

Modeling Electrochemistry in Metallurgical Processes

Adam C. Powell IV, Yasushi Shibuta, Jonathan E. Guyer, and Chandler A. Becker

Enhanced for the Web

Read this article on the JOM web site (www.tms.org/JOMPT) to see video clips of the simulations.

Editor's Note: Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.

Mathematical modeling is an important tool for the development of materials and processes for making them. Modeling electrochemical processes for smelting or plating metals presents several particularly difficult challenges. Boundary conditions are nonlinear and time-dependent, often because phenomena at multiple length scales are inextricably linked. For example, the Ångström-scale double layer gives rise to nonlinear voltage-current behavior, which is a boundary condition for macroscopic models. And development of micrometer-scale dendrites dramatically changes both the product form and the apparent resistance at the interface; chemical additives can suppress dendrites and produce superconformal filling of very rough surfaces. This paper gives an overview of modeling approaches at all length scales from Ångströms to meters, including both mean field and atomistic approaches.

INTRODUCTION

Electrometallurgy dominates aluminum extraction, is significant in magnesium production, and has wide applications in the refining of copper and many other metals. In many metallurgical reduction processes, electron transfer provides a pathway for reduction and oxidation reactions to happen at different locations, providing more reaction area and improving kinetics. On a much

smaller scale, integrated circuit copper metallization uses electroplating, not evaporation or chemical vapor deposition, because of its superconformal filling ability. All of these processes share the use of electrons to change the oxidation state of ions and atoms.

Engineers designing these processes face a wide variety of challenges. At the largest scales, uneven current distribution leads to uneven plating rate or uneven heating of cell components. At smaller scales, the deposit often forms dendrites, which are usually a poor product and can even stretch across the electrolyte and create a short circuit. In the Hall cell, aluminum forms streamers which are the liquid equivalent of dendrites; these break into tiny droplets or "metal fog" that increase the electronic conductivity of the electrolyte, reducing cell efficiency.

Electrochemistry also creates significant opportunities. Additives can eliminate dendrites and help to fill rough surfaces and deep trenches more uniformly than with other thin film techniques. Alternating current with a carefully chosen waveform can create a powder or flake product. And on a small scale a carefully controlled short circuit can be used as a switch.

As with any engineering pursuit, mathematical models can facilitate the design of electrochemical cells around these challenges and opportunities. Such models fall into three categories based roughly on length scale (Figure 1). Macroscopic models predict current densities and plating rates over centimeter to meter lengths. Meso-scale models predict interface stability and the shape of dendrites or streamers at submicrometer to millimeter scales; some also resolve nanometer-scale double layer phenomena and estimate non-ohmic charge transfer resistance. And finally, atomistic models

explicitly track the motion of individual atoms, sometimes even their bonding electrons, to study fundamental mechanisms of bonding and charge transfer at interfaces.

The following sections that describe these models and their applications will focus on processes for making metals, leaving aside topics such as batteries and corrosion.

MACROSCOPIC MODELS

The purpose of macroscopic models is to help engineers lay out electrochemical cells on centimeter or larger scales in order to achieve a desired plating rate profile. They calculate the electrical potential, concentration, and sometimes electrolyte flow velocity fields, which determine the ionic current from anode to cathode. The current is driven by the applied voltage and limited by resistance to ionic conduction throughout the electrolyte, resistance due to slow mass transfer (if applicable), and non-ohmic (nonlinear) resistance to electrochemical reaction kinetics at the cathode and anode surfaces. Generally the macroscopic models assume smooth electrode surfaces, ignoring any roughening due to uneven plating.

The Nernst-Planck equations¹ describe transport of ions in the electrolyte (e.g., of Cu^{2+} ions in aqueous solution for copper plating). Equation 1 shows the rate of change of local copper concentration C_{Cu} due to its flux. (All equations are presented in the table on page 38.) Many electrochemical cells rapidly establish a steady state where the local concentration changes very slowly, thus $\partial C_{\text{Cu}}/\partial t = 0$. In the most general case, the flux has terms for diffusion with diffusivity D_{Cu} , convection fluid flow due to velocity field \vec{u} , and electromigration due to electric field \vec{E} as shown in Equa-

tion 2, where z_{Cu} is the ionic charge (two for Cu^{2+}) and μ_{Cu} is mobility given by the Einstein relation $D_{Cu} = (RT/F)\mu_{Cu}$. R is the gas constant, T is the absolute temperature, and F is Faraday's constant.

Put in words, flux follows the flow, goes down the concentration gradient (from high to low concentration), and (positive) cations follow the electric field while anions go the opposite way. In many

plating and smelting operations, electromigration is much faster than diffusion and flow mixes the electrolyte rapidly, such that the electromigration term dominates the flux. Generally, macro-scale simulations solve Equation 2, along with conservation equations for other ions and an equation for conservation of charge, to compute the distributions of concentrations and electrical potential.

Figure 2 shows the result of a calculation which estimates the distribution of plating current driven by the imposed potential based on electrolyte resistance (using electromigration flux alone) and charge transfer resistance at the electrode surfaces. A process engineer can use this model to position the electrodes in order to make the current density relatively uniform, and to determine at what total current the highest local plating current density might lead to a rough deposit.

The paper by U. Pal and A. Powell in this issue gives another example of this type of model. In the magnesium oxide reduction cell described there, the design objectives are to minimize overall cell resistance and to avoid high local current density through the solid oxide membrane anodes in order to prevent excessive local heating. Again, the model provides guidance for electrode placement that best meets these criteria.

These models are thus very useful design tools for estimating plating rates when the deposit is smooth. However, in many cases, particularly with additives, it is hard to know a priori when the deposit will be smooth or rough. And in some cases, one wants a rough deposit and needs to know how the process parameters determine the shape of dendrites or whether they break off (e.g., for making powder or flake product). For these cases, meso-scale models are necessary.

MESO-SCALE MODELS

Models at the micrometer to millimeter scale simulate shape and topology dynamics at the deposit surface. Such models often assume simplified charge transfer resistance at the interface, such as first-order (linear, ohmic) kinetics or, at high temperature, negligible charge transfer resistance.

Typically, boundary conditions apply at the phase interface that depend on the shape and local environment of that

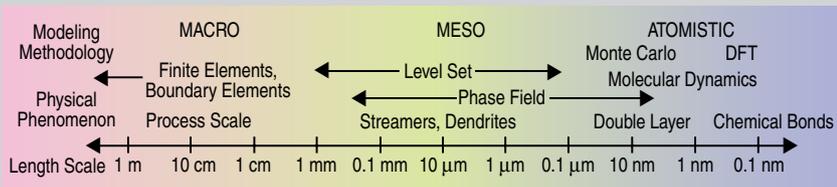


Figure 1. The spectrum of models to describe electrochemical phenomena at various length scales.

