Coadsorption of Copper and Sulfate on Au(111) Electrodes:
Monte Carlo Simulation of a Lattice-Gas Model*

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Abstract. We report ground-state calculations and Monte Carlo simulations for a lattice-gas model of the underpotential deposition of copper on Au(111) in sulfate-containing electrolytes. In a potential range of approximately 100∼150 mV, this system exhibits a \( (\sqrt{3} \times \sqrt{3}) \) mixed phase with 2/3 monolayer (ML) copper and 1/3 ML sulfate. Our simulation results agree well with experimental results and with other theoretical work.

1. Introduction

Underpotential deposition (UPD) is a process whereby a monolayer (ML) or less of one metal is electrochemically adsorbed onto another in a range of electrode potentials more positive than those where bulk deposition would occur [1]. The UPD of copper on Au(111) electrodes in sulfate-containing electrolytes has been intensively studied, both experimentally (see detailed discussion in Ref. [2]) and theoretically [3,4]. In cyclic voltammetry (CV) experiments the potential is scanned slowly while the current density is recorded. The most striking feature of the CV currents observed with a Au(111) electrode in sulfate-containing electrolyte is the appearance of two peaks, separated by about 100∼150 mV, upon the addition of Cu\(^{2+}\) ions [5,6]. Typical CV profiles are shown in Fig. 1a [2], together with our simulation results. In the potential range between the peaks, the adsorbate layer is believed to have a \( (\sqrt{3} \times \sqrt{3}) \) structure consisting of 2/3 ML copper and 1/3 ML sulfate. This picture is based on a variety of both ex situ and in situ experimental evidence, as discussed in Ref. [2].

2. Model and theoretical methods

Our lattice-gas model for UPD of copper on Au(111) in sulfate-containing electrolyte is a refinement of the Huckaby-Blum model [3,4]. It is defined by a

* To appear in Computer Simulation Studies in Condensed-Matter Physics VIII, edited by D. P. Landau, K. K. Mon, and H. B. Schüttler (Springer, Berlin, in press).
standard three-state lattice-gas Hamiltonian [7,8],

\[
\mathcal{H}_{\text{LG}} = \sum_l \left[ -\Phi_{SS}^{(l)} \sum_{ij} n_i^S n_j^S - \Phi_{SC}^{(l)} \sum_{ij} \left( n_i^S n_j^C + n_i^C n_j^S \right) - \Phi_{CC}^{(l)} \sum_{ij} n_i^C n_j^C \right] - \Phi_{SS}^{(l)} \sum_{i} \Delta n_i n_j n_k - \bar{\mu}_S \sum_i n_i^S - \bar{\mu}_C \sum_i n_i^C.
\]

(1)

Here \( n_i^X \in \{0,1\} \) is the local occupation variable for species \( X \) [\( X = S \) (sulfate) or \( C \) (copper atom)], and the third adsorption state ("empty" or "solvated") corresponds to \( n_i^S = n_i^C = 0 \). The sums \( \sum_{(ij)}^{(l)}, \sum_{\Delta}, \) and \( \sum_i \) run over all \( l \)-th-neighbor bonds, over all equilateral next-nearest-neighbor triangles [9], and over all adsorption sites, respectively. \( \Phi_{XY}^{(l)} \) denotes the effective \( XY \) interaction through an \( l \)-th-neighbor bond, and \( \sum_l \) runs over the interaction ranges. The change in electrochemical potential when one \( X \) particle is removed from the bulk solution and adsorbed on the surface is \( -\bar{\mu}_X \). The sign convention is such that \( \Phi_{XY}^{(l)} > 0 \) denotes an effective attraction, and \( \bar{\mu}_X > 0 \) denotes a tendency for adsorption in the absence of lateral interactions. The bonds that correspond to finite lateral interaction energies are shown in Fig. 2. For large separations the interactions vanish, and \( \Phi_{SS}^{(l)} \) is an infinite repulsion corresponding to nearest-neighbor sulfate-sulfate exclusion ("hard hexagons" [3,4,10]). We emphasize that the \( \Phi_{XY}^{(l)} \) are effective interactions through several channels, including electron-, phonon-, and fluid-mediated mechanisms [7].

