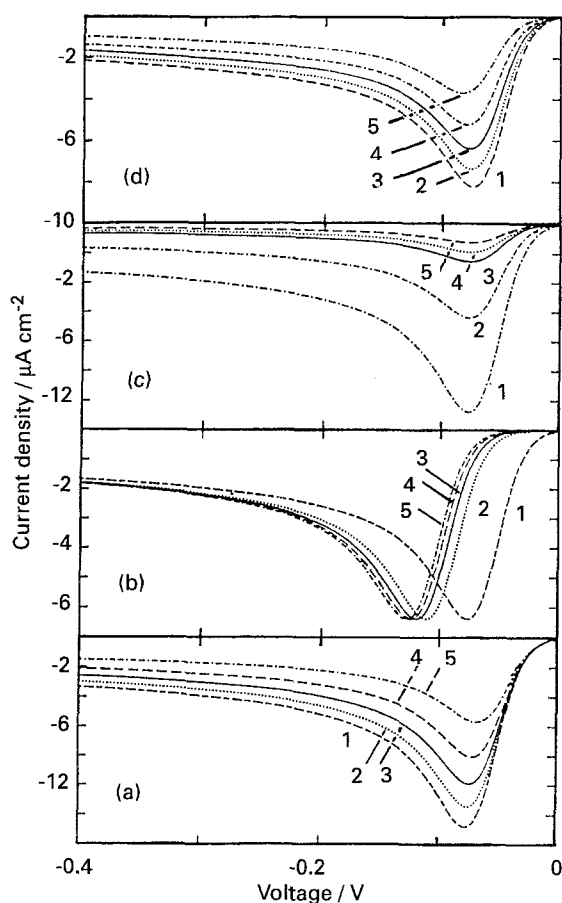


Fig. 1. Current ( $i$ )/voltage ( $E - E_0$ ) characteristics of diffusion controlled UPD. Effects of  $D$ ,  $f$ ,  $C_b$  and  $v$  on DLD are shown in (a), (b), (c) and (d), respectively.  $D = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for all graphs in (b), (c) and (d). In (a): curves 1–5 represent different values of  $D$  ( $\text{cm}^2 \text{ s}^{-1}$ ): (1)  $2 \times 10^{-5}$ , (2)  $1.6 \times 10^{-5}$ , (3)  $1.2 \times 10^{-5}$ , (4)  $8.0 \times 10^{-6}$ , and (5)  $4.0 \times 10^{-6}$ . In (b):  $f =$  (1) 0.01, (2) 0.20, (3) 0.40, (4) 0.60, and (5) 0.80;  $f = 0.01$  for all graphs in (a), (c) and (d).  $C_b =$  (1)  $5.0 \times 10^{-5}$ , (2)  $2.5 \times 10^{-5}$ , (3)  $1.0 \times 10^{-5}$ , (4)  $7.5 \times 10^{-6}$ , and (5)  $5.0 \times 10^{-6} \text{ M}$ , in (c): and  $2.5 \times 10^{-5} \text{ M}$  for all graphs in (a), (b) and (d). In (d),  $v =$  (1) 10, (2) 8, (3) 6, (4) 4 and (5)  $2 \text{ mV s}^{-1}$ ,  $v = 6 \text{ mV s}^{-1}$  in (a) and (b), and  $10 \text{ mV s}^{-1}$  in (c).

with  $a = B(E_i - E_0)$ . By using Equations 10 and 11 in Equation 9 we obtain

$$\int_0^{\sigma t} [(\sigma t - Z)^{-1/2} + \alpha e^{-\sigma t}] \chi(Z) dZ = -1 \quad (12)$$

where  $\sigma$ ,  $Z$ ,  $\chi$ , and  $\alpha$  are dimensionless parameters;  $\sigma = Bv$ ,  $Z = \sigma\tau$ , and

$$\chi(Z) = i(Z)/[nFC_b(\pi D\sigma)^{1/2}] \quad (13)$$

$$\alpha = \left( \frac{Ff}{f_b} \right) \left( \frac{\pi D}{\sigma} \right)^{1/2} \exp[B(E_i - E_0)] \quad (14)$$

Equation 12 can be solved numerically for a given set of  $v$ ,  $C_b$ ,  $f$ , and  $(E_i - E_0)$ . The resulting solution represents the ( $i - E(t)$ ) characteristics (voltammogram) of DLMT influenced UPD. The corresponding response of  $\theta$  can be calculated by using the solution to Equation 12 in Equation 3. In the following, we present numerically simulated ( $i - E$ ) and ( $\theta - E$ ) plots of UPD obtained from Equations 12–14.