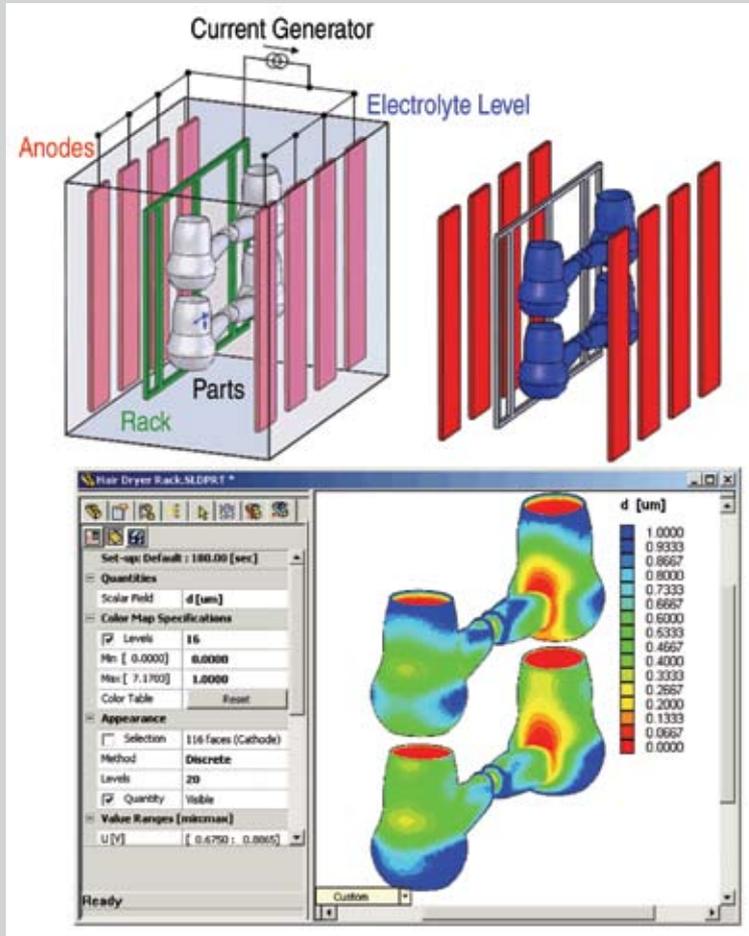


Figure 2. A hair dryer plating simulation: schematic (upper left), electrical potential (upper right), computed plating thickness (lower).^{2,3}

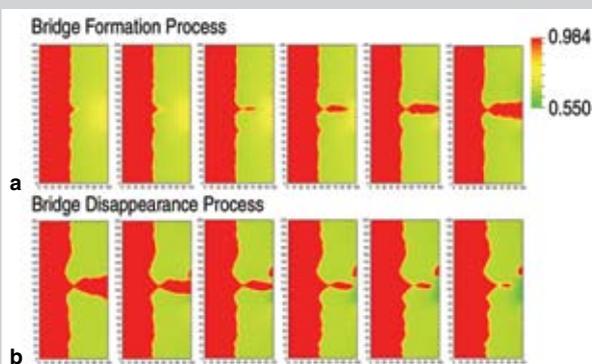


Figure 3. Snapshots of the process of bridge formation and disappearance in a nanometer-scale switch by phase field modeling. (a) Bridge-forming process, (b) bridge-disappearance process.⁴ [See animation on-line.]



interface. These boundary conditions cause the interface to evolve by deposition or dissolution, which changes its shape and local environment, which again causes it to evolve, forming structures such as solid dendrites or liquid streamers. Such complicated morphologies present significant challenges for traditional sharp interface methods as sections of the interface either impinge or break off. Complex algorithms are needed to determine whether, and where, to insert or delete mesh points along the changing interface.

The class of “diffuse interface” methods overcomes this topological difficulty by not attempting to explicitly track the position of the interface. Rather, they introduce a continuously varying field. Contours on this field with a particular value (sometimes called “level sets”) are taken to represent the position of the interface. Changes in topology (impingement, voids, nucleation of new phases) present no difficulty for these methods because the changing contour plays no role in the calculation; it is simply a visualization tool.

There are two broad classes of diffuse interface techniques for electrochemical modeling. Phase field models begin with fundamental thermodynamic and kinetic principles and derive governing equations that may or may not be directly compared to their empirical counterparts, but which often predict the rich behavior observed in experiments. Level set models start with known empirical relationships and model the evolution of complex morphologies.

Transport-Limited Phase Field Models

Y. Shibuta et al.^{4,5} and A. Powell et al.^{6–12} developed phase field models for electrochemical processes with negligible interface effects on current flow. These models use Laplace’s equation (Shibuta) or continuity of current density (Powell) to calculate the electrostatic potential. The gradient of the potential, which is the electric field, then drives the metal ions in the electrolyte phase and the electronic current in the metal phase.

At high temperature or in situations with slowly flowing or stagnant electrolytes, charge transfer at the interface is much faster than mass transfer to the

interface. Under these mass transfer-limited conditions, models may assume that charge transfer resistance at the interface is negligible. When charge accumulation at interfaces is faster than other changes affecting the electric field (e.g., not high-frequency alternating current), models may further assume that net charge at the interface is quasi-steady-state, so

normal charge density is the same on both sides.

Shibuta⁴ begins with a Ginzburg-Landau free energy functional that includes the electrostatic potential. The phase field order parameter ξ ranges from 1 in the electrode (α) to 0 in the electrolyte (β). The model assumes that the electrode is an ideal metal M and the electrolyte is

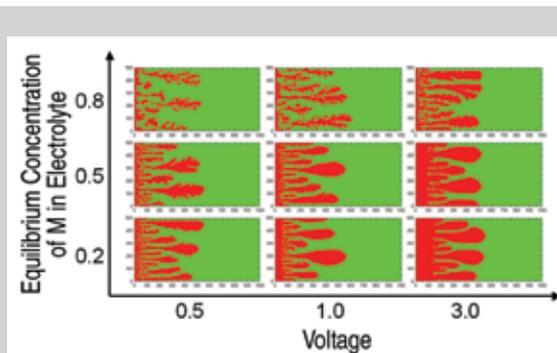


Figure 4. Morphological transition as a function of applied voltage and equilibrium mole fraction of cation in the electrolyte. [See animation on-line.]⁵

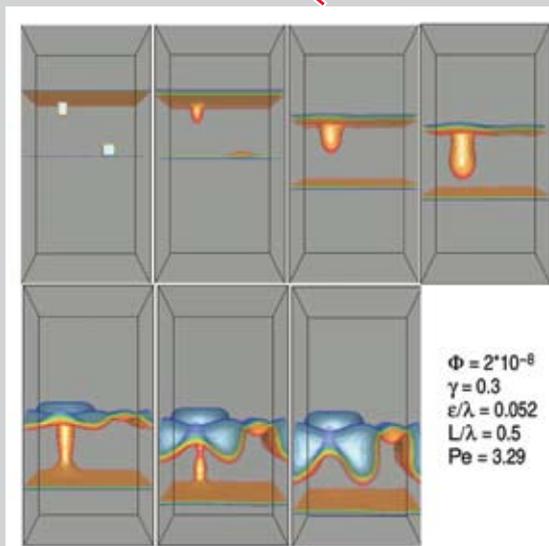


Figure 5. The three-dimensional simulation of migration of an FeO layer in iron on a 60x120x60 grid.¹² Blue, green, yellow, and red contours represent FeO fractions of 0.2, 0.4, 0.6, and 0.8, respectively, illustrating the diffuse interface. [See animation on-line.]