The electrochemical potentials in Eq. (1) are (in the weak-solution approximation and here given in molar units) related to the bulk concentrations \([X]\) and the electrode potential \(E\) as

\[
\bar{\mu}_X = \bar{\mu}_X^0 + RT \ln \frac{[X]}{[X]^0} - z_X F E.
\]

(2)

Here \( z_X \) (\( X = S,C \)) are the effective electrovalences of sulfate and copper, \( R \) is the molar gas constant, \( T \) is the absolute temperature, and \( F \) is the Faraday constant. The quantities superscripted with a 0 are reference values which contain the local binding energies to the surface. They are generally temperature dependent if the effects of rotational and vibrational modes are considered.

The coverages of sulfate and copper are defined as \( \theta_X = \frac{N}{\sum_i n_i^X} \), where \( N \) is the total number of unit cells in the lattice. However, it is experimentally observed that sulfate remains adsorbed on top of the copper monolayer in the negative-potential region, rather than becoming reduced and entering the solution. A simple estimate of the sulfate coverage in this second layer can be obtained as \( \theta_S^{(2)} = \alpha \theta_C (1/3 - \theta_S) \), which allows the difference between the first-layer coverage \( \theta_S \) and its saturation value of 1/3 to be transferred to the
top of the copper layer. The factor $\alpha$ is a phenomenological constant expected to be between zero and one. Since the transfer of sulfate between the gold and copper surfaces does not involve an oxidation/reduction process, the total charge transport per unit cell during the adsorption/desorption process is $q = -e(z_S(\theta_S+\theta_S^{(2)}) + z_C\theta_C)$, where $e$ is the elementary charge. In the absence of diffusion and double-layer effects and in the limit that the potential scan rate $dE/dt \to 0$ [1], the voltametric current $i$ per unit cell of the surface is the time derivative of $q$. Using differentiation by parts involving the relations between the $E$ and $\bar{\mu}_X$, Eq. (2), as well as the Maxwell relation $\partial \theta_S/\partial \bar{\mu}_C = \partial \theta_C/\partial \bar{\mu}_S$, we find the current density $i$ in terms of the lattice-gas response functions:

$$i = eF \left\{ \frac{\zeta_S^2(1-\alpha \theta_C)}{\bar{\mu}_C} \left| \frac{\partial \theta_S}{\partial \bar{\mu}_S} \right| \bar{\mu}_S + z_C(z_C - 2\alpha z_S\theta_S/3) \left| \frac{\partial \theta_C}{\partial \bar{\mu}_C} \right| \bar{\mu}_S \right\} + eF \left\{ z_S \left( 2z_C + \alpha z_S(1/3 - \theta_S) - \alpha z_C \theta_C \right) \left| \frac{\partial \theta_S}{\partial \bar{\mu}_C} \right| \bar{\mu}_S \right\} \frac{dE}{dt},$$

which reduces to its standard form for $\alpha=0$ [11].

Although the experimental studies are carried out at room temperature, the zero-temperature phase diagram serves as a quite accurate guide to the path in the $(\bar{\mu}_S, \bar{\mu}_C)$ plane that the isotherms should follow. At constant temperature and $pH$, two factors influence the path: the adsorbate concentrations in the electrolyte and the electrovalences. As seen from Eq. (2), $\bar{\mu}_S$ and $\bar{\mu}_C$ depend linearly on $E$, with slopes determined by $z_S$ and $z_C$, whose values must be determined from experiments. Here we use $z_C=+2$, $z_S=-2$. Thirty-two ordered phases were found by applying the group-theoretical arguments of Landau and Lifshitz [12], nine of which (denoted by $(X \times Y)^{\theta_S}_{\theta_C}$ in Fig. 3) are realized as ground states for interactions in the region of experimental interest. The ground-state energies depend on $\bar{\mu}_S$ and $\bar{\mu}_C$ and the lateral interactions. The repulsive second-neighbor three-particle interaction $\Phi^{(t)}_{SS}$ disfavors the pure sulfate $(\sqrt{3} \times \sqrt{3})0/3$ phase, which has not been experimentally observed in this system. For a fixed set of interactions, the zero-temperature phase boundaries are exactly determined by pairwise equating the ground-state energies. In order to easily explore the effects of changing the interactions, a program was developed which numerically determines the zero-temperature phase diagram by scanning $\bar{\mu}_S$ and $\bar{\mu}_C$ and determining the phase of minimum energy [13].

