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Kinetics of Cu\(^{2+}\) Reduction and Nanoparticle Nucleation at Micro-scale 1,2-Dichlorobenzene-water Interface Studied by Cyclic Voltammetry and Square-wave Voltammetry

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Abstract: Reduction and nanoparticle nucleation of Cu\(^{2+}\) by decamethylferrocene was studied with cyclic and square-wave voltammetry at a microscale liquid–liquid interface established at the tip of a micropipette. With square-wave voltammetry, two reduction steps could be distinguished as two separate current waves. Comparing the experimental results of cyclic voltammetry with finite element method simulations, particle growth could be observed as an increasing limiting current. Furthermore, kinetic parameters could be estimated with square-wave voltammetry simulations following Butler-Volmer kinetics.

Keywords: square-wave voltammetry · liquid–liquid interface · micropipette · metal reduction · finite element simulation

1 Introduction

As metallic nanoparticles often show catalytic properties that do not exist in bulk materials, much interest has been attracted to synthesis and characterisation of these materials. Electrodeposition of metals at liquid-liquid interfaces, i.e., interfaces between two immiscible electrolyte solutions (ITIES), is a relatively long known phenomenon, the earliest discoveries dating back to the 1970’s by Guainazzi et al. [1]. For NP synthesis ITIES provide an easily reproducible and electrochemically controllable platform. In addition to this, containing the metal cation and the reducing agent in separate phases facilitates separation of the product [2].

During the last 15 years, Cu nanoparticles that are usually supported on different carbon structures have been researched immensely as a catalyst for CO2 reduction to C–C products such as ethanol [3–7] and their catalytic properties for hydrogen evolution reaction (HER) have also been studied [8–10]. These nanoparticles can be formed via an interfacial redox reaction at an ITIES that is electrochemically polarized with a common ion, namely tetraakis(pentafluorophenyl)borate (TB·) [9,10]. Because of these catalysing properties of Cu NPs, and copper being a relatively abundant material compared e.g. to rare earth elements which conventional HER catalysts consist of, Cu NPs have become promising in the research of future hydrogen economy applications, and understanding the kinetics of NP nucleation and controlling their growth has become increasingly relevant.

Differential electrochemical techniques, such as square-wave voltammetry (SWV) that uses a signal in which square-wave and staircase functions are combined, have been presented to determine kinetic parameters of redox reactions and their theory has been discussed in literature [11,12]. In practice, SWV has been utilized e.g. by Mirčeski et al. [13] who estimated kinetic parameters of reduction of azobenzene and hexacyanoferrate at hanging drop mercury and glassy carbon electrode, respectively.

Electron/ion transfer reactions at ITIES are conventionally studied at a macroscopic ITIES with four-electrode voltammetry that has been used intensively since its discovery in the 1970’s [14]. Alternatively, a microscale interface can be established at e.g. a tip of a micropipette, in which case only two electrodes are needed. Miniaturizing the ITIES increases the mass-transfer rate due to higher diffusion rates, which enables probing reaction kinetics [15]. Additionally, smaller currents decrease the Ohmic loss which is an inherent problem when working with organic solvents with high resistance [16].

Deposition of Pt and Pd nanoparticles has been demonstrated at micro- and macroscopic ITIES [17–21] and nucleation of mesoscopic Ag particles at the tip of a micropipette has been shown by Guo [22]. More recently Moshrefi et al. [23] studied Au NP nucleation by micropipette voltammetry. To our knowledge, while the EE mechanism has been researched in the literature [24–28], no studies have been published in which Cu\(^{2+}\) reduction at micropipette ITIES have been studied with SWV.

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In our previous work [29], scanning electrochemical microscopy was utilized to measure the kinetics of Cu²⁺ reduction by reduced 7,7,8,8-tetracyanoquinodimethane (TCNQ⁻) formed at a Pt disk ultramicroelectrode, which was detected as a positive feedback loop. The measurements were obscured by a film that was formed at the interface when the common ion was present in both phases, which would generate a positive feedback loop at high common ion concentrations. It is likely that the reason behind this was the choice of the organic solvent, methyl isobutyl ketone, which was selected due to its density lighter than that of the aqueous phase and adequate solubility of TCNQ to it. Therefore, only low common ion concentrations could be used to determine the Galvani potential.

