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Correction to “Anions in Corrosion: Influence of Polymer Electrolytes on the Interfacial Ion Transfer Kinetics of Cu at Au(111) Surfaces”

Permalink

<https://escholarship.org/uc/item/34w5k3hx>

Journal

ACS Electrochemistry, 1(9)

ISSN

2997-0571

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Publication Date

2025-09-04

DOI

10.1021/acselectrochem.5c00298

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Anions in corrosion: Influence of polymer electrolytes on the interfacial ion transfer kinetics of Cu at Au(111) surfaces

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Abstract

The corrosion kinetics of metals in the presence of polymer electrolytes—which are frequently used in devices for the electrochemical production of hydrogen, hydrocarbons, and alcohols—is convoluted by transport and ill-defined reactive interfaces which mask the fundamental reaction kinetics. Underpotential-deposited monolayers of Cu at Au(111) surfaces provide a structurally well-defined active site for interfacial ion transfer, with a fixed number of sites available for adsorption. Here, we investigate the adsorption behavior of Cu at Au(111) surfaces across a series of sulfate and sulfonate electrolytes, to understand how anion structure influences the kinetics of elementary interfacial ion-transfer reactions. The influence of anion structure is most significant at high adsorbate coverage, with similar adsorption isotherms and kinetics observed for all three molecular sulfates and sulfonates. In contrast, a suspended perfluorosulfonic acid ionomer reduced both the equilibrium coverage of Cu as well as the standard exchange rate at Au(111) at low coverages of Cu. These results suggest that electrocatalyst corrosion is inhibited for metal nanoparticles supported at polymer electrolytes due to changes in adsorbate coverage as well as suppressed kinetics for interfacial ion transfer.

Keywords: Interfacial ion transfer, corrosion kinetics, durability, copper

Introduction

Corrosion reactions limit the operational environments available to electrocatalysts,¹⁻⁵ conductive supports,^{6, 7} semiconducting light absorbers,⁸⁻¹⁰ and protective transparent conducting oxides used in (photo)electrochemical cells.^{11, 12} These reactions are generally controlled by the transfer of ions—not electrons—through the double layer, so measurements of ion-transfer kinetics are thus critical for understanding the durability of (photo)electrochemical cells. Corroding electrode/electrolyte interfaces present many possible active surface sites, having varied free energies of adsorption and unknown activation energies for interfacial ion transfer, whereas adatoms and monolayers prepared via underpotential deposition (UPD)^{13, 14} on uniform metal surfaces are limited by a fixed number of surface sites for adsorption events. Because UPD reactions are inherently self-limiting, electrodes prepared from (sub)monolayer metal adatoms are well-suited for studying the fundamentals of interfacial ion transfer.

Despite the broad importance of both corrosion and electrodeposition reactions, many basic aspects of ion-transfer kinetics remain poorly understood.¹⁵ The behavior of electrode/electrolyte interfaces is controlled by adsorbates that define the electric field. These species often bear a partial charge that is challenging to measure experimentally, but a crucial component of any robust model of the polarized interface.¹⁶ For many transition metals where a stable, solvated, monovalent state is energetically disfavored (Zn, Ni, Fe), the exact intermediate crossing the double layer is still not known.^{17, 18} However, free and adsorbed anions, as well as the organization of the solvent in the double-layer region, are believed to play a critical role in controlling ion-transfer kinetics.¹⁹⁻²² An ideal system for measuring ion-transfer kinetics would include a single, well-defined active site for adsorption at an electrochemically inert metal, such as a three-fold hollow site at an Au(111) surface.

Cu is an interesting species for studying interfacial ion transfer because it exists as stable Cu^{2+} and Cu^+ species in solution and forms UPD adlayers on many noble metal surfaces.¹³ Perhaps one of the most-studied adsorption systems is the Au(111)/Cu electrode in H_2SO_4 , which yields a distinct set of two, chemically reversible adsorption peaks at potentials positive of the equilibrium potential for Cu/Cu^{2+} (E_{rev}).^{13, 23-25} Co-adsorbed species have been shown to disrupt the equilibrium structure of Cu UPD layers, in particular halides, but the influence of anions on the kinetics of adsorption has received less attention.²⁶⁻²⁸ Schlaup et al. showed that introducing chloride as a co-adsorbed species in the UPD process leads to stable submonolayers which collapse at electrode potentials where Cl^- is desorbed from the Au(111)/Cu surface.²⁹ Coadsorbed anions do not appear to be necessary to stabilize a complete monolayer of Cu at E near E_{rev} . Cu is also the only pure metal shown to facilitate the CO_2 reduction (CO_2R) reaction with substantial activity towards multi-carbon products,^{30, 31} and may be integrated in gas-diffusion-electrode microenvironments where anions exist exclusively as pendant side chains.³²⁻³⁴ For this reason, we used Cu^{2+} as a model system to understand how free and fixed anions influence the possibly rate-limiting step of corrosion reactions occurring in cells forming multi-carbon products from CO_2 .

A series of sulfonic acid electrolytes were selected to systematically modify supporting anion structure: sulfuric acid, methanesulfonic acid (MSA), triflic acid (TFMSA), and an aqueous suspension of perfluorosulfonic acid (PFSA) ionomer (Nafion® 1100). When dispersed in water, PFSA ionomers are believed to form colloidal suspensions with tightly packed rod-like structures; the hydrophobic perfluorinated backbone aggregates to create a water-free core while the hydrophilic sulfonate groups are facing outward.³⁵⁻³⁷ Here, we report the corrosion and deposition behavior for Cu monolayers on Au(111) in electrolytes containing only polymeric cation-conducting polymers, with no metal cations other than Cu^{2+} as the bulk redox couple. The

interfacial ion-transfer kinetics of Cu^{2+} on Au(111) were quantified and compared for sulfonates to determine the specific chemical factors that influence this important elementary step associated with corrosion reactions.

Methods

Chemicals: Deionized water having a resistivity $>18.2 \text{ M}\Omega\text{-cm}$, DI H_2O , was obtained from a laboratory water purification system (Barnstead Ultrapure). Sulfuric acid (H_2SO_4 96%, TraceMetal Grade) was obtained from Fisher Chemical, methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$, 70.6%) was obtained from Alfa Aesar, and triflic acid ($\text{CF}_3\text{SO}_3\text{H}$, 99% extra pure) was obtained from Acros Organics. A 10% aqueous suspension of perfluorosulfonic acid, PFSA, ionomer (10 w%) was obtained from the Fuel Cell Store. Cuprous oxide was obtained from Acros Organics (ACS reagent) and was used as a consistent source of Cu^{2+} for all other anions present in supporting electrolytes and was added in concentrations well below the solubility limit of $\text{Cu}^{2+}(\text{aq})$. Typical Cu^{2+} containing electrolytes were prepared by dissolving CuO (1 mM Cu equivalent) in 10 mM acid such that the final $[\text{Cu}^{2+}]$ was 1 mM and the final pH was ~ 2.1 .

Electrodes: Au(111) surfaces were prepared from thermally evaporated films of Au on titanium-coated glass substrates (**Supporting Information**).^{38, 39} Glass slides were cleaned in an O_2 plasma and transferred to a thin-film deposition system (Angstrom Engineering) with a base pressure of 10^{-6} torr. Ti was deposited via electron-beam evaporation at $0.2 \text{ \AA s}^{-1}$ to a nominal thickness of 17 nm followed by Au deposited via thermal evaporation at $0.2 \text{ \AA s}^{-1}$ to $0.5 \text{ \AA s}^{-1}$ to a nominal thickness of 200 nm; a shadow mask defined the working area of the electrode surface. Electrodes were carefully annealed in a butane gas flame and cooled under Ar immediately before transferring the surface to the cell environment.