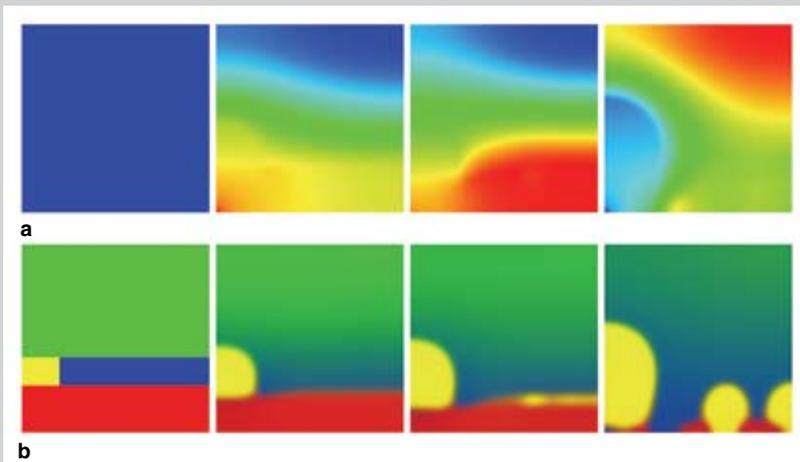


Figure 6. A simulated reaction between TiCl_2 and magnesium to produce titanium and MgCl_2 , illustrating electronically mediated reaction on the initial titanium seed and nucleation of titanium particles at the interface. (a) Relative electrical potential: blue at maximum, red at minimum. (b) Composition: red = Mg, yellow = Ti, green = TiCl_2 , blue = MgCl_2 . [See animation on-line.]

an ideal sulfide M_2A or MA . This is thus a binary M - A system. For simplicity, the model uses a dilute-solution approximation in the electrode and an ideal-solution approximation in the electrolyte phase. It also assumes that the molar volumes of M and A are the same. Hence, the free-energy density is expressed using C_{M^+} , the mole fraction of M , and the phase field parameter ξ . Based on the binary alloy model by S.G. Kim et al.¹³ with the above conditions, the governing equations are Equations 3 and 4⁴ where M_ξ is the mobility of the phase field, κ_ξ characterizes the energy of gradients in the phase field, $p(\xi)$ is an interpolation function, $g(\xi)$ is a double well potential energy function, W is the height of that double well, $G(C_{M^+}^\alpha, C_{M^+}^\beta)$ is the thermodynamic driving force for phase transformation, and $H(\xi, C_{M^+}^\alpha, C_{M^+}^\beta)$ is a thermodynamic factor relating diffusivity to mobility. The superscript α and β denote the value of C_{M^+} projected into the bulk electrode or electrolyte phase, respectively.

In addition to Equations 3 and 4, Laplace's Equation 5 with an applied voltage at the boundary is solved for the distribution of the electrostatic potential. Shibuta et al. use this model to simulate two processes:

- Bridge formation in a nanometer scale switch
- Electrochemical deposition of metals from an unsupported electrolyte solution

K. Terabe et al.¹⁴ and T. Sakamoto et al.¹⁵ developed nanometer-scale switches in ionic/electronic conductor systems such as Cu/CuS and Ag/Ag_2S . They operate by electrochemically depositing a metal bridge through the sulfide. However, experiments have shown that these switches have limited lifetimes, and the reason for this is still unknown. A numerical simulation may help with their development.

Figure 3a shows snapshots of the electrolyte concentration during bridge formation. The voltage signal at the right boundary amplified the disturbance of the interface caused by noise. Then, a cusp made by the disturbance of the interface rapidly grew by plating toward the right edge where voltage was largest, and eventually reached the right boundary. The narrowest part of the bridge was against the bulk electrode. Next, the voltage reversed polarity for 23.5 μs . Figure 3b shows snapshots of the bridge disappearance process in response to the positive applied voltage. The electrode cusp dissolved from the right side and the

bridge structure was separated. Though this calculation used parameters for ideal metal/sulfide M/M_2A , it can provide insight into the bridge formation process to guide experiments.

The next application was electrodeposition.⁵ Plating morphologies come in many varieties, including homogeneous, dendritic, fractal, open-ramified, finger-like, and other complex structures depending on applied voltage and electrolyte concentration.^{16–20} Others have used diffusion-limited aggregation²⁰ and mean-field lattice gas^{21,22} approaches to study these phenomena. Shibuta et al.^{5,23} applied a phase field model to analyze the morphological transition of electrodeposits.

Figure 4 shows deposit morphologies calculated by this method as a function of the applied voltage and equilibrium mole fraction of M^+ in the electrolyte. For a given applied voltage, deposits tended to be dendritic at higher concentrations. Growth velocity of the deposits was proportional to the applied voltage at each concentration. These parameters need to be revised²³ for real materials such as $Cu/CuSO_4$ or $Zn/ZnSO_4$ in order to make them physically meaningful.

The models of Powell and W. Pongsaksawad use a very similar methodology toward several ends. First, they model migration and breakdown of an FeO layer in iron under an electric field in three dimensions, as shown in Figure 5. The perturbation on the anode shrinks because dissolution is faster there, making the anode unconditionally stable, whereas the perturbation on the cathode grows because plating is faster there.

Second, they use numerical simulations to extend traditional linear stability analysis of electrodeposition. Stability of a sinusoidal perturbation of wavelength λ is determined by the Péclet number, which is given by Equation 6. This indicates that the surface is more likely to roughen at wavelength λ if the deposit is growing fast (large u_{int} plating velocity) and ion diffusivity D is small. The linear stability theory by D.P. Barkey²⁴ assumes that electrodes are infinitely far apart and have perfect conductivity relative to the electrolyte, and that the interface is perfectly sharp. Under these conditions, the interface is unstable when the Péclet number is above a critical value of 0.116. This gives the smallest wavelength λ

Equations

$$\frac{\partial C_{Cu}}{\partial t} = -\nabla \cdot \bar{J}_{Cu} (=0) \quad (1)$$

$$J_{Cu} = \bar{u}C_{Cu} - D_{Cu} \nabla C_{Cu} + z_{Cu} C_{Cu} \mu_{Cu} \bar{E} \quad (2)$$

$$\frac{\partial \xi}{\partial t} = M_\xi \left[\kappa_\xi \nabla^2 \xi + \frac{\partial p(\xi)}{\partial \xi} G(C_{M^+}^\alpha, C_{M^+}^\beta) - W \frac{\partial g(\xi)}{\partial \xi} \right] \quad (3)$$

$$\frac{\partial C_{M^+}}{\partial t} = \nabla \cdot \left[D(\xi) H(\xi, C_{M^+}^\alpha, C_{M^+}^\beta) \nabla \left(\ln \frac{C_{M^+}^\beta}{1 - C_{M^+}^\beta} + \frac{z_{M^+} F \phi}{RT} \right) \right] \quad (4)$$

$$\nabla \cdot \epsilon(\xi) \nabla \phi = 0 \quad (5)$$

$$Pe = \frac{u_{int} \lambda}{D} \quad (6)$$

$$i_j(\theta_j) = \frac{C_{Cu^{2+}}}{C_{Cu^{2+}}^\infty} z_j^0 \left[\exp \frac{-\alpha_j F \eta}{RT} - \exp \frac{(1 - \alpha_j) F \eta}{RT} \right] \quad (7)$$

$$\frac{d\theta_a}{dt} = \frac{iV_m}{zF} \kappa \theta_a \quad (8)$$

$$\nabla \bar{\mu}_j = \Delta \mu_j^{\alpha\beta} \nabla p(\xi) + RT \nabla \ln C_j V_m - z_j F \bar{E} + W_j \nabla g(\xi) \quad (9)$$

which will grow for a given plating rate u_{int} and diffusivity D .

