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Parameter Sensitivity Analysis of Monte Carlo Simulations of Copper Electrodeposition with Multiple Additives

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Monte Carlo simulations are typically characterized by a large number of unknown parameters, many of which are difficult to obtain experimentally. Parameter sensitivity analysis can be used to quantify the effect of the unknown parameters. This information can be used to decide which parameters should be optimized or determined more accurately through further experimental or simulation studies. The parameter sensitivity analysis for Monte Carlo simulations is complicated by the stochastic nature of the simulations, making it difficult to isolate responses from background noise. In the present study, a stochastic optimization problem was formulated and solved, which produced a first-order accurate equation for computing the sensitivities that optimally accounts for the simulation noise. This new approach for computing sensitivities for stochastic simulations significantly increases the accuracy over existing methods. The approach is illustrated by application to a Monte Carlo code that simulates copper electrodeposition from a sulfate bath onto a flat copper substrate in the presence of a three-additive system of chloride, polyethylene glycol, and mercapto propane sulfonic acid.
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Copper electrodeposition with complex additive systems is used to fill on-chip nanoscale trenches. In this application, the product quality is determined by events at the molecular scale that influence surface roughness, morphology, and shape evolution phenomana that span multiple time and length scales. Therefore, traditional continuum models are inadequate for capturing the effect of near-surface small-scale events on the product quality. Noncontinuum methods, such as Monte Carlo, are appropriate for simulating these near-surface events, but often require the specification of large numbers of physical parameters. Obtaining physical parameters from *ab initio* calculations or direct experiments is not usually feasible for complex electrochemical systems. Furthermore, noncontinuum methods are computationally intense, which poses problems in performing parameter assessment techniques that explore large regions of parameter space to attain the unknown parameters.

Parameter sensitivity analysis can be used to decide which parameters should be optimized or determined more accurately through further modeling or experimental studies.[1,2] Here, parameter sensitivity analysis was used to quantify the effect of unknown kinetic parameters on the surface roughness and additive entrapment in the deposit. The parameter sensitivities were computed using the finite difference method, which involved running multiple simulations, in which each simulation corresponded to a perturbed set of parameters.[3,4] High throughput computing tools are used to perform parameter sensitivity analysis of Monte Carlo simulations in this study. Due to their computationally intense nature and the need to run multiple sets of simulations with the same parameters to average the results, high throughput computing was essential to performing parameter assessment with noncontinuum simulation codes. High throughput computing can lead to more efficient pathways for evaluating hypotheses of complex additive mechanisms.

Parameter sensitivity analysis determines the attributes of certain additives that have the greatest influence on the deposit morphology evolution and the quality of the deposit. Once these additive attributes are identified, it is possible to tailor additive systems to have the most desirable qualities for a specific application (*i.e.*, develop optimal additive systems for a specific application).

The parameter sensitivity approach was applied to a kinetic Monte Carlo code that simulates copper electrodeposition from a sulfate bath onto a flat copper substrate in the presence of a three-additive system of chloride (Cl^-), polyethylene glycol (PEG), and mercapto propane sulfonic acid (MPSA). In the experimental system, copper electrodeposition with the PEG-Cl-MPSA additive system resulted in an extremely flat deposit. 3,3′-Dipropanesulfonic acid (DDDS), the oxidized form of MPSA, is a brightener that causes grain refinement during the deposition process, which with PEG-Cl, leads to the flat surface morphology.[5] In the trench geometry, copper electrodeposition with this additive system results in superfilling of the trench.[6]

Derivation of the Sensitivity Equations

Twenty-two independent parameters in the multiple additive mechanism were perturbed both positive and negative of their base case values to determine the effect on the outputs. The size of the perturbation should be selected with care when determining the effect of the parameter on the outputs. Monte Carlo simulations of realistic mechanisms typically have significant stochastic fluctuations in their outputs. The parameter perturbations have to be large enough to isolate the effect of the parameter perturbation from the simulation noise. In the case at hand, it was found that the perturbation of +100% and −50% of the parameter made it possible to distinguish most output responses from the simulation noise. At these perturbation values, it was possible to discern the effect of the perturbation from the simulation noise for many output parameters, provided that averages from multiple sets of simulations were used.