Electrochemical characterization:

All glassware was cleaned in sulfuric acid with a persulfate-based oxidizing agent (Alnochromix) and boiled and washed in deionized water at least three times before use to remove trace organic and inorganic contaminants, including sulfate, which could interfere with adsorption behavior. A Pt wire (Alfa Aesar 99.95%) served as the counter electrode and a reference electrode, $\text{Cu}/\text{Cu}^{2+}(\text{aq}, 10 \text{ mM})$, was prepared from a clean Cu wire (Alfa Aesar, 99.999% metals basis) in a supporting electrolyte identical to

the working electrochemical cell but maintained behind a microporous glass frit. All potentials are reported versus the equilibrium potential for Cu deposition from $\text{Cu}^{2+}(\text{aq})$, E_{rev} . Solutions were purged with ultra-high-purity Ar (99.999%) and maintained under a blanket of flowing Ar gas throughout the experiments. All Cu-containing solutions were prepared by dissolving 1 mM CuO in 10 mM HA where A was HSO_4^- (HSA), CH_3SO_3^- (MSA), CF_3SO_3^- (TFMSA), except for the polymer solution which was prepared as a 10 meq suspension of perfluorosulfonic acid ionomer electrolyte (PFSA). More-concentrated suspensions of PFSA could not be purged with Ar due to the generation of persistent foams. Surfaces were conditioned by sweeping the potential at 20 mV s^{-1} in 1 mM Cu^{2+} dissolved from CuO in 10 mM H_2SO_4 from 0.95 to 0 V vs E_{rev} until a steady electrochemical response was reached (4-10 cycles).

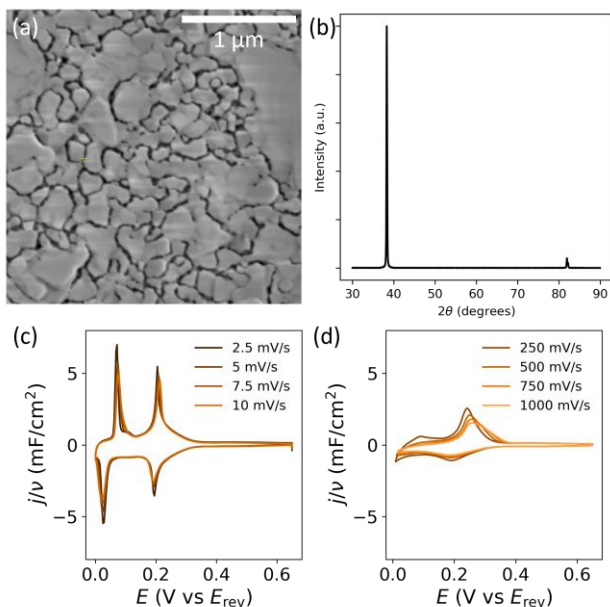


Figure 1: Physical and electrochemical characterization of Au(111) surfaces. **(a)** Scanning electron micrograph of annealed Au surface. **(b)** X-ray diffraction pattern from the Au surface collected at normal incidence. **(c)** Representative voltammetry of annealed Au(111) electrodes in 1 mM CuO, 10 mM H_2SO_4 at slow scan rates ($\nu = 2.5, 5, 7.5, 10 \text{ mV s}^{-1}$) **(d)** Representative voltammetry of annealed Au electrodes in 1 mM CuO, 10 mM H_2SO_4 at fast scan rates ($\nu = 250, 500, 750, 1000 \text{ mV s}^{-1}$)

Results

Scanning-electron microscopy of the annealed Au electrode surfaces revealed the presence of terraces ranging from 10s to 100s of nm in width (**Figure 1a**) and surface X-ray diffraction displayed only the diffraction peaks expected from an Au(111) surface (**Figure 1b**). All Au(111) electrodes were first characterized in 1 mM Cu²⁺(aq), 10 mM SO₄²⁻(aq) to verify the consistency of the annealing process. Whereas as-deposited Au films yielded multiple, broad cathodic peaks (**Figure S1**), the voltammetric response of annealed Au surfaces displayed a single pair of sharp cathodic peaks at 0.19 and 0.03 V vs. E_{rev} ($\nu = 2.5 \text{ mV s}^{-1}$) with charge-balanced anodic peaks at 0.07 and 0.20 V, respectively, characteristic of UPD of Cu on Au(111) (**Figure 1c**). The reference potentials for these two adsorption processes were measured as $E_{1/2}$, the average of the anodic and complementary cathodic peak potential, which were 0.051(4) and 0.202(3) V vs. E_{rev} .⁴⁰

Because our focus is on adsorptive processes, voltammetry is presented as current density normalized to scan rate, j/ν , as a function of potential, E , which as the units of areal capacitance. The cathodic charge passed was integrated from $E = 0.0\text{--}0.6 \text{ V vs. } E_{\text{rev}}$ and compared against the theoretical charge for complete adsorption of Cu²⁺ onto the Au(111) surface ($Q_{\text{Cu}}^* = -0.44 \text{ mC cm}^{-2}$) to estimate the Cu coverage, θ_{Cu} (**Figure S2a**, Equation 1)

$$\theta_{\text{Cu}}(E) = \frac{1}{Q_{\text{Cu}}^*} \int_{0.360}^E j/\nu dE \quad (1)$$

$\theta_{\text{Cu}}(0.0 \text{ V})$ was >0.9 for $\nu \leq 25 \text{ mV s}^{-1}$ and then decreased steadily with increasing ν to < 0.45 at 1000 mV s^{-1} (**Figure 1d**). At increased scan rates ($\nu > 100 \text{ mV s}^{-1}$) a single quasi-reversible wave was observed, with $E_{1/2}$ systematically increasing from 0.204 to 0.240 V with increasing scan rates ν . Based on characterization via scanning tunneling microscopy,^{27, 41, 42} *in-situ* X-ray diffraction,⁴³ and X-ray absorption spectroscopy^{23, 24} of similar surfaces, the more positive

adsorption peak was assigned to the UPD of Cu^{2+} along with SO_4^{2-} and the second peak was ascribed to the formation of a nearly complete monolayer of Cu on the Au(111) surface.

The Au(111) electrodes cleaned in DI H_2O and transferred to a cell containing 1 mM CuO, 10 meq PSFA produced a voltammetric response that was distinct from electrodes in H_2SO_4 electrolyte at all scan rates (**Figure 2a**). Characterization of the electrolyte using dynamic light scattering suggested that it was described by a suspension of ~ 100 nm dispersed colloidal ionomer, which was acidic enough to dissolve the solid CuO (**Figure S3**). No scattering particles were observed for CuO dissolved in any other electrolytes tested in this work. At $\nu = 5 \text{ mV s}^{-1}$, the onset of Cu adsorption occurred at $E_{\text{rev}} < 0.3 \text{ V}$ with a minor cathodic peak at $\sim 0.15 \text{ V}$ and a larger cathodic wave that could not be resolved prior to bulk Cu deposition. A sharp and well-defined anodic peak was evident for $\nu = 5\text{--}25 \text{ mV s}^{-1}$, with E_p shifting positively from 0.17–0.22 V. For $\nu = 50\text{--}1000 \text{ mV s}^{-1}$ a single anodic and cathodic wave was observed, with a peak capacitance and integrated area that quickly decreased with increasing ν . For all ν , the integrated charge was less than the expected charge for a complete Cu monolayer and E was kept positive of potentials where bulk Cu is thermodynamically stable on the electrode surface. The anodic peak potential, E_{pa} , shifted negatively by 0.040 V from 0.192 to 0.152 V, while the cathodic peak potential, E_{pc} , shifted positively by $> 0.130 \text{ V}$ from 0.232 to 0.368 V. Less Cu was adsorbed onto the Au(111) surface from PFSA electrolytes compared to H_2SO_4 electrolytes and the adsorption kinetics were more-strongly affected by increasing ν at both low and high coverages (**Figure 2b**). At slow scan rates ($\nu = 2.5 \text{ mV s}^{-1}$), an incomplete monolayer was formed ($Q_{\text{ad}} \sim 0.3 \text{ mC cm}^{-2}$) and

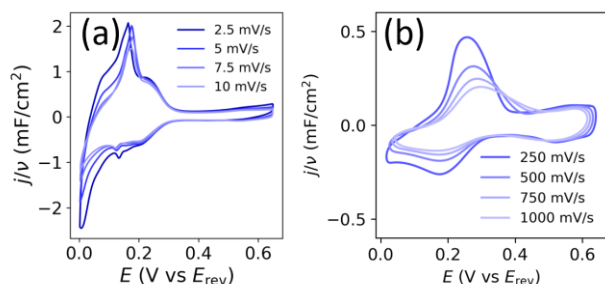


Figure 2: Cu UPD in aqueous PFSA electrolyte. **(a)** Voltammetry of annealed Au(111) electrodes in 1 mM CuO, 10 meq PFSA at slow scan rates ($\nu = 2.5, 5, 7.5, 10 \text{ mV s}^{-1}$) **(b)** Voltammetry in 1 mM CuO, 10 mM H_2SO_4 at fast scan rates ($\nu = 250, 500, 750, 1000 \text{ mV s}^{-1}$)

at the fastest scan rates $Q_{\text{ad}} < 0.041 \text{ mC cm}^{-2}$, corresponding to $\theta_{\text{Cu}} < 0.10$ (**Figure 2b**, **Figure S2d**).

To understand the differences caused by the polymeric nature of PFSA and those resulting from chemical differences between sulfonate and sulfate anions, we measured the UPD and corrosion behavior of Cu in two additional electrolytes (**Figure 3**). Methane sulfonic acid (MSA), $\text{CH}_3\text{SO}_3\text{H}$, and triflic acid (TFMSA), $\text{CF}_3\text{SO}_3\text{H}$, were selected as representative hydrocarbon and fluorocarbon sulfonate anions. The voltammetry of Au(111) in 1 mM CuO, 10 mM MSA is presented in **Figure 3a**, where at $\nu = 2.5\text{--}20 \text{ mV s}^{-1}$ sharp cathodic peak was observed at $E_{\text{pc}} = 0.017\text{--}0.075 \text{ V}$ with a corresponding anodic peak at $E = 0.15\text{--}0.24 \text{ V}$. $Q_{\text{ad}} \sim 0.4 \text{ } \mu\text{C cm}^{-2}$ at $\nu = 2.5 \text{ mV s}^{-1}$ (**Figure S2b**) suggesting that nearly a complete Cu monolayer could be formed from sulfonate solutions at sufficiently slow ν . At increased ν ($75\text{--}1000 \text{ mV s}^{-1}$) only a single, broad cathodic wave at $E_{\text{pc}} = 0.23\text{--}0.17 \text{ V}$ was connected to an anodic peak, which shifted positively with increasing scan rates from $E_{\text{pa}} = 0.24\text{--}0.35 \text{ V}$. The voltammetric response was similar in both MSA and TFMSA, particularly at high ν , with similar $E_{1/2} = 0.243(8)$ and $0.239(5) \text{ V}$ for MSA and TFMSA, respectively, measured at $\nu = 75 \text{ mV s}^{-1}$. The Au(111) in 1 mM CuO and 10 mM TFMSA yielded a single desorption peak at all ν , but a sharp adsorption peak was observed for $\nu \leq 25 \text{ mV s}^{-1}$. For both MSA and TFMSA electrolytes, Q_{ad} decreased with increasing ν , with a

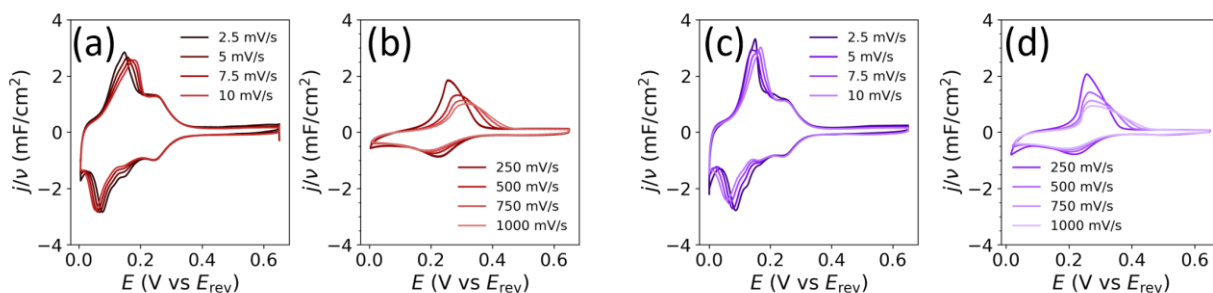


Figure 3: Cu UPD in representative molecular sulfonate electrolytes. Scan rate dependence (a) 2.5, 5, 7.5, 10 mV s^{-1} and (b) 250, 500, 750, and 1000 mV s^{-1} for Cu adsorption on Au(111) electrodes in 1 mM CuO, 10 mM MSA (c,d) Scan rate dependence in 1 mM CuO, 10 mM TFMSA.

maximum of 0.16 and 0.14 mC cm⁻² at $\nu = 1000$ mV s⁻¹ ($\theta_{\text{Cu}} \sim 1/3$) (**Figure S2b,c**). At high ν , the positive shift in the anodic peak potential was greater than the commensurate negative shift in cathodic peaks, which could be related to the more substantial changes in the surface composition during Cu stripping as compared to the early stages of the adsorption process (**Figure 1d**, **Figure 2d**, **Figure 3b,d**).

At positive E (corresponding to low θ_{Cu}), the onset of Cu adsorption and the tail end of Cu desorption were similar ($E \sim 0.3$ V) across all four electrolytes despite the varied j - E behavior at increasing θ_{Cu} (**Figure 4**). At low ν , the adsorption and desorption capacitance were nearly symmetric in E and invariant with ν , indicating reversible kinetics for Cu adsorption and desorption. The broad adsorption wave in this potential region has previously been assigned to “random” adsorption of Cu onto the Au(111) surface.²⁵ We interpret the similar peak character for the four anions to suggest that at low coverages the adsorption sites for Cu at Au(111) are invariant with the supporting anion.

