A THEORETICAL INTERPRETATION OF CURRENT SPIKES DURING UNDERPOTENTIAL DEPOSITION*

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During the deposition of a metal on a crystalline electrode, a first-order phase transition can occur at the electrode surface as the applied potential is changed. Such a transition will cause a sharp spike in the associated current density versus potential plot, or voltammogram. We have developed a statistical mechanical theory within which a voltammogram spike is interpreted as being an average spike resulting from a large collection of crystals on the electrode surface. We describe how spikes in the voltammogram of the underpotential deposition of Cu on Au(111) in sulfuric acid solution can be interpreted using this theory, and we discuss plans for generalizing the theory.

1. INTRODUCTION

During an adsorption or deposition process of charged species on crystalline electrode surfaces first-order phase transitions may occur as the applied electric potential varies. In the corresponding voltammogram, i.e., the current vs. electric potential plot, sharp spikes are then observed. In this paper we discuss how the voltammogram spikes can be obtained from statistical mechanical considerations.

The early statistical mechanical studies of adsorption or deposition of charged species on a crystalline electrode were worked out by Blum and Huckaby [1, 2, 3, 4, 5]. They introduced a microscopic model [1], mathematically equivalent to a two dimensional lattice gas, that can be used to construct the associated voltammograms. They applied their theory to the deposition of Cu on the crystalline electrode of Au(111) and successfully described the structure of the involved phases, resolving thus a controversy stemming from contradictory experimental observations. Nevertheless, their description of the voltammogram spikes was not completely satisfactory. They considered an infinite lattice of adsorption sites, which necessarily led to infinitely tall and sharp spikes of the


δ-function type. They could resolve the difficulty only by adding a “switching function” to produce spikes of finite height and width.

The problem of modeling voltammograms has also been intensively investigated with the help of computer simulations [6, 7, 8, 9]. Although a finite lattice of adsorption sites is inevitably used, the results have been inconclusive, producing spikes that are still too tall and sharp.

After formulating the problem in Section 2, we overview the main points of our statistical mechanical theory of voltammogram spikes in Section 3. In Section 4 we discuss the application of the theory to the underpotential deposition of copper on the (111) surface of a gold electrode in the presence of bisulfate. Finally, in Section 5 we point out how our theory can be used to obtain voltammogram spikes in a rather general fashion.

2. FORMULATION OF THE PROBLEM

Let us consider an electrode interface $E$ with a flow of current in it. We assume the Faradaic part of the current is entirely due to the discharge of a single type of ion $ι$ and neglect any capacitive contributions. Assuming also that the effective electrovalence $γ$ of $ι$ is independent of the applied electric potential $ψ$, the current density at $E$ is given as [4]

$$J(ψ) = -\kappa e_0 γ ν \frac{\Theta}{\partial ψ}.$$  \hspace{1cm} (1)

Here $κ$ is the surface density of adsorption sites on $E$, $e_0$ is the elementary charge, $ν$ is the scan rate, and $Θ$ is the total coverage (the average values of the fraction of adsorption sites on $E$ occupied by $ι$). A voltammogram is a plot of the current density $J$ as a function of $ψ$. In order to have a spike in $J$, it is supposed that a first-order phase transition occurs between two phases at the interface, denoted as $+$ and $-$, at some point $ψ_t$.

The aim is, therefore, to obtain, from microscopic analysis, the dependence of $J$ on $ψ$ that would well match with experimental observations. An ideal experimental scenario for studying two dimensional phase transitions at the fluid-electrode interface is provided by underpotential deposition (UPD). This is the phenomenon when $ι$ can deposit on a “more noble” metal substrate at a more positive potential $ψ$ than the potential that causes bulk deposition of the metal, and, for a range of $ψ_t$, only monolayer or submonolayer deposition takes place.

3. CURRENT DENSITY AS AN AVERAGE

The main point of our statistical mechanical approach [10, 11] is the observation that an electrode surface consists of a huge number of relatively
current spikes during underpotential deposition

small crystalline domains that we call *crystals*. Each crystal produces its own contribution to the overall current density \( J \). Thus, we interpret \( J \) as a sum of contributions coming from various crystals on the electrode surface.

Let us write \( S \) for the crystal size (the number of its adsorption sites), \( \xi \) for the shape factor (the dimensionless ratio of the crystal boundary size and \( \sqrt{S} \)), and \( \tau \) for the “surface tension” (determined by the boundary conditions). Assuming for simplicity that the crystals do not mutually interact, the total current density \( J \) can be expressed as a triple average over the crystal current densities. Namely [11],

\[
J(\psi) = \mathbb{E}_S \mathbb{E}_\xi \mathbb{E}_\tau \, J_{S,\xi,\tau}(\psi),
\]

where \( J_{S,\xi,\tau}(\psi) = -\kappa e_0 \gamma \nabla \cdot \frac{\partial \Theta_{S,\xi,\tau}(\psi)}{\partial \psi} \) is the current density from a crystal with the size \( S \), the shape factor \( \xi \), and the surface tension \( \tau \) (c.f. (1)). The crystal coverage \( \Theta_{S,\xi,\tau}(\psi) \) is the average value of the fraction of adsorption sites in the crystal occupied by the ion \( \iota \).

The crystal current density \( J_{S,\xi,\tau}(\psi) \) can be rigorously controlled with the help of the Borgs-Kotecký theory of finite-size effects near first-order phase transitions [12]. It turns out that \( J_{S,\xi,\tau} \) is a spike-shaped function with a unique maximum at the potential

\[
\psi_{S,\xi,\tau} = \psi_1 - \frac{\tau \xi}{\sqrt{S}}, \quad \lambda = \frac{1}{\kappa e_0 \gamma (\theta_+ - \theta_-)},
\]

where \( \theta_\pm \) is the infinite-crystal coverage in the phase \( \pm \). Moreover, one has

\[
J_{S,\xi,\tau}(\psi) \approx h_S \cosh^{-2} \left( 2h_S \frac{\psi - \psi_{S,\xi,\tau}}{a} \right)
\]

with

\[
a = \kappa e_0 \gamma \nu (\theta_+ - \theta_-), \quad h_S = h_1 S, \quad h_1 = \kappa (e_0 \gamma)^2 \nu \beta \left( \frac{\theta_+ - \theta_-}{2} \right)^2.
\]

The approximation (4) is valid for crystals of a square-like shape (i.e., crystals that are not too oblong so that \( \xi \) is not large) and boundary conditions that do not strongly prefer any of the involved phases (the surface tension \( \tau \) must be small enough). The temperature must also be sufficiently small (this is not a serious restriction, though).

Knowing the behavior of the current density from a single crystal, the dependence of the total current density \( J \) on \( \psi \) is to be obtained by taking the triple average given by Eq. (2). To this end, it is necessary to estimate, in a
physically plausible way, the distributions of crystal sizes, shapes and surface tensions across the electrode surface. In [10, 11, 13] we derived approximative formulas for macroscopic characteristics of the resulting spike exhibited by $J$. Namely, the spike area $A$, maximum position $\psi_{\text{max}}$, height $H$, and asymmetry index $\alpha$ (the latter being defined as the ratio of the area of the spike to the left of the maximum point $\psi_{\text{max}}$ with respect to the total area $A$). In [11] we even obtained an approximation of the function $J(\psi)$ itself. These approximative formulas are important in fitting a theoretical voltammogram to an experimental one (see Section 4). Moreover, they link the macroscopic parameters of a voltammogram with the parameters (such as the energy interactions) of the statistical mechanical model used to simulate the deposition process. In this way a voltammogram spike informs one about the microscopic behavior on the electrode surface.

4. UPD OF Cu ON Au(111)

One of the most studied underpotential deposition processes is that of copper on the (111) surface of a crystalline gold electrode in sulfuric acid solution. The associated voltammogram has two spikes [14]: the spike at a higher potential has a broad foot and its total area is about twice as large as the spike at a lower potential (see Fig. 1).

![Fig. 1. – UPD of Cu on Au(111) in 0.05 M of H$_2$SO$_4$ and 1 mM of Cu$_2$SO$_4$ at the scan rate 1 mV s$^{-1}$. The experimental voltammogram (gray line) from [15] is compared with the theoretical one (black line) from [11].](image-url)
In [11] we applied our theory based on Eqs. (2) and (4) to this deposition process. As usual, we attributed the spike at a lower potential to the transition between the phase \( CCC \) and the phase \( SCC \). However, contrary to the generally accepted view, we attributed the spike at a higher potential to the \( SCC - SCO \) phase transition. Even more surprisingly, we associated a first-order phase transition also with the foot region, namely, the \( SCO - OOO \) transition (see Fig. 2).

Microscopically, we modeled the deposition process by a two-component lattice gas in which first neighbors \( X \) and \( Y \) interact with the energy \( \epsilon_{XY}^{(1)} \) that is (i) infinitely repulsive if both the neighbors are \( S \) ions, (ii) repulsive if both the neighbors are \( C \)'s, and (iii) attractive if one neighbor is \( S \) and the other is \( C \). In order to guarantee that the involved phase transitions are all of the first order, we also introduced attractive second-neighbor interactions \( \epsilon_{SS}^{(2)} \) and \( \epsilon_{CC}^{(2)} \) between the pairs of \( S \)'s and the pairs of \( C \)'s, respectively.

Each of the three phase transitions \( CCC - SCC \), \( SCC - SCO \), and \( SCO - OOO \) gives rise to a spike that we attributed to the two voltammogram spikes and the foot region, respectively. Therefore, the total current density is approximated by the sum of three components,

\[
J(\psi) \approx J_{CCC - SCC}(\psi) + J_{SCC - SCO}(\psi) + J_{SCO - OOO}(\psi).
\]

Each component can be analyzed separately with the help of (2) and (4).

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1 Phases on the triangular lattice of the electrode surface can be described just by their local configuration, \( XYZ \), on every elementary triangle of the lattice. We use \( C \), \( S \), and \( O \) to represent copper, (bi)sulfate, and vacancy, respectively.
The fitting of the plot of our theoretical current density (5) to the experimental voltammogram from [15] is carried out in two steps. First, we use the approximative formulas for the area, maximum point, height, and asymmetry index (and, in fact, for the current density itself) of each of the three spikes to obtain a good match with experiment (see Fig. 1). In the second step we use the corresponding values of these macroscopic parameters to find the values of the microscopic parameters.

5. A WAY TO A GENERAL THEORY OF VOLTAMMOGRAM SPIKES

Eq. (4) shows that the single-crystal current density \( j_{\theta,\xi,\tau}(\psi) \) behaves, under rather general conditions, in a remarkably universal manner. It basically depends only on three “mesoscopic” parameters (the crystal size, shape factor, and surface tension). Therefore, it is not necessary to start a microscopic analysis of a deposition process by introducing an appropriate statistical mechanical model. Rather, one can work with the “mesoscopic” parameters to fit the theoretical voltammogram to an experimental voltammogram. This is, evidently, a much less complicated problem to solve. Only in the end, when interpreting the obtained results microscopically, may one construct a suitable lattice-gas model. Using then the values of the three “mesoscopic” parameters, as given by the fit, one can also find the (equations for the) values of the microscopic parameters of the model.

This strategy is worked out in detail in [13, 16]. Applying it to the simple process of the UPD of Cu on Pt (111), we obtained the same results as in our earlier work [10] (see also [17]).

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REFERENCES