The sensitivities were first computed using first- and second-order accurate finite difference expressions,[2,3] which were rederived to account for the size of the positive and negative perturbation values used in this study. The first-order accurate backward difference formula is

$$f'(x) = \left(\frac{2}{h}\right)\left[f(x) - f\left(x - \frac{1}{2}h\right)\right] \quad [1]$$

where $f(x)$ is the simulation output of interest, and x is a parameter that is perturbed. The first-order accurate forward difference formula is

$$f'(x) = \left(\frac{1}{h}\right)[f(x + h) - f(x)] \quad [2]$$

Combining Eq. 9 and 10 gives the first-order accurate central difference formula

$$f'(x) = \left(\frac{2}{3h}\right)\left[f(x + h) - f\left(x - \frac{1}{2}h\right)\right] \quad [3]$$

The second-order accurate central difference formula was derived using Lagrange interpolation

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$$f'(x) = \left(\frac{1}{3h}\right)\left[f(x + h) + 3f(x) - 4f\left(x - \frac{1}{2}h\right)\right] \quad [4]$$

Although Eq. 1-4 are adequate for deterministic/continuum models that do not contain significant simulation noise, they do not account for the effect of the significant simulation noise typically encountered in Monte Carlo simulations. An optimized first-order accurate sensitivity equation was derived to minimize the variance in the estimated derivative (sensitivity). In the derivation that follows, it is assumed that the random fluctuations in the simulations are independent for each simulation and that the fluctuations in each output of the simulations can be represented by an additive stochastic error term, with equal variance for all simulations. Then each simulation output of interest, $\hat{f}(x)$, is composed of a deterministic component and a stochastic error component, $\varepsilon_{f(x)}$. Therefore, the outputs for the positive perturbation, base case, and negative perturbation simulations, can be written as

$$\hat{f}(x + h) = \varepsilon_{f(x+h)} + f(x) + hf'(x) + \frac{h^2}{2}f''(x) + \ldots \quad [5]$$

$$\hat{f}(x) = \varepsilon_{f(x)} + f(x) \quad [6]$$

$$\hat{f}\left(x - \frac{h}{2}\right) = \varepsilon_{f(x-h/2)} + f(x) - \frac{h}{2}f'(x) + \frac{h^2}{8}f''(x) + \ldots \quad [7]$$

Then the estimate of the derivative, $\hat{f}'(x)$, can be written as a function of the three simulation outputs

$$\hat{f}'(x) = \alpha\hat{f}(x + h) + \beta\hat{f}(x) + \gamma\hat{f}\left(x - \frac{h}{2}\right) \quad [8]$$

where α, β, and γ are constants. Substitution of Eq. 5-7 into Eq. 8 gives

$$\hat{f}'(x) = [\alpha\varepsilon_{f(x+h)} + \beta\varepsilon_{f(x)} + \gamma\varepsilon_{f(x-h/2)}] + [\alpha + \beta + \gamma]f(x) + \left[\alpha h - \frac{\gamma h}{2}\right]f'(x) + \left[\frac{\alpha h^2}{2} + \frac{\gamma h^2}{8}\right]f''(x) + \ldots \quad [9]$$

Thus the expected value of $\hat{f}'(x)$ is

$$E[\hat{f}'(x)] = [\alpha + \beta + \gamma]f(x) + \left[\alpha h - \frac{\gamma h}{2}\right]f'(x) + \left[\frac{\alpha h^2}{2} + \frac{\gamma h^2}{8}\right]f''(x) + \ldots \quad [10]$$

and the variance of $\hat{f}'(x)$ is

$$V[\hat{f}'(x)] = \alpha^2 V(\varepsilon_{f(x+h)}) + \beta^2 V(\varepsilon_{f(x)}) + \gamma^2 V(\varepsilon_{f(x-h/2)}) \quad [11]$$