To characterize the adsorption behavior of anions present in Cu adsorption/desorption experiments, we collected voltammetry for Au(111) electrodes in acids that were free of CuO and at a comparable ionic strength (**Figure S4**). Au(111) exhibited $C_{\text{dl}} > 80$ $\mu\text{F cm}^{-2}$ for all E in 10 mM H₂SO₄ and showed pseudocapacitive peaks at $E = 0.24$ and 0.48 V vs E_{rev} (**Figure S4a**). In contrast, the PFSA electrolyte yielded a nearly constant $C_{\text{dl}} \sim 30$ $\mu\text{F cm}^{-2}$ until the onset of oxidation of the Au(111) surface at $E > 0.5$ V (**Figure S4d**). Au(111) surfaces in H₂SO₄ were stable at $E < 1.0$ V with a small set of peaks at 0.84 and 0.88 V previously attributed to an ordered-to-disordered phase transition of adsorbed HSO₄⁻ (**Figure S5a**).⁴⁴ Voltammetry of Au(111) surfaces in aqueous 10 mM MSA or 10 mM TFMSA did not show prominent current peaks indicative of specific adsorption, with C_{dl} between 50 and 125 $\mu\text{F cm}^{-2}$ for MSA and between 30 and 85 $\mu\text{F cm}^{-2}$ for TFMSA (**Figure**

S4b,c). The Au(111) surface in the presence of the sulfonate anions, or possibly the anions themselves, showed a reduced oxidative stability relative to sulfate, with irreversible faradaic currents observed for $E > 0.8$ V. Similar decomposition products from polymer electrolytes have been shown to impact catalyst activity (**Figure S5**).⁴⁵

Discussion

$\text{Cu}^{2+}(\text{aq})$ prepared from CuO dissolved in an aqueous suspension of PFSA⁻ anions facilitated direct measurements of the potential dependence of θ_{Cu} , as well as Cu^{2+} adsorption kinetics, without competing transport limitations through solid-polymer electrolytes and *without the competing influence of other anions*. The equilibrium adsorption behavior of Cu at Au(111) in the presence of PFSA (**Figure 2a**) is substantially different from behavior observed in the presence of HSO_4^- (**Figure 1a**). Cu adsorption from PFSA electrolytes led to lower θ_{Cu} and impeded the formation of an ordered Cu monolayer despite yielding similar $\theta_{\text{Cu}}-E$ behavior at low θ_{Cu} (**Figure 4**).

These data highlight the role of charge-balancing anions in enabling increased coverage of charged surface intermediates. Co-adsorbed sulfate is associated with higher θ_{Cu} at more-positive potentials in comparison to singly-charged MSA and TFMSA (**Figure 3a,c**). Despite similarities in structure, sulfonate anion groups are expected to interact differently with multivalent corrosion products such as Cu^{2+} . Moreover, polymer chains with PFSA acid groups have been observed via electrochemical quartz-crystal microbalance and atomic-force microscopy to specifically adsorb to the Au(111) surface, and can thus compete with Cu for adsorption sites.⁴⁶ Uncharged polymer backbones may suppress interfacial ion transfer and reduce the surface coverage of Cu^{2+} via direct competition for adsorption sites or also by displacing charge-balancing anions at the surface or

within the double layer.⁴⁷ The absence of the typical voltage-driven surface phase transition observed for CuSO₄ electrolytes at Au(111) at $\nu \geq 250 \text{ mV s}^{-1}$ (**Figure 1c**), and qualitatively similar voltammetry across all three anions, indicates that the voltametric response at fast scan rates was governed by the adsorption of Cu²⁺ only (**Figures 2, 3**).

The scan rate dependence of anodic and cathodic waves indicate differences in the deposition and corrosion process for Cu at Au(111). Greater changes in E_{pa} were observed for all three anions compared to the corresponding shift in E_{pc} , potentially caused by hysteresis in the potential-dependent surface composition. We did not attempt to definitively assign the surface phase of Cu species formed at fast scan rates; it could comprise incomplete islands of ordered RSO₃⁻/Cu or Cu(111)/Au(111) phases, with the latter being formed in a zero-current process during the potential excursion near $E = 0.0 \text{ V}$ vs E_{rev} . The corrosion of electropolished, polycrystalline Cu was accelerated in MSA compared to similar concentrations of H₂SO₄ (**Figure S6**). Differences in the structure of the ordered adsorbed layers of Cu²⁺ and anions could play an important role in the corrosion behavior of bulk Cu metal.

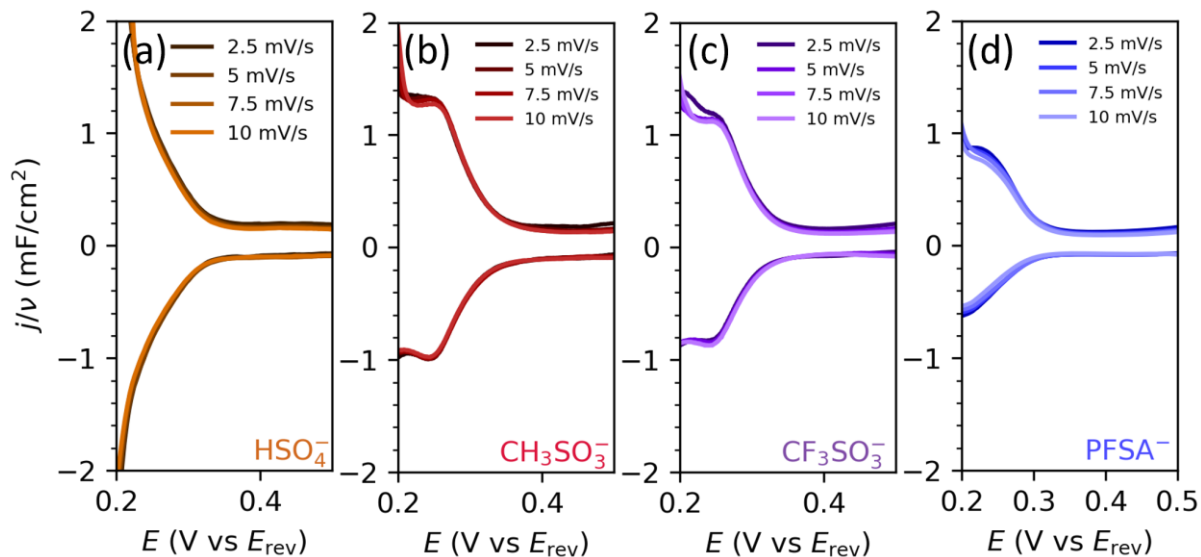
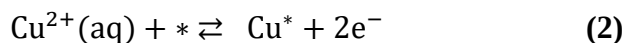


Figure 4: Comparison of adsorption onset for sulfate and sulfonate electrolytes. Kinetically reversible adsorption behavior was observed for Cu²⁺ in (a) H₂SO₄, (b) MSA, (c) TFMSA, and (d) PFSA, for scan rates $\nu = 2.5\text{--}10 \text{ mV s}^{-1}$.

Adsorption of Cu at low θ_{Cu} is quasi-reversible and allowed for the direct measurement of Cu interfacial ion-transfer kinetics as a function of the anion environment. At low θ_{Cu} ($E > 0.3$ and $\theta_{\text{Cu}} < 0.05$), the influence of processes related to nucleation and growth is minimized and the equilibrium adsorption behavior was similar for all sulfonate electrolytes (**Figure 4**), consistent with mechanism described by Equation 4 which is independent of the anion identity (**Equation 2**).