Pongsaksawad and Powell extend this theory by calculating the critical Péclet number of a solid cathode as a function of interface thickness, electrode/electrolyte conductivity ratio, and electrode separation/wavelength ratio. They also model a fully liquid system, like liquid aluminum electrolysis in the Hall cell, and show that at low viscosity, flow provides another mechanism to stabilize the interface.

Finally, they extend the model to a ternary system. This model can capture electronically mediated reactions, such as metallothermic reduction. The simulation shown in Figure 6 illustrates the reaction between titanium dichloride and magnesium to produce titanium and magnesium chloride. In this simulation, electrical potential is low at the Mg-MgCl₂ interface where electrons are produced and high at the Ti-TiCl₂ interface where they are consumed.

CEAC

In the last decade, the “Damascene” process of electrodepositing copper²⁵ has supplanted evaporated aluminum for forming the conducting pathways between the individual semiconductor devices of integrated circuits. With an appropriate combination of additives (accelerators, suppressors, and levelers), electrodeposited metals can “superfill” the small (tens of nanometers), high aspect ratio features found in modern integrated circuits without forming voids or seams.

Although traditional leveling models were initially applied to this process, they failed to account for the unique features of bottom-up superfill that make Damascene viable for this application. The process works because the metal is deposited superconformally, filling from the bottom of a feature faster than on the sides or the surface of the wafer, to such a degree that a bump actually forms over the top of a trench or via (known as momentum plating). The curvature enhanced accelerator coverage (CEAC) mechanism has been proposed^{26–29} to explain the phenomenon of electrodeposited superfill. The essence of the model is that when a suppressor, such as polyethylene glycol (PEG), is displaced by an accelerating surfactant such as SPS (Na₂(S(CH₂)₃SO₃)₂), faster

deposition occurs in regions of higher accelerant coverage and that an advancing concave surface will tend to concentrate this accelerant while an advancing convex surface will tend to dilute it. The velocity of the growing interface is directly related to the total current passing through it, which is the sum of the partial currents i_j mediated by each additive j . Each i_j is assumed to depend on the applied overpotential η and the additive surface concentration θ_j through a relation like Equation 7, commonly called the Butler–Volmer equation. $i_j^\circ = i_j^\circ(\theta_j)$ is the exchange current and $\alpha_j = \alpha(\theta_j)$ characterizes the symmetry of the forward and reverse reactions, $C_{\text{Cu}^{2+}}$ is the concentration of cupric ions at the electrode surface and $C_{\text{Cu}^{2+}}^\infty$ is the cupric concentration in the far-field. In its simplest form, the conservation for the accelerant a is governed by Equation 8, where the right-hand side is the key to the mechanism, with concave curvature κ leading to increasing surface coverage of accelerant (inducing even faster growth of the concave surface) and convex κ leading to decreasing surface coverage. The CEAC model has also been extended to treat surface diffusion, adsorption, and finite additive consumption.

The exchange current i° and the reaction symmetry α are determined by fitting voltammetric and chronoamperometric experiments performed on planar electrodes. These parameters are then used, without further adjustment, when modeling filling of features of different aspect ratios. The electrode surface is advanced, using the level set technique, in accordance with the current passed in Equation 7. This model has enjoyed considerable success in predicting desirable superfill versus void and seam formation in the electroplating of copper, as illustrated in Figure 7. The same mechanism has also been found to describe the electrodeposition of silver and gold, as well as the chemical vapor deposition of copper.³⁰

Modeling the Double Layer

When transport in the electrolyte does not control deposition kinetics, phenomena in the double layer create non-ohmic (nonlinear) charge transfer kinetics. G.M. Gouy³¹ and D. Chapman³² undertook the first attempt to model the double layer. They treated the electrode

as an impenetrable boundary with some imposed potential at its surface and assumed that ions in the electrolyte obey a Boltzmann distribution and that the electrostatic potential was coupled to the distribution of charges via Poisson’s equation ($\nabla \cdot \epsilon \nabla \phi = \rho$, where ρ is the local charge density). The result was a prediction for the distribution of ions in the electrolyte, the decay length of the electrostatic potential, and relationships between the applied potential and the surface energy of the electrode, the charge on the surface of the electrode, and the differential capacitance of the charged layers. It is interesting to note that the Gouy and Chapman treatments of the electrochemical interface predate the more widely known Debye–Hückel³³ model of charged interfaces by a decade.

One weakness of the Gouy–Chapman model, corrected by O. Stern,³⁴ was that they assumed ions to be infinitesimal points, allowing them to pack without constraint near the electrode surface. Among other things, this caused the differential capacitance to diverge to infinity as the imposed surface potential (or surface charge) was increased. By accounting for the finite size of the ions, Stern showed that the differential capacitance could be considered as two capacitors in series, one as predicted by Gouy–Chapman at low biases and another of constant capacitance that dominates at high biases, when ions at the surface reach their packing limit.

Although Gouy–Chapman–Stern (GCS) captures the qualitative characteristics of the double layer, it does not account for many of the details of real electrochemical interfaces. This has motivated the development of more sophisticated computational models similar to GCS, but which capture more of the details observed in experimental studies.

Recent density functional treatments, such as those of Z. Tang et al.³⁵, have expanded on the essential elements of the GCS model and demonstrated rich electrocapillary behavior reminiscent of experimental measurements. Like GCS, these density functional models cannot treat electroplating or electrodisolution because the electrode is just a simple abstraction provided as a boundary condi-

tion to the model.

J.E. Guyer et al.^{36,37} noted the many analogies between electrodeposition and solidification, where the phase field method has enjoyed considerable success, and developed a phase field treatment of the electrochemical interface. This treatment considered the same basic physics as the GCS and Tang models, but also allowed for the plating or dissolution of the electrode. They considered four components: cations, anions, solvent, and electrons. All species had the same molar volume, except electrons were assumed to have no molar volume, allowing them to move freely in the electrode without having to displace other species. Although an inert electrochemical interface could be modeled

with three components in this formalism, four are necessary to describe plating or dissolution. All species were assumed to obey ideal solution thermodynamics (equivalent to the Boltzmann distribution assumed in GCS). They included the electrostatic contribution to the total free energy and showed that the phase field gradient energy coefficient and the dielectric constant are completely analogous, one penalizing gradients in the phase field and the other penalizing gradients in the electrostatic potential. They did not similarly penalize gradients in concentration.