In this work, cyclic voltammetry (CV) and square-wave voltammetry (SWV) at an ITIES established at a tip of a micropipette was utilized to provide insight into the Cu²⁺ reduction to Cu⁺ and the subsequent Cu NP formation at a μ-ITIES, i.e. the EE mechanism. The experimental data was interpreted with finite element method (FEM) simulations [29–31]. When the current is not limited by the reducing species in the organic phase, the two reduction steps of Cu²⁺ could be distinguished with SWV as two separate waves. This is unique for SWV at μ-ITIES as at a macroscopic electrode these reduction steps are not readily distinguishable. The FEM simulations presented in this study provide estimations for kinetic parameters of the reactions.

2 Materials and Methods

All aqueous solutions were prepared in ultrapure MQ water (specific resistivity 18.2 MΩcm). The organic phases were prepared from 1,2-dichlorobenzene (DCB, Sigma-Aldrich), which was purchased from Sigma-Aldrich. Decamethylferrocene (DcMFc) was purchased from Alfa Aesar. Lithium tetraakis(pentafluorophenyl)borate (LiTB) was purchased from Chemdex and bis-triphenylphosphoranylidene)ammonium chloride (BACl, 97% purity) from Sigma-Aldrich. Bis (triphenylphosphoranylidene)ammonium tetraakis (pentafluorophenyl)borate (BATB) was obtained by metathesis from LiTB and BACl and it was recrystallized in acetone as described in literature [32]. Trimethylchlorosilane was purchased from Sigma-Aldrich.

The micropipettes were prepared with P-2000 pipette puller (Sutter Instruments, the USA). The instrument utilizes laser light to melt a glass capillary and pull it apart to create a micropipette. The shape of the micropipette could be controlled by varying five parameters in the pulling programme: heat, filament, velocity, delay, pull. In order to reduce the iR drop inside the pipette, the aim was to pull micropipettes with a short taper [33,34] and with micrometer scale tip diameter. The quality of the tip and its diameter was determined with a light microscope. In this work quartz glass capillaries with outer diameter of 1.5 mm and inner diameter of 0.75 mm were used. The capillaries were purchased from Sutter Instruments.

Since the aqueous phase was inserted inside the micropipette, its external surface was rendered more hydrophobic by silanizing it by immersing it to a trimethylchlorosilane solution while having a constant flow of N₂ directed through the pipette. The pipette was left to dry overnight. The aqueous phase was inserted into the micropipette with a Hamilton syringe.

The electrochemical measurements were carried out with an Autolab potentiostat (PGSTAT100, Eco Chemie, the Netherlands). In all experiments, the aqueous phase inside the micropipette contained 100 mM Li₂SO₄ as a supporting electrolyte in order to decrease the iR drop.

DiMFc was used as a reducing agent instead of TCNQ⁻ in our previous paper [29] since TCNQ⁻ would have needed to be reduced from readily available TCNQ. DiMFc was also convenient due to its low solubility to the aqueous phase and it has been used in Ag deposition experiments at liquid-liquid interfaces [35]. Pt electrode was utilized both in the aqueous phase inside the micropipette and as a counter/quasireference electrode (QRE) in the organic phase. Using QRE is often justified in electrochemical measurements at a microscopic ITIES because of its convenience and since the currents at nA scale should not affect the reference potential dynamically during measurements: the potential scale can be calibrated by measuring transfer of an ion with a known standard transfer potential [29,36,37]. The structure of the cell for measuring Cu²⁺ reduction at the tip of the micropipette is shown in Scheme 1.

The CuSO₄ concentration was varied (between 0–50 mM) while the concentration of DiMFc was kept at 4 mM throughout the experiments. In the CV measurements, sweep rate 25 mV/s was used. (in the micro-electrode experiments, sweep rate should not play a remarkable role since the limiting current does not depend on it as long as the sweep rate is low). In the SWV, the frequency of the signal was varied between 5–25 Hz and amplitude between 10–50 mV.