The distinct adsorption behavior for Cu^{2+} in the presence of sulfate as compared to sulfonates converged to a qualitatively similar set of peaks at the fastest scan rates, which was commensurate with a decrease in the maximum coverage to $\theta_{\text{Cu}} < 0.2$ (**Figures 1, 3, S2**). This is consistent with a model for UPD where ordered adlayers of Cu and supporting anions are necessary to stabilize the excess surface charge associated with $\theta_{\text{Cu}} > 0.2$ when $E \gg E_{\text{rev}}$.

The exchange rate for Cu adsorption and desorption was estimated using a method of analysis developed by Kuo et al. for quantifying the rates of proton adsorption onto Pt(111).⁴⁸ Cu adsorption rates were estimated from the current during the cathodic sweep from $E = 0.36$ V to 0.2 V, which ensured that Cu adsorption primarily occurs on isolated Au(111) adsorption sites, with the further assumption that Cu^{2+} completely transferred through the double layer to coordinate with the Au surface. Although *in-situ* x-ray absorption near-edge structure measurements (XANES) suggest the oxidation state of Cu at these potentials is approximately +1,⁴⁹ the total integrated charge ($\sim 440 \mu\text{C cm}^{-2}$) is consistent with complete transfer of Cu^{2+} through the electrochemical double layer ($\mu\text{C cm}^{-2}$).¹³

A baseline correction to the current is applied using the capacitance at 0.36 V vs E_{rev} and θ_{Cu} is then estimated from the remaining integrated charge normalized to Q_{Cu}^* .¹³ The apparent interfacial ion transfer rate (k_{app}) was calculated by **Equation 3**

$$k_{\text{app}} = \frac{j(E)}{|Q_{\text{Cu}}^*|} \quad (3)$$

where j is the current density corrected for double layer charging in the absence of Cu^{2+} , (**Figure 5**). We fit interfacial ion-transfer kinetics to a Butler-Volmer-type equation (Equation 2) where the driving force, ξ ($E - E_{\text{eq}}$), is assumed to vary with the difference in the applied electrode potential from the experimentally observed equilibrium potential (**Equation 4**)

$$k_{\text{app}} = k_0 \sqrt{\theta_{\text{Cu}}(1 - \theta_{\text{Cu}})} \left[\exp\left(\frac{\alpha e \xi}{k_b T}\right) - \exp\left(-\frac{(1-\alpha)e \xi}{k_b T}\right) \right] \quad (4)$$

where α , e , k_b , T , and k_0 are the transfer coefficient, elementary charge, Boltzmann constant, temperature, and standard exchange rate. The E_{eq} are measured at a sweep rate of 7.5 mV s^{-1} , sufficiently slow to give a response that well approximates the equilibrium response, that is, the

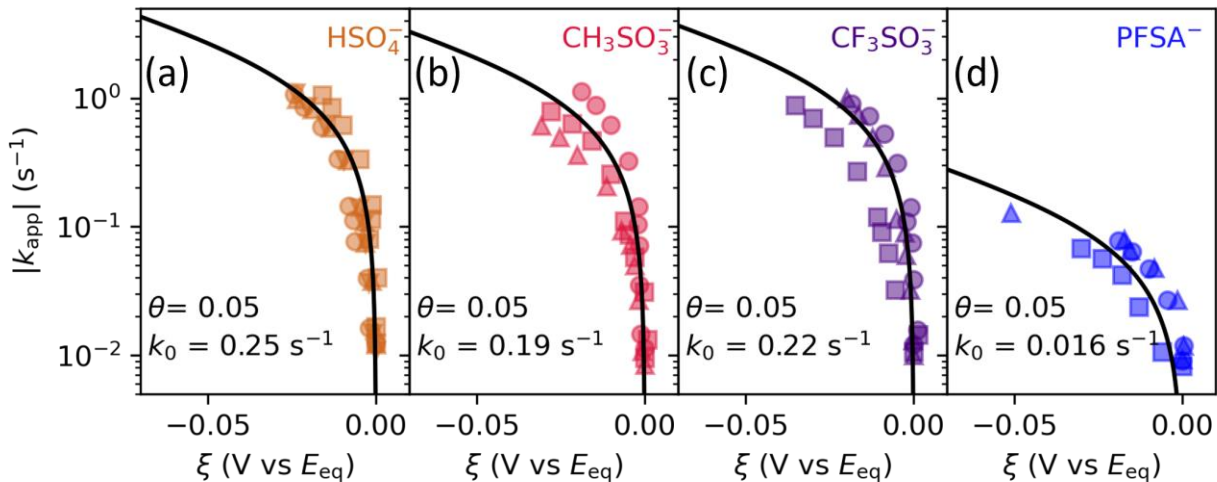


Figure 5. Interfacial Cu transfer apparent interfacial ion transfer rate vs driving force at 5% coverage of Cu on an Au(111) surface in 1 mM CuO in (a) 10 mM H_2SO_4 , (b) 10 mM MSA (c) 10 mM TFMSA and (d) 10 meq PFSA⁻ ionomer electrolyte. Data were fit with **Equation 4** (solid black line) to calculate k_0 . Independent replicates for freshly cleaned Au(111) electrodes are represented by circles, squares, or triangles.

collected j/v data is no longer a strong function v . The experimental data were fit to (4) using a non-linear least-squares algorithm to determine k_0 , assuming $\alpha = 0.5$.^{48, 50}

When Cu occupied 5% of the available surface sites, k_0 for Cu^{2+} interfacial ion transfer is $0.25(6) \text{ s}^{-1}$ in the presence of HSO_4^- and was $0.19(9) \text{ s}^{-1}$ and $0.22(7) \text{ s}^{-1}$ for Cu^{2+} in the presence of MSA and TFMSA, respectively (**Figure 5**). We similarly fit the data for HSO_4^- for α values between 0.1 and 0.9, which led to estimated values for k_0 between 0.33 s^{-1} and 0.19 s^{-1} , respectively (**Figure S7**). Although this fitting procedure was not able to discriminate for different values of α , this parameter had only a modest effect on the apparent k_0 . Thus, despite the significant changes to the adsorption behavior in the high θ_{Cu} limit, differences in the identity of non-polymer sulfonate anions had no significant influence on the interfacial ion-transfer kinetics at low θ_{Cu} . However, when PFSA served as the supporting anion, the standard exchange rate is reduced by approximately one order of magnitude ($k_0 = 0.016(5) \text{ s}^{-1}$).

Difference in interfacial ion transfer kinetics could be caused by a lower number of available surface sites for adsorption (**Figure 2**) and/or a greater free energy barrier for reorganization during interfacial ion transfer due to the additional steric and rotational constraints on polyanions. The total adsorbed charge for Cu on Au(111) in the PFSA electrolyte was reduced by $\sim 30\%$ at $v = 2.5 \text{ mV s}^{-1}$ relative to the expected coverage for a complete monolayer (**Figure S2**) which is consistent with obstruction of the Au(111) surface by polymer chains. Regardless of the underlying mechanism, the consequence of this change should be lower rates of Cu corrosion into PFSA electrolytes, which is consistent with studies finding reduced corrosion rates of kinetically stable catalysts such as IrO_2 when operated in a membrane-electrode assembly as compared to conventional acid electrolytes.⁵¹ Previous studies have shown that the interaction of PFSA with electrocatalyst surfaces can be modified by adsorbed transition metals and electrolyte additives.^{52,}

