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Microelectrode Studies of S-NDR Copper Electrodeposition: Potentiodynamic and Galvanodynamic Measurements and Simulations

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Copper electrodeposition from a $CuSO_4$ — H_2SO_4 electrolyte containing a polyether suppressor and (0 to 100) μ mol·L⁻¹ Cl⁻ is examined using a 25 µm diameter microdisk electrode. Optical imaging during cyclic voltammetry and galvanodynamic measurements reveal hysteresis, overpotential inversions, and the morphological evolution accompanying breakdown of the polyether-chloride inhibition layer. Simulations involving co-adsorption of the suppressor-halide adlayer and its subsequent breakdown capture the positive feedback and negative differential resistance (S-NDR) evident in electroanalytical measurements as well as important aspects of electrode shape evolution. The impact of electrode shape change on simulations of electroanalytical experiments is quantified in comparison to a stationary interface approximation. For potentiodynamic conditions, adlayer breakdown propagates rapidly from the center of the microelectrode surface although the final deposit profile is non-uniform due to enhanced transport to the disk perimeter. In contrast, galvanodynamic experiments in more concentrated Cl⁻ solutions reveal spatially selective suppressor breakdown with deposition initially localized to the microelectrode center followed by outward expansion as applied current is increased. The difference between potentiodynamic and galvanodynamic responses reflects the convolution of S-NDR critical behavior with the respective control-loop load lines. Microelectrodes constrain or frustrate the otherwise random bifurcation process giving rise to predictable morphologies unattainable on macroscale electrodes. © 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, http://creativecommons.org/licenses/by-nc-nd/4.0/), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse. please email: oa@electrochem.org. [DOI: 10.1149/1945-7111/ab8e86]



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Significant research efforts and commercial resources have focused on development of efficient processes for fabricating electronic circuitry that range in length-scale from sub-10 nm transistor interconnects to millimeter-scale wiring in printed circuit boards (PCBs). Central to this and other manufacturing applications is void-free electrodeposition of Cu in high-aspect ratio features, accomplished using electrolyte additives that selectively inhibit and accelerate the deposition rate to enable superconformal or bottom-up filling of recessed surface features.¹⁻¹⁶ For on-chip damascene interconnects as well as blind via PCB metallization, organic additive combinations are often used in either two (suppressoraccelerator) or three (suppressor-accelerator-leveler) component combinations.^{1–11} In these systems, superconformal filling of highaspect ratio features occurs by the Curvature Enhanced Adsorbate Coverage (CEAC) mechanism in which area loss during deposition in regions of high concavity leads to the accumulation of the more strongly bound accelerating adsorbates resulting in enhanced deposition on such recessed surfaces.^{4,17–19} More recently, explorations of suppressor-only systems have revealed a different filling mechanism where high aspect ratio features that are tens of micrometers to millimeters in scale are readily filled from the bottom-up.^{12–16} For suppressor-only Cu deposition systems, electroanalytical and surface science measurements demonstrate the importance of halide coadsorption in the formation of the blocking polyether layer that inhibits metal deposition by restricting access of Cu²⁺ to the surface.^{20–33} These systems exhibit critical behavior where potential-dependent suppressor breakdown manifests as an S-shaped negative differential resistance (S-NDR). Operating within the S-NDR region leads to bifurcation of the electrode surface into active plating and passive zones. For substrates with significant topological variation the active zones preferentially develop in the most recessed regions, giving rise to bottom-up filling of high aspect

ratio features demonstrated for through-silicon vias (TSV) or "butterfly" filling of PCB through-hole features.^{12–16,34}

Bifurcation of electrochemical reactions into passive and active surface regions is not uncommon; the phenomenon derives from competition between inhibited and catalytic pathways. For example, Turing patterns develop spontaneously from the mismatch between material transport that is temporally slow relative to more rapid variations in the electrical response. For deposition reactions this competitive transport response leads to continuous restructuring of the electrode geometry with time. Spatiotemporal patterns develop when the control parameter falls within the S-NDR region where a decrease in the driving force (i.e., reaction overpotential) is correlated with an increase in the reaction rate (i.e., current), or vice versa. Depending on the control mode, i.e., potentiodynamic versus galvanodynamic, critical phenomena manifest from a multiplicity of control points and/or oscillations.^{39–43} During potentiodynamic deposition parasitic processes such as ohmic losses in the electrolyte can obscure the NDR region, effectively unwinding the inversion to provide single valued control points for maintaining stable global operation while local pattern formation evolves freely. Absent such losses, single-valued potential control points for planar electrodes within the NDR regions are not accessible, and the electrode rapidly switches between the passive and active states. However, when electrode topography varies on a length scale commensurate with the boundary layer a sustained release from the above condition is available whereby the planar field is passive due to a higher additive flux while recessed surface areas adopt the active state as seen for TSV filling. Importantly, regardless of the electrode geometry, galvanostatic regulation within the NDR inverted region does not require the ohmic losses necessary in potentiostatic operation to define stable control points for passiveactive bifurcation.

On planar electrodes, reaction bifurcation is usually triggered and guided by inhomogeneities at the electrode surface or within the electrochemical cell. The variations can range from microstructure and roughness of the electrode to its coupling with convection, diffusion, migration, and related gradients in the system. The resulting ensemble of active regions typically vary in shape and

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area and are usually distributed on the otherwise passive surface with a bias reflecting the constraint of the primary and tertiary current distribution. Under such conditions the accurate determination of kinetics for the actively growing region is exceedingly difficult (if not impossible in practice). Restricting the dimensions of the working electrode down to micrometer scale offers several important advantages. In particular, continuous optical imaging of the surface during metal deposition is possible, allowing real time assessment of the evolution of active and passive areas.⁴⁴ Recently, imaging of a 100 µm diameter electrode under microfluidic flow conditions examined the effect of rapid change in additive concentration on Cu deposition behavior on the disk.⁴⁵ This development builds upon prior studies examining the impact of rapid additive changes on the global electrochemical response.²⁹ Transport to small size electrodes, $\approx 25 \ \mu m$ diameter, is dominated by a hemispherical field capable of providing steady-state deposition rates that can only be matched by forced convection, e.g. at high RDE rotation rates, for macroscale electrodes. This difference enables the importance of shear in the adsorption and desorption of the polymer suppressor to be assessed. An additional benefit of microscale electrodes is the relative ease of correcting for losses associated with electrolyte resistivity, thereby helping to clarify the nature of S-NDR behavior. Furthermore, as microelectrode dimensions shrink, bifurcation into active-passive zones will be constrained and possibly channeled or templated by the finite geometry.^{44–46} In the extreme limit the bifurcation process itself might be frustrated. Indeed, this approach has been used to explore electrode size effects on the bifurcation of a Pt microelectrode surface during CO oxidation including an analysis of the electrochemical noise associated with the process.⁴⁵ Taking a similar approach to examine processes such as nucleation, growth, and phase separation during electrodeposition reactions represents a promising avenue for future research.

In the present study, microelectrodes are used to examine S-NDR phenomena associated with Cu electrodeposition in the presence of a representative polyether additive, poloxamine, and a range of Clconcentrations in acid CuSO₄-H₂SO₄ electrolyte. Cyclic voltammetry captures the characteristic hysteresis response, and linear galvanodynamic sweeps reveal the negative differential resistance associated with breakdown of the polyether-Cl⁻ suppressor phase. A two-additive model describing co-adsorption and deactivation/ consumption of the respective components of the suppressor phase and their impact on copper deposition kinetics is used to simulate the electroanalytical measurements. Simulations tracking changes in the electrode shape (i.e., moving boundaries) during electroanalytical measurements are compared with predictions calculated using a stationary interface approximation. While all the simulations assume a microstructurally homogeneous electrode surface, predictions of the deposit growth profiles are used to explore the effect of inhomogeneities in the current distribution and chemical transport on the regulation/operation mode used during growth. Importantly, the shape change simulations show favorable agreement with in situ imaging experiments. Distinct and important differences as a function of the regulation mode are revealed that contribute to a deeper understanding of spatiotemporal patterning that develops during suppressor breakdown in additive derived S-NDR electrodeposition systems.

Experimental Methods

Cyclic voltammetry (CV) and linear galvanodynamic sweeps (GD) exploring the impact of Cl⁻ concentration and a polyether additive on copper deposition were conducted in an electrolyte comprised of 0.24 mol·L⁻¹ CuSO₄ and (0.01 to 1.8) mol·L⁻¹ H₂SO₄. The chemicals CuSO₄·5H₂O (Sigma Aldrich,^a \ge 98.0 % by wt.), concentrated H₂SO₄ (Taylor Chemical Company, 95.0–98.0 % by wt.), and NaCl (Fisher Scientific, \ge 99.0 % by wt.) were used in the as-received condition. A poloxamine suppressor, ethylenediamine

tetrakis (propoxylate-block-ethoxylate) tetrol, (PEO₄PPO₁₂)₂ED $(PPO_{12})PEO_{4})_2$ ($M_{n avg} \approx 3600$, Tetronic 701, Sigma Aldrich product no. 435511) was used with the concentration fixed at 80 μ mol·L⁻¹ (or, equivalently 0.288 g·L⁻¹). Solutions with different chloride concentrations were made using aliquots from a master solution of 20 mmol·L⁻¹ NaCl. The 0 μ mol·L⁻¹ Cl⁻ experiments likely have a trace amount of chloride in solution, a result of the limited purity specification of the as-received CuSO₄ salt ($\leq 0.001 \%$ Cl⁻ by wt.) and the affinity of copper metal for chloride adsorption due to its negative potential of zero charge. All electrolytes, polishing, and rinsing solutions were prepared with 18 M Ω ·cm water. A Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (SSE) was used in all experiments. All potentials are referenced versus SSE which is pH sensitive due to the sulfate/bisulfate equilibrium. The pH dependence was evaluated by direct comparison to Hg/Hg₂Cl₂/saturated KCl (SCE) and H₂/H₃O⁺/Pt (RHE) reference electrodes poised in the same solution. For experiments performed in 10 mmol L^{-1} and 100 mmol·L⁻¹ H₂SO₄ solutions the SSE reference shifted by -63 mVand -48 mV in comparison to experiments performed in $1.8 \text{ mol} \cdot \text{L}^{-1}$ solution and thus, the potential of the respective data sets were shifted accordingly in Fig. 1. To avoid concerns with Pt dissolution in the Cl⁻containing electrolyte, an iridium wire was used as the counter electrode.

Electroanalytical measurements were performed on a 25 μ m diameter gold microelectrode (CH Instruments, Austin, TX) and a 0.5 cm diameter gold rotating disk electrode (RDE) using a Biologic model VSP potentiostat. The microelectrodes were polished using sequentially finer diamond lapping paper, ending with a 0.1 μ m grit. The RDE was similarly polished using silicon carbide paper in 18 M Ω ·cm water, ending with 5 μ m grit. Electrodes were only polished before each electroanalytical campaign to limit microstructural variation of the gold electrode between experiments; thus, all experiments in Fig. 2 use the same pre-polished microelectrode. Voltammetric studies of Cu deposition in the various CuSO₄ solutions were performed at $10 \text{ mV} \cdot \text{s}^{-1}$, initiating at -0.15 V and sweeping to -0.72 V or -0.75 V (as shown). Linear galvanodynamic sweeps were performed on microelectrodes at a scan rate of 14.48 nA·s⁻¹, initiating at 0 nA and ending at -579 nA. Prior to voltammetric and galvanodynamic measurements the Au microelectrodes were held for 30 s at -0.15 V and 0 nA (the open circuit potential ranged from -0.41 V to -0.48 V), respectively, to allow the polyether-chloride adlayer to form. To refresh the electrodes between individual experiments, the deposited Cu was removed by voltammetric cycling between -0.35 V and 0 V at 10 mV s⁻¹ in the CuSO₄—H₂SO₄—additive containing solution followed by immersion of the electrode in concentrated nitric acid for a few seconds (the same 20 ml nitric acid solution was used throughout each day). Then, the electrodes were electrochemically annealed by cyclic voltammetry in 1.8 mol·L⁻¹ H₂SO₄, sweeping between 1.25 V and -0.45 V for 10 cycles at a 100 mV s⁻¹ scan rate. Electrodes were rinsed for ≈ 10 s in a stream of 18 M Ω ·cm water after removal from each electrolytic or cleaning solution. Voltammetry and galvanodynamic measurements for each Cl⁻ concentration were accomplished in the same electrolyte solution, the relevant concentration being subsequently increased for measurements under other conditions. Currents measured in all electroanalytical experiments are converted to current densities based on the projected microelectrode (4.91 \times 10^{-6} cm²) and RDE (0.196 cm²) areas. Solution conductivity and cell impedance were derived from high frequency impedance measurements using a standard electrolyte conductivity cell with two circular Pt electrodes. The conductivities of 0.01 mol·L⁻ H_2SO_4 , 0.1 mol·L⁻¹ H_2SO_4 , and 1.8 mol·L⁻¹ H_2SO_4 solutions were 1.43 S·m⁻¹, 4.34 S·m⁻¹, and 49.3 S·m⁻¹, respectively.

For in situ optical measurements, cyclic voltammetry and linear galvanodynamic sweeps were performed in a pool (<1 mL) of electrolyte supported on a silica plate (thickness of 0.5 mm, Valley Design East, Shirley, MA) placed on the stage of an inverted Nikon Epiphot 300 microscope. The Au microelectrode was suspended above the plate, with less than 2 mm distance between the

^aIdentification of commercial products in this paper was done to specify the experimental procedure. In no case does this imply endorsement or recommendation by the National Institute of Standards and Technology.



Figure 1. (a) Cyclic voltammetry measurements at 10 mV·s⁻¹ and (b) galvanodynamic sweep at 0.288 mA·s⁻¹ in 0.24 mol·L⁻¹ CuSO₄, 80 μ mol·L⁻¹ poloxamine (Tetronic 701), 10 μ mol·L⁻¹ NaCl, and the indicated H₂SO₄ concentrations on a 0.5 cm diameter Au rotating disk electrode (RDE) at 1600 rpm. The polymer-free measurement is in 0.24 mol·L⁻¹ CuSO₄, 1.8 mol·L⁻¹ H₂SO₄, and 10 μ mol·L⁻¹ NaCl. The 1.8 mol·L⁻¹ H₂SO₄ data in (a) is re-plotted with the corresponding post-experimental iR-corrected voltammogram in (b). The measured current is normalized to the geometric area of the polished RDE.

microelectrode tip and silica plate. The same Hg/Hg₂SO₄/saturated K_2SO_4 reference electrode (SSE) and iridium wire counter electrodes used for other electroanalytical measurements were also suspended in solution a few millimeters from the microelectrode. Microelectrodes were viewed with a 50 × LWD (long-working distance) Nikon objective through the silica plate and electrolyte solution. Images were recorded using a Model OCS-5.0 OptixCam Summit Series CMOS Camera (Microscope Store, LLC, Roanoke, VA) with OCView (version 7.3.1.7) and then processed using ImageJ (version 1.52a). Mean gray values measured by ImageJ are the average grayscale value (between 0 and 255) of the colorized images. The default ImageJ thresholding algorithm was used to produce binary images estimating the fraction of the microelectrode area covered with copper deposits.

Experimental Results

RDE measurements.—Copper electrolytes used for filling highaspect ratio features in electronics manufacturing are typically evaluated by a variety of electroanalytical measurements (e.g., cyclic voltammetry, chronoamperometry, chronopotentiometry) to understand how the additives influence the kinetics of copper deposition. Prototypical cyclic voltammetry for copper electrodeposition in the presence of sub-millimolar concentrations of sodium chloride and a polyether additive (suppressor)^{13,16,47} in electrolytes of different sulfuric acid concentrations, with forced convection provided by a rotating disk electrode at 1600 rpm $(3200\pi \text{ rad}\cdot\text{min}^{-1})$, are shown in Fig. 1. Cyclic voltammetry in an additive-free electrolyte or an electrolyte containing only NaCl (--) produces a monotonic i-V relationship, the current exponentially dependent on electrode overpotential congruent with the Butler-Volmer equation. In contrast, in the presence of chloride and the polyether additive, the rate of copper deposition is inhibited due to the formation of a polyether-chloride adlayer that hinders cupric ion reduction by blocking its access to the electrode surface (-). The reduced current densities associated with the passive state are evident on the forward sweep. Eventually, the electrode reaches a critical potential where the polyether-chloride adlayer is disrupted and cupric ion reduction occurs with positive feedback leading to a further rapid increase in current. On the reverse sweep, sustained copper deposition prevents the polyether-chloride adlayer from reforming on the electrode so that the polarization branch resembles that of the polymer-free solution. As the overpotential decreases further, the driving force for adsorption of polymer and chloride ultimately exceeds the potential (or metal deposition rate) dependent disruption of the adlayer, and the suppressor layer reforms once again.