2.1 FEM Simulations: Geometry, Mesh, Methods

The FEM simulations for analysing the electrochemical measurements were run with Comsol Multiphysics software. Similarly to the simulation model in our previous paper [29], the geometry of the micropipette being axisymmetrical, it was sufficient to run the simulations in a two-dimensional geometry with the symmetrical axis placed through the centre of the micropipette. To minimize the simulation error, an extremely dense mesh

![Scheme 1. The composition of the used cell.](image-url)
was used: the model was divided in ca. $3 \cdot 10^5$ elements. The mesh density was largest near the interface and specifically at its edge where the theoretical current density increases infinitely. The geometry, including the RG value (ratio of the radii of the tip of the micropipette including the glass) and the orifice (excluding the glass), the shape of the micropipette was obtained from light microscopy images. An example of a typical micropipette is shown in Figure 1.

The electron transfer from organic DcMFc to Cu$^{2+}$ takes place in two steps, reactions 1 and 2:

$$\text{DcMFc}(a) + \text{Cu}^{2+}(w) \underset{k_{\text{ox} \rightarrow \text{red} \rightarrow \text{ox}}}{\overset{k_{\text{red} \rightarrow \text{ox}}}{\rightleftharpoons}} \text{DcMFc}^+(a) + \text{Cu}^+(w)$$ (1)

$$\text{DcMFc}(a) + \text{Cu}^+(w) \underset{k_{\text{red} \rightarrow \text{ox} \rightarrow \text{red} \rightarrow \text{ox}}}{\overset{k_{\text{red} \rightarrow \text{ox}}}{\rightleftharpoons}} \text{DcMFc}^+(a) + \text{Cu}^+(ads)$$ (2)

where $k_{\text{ox} \rightarrow \text{red} \rightarrow \text{ox}}$ and $k_{\text{red} \rightarrow \text{ox} \rightarrow \text{red} \rightarrow \text{ox}}$ are the forward and reverse reaction rate coefficients for reactions $i=1$, 2, which are defined with their respective standard reaction rate coefficients $k_i^0$ as:

$$k_{\text{ox} \rightarrow \text{red} \rightarrow \text{ox}} = k_i^0 \exp \left( \frac{\Delta E_i^0}{RT} \right)$$ (3)

$$k_{\text{red} \rightarrow \text{ox} \rightarrow \text{red} \rightarrow \text{ox}} = k_i^0 \exp \left( \frac{\Delta E_i^0}{RT} \right)$$ (4)

where $a_i$ is the electron transfer coefficient and $\Delta E_i^0$ the standard redox potential for reaction $i$:

$$\Delta E_i^0 = E_{0i,\text{Rg}} - E_{\text{DcMFc}}^0$$ (5)

O$_i$ and R$_i$ are the oxidized and reduced aqueous species of reaction $i$, respectively. The values for these potentials vs. SHE in their respective solutions were acquired from literature ($E_{\text{DcMFc}}^0$-$E_{\text{DcMFc}}^0 = 0.06$ V [37], $E_{\text{Cu}^{2+}/\text{Cu}^{0}}^0 = E_{\text{Cu}^{2+}/\text{Cu}^{0}}^0 = 0.52$ V [38]) was used. Throughout the simulations, the difference of $E_1^0$ and $E_2^0$ was kept constant (0.361 V).

To model the reactions taking place at the μ-ITIES and at the substrate interface, transport of diluted species physics module was used, where the reactions were modeled as a flux of the corresponding species following the Butler-Volmer kinetics [39, 40]:

$$i = \frac{Fk_i^0}{A} \exp \left( \frac{-\Delta G_i^0}{RT} \right) - \frac{Fk_i^0}{A} \exp \left( \frac{\Delta G_i^0}{RT} \right)$$ (6)

where $i$ is the current density over area $A$ and $c$ are the surface concentrations of the species indicated by the lower index.

For the CV simulations, the potential signal was built by utilizing a built-in time-dependent triangle wave function, which was set to the initial potential $E_{\text{im}}$ at $t=0$ and reaches the vertex potential $E_{v}$ at $t = v(E_{v} - E_{\text{im}})$ where $v$ is the sweep rate.