⁵³ The dependence of k_0 on θ_{Cu} is presented in **Figure 6**. In contrast with previous measurements for proton adsorption at Pt(111), which found that k_0 was constant after correcting for proton coverage (and thus electrode potential), we find that an uncorrected k_0 is approximately constant for $\theta_{\text{Cu}} < 0.1$ in H_2SO_4 electrolytes whereas k_0 is weakly dependent on θ_{Cu} for both MSA and TFMSA. The standard exchange rate, k_0 , can be multiplied by the available adsorption sites and the formal charge on dissolved Cu^{2+} to be expressed as an equivalent exchange current density, j_0 . This value facilitates comparison to other reactions involving interfacial ion transfer. The observed j_0 for the molecular sulfate and sulfonates is 0.11 mA cm^{-2} (**Figure 5**) which is only slightly lower than the j_0 (0.35 mA cm^{-2}) reported for the electrocrystallization of Cu from sulfate electrolytes at Cu(111) and is consistent with a kinetic model where interfacial ion transfer is the rate determining step for metal deposition.⁵⁴

Our implicit assumption in this work is that a single site for Cu^{2+} adsorption at Au(111) dominates the electrochemical response. Due to the size of Au(111) grains available for adsorption, we expect these data to represent the rate associated with ion transfer to isolated sites on terraces, but different electrode kinetics may be expected at the edges of actively growing Cu(111) terraces or Au(111) step edges and grain boundaries.³⁸ While we do not expect the terrace size to directly impact k_0 , the apparent k_0 at high $\theta_{\text{Cu}} >$ is likely dependent on the surface density of defects and the rate of adsorption and desorption of higher Cu coverages is known to be influenced by the rate of nucleation.²⁵ All of

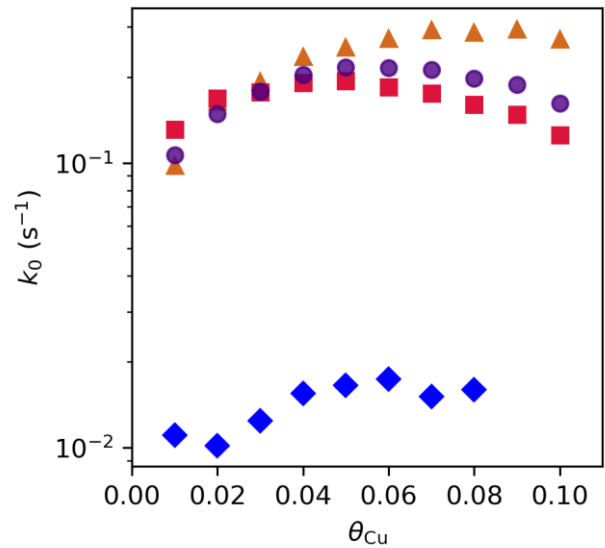


Figure 6: Coverage dependence for k_0 for various supporting anions, H_2SO_4 (orange triangles), MSA (red squares), TFMSA (purple circles), PFSA (blue diamonds).

these factors are likely to have a more substantial impact on k_0 for more complex Au surfaces other than Au(111), where the active site for interfacial ion transfer is difficult to assign. The j_0 values measured for H adsorption at Pt(111) from H_3O^+ ($253 \pm 75 \text{ mA cm}^{-2}$) and also $\text{H}_2\text{O}/\text{OH}^-$ ($2.2 \pm 0.3 \text{ mA cm}^{-2}$) highlight the substantial difference in kinetics between proton-coupled adsorption reactions and interfacial ion-transfer of multivalent transition metals.⁴⁸ Similar $j_0 = 0.39$ and 0.19 mA cm^{-2} have been reported for divalent Pb^{2+}/Pb and Cd^{2+}/Cd , respectively and these cations may serve in future studies on the influence of cation identity underpotential deposition kinetics at Au(111).⁵⁵ For monovalent ions, such as Ag/Ag^+ on gold-supported Ag nanoclusters, much larger j_0 ($\sim 50 \text{ mA cm}^{-2}$) were found at room temperature, consisting of a lower solvation/desolvation barrier.⁵⁶ However, quantitative comparison of j_0 for polycrystalline systems is difficult because the exact number of deposition and stripping sites cannot be directly determined. Future studies comparing interfacial ion transfer exchange rates as a function of formal charge can address this gap.

Conclusions

Cu^{2+} adsorption at Au(111) was chosen as a model system for studying the effects of molecular and polymeric anions on the kinetics for interfacial ion transfer, an elementary step associated with corrosion, and the reverse reaction, electrodeposition. We find that simple changes to the structure of the anion have a substantial difference on the equilibrium adsorption voltammetry of Cu, with the stabilization of ordered adlayers at positive potentials disrupted by the substitution of the $-\text{OH}^-$ on sulfate with either a $-\text{CH}_3$ or $-\text{CF}_3$. The interfacial ion-transfer kinetics of Cu adsorption were quantified in the limit of random adsorption and found to be independent of anion identity for molecular sulfate and sulfonates. Suspended perfluorosulfonic acid ionomer electrolytes inhibited the equilibrium coverage of Cu at Au(111) and also suppressed

interfacial ion transfer kinetics by roughly an order of magnitude. This indicates that the direct consequence of an electrochemical double layer containing only polymer-tethered anions is to diminish the standard rate constant for metal corrosion, which could contribute to the improved durability of electrocatalysts operated polymer electrolyte membrane devices.

Supporting Information

Additional details on experimental methods, dynamic light scattering and electrochemical characterization of materials, measurements at electropolished Cu surfaces, and alternative fitting results are available.

Acknowledgments

This material is based on work performed by the Liquid Sunlight Alliance, which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub under Award Number DE-SC0021266. We thank Aaron Kaufman, Jason Prachar, and Fuding Lin for assistance with preparation of Au thin films and Nicole Sagui for assistance with dynamic light scattering measurements.

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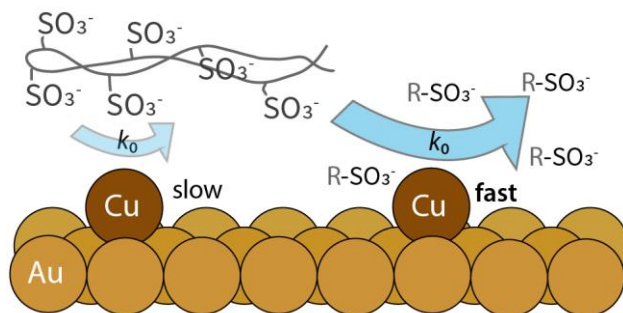
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Table of Contents graphic



Anions in corrosion: Influence of polymer electrolytes on the interfacial ion transfer kinetics of Cu at Au(111) surfaces

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S1. Electrode preparation

S1.1 Au(111) electrode preparation

Gold single-crystal-like electrodes were prepared by evaporating gold onto plasma-cleaned glass microscope slides.^{1,2} Glass slides (EMS GOLD SEAL®) were plasma cleaned using PlasmaEtch plasma cleaner for 15 minutes, with a negative titanium mask applied to the clean surface of glass slides and electrode materials deposited using an AMOD physical vapor deposition platform at a base pressure of 10^{-6} Torr. A 10 nm titanium adhesion layer was deposited at rate of 0.3 Å/s followed by thermally evaporating 200 nm gold starting at a rate of 0.25 Å/s, increasing up to 0.5 Å/s, and decreasing to finish at 0.25 Å/s. The glass electrode sheet was scored and cleaved to obtain individual electrodes.