Since it is assumed that the variance in the stochastic error terms is the same for all simulations (this assumption has been confirmed to be true in all Monte Carlo simulations for which we have applied this approach), $V(\varepsilon_{f(x+h)}) = V(\varepsilon_{f(x)}) = V(\varepsilon_{f(x-h/2)})$, Eq. 11 reduces to

$$V[\hat{f}'(x)] = [\alpha^2 + \beta^2 + \gamma^2]V(\varepsilon_{f(x)}) \quad [12]$$

The optimization problem that minimizes the variation of the estimate for the derivative is then

$$\min_{\alpha,\beta,\gamma}(\alpha^2 + \beta^2 + \gamma^2) \quad [13]$$

Table I. Variances of finite difference expressions for parameter sensitivities (under the assumption that the variance of the stochastic error terms are the same for all simulations).

Variance	Expression
Eq. 9	$(8/h^2)V(\varepsilon_{f(x)})$
Eq. 10	$(2/h^2)V(\varepsilon_{f(x)})$
Eq. 11	$(8/9h^2)V(\varepsilon_{f(x)})$
Eq. 12	$(26/9h^2)V(\varepsilon_{f(x)})$
Eq. 24	$(6/7h^2)V(\varepsilon_{f(x)})$

subject to the constraint that any bias terms are not a function of $f(x)$ or $f'(x)$, so that the resulting sensitivity equation is first-order accurate. This approach is appropriate when the magnitude of the stochastic noise in the simulation output of interest is significantly larger than the higher order terms in the series expansion of the deterministic component of the simulation output. The constraint of having first-order accuracy for the deterministic component of the simulation output implies that

$$\alpha + \beta + \gamma = 0 \quad [14]$$

$$\left(\alpha - \frac{\gamma}{2}\right)h = 1 \quad [15]$$

These equations are solved to obtain equations for α and β in terms of γ, which are substituted into Eq. 12 and the coefficient $\alpha^2 + \beta^2 + \gamma^2$ is minimized (*i.e.*, compute the derivative with respect to γ and set it equal to zero). This gives $\alpha = 5/7h$, $\beta = -1/7h$, and $\gamma = -4/7h$. The resulting sensitivity equation is

$$f'(x) = \left(\frac{1}{7h}\right)\left(5\mathrm{f(x + h)} - \mathrm{f(x)} - 4\mathrm{f}\left(\mathrm{x} - \frac{1}{2}\mathrm{h}\right)\right) \quad [16]$$

It is instructive to compare the accuracy of expression 16 for computing parameter sensitivities compared to the other Eq. 1-4. Recall an assumption in deriving expression 16 is that the stochastic term is much larger than the higher order deterministic terms in the series expansion. Hence the accuracy of the expressions can be compared in terms of their variances, which are reported in Table I. The accuracy can vary by an order-of-magnitude between finite difference expressions (compare Eq. 1 and 16). Although textbooks and papers on finite differences and parameter sensitivity calculations[2-4] indicate that the higher order expression should be more accurate, the variance for the second-order expression is more than three times larger than the variance of the optimal first-order expression (16). The reason for the apparent discrepancy is that existing papers and books on these subjects[2-4] implicitly assume that the higher order terms are larger than any stochastic noise terms, which is not true for many, perhaps most, stochastic simulation codes. Equation 16 gives more accurate parameter sensitivities when applied to simulation codes with significant stochastic fluctuations, as shown below in the results and discussion section. Note also the strong dependence of the accuracy of the parameter sensitivities to the step size, h. This implies that, for highly stochastic simulation outputs, the step size may have to be large to counteract the deleterious effect of the noise. Also, additional averaging of simulation outputs may be necessary as shown in the example below to reduce the effect of the noise on the accuracy of the computed parameter sensitivities.