The square-wave potential signal was given as a sum of $E_{\text{im}}$, step function ($E_{\text{sw}}$) and a square-wave signal $E_{\text{sw}}$ that alternates at each step between a given amplitude $E_{\text{am}}$ and its additive inverse with a duty cycle 0.5. Naturally, $E_{\text{im}}$, $E_{\text{sw}}$ and $E_{\text{am}}$ must have the same frequency $f_{\text{sq}}$:

$$E = E_{\text{im}} + E_{\text{sw}} + E_{\text{am}}$$

$$E_{\text{am}} + \Delta E \text{ floor } ((m(t) - 1)/2) + E_{\text{am}} \text{ SW}(m(t))$$ (7)

where $\Delta E$ is the potential step size and $m(t)$ is a function that discretizes $t$ into integers:

$$m(t) = \text{ceil} \left( 2f_{\text{sq}} \right)$$ (8)

$i.e.$ the first half of each period is represented by an odd integer and second half by an even one. SW is a built-in function in COMSOL that returns 1 when it is odd. Each potential step ($i.e. m(t)$) of this signal was further divided into $n$ time steps out of which the flux at the last step at each potential was extracted. The time difference between the last time step and the end of the step is equal to $(f_{\text{sq}}n)^{-1}$. Curiously, if this time difference was set too small by growing $n$, the simulations would become more unstable and result in noisy voltammograms. The reason for this remained unknown to us. However, if $n$ was too small, the extracted current would not correspond to the given $f_{\text{sq}}$. The value $n = 5$ was selected as it was the smallest division of the potential steps that would result in stable voltammograms while the error remained negligible.

The CV and SWV simulations were run with various standard reaction rate constants of reactions 1 and 2. To facilitate the distinction of the reversible, quasireversible and irreversible regimes, $k_i^0$ was expressed in a non-dimensional form $k_i^0$:

$$k_i^0 = \frac{Fk_i^0}{A} \exp \left( \frac{-\Delta G_i^0}{RT} \right)$$ (9)
where $c_{\text{DMFc}}$ and $D_{\text{DMFc}}$ are the concentration and diffusion coefficient of DcMFc, respectively. The diffusion coefficients of DcMFc and Cu$^{2+}$ were obtained from literature ($4.5 \times 10^{-10}$ m$^2$/s [37] and $5.4 \times 10^{-10}$ m$^2$/s [41], respectively). The diffusion coefficients of the reduced and oxidized species of each component were assumed to be equal.

### 3 Results and Discussion

For macroscopic electrodes, the Galvani potential scale ($\Delta_{o}^{w} \phi$) can be determined by measuring with CV the half-wave potential ($\Delta_{o}^{w} \phi_{1/2}$) of an ion that has a known standard formal transfer potential ($\Delta_{o}^{w} \phi_{0}$), e.g. TEA$^+$ (0.116 V [37]), by using equation 10 [42]:

$$
\Delta_{o}^{w} \phi_{1/2} = \Delta_{o}^{w} \phi_{0} + \frac{RT}{2F} \ln \left( \frac{\eta_o}{\eta_w} \right)
$$

(10)

where $\eta_o$ and $\eta_w$ are the viscosities of DCB and water, respectively, and $F$, $R$, and $T$ have their usual meanings. Usually it is estimated that the ratio of the viscosities is unity, from which follows that $\Delta_{o}^{w} \phi_{\text{TEA},1/2} \approx \Delta_{o}^{w} \phi_{\text{TEA},0}$.

However, at $\mu$-ITIES the relation of the half-wave potential and the standard transfer potential is more complex [43]. The $\Delta_{o}^{w} \phi$ scale was therefore determined by comparing simulated CV of TEA$^+$ transfer to the experimentally measured CV (Figure 2a). The transfer was modeled as reversible Butler-Volmer kinetics with $\alpha=0.5$ and $\Delta_{o}^{w} \phi_{\text{TEA}}=0.116$ V (analogously to equation 6). In Figure 2b, the same potential window at $\Delta_{o}^{w} \phi$ scale is shown for SWV.

