

Hysteresis effects and roughness suppression efficacy of polyethylenimine additive in Cu electrodeposition in ethaline

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ABSTRACT

Deep eutectic solvents (DES) are environmentally-friendly electrolytes that are gaining interest for electro-deposition and energy storage applications. In these applications, metal electrodeposits with smooth, non-dendritic morphology are desired and thus effective strategies for suppressing roughness evolution are critically needed. A commonly employed and rather effective strategy for suppressing roughness evolution in metal electrodeposition is the use of electrolyte additives; however, the availability of such additives in DES electrolytes is limited and so is the understanding of the mechanisms through which additives suppress roughness amplification in DES media. In the present contribution, we demonstrate that polyethylenimine (PEI) is an effective electrolyte additive that suppresses roughness evolution during Cu electrodeposition in ethaline DES. PEI, due to its adsorption–deactivation properties, exhibits a unique hysteresis response during voltammetric studies of Cu electrodeposition – this response is analyzed using a mathematical model incorporating the relevant PEI transport, surface adsorption and deactivation processes. The model provides guidelines for selection of optimal conditions (e.g., PEI concentration) for effective suppression of roughness amplification in Cu electrodeposition.

1. Introduction

Deep eutectic solvents (DESs) are gaining interest as emerging electrolytes for next-generation energy storage and thin-film deposition applications [1–3]. A DES is formed by mixing a hydrogen bond donor with a hydrogen bond acceptor. At the eutectic composition, the mixture exhibits a freezing point depression that results in liquid-like physical properties under ambient conditions [3]. DESs are advantageous over organic electrolytes due to their large electrochemical stability windows [1,3], biodegradability [4,5], the low-cost of the constituent materials [4], and their environmental benignity [1,3]. Despite the considerable interest in DESs, practical applications of DESs are limited by their highly viscous nature, which manifests in inferior transport properties, i.e., low ionic conductivity and low diffusivity.

Ethaline, a mixture of choline chloride and ethylene glycol (ChCl:EG = 1:2 M ratio), is a commonly studied DES owing to its low viscosity (~50 cP at 25 °C) compared to other DES mixtures. The physical properties of ethaline are known [5], and it exhibits an electrochemical stability window of ~ 2 V [6]. A variety of metals including

Zn [7,8] and Ni [9] have been electrodeposited using ethaline as the electrolyte medium. Cu has also been electroplated successfully with high current efficiencies (> 90%) [10,11]. While researchers have studied the effect of electrolyte additives in DESs on the electrodeposition of a variety of metals, including Zn [8,12] and Ni [13], a limited number of researchers have investigated the effect of additives on Cu electrodeposition in ethaline [14].

Metal electrodeposition under conditions approaching the mass transport limit produces morphological changes such as the evolution of roughness and dendrite formation [15]. The mechanisms underlying roughness evolution were first investigated by Ibl et al. [16]. Under practical conditions, micro-scale irregularities or ‘roughness elements’ are present on an electrode surface undergoing electrodeposition. When deposition is carried out under mass-transport limited conditions, the tips of the roughness elements experience enhanced local plating relative to the recessed portions. This amplifies roughness as plating progresses. While a variety of methods are available to mitigate roughness evolution, ppm levels of additives are routinely included in electrolytes to act as leveling agents [15,17,18]. Polymeric additives

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with polarizing characteristics such as polyethylene glycol (PEG) and polyethylenimine (PEI) are commonly used in Cu electrodeposition in aqueous media [17,19]. Roha and Landau [20] modeled the steady-state mass transport of leveling agents to an electrode surface during metal electrodeposition. They studied the specific case of a strongly adsorbing additive molecule that is buried in the deposited metal at a rate proportional to the current density. Other modes of electrode potential-dependent additive deactivation have also been proposed [19,21]. The additives' adsorption – deactivation processes are known to produce unique features such as hysteresis in voltammograms.

In the present work, we report on Cu electrodeposition in ethaline DES. We investigate the effect of an additive, i.e., branched PEI, on voltammetric response and roughness evolution during electrodeposition. Unlike typical polarizing additives used in electrodeposition in DES [8,12,13], PEI introduces hysteresis behavior during cyclic voltammetry (CV). A mathematical model describing the interplay between the additive adsorption – deactivation processes is presented. The model qualitatively explains the observed hysteresis and its relevance to the efficacy of PEI in suppressing roughness evolution during Cu electrodeposition.

2. Materials and methods

2.1. Materials

Ethaline was prepared by mixing choline chloride (ChCl, 99% purity, Acros Organics) and ethylene glycol (EG, anhydrous, 99.8% purity, Sigma-Aldrich) in a 1:2 M ratio at 80 °C for 3 h until a homogeneous, clear solution formed. The resulting DES was allowed to cool down to room temperature. Cuprous chloride (CuCl, anhydrous, 99% purity, Acros Organics) was added to ethaline to obtain 100 mM Cu¹⁺-containing electrolyte. Branched polyethylenimine (PEI, average MW: 1300 g/mol, 50% w/v in H₂O, Sigma-Aldrich) was added to the electrodeposition electrolyte from a stock solution containing 10,000 ppm PEI in ethaline.

2.2. Methods

All electrochemical measurements were performed on a rotating disc electrode (RDE, Pine Research). An electrochemical cell with a three-electrode configuration was used. The working, counter and reference electrodes were connected to a Princeton Applied Research PARSTAT-4000 potentiostat. The Ag/AgCl reference electrode was prepared using a silver wire (99.9% purity, Rio Grande) anodized in ethaline using the procedure described by Shen et al. [1] The counter electrode was a porous graphite rod (Graphite store). Electrolyte temperature was maintained at 25 ± 1 °C.

Cyclic voltammograms were collected on a 5 mm diameter Cu RDE working electrode. Prior to each experiment, the exposed Cu surface was polished in a stepwise manner using 600 grit and 1000 grit sandpapers followed by 1 μm and lastly 0.3 μm alumina slurries. The electrode potential was scanned cathodically from the initial equilibrium potential, E_{eq} , to various switching potentials, E_s , then returned back to the initial potential. As the electrode potential was scanned, the activation overpotential, η_a , varied as:

$$\eta_a = V_{app} - IR_{\Omega} - E_{eq} - \eta_c \quad (1)$$

where V_{app} is the applied potential, IR_{Ω} is the ohmic loss due to electrolyte resistance, and η_c is the concentration overpotential. The ohmic resistance, R_{Ω} (= 110 Ω) was measured using electrochemical impedance spectroscopy (EIS) and remained unchanged on the addition of PEI. E_{eq} was measured under open circuit conditions to be -0.187 V vs. Ag/AgCl.

Roughness evolution was quantified using chronopotentiometry in which the Cu RDE was sequentially held at three fixed currents: (i) -0.05 mA for 250 s; (ii) -0.6 mA for 250 s; (iii) -0.05 mA for 250 s. The

low current and prolonged time in steps (i) and (iii) allowed for uniform Cu deposition over the electrode, whereas the high current in step (ii) produced roughness. By comparison of the measured overpotentials in steps (i) and (iii), surface area evolution during step (ii) could be quantified.

A Zygo NewView 7300 optical profilometer was also used to quantify surface roughness. Samples for profilometry were prepared using a silicon wafer substrate (1 cm diameter) coated with 100 nm of sputter-deposited Cu. Prior to Cu deposition from the DES electrolyte, surface oxides were electrochemically reduced in a 100 mM HClO₄ electrolyte. Here, a three-electrode configuration was used with a saturated Ag/AgCl (Fisher Scientific) reference electrode, a porous graphite counter electrode, and the substrate mounted on a RDE set at a rotation speed of 500 rpm. The potential of the RDE working electrode was scanned in the cathodic direction from 0 to -1 V vs. Ag/AgCl to reduce surface oxides. The electrode was then removed from the acidic electrolyte, rinsed with 18 MΩ deionized water, and dried with nitrogen before transferring it to the DES electrolyte. Cu was electrodeposited from the Cu¹⁺-containing ethaline at -2.1 mA for 250 s. The substrate was then removed from ethaline, submerged in 18 MΩ deionized water to remove residual ethaline, then dried in a vacuum oven at 30 °C for 20 h. Optical images were collected immediately after drying.

3. Results and discussion

3.1. Hysteresis during Cu electrodeposition from ethaline in the presence of PEI

Fig. 1 (red curves) shows the CV responses obtained under different conditions, i.e., varying PEI concentrations (left column), rotation speeds (middle column), and switching potentials (E_s , right column). For comparison, the additive-free CV responses (in black) are also shown. With the addition of 10 ppm PEI, the current during the cathodic (forward) scan direction is lowered compared to the additive-free electrolyte, indicating surface polarization by PEI. Increasing the PEI concentration to 200 ppm further suppresses the deposition current and polarizes the surface. Interestingly, PEI does not further polarize the surface at 1000 ppm, suggesting that the Cu surface is saturated with PEI at concentrations in excess of 200 ppm. While the surface is polarized in the cathodic (forward) scan, it exhibits depolarization on the reverse scan, particularly for 200 ppm PEI. This hysteresis signature is absent in the additive-free CVs, which suggests that hysteresis caused by PEI is not the result of electrochemically active surface area changes during CV. At very low PEI concentrations (e.g., 10 ppm), polarization is weak whereas at high PEI concentrations (e.g., 1000 ppm) polarization is strong but hysteresis is dampened. The switching potential has been shown previously to affect hysteresis [19]. Here too, we observed that the switching potential modulated the degree of hysteresis (right column of Fig. 1) with essentially no hysteresis observed when the potential scan was switched at more positive potentials (i.e., lower overpotentials in magnitude) to a gradual increase in the hysteresis as the switching potential was shifted to more negative values. The effect of hydrodynamics on the CV response is shown in the middle column of Fig. 1. While the current is suppressed in the cathodic scan direction under all conditions, hysteresis is magnified at moderate rotation speeds (500 rpm); however, the effect of hydrodynamics is convoluted with that of the switching potential since increasing the RDE speed produced higher rates of Cu deposition. This impacts the post-experimentally compensated ohmic drop, and thus shifts the switching overpotential as per Eq. (1).

3.2. Modeling of PEI transport, adsorption and deactivation processes

To characterize the hysteresis observed in CVs in the presence of PEI (Fig. 1), a quantitative analysis of the PEI adsorption and surface deactivation processes is required. Here, we follow the modeling approach

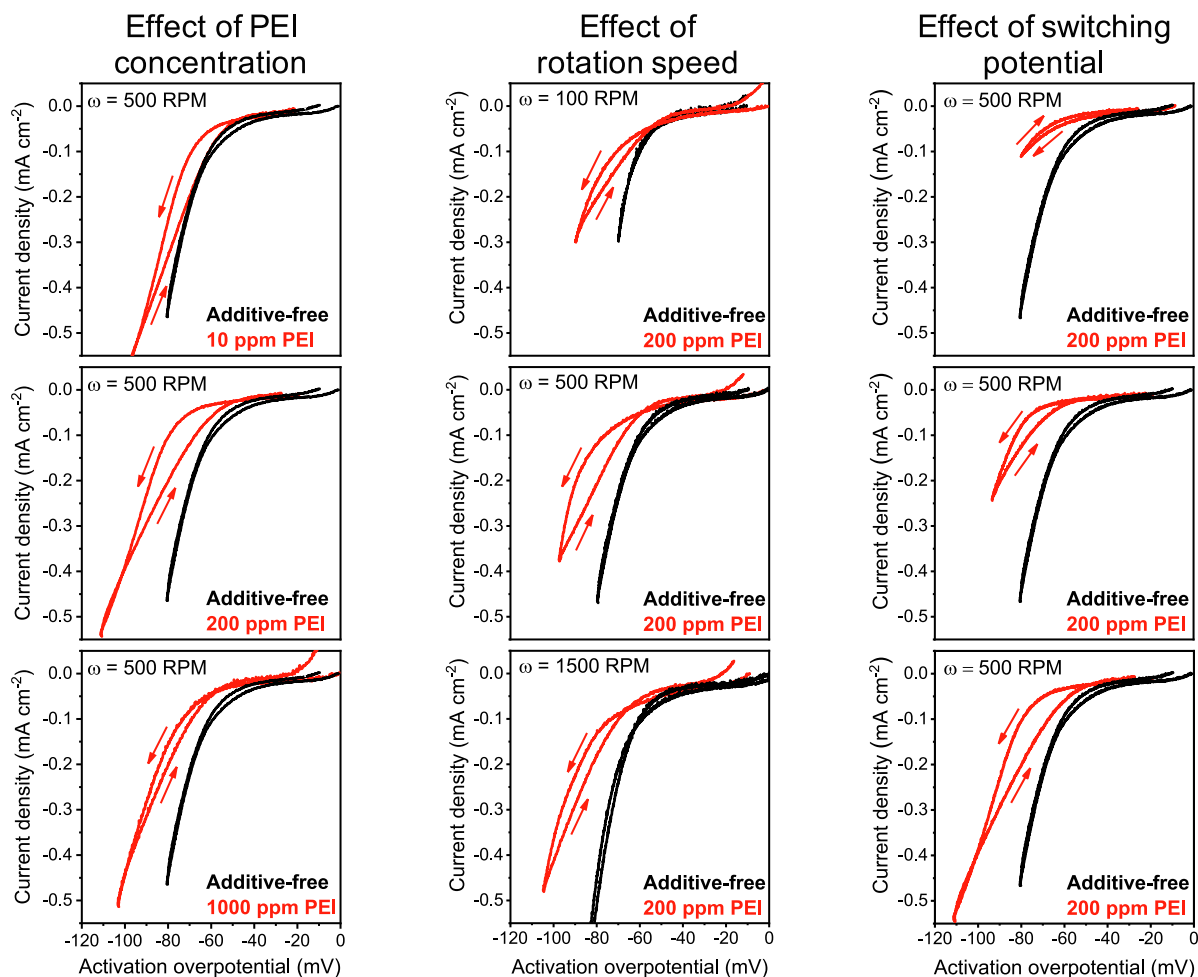


Fig. 1. Cyclic voltammetry (scan rate = 1 mV/s) during Cu electrodeposition on RDE in ethaline electrolyte containing 100 mM Cu^{1+} . CVs obtained in the additive-free electrolyte are shown in black, and those obtained in the PEI-containing electrolyte are in red. The three columns depict the effect of PEI concentration, RDE rotation speed, and switching potential on CV response.

presented by Liu and co-workers [22] for investigating the additive-induced hysteresis behavior in Zn electrodeposition. Following their approach, a mass balance providing the PEI coverage θ of the electrode surface at steady state may be written as:

$$k_{\text{ads}} C_b (1 - \theta) = k_{\text{deac}} \hat{c}_{\text{Cu}} \quad (2)$$

In Eq. (2), the expression on the left-hand side represents the first-order adsorption of PEI onto the Cu electrode whereas the expression on the right-hand side represents PEI deactivation. The parameters k_{ads} and k_{deac} represent the PEI adsorption and deactivation rate constants, respectively. The concentration of PEI near the electrode is assumed to be its bulk value (C_b). The deactivation rate is assumed to be proportional to the magnitude of the Cu deposition current density (i_{Cu}) and the PEI surface coverage (θ) consistent with the approach taken by Liu et al. [22]. The current density i_{Cu} is related to the surface overpotential η (–ve) and PEI coverage:

$$i_{\text{Cu}} = i_0 (1 - \theta) e^{-b\eta} \quad (3)$$

i_0 is the exchange current density of Cu deposition under additive-free conditions, and b is a constant relating to the Tafel slope. Combining Eqs. (2) and (3), we get:

$$\xi \theta^2 - (1 + \xi) \theta + 1 = 0 \quad (4)$$

Eq. (4) is a quadratic in θ in which the dimensionless parameter ξ is defined as the ratio of the PEI deactivation rate to its adsorption rate:

$$\xi = \frac{k_{\text{deac}} i_0 e^{-b\eta}}{k_{\text{ads}} C_b} \quad (5)$$

Eq. (4) has two roots: (i) $\theta = 1$ which is stable only when $\xi < 1$, and (ii) $\theta = \xi^{-1}$ which is stable only when $\xi > 1$. A plot of θ vs. ξ is shown in Fig. 2. In a CV experiment, as the electrode potential is scanned in the negative direction, ξ gradually increases as the overpotential η increases (Eq. (5)). The maximum ξ represents the maximum overpotential (η_{max}) reached:

$$\xi_{\text{max}} = \frac{k_{\text{deac}} i_0 e^{-b\eta_{\text{max}}}}{k_{\text{ads}} C_b} \quad (6)$$

From Fig. 2, it is evident that, if ξ_{max} is small ($\xi_{\text{max}} < 1$ because η_{max} is small, or C_b is large), the PEI coverage of the electrode remains at $\theta = 1$, implying that the surface remains polarized during the entire CV scan. A small ξ_{max} represents PEI adsorption that is much faster than its deactivation – a condition that would saturate the surface with PEI and not result in hysteresis. If ξ_{max} is large ($\xi_{\text{max}} > 1$ because η_{max} is large, or C_b is small), the PEI coverage of the electrode would evolve with the surface potential and eventually reach a low value of ξ_{max}^{-1} . For example, if $\xi_{\text{max}} = 4$, $\theta = 0.25$. The depolarized surface condition is the result of gradual dominance of the rate of PEI deactivation over its adsorption. This surface coverage evolution manifests as hysteresis during a CV experiment. Fig. 2 allows us to explain qualitatively the observations in Fig. 1. For example, the dampening of hysteresis at very high concentrations of PEI (i.e., $C_b = 1000$ ppm) is the result of smaller ξ_{max} as

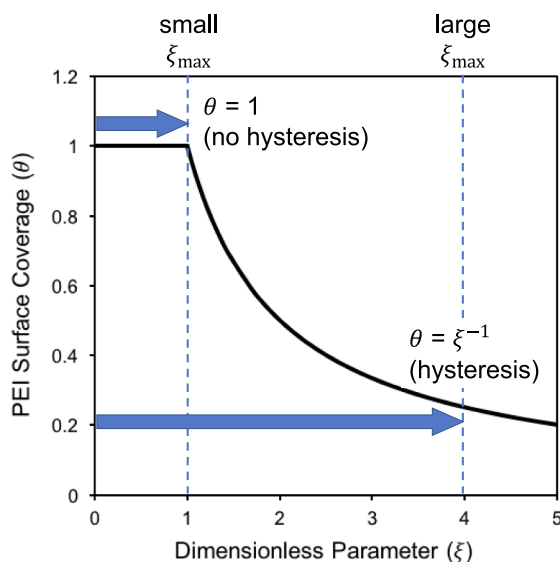


Fig. 2. PEI surface coverage as a function of the dimensionless parameter ξ . When ξ_{\max} is low, PEI adsorption dominates over its deactivation and the Cu surface remains saturated ($\theta = 1$) and thus polarized. When ξ_{\max} is large, the PEI is deactivated at a rate faster than its adsorption, resulting in a low surface coverage.

per Eq. (6). Furthermore, the gradual amplification of hysteresis as the switching potential is shifted to more negative values (higher η_{\max}) is again the result of an increase in ξ_{\max} as per Eq. (6).

3.3. Effect of PEI on roughness evolution

The above dimensionless parameter ξ (Fig. 2) assists one in understanding how the interaction between PEI adsorption and deactivation rates results in a polarized (large θ) or depolarized (small θ) surface condition. The PEI surface coverage θ is responsible for modulating deposit properties such as roughness. Following the work of Barkey [23] and Landau [24], a dimensionless parameter L representing the micro-scale non-uniform current distribution leading to roughness evolution can be defined as:

$$L = \left(\frac{i_L - i}{i_0} \right) \left(\frac{1}{1 - \theta} \right) \quad (7)$$

In Eq. (7), i_L is the limiting current and assumes linear kinetics of Cu deposition with exchange current density i_0 . The second term in Eq. (7) represents the surface blocking effect of PEI which can be viewed as an apparent lowering of the deposition exchange current density. Roughness amplification is minimal when $L \gg 1$ and it is significant when $L \ll 1$. Under fixed hydrodynamic conditions and applied current density, roughness can be suppressed by increasing the PEI surface coverage θ .

An electrochemical diagnostic test was performed to better understand the conditions that favor polarization (roughness suppression) over depolarization (roughness amplification). The test comprised the galvanostatic deposition of Cu using a waveform shown in the top panel of Fig. 3. First, Cu was plated at -0.05 mA for 250 s to uniformly coat the substrate electrode. Next, Cu was deposited at a higher current -0.6 mA for 250 s to evolve roughness. This current was about 75% of the mass-transport limited deposition current. Following this step, current was returned back to -0.05 mA for 250 s to measure the change in the surface overpotential compared to that before evolving roughness. Since the first and the last steps were carried out at a very low current, the micro-scale current distribution is expected to be uniform and any changes in the measured overpotential can be attributed to surface area evolution due to roughness generated in the intermediate step. The potential response corrected as per Eq. (1) resulted in the time

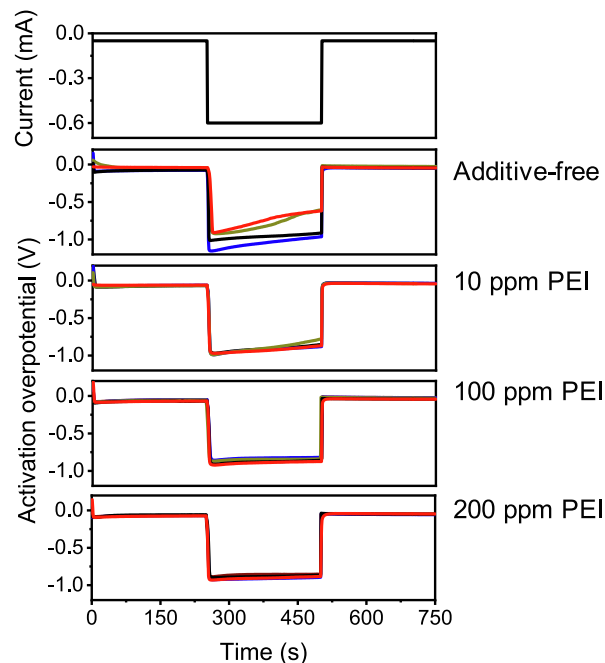


Fig. 3. Potential responses to the applied current step (top) during Cu electrodeposition from 100 mM Cu^{1+} -containing ethaline with 0, 10, 100, and 200 ppm PEI on Cu RDE (500 rpm). As the concentration of PEI increases toward 200 ppm, roughness evolution is suppressed. Colors represent multiple trial runs.

evolution of the activation overpotential, which is given in Fig. 3 for PEI concentrations of 0, 10, 100, and 200 ppm.

We observe in Fig. 3 that the activation overpotential during the intermediate roughness development step gradually decreases in the absence of PEI and becomes relatively constant as the PEI concentration approaches 200 ppm. The changes in η_a with time are indicative of surface area evolution in the absence of PEI. Furthermore, the difference in activation overpotential measured between the first and third steps can be used to compute the electrochemically active surface area ratio (i.e., the roughness factor R_f) before and after roughness evolution:

$$R_f = \frac{A_{\text{after}}}{A_{\text{before}}} = e^{-b\Delta\eta_a} \quad (8)$$

In Eq. (8), b was taken as 37 V^{-1} . This value was determined from polarization data in Fig. 1. Taking $\Delta\eta_a$ from Fig. 3, R_f was calculated for each PEI concentration (Fig. 4 left). R_f is observed to decrease gradually with increasing PEI concentration. The effect of PEI concentration on deposit roughness was also confirmed via RMS roughness analysis using an optical profilometer (Fig. 4 right), which also confirmed that roughness decreased with increasing PEI concentration. As the PEI concentration (C_b) increases, ξ decreases as per Eq. (5). Since $\theta = \xi^{-1}$, we see that the PEI coverage of the Cu surface increases as PEI concentration increases. In accordance with Eq. (7), the dimensionless parameter L increases (i.e., roughness suppression) as θ increases. This explains how increasing PEI concentration lowers roughness during plating (Fig. 4).

4. Conclusions

This study leads to the following conclusions:

- Electrolyte additive PEI exhibits hysteresis during CV studies of Cu electrodeposition in ethaline DES. The extent of hysteresis is

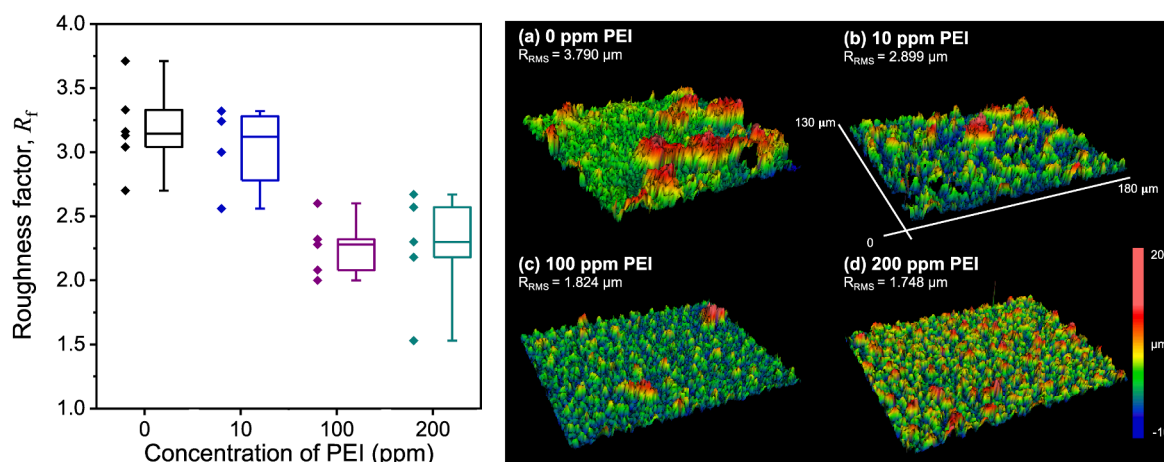


Fig. 4. Effect of PEI concentration on suppressing roughness during Cu deposition from a 100 mM Cu^{1+} -containing ethaline. The dots represent individual data points, the whiskers represent 1 standard deviation, the box indicates interquartile range, and the inner bar indicates the median. (left) R_f was calculated using Eq. (8) and data in Fig. 3; (right) RMS roughness measured using profilometry.

modulated by the PEI concentration and the switching potential.

- (ii) A mathematical model incorporating the PEI adsorption and deactivation processes is presented. The model explains why pronounced hysteresis is seen at low or moderate PEI concentrations and more cathodic switching potentials.
- (iii) PEI suppresses roughness amplification during Cu electrodeposition in ethaline DES. Suppression occurs when PEI adsorbs on the Cu surface at a rate that exceeds its deactivation rate, i.e., ξ is small.

CRediT authorship contribution statement

Nora A. Shaheen: Conceptualization, Data curation, Formal analysis, Investigation, Writing - original draft. **Ijjada Mahesh:** Investigation, Data curation, Methodology. **Miomir B. Vukmirovic:** Conceptualization, Funding acquisition, Investigation, Resources. **Rohan Akolkar:** Conceptualization, Funding acquisition, Project administration, Investigation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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