The simplest set of assumptions was made, consistent with conserving each species and minimizing free energy, to obtain the governing equations for the

model. In the absence of variations in the dielectric constant, the treatment of the phase field is identical to that used by Shibuta et al.^{4,5} and by Powell et al.⁶⁻¹² Diffusion equations were obtained in the manner of Equation 1, with fluxes defined by $\vec{J}_{e^-} = -M_{e^-} \nabla \bar{\mu}_{e^-}$ for electrons and $\vec{J}_j = -M_j \nabla (\bar{\mu}_j - \bar{\mu}_N)$ for all species other than electrons and species N (chosen arbitrarily). They related the mobilities M_j to the diffusivities D_j and defined gradients of the electrochemical potential of species j by Equation 9.

For each component j , W_j is the energy barrier of the activated state and $\Delta\mu_j^{o\alpha\beta}$ is the standard chemical potential difference between the electrode and electrolyte. V_m is the molar volume. $\Delta\mu_j^{o\alpha\beta}$ depends on the standard state bulk concentrations in each phase and on the Galvani potential $\Delta\phi^o$ (the difference between the internal potential or work function of the electrode and that of the electrolyte). Although really a property of the electrode material and electrolyte chemistry, the Galvani potential is an adjustable parameter in this model that dramatically affects the structure of the double layer.

The model solves the phase field and diffusion equations in conjunction with Poisson's equation. The fundamental difference from GCS or the Tang model is that the same set of equations govern both the electrolyte and the electrode, the difference being that Guyer et al. chose thermodynamic parameters to favor an electrode rich in cations and electrons and an electrolyte rich in solvent, cations, and anions. They consider both a charge-free solvent as a simple model of aqueous solutions (while ignoring the important effects of polar solvent molecules) and a charged solvent system as a simple model of molten salts.

When studying electrode-electrolyte interfaces at open circuit (in equilibrium), Guyer et al. found that sweeping the Galvani potential (effectively changing the electrode material) produced changes in surface energy, surface charge, and differential capacitance that were qualitatively consistent with the electrocapillary theory for sweeping the voltage applied to an inert electrode. [See

[animation on-line.](#)] As seen in Figure 8, however, the detailed predictions are markedly different from the GCS models but bear a striking resemblance to the

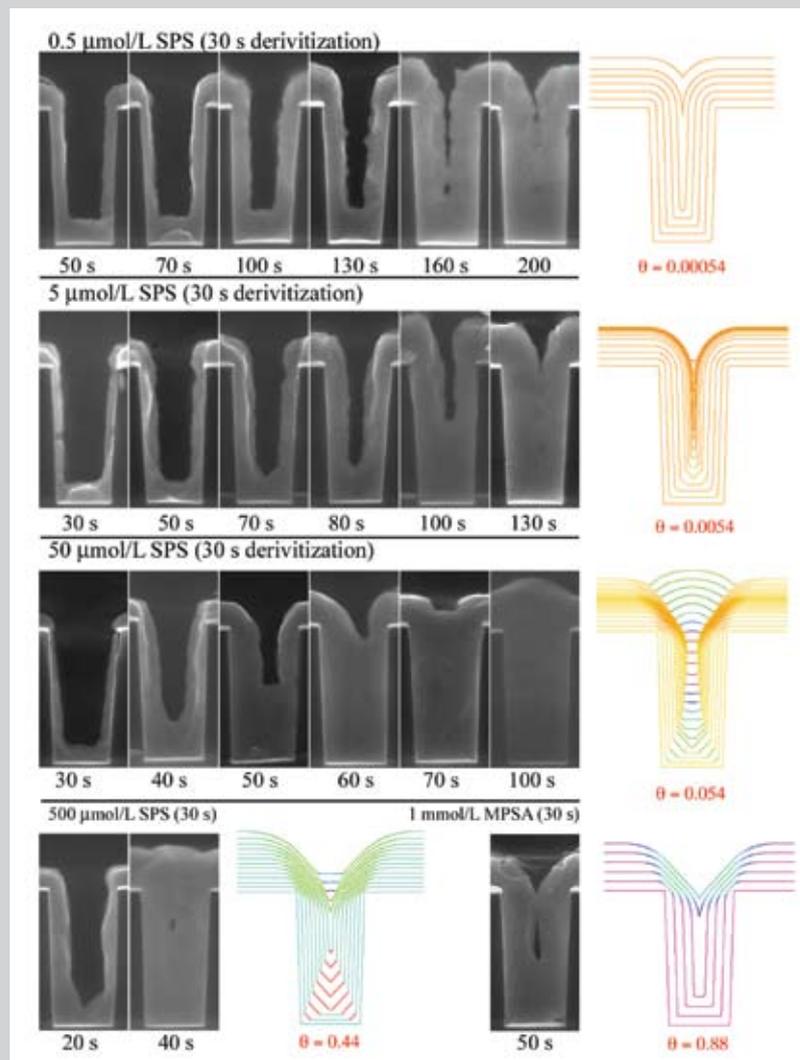


Figure 7. The superfilling of trenches that were pre-treated with catalyst prior to copper plating in a PEG-Cl electrolyte at 0.25 V. The conditions used for electrode derivitization are indicated above the features. Simulations of feature filling for the respective derivitization conditions are shown to the right of the experiments. The contour lines are colorized to reflect the local catalyst coverage.²⁸ [See [animation on-line.](#)]



behavior observed in experimental studies of solid metal electrodes.

On examining moving interfaces (plating or dissolution), Guyer et al. showed that the model yields expected behavior such as limiting current and alloy plating. [See *animation on-line*.] Most dynamic models of electrodeposition, including the level set treatment described, assume that the Butler–Volmer equation governs the relationship between current and overpotential and use it to evolve the shape of the interface. This model assumed a linear relationship between phase evolution rate and driving force, but gave rise to a non-linear relationship between current and overpotential, consistent with the empirical Butler–Volmer relation. This is the power of phase field: simple physical relationships, applied rigorously, give rise to complex phenomena, but without having to hypothesize complex origins.

Although the model is not intrinsically limited to one dimension, higher dimensions have proven computationally intractable without choosing a number of unphysical parameters. Reasons for this include very small Debye length (separation between charged planes in the double layer) requiring very fine spatial resolution, and abrupt changes in concentration of many orders of magnitude in order to capture an intuitively acceptable approximation of a real metal-electrolyte interface (i.e., no water in the electrode, no free electrons in the water). Although not considered in this treatment, the anisotropy of adsorption behavior on different crystallographic surfaces can be incorporated in the thermodynamic derivation of a phase field model.

The phase field treatments of Powell et al. and Shibuta et al. avoid these difficulties (at the loss of some details about the interface) by replacing Poisson's equation with Laplace's and by modeling a different set of concentration variables that do not experience such extreme changes in magnitude. It remains to be seen if the approaches can be successfully merged to model larger systems, in higher dimensions, while retaining the electrocapillary phenomena of the double layer.

Summary

Meso-scale models provide important insights into physical phenomena at the

scale of dendrites and microfabricated features. They are thus useful as design tools for engineers seeking to avoid or utilize spontaneous roughness formed by electrodeposition. Continuum theories can even shed new light on nanometer-scale phenomena such as the electrochemical double layer. However, many of these models require parameters that are very difficult to measure, such as homogeneous free energy at compositions which are not homogeneous, and bonding energies. For these parameters and fundamental understanding at smaller scales, we turn to atomistic models.