To obtain adsorption isotherms and CV currents at room temperature, we performed Monte Carlo (MC) simulations on a $30 \times 30$ triangular lattice, using a heat-bath algorithm [14] with updates at randomly chosen sites. In order to avoid getting stuck in metastable configurations (a problem which is exacerbated by the nearest-neighbor sulfate-sulfate exclusion), we simultaneously updated clusters consisting of two nearest-neighbor sites. Each data point was obtained as an average over $2 \times 10^6$ Monte Carlo Steps per spin (MCSS), sampling at intervals of 50 MCSS and discarding the first 4000 MCSS.
3. Numerical results

The zero-temperature phase diagram corresponding to the interactions used in this work is shown in Fig. 3. For large negative $\mu_S$ only copper adsorption is possible, and the phase diagram is that of the lattice-gas model corresponding to the triangular-lattice antiferromagnet with next-nearest neighbor ferromagnetic interactions [15]. Similarly, in the limit of large positive $\mu_S$ and large negative $\mu_C$ the zero-temperature phase is the $\left(\sqrt{3} \times \sqrt{7}\right)^{1/5}_0$ sulfate phase characteristic of the hard-hexagon model [3,4,10]. The phase diagram for intermediate electrochemical potentials is quite complicated. For $\mu_S < -22 \text{ kJ/mol}$, no sulfate adsorption occurs in the first adlayer, while if $\mu_C < -18 \text{ kJ/mol}$, no copper is adsorbed. The $\left(\sqrt{3} \times \sqrt{7}\right)^{1/5}_0$ phase corresponds to experimental observations in copper-free systems [16,17]. It is enhanced by the fourth-neighbor sulfate-sulfate attraction, $\Phi_{SS}^{(4)}$, and the $\left(\sqrt{3} \times \sqrt{3}\right)^{1/3}_0$ phase is disfavored by the second-neighbor repulsive trios, $\Phi_{SS}^{(t)}$. The $\left(\sqrt{3} \times \sqrt{3}\right)^{2/3}_0$ mixed-phase region in the upper right-hand part of the diagram is relatively large, due to the nearest-neighbor attraction between copper and sulfate, $\Phi_{SC}^{(1)}$. The isothermal path is chosen such that the distance between points A and B (measured by the electrode potential) equals the peak separation in the CV current shown in Fig. 1a. The narrow strip of $\left(\sqrt{3} \times \sqrt{7}\right)^{1/5}_0$ phase lies closely above the $\left(\sqrt{3} \times \sqrt{3}\right)^{1/3}_2$ phase and is quite sensitive to the fourth-neighbor attraction, $\Phi_{SS}^{(4)}$, and the second-neighbor trio sulfate repulsion, $\Phi_{SS}^{(t)}$. The nearest-neighbor copper repulsion causes the appearance of the $\left(\sqrt{3} \times \sqrt{3}\right)^{1/3}_1$ phase.

The potential scan path corresponding to the CV current and adsorption isotherms shown in Fig. 1 is indicated by the dashed line in Fig. 3. With the aid of the ground-state diagram, it is easy to analyse the simulation results. Starting from the positive potential end (lower right in Fig. 3), where $\theta_C \approx 0$, $\theta_S$ drops from its saturated hard-hexagon value of $1/3$ to approximately $1/5$ in the $\left(\sqrt{3} \times \sqrt{7}\right)^{1/5}_0$ phase region. This is in reasonable agreement with the experimental results for the same electrochemical system in the absence of copper, where the $\left(\sqrt{3} \times \sqrt{7}\right)^{1/3}_0$ structure has been observed, but not that of $\left(\sqrt{3} \times \sqrt{3}\right)^{1/3}_0$ [16,17]. As $E$ is scanned in the negative direction, the cations are attracted toward the electrode. Since there are strong effective attractions between the two types of adsorbed particles, the adsorption of copper induces the readsoption of sulfate: they both increase their coverages in a narrow potential range near $175 \text{ mV}$ to form the mixed $\left(\sqrt{3} \times \sqrt{3}\right)^{1/3}_2$ phase. This is exactly the scenario proposed by Huckaby and Blum [3,4], and it is an example of the enhanced-adsorption phenomenon discussed by Rikvold and Deakin [7]. This phase remains stable in a potential range indicated by the separation of the two CV peaks, until the electrode potential is sufficiently negative that
the sulfate adsorption on the gold surface is disfavored in comparison with completion of the copper monolayer. The replacement causes another sharp change in the surface coverages, corresponding to the left CV peak. However, there is experimental evidence that part of the sulfate desorbed from the gold surface is not reduced and dissolved, but rather remains adsorbed in a formally neutral submonolayer on top of the monolayer of copper, with a coverage \( \theta_S^{(2)} \approx 0.2 \) [6]. This corresponds to \( \alpha=0.6 \) in Eq. (3), which was used to obtain the simulated CV current and surface-charge densities shown in Fig. 1. Figure 1b shows a comparison of the simulation results for the charge transfer and the integral of the experimental CV current.

The agreement between the experimental and theoretical results is reasonable, except for large positive \( E \), where the model predicts less copper and more sulfate on the surface than indicated by the experiments. The disagreement between the theoretical and experimental maximum currents may be due to defects on the electrodes used in the experiments.

Acknowledgements

We have enjoyed enlightening conversations with L. Blum. This work was supported by Florida State University through the Supercomputer Computations Research Institute (funded in part by US Department of Energy Contract No. DE-FC05-85-ER25000) and the Center for Materials Research and Technology, and by NSF grant No. DMR-9315969. Work at the University of Illinois was supported by the Frederick Seitz Materials Research Laboratory under US Department of Energy Contract No. DE-AC02-76-ER01198.
Figure Captions

Figure 1: Experimental (dashed curves) and simulated (solid curves) results.
(a): CV currents for a positive-going potential scan at 2 mV/s. (b): Integrated charge density. Also shown are $z_C\theta_C$ (long dashed), $z_S\theta_S$ (dotted) and $z_S(\theta_S + \theta_S^{(2)})$ (dotdash).

Figure 2: The relative positions of copper (filled circles) and sulfate (triangles) corresponding to the effective interactions used in Eq. (1). The numbers are the corresponding values of $\Phi^{(l)}_{XY}$ used in this work, given in kJ/mol. The interactions are invariant under symmetry operations on the lattice.

Figure 3: The zero-temperature phase diagram. Solid lines are phase boundaries and the dotted line is the path along which the isotherms are calculated (positive E towards the lower right). The phases are indicated as $(X \times Y)_{\theta_C}^{\theta_S}$. 
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| \( \Phi_{CC}^{(1)} \) | \( \Phi_{CC}^{(2)} \) | \( \Phi_{SC}^{(1)} \) | \( \Phi_{SS}^{(3)} \) | \( \Phi_{SS}^{(4)} \) | \( \Phi_{SS}^{(5)} \) |
|---|---|---|---|---|---|
| o o o | o o o | o o o | △ o o | o o △ | o o △ |
| o o o | o o o | o o o | △ o o | o o △ | o o △ |
| -1.8 | +1.5 | +4.0 | -1.8 | +0.54 | -1.1 |