As-deposited polycrystalline Au surfaces were flame annealed in a propane micro torch for 3-5 minutes to obtain an Au(111) surface. After allowing the glass to cool to room temperature under an Ar stream, the electrode was annealed again by briefly passing the flame from the micro torch over the surface, just enough to see condensation (about 15 seconds). The electrode was then cycled at 50 mV/s in 1 mM CuO in 10 mM H₂SO₄ at potentials covering the full Cu UPD range plus 250 mV in the capacitance region to ensure sustained single crystalline behavior (0.65 V vs E_{rev} to 0V vs E_{rev}).

S1.2 Polycrystalline Cu preparation

A polycrystalline Cu rod (Fisher Scientific, 99.999%) was mechanically polished to a 1 µm finish and then insulated within a (poly)tetrafluoroethylene shroud and electropolished in 66% H₃PO₄ at +2 V versus a high purity graphite rod counter electrode (Alfa Aesar, 5N) for 5 min under continuous N₂ gas bubbling.⁴ *J-E* data for the Cu surface was collected at 5 mV s⁻¹ immediately after submerging the surface in 10 mM H₂SO₄ or CH₃SO₃H under 1 atm N₂. Data was reported for the first scan.

S2. Characterization

S2.1 XRD analysis

Xray diffraction (XRD) data was collected on a Rigaku Smartlab diffractometer. The diffraction pattern was collected with Cu Kα radiation with a nickel filter used to remove any Cu Kβ radiation.

S2.2 SEM imaging

SEM images were collected using an Aperos SEM equipped with an ETD detector, operated at an accelerating voltage of 5 kV.

S2.3 Dynamic Light Scattering

Mobius Wyatt Technology was used to characterize electrolyte solutions both with and without CuO using 532 nm laser excitation at room temperature. All scans were collected using deionized water as a blank.

S3. Supporting Figures

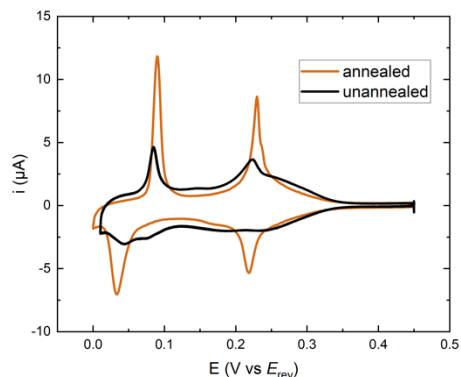


Figure S1. Cu UPD on Au surfaces in 10 mM H₂SO₄ and 1 mM CuO at 5 mV/s: unannealed polycrystalline electrode (black) vs electrode annealed in micro torch (orange). The annealed electrode yielded an electrochemical response consistent with an Au(111) surface.^{1, 2}

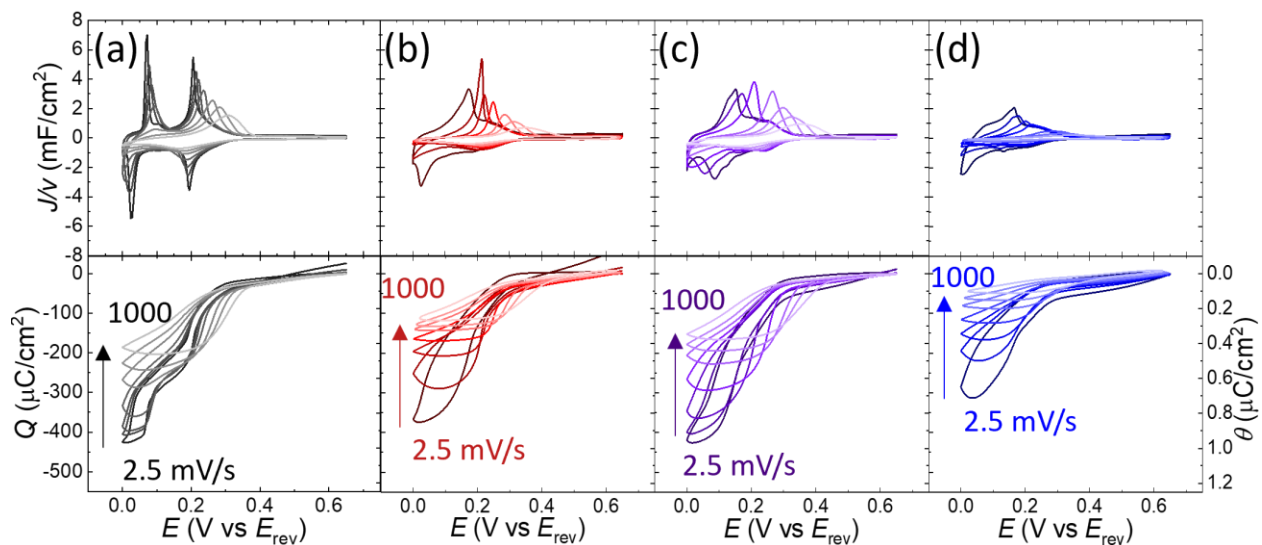


Figure S2: Effect of increasing scan rate on the scan-rate normalized current density and integrated charge density for Cu adsorption in the presence of (a) H₂SO₄ (b) MSA (c) TFMSA and (d) PFSA at scan rates between 2.5–1000 mV s⁻¹.

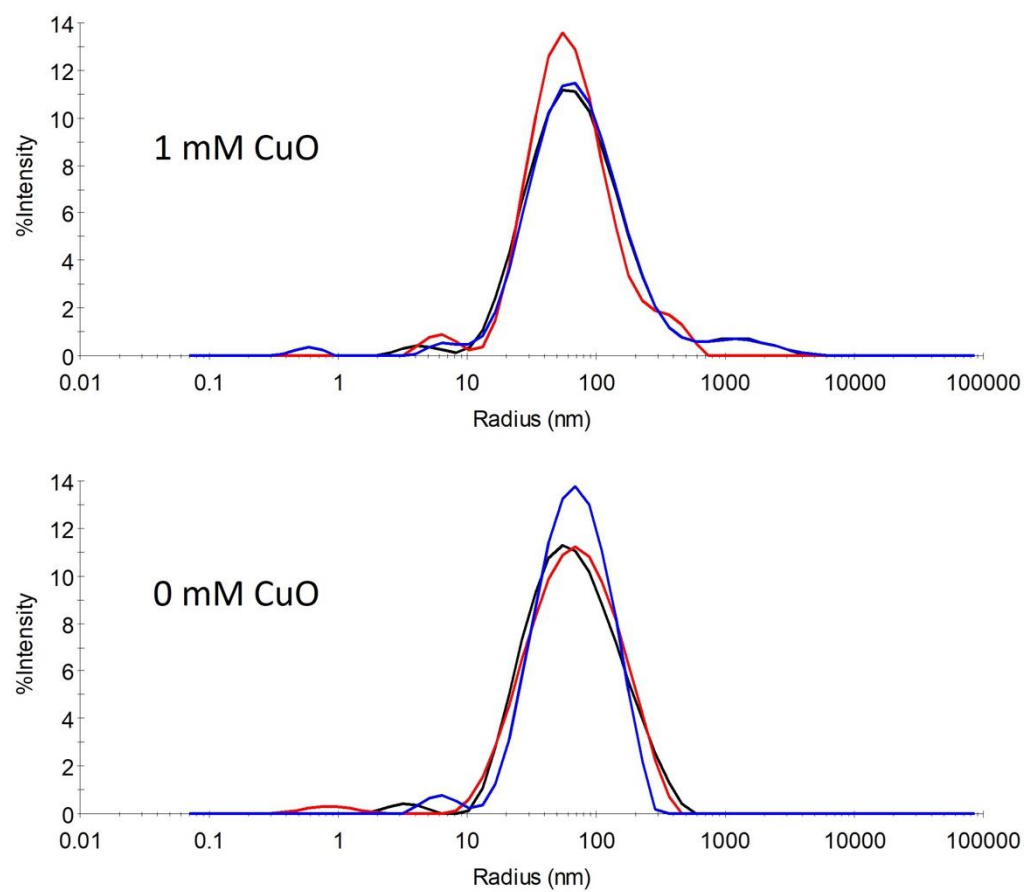


Figure S3: Dynamic light scattering for suspensions of Nafion 1100 with and without dissolved CuO.