ATOMISTIC MODELS

Atomistic and first-principles methods help provide insight into processes that

occur on the atomic or subatomic scale in order to better understand fundamental processes, aid in the design of materials, and estimate parameters for use in other models. For example, they can be used to examine the formation of adlayers at interfaces during electrodeposition and properties of the electrical double layer that forms due to charge separation, and they can be used to calculate materials parameters such as the binding energy of an atom on a surface. These methods provide information about atomic- and electronic-scale phenomena that is unavailable from models on larger length and time scales. However, they can also be limited by small sizes, short times, and the dependence of results on the physical approximations used in the

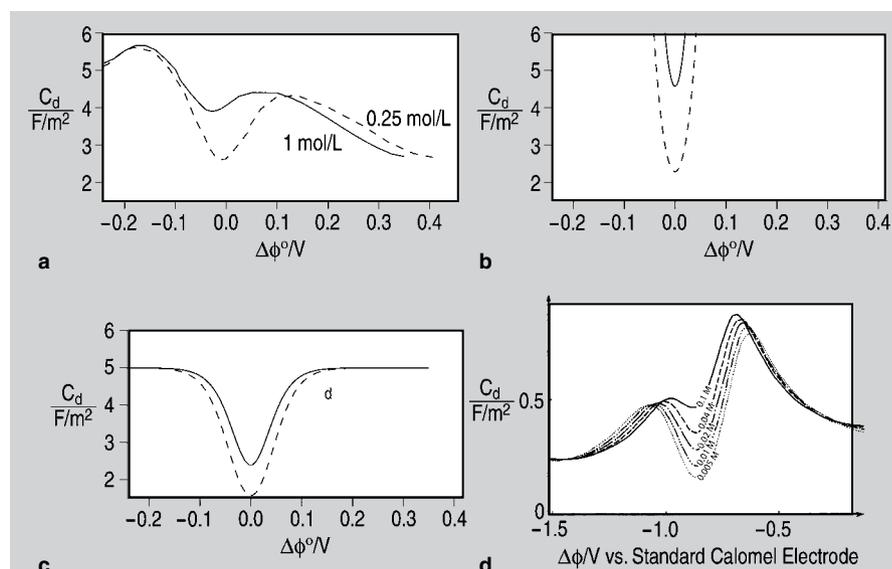


Figure 8. A comparison of the differential capacitance results of Reference 36 with the predictions of sharp interface theories^{31,32,34} and the experimental measurements of Ag(100) electrodes in aqueous solutions of NaF. (Reprinted from Reference 38 with permission from Elsevier.) (a) Guyer et al., (b) Gouy–Chapman, (c) Gouy–Chapman–Stern (d) experiment.

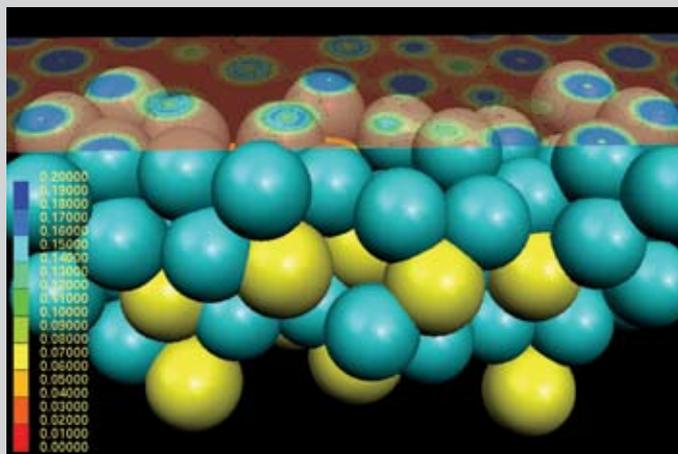


Figure 9. An electron density map of the Ag/Ag₂S/Ag junction system by first principles calculation with schematic atomic models.⁵³ Sky-blue and yellow spheres represent silver and sulfur atoms, respectively.

calculations. The computational methods of interest include molecular simulation techniques such as Monte-Carlo (MC) and molecular dynamics (MD), and electronic structure, or first-principles, methods.

Monte-Carlo simulations are grounded in a statistical-mechanical treatment of particles where system evolution is based on how random moves (such as changes in atomic coordinates) affect the state of the system. Equilibrium (or static) MC methods cannot be associated with real time, but kinetic (or dynamic) MC methods use attempt frequencies of moves to relate the simulation evolution to physical time.³⁹ Classical MD techniques solve Newton's equations of motion to model the evolution of particles (usually atoms) under conditions such as constant temperature.⁴⁰ Since MC moves are not tied to particle trajectories, it is often possible to treat larger systems for longer periods of time than can be achieved with MD, though the two techniques can be used in parallel or in series for some problems. First-principles (or ab-initio) methods use quantum-mechanical descriptions of atoms to calculate materials properties and examine chemical reactions (e.g., Reference 41). First-principles methods provide very detailed information about individual atoms, but the computational cost is high, leading to small system sizes. This section is intended to provide examples of interesting work and is not exhaustive.

To understand the origins of ordered overlayers and surface phase transitions, first-principles and atomistic simulations have been used in combination with experimental methods such as cyclic-voltammetry and chronocoulometry. These systems can be viewed as model systems for the interfaces between electrodes and aqueous electrolytes. A review of the behavior and importance of ordered anion adlayers on metal electrode surfaces can be found in Reference 42. Using kinetic MC and equilibrium MC, the origins of ordered overlayers and surface phase transitions have been examined. For example, N. Garcia-Araez et al. recently compared dynamic MC simulations and mean-field approximations with experimental results to examine the competitive adsorption of hydrogen and bromine on Pt(100), finding that the MC results could adequately model the

system, but that the mean-field approach could not.⁴³ S. Frank and P.A. Rikvold studied how lateral adsorbate diffusion affects first-order phase transitions in a two-dimensional Ising lattice gas model with attractive nearest-neighbor interactions.⁴⁴ Some models have coupled MC simulations with continuum models in order to bridge size and time scales such as in the study of a potential step test in a copper sulfate bath to examine electrodeposition and electrodisolution of copper at an electrode.⁴⁵ Materials parameters used to parameterize the interatomic interactions, such as binding energies between atoms, have been calculated with ab-initio methods and often compared with experimental methods.

While the double layer is a phenomenon of great interest, continuum models provide little insight into the atomic-scale mechanisms at interfaces such as the orientation of the dipolar water molecules and the effect of ions on interfacial structure. Many theoretical and simulation (including MC and MD) studies have examined the double layer (e.g., References 46–50). Recently P. Taboada-Serrano et al. examined mixtures of symmetric and asymmetric electrolytes near discretely charged planar surfaces using MC methods to examine the effects of surface charge distribution and asymmetry in charge and size on the structure of the double layer, finding that the thickness and ionic distribution in the double layer were strongly affected by them.⁵¹ C. Hartnig and M.T.M. Koper used MD to simulate ion transfer reactions of chlorine in water at metal electrodes, where they found that solvent reorganization related to the electron transfer and ion transfer behaved differently—the first was dominated by long-range electrostatics while the latter was influenced by shorter-range solvent effects.⁵²

As mentioned, ab-initio methods have been used to calculate materials parameters (cohesive energies, preferred binding sites, etc.) and to examine electrochemical reactions. The information gained from these methods can then be used to inform higher-level simulations and models for a more complete understanding of electrochemical interfaces. For example, Z.C. Wang et al.⁵³ have been studying the electrical properties of the Ag/Ag₂S/Ag junction nanometer-scale switch mentioned previously. They used

density functional theory and a nonequilibrium Green's function method to calculate current-voltage characteristics, as shown in Figure 9. A. Migani et al. studied halogens on low-index surfaces of transition metals, calculating atomic structure, adsorption energies, vibrational frequencies, and net charges.⁵⁴ While the halogen study was performed in vacuum, with results to be extrapolated to aqueous solutions, C. Taylor et al. studied electrochemical reactions at the Ni(111)/H₂O interface to determine interfacial structure and when water and its activation products are stable.⁵⁵ Further review of work related to aqueous/metal interfaces can be found in Reference 56.

Atomic- and molecular-scale methods have become much more useful for both the design of materials and the fundamental understanding of materials behavior. Coupled with models on higher length scales and compared with experimental results, they can provide a more complete picture of electrochemical behavior.

CONCLUSION

Electrochemistry plays several key roles in metallurgy, including processes for extracting and fabricating metals at all length scales. In terms of extraction, it will likely grow in importance as the price of carbon emissions tips the balance from carbothermic to electrochemical processes in some applications. Models such as those described in this paper will play an increasing role in the rapid design and development of these processes.

Furthermore, these models are useful for studying corrosion and designing a wide range of electrochemical devices. Batteries come to mind here, as do hybrid photo-electric hydrolysis devices for generating hydrogen and electrochemical solar cells. For all of these applications, models can provide understanding and predict behavior to inform intelligent design of new devices and products.

ACKNOWLEDGEMENTS

Adam Powell would like to thank Donald Sadoway and James Warren for discussions that influenced this work, and much of W. Pongsaksawad's and Powell's meso-scale work described here was supported by the National Science Foundation (Award DMI-0457381) and a Royal Thai Government Fellowship.

Yasushi Shibuta would like to thank Prof. Toshio Suzuki, Prof. Shu Yamaguchi, and Mr. Yoshinao Okajima (The University of Tokyo) for their help in modeling and calculations, and MEXT, Japan for financial support of the Grant-in-Aid for Scientific Research on Priority Area "Nanoionics (439)." Chandler A. Becker would like to thank the National Research Council-National Academy of Sciences Postdoctoral Research Associate program for support. We are grateful to Tom Moffat and Daniel Wheeler for many helpful comments on this manuscript.