#### 3.1 Two-step Reduction of Cu$^{2+}$ at the Tip of the Micropipette

In Figure 3, reduction of aqueous Cu$^{2+}$ at the tip of the micropipette by 4 mM DcMFc in the organic phase was observed in a CV converted to $\Delta_{o}^{w} \phi$ scale. At CuSO$_4$ concentrations from 2.5 to 10 mM (ratio of DcMFc and Cu$^{2+}$ concentration between 0.4–1.6), a current loop characteristic to particle nucleation could be observed.

At the lowest Cu$^{2+}$ concentration (0.5 mM) (excess DcMFc), the curves of the forward and reverse sweeps did not loop, which implies that the low metal cation concentration was unable to trigger nucleation. At excess Cu$^{2+}$ concentrations (25 and 50 mM) the nucleation loop did not emerge and doubling the Cu$^{2+}$ concentration from 25 to 50 mM did not double the limiting current, both of which indicate that the current is limited by DcMFc. This is also shown by the shape of the voltammograms that is characteristic to diffusive flux from the bulk solution onto an ultramicroelectrode [41].

The SWV measurements of reduction of aqueous 10 mM CuSO$_4$ inside the micropipette by 4 mM DcMFc in the bulk organic phase are shown in Figures 4 and 5. In Figure 4, $f_{\text{sg}}$ was varied between 5–25 Hz and $E_{\text{am}}$ was kept at 25 mV. With the used increment between the potential steps $dE=4$ mV, this frequency regime corresponds to 20–100 mV/s. Both sweep directions show two waves which are attributed to the Cu$^{2+}$ reduction to Cu$^+$ and Cu$^+$ reduction to Cu with peak potentials at $-0.10$ V and 0.16 V, respectively. When swept to the positive direction, the second wave showed irregularities as the peak $i_\text{p}$ decreased after reaching a peak of 2.2 mA/cm$^2$ at 10 Hz which corresponds to sweep rate of 40 mV/s. Too high frequencies decrease the wavelength of the square-wave signal which allows less time for the electron transfer to take place and the transient capacitive currents become more prevalent, which caused the peak currents to plateau. $f_{\text{sg}}$ did not have similar effect on the SWV when swept to the reverse direction and the absolute values of the peak current densities were larger, which can imply faster reaction at reverse sweep.

Figures 5a and 5b show the effect of the Cu$^{2+}$ concentration and the amplitude $E_{\text{am}}$ on the forward sweep SWV while $f_{\text{sg}}$ was kept at constant 10 Hz. Also in Figure 6a, $f_{\text{sg}}$ was decreased down to 1 Hz, while $E_{\text{am}}$ was varied between 10–40 mV: the lower frequency enabled clearer separation of the two waves. Additionally, the forward and backward components that the SWV sweep consists of are shown in Figure 6b in which the two reaction steps are also clearly distinguishable.
In contrast to the unpredictable effect of $f_{sw}$ on the peak currents in Figures 4a and b, the peak currents increased linearly as $E_{am}$ was increased from 10 to 50 mV at 10 mV interval at both concentrations. However, at excess Cu$^{2+}$ concentration (50 mM in Figure 5b), as the current is limited by DcMFc, the two waves could no longer be distinguished, which is analogous to the CVs in Figure 3b. Similar behaviour can be observed in the reverse sweep in Figure 5c.

3.2 FEM Simulations

The theoretical limiting current density at an ultramicroelectrode (UME) is given by equation 11: [41]

$$i_{lim} = xDFc_br$$  \hspace{1cm} (11)

where $r$ is the radius of the UME, $c_b$ is the bulk concentration of the reacting species and $x$ is a constant that depends on the geometry of the electrode, e.g. $RG$ value: for a hemispherical geometry $x = 2\pi$ and for a disk UME, $x = 4$ [41]. Figure 7 shows the dependence of $x$ on the $RG$ value in time-dependent CV and steady state simulations. At larger $RG$ values $x$ approaches 4, and at $RG = 30$, the difference of $x$ and 4 was < 0.5% which is low enough to be attributed to simulation error. The $RG$ value of the used micropipettes according to the microscopy images (Figure 1) was very thin, and in the simulations, including the ones in Figure 2, it was estimated to be 1.1 which corresponds to $x = 5.0$.