The linear i-V character evident for the activated surface (i.e., the positive-going return scan) at negative potentials, in combination with its offset to more negative potentials with decreasing sulfuric acid concentration, reflects the impact of significant ohmic losses in the electrolyte. In the 1.8 mol·L⁻¹ H₂SO₄-0.24 mol·L⁻¹ CuSO₄ solution, the high frequency cell resistance of 1.5 Ω results in a modest iR-shift of 12 mV for the 0.196 cm² RDE at 40 mA cm⁻². For the 0.1 mol·L⁻¹ and 0.01 mol·L⁻¹ H₂SO₄ containing electrolvtes, the larger 15.2 Ω and 46.2 Ω impedances, respectively, result in more significant ohmic losses in the electrolyte of 119 mV and 362 mV at 40 mA cm⁻². Post-experiment correction for the associated iR-drop shown in Fig. 1b and Fig. S1 (available online at stacks.iop.org/JES/167/082509/mmedia) (and discussed previously in Ref. 12) reveals the s-shaped NDR and multiplicity of current values over the relevant potential range. Even these large ohmic losses are likely underestimates, as the electroactive area, particularly in the earliest stage of breakdown, is substantially smaller than the geometric area of the electrode. The potential range of the hysteretic zone appears to decrease with lower sulfuric acid concentration, but this behavior is, at least partly, due to significant distortion of the actual overpotential waveform at the electrode. Use of active iR-compensation during the voltammetric sweep can help partially mitigate these effects. Nevertheless, the remaining uncompensated ohmic loss is still convolved with the current rise during the potentiodynamic scan thereby obscuring the S-NDR.

In contrast to cyclic voltammetry, current control is single valued over the S-NDR regime as demonstrated in Fig. 1b for the $0.288 \text{ mA} \cdot \text{s}^{-1}$ galvanodynamic sweep for the same RDE configuration in 1.8 mol·L⁻¹ H₂SO₄. As the current increases in magnitude the electrode polarizes sharply until the breakdown potential is reached. This breakdown is followed by potential relaxation as the current increases. As the current is ramped further the whole electrode eventually activates, and the i-V curve merges with that observed for the fully activated voltammetric branch. Morphology development during electrodeposition is path dependent and, for certain conditions, coupling with an RDE flow field can give rise to spiral and striated patterns, as demonstrated in previous reports. ^{16,22,48–50}

Microelectrode measurements.—The characteristic length scale of spontaneous pattern formation on macroscale electrodes is on the order of tens of micrometers with multiple sites developing across the electrode.^{12,22,48–50} By constraining the available area, micrometer scale electrodes offer the promise of examining a limited number of (or even individual) active domains, thus minimizing the



Figure 2. Cyclic voltammetry at 10 mV·s⁻¹ and linear galvanodynamic sweeps at 14.48 nA·s⁻¹ in 0.24 mol·L⁻¹ CuSO₄, 1.8 mol·L⁻¹ H₂SO₄, 80 μ mol·L⁻¹ poloxamine (Tetronic 701) with the indicated chloride concentrations on a 25 μ m diameter Au microelectrode. The measured current is normalized to the geometric area of the mechanically polished microelectrode.

dispersion effects associated with ensemble development and implied competition therein. Furthermore, the hemispherical field that surrounds microelectrodes provides high steady-state transport rates without the need for forced convection. The smaller electrode size also mitigates measurement challenges associated with resistive electrolytes as the uncompensated resistance is concentrated within a well-defined region of the electrolyte immediately adjacent to the electrode. The inverse radial dependence of the ohmic resistance combined with the decreased capacitance proportional to radius squared give an improved time response associated with smaller electrodes.

Cyclic voltammetry and linear galvanodynamic sweeps of Cu deposition on a 25 μ m diameter Au microelectrode from solutions containing 0.24 mol·L⁻¹ CuSO₄, 1.8 mol·L⁻¹ H₂SO₄, 80 μ mol·L⁻¹ poloxamine, and different Cl⁻ concentrations are shown in Fig. 2. At potentials positive of -0.5 V, a wetting Cu underpotential deposited layer forms on the Au electrode. As the potential is swept more negative a monotonic polarization curve of unrestrained Cu2+ reduction on the Cu covered surface is observed for the additivefree electrolyte. In the presence of 5 μ mol·L⁻¹ Cl⁻ reduction kinetics are actually enhanced, with a small peak evident near -0.54 V due to Cl accelerated reduction of Cu²⁺ to Cu^{+,5} Thereafter the polarization curve is monotonic with potential for Cu^{2+} reduction to Cu. Interestingly, the dilute Cl^{-} coverage leads to acceleration of the metal deposition reaction yet is insufficient to support co-adsorption of the polyether suppressor. As the Clconcentration is increased to 10 μ mol·L⁻¹, and higher, strong inhibition of the deposition is evident in the negative sweep until the critical potential is reached and the polyether-Cl⁻ suppressor layer is disrupted. With further polarization, the reaction rate sharply accelerates as the electrode surface fully activates, and the curve inflects to a linear i-V response. On the return sweep the deposition rate on the fully activated surface mirrors the suppressor-free kinetics with decreasing overpotential for concentrations less than 25 μ mol·L⁻¹ Cl⁻. For higher Cl⁻ concentrations the suppressor layer reforms at successively more negative potentials as the flux driving reformation of the suppressor overcomes the weakening driving force for metal deposition, a trend more clear when comparing all the voltammetry data as shown in Fig. S2. The dependence of the breakdown potential on Cl⁻ concentration, related to the halide coverage and/or related structural phase transitions,⁵ is also evident in Fig. S2. The critical potential, or activation threshold defined at $-10 \text{ mA} \cdot \text{cm}^{-2}$, shifts by $\approx -66 \text{ mV}$ between $10 \ \mu\text{mol}\cdot\text{L}^{-1}$ Cl⁻ and $100 \ \mu\text{mol}\cdot\text{L}^{-1}$ Cl⁻, (Fig. S2b) consistent with previously reported data using RDEs in a solution of 1 mol·L⁻¹ CuSO₄, 0.5 mol·L⁻¹ H₂SO₄, and 40 μ mol·L⁻¹ poloxamine, Tetronic 701, over a similar range of chloride concentrations.¹³ During the reverse sweep repassivation of the active branch is dependent on Cl⁻ concentration reflecting the importance of co-adsorption in formation of the suppressor phase; the trend is pictured more clearly in Fig. S2b. This is true even when the concentration of the polyether and Cl⁻ are in the same range (i.e., at (75 to 100) μ mol·L⁻¹ Cl⁻). The voltammetric sequence of breakdown and repassivation gives rise to the \approx 100 mV wide hysteresis loop that reflects the balance between the kinetics of Cl⁻ adsorption versus the metal deposition rate dependent incorporation in the growing deposit.^{13,23,36,47}

As with the RDE data, the S-NDR region is not evident in the microelectrode cyclic voltammetry. However, unlike the RDE measurements, imposing a post-experimental correction for the iR-drop based on the microelectrode geometric area does not reveal the S-NDR. The primary current distribution resistance, $\Omega_{\rm UME}$, for current flow to a disk follows⁵³

$$\Omega_{UME} = \frac{1}{4\kappa r}$$
[1]

where κ is the solution conductivity and *r* is the radius of the microelectrode disk. The calculated iR-drop for the highest current value in Fig. 2 (-220 mA·cm⁻²) is only 0.4 mV by Eq. 1, versus 26 mV on the RDE in Fig. 1 estimated from cell impedance. Even for the more resistive solutions, such as 0.01 mol·L⁻¹ H₂SO₄, the estimated iR-drop at similar current levels on a microelectrode is only 14 mV, substantially less than the corresponding >300 mV potential shift on the RDE.

Optical imaging of the microelectrode during cyclic voltammetry reveals that the sharp transition between the fully passive surface and the active branch corresponds to nucleation of a high density of small active regions concentrated near the center of the microelectrode, as shown in Fig. 3 for an electrolyte containing 100 μ mol·L⁻¹ Cl⁻. The bifurcation begins with the formation of active clusters that by -0.724 V (corresponding to halfway between the fully passive and activated state) represents only a modest fraction of the electrode surface. Each actively growing region may be considered an individual microelectrode. As the clusters are growing on a conductive surface high frequency impedance measurements do not properly capture the nature of the ohmic losses associated with current flow to the much smaller active region. Rather, the ohmic losses for current flow to these smaller regions will be greater, as



Figure 3. Cyclic voltammetry at 10 mV·s⁻¹ and corresponding in situ optical micrographs of copper deposition on a 25 μ m microelectrode in 0.24 mol·L⁻¹ CuSO₄, 1.8 mol·L⁻¹ H₂SO₄, 80 μ mol·L⁻¹ poloxamine (Tetronic 701), and 100 μ mol·L⁻¹ NaCl. The mean grey value for each image is scaled between 0 and 255 as determined from the color images. The percentages representing Cu coverage listed in each optical micrograph are estimated from binary thresholding in ImageJ software.

suggested by the radius-dependent relationship described in Eq. 1. By -0.731 V the whole electrode is actively growing, although evidence of a higher initial nucleation density toward the center remains, and at this juncture the ohmic losses associated with the full microelectrode area are relevant. The evolution of the bifurcation, although occurring within a 29 mV range, is such that the S-NDR region must exist; however, quantitative analysis of the likely dynamic ohmic losses during expansion of the active regions remains to be fully determined.

The critical instability of the potentiodynamic control loop is such that the shift of the electrode from the fully passive to fully active state occurs in less than 3 s for the 10 mV \cdot s⁻¹ scan rate; analysis of greyscale images using binary thresholding in ImageJ software indicates transition of a microelectrode from 7% copper coverage to 100% coverage occurs within 29 mV. Current control measurements provide the means to slow down and stabilize the S-NDR bifurcation on the microelectrode surface. Accordingly, Fig. 2 shows linear galvanodynamic sweeps from 0 to -579 nA at 14.48 nA·s⁻¹ in the same electrolytes used in the voltammetric experiments. The galvanodynamic sweeps clearly show a negative differential resistance as the potential depolarizes upon partial breakdown of the suppressor layer. That the current sweep with 0 μ mol·L⁻¹ Cl⁻ also shows a small inversion might be associated with 3D nucleation of Cu metal on Au during the fast galvanodynamic polarization or possibly related to Cl⁻ contamination and thereby some partial coverage of the suppressor phase. Contamination is suggested by the subsequent polarization after the inversion being similar to that observed for the full activated surface during voltammetry in the 5 μ mol·L⁻¹ Cl⁻ CV measurement; that said, the voltammetry and galvanodynamic data were obtained sequentially from the same electrolyte so that such contamination would have to arise from carry-over from the nitric acid immersion, electrochemical annealing, and rinsing steps between each individual measurement.

Following the addition of 5 μ mol·L⁻¹ Cl⁻ to the electrolyte a sharper inversion with larger depolarization (decrease of overpotential) is observed even though the corresponding voltammetric



Figure 4. Galvanodynamic sweeps at 14.48 $nA \cdot s^{-1}$ and corresponding in situ optical micrographs of copper deposition on a 25 μ m microelectrode in 0.24 mol·L⁻¹ CuSO₄, 1.8 mol·L⁻¹ H₂SO₄, and 80 μ mol·L⁻¹ poloxamine (Tetronic 701) for (a) 5 μ mol·L⁻¹ and (b) 100 μ mol·L⁻¹ NaCl. The mean grey value for each image is scaled between 0 and 255 as determined from the color images. The percentages representing Cu coverage listed in each optical micrograph are estimated from binary thresholding in ImageJ software.



Figure 5. Schematic (a) of the 2D axisymmetric geometry used in the S-NDR model to simulate electroanalytical measurements of copper electrodeposition on the microelectrode. Relevant domains and boundaries are indicated. (b) Linear sweep voltammetry at 10 mV·s⁻¹ in 0.24 mol·L⁻¹ CuSO₄ and 1.8 mol·L⁻¹ H₂SO₄ for polymer-free electrolyte (100 μ mol·L⁻¹ NaCl) and fully suppressed electrolyte (1000 μ mol·L⁻¹ NaCl and 80 μ mol·L⁻¹ Tetronic 701). Time-dependent, 2D axisymmetric simulations are used to approximate best fits to extract the electrochemical kinetic parameters for both electrolytes.

experiment showed no hysteresis. For 10 μ mol·L⁻¹ Cl⁻ two inversions are evident in the galvanodynamic curves that might be related to a frequency doubling phenomenon seen in many bifurcating reactions.^{45,54} Alternatively, this feature may be related to the non-uniform current distribution caused by variations in both migration and diffusion to the disk electrode versus the more uniform conditions offered by a hemispherical electrode geometry, a testable hypothesis for a future study. The galvanodynamic curve for 20 μ mol·L⁻¹ Cl⁻ only exhibits a single inversion whereas concentrations greater than 20 μ mol·L⁻¹ again exhibit two inversions. Optical imaging of the microelectrode surface during current ramping reveals that the single and double inversions in the Cl⁻-dependent galvanodynamic curves are associated with distinctive growth morphologies. As shown in

Fig. 4a, suppressor breakdown in 5 μ mol·L⁻¹ Cl⁻ is followed by depolarization reaching a maximum that is coincident, within the limits of resolution, to uniform activation of the electrode surface. The darkened surface in the bright field image at 6.7 s indicates that the film is rough, suggestive of a high density of 3D clusters growing, more or less uniformly, across the surface; the associated deposition charge is equivalent to a uniform film thickness of ≈ 24 nm. The surface becomes progressively brighter with time as the polarization then increases more gradually. By 40 s the polarization matches that at the initial breakdown of the passive state but now corresponds to an entirely actively growing surface; the respective passive and active surfaces grow at 5.31 mA·cm⁻² and 118 mA·cm⁻² assuming a 100 % current efficiency. In contrast, suppressor breakdown in 100 μ mol·L⁻¹ Cl⁻ shown in Fig. 4b is associated with a localized active region that is well developed by the maximum observed depolarization of the galvanodynamic curve at 7.8 s. Subsequent repolarization of the electrode is accompanied by a modest increase of the diameter of the circular active region through 14.6 s, indicating that the applied current during this time interval is associated primarily with vertical growth. A second, albeit weaker, depolarization event occurs at this time, marking the start of lateral expansion of the active region that eventually covers the entire electrode by 40 s. The rich interplay between the control mode and resulting morphological evolution is worthy of additional experimental exploration; however, in the present work, these differences will be further explored using simulation based on a simple positive feedback model employing metal deposition stimulated breakdown of the polyether-Cl⁻ suppressor layer.

Computational Methods

Existing theory of chemical transport and potential variation in solution for microelectrodes makes this experimental system ideal for comparison to simulation. The microdisk geometry provides sustained mass transport without requiring convective flow calculations, and positioning of the counter and reference electrodes in solution is unimportant as long as they are sufficiently far from the working electrode.^{53,55,56} Equally important, prior work has detailed a model for co-adsorption of chloride and polyether additives during copper deposition that captures experimental trends observed in feature filling for through-silicon-via (TSV) and through-hole (TH) structures.^{13,34} Here we apply that construct to capture experimental trends of cyclic voltammetry and linear galvanodynamic sweeps on microelectrodes.

Finite element method (FEM) computations of microelectrode electroanalytical measurements are performed in the 2D axisymmetric configuration depicted in Fig. 5a, with symmetry imposed at the centerline of the microelectrode. The microelectrode radius (R_{UME}) is 12.5 μ m and the total simulated domain extends to $20R_{UME}$. In the 2D electrolytic domain, the concentration and flux N_i of each species (Cu²⁺, Cl⁻, and polymer) are related through the Nernst-Planck equation, capturing both diffusion and electromigration by

$$\frac{dC_i}{dt} = -\nabla \cdot \overrightarrow{N_i} = -\nabla \cdot (-z_i u_{m,i} F C_i \nabla \phi - D_i \nabla C_i)$$
[2]

given the charge z_i and mobility $u_{m,i}$ calculated by the Einstein relationship

$$u_{m,i} = \frac{D_i}{RT}$$
[3]

The simulated electrolyte consists of 0.24 mol·L⁻¹ CuSO₄, 1.8 mol·L⁻¹ H₂SO₄, 80 μ mol·L⁻¹ polymer, and NaCl concentration ranging from 0 μ mol·L⁻¹ to 100 μ mol·L⁻¹. Full dissociation of CuSO₄ and NaCl is assumed for the concentrations of Cu²⁺ and Cl⁻. The suppressing polyether molecule (P) is assumed to be neutral in charge ($z_p = 0$). Diffusion coefficients listed in Table I for Cu²⁺, Cl⁻, and polyether are taken or estimated from literature sources.^{13,56-60} The diffusion coefficient for the polymer was

Table I. Parameters for electroanalytical simulations.

Parameter	Name	Units	Value	References
Electrochemical Cell Geometry				
Microelectrode radius	Rung	um	12.5	
Cell radius/distance to reference electrode	R.	µm	$20 \times R_{max}$	
Initial microelectrode area	AUME	m^2	4.91×10^{-10}	_
Electrolyte Parameters	OWE			
Bulk concentration Cu ²⁺	C^o_{Cu}	mol·L $^{-1}$	0.24	_
Bulk concentration Cl ⁻	C_{Cl}^{o}	$\mu \text{mol} \cdot \text{L}^{-1}$	0 to 100	_
Bulk concentration polyether (Poloxamine Tetronic 701)	C_{P}^{o}	μ mol·L ⁻¹	80	_
Diffusion coefficient Cu^{2+}	$D_{C''}$	$cm^2 \cdot s^{-1}$	$3.6 imes 10^{-6}$	Ref. 57
Diffusion coefficient Cl ⁻	D_{Cl}	$cm^2 \cdot s^{-1}$	9×10^{-6}	Ref. 13
Diffusion coefficient polyether (Poloxamine Tetronic 701)	D_P	cm ² ·s ⁻¹	1×10^{-6}	Refs. 58-60
Electrolyte conductivity	ĸ	$S \cdot m^{-1}$	49.3	Measured
Reversible Potential	E_{rev}	V	-0.41	Measured
Adsorbate Parameters				
Saturation chloride coverage	Γ_{Cl}	$\text{mol}\cdot\text{m}^{-2}$	$1.62 imes 10^{-5}$	Ref. 13
Saturation suppressor coverage	Γ_P	$mol \cdot m^{-2}$	$9.2 imes 10^{-8}$	Ref. 61
Chloride adsorption kinetics	k_{Cl}^+	$m^3 \cdot (mol \cdot s)^{-1}$	120	Fit
Chloride deactivation kinetics	k_{Cl}^{-}	m^{-1}	$7 imes 10^7$	Fit
Suppressor adsorption kinetics	k_P^+	$m^3 \cdot (mol \cdot s)^{-1}$	2500	Ref. 13
Suppressor deactivation kinetics	k_P^-	m^{-1}	$1 imes 10^7$	Ref. 13
Initial chloride & polymer coverages	$\theta_{i,o}$		0.99	_
Electrochemical Kinetics	1,0			
Unsuppressed Cu exchange current density	j_0^o	$A \cdot m^{-2}$	2.5	Fit
Suppressed Cu exchange current density	j_1^o	$A \cdot m^{-2}$	0.0047	Fit
Unsuppressed charge transfer coefficient	α_0	_	0.64	Fit
Suppressed charge transfer coefficient	α_I	_	0.64	Fit
Cu ionic charge	n	—	2	—
Cu molar volume	Ω	$m^3 \cdot mol^{-1}$	$7.1 imes 10^{-6}$	—
Miscellaneous				
Cyclic voltammetry ramp rate	V_{ramp}	$mV \cdot s^{-1}$	10	—
CV vertex potential	Vvertex	V	-0.72 to -0.75	—
Galvanodynamic sweep rate (microelectrode)	I _{ramp}	$nA \cdot s^{-1}$	-14.48	—
GD end current (microelectrode)	Iend	nA	-579	
Temperature	Т	K	298	—

estimated to be $1 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ based on literature data for polyethylene glycol of similar molecular mass. Conductivity κ , determined by high-frequency impedance in a standard conductivity cell, is 49.3 S·m⁻¹.

Due to the high concentration of supporting electrolyte (H₂SO₄), the model neglects potential variation in solution (ϕ) due to ionic gradient effects and is defined by Laplace's equation

$$\nabla^2 \phi = 0 \tag{4}$$

The current density j associated with the Cu²⁺ flux through the electrolyte is given by ohms law

$$\vec{j} = -\kappa \nabla \phi \tag{5}$$

The counter/reference electrode is imposed at the boundary with a position of $r^2 + z^2 = (20R_{UME})^2$; the solution potential (ϕ) is therefore set equal to the equilibrium potential (E_{rev}) at this boundary. At this position, the potential drop across the solution to the working electrode is estimated to be 97 % of the total iR-drop were the counter/reference electrode placed infinitely far from the working electrode. Additional simulations with the counter/reference electrode boundary located at $r^2 + z^2 = (65R_{UME})^2$ (corresponding to >99 % of the estimated iR-drop for infinite separation) yielded essentially identical cyclic voltammetry and galvanodynamic sweep calculations but required more than 3× the computing time due to the additional mesh. The $20R_{UME}$ geometry was therefore used for the analysis that follows.

Accumulation of the adsorbates on the electrode follows Langmuir adsorption kinetics with adsorbate removal related to metal deposition by deactivation and/or incorporation into the growing metal deposit. Evolution of the fractional chloride coverage θ_{Cl} , defined as the surface concentration divided by the saturation coverage Γ_{Cl} , is described by

$$\frac{d\theta_{Cl}}{dt} = k_{Cl}^+ C_{Cl} (1 - \theta_{Cl}) - k_{Cl}^- \theta_{Cl} \nu$$
[6]

where k_{Cl}^+ is the adsorption rate constant, C_{Cl} is the chloride concentration at the evolving metal/electrolyte interface, k_{Cl}^- is the deactivation rate constant and ν is the metal deposition rate. Values for k_{Cl}^+ and k_{Cl}^- listed in Table I are fit to experimental cyclic voltammetry in Fig. 2. Evolution of the fractional polyether coverage θ_P is described by

$$\frac{d\theta_P}{dt} = k_P^+ C_P (\theta_{Cl} - \theta_P) - k_P^- \theta_P \nu$$
^[7]

where the polyether is restricted to adsorption on top of the halide covered sites and thereby implicitly subject to the requirement that θ_P cannot exceed θ_{CI} through adsorption. Fractional chloride and polyether coverage are both limited to values between 0 and 1. Estimated values for k_P^+ and k_P^- listed in Table I are taken from prior model fits to voltammetric experiments performed using a rotating disk electrode.¹³ The metal deposition rate is assumed to be proportional to the suppressor coverage θ_P (or equivalently, coverage of the polyetherchloride bi-layer) and metal ion concentration C_{Cu} , as well as depending on overpotential η at the interface, thus

$$\nu(\theta_P, C_{Cu}, \eta) = \frac{\Omega}{nF} \frac{C_{Cu}}{C_{Cu}^{\theta}} [j_{\theta=0}(\eta)(1-\theta_P) + j_{\theta=1}(\eta)\theta_P]$$
[8]

The current densities on unsuppressed $(j_{\theta=0})$ and suppressed $(j_{\theta=1})$ surfaces are only associated with metal deposition (i.e., ignoring parasitic contributions) and directly reflect the growth velocity, ν , using Faraday's constant ($F = 96485 \text{ C} \cdot \text{mol}^{-1}$), the ionic charge *n*, and the molar volume Ω of solid copper. The current densities $(j_{\theta=i})$ are assumed to exhibit the conventional exponential dependence on overpotential η by

$$j_{\theta=0,1}(\eta) = j_i^o \left(e^{\frac{(1-\alpha_i)F}{RT}\eta} - e^{\frac{-\alpha_i F}{RT}\eta} \right)$$
[9]

where the subscript *i* in Eq. 9 refers to the active state (0) and suppressed state (1) of the metal/electrolyte interface. The applied potential V_{app} is related to the overpotential η at the working electrode through

$$V_{app} = \eta + \phi + E_{rev}$$
[10]

where the potential ϕ within the electrolyte evaluated at the electrolyte/deposit interface captures the potential drop between the working and reference electrodes due to electrolyte resistivity. The overpotential driving electrodeposition is referenced to the reversible Nernst potential for the reaction, estimated to be -0.41 V from open circuit potential measurements in polymer-free solution containing 10 μ mol·L⁻¹ NaCl. As defined by Eq. 9, the exchange current densities $j_{\theta=i}^{o}$ for the bare, $\theta_P = 0$, and fully inhibited, $\theta_P = 1$, surfaces are for bulk metal ion concentration C_{Cu}^{o} at the interface. Figure 5b shows linear sweep voltammetry on a 25 μ m diameter microelectrode and simulated fits for the indicated values of the parameters j_i^o and α_i . Parameters for the suppressed surface are estimated from the experimental voltammetry in electrolyte con-taining 1 mmol·L⁻¹ NaCl and 80 μ mol·L⁻¹ polyether; the active surface kinetic parameters are fit to the experimental voltammetry in polymer-free solution and 10 μ mol·L⁻¹ NaCl. The kinetics of metal deposition on polymer-free surfaces are known to depend on halide coverage; however, for simplicity, the present work uses a single set of j_0^o and α_0 for deposition on the polymer free surface. The fits in Fig. 5b employ the full, time-dependent computational method outlined here.

The local current density at the electrode (\vec{j}_{Cu}) is equated to the Cu²⁺ flux from the electrolyte onto the interface (outward surface normal \hat{n}) according to

$$\frac{1}{nF}\vec{j}_{Cu}\cdot\vec{n} = -(z_{Cu}u_{m,Cu}FC_{Cu}\nabla\phi + D_{Cu}\nabla C_{Cu})\cdot\vec{n}$$
[11]

Similarly, the normal fluxes of chloride and polyether from the electrolyte onto the interface are equated to the rates of their adsorption yielding

$$-(z_{Cl}u_{m,Cl}FC_{Cl}\nabla\phi + D_{Cl}\nabla C_{Cl})\cdot\vec{n} = \Gamma_{Cl}k_{Cl}^+C_{Cl}(1-\theta_{Cl}) \quad [12]$$

and

$$-D_P \nabla C_P \cdot \vec{n} = \Gamma_P k_P^+ C_P (\theta_{Cl} - \theta_P)$$
[13]

Saturation coverages Γ_i are estimated from literature: $\Gamma_{Cl} = 1.62 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2}$, which corresponds to half of the sites on a smooth Cu (111) surface, and $\Gamma_P = 9.2 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2}$, based on the poloxamine molecule lying flat like a pancake on the interface. The latter value is based on the correlation between surface pressure behavior and the number of ethylene oxide and propylene oxide

groups comprising poloxamines^{62,61}; data from a similar poloxamine, Tetronic 901, indicate that with a strong increase in surface pressure the polymer could be compressed towards a brush conformation, although the associated saturation coverage is unlikely to exceed 2.5×10^{-7} mol·m⁻². As stated previously, the $(\theta_{CI} - \theta_P)$ term in Eq. 13 captures the requirement that the suppressor only adsorbs on chloride.

The full system of equations is solved numerically using a finite element method employing the COMSOL Multiphysics version 5.4 software package and the default MUMPS solver, implementing the following modules: tertiary current distribution, separate coefficient form boundary partial differential equations for both chloride and suppressor, and deformed geometry. Mesh was more highly refined in the area of highest gradient (i.e., near the microelectrode), with triangular elements along the microelectrode interface initially having 0.125 μ m on each side. Typical simulations have 5500 total mesh elements and take on the order of minutes to compute. The overall charge imbalance (the fractional difference between the total integrated currents at the counter electrode and working electrode), which reflects evaluation error, was less than 0.5 %. All simulations were performed on a Dell Precision 3630 desktop computer with an Intel Xeon E-2186G CPU @ 3.80GHz and 64 GB RAM using a Windows 10 Enterprise 64-bit operating system. A moving boundary smoothing parameter of 0.5, geometry shape order of 1, and hyperelastic mesh smoothing type are used in the deformed geometry module (see COMSOL documentation for detailed explanation on how these parameters impact moving boundary convergence).

Computational Results and Discussion

Model validation: comparison to experiment.-The S-NDR model has previously demonstrated quantitative prediction of experimental filling of copper¹³ and nickel³⁵ in through-siliconvias and has also been shown to yield experimentally observed "butterfly" copper deposition in through-hole features.³⁴ However, the fully time-dependent chemical process model has not yet been tested against electroanalytical measurements on planar electrodes. Figure 6 shows simulations of cyclic voltammetry (---) using the two-additive S-NDR model for copper deposition, including the experimental voltammetry from Fig. 2 (-) for comparison. Values for k_{Cl}^+ and k_{Cl}^- were obtained by parametrically fitting the slope and breakdown of the data over the range of NaCl concentrations examined; the complete list of parameters used in the model is outlined in Table I. The values for k_{Cl}^+ and k_{Cl}^- in this electrolyte are 120 m³·(mol·s)⁻¹ and 7 × 10⁷ m⁻¹. The values vary slightly from prior estimates of 20 m³·(mol·s)⁻¹ and 1.5 × 10⁷ m⁻¹, respectively, that were determined using RDE measurements in a higher Cu, lower acidity electrolyte (1 mol·L⁻¹ CuSO₄ and 0.5 mol·L⁻¹ H₂SO₄).¹³ The single pair of k_{Cl}^+ and k_{Cl}^- values captures the range of the experimental data quite well. The simulations predict the observed negative shift in breakdown potential between 10 μ mol L⁻¹ and 100 μ mol·L⁻¹ Cl⁻ as well as the profile of the reverse sweep in most cases. The latter aspect is particularly important as deposition on macroscale RDEs is often non-uniform, with the current values after breakdown reflecting the average across the spatially bifurcated electrode; the discrepancy in the electrochemically active surface area relative to the geometric electrode area makes accurate comparison to kinetic models difficult. The strong correlation between experimental and simulated voltammetry in Fig. 6 suggests that deposition on the microelectrode surface is homogeneous after breakdown, which permits more meaningful estimation of active current density using the known geometric area $(4.91 \times 10^{-6} \text{ cm}^2)$ of the microelectrode. This is further supported by the in situ optical microscopy in Fig. 3 that showed the rapid transition from a fully passive to fully active microelectrode surface. There is some deviation in predictions of the return sweep for 50 μ mol·L⁻¹ and 75 μ mol·L⁻¹ Cl⁻ experiments that also exhibit higher peak current



Figure 6. Comparison of experimental cyclic voltammetry (---) to S-NDR model using a moving interface calculation (---) for the indicated chloride concentrations.

density at -0.75 V (\approx 15 % higher) than that observed for 25 μ mol·L⁻¹ and 100 μ mol·L⁻¹ Cl⁻. The cause of this discrepancy is not certain but might indicate lateral overgrowth of Cu on the microelectrode that was not removed completely during the electrochemical cleaning step before these two experiments. The model also predicts suppression and hysteresis at 5 μ mol·L⁻¹ Cl⁻ where the experimental voltammetry shows none. That the experimental galvanodynamic experiment from Fig. 2 shows a clear NDR inversion for this same concentration might indicate the condition is near a threshold value for inducing significant polymer adsorption and formation of a suppression layer. That the 0 μ mol·L⁻¹ Cl⁻ prediction differs significantly from the corresponding experimental data is not surprising; copper kinetics are known to be accelerated by chloride adsorption and the kinetic parameters estimated from a solution containing 10 μ mol·L⁻¹ Cl⁻ are expected to provide a poor fit to behavior in nominally chloride-free electrolyte.

Figure 7 compares S-NDR model simulations of galvanodynamic sweeps to the experimental data from Fig. 2. The voltammetric simulations are included as a visual frame for the galvanodynamic curves. The computations qualitatively capture the trends in the experimental data. At lower Cl⁻ concentrations the simulated curves predict a single NDR inversion (decreasing overpotential with increasing current) following the onset of suppressor breakdown that occurs within 1 s of initiation of the current ramp. Thereafter the electrode depolarizes to reach a maximum potential followed by a slower increase in polarization as the galvanodynamic curve progresses monotonically on a path similar to the reverse branch of the simulated voltammetric curve. At higher chloride concentrations the simulated galvanodynamic curves display two NDR inversions, the second inversion being less pronounced than the first. As in the low Cl⁻ simulations, the galvanodynamic curve tends to merge with the active branch of the simulated voltammograms at higher currents. For Cl⁻ concentrations <50 μ mol·L⁻¹ the galvanodynamic simulations predict a breakdown potential only slightly negative (10 to 20) mV of that in the simulated voltammetry; at higher concentrations the simulated galvanodynamic breakdown potentials are equal to, or more positive than, those in the corresponding simulated voltammetry. These trends are consistent with experimental data in Fig. 2, although to a lesser extent, where the measured galvanodynamic breakdown potential is (30 to 60) mV more negative than the corresponding voltammetric result for Cl- $<50 \ \mu mol \cdot L^{-1}$. Neglect of the double layer capacitance of the electrode in simulations, and variation thereof, may contribute to the underestimation of the experimental potential shift.

The combination of micrometer-sized electrodes and electroanalytical methods provide important opportunities to gain new insight into bifurcation reactions. This includes optical imaging of the entire electrode area with suitable resolution to allow cross correlation with the electrochemical data. The hemispherical transport fields also supply high flux conditions analogous to those provided by forced convection on planar electrodes, thereby enabling the relative roles of transport and shear in adsorption and desorption processes to be examined, understanding that may be particularly important for predicting the impact of polymer suppressors in filling of patterned features. Likewise, microelectrodes enable the exploration of finite size effects, relative to pattern formation, on bifurcation reactions, again highly relevant for polymer-containing electrolytes used in feature filling, along with examination of the coupling to ohmic losses associated with current flow in the electrolyte.

Stationary approximation versus moving interface.—Changes in electrode shape and area are important complications in the analysis of deposition reactions. To minimize this effect in the present work the experimental voltammetry was collected at a 10 mV·s⁻¹ scan rate rather than the 2 mV·s⁻¹ or less scan rates often used for pseudo steady-state measurements on macroscale RDEs. For the galvanodynamic experiments swept at 14.48 nA·s⁻¹ to 579 nA (I_{end}), a simple estimate of the build-up is provided by Faraday's law, converting mass to thickness using the density of copper (ρ_{Cu}) and surface area of the microelectrode (A_{UME}) through

$$Thickness = \frac{(0.5I_{end}t)M_{w,Cu}}{z_{Cu}F} \cdot \frac{1}{\rho_{Cu}A_{UME}}$$
[14]

which predicts 0.87 μ m of uniform growth on the microelectrode for the total measurement charge, Q, of 11.58 μ C. While this thickness is only 3.5 % of the microelectrode diameter, the associated area change can measurably alter the predicted voltammetry if a stationary interface approximation is used. Figure 8 shows simulated voltammetry and galvanodynamic responses for 10 μ mol·L⁻¹ and 100 μ mol·L⁻¹ Cl⁻ conditions using both the moving interface calculation used in all Fig. 6 and Fig. 7 simulations and a stationary interface approximation also with parameters from Table I. The two methods produce qualitatively similar voltammetry and galvanodynamic predictions but with clear, albeit minor, quantitative differences. Prior to voltammetric suppressor breakdown the two simulation methods are identical as negligible deposition has occurred. After breakdown the stationary approximation deviates from the



Figure 7. Comparison of experimental galvanodynamic sweeps (gray) to model (—) at the indicated chloride concentrations. Simulated cyclic voltammetry (—) is included to frame the GD data.

moving interface calculation, exhibiting slightly lower peak currents and a small secondary hysteretic loop. Rapid depletion of Cu^{2+} after breakdown reduces the current more for the stationary approximation; this difference is accentuated by higher currents arising from the increase in surface area that includes lateral overgrowth of the electrodeposits. The higher current levels for the moving interface calculation are likewise maintained during the return sweep. The galvanodynamic sweeps also show little variation between the moving interface and stationary calculations at early times due to negligible deposition at the lowest applied currents. As the galvanodynamic sweep progresses the stationary approximation ultimately diverges from the moving interface calculation by 10 mV to 20 mV for both Cl^- concentrations; the expanding surface area of the growing deposit reduces the current density relative to that for the stationary approximation, thereby providing additional depolarization.

Simulations with a stationary approximation were also done for polymer-free and suppressed solutions (Fig. **S3**) to examine the impact on the fitted values of the electrochemical kinetic parameters j_i^o and α_i . The best fit for the fully suppressed parameters did not change using a stationary interface approximation. This is unsurprising, as relatively little deposition occurs over the course of the linear voltammetric sweep. Failure to account for shape change during growth when fitting the voltammetry for the fully active



Figure 8. Simulations of cyclic voltammetry (top) and galvanodynamic sweeps (bottom) using moving interface calculations (-) and a stationary electrode approximation (-) at the indicated chloride concentrations.



Figure 9. Simulated copper growth profiles during (a) cyclic voltammetry at 10 mV·s⁻¹ and (b) linear galvanodynamic sweeps at 14.48 nA·s⁻¹ in 0.24 mol·L⁻¹ CuSO₄, 1.8 mol·L⁻¹ H₂SO₄, and 80 μ mol·L⁻¹ poloxamine (Tetronic 701) at the indicated chloride concentrations. For voltammetry the reverse potential is -0.75 V for each concentration, resulting in a total measurement time of 68 s. For the galvanodynamic sweep current is sweet from 0 to -579 nA, resulting in a total time of 40 s. The images above the charts show the cross-section of the copper deposit for the 100 μ mol·L⁻¹ Cl⁻ concentration (—) and the final growth profile for the 0 μ mol·L⁻¹ Cl⁻ concentration (—).

surface, however, did result in a significant change of the exchange current density: a value of $j_0^o = 3.25 \text{ A} \cdot \text{m}^{-2}$ for the fixed interface rather than $j_0^o = 2.5 \text{ A} \cdot \text{m}^{-2}$ for the moving interface. This 30 % increase in j_0^o also resulted in a slight decrease in the best fit for k_{Cl}^- from $7 \times 10^7 \text{ m}^{-1}$ to $5.2 \times 10^7 \text{ m}^{-1}$, although k_{Cl}^- remained the same at 120 m³·(mol·s)⁻¹. Experimental and simulated cyclic voltammetry across the (0 to 100) μ mol·L⁻¹ range of Cl⁻ concentrations, using the above parameters for the stationary electrode, are shown in Fig. **S4**.

Microelectrode shape evolution during electrodeposition.—In both rotating disk electrode and microelectrode experiments the primary current distribution leads to enhanced deposition at the disk edges and non-uniform deposition profiles. Simulations using a moving interface calculation provide an estimate of the crosssectional profile resulting from such edge effects. Simulations of cyclic voltammetry in Fig. 6 were therefore re-computed using a vertex potential of -0.75 V for each Cl⁻ concentration; the profiles of the resulting deposits are presented in Fig. 9a. Increased deposition is predicted at the edge of the microelectrode for all Cl^{-} concentrations, the suppressor-free (i.e., 0 μ mol·L⁻¹ Cl⁻) case showing the most deposition overall. As chloride concentration increases the suppression breakdown potential shifts negative, reducing the total charge generated by the voltammetry and thereby the amount of deposition. Addition of chloride reduces the deposit height fairly evenly across the microelectrode; the ratio of peak deposit height to that at the deposit center only changes from 1.67 to 1.53 upon an increase from $0^{-}\mu$ mol·L⁻¹ to 100 μ mol·L⁻¹ Cl⁻. The different scales of the x-axis and y-axis make the deposit appear more non-uniform in Fig. 9a than in reality; profiles to scale for the $0 \ \mu \text{mol} \cdot \text{L}^{-1}$ and $100 \ \mu \text{mol} \cdot \text{L}^{-1} \text{ Cl}^{-}$ simulations are shown above the plot. The ratio of average deposit height to microelectrode diameter is 3.7 % and 2.4 % for the 0 μ mol·L⁻¹ and 100 μ mol·L⁻¹ Cl⁻ cases, respectively.

Deposit profiles for the 40 s linear galvanodynamic sweeps in the same electrolytes are shown in Fig. 9b with scale profiles for the 0 μ mol·L⁻¹ and 100 μ mol·L⁻¹ Cl⁻ concentrations shown above. In contrast to the cyclic voltammetry, the total charge in the linear current ramp (11.58 μ C) is the same for all Cl⁻ concentrations. Despite this nominally greater similarity, the simulations show far more variation in deposit profile as a function of chloride concentration. With no Cl⁻ in solution the deposit has a shape analogous to that which results from the voltammetric measurement but with a slightly more uniform profile across the disk (edge-to-center thickness ratio of 1.26). Increasing chloride concentration up to 25 μ mol·L⁻¹ flattens the profile further, leaving an edge-to-center thickness ratio of just 1.08. However, Cl⁻ concentrations between 50 μ mol·L⁻¹ and 100 μ mol·L⁻¹ invert the deposit non-uniformity, producing thicker profiles at the center than at the edge; the 1.34 μ m deposit thickness at the center for the 100 μ mol·L⁻¹ Cl⁻ simulation is 54% thicker than anticipated for uniform deposition. This reverse in the trend suggests a value for chloride concentration exists between 25 μ mol·L⁻¹ and 50 μ mol·L⁻¹ that would result in a nominally uniformly growing interface (i.e., edge-to-center thickness ratio approaching unity) with nearly uniform deposit thickness of 0.87 μ m for the given galvanodynamic measurement charge.

The profiles shown in Fig. 9 correspond to those at the end of the measurements and thus reflect the integrated time-dependent current distributions. However, the significant variations of chemical transport and electric fields during voltammetric and galvanodynamic measurements lead to dynamic current density profiles during deposition on the microelectrode. Figure 10 shows normalized current density profiles (the ratio of local current density to global current divided by the electrode geometric area) at several times during the voltammetric and galvanodynamic measurements in 100 μ mol·L⁻¹ Cl⁻ that correspond to specific features in the associated current and potential transients. For the voltammetry, the first profile at 27.3 s (\bullet) is uniform and reflects the slow kinetics of deposition on the fully passivated electrode interface prior to suppression breakdown. Shortly after suppression breakdown (•) the normalized current profile exhibits slightly more deposition at the center than the edges, matching the observations of increased Cu nucleation density during in situ voltammetry in Fig. 3. This pattern is attributed to the higher flux of Cl⁻ that helps inhibit suppressor breakdown at the microelectrode edge. As the potential is swept negative sustained copper deposition drives full deactivation of the inhibition layer, leading to increased cupric ion depletion. By 34.0 s the current maximum (\bullet) is reached and the current density profile inverts, exhibiting over $3 \times$ higher current density at the microelectrode edge than the center due to the non-uniform electric field and enhanced (chemical) transport of Cu^{2+} to the edge of the disk. However, after the initial "shock" of adlayer breakdown, the cupric ion gradient relaxes so that the variation of deposition rate from the



Figure 10. Normalized instantaneous current density profiles for (a) cyclic voltammetry and (b) a linear galvanodynamic sweep with corresponding (c) i-t and (d) V-t transients in 100 μ mol·L⁻¹ Cl⁻. Current density profiles are normalized by the average current density determined by the initial microelectrode surface area. Local current density for cyclic voltammetry is sampled at -1 mA·cm⁻², -100 mA·cm⁻², the peak current (-172 mA·cm⁻²), -100 mA·cm⁻² on the reverse sweep, and at the end of the measurement. Current density profiles for the GD sweep correspond to potentials at local minima (1.4 s and 9 s), local maxima (5 s and 25 s), and the end of the measurement (40 s).

edge to the center is less pronounced during the return sweep. The electrode surface remains mostly active (\bullet), although enhanced deposition at the edge weakens as the overpotential is reduced and the first signs of inhibition develop at the edge of the disk where the Cl⁻ flux is highest. As the overpotential is reduced further complete repassivation of the electrode occurs, suppression propagating inward from the outer edge of the disk (not shown) due to enhanced Cl⁻ transport. By the end of the voltammogram (\bullet) the current distribution is flat across the disk. The distribution associated with the peak deposition current and subsequent repassivation process is reflected in the final profile depicted in Fig. 9a. The offset from unity for the final current density profile in Fig. 10a reflects the predicted 17 % increase in surface area of the microelectrode from the original geometric area (4.91×10^{-6} cm²).

The earliest current density profile at $1.4 \text{ s}(\bullet)$ for the galvanodynamic sweep in Fig. 10b corresponds to the minimum potential (maximum overpotential) at the first S-NDR inversion and depicts the flat profile of an evenly passivated surface like that seen in voltammetric simulations prior to inhibition breakdown. This sharp potential extremum marks the onset of breakdown of the polymer-Cl⁻ suppression layer. The breakdown is followed by depolarization, reaching a local potential maximum (overpotential minimum) at 5 s (\bullet) . The corresponding simulated chloride surface coverages, shown in Fig. S5, reveal a rapid decrease that is localized to the center 10 μ m of the 25 μ m diameter microelectrode. At 5 s the current density at the center exceeds the global average value by more than a factor of seven. The active central area is surrounded by a passive annular region with current density less than 10 % of the average that extends inward as far as 3 μ m from the microelectrode edge. This substantial non-uniformity reflects the bifurcation of the electrode such that activation or passivation is biased by the local variation in chemical transport provided by the microelectrode

geometry. As the applied current increases the electrode begins to polarize again, reaching a local extremum at 9 s (•). Localization of current density at the microelectrode center remains, although now only five times the average and with a more sharply defined transition to the neighboring passive region. As the applied current increases further, the electrode slowly depolarizes to reach a local overpotential minimum at 25 s (•). The current profile captures the lateral expansion of the active zones coincident with weakened current density at the center that is only 25 % larger than the global average while the outermost 1 μ m of the microelectrode surface still exhibits a passive character. By the end of the galvanodynamic sweep (•) the entire interface is activated, and the peak local current density near the microelectrode edge is 33 % larger than the minimum at the center.

The combination of in situ imaging during cyclic voltammetry (Fig. 3) and galvanodynamic sweeps (Fig. 4) with simulations of the spatiotemporal current distribution (Fig. 10) indicate that the operating mode, i.e., galvanodynamic or potentiodynamic, results in substantially different growth profiles due to variation in the local current density at the microelectrode-electrolyte interface during S-NDR bifurcation. In each case, non-uniform deposition reflects spatially varying chemical concentrations and gradients as well as competition between the adsorbed polymer-chloride suppression layer and potential-driven activation of copper deposition. For cyclic voltammetry, potentiodynamic control (as well as freely evolving current) permits sustained activation of the electrode after critical breakdown of the suppression layer, only iR drop within the system prevents a truly instantaneous activation. The bifurcation into active and passive zones that precedes full activation is correspondingly rapid. In contrast, the defined current provided by galvanodynamic operation enforces a clearer and more extended view of the spatial bifurcation as long as the applied current remains insufficient to



Figure 11. Normalized instantaneous current density profiles for a linear galvanodynamic sweep with corresponding V-t transient in 20 μ mol·L⁻¹ Cl⁻. Current density profiles are normalized by the average current density determined by the initial microelectrode surface area.

activate the full surface. At higher Cl⁻ concentrations, two S-NDR elements are then evident. The first instance of breakdown is localized to the center of the microelectrode, leaving an annular passive perimeter. Progression of the linear current ramp to more negative values leads to further polarization and sharpening of the active-passive boundary at the second polarization extremum. Only further increases in current drive lateral expansion of the active zones, with full activation achieved by the end of the measurement. Experimental images of galvanodynamic sweeps in 100 μ mol·L⁻¹ Cl⁻ showed the first instance of breakdown occurring slightly off-center for this particular specimen, in contrast to the simulated profiles; the simulations do not account for microstructural inhomogeneities in the electrode surface that can favor experimental adlayer disruption.

In both simulations and experiments (Fig. 7) multiple NDR inversions are generally a characteristic feature of electrolytes with higher Cl⁻ concentrations whereas lower concentrations typically exhibit a single NDR inversion. In situ optical microscopy of a galvanodynamic sweep with a single inversion (Fig. 4a) reveals a relatively rapid transition from passive to active deposition by lateral propagation of the activation front across the entire microelectrode surface. Similarly, simulations of the instantaneous current density profiles in Fig. 11 for the 20 μ mol L⁻¹ Cl⁻ galvanodynamic sweep (also exhibiting a single NDR inversion) indicate that the current density at all locations remains over 35 % of the global average current density for the entire measurement. Furthermore, the local current density only drops below 50 % of the average value for a period of 8 s (between 5 s and 12 s) on the outermost 1 μ m of the microelectrode. Finally, the peak normalized current is never greater than 55 % of the average current density $(1.55\times)$, much less than the peak current density observed for the 100 μ mol·L⁻¹ Cl⁻ simulation in Fig. 10b, with its maximum value locally exceeding 7× the average current. These simulations and experimental observations indicate that electrolytes yielding multiple NDR inversions in a galvanodynamic sweep provide greater localization and stability to the deposited Cu as well as additional insight into the bifurcation process and its application to the current controlled filling of recessed surface features.

Finally, it is noteworthy that the localization of deposition associated with S-NDR systems may have applications in technologies beyond the filling of recessed surface features. Specifically, the link between galvanodynamic measurements and simulations of metal deposition on microelectrodes demonstrates how S-NDR systems can naturally give rise to spontaneous whisker growth. With optimization this might be employed in additive manufacturing of micro- to conceivably nano-wires⁶³ and/or the controlled formation of convex bumps for interconnect packages provided the effect can extend uniformly over arrays of a feature. Alternatively, absent a

taming of the associated instabilities, such whisker-like growth can have a negative impact in electrochemical technologies such as metal/metal ion batteries. Specifically, the reliability of these systems is often associated with the formation and stability of a solid-electrolyte interface that serves to passivate the surface and mediate charge transfer reactions. Unfortunately, defects and related instabilities in the passivation layers often lead to whisker-like metal growths that can result in catastrophic short-circuiting. The coupling between galvanodynamic control and morphological evolution in S-NDR systems detailed herein provides a new avenue for fundamental understanding of whisker growth, a topic that has received limited attention to date.

Conclusions

Copper deposition in the presence of a single organic additive and chloride exhibits dynamic instabilities characteristic of S-shaped negative differential resistance (S-NDR) systems. Cyclic voltammetry on a microelectrode shows features similar to previous experimental results using rotating disk electrodes; namely, a potential-dependent breakdown of the polyether-chloride adlayer that shifts negatively with increased Cl⁻ concentration accompanied by a sharp increase in current that is subsequently guenched on the return sweep resulting in large hysteretic voltammetry. In contrast to the RDE experiments, correction of the ohmic losses for microelectrode measurements based on the geometric area does not produce a clear inversion in the post-experimental corrected i-V curve. However, in situ optical imaging of the microelectrode during voltammetric measurements reveals that copper deposition is initially localized towards the center of the microelectrode; this localized Cu deposit effectively corresponds to a smaller diameter microelectrode and thus higher ohmic electrolyte losses. Subsequently, lateral propagation of adlayer breakdown follows leading to complete activation of the entire electrode. Simulations of the morphological evolution during breakdown of the two-additive suppressor model are consistent with experimental observations, exhibiting an initial rise in the current density profile at the center of the microelectrode followed by complete activation to the perimeter. Nonetheless, the predicted current density profile following voltammetric measurements remains non-uniform for all chloride conditions examined as a result of the primary current distribution and enhanced hemispherical transport to the disk edges.

Linear galvanodynamic sweeps, in contrast to voltammetry, allow the potential to adjust freely revealing the negative differential resistance and associated breakdown of the polyether-Cl⁻ adlayer over the entire range of Cl⁻ concentrations examined. For more concentrated Cl⁻ solutions multiple NDR inversions are evident during both experimental and simulated galvanodynamic sweeps. In situ optical microscopy reveals that systems exhibiting the single NDR inversion transition rapidly from the passive to active state by lateral propagation of suppressor breakdown from the center of the microelectrode. In contrast, systems manifesting the double NDR inversion show sustained bifurcation of the microelectrode into passive and active zones with significant vertical growth of the active region before the second inversion leads to lateral expansion of the active area; given sufficient applied current, the microelectrode surface is fully activated. Simulations of the deposit growth profiles and instantaneous current density profiles are in good agreement with the experimental observations.

Additive suppressed electrodeposition systems that bifurcate into active and passive domains have proven to be valuable for filling of high-aspect ratio recessed surface features relevant to the metallization of microelectronics. The results presented herein demonstrate that the operating mode (potentiodynamic or galvanodynamic) significantly impacts the morphological evolution of bistable S-NDR systems. Process stability and ease of control associated with galvanodynamic sweeps provide important insight into the operation of the S-NDR systems. The localization of deposition for S-NDR systems observed under galvanodynamic control offers additional insight into dynamics observed during bottom-up filling of recessed surface features used in microfabrication applications. The present construct may also provide a theoretical basis for understanding non-uniform growth of whiskerlike structures in many inhibited metal deposition systems.

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