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Probing TCNQ-Mediated Metal Reduction Reactions at Liquid-Liquid Interface with SECM

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Abstract

Metal reduction at the interface between two immiscible electrolyte solutions (ITIES) has been studied with scanning electrochemical microscopy (SECM). Metal cations in the aqueous phase are reduced by 7,7,8,8-tetracyanoquinodimethane anion (TCNQ^-) residing in the oil phase, methyl isobutyl ketone (MIBK). TCNQ^- is formed at the SECM tip by reducing TCNQ, which results in a positive feedback loop between the tip and the ITIES when an electron is donated to a metal cation. The effect of the Galvani potential difference on the rate of the interfacial electron transfer was investigated, establishing the potential difference either by an additional substrate electrode in the aqueous phase or by an a common ion in both phases. It is shown that the Galvani potential difference as a driving force does enable TCNQ^- mediated Cu^{2+} reduction. Finite element method (FEM) simulations were run to provide information on the reaction kinetics and stoichiometry.

1 Introduction

The interface between two immiscible electrolyte solutions (ITIES) has now been studied for ca 40 years [1, 2] but has mainly remained as an analytical tool due to the small interfacial area of electrochemical cells. However, electrochemistry at the ITIES can be scaled up from the laboratory to the preparative scale by establishing the Galvani potential difference across the ITIES with a common ion in the phases. In this way, the interfacial area is not limited by the configuration of the electrochemical cell. Preliminary studies have been made on metal transfer across the ITIES driven by the Galvani potential difference established by tetrakis(pentafluorophenyl)borate, TB^- [3]. In addition to metal extraction

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experiments, investigations have been made to study the effect of the polarization of the ITIES on O_2 and H_2O_2 reduction [4, 5], and hydrogen evolution reaction catalysed by Pt nanoparticles formed at the ITIES [6, 7].

Solvent extraction is an elementary process in hydrometallurgy, in which metals are extracted from an aqueous phase to an organic phase using a suitable and preferably selective ligand that binds with the metal and increases its solubility to the organic phase. Solvent extraction is an interesting candidate for applying electrochemistry at the ITIES at an industrial scale. However, many of the organic solvents used in the industry (e.g. kerosene [8–11]) have a low relative permittivity ($\epsilon_r = 1.8$ [12]) [13] and therefore do not allow conventional electrochemical study which requires dissociation of electrolytes. A convenient candidate would be *e.g.* methyl isobutyl ketone (MIBK), which is an industrially relevant solvent [14–16] that can also be used in electrochemistry because of its higher relative permittivity ($\epsilon_r = 13.11$ [13]), allowing the dissolution and dissociation of electrolytes. The potential window of the water-MIBK interface is also quite wide, of the same order of magnitude as with 1,2-dichloroethane that is commonly used in the ITIES studies.

Scanning Electrochemical Microscope (SECM) is a modern analytical tool that can be used in various ways to study electrochemical reactions [17]. Pt ultramicroelectrodes (UMEs) are commonly used as the SECM tip also at the ITIES. For example, electron transfer [18–22] and ligand-assisted metal transfer at the ITIES [23, 24] have been studied. In the work by Slevin *et al.*, a complexation equilibrium between aqueous Cu^{2+} and an organic ligand, oxime, was first allowed to settle, after which the SECM tip residing in the aqueous phase was set to approach the interface while reducing copper on the tip, producing a descending approach curve analogously to a relatively slow electrochemical reaction on a solid substrate. No potential control across the ITIES was imposed. Wei *et al.* [18] studied electron transfer across the ITIES, between an aqueous ruthenium bipyridine and organic ferrocene redox couples. Tetraethylammonium perchlorate (TEAP) was dissolved in both the aqueous and nitrobenzene phase, making the Galvani potential difference across the interface approximately equal to the average value of the standard transfer potentials of TEA^+ and P^- . The set-up was complicated by the possible ion transfer of the aqueous redox species into the oil phase or the transfer of the ferrocenium cation into the aqueous phase. Barker *et al.* [20] measured electron transfer across the ITIES using perchlorate anion to fix the Galvani potential.

Metal reduction at the ITIES induced by a direct current has been shown as early as 1975 [25], and metal nanoparticle deposition at ITIES has been reported earlier [26, 27]. Aslan *et al.* [28] reported LiTB-catalyzed (Lithium tetrakis(pentafluorophenyl)borate) reduction of Cu^{2+} by decamethylferrocene and subsequent formation of spherical Cu nanoparticles at water/dichloroethane interface without an external current source. The synthesis of the nanoparticles did not require a well-determined Galvani potential difference at the ITIES since the TB^- counterion was not present in the organic phase. This type of nanoparticle formation at ITIES has been studied with SECM by Li *et al.* [29] who used Ag UME that supplied Ag^+ cations which would be re-reduced by

hydrophobic decamethylferrocene at the ITIES.

Jedraszko *et al.* [30] utilized SECM to study light-driven hydrogen evolution reaction (HER) at a chemically polarized ITIES, having decamethylruthenocene in the organic phase as the electron donor. A bipotentiostat was used with a substrate tip in the organic phase that re-reduced decamethylruthenocenium, providing a constant supply of electrons for the HER that was detected at a Pt UME in the aqueous phase. SECM has also been utilized by Rastgar *et al.* [31, 32] to study $[\text{Co}(\text{bpy})_3]^{3+}$ mediated light-driven oxygen evolution reaction at a liquid-liquid interface polarised with a common tetrabutylammonium (TBA^+) ion as well as the photocatalytic effect of BiVO_4 on electron transfer at electrochemically polarized ITIES.

In this communication, the target is to investigate novel means to separate precious and rare earth metals in recycling processes, *i.e.* Galvani potential control by potential determining ions. The effect of Galvani potential difference on the reduction of various metals at the water-MIBK interface is studied with SECM. The potential control across the ITIES is realized with external polarization via a Pt electrode in the aqueous phase; the SECM tip approaches the interface from the organic phase. Furthermore, the Galvani potential difference could also be established by incorporating a common ion (*e.g.* TB^-) in the both phases, as given by the Nernst-Donnan equation [33, 34].

2 Materials and Methods

All measurements were performed in an ambient temperature in atmospheric conditions. The aqueous solutions were prepared from ultrapure MQ water (specific resistivity 18.2 M Ω cm), and the organic phases from ethyl isobutyl ketone (MIBK), which was purchased from Fluka. 7,7,8,8-tetracyanoquinodimethane (TCNQ) and bis(triphenylphosphoranylidene)ammonium chloride (BACl , 97 % purity) were purchased from Sigma-Aldrich and lithium tetrakis(pentafluorophenyl)borate (LiTB) *n*-etherate from Chemodex (Switzerland). Bis(triphenylphosphoranylidene)ammonium tetrakis (pentafluorophenyl)borate (BATB) was formed by metathesis of BACl and LiTB as described in the literature [35]. NiSO_4 , CuSO_4 and CoSO_4 were all purchased from Merck. All chemicals were used as received.

SECM measurement were carried out with CHI900 workstation (CH Instruments, Austin, USA). A Pt disk UME with the diameter of 30 μm (RG value 17) was used as the SECM tip, and it was prepared as previously described in literature [17]. The tip was polished with FiberMet Abrasive disk (0.3 MIC, Buehler) until its surface had no stains that could be seen with light microscopy. A Pt wire was used as the counter electrode and a Ag wire as a quasi-reference electrode (AgQRE). The liquid-liquid interface was established inside a 30 ml vial by injecting on top of the water phase 5 ml of the organic phase containing 0.1 or 1 mM BATB and TCNQ (1.0, 2.5 or 5.0 mM). BATB is used to insert the common ion into the organic phase and it also acts as a supporting electrolyte. All the electrodes were placed in the organic phase. The ITIES was approached

with the tip that was set to a sufficiently negative potential to reduce TCNQ under limiting current condition. Negative or positive feedback was detected, depending on the reaction occurring at the ITIES. The tip should not penetrate the ITIES, since it would leave residues of water onto the UME surface, distorting the measurements. After finding the location of the ITIES the probe was withdrawn by 300 μm and CVs were measured at various distances from the surface with the scan rate of 25 mV/s. The distances d were normalized by the tip diameter r_0 and the current by the limiting current of TCNQ reduction in the oil phase i_{lim} .

Since the SECM instrument is equipped with a bipotentiostat, the Galvani potential difference across the ITIES could also be established by a substrate electrode, which effectively emulates the common ion and provides a means to vary the potential difference continuously. Thus, an additional aqueous Pt wire substrate electrode was polarized to various potentials vs. Ag|AgCl, which would effectively alter the Galvani potential difference at the ITIES. These potentials were converted to an approximate Galvani potential scale ($\Delta_o^w \phi$) with the following equation:

$$\Delta_o^w \phi = E_{\text{Pt}(w)}^{\text{Ag|AgCl}} + E_{\text{Ag|AgCl}}^0 + \Delta_o^w \phi_{\text{BA}^+}^0 + \frac{RT}{F} \left(\ln \frac{a_{\text{BA}^+}^o}{a_{\text{Cl}^-}^w a_{\text{BA}^+}^w} - 2.3\text{pH} \right) \quad (1)$$

where $E_{\text{Pt}(w)}^{\text{Ag|AgCl}}$ is the measured cell potential between aqueous Pt electrode and the Ag|AgCl reference electrode, $E_{\text{Ag|AgCl}}^0$ is the standard potential of the aqueous Ag|AgCl electrode, and $\Delta_o^w \phi_{\text{BA}^+}^0$ is the standard transfer potential of BA^+ . $\Delta_o^w \phi_{\text{BA}^+}^0$ is not known precisely and it is estimated as the standard transfer potential from dichloroethane to water that is -700 mV [35]. Since the measurements were performed with a Ag wire as a quasi reference electrode, $\Delta^{ref} E$ describing the shift from Ag|AgCl scale to AgQR scale was determined as the potential difference of the half-wave potentials of TCNQ reduction between these two scales.

$$\Delta^{ref} E = E_{1/2}^{\text{Ag|AgCl}} - E_{1/2}^{\text{AgQRE}} \quad (2)$$

The potential at the AgQRE scale can be thus converted to the Ag|AgCl scale when $\Delta^{ref} E$ is known:

$$E_{\text{Pt}}^{\text{Ag|AgCl}} = E^{\text{AgQRE}} + \Delta^{ref} E \quad (3)$$

The difference between the half-wave potentials on the AgQRE and the Ag|AgCl liquid junction scale was found to be 540 mV (Figure 1). It should be noted that, although not shown in the figure, the second reduction wave of TCNQ $^-$ at more negative potentials [36,37] could not be seen in MIBK. The reason for this might be that the second reduction takes place outside of the potential window limited by MIBK decomposition.

Figure 1: TCNQ reduction at the Pt UME in MIBK using either the Ag|AgCl reference electrode with the liquid junction (dashed line) or the AgQRE (solid line). Sweep rate was 25 mV/s.

The substrate potential was varied between -200 mV and 700 mV while the tip was kept at -300 mV vs. AgQRE; both the tip and the substrate currents were recorded during the tip approach. Additionally, tip CVs were measured at various substrate potentials, while it was positioned in the bulk or close to the interface.

Next, LiTB was included to the aqueous phase to determine the $\Delta_o^w \phi$ instead utilizing the substrate electrode in the aqueous phase. The approach curves and CVs with this setting were performed similarly as described above.

To analyse the results, FEM simulations of the probe approach curves were carried out with a commercial COMSOL Multiphysics software. Since the geometry of the probe and the entire system is axi-symmetric, simulating a 2D model that has been described earlier [38] suffices. Similarly to the experimental results, the model was made dimensionless by dividing the lengths by the tip radius r ($15 \mu\text{m}$). The ratio of the glass sheath radius to r , RG , was ca 17, as determined with microscope image. An extremely dense mesh was used: the density was set to be larger in the relevant areas in the model, namely in the vicinity of the electrode, the insulating sheath and the ITIES. The number of elements depends on the distance of the electrode from the ITIES, thus it varied from 200.000 to 300.000 elements.

3 Results and Discussion

3.1 Probe Approach Curves Against Externally Polarized ITIES.

First, a set of blank experiments were carried out to exclude artefacts from the approach curves. Increasing the TCNQ concentration from 1.0 mM to 5.0 mM the (aqueous phase 5.0 mM H_2SO_4 , tip potential -0.3 V vs. AgQRE) changed the feedback gradually from negative to positive (not shown), which can probably be attributed to TCNQ adsorption on the ITIES. Knowing this, TCNQ concentration was kept at 1.0 mM so that the possible TCNQ adsorption would not interfere with the measurements. Figure 2 shows the approach curves in the absence of TCNQ in MIBK, while the aqueous phase contains 5.0 mM CuSO_4 . Far from the interface, there is naturally no current, but when approaching the ITIES current rises to 28 pA at the closest distance. This can be attributed to Cu^{2+} partitioning across the ITIES and reducing at the tip. Since the value of the transfer potential of Cu^{2+} and the $\Delta_o^w\phi$ in the absence of potential determining ions are not known, it is impossible to evaluate conclusively the partitioning and its effect on the feedback. However, although this feedback cannot be quantum mechanical tunnelling, the current i appears to decay exponentially as a function of the distance according to $i = (2.46\text{pA}) \cdot e^{-0.57d/r_0}$. This feedback is, however, negligible since the limiting current of TCNQ reduction is at nA scale.

Figure 2: Approach curve against water phase with 5 mM CuSO_4 when no TCNQ was present in the organic phase. The dashed line shows the best fit of the exponential decay. The tip potential was *ca* -100 mV vs. aqueous Ag|AgCl.

The probe approach experiments were performed first by having a substrate electrode immersed in the water phase, which would establish the Galvani potential difference across the ITIES instead of the distributing ion. The potential between the reference and substrate electrode was set between -100 and

500 mV, -400 to 200 mV on the χ scale. The TCNQ and BATB concentrations in the oil phase were kept at 1 mM and 0.1 mM, respectively. Since the Galvani potential was established externally, no LiTB was added to the water phase, and BATB would act merely as a supporting electrolyte. The actual Galvani potential was calculated with equation 1 and subsequently converted to the χ scale with equation 9.

Figure 3: Probe approach curves at various substrate potentials against water phase with 5 mM CuSO_4 . The substrate potentials were converted to the χ scale.

Although not shown, the Galvani potential fixed by the substrate electrode had negligible effect on the feedback when no metal cations were present in the water phase, and the feedback remains negative at the studied potential range. Approach curves with 5 mM CuSO_4 are shown in Figure 3. Similar approach curves with NiSO_4 and CoSO_4 did not generate a positive feedback at the studied substrate potential range; neither Ni^{2+} nor Co^{2+} could be reduced even when the substrate potential of 700 mV, whereas the presence of CuSO_4 generated a positive feedback after a certain threshold potential.

Additionally, tip CVs were performed close to the ITIES at various χ . As the exact location of the ITIES could not be known without penetrating the interface, "close to the interface" was defined as the distance where the tip current drops to 70% of i_{lim} when the substrate potential in the organic phase was -100 mV vs. AgQRE, which corresponds to ca -400 mV on the χ scale. The dimensionless currents at the vertex potential were recorded (-100 mV against $\text{Ag}|\text{AgCl}(\text{w})$). The results are shown in Figure 4. Similarly, CVs were run at the substrate electrode while the current flowing through the tip was recorded. The tip potential was the same as the vertex potential in CVs run for Figure 4. Although not shown here, the continuous substrate potential sweep results in a similar behaviour of the tip current, where the feedback changes from negative to positive after the threshold potential ($\chi \approx -230$ mV).

Figure 4: Tip currents at vertex potentials (-100 mV vs. $\text{Ag}|\text{AgCl}(\text{w})$) close to the ITIES at various substrate potentials, converted to χ scale. Purple triangles: CuSO_4 , yellow diamonds: NiSO_4 , red squares: CoSO_4 , blue circles: H_2SO_4 only.

3.2 Probe Approach Curves At ITIES Polarized by Common Ion.

The effect of increasing LiTB concentration on the feedback is shown in Figure 5. Similarly to TCNQ, increasing the LiTB concentration changes the feedback from negative to positive. Above 1 mM, the approach curves became increasingly more unstable and unrepeatable. Again, this is probably due to LiTB adsorption at the interface, since LiTB forms spontaneously a visible film-like structure at the interface. Therefore, in all experiments where LiTB was used, its concentration was limited to 0.1 mM.

Figure 5: Approach curves against water phase with various LiTB concentrations and with no metal salts.

In the first plot of Figure 6 the effect of Galvani potential established by the potential determining ions on the Cu^{2+} reduction is shown. When 5 mM CuSO_4 but no LiTB was present in the water phase, a sharp positive feedback near the interface was observed. A monotonous positive feedback could be detected only if both LiTB and CuSO_4 were present in the water phase. The kinetics of the Cu^{2+} reduction was studied by approaching the interface in various TCNQ concentrations while having 5 mM CuSO_4 in the organic phase. The obtained approach curves are presented in the second plot of Figure 6, showing that increasing the TCNQ concentration changes the feedback from negative to positive.

Figure 6: a) Pt UME approach curves showing the synergistic effect of the Galvani potential on the Cu^{2+} reduction at the ITIES. The TCNQ concentration in the organic phase was 1 mM. b) Approach curves at various TCNQ concentrations. CuSO_4 concentration was 5 mM, LiTB and BATB concentrations were 0.1 mM in the water and organic phase.

3.3 FEM Simulations of the SECM Measurements.

In the SECM experiments, a water-MIBK interface was probed by using a Pt disk UME. At a sufficiently low tip potential, TCNQ in the organic phase is reduced:

TCNQ^- acts as an electron donor to the metal cation in the aqueous phase. Thereafter, it is available to be reduced again at the tip, thus resulting in a positive feedback in the approach curves. Two possible loop patterns are shown in Figure 7. In 7a, the electron transfer takes place directly at the interface without transfer of TCNQ^- or M^{2+} . Alternatively, in 7b, the reduced TCNQ^- is transferred to the aqueous phase where it donates the electrons to the metal cation and the oxidized TCNQ, being hydrophobic, is transferred passively back to the oil phase to establish the positive feedback loop.

Figure 7: Possible reaction patterns that can take place at the ITIES: a) heterogeneous reaction, where the metal is reduced at the ITIES; b) homogeneous reaction, where TCNQ^- formed at the tip is transferred to the organic phase, where it reduces the metal cation.

In the FEM simulations, the reaction at the microelectrode under limiting current conditions is usually modelled by setting the surface concentration of the reactant (here TCNQ) to zero and the product (TCNQ^-) to the bulk concentration of the reactant. However, here, this appeared to cause convergence problems or mass balance violations. Therefore, Butler-Volmer equation [34] was applied at the tip.

The redox reaction between TCNQ^- produced at the tip and the metal cation (M^{2+}) was assumed to be irreversible and the reaction rate characterized by the reaction rate constant k_r . In the simulation, a heterogeneous reaction takes place at the ITIES:

The reaction rate v_r is described by an equation:

$$v_r = k_r [\text{TCNQ}^-]_{\text{o}}^2 [\text{M}^{2+}]_{\text{w}} \quad (7)$$

where k_r is the apparent reaction rate constant. Since the reaction is heterogeneous, its rate depends on the Galvani potential and the rate equation can be written as:

$$-\frac{i_r}{2Fk_r^0} = [M^{2+}]_w [TCNQ^-]_o^2 e^{\alpha f \chi} \quad (8)$$

where i_r is the current density flowing through the ITIES, $f = F/(RT)$, α is the charge transfer coefficient and k_r^0 is the standard reaction rate constant, *i.e.* the reaction rate constant when the driving force $\chi = 0$. χ is defined as:

$$\chi = \Delta_o^w \phi - E_{TCNQ/TCNQ^-}^{0,o} + E_{M^{2+}/M}^{0,w} \quad (9)$$

where $\Delta_o^w \phi$ is the Galvani potential difference and $E_{TCNQ/TCNQ^-}^{0,o}$ and $E_{M^{2+}/M}^{0,w}$ are the standard redox potentials of TCNQ in the organic phase and M^{2+} in the aqueous phase, respectively. $E_{TCNQ/TCNQ^-}^{0,o}$ can be calculated from the half-wave potential of TCNQ reduction at Ag|AgCl scale (Figure 1) and $E_{M^{2+}/M}^{0,w}$ can be obtained from literature [34]. Since the reverse reaction is omitted, equation 9 can be simplified by incorporating the constants and unknown variables into a single parameter κ :

$$\frac{i_r}{F} = \kappa [M^{2+}]_w [TCNQ^-]_o^2 \quad (10)$$

where

$$\kappa = 2k_r^0 e^{\alpha f \chi} \quad (11)$$

Simulations were also attempted with 1:1 reaction stoichiometry, meaning a rate determining step with Cu^{2+} and $TCNQ^-$. The approach curves were simulated sweeping the tip-ITIES separation (d), starting from $25r$, along with the parametric sweep of κ , in order to study the effect of $\Delta_o^w \phi$ on the current feedback.

It is also possible to simulate the mechanism where reduced $TCNQ^-$ is first transferred to the aqueous phase, depending on its standard formal transfer potential $\Delta_o^w \phi_{TCNQ^-}^{0'}$ (Figure 7b). Then the metal cation would be reduced in water and oxidized TCNQ, being hydrophobic, would return to the organic phase, establishing a positive feedback loop. Possible interfacial mechanisms have been discussed by Girault *et al.* already in the 1990s [39]. The distribution of $TCNQ^-$ between the phases depends on the Galvani potential difference:

$$[TCNQ^-]_w = [TCNQ^-]_o e^{f(\Delta_o^w \phi - \Delta_o^w \phi_{TCNQ^-}^{0'})} \quad (12)$$

where $\Delta_o^w \phi_{TCNQ^-}^{0'}$ is the standard transfer potential of $TCNQ^-$. In this approach, the reaction and its kinetics are mathematically analogous to 7 except that the reaction is homogeneous. Although the reaction rate constant k_r does not depend on $\Delta_o^w \phi$, the distribution of $TCNQ^-$ brings about the $\Delta_o^w \phi$ dependency via equation 12. Butler-Volmer kinetics with a large reaction rate constant was used to model the ion transfer, which allowed the concentrations to reach electrochemical equilibrium rapidly. The metal reduction itself would take place in the aqueous phase and thus for irreversible reaction with reaction rate constant k_r , rate equation would be:

$$-\frac{i_r}{2Fk_r} = [M^{2+}]_w [TCNQ^-]_o^2 e^{2f(\Delta_o^w \phi - \Delta_o^w \phi_{TCNQ^-}^{0'})} \quad (13)$$

The simulations were carried out by varying k_r and $\Delta_o^w \phi$, which would determine the TCNQ⁻ concentration in the aqueous phase.

Figure 8: The fitted COMSOL simulations of the approach curves against a water phase with 1 mM CuSO₄ and the extracted $\ln(\kappa/\kappa_0)$ values plotted against the corresponding χ . $\kappa_0 = 10^{-8}$ m⁴/mol/s was used to κ to make the argument of the logarithm dimensionless. The dashed lines represent the experimental data and the solid lines the COMSOL simulations.

The FEM simulations could reproduce the approach curves obtained from the experiments only when the heterogeneous redox reaction was assumed. With the homogeneous approach, none of the simulated curves could be matched with the experimental ones. The best fits of the approaches against the water phase with 1 and 5 mM CuSO₄ and the obtained κ values in logarithmic scale are shown in Figures 8 and 9, respectively. For the lower Cu²⁺ concentration, the approach curves were compatible with the experimental data only, when 1:1 stoichiometry was applied, while at 5 mM Cu²⁺ concentration 2:1 stoichiometry was required. For the 1:1 stoichiometry, reaction rate coefficient could be extracted from the intercept of the line fitted for the $\ln(\kappa/\kappa_0)$ data ($2.2 \cdot 10^{-6}$ m⁴/mol/s) and α from the slope (0.09). κ_0 is an arbitrary quantity to scale κ . The reaction rate constants obtained from the 5 mM Cu²⁺ approaches showed more ambiguous non-linear behaviour as χ was varied. After the threshold potential after which the feedback becomes positive, κ does not exhibit χ dependency.

Obviously, there are some deviations between the experimental and modelled approach curves, which can be explained by phenomena, which were not taken into account in the simulations, *e.g.* changes in the ITIES geometry as the approaching UME interacts with it by pushing it without penetrating it. The imperfect geometry and deviations from the axial symmetry of the UME itself can also cause error in the simulations. Additionally, the repeatability of the experiments with SECM against a liquid/liquid interface can be inadequate, as has been discussed earlier *e.g.* by Deng *et al.* [40] Cu nanoparticles have catalytic properties, which are likely to affect the reaction kinetics. Additionally, it should be mentioned especially in the case of Figure 8 that simulations of negative feedbacks are more sensitive to the RG values. Also the used mesh can result in some error, even though an extremely dense mesh was generated.

Figure 10 shows the tip currents converted to $\ln(\kappa/\kappa_0)$ scale similarly to

Figure 9: The fitted COMSOL simulations of the approach curves as in Figure 8, while the CuSO_4 concentration in the water phase was 5 mM. Similarly to Figure 8, $\kappa_0 = 10^{-8} \text{ m}^7/\text{mol}^2/\text{s}$ was used to make the argument of the logarithm dimensionless. The dimension of κ_0 is different from that in Figure 8 due to different reaction stoichiometry. The dashed lines represent again the experimental data and the solid lines the COMSOL simulations.