When the step size is large, as it is here, the higher order terms can become significant. There is not necessarily a drawback in using large step sizes, since the magnitudes of the parameters in Monte Carlo simulation are so poorly known that it is often of more interest to know the effect on the simulation outputs of large changes in parameters rather than small changes. It is much more valuable to have statistically reliable estimates of the changes in the simulation outputs to changes in the simulation parameters than it is to have statistically unrealiable sensitivities computed from small enough

step sizes that the higher order terms are nearly zero. Also, in early parameter sensitivity studies, such as conducted here, order-of-magnitude effects are more of interest, in which case the possibility of nonzero higher order terms are less important.

Additive Mechanism

It was the goal here neither to evaluate existing mechanisms, nor to propose new mechanisms. The mechanism was selected to illustrate the utility of the parameter sensitivity tools in identifying the most sensitive physical parameters of additives in complex additive systems. Here a three-additive mechanism was used and the steps in the three-additive mechanism were developed from the literature or are inferred by us if the literature was unclear about the exact mechanism steps. Currently there is much debate about the steps in additive mechanisms. With the foregoing system, we wish to show that noncontinuum simulations, performed in conjunction with high-throughput computing, are useful in analyzing complex systems, even with incomplete knowledge of the physical parameters.

In the present parameter sensitivity study, simulations are performed for copper electrodeposition on a flat surface with an electrolyte containing 0.5 M Cu^{2+}, 1 mM Cl^-, 1 mM PEG, and 4 mM MPSA and operating under galvanostatic control at -20 mA/cm^2. In previous work, small-scale experimental data of flat surface copper electrodeposition with additives combined with hypothesis additive mechanisms from the literature were encoded in Monte Carlo simulations.[7] The experiments were performed on a flat Cu(111) surface to eliminate the geometry as a complicating factor in the experiments, making it easier to develop hypothesis mechanisms.

The mechanism used in the present simulations assumed that at the beginning of the experiment, when the system was at the open circuit potential (OCP), there was an ordered layer of Cl^- on the surface.[8] The PEG was held at the electrode surface by the Cl^-.[6,8,9] The Cl^- was assumed to be necessary for the adsorption of PEG on metal surfaces.[10] It has been proposed that the PEG is complexed with Cu^+,[9] but this has been a subject of debate and is not included in the mechanism used here. When the MPSA was added to the deposition bath, most of it was immediately oxidized to DDDS.[11] The DDDS was then oxidized by cupric ions to form a cuprous-thiolate complex.[11]

After the system was held at the OCP, a cathodic current was applied. The PEG-Cl film hinders copper deposition by blocking access to surface sites.[6,8-10] However, when a cathodic current was applied in the current region where copper deposition occurs, the PEG began to leave the surface, making it more facile for copper deposition to occur.[6,10] Charge transfer through the PEG-Cl film was unlikely because the film was thick, meaning that a transport mechanism through the film was required for copper deposition to occur.[8] Therefore, cupric ions reach the cathode surface by traveling through nucleated holes in the PEG-Cl film.[12] Furthermore, only a minimal amount of PEG was expected to be incorporated into the copper deposit.[6] It was assumed in the mechanism that the PEG and Cl^- would exist in the bulk solution after they left the surface and would not break down to some other compound. Some authors[6,9] suggest that the PEG-Cl film breaks down at cathodic potentials due to the reduction of the adsorbed complex or the potential induced disruption of the Cl^- layer, but this phenomenon was not included in the current mechanism as it has been the subject of some debate.[8]

After the cupric ions adsorbed onto the electrode surface, they underwent charge transfer to become cuprous ions, which surface diffuse and compete with PEG for adsorption sites on the electrode surface.[10] It was assumed in the mechanism that the cuprous-thiolate complex competes with PEG and cuprous ions for the same surface sites. It was further assumed that the cuprous-thiolate complex was formed outside the Monte Carlo domain and diffused through the Monte Carlo domain where it adsorbed. Experiments have been interpreted to suggest that peaks of copper will grow through the holes in the adsorbed PEG-Cl film.[13] The cuprous-thiolate complex, which existed in low concentrations in the bulk solution, was mass-transfer limited, and adsorbed at sites of high local current density (*i.e.*, the peaks of copper).[5] The cuprous-thiolate complex reacted with cuprous ions at the surface to reform DDDS. The DDDS acted as a blocker to shut off the peaks, thereby reducing the high local current density. The DDDS was not allowed to desorb, but remained at the surface, where it could regenerate the cuprous-thiolate complex. Adsorbed cupric ions that contacted the DDDS could react with it to generate the cuprous-thiolate complex, which was permitted to diffuse from the surface.