References

- Max Planck, "Ueber die Erregung von Electricit"at und Wärme in Electrolyten," *Ann. Physik. u. Chem.*, 39 (1890), p. 161.
- Elsyca, www.elsyca.com/
- The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.
- Y. Shibuta, Y. Okajima, and T. Suzuki, "A Phase-Field Simulation of Bridge Formation Process in a Nanometer-Scale Switch," *Scripta Materialia*, 55 (2006), pp. 1095–1098.
- Y. Okajima, Y. Shibuta, and T. Suzuki, "Phase-Field Simulation of an Electrodeposition Process," *Electrochemistry and Thermodynamics on Materials Processing for Sustainable Production: Masuko Symposium*, ed. Shu Yamaguchi (Tokyo: The University of Tokyo, 2006), pp. 829–834.
- David Dussault, "A Diffuse Interface Model of Transport Limited Electrochemistry in Two-Phase Fluid Systems with Application to Steelmaking" (S.M. Thesis, Massachusetts Institute of Technology, Department of Mechanical Engineering, January 2002).
- David Dussault and Adam C. Powell, "Phase Field Modeling of Electrolysis in a Slag or Molten Salt," *Proc. Mills Symp.* (London: The Institute of Materials, 2002), pp. 359–371.
- Adam C. Powell and David Dussault, "Detailed Mathematical Modeling of Liquid Metal Streamer Formation and Breakup," *Metalurgical and Materials Processing Principles and Technologies (Yazawa International Symposium)-Vol. 3: Aqueous and Electrochemical Processing*, ed. F. Kongoli et al. (Warrendale, PA: TMS, 2003), pp. 235–250.
- Wanida Pongsaksawad, *Numerical Modeling of Interface Dynamics and Transport Phenomena in Transport-Limited Electrolysis Processes* (Ph.D. Thesis, Massachusetts Institute of Technology, Department of Materials Science and Engineering, May 2006).
- Adam C. Powell, Wanida Pongsaksawad, and Uday B. Pal, "Phase Field Modeling of Phase Boundary Shape and Topology Changes Due to Electrochemical Reactions in Solid and Liquid Systems," *Advanced Processing of Metals and Materials Vol. 3: Thermo and Physicochemical Principles: Special Materials; Aqueous and Electrochemical Processing* (Warrendale, PA: TMS, 2006), pp. 623–640.
- Adam C. Powell, Wanida Pongsaksawad, and Uday B. Pal, "Phase Field Modeling of Phase Boundary Shape and Topology Changes Due to Electrochemical Reactions in Solid and Liquid Systems," *Electrochemistry and Thermodynamics on Materials Processing for Sustainable Production: Masuko Symposium*, ed. Shu Yamaguchi (Tokyo: University of Tokyo, November 2006), pp. 793–814.
- Wanida Pongsaksawad, Adam C. Powell, and David Dussault, "Phase Field Modeling of Transport-Limited Electrolysis in Solid and Liquid States," *J. Echem. Soc.*, 154 (6) (June 2007).
- S.G. Kim, W.T. Kim, and T. Suzuki, "Phase-Field Model for Binary Alloys," *Phys. Rev. E*, 60 (6) (1999), pp. 7186–7197.
- K. Terabe et al., "Formation and Disappearance of a Nanoscale Silver Cluster Realized by Solid Electrochemical Reaction," *J. Appl. Phys.*, 91 (12) (2002), pp. 10110–10114.
- T. Sakamoto et al., "Nanometer-Scale Switches Using Copper Sulfide," *Appl. Phys. Lett.*, 82 (18) (2003), pp. 3032–3034.
- Y. Sawada, A. Dougherty, and J.P. Gollub, "Dendritic and Fractal Patterns in Electrolytic Metal Deposits," *Phys. Rev. Lett.*, 56 (12) (1986), pp. 1260–1263.
- F. Sagues, M.Q. Lopez-Salvans, and J. Claret, "Growth and Forms in Quasi-Two-Dimensional Electrocrystallization," *Physics Reports*, 337 (2000), pp. 97–115.
- G. Gonzalez et al., "Viscosity Effects in Thin-Layer Electrodeposition," *Journal of the Electrochemical Society*, 148 (7) (2001), pp. C479–C487.
- C. Leger, J. Elezgaray, and F. Argoul, "Internal Structure of Dense Electrodeposits," *Phys. Rev. E*, 61 (5) (2000), pp. 5452–5463.
- M. Matsushita et al., "Fractal Structure of Zinc Metal Leaves Grown by Electrodeposition," *Phys. Rev. Lett.*, 53 (3) (1984), pp. 286–289.
- J. Elezgaray, C. Leger, and F. Argoul, "Dense Branching Morphology in Electrodeposition Experiments: Characterization and Mean-Field Modeling," *Phys. Rev. Lett.*, 84 (14) (2000), pp. 3129–3132.
- M.O. Bernard, M. Plapp, and J.F. Gouyet, "Mean-Field Kinetic Lattice Gas Model of Electrochemical Cells," *Phys. Rev. E*, 68 (2003), p. 011604.
- Y. Shibuta, Y. Okajima, and T. Suzuki, in preparation.
- D.P. Barkey, R.H. Muller, and C.W. Tobias, "Roughness Development in Metal Electrodeposition: II. Stability Theory," *J. Electrochem. Soc.*, 136 (1989), pp. 2207–2214.
- P.C. Andricacos et al., "Damascene Copper Electroplating for Chip Interconnections," *IBM J. Res. Develop.*, 42 (5) (1998), pp. 567–574.
- D. Josell et al., "Superconformal Electrodeposition in Submicron Features," *Phys. Rev. Lett.*, 87 (1) (2001), p. 016102.
- D. Wheeler, D. Josell, and T.P. Moffat, "Modeling Superconformal Electrodeposition Using the Level Set Method," *J. Electrochem. Soc.*, 150 (5) (2003), pp. C302–C310.
- T.P. Moffat, D. Wheeler, and D. Josell, "Superfilling and the Curvature Enhanced Accelerator Coverage Mechanism," *Interface* (Winter 2004), pp. 46–52.
- T.P. Moffat et al., "Superconformal Film Growth: Mechanism and Quantification," *IBM J. Res. Develop.*, 49 (1) (2005), pp. 19–36.
- D. Josell, D. Wheeler, and T.P. Moffat, "Superconformal Deposition by Surfactant-Catalyzed Chemical Vapor Deposition," *Electrochemical and Solid State Letters*, 5 (3) (2002), pp. C44–C47.
- G.M. Gouy, "Sur la Constitution de la Charge Électrique à la Surface d'un Électrolyte," *Compt. Rend.*, 149 (1910), p. 654.
- David Leonard Chapman, "A Contribution to the Theory of Electrocapillarity," *Phil. Mag.*, 25 (1913), p. 475.
- P. Debye and E. Hückel, "Zur Theorie der Elektrolyte I. Gefrierpunktserniedrigung und verwandte Erscheinungen," *Physik. Z.*, 24 (1923), pp. 185–206.
- Otto Stern, "Zur Theorie der Elektrolytischen Doppelschicht," *Z. Elektrochem.*, 30 (1924), p. 508.
- Zixiang Tang, L.E. Scriven, and H.T. Davis, "A Three-Component Model of the Electrical Double Layer," *J. Chem. Phys.*, 97 (1992), pp. 494–503.
- J.E. Guyer et al., "Phase Field Modeling of Electrochemistry I: Equilibrium," *Phys. Rev. E*, 69 (2004), p. 021603.
- J.E. Guyer et al., "Phase Field Modeling of Electrochemistry II: Kinetics," *Phys. Rev. E*, 69 (2004), p. 021604.
- G. Valette, "Double Layer on Silver Single Crystal Electrodes in Contact with Electrolytes Having Anions Which are Slightly Specifically Adsorbed Part II. The (100) Face," *J. Electroanal. Chem.*, 138 (1982), pp. 37–54.
- M.E.J. Newman and G.T. Barkema, *Monte Carlo Methods in Statistical Physics* (Oxford, U.K.: Clarendon Press, 1999).
- D.C. Rapaport, *The Art of Molecular Dynamics Simulation*, second edition (Cambridge, U.K.: Cambridge University Press, Cambridge, 2004).
- D.G. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford, U.K.: Clarendon Press, 1995).
- O.M. Magnussen, "Ordered Anion Adlayers on Metal Electrode Surfaces," *Chem. Rev.*, 102 (2002), pp. 679–725.
- N. Garcia-Araez et al., "Competitive Adsorption of Hydrogen and Bromide on Pt(100): Mean-Field Approximation vs. Monte Carlo Simulations," *J. Electroanalytical Chem.*, 588 (2006), pp. 1–14.
- S. Frank and P.A. Rikvold, "Kinetic Monte Carlo Simulations of Electrodeposition: Crossover from Continuous to Instantaneous Homogeneous Nucleation within Avrami's Law," *Surf. Sci.*, 600 (2006), pp. 2470–2487.
- A. Saedi, "A Study on Mutual Interaction between Atomistic and Macroscopic Phenomena during Electrochemical Processes Using Coupled Finite Difference–Kinetic Monte Carlo Model: Application to Potential Step Test in Simple Copper Sulfate Bath," *J. Electroanalytical Chem.*, 588 (2006), pp. 267–284.
- R. Guidelli, "Recent Developments in Models for the Interface between a Metal and an Aqueous Solution," *Electrochimica Acta*, 45 (2000), pp. 2317–2338.
- W.R. Fawcett and T.G. Smagala, "New Developments in the Theory of the Diffuse Double Layer," *Langmuir*, 22 (2006), pp. 10635–10642.
- E. Spohr, "Some Recent Trends in Computer Simulations of Aqueous Double Layers," *Electrochimica Acta*, 49 (2003), pp. 23–27.
- R.R. Netz, "Theoretical Approaches to Charged Surfaces," *J. Phys. -Cond. Matter*, 16 (2004), pp. S2353–S2368.
- M.T.M. Koper, "Combining Experiment and Theory for Understanding Electrocatalysis," *J. Electroanalytical Chem.*, 574 (2005), pp. 375–386.
- P. Taboada-Serrano, S. Yiacoumi, and C. Tsouris, "Behavior of Mixtures of Symmetric and Asymmetric Electrolytes Near Discretely Charged Planar Surfaces: A Monte Carlo Study," *J. Chem. Phys.*, 123 (2005), p. 054703.
- C. Hartnig and M.T.M. Koper, "Molecular Dynamics Simulation of Solvent Reorganization in Ion Transfer Reactions near a Smooth and Corrugated Surface," *J. Phys. Chem. B*, 108 (2004), pp. 3824–3827.
- Z.C. Wang et al., in preparation.
- A. Migani and F. Illas, "A Systematic Study of the Structure and Bonding of Halogens on Low-Index Transition Metal Surfaces," *J. Phys. Chem. B*, 110 (2006), pp. 11894–11906.
- C. Taylor, R.G. Kelly, and M. Neurock, "First-Principles Calculations of the Electrochemical Reactions of Water at an Immersed Ni(111)/H₂O Interface," *J. Electrochemical Soc.*, 153 (2006), pp. E207–E214.
- C.D. Taylor and M. Neurock, "Theoretical Insights into the Structure and Reactivity of the Aqueous/Metal Interface," *Current Opinion in Solid State and Materials Science*, 9 (2005), pp. 49–65.

Adam C. Powell IV is managing engineer at Veryst Engineering LLC, 47A Kearney Rd., Needham, MA 02494-2503, USA. Yasushi Shibuta is an assistant professor at the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. Jonathan Guyer and Chandler A. Becker are materials research engineers at the National Institute of Standards and Technology, Gaithersburg, MD 20899, USA. Dr. Powell can be reached at (781) 433-0433, ext. 12; fax (781) 433-0933; e-mail apowell@veryst.com.