#### 4. Results

Our goal here is to bring out the effects that are intrinsic to diffusion-limited mass transfer alone. Hence, we choose a simple, linear isotherm,  $f = \text{constant}$ , which is free of any shape-determining contributions to the

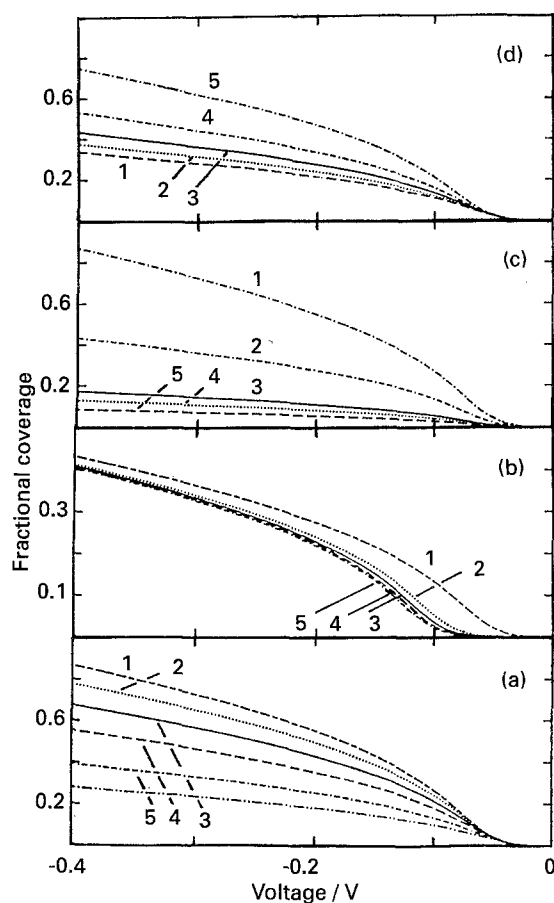


Fig. 2. Coverage ( $\theta$ )/voltage ( $E - E_0$ ) characteristics of metal UPD, calculated from the diffusion-limited deposition model. Graphs 1–5 in each of (a)–(d), are obtained by integrating [Equation 3] the corresponding plots in Fig. 1.

$(i - E)$  plots [5]. We consider the prevalence of diffusion by choosing low values of  $C_b$  ( $\sim 10^{-5} - 10^{-6}$  M). We take the 'base line' of the double layer charging current [5, 6] to be zero, and focus only on the behaviour of  $i(t)$ . For our numerical calculations we choose parameters that are typical of UPD by LSV (such as in lead deposition on silver [15]):  $D = 10^{-5} - 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>,  $v = 2 - 10$  mV s<sup>-1</sup>,  $f_b = 1$ ,  $E_i = E_0$ ,  $Q_0 = 210$   $\mu$ C cm<sup>-2</sup>,  $n = 2$ , and  $F/RT = 40$  V<sup>-1</sup>.  $D$  and  $f$  characterize the substrate-adsorbate pair;  $C_b$  and  $v$  describe the experimental conditions of LSV. We also choose a range of  $E - E_0$ , from 0.0 to  $-0.4$  V vs SCE, to calculate the voltammograms. In practice, the UPD voltage range depends on the detailed electronic structure of the interface, and therefore, on surface preparation, crystal face, and supporting electrolyte composition [16]. Since these latter effects are not separately treated here, the UPD range is not uniquely specified in our present formulation. We find that the essential features of DLMT characterized by Equations 12–14 are present in all realistic voltage ranges around the values chosen above.

Figure 1 shows the effects of (a)  $D$ , (b)  $f$ , (c)  $C_b$ , and (d)  $v$  on the  $(i - E)$  plots obtained from Equation 12. The corresponding  $(\theta - E)$  graphs are presented in Fig. 2(a)–(d). All parameters used in the individual graphs of Figs 1 and 2 are noted in the captions. The predominant effects of DLMT in these Figures can be summarized as follows. (i) The current peaks are asymmetric on the voltage axes in all graphs of Fig. 1. The width and the asymmetry of these peaks are sensitive to the values of  $D$ ,  $f$ ,  $C_b$ , and  $v$ ; (ii) With the other variables fixed, when  $C_b$  is increased, the UPD current increases. Note the increasing trend in  $i$  when  $v$  increases in Fig. 1(d). This latter effect is intrinsic to the working principle of LSV [1], and not a result of DLMT. (iii) The coverage at a given voltage (and a given  $f$ ) increases with increasing values of  $D$  and  $C_b$  and with decreasing values of  $v$ . (iv) The coverage is not a linear function of  $E$  and the shape of a  $(\theta - E)$  plot is particularly sensitive to the choices of  $D$ ,  $C_b$  and  $v$ .

The above listed features of the  $(i - E)$  and  $(\theta - E)$  plots have been observed in several UPD experiments with LSV [5, 9, 15–18]. The present analysis shows that

DLMT (in addition to the adsorption isotherm) may have a significant contribution to these observed features.

## 5. Summary

A simple method is presented to separate the DLMT effects from those of the actual adsorption isotherm in UPD experiments. The DLMT features of UPD are resolved explicitly in terms of  $C_b$ ,  $D$ , and  $v$ . The latter quantities are known variables of an experiment, and hence, the surface effects can be analysed by independently fitting  $f$  with the experimental voltammograms. This procedure of data analysis including DLMT can simplify the task of choosing adsorption isotherms in UPD studies.

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