Description of Numerical Programs

Monte Carlo code.—Numerical simulations of electrochemical deposition of a copper blanket film onto a featureless flat copper surface were carried out. To simulate the effect of additives on surface roughness a kinetic Monte Carlo method[14] was used since traditional continuum codes are not convenient for simulating roughness evolution. The roughness was characterized by scaling analysis of the interface width. Two exponents, α and β, characterize the spatial and temporal evolution of the surface roughness, respectively.[15] The spatial scaling exponent, α, was determined by computing the slope of the initial points in a plot of the surface roughness as a function of distance across the surface. The temporal scaling exponent, β, was determined by computing the slope of a log plot of saturation roughness, which is the limit of the roughness over large distances across the surface, as a function of time.

In pristine systems, scaling exponents are obtained from limits which can be characteristic of various growth phenomena. The difficulty in obtaining exponents from asymptotic limits is that there needs to be data collected over a very broad range of parameter space. In this work, Monte Carlo simulations were performed over as broad of a range of parameter space as could be made experimentally. This work is not concerned with reaching asymptotic scaling exponents and cross-over effects where multiple growth modes can arise.

The Monte Carlo code described the pseudo-molecular scale with a cubic lattice, whose blocks (or ''particles'') in the simulation space represented clusters of molecules of a given species in the deposition bath. Blocks were assumed to be homogeneous in both phase and composition. This ''pseudoparticle'' approach has been used in other fields.[16-18] The block size used for simulations in this study was 100 nm. The size of the Monte Carlo domain used here was 50 blocks wide, 50 blocks high, and 50 blocks deep.

The Monte Carlo code is coupled to a 1-D continuum code that simulates diffusion in the diffusion boundary layer above the Monte Carlo domain. The continuum code provides fluxes of copper and additives into the Monte Carlo domain. The diffusion boundary layer thickness is set to 50 μm in this study.

Computational requirements.—Condor,[19] a high throughput computing environment, is advantageous for studies where large, computationally intense sweeps of parameter space are required. The Condor system seeks unused computers in a Condor flock and sends jobs to these computers. When the owner of the computer returns to use it, the job is moved from that computer to another computer. The Linux-based Condor flock, where most of the simulations ran, is located at the University of Wisconsin at Madison and contains approximately 660 computers. Many of the computers on the Condor flock are 550 MHz Pentium III Xeon processors with 128 MB to 1 GB RAM.

The simulations performed here consisted of 45 simulations per random seed number. These simulations consisted of a base-case simulation and a positive and negative perturbation simulation for each of the 22 independent parameters analyzed. The independent parameters perturbed are listed in Table II. Identical sets of simulations were performed with 32 random seed numbers. Each simulation took an average of 64 h to complete per simulation and 1440 total simulations were performed. The total simulation time was approximately 92,547 h (or about 10.6 years if run sequentially on one computer). One set of 45 simulations typically required about six days to complete once they started running. Approximately 200

Table II. Physical parameter data used in the three-additive mechanism, with corresponding reactions and descriptions.

Parameter number	Reaction	Parameter description	Base case value
1	$Cu^{2+} + e^- \rightarrow Cu^+$	Reaction rate constant	150 nm/s
2	$Cu^{2+} + e^- \rightarrow Cu^+$	Charge transfer coefficient	0.339
3	$Cu^+ + e^- \rightarrow Cu$	Reaction rate constant	2×10^4 nm/s
4	$Cu^+ + e^- \rightarrow Cu$	Charge transfer coefficient	−0.40
5	$Cu^{2+} \rightarrow Cu^{2+}$	Bulk diffusion coefficient	6×10^8 nm^2/s
6	$Cu^+ \rightarrow Cu^+$	Surface diffusion coefficient	2×10^8 nm^2/s
7	Cu(I)-thiolate → Cu(I)-thiolate	Bulk diffusion coefficient	6×10^8 nm^2/s
8	Cu(I)-thiolate → Cu(I)-thiolate (1)	Adsorption reaction rate coefficient	5×10^2 nm/s
9	Cu(I)-thiolate (1) → Cu^+ + DDDS	Reaction rate constant	5×10^3 nm/s
10	DDDS + Cu^{2+} → Cu(I)-thiolate	Reaction rate constant	1×10^4 nm/s
11	PEG-Cl → PEG-Cl(1)	Desorption rate constant (in presence of Cu^{2+})	10 nm/s
12	PEG-Cl(1) → PEG-Cl(1)	Bulk diffusion coefficient	1×10^5 nm^2/s
13	PEG-Cl → PEG-Cl(1)	Desorption rate constant	0.5 nm/s
14	PEG-Cl(1) → PEG-Cl	Adsorption rate constant	50 nm/s
15	Cu(s)	Broken face energy barrier	-0.5×10^{-21} J/(molecule K)
16	Cu(s)	New face energy barrier	0.5×10^{-21} J/(molecule K)
17	Cu(s)	Step energy barrier	-1.5×10^{-20} J/(molecule K)
18	Initial substrate	Broken face energy barrier	-0.5×10^{-21} J/(molecule K)
19	Initial substrate	New face energy barrier	0.5×10^{-21} J/(molecule K)
20	Initial substrate	Step energy barrier	-1.5×10^{-20} J/(molecule K)
21	$Cu^+ + e^- \rightarrow$ Cu on Cu(s)	Modified charge transfer coefficient	0.2
22	$Cu^+ + e^- \rightarrow$ Cu on initial substrate	Modified charge transfer coefficient	0.2

simulations ran on the Condor system at a time. Automation of the parameter sensitivity routines, in conjunction with the Linux-based Condor system, was key to managing the large number of simulations required for this study.

Results and Discussion

Averaging was necessary due to the significant stochastic fluctuations in the simulation outputs. It was assumed that the stochastic noise terms were normally distributed, which was confirmed in Monte Carlo simulations for the particular system under investigation. Parameter sensitivities were computed for each set of 32 identical simulations, averaged, and the standard error (which was computed as the standard deviation divided by the square root of the number of simulations) was computed.

In this analysis, hypothesis testing was performed to determine whether or not the sign of the sensitivity was known with confidence. The null hypothesis used here was that the sensitivity was zero. A two-sided t test with $n - 1$ degrees of freedom was then performed to test the null hypothesis. The sensitivities were deemed statistically significant if the p value (presented in percentages) was at least 90% (approximately two standard deviations) away from the mean. If a sensitivity was nonzero and had a p value greater than 90%, this implies that the tail probability was less than 10% and we were quite confident of the sign of the sensitivity.

The parameter sensitivities computed with Eq. 24 for 32 averaged sets of simulations are shown in Table III. In this table the italicized cells are considered to be statistically significant results. Here, 40 sensitivities were statistically significant. For each output variable there were usually one or two sensitivities that were much larger than the others that are statistically significant; these sensitivities are bold and italicized. Base case values of all the output parameters are shown in Table IV.

Table III. Mean sensitivities and standard errors for 32 sets of simulations. The parameter sensitivities are computed using Eq. 24. Italicized cells are statistically significant. Bold and italicized cells are the most important parameters for each output.

Parameter number	α-mean	α-std error	*t*-Test probability for α	β-mean	β-std error	*t*-Test probability for β	Entrapped Peg-Cl-mean	Entrapped Peg-Cl-std error	*t*-Test probability for entrapped Peg-Cl	Entrapped DDDS-mean	Entrapped DDDS-std error	*t*-Test probability for entrapped DDDS
1	***−0.06091***	***0.00473***	***100.00***	*0.01387*	*0.00531*	*98.62*	*0.00015*	*0.00002*	*100.00*	*0.00064*	*0.00009*	*100.00*
2	***−0.08542***	***0.00446***	***100.00***	*0.02712*	*0.00742*	*99.91*	*0.00013*	*0.00003*	*100.00*	*0.00111*	*0.00010*	*100.00*
3	*−0.01911*	*0.00438*	*99.99*	*−0.02322*	*0.00647*	*99.89*	−0.00002	0.00002	66.97	−0.00013	0.00009	83.74
4	*0.01571*	*0.00429*	*99.91*	*0.01815*	*0.00785*	*97.24*	*0.00006*	*0.00002*	*99.45*	*0.00045*	*0.00008*	*100.00*
5	*−0.01272*	*0.00341*	*99.92*	−0.00462	0.00687	49.38	*−0.00006*	*0.00002*	*97.73*	*−0.00040*	*0.00010*	*99.97*
6	*0.01219*	*0.00443*	*99.02*	*0.02123*	*0.00796*	*98.80*	*0.00004*	*0.00002*	*90.94*	0.00008	0.00009	63.50
7	0.00572	0.00436	80.10	−0.00258	0.00726	27.54	0.00000	0.00002	19.78	*0.00071*	*0.00011*	*100.00*
8	*−0.01527*	*0.00423*	*99.89*	0.00160	0.00626	20.01	***0.00069***	***0.00002***	***100.00***	***0.01472***	***0.00010***	***100.00***
9	0.00322	0.00519	46.03	−0.00221	0.00379	43.62	0.00000	0.00002	11.24	−0.00001	0.00008	10.05
11	−0.00214	0.00501	32.82	−0.00556	0.00659	59.43	−0.00001	0.00003	37.48	*0.00031*	*0.00008*	*99.93*
12	*−0.01658*	*0.00499*	*99.77*	***0.10919***	***0.00748***	***100.00***	*0.00014*	*0.00002*	*100.00*	*−0.00252*	*0.00010*	*100.00*
13	−0.00450	0.00426	70.17	0.00861	0.00677	78.73	***0.00035***	***0.00002***	***100.00***	*0.00117*	*0.00009*	*100.00*
14	*−0.01193*	*0.00416*	*99.26*	***−0.06273***	***0.00696***	***100.00***	*0.00008*	*0.00002*	*99.98*	*−0.00205*	*0.00011*	*100.00*
21	*0.02677*	*0.00467*	*100.00*	***−0.08589***	***0.00490***	***100.00***	*−0.00008*	*0.00002*	*99.91*	*−0.00138*	*0.00008*	*100.00*
22	0.00126	0.00424	23.19	*0.01615*	*0.00463*	*99.85*	0.00002	0.00002	69.64	−0.00016	0.00011	84.15

Table IV. Mean and standard deviation of all output parameters for the base case simulation.

	α	β	Entrapped PEG-Cl fraction	Entrapped DDDS fraction	RMS roughness (nm)
Mean	0.705	0.04961	0.00104	0.01879	269
std deviation	0.018	0.04386	0.00011	0.00044	25

The parameters associated with the reduction of Cu^{2+} (parameters 1 and 2) have the strongest effect on the spatial scaling exponent α. The sensitivities of both of these parameters are negative, which suggests that the surface becomes smoother when these parameters are increased. An explanation for these sensitivities is that increasing these parameters results in an increase in the rate of the rate-limiting step, which results in a lower potential because the potential does not have to be driven as negative to maintain the current. Lowering the potential would allow cuprous ions more time to traverse the surface to find low energy sites on the deposit to incorporate into the metal, which results in a smoother deposit.

However, quantifying variations in the roughness in terms of α can be misleading and care must be taken when making physical interpretations of their significance. To verify the correctness of the physical interpretations suggested by the sensitivities, the root-mean-square (rms) roughness was calculated over the entire simulation domain for the simulations where parameters 1 and 2 were perturbed. For parameter 1, the mean sensitivity was −0.14, the standard deviation was 3.20, and the p value was 3.55%. For parameter 2, the mean sensitivity was 4.46, the standard deviation was 3.59, and the p value was 77.69%. The rms parameter sensitivity results indicate that neither of these sensitivities is statistically significant, for a p-value of 90%. Furthermore, if the cut-off were lowered to one standard deviation (*i.e.*, p value of 67%), the parameter sensitivity for parameter 2 has the opposite sign of the sensitivity for α for that same parameter, indicating that the surface roughens as parameter 2 is increased. From the rms roughness data, it is clear that the interpretation of the scaling exponents must be done with caution.

The PEG-Cl bulk diffusion coefficient (parameter 12) had the largest effect on the temporal scaling exponent β. Increasing the PEG-Cl bulk diffusion coefficient resulted in more PEG-Cl making it to the surface where it can adsorb, leading to a higher concentration of PEG-Cl on the surface. Recall that PEG-Cl blocks the adsorption of copper at that location on the surface, which clearly has a direct effect on surface roughness. Increasing the PEG-Cl adsorption rate constant (parameter 14) led to a decrease in the temporal scaling coefficient β. Increasing the rate of adsorption relative to surface diffusion led to more PEG-Cl located at the most readily available sites on the surface, which are peaks. The PEG-Cl on the peaks blocks further copper deposition onto those peaks and smoothens the surface so the surface does not get as rough over time.

The cuprous-thiolate complex adsorption rate coefficient (parameter 8) and the PEG-Cl desorption rate coefficients (parameter 13) have the strongest effect on the amount of entrapped PEG-Cl, though these effects are comparatively small due to the low amount of entrapped PEG-Cl. Increasing either of these parameters results in an increase in the amount of entrapped PEG-Cl. For the amount of entrapped DDDS, the cuprous-thiolate complex adsorption rate constant is about a factor of six larger than the next largest statistically significant parameter sensitivity. It is physically intuitive that this relationship would be significant, since increasing the rate constant for cuprous-thiolate complex adsorption directly increases the concentration of the DDDS on the surface that can be entrapped during deposition.

Conclusions

A parameter sensitivity analysis of a three-additive copper electrodeposition system was performed with the use of a multiscale Monte Carlo simulation code. An optimized sensitivity equation was used to identify the particular parameters that had a significant effect on the outputs. The sensitivity equation is generic and can be applied to any stochastic simulation. The overall approach of deriving a finite difference parameter sensitivity equation based on the solution of a stochastic optimization problem is generic, and can be used to derive expressions in terms of backward and forward differences, or for higher order parameter sensitivities. With the use of high throughput computing, such as Condor, it is possible to perform a massive number of computationally expensive simulations in a reasonable amount of time.

With parameter sensitivities available, an efficient parameter estimation study can be performed, where only the most sensitive parameters to the output parameters of interest are perturbed. Furthermore, the parameter sensitivity techniques used here pave the way for testing multiple additive mechanism hypotheses in the Monte Carlo simulation code. It is shown here that it is not necessary for all of the physicochemical parameters in the noncontinuum simulations to be known accurately, since many parameters have a small effect on the simulation outputs. It was found that of the 22 parameters studied, the outputs were sensitive to the magnitudes of only 7 parameters, if the mechanism hypothesis is correct. The parameter sensitivities can also be useful for determining where future computational and experimental efforts should be focused; that is, do not spend a lot of effort calculating or measuring physical parameters that do not have a significant effect on the product quality.

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List of Symbols

f Deterministic component of a function, dimensions vary
$\hat{f}$ Deterministic and stochastic components of a function, dimensions vary
h Forward perturbation size, dimensionless

Greek

α Coefficient, dimensionless
α Spatial scaling exponent, dimensionless
β Coefficient, dimensionless
β Temporal scaling exponent, dimensionless
ε Stochastic error term, dimensions vary
γ Coefficient, dimensionless

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