Figures 8 and 9, scanning the substrate electrode potential. From this, 4 regimes of χ of different slopes can be observed (a, b, c and d as named in the Figure). The k_r^0 values obtained from the intercepts for a, b, c and d were $6.1 \cdot 10^{-3}$, $5.3 \cdot 10^{-6}$, 180 and $72 \cdot 10^{-6} \text{ m}^7/\text{mol}^2/\text{s}$, respectively, and the α values for a, b, c and d were 0.71, 0.17, 1.87, and 0.27, respectively.

Figure 10: $\ln(\kappa/\kappa_0)$ values juxtaposed with the recorded tip currents while the substrate electrode potential was swept. CuSO_4 concentration was 5 mM and the substrate potentials were converted to χ scale.

4 Conclusions

In this work, TCNQ-mediated metal reduction and the effect of $\Delta_o^w\phi$ on it was studied with SECM. From Co^{2+} , Cu^{2+} and Ni^{2+} , only Cu^{2+} produced a positive feedback and could be reduced to Cu. This is obviously expected due to a large difference between the standard redox potential of Cu^{2+} and the other metal cations. The redox potentials of Co, Cu and Ni are -0.277 V, 0.340 V and -0.257 V (vs. NHE), respectively, and the redox potential of TCNQ vs. aqueous SCE is 0.13 V [34]. As equation 9 shows, χ increases as the $E_{\text{M}^{2+}/\text{M}}^{0,w}$ increases, thus increasing the reaction rate.

The Galvani potential difference at the ITIES was established by dissolving potential determining salts to the both phases as well as by utilizing an additional electrode. The results are in agreement with the earlier results of the shake-flask experiments [3, 28] in which the Galvani potential difference at the ITIES established by the common ion TB^- could promote Cu^{2+} reduction by decamethylferrocene. The reduction of Cu^{2+} started to take place when $\chi > -230$ mV. From the FEM simulations it can be deduced that the heterogeneous electron transfer with $\Delta_o^w\phi$ contributing to the driving force χ is the likeliest mechanism for the metal reduction (Figure 7a). Furthermore, the ratio of the TCNQ and Cu^{2+} concentrations have an impact on the redox reaction stoichiometry: when the ratio of TCNQ and Cu^{2+} concentrations was 1, the FEM models agreed with the experimental approach curves when 1:1 stoichiometry was applied. With excess Cu^{2+} , the stoichiometry shifted to 2:1. The reason for this remains unknown, but it can be speculated that they are related to nucleation overpotential, *i.e.* the catalysing effect of the formed Cu nanoparticles of the redox reaction. It is also possible that the nanoparticles can block the diffusion of the reactants, which complicates the system. Also, no adsorption phenomena were taken into account in the simulations, either.

Simulations of the model with homogeneous metal reduction reaction shown in Figure 7b were attempted but no similar behaviour of the approach curve was obtained with this mechanism. The differences of $\Delta_o^w\phi$ sweeps obtained from the simulations and experimental data could be explained by the formation of nanoparticles, which start to catalyse the metal reduction as they are formed. This effect was not included in the simulations. The catalytic effect could be modelled *e.g.* as a step function applied to the relevant boundary conditions.

Both ways of establishing the Galvani potential resulted in similar feedbacks when Cu^{2+} was present in the water phase. However, when the Galvani potential was controlled by a common ion, the feedback was prone to be positive even when no metals were dissociated into the water phase. This is likely not to be due to HER since the pH did not affect the frequency of this phenomenon. It is however worth noting that the presence of LiTB in the water phase resulted in formation of a cloudy layer to the water phase in the vicinity of the ITIES. Additionally, LiTB causes a visible film-like layer to form at the interface, which can be the actual cause for the occasional positive feedback. It was shown that the LiTB concentration has a clear effect on the feedback: higher LiTB concentrations resulted exclusively in positive feedback. The layer is most likely to be

attributed to the surface-active properties of LiTB, resulting in a microemulsion layer formation at the interface. This issue has been recently studied by Holub *et al.* [41] using 1,2-dichloroethane as the organic solvent.

Nevertheless, the probe approach curves against the externally polarized ITIES support the hypothesis of TCNQ⁻-mediated Cu²⁺ reduction and the reaction rate constant for it could be obtained from the COMSOL simulations. When external polarization was used, there would be no potential determining ions in the aqueous phase to cause layer or precipitate formation at the ITIES. In this sense, approach curves against externally polarized ITIES can be regarded as more reliable than the ones against the ITIES with Galvani potential difference determined by a common ion.

Conflicts of Interest

There are no conflicts to declare.

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