A Statistical Mechanical Study of Phase Transitions on Crystalline Electrodes

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Abstract

A microscopic statistical mechanical lattice gas model is used to study phase transitions that occur at the fluid-crystal interface during electrodeposition on a crystalline electrode surface. Current versus voltage plots, or voltammograms, constructed from the adsorption isotherms of the model agree quite well with experiment. The effects of finite sized electrode crystals on the shapes of voltammogram spikes associated with first order phase transitions are studied using the rigorous Pirogov-Sinai theory.

1 Introduction

First order phase transitions often occur as the electric potential is changed during adsorption or deposition of charged species on a crystalline electrode surface. These transitions produce spikes in the voltammogram current.

Blum and Huckaby[1] introduced a microscopic statistical mechanical model which can be used to generate model voltammograms associated with the adsorption or deposition of such charged species on a crystalline electrode. The model is an adaptation of an earlier three dimensional model for adsorption of hard spheres[2, 3, 4, 5, 6]. In that model, the spheres can come in contact with a planar wall containing a lattice of sticky sites. The adsorption model is mathematically equivalent to a two dimensional lattice gas. The fugacity of a sphere in the lattice gas equals the product of the stickiness parameter associated with a sticky lattice site times the hard sphere contact density in the three dimensional model. The Boltzmann factor for the n-body interaction energy in the two dimensional lattice gas equals an n-body contact correlation function in the equivalent three dimensional model.

The adsorption model was modified to treat charged species by assuming that the stickiness parameter, the contact density, the fugacity, and perhaps the interaction energies are voltage dependent. Assuming a reasonable form for this dependence on the potential, a voltammogram can be constructed. For the special case of Faradaic current, the current intensity in the voltammogram is proportional to the derivative, with respect to the potential, of the adsorption isotherm of the lattice gas.

In Section 2 we discuss the application of the model to the underpotential deposition of copper on the (111) surface of a gold electrode in the presence of bisulfate and to the reduction of hydrogen on the (111) surface of a platinum electrode in the presence of bisulfate. In Section 3 we discuss our recent treatment of the effects of finite size electrode crystals on the shape of voltammogram spikes. These results are applied to produce a model voltammogram for the underpotential deposition of copper on the (111) surface of a platinum electrode in sulfuric acid solution.

2 Application of the Model

In some cases, a metal ion can deposit on a "more noble" metal substrate at a more positive potential than the potential that causes bulk deposition of the metal. Thus, for a range of potential, only monolayer or submonolayer deposition will occur. This phenomenon, called underpotential deposition (UPD), provides an ideal experimental scenario for studying two dimensional phase transitions at the fluid-electrode interface.

One of the most studied systems is the UPD of copper on the (111) surface of a crystalline gold electrode in sulfuric acid solution. The voltammogram[7] has two spikes, the spike at higher potential having a broad foot and an overall area about twice as large as the spike at lower potential (see Fig. 1). Huckaby and Blum proposed that the following sequence of voltage-dependent phase transitions occurs on the electrode surface[8, 9, 10]. At high potentials, bisul-

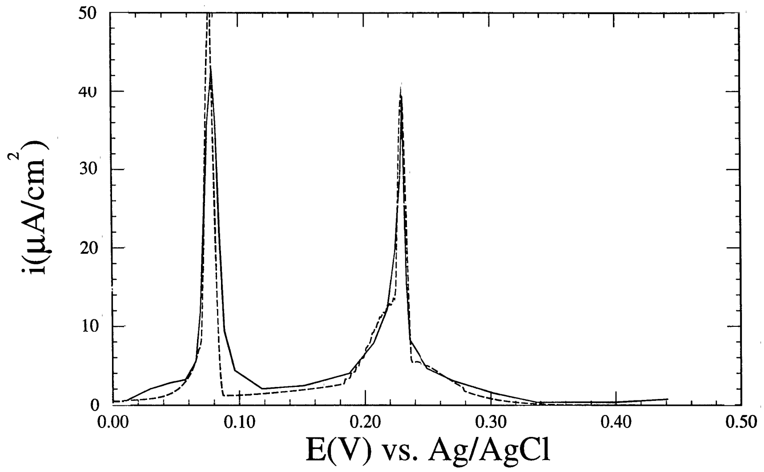

Figure 1: Voltammogram of the underpotential deposition of copper on the (111) surface of a gold electrode in the presence of bisulfate. The model voltammogram (dashed line) is compared with the experimental one (full line) from [7].

fate ions form a phase in which bisulfates are above all the lattice sites of one triangular sublattice of the triangular lattice of adsorption sites. Three of the oxygens of each bisulfate interact with the triangle of three gold atoms that neighbor the adsorption site. As the potential is decreased, the bisulfate leaves the lattice and then returns due to its attraction to the copper ions that are being deposited. A phase is then formed in which one sublattice is again occupied by bisulfate, and the remaining honeycomb lattice is occupied by copper. The voltammogram spike at higher potentials is associated with the transition to this phase. As the potential is further reduced, the bisulfate is replaced by copper, this phase transition being associated with the voltammogram spike at lower potentials. We treated the system using series expansions of the partition function[8, 9, 10], by studying the low temperature phases in the thermodynamic limit using the rigorous Pirogov-Sinai theory[11], by introducing and using a mean neighbor approximation[12, 13, 14], and by using a cluster variation method[15, 16]. The results given by the latter method are presented in Fig. 1, and the agreement with experiment is quite good.

We have recently applied the lattice gas model, using a new effective cluster approximation, to study the reduction of hydrogen on the (111) surface of a platinum electrode in sulfuric acid solution[17, 18]. The voltammogram of this process, first obtained for a crystalline (111) platinum electrode by Clavilier[19, 20], consists of three regions. We proposed that the high potential region corresponds to water-bisulfate coadsorption in which the water forms hydrogen bonded chains. There is no phase transition in this region. At lower potentials, the bisulfate occupies one sublattice of the triangular lattice of adsorption sites, the remaining honeycomb lattice of adsorption sites being occupied by a two dimensional "ice-like" structure composed of hydrogen bonded $H_5O_2^+$ species. As the potential is reduced, the bisulfate can leave, but the honeycomb ice-like structure remains, being stabilized by the hydrogen bonding. As the potential is further reduced, the $H_5O_2^+$ species is reduced to $H_3O_2^-$ and one molecule of H_2 gas is evolved. Recent density functional calculations are consistent with this reaction[18]. The model thus provides a robust explanation for the well-known experimental observation that the (111) platinum surface gives only a 2/3 yield of H_2 gas. The calculated model voltammogram agrees quite well with the experimental voltammogram[19, 20].

3 Effects of finite sizes of electrode crystals

In this section we discuss how the finite-size effects for crystals that are formed on electrode surfaces can be used to interpret the voltammogram spikes. We consider the underpotential deposition of copper on platinum(111) in sulfuric acid medium. Its voltammogram shows a single, symmetric-shaped spike that corresponds to the first order phase transition that occurs when the copper ions discharge and form a full monolayer that is commensurate with the (111) surface of the underlying substrate[21].

We modeled this deposition process[22] by using the standard, one component lattice gas on the triangular lattice with an attractive nearest-neighbor interaction $\varepsilon < 0$ and a chemical potential μ. We considered parallelogram-shaped crystals and fixed boundary conditions with an attractive boundary interaction $\omega < 0$ constant along the boundary of the crystal. The model is equivalent to the Ising model with a bulk coupling $-\varepsilon/4$, a magnetic field $(\mu - 3\varepsilon)/2$, and a boundary coupling $-(2\omega - \varepsilon)/4$. Given a crystal containing $n \times n$ adsorption sites that has a boundary interaction ω, the Faradaic current density from the crystal is given as $j_n^{\omega}(\psi) = -\kappa e_0 \gamma \nu \, \frac{\partial \theta_n^{\omega}}{\partial \psi}$ [10]. Here ψ is the electric potential, and θ_n^{ω} is the crystal copper coverage (the average value of the fraction of adsorption sites on the crystal occupied by copper). Moreover, κ is the number of adsorption sites on the electrode per unit area, γ is the effective electrovalence of copper, e_0 is the elementary charge, and ν is the sweep rate.

It is instructive to find the crystal current density $j_1^{\varepsilon/2}(\psi)$ for the trivial case of a crystal containing just a single site ($n = 1$) and having fixed constant boundary conditions with $\omega = \varepsilon/2$. The partition function of the system is

$Z_1^{\varepsilon/2}(\mu) = e^{\beta(\mu-3\varepsilon)}+1$, with $\beta = 1/(k_B T)$, which yields the coverage $\theta_1^{\varepsilon/2}(\mu) = e^{\beta(\mu-3\varepsilon)}/Z_1^{\varepsilon/2}(\mu) = \{1+\tanh[\beta(\mu-3\varepsilon)/2]\}/2$. Since the chemical potential μ is related to ψ by $\mu = -\gamma e_0(\psi - \bar{\psi})$ [11], where $\bar{\psi}$ is the reference potential, we readily find $j_1^{\varepsilon/2}(\psi) = \kappa(\gamma e_0)^2 \nu\beta \cosh^{-2}\{\beta\gamma e_0[\psi + (3\varepsilon)/(\gamma e_0) - \bar{\psi}]/2\}/4$. Thus, this current density has the shape of a spike described by the function $\cosh^{-2}$ with a maximum at $\psi = -(3\varepsilon)/(\gamma e_0) + \bar{\psi}$.

In order to analyze the behavior of a finite sized crystal containing more than just a single site and to obtain an accurate estimate of the corresponding single-crystal current density, we used the rigorous statistical mechanical techniques of Borgs and Kotecký[23] based on the Pirogov-Sinai theory[24, 25]. They show that the tanh and $\cosh^{-2}$ formulas are in fact a very general result that is true for a large class of lattice models in a (hyper)cubic-like volume that exhibit a two-phase coexistence. The application of their techniques requires that the imposed boundary conditions do not strongly prefer any of the involved phases. For our one component lattice gas this means that the boundary interaction ω has to be close to the neutral value $\omega = \varepsilon/2$ [22]. Then, in complete analogy with the above case of a single-site crystal, we were able to rewrite the partition function of the crystal of size n as the sum $Z_n^\omega = e^{-\beta F^\omega_{n,o}} + e^{-\beta F^\omega_{n,v}}$, where $F^\omega_{n,o}$ (resp. $F^\omega_{n,v}$) is some well controlled finite-volume free energy associated with the fully occupied (resp. fully vacant) phase. This again allowed us to prove that the shape of a spike of the single-crystal current density is given by the function $\cosh^{-2}$, namely,

$$j_n^\omega(\psi) \approx \kappa\,(\gamma e_0)^2\,\nu\,\beta\,n^2\Big(\frac{m^*}{2}\Big)^2 \cosh^{-2}\Big[\beta\,\frac{m^*}{2}\,\gamma e_0(\psi - \psi_n^\omega)\,n^2\Big], \qquad (1)$$

the error term being of order n. Here m^* is the Ising spontaneous magnetization on the triangular lattice. The point ψ_n^ω is the potential at which the current density j_n^ω attains its maximum. It is shifted with respect to the infinite-volume transition point $\psi_t = -(3\varepsilon)/(\gamma e_0) + \bar{\psi}$ by an amount proportional to n^{-1}, more precisely, $\psi_n^\omega - \psi_t \approx [4(2\omega - \varepsilon)]/(m^*\gamma e_0 n)$. Obviously, the symmetry of our model implies $\psi_n^{\omega=\varepsilon/2} = \psi_t$. Notice that Eq. (1) holds exactly for the above described trivial case $n = 1$ and $\omega = \varepsilon/2$, taking $m^* = 1$.

It is natural to imagine that a voltammogram spike can be microscopically interpreted as a spike in the current density that results from a first order phase transition on a *single* ("typical") crystal of finite size. However, Eq. (1) implies that this idea turns out to be erroneous: such a single-crystal spike would be taller and sharper than an experimental spike by a factor of about 100. As a matter of fact, this conclusion is true for a whole variety of boundary conditions for which the Borgs-Kotecký theory of finite-size effects

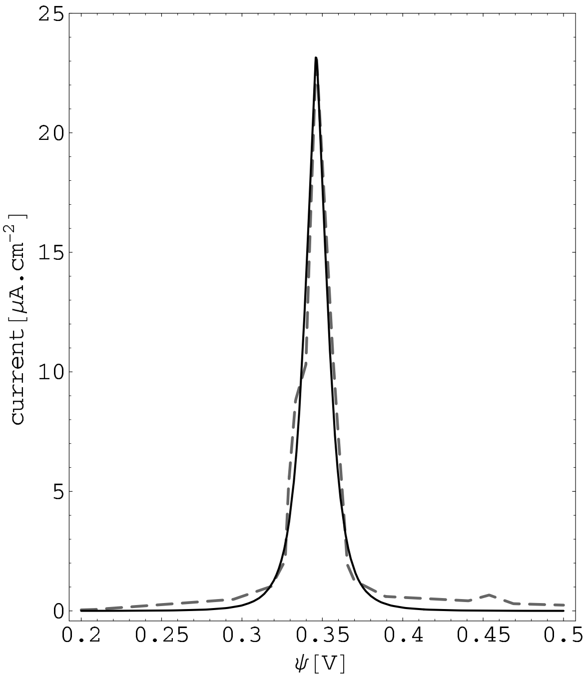

Figure 2: Voltammogram of the underpotential deposition of copper on the (111) surface of a platinum electrode in the presence of bisulfate. The model voltammogram (full line) is compared with the experimental one (dashed line) from [21].

is applicable (e.g., periodic, fixed constant, a mean-field type, or possibly random boundary conditions) because the spike shape (in particular, its height, width, and area) is predominantly determined by the bulk properties of the crystal.

Nevertheless, a real electrode surface actually contains many crystalline domains. Therefore, one should rather view the surface as a huge collection of crystals, and interpret a voltammogram spike as an *average* of the contributions coming from various sized crystals. Besides taking the average over the crystal sizes, one must also take the average over crystal boundary interactions ω, for these vary in general from crystal to crystal. Whereas the $\cosh^{-2}$ shape of a crystal spike is determined by the bulk properties of the crystal, the boundary conditions determine the maximum position ψ_n^ω of the spike. Thus, as a result of the double average, our interpretation of a voltammogram spike is that it is an envelope of mutually shifted (but closely spaced) spikes associated with first order phase transitions that occur in various crystals formed on the electrode surface.

To calculate the double average, we introduced a simple but realistic distribution of crystal sizes by assuming that the crystals were a result of line defects occurring on the electrode surface. Moreover, we used the simplest possible distribution of boundary interactions ω leading to a symmetric voltammogram spike, namely, a wedge-shaped distribution that was symmetric around $\omega = \varepsilon/2$. Accurate explicit estimates of the area and the height of the resulting model voltammogram spike in terms of the microscopic parameters of our model — ε, γ, and $\bar{\psi}$ — allowed us to choose their values so that the calculated spike agreed very well with experiment (see Fig. 2).

Very recently we have applied the idea of interpreting voltammogram spikes as envelopes of spikes resulting from various sized electrode crystals to the underpotential deposition of copper on the (111) surface of a gold electrode in sulfuric acid medium[26], and we again achieved very good agreement with experiment. In the future we plan to apply this idea to analyze the reduction of hydrogen on the (111) surface of a platinum electrode in the presence of bisulfate.

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