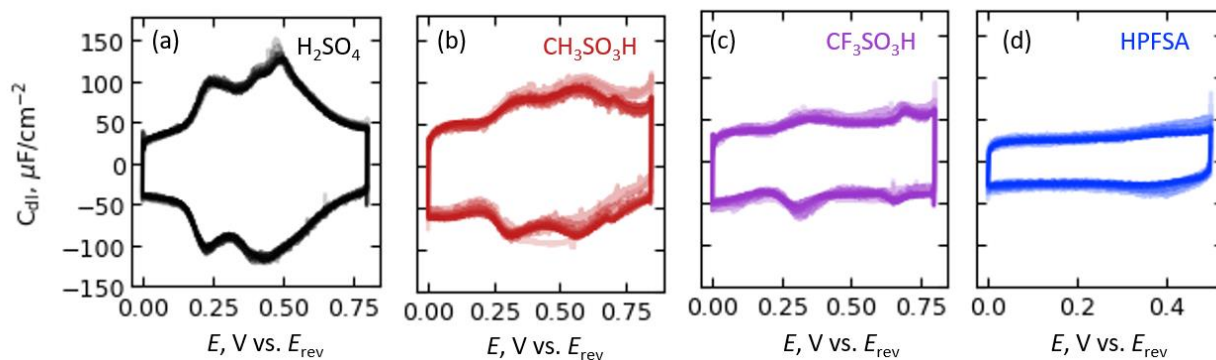


Figure S4: Capacitance vs voltage behavior of supporting electrolytes at 10 mM concentration. $\nu = 50, 100, 250, 500, 750,$ and 1000 mV s^{-1} are overlaid to demonstrate that the apparent capacitance (j/ν) was invariant with scan rate of (a) sulfuric acid, (b) MSA, (c) TFMSA, and (d) PFSA ionomer electrolyte.

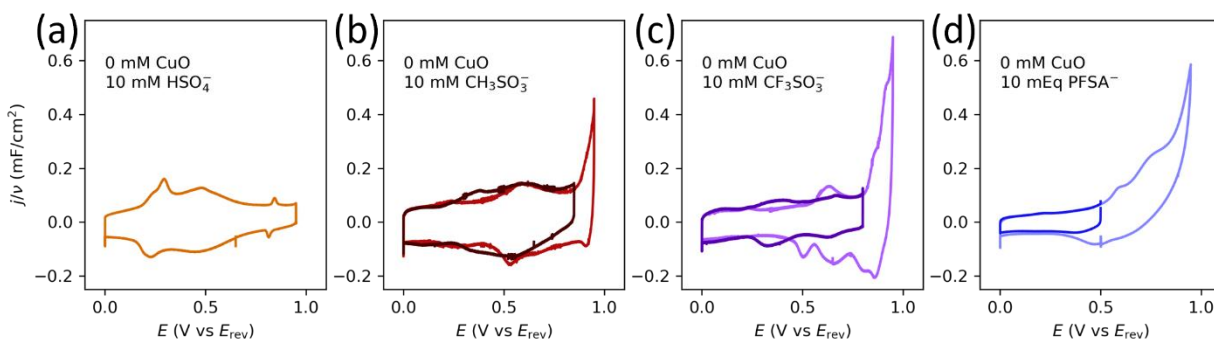


Figure S5: Capacitance vs voltage behavior of supporting electrolytes at 10 mM concentration. Irreversible oxidation is observed in the sulfonate electrolytes, including the PFSA ionomer. Light traces show the CV swept to $0.95 \text{ V vs } E_{\text{rev}}$, and the dark traces show the CV swept until the onset of Au oxidation. Scans at $\nu = 25 \text{ mV s}^{-1}$ shown for (a) sulfuric acid, (b) MSA, (c) TFMSA, and (d) PFSA ionomer electrolyte.

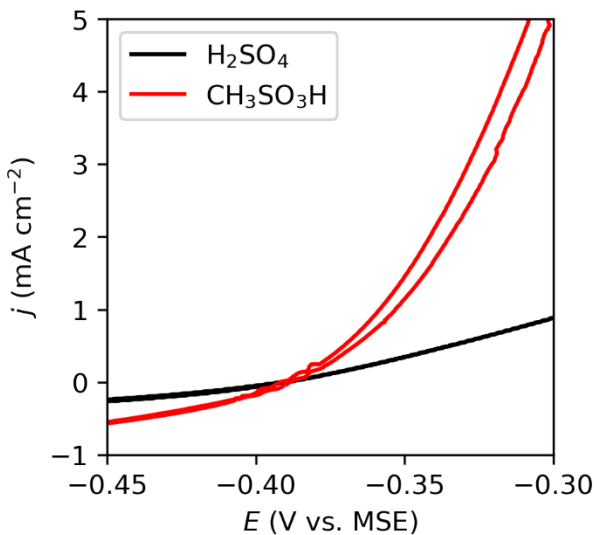


Figure S6: Corrosion behavior for a Cu disk freshly electropolished in H₃PO₄(aq). The potential was swept in N₂-purged H₂SO₄(aq) (black) or CH₃SO₃H (red) at $\nu = 5 \text{ mV s}^{-1}$ at a constant rotation rate of 1600 rpm.

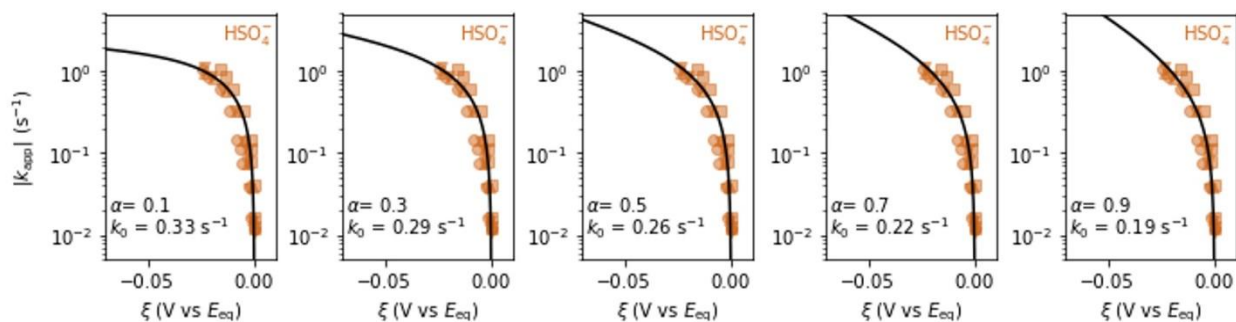


Figure S7: Sensitivity analysis of the parameter α on the calculated k_0 via curve-fitting for 1 mM Cu²⁺ dissolved in 10 mM H₂SO₄ with rates measured at $\theta = 0.05$.

S4. Supporting References

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