### 3.2.1 SWV Simulations

Figure 8 shows the forward sweep SWV simulations of reactions 1 and 2 with 10 mM Cu$^{2+}$ and 4 mM DcMFc ($f_{sw} = 5$ Hz) while $k_1$ was varied between 0.01 and 10. At values of $k_1$ larger than 10 the reaction 1 is reversible and the peak potential reaches a constant value of $-0.1$ V. At the regime of $k_1 < 1$ presented in Figure 8, the peak potential shifts to the positive direction logarithmically, i.e. constant positive shift by each decade. This is characteristic to the dependence of peak potential on the reaction rate constant and it has been shown in literature [11,44]. The first wave coincides with the experimental data of Figure 4 in terms of current and peak potential when $k_1 = 1$ which corresponds to $k_1^{0} = 1.2 \cdot 10^{-3}$ m/(s mM).

Using this value for $k_1$, SWV simulations for estimating $k_2^{0}$ were performed and shown in Figure 9. In the
Figure, the ratio of $k_0^2$ and $k_0^1$ was varied between 1 and 100. As the peak potential of the second reaction reaches its plateau as the reaction rate constant is increased to $k_0^2 > 5k_0^1$, it is still ca. 0.11 V higher than in the experimental SWV. The difference could only match the experimental results if $k_0^1$ was low enough to have its corresponding peak potential at 0.1 V, or if the difference of $E_0^1$ and $E_0^2$ was smaller than the value used in the simulations. Cu$^{2+}$ could also be reduced to Cu with $E_{Cu^{2+}Cu} = 0.34$ V vs. SHE [41], but simulations of this reaction pathway did not produce a second wave at any reaction rate constant (the data not included in this work).

3.2.2 CV Simulations

In Figures 10a and 10b, the value $k_0^0 = 1$ was used to produce the forward sweep voltammetric simulations at high and low Cu$^{2+}$ concentrations (10 mM and 50 mM in Figures 10a and 10b, respectively) while the ratio of $k_0^2$ and $k_0^1$ was varied similarly as in Figure 9. At both concentrations, $k_0^2$ had little effect on the CVs. At 50 mM Cu$^{2+}$, the shape of the forward sweep matches the experimental sweep in Figure 3b but the measured and modelled half-wave potentials are off by ca. 0.1 V.

The limiting current densities of the CV with excess Cu$^{2+}$ are consistently lower in the FEM simulations (5.5 mA/cm$^2$ in Figure 10) than in the experiments (up to 28 mA/cm$^2$ in Figure 3). This can only be explained by growth of the surface area due to Cu nucleation. Comparing the theoretical and experimental limiting currents indicates that the area grows to 5 A; at 10 mM CuSO$_4$, the limiting current in Figure 3 was 10 mA/cm$^2$, which was ca. 4.3 times larger than the current density acquired from the simulations (2.3 mA/cm$^2$). The expansion of the reaction area could also explain the difference between measured and modelled half-wave potentials: both sweeps have the same off-set potentials, but as the reaction 2 starts producing NPs and thus increases $A$, the current increases to its new limiting current shifting the half-wave potential. This effect is not visible in the SWV measurements, as it is a differential technique. The
expansion of the reaction area caused by the growing NPs was not included in the geometry of the model, which also explains the difference between the experimental and modeled CV of 10 mM Cu$^{2+}$: the experimental CV did not produce similar clear two waves that are shown in Figure 10b but rather a steadily increasing current starting from an off-set at ca. −0.1 V.

4 Conclusions

In this work, Cu$^{2+}$ reduction was studied by CV and SWV at a μ-ITIES formed at a tip of a micropipette. The experimental measurements were analysed with FEM simulations in two-dimensional geometry. In the CVs, a characteristic nucleation loop could be observed and its emergence depended on the concentration ratio of DcMFc and Cu$^{2+}$. Similar loop for Cu$^{2+}$ reduction by DcMFc has been detected also at macroscopic four-electrode CV [9]. At excess Cu$^{2+}$ concentrations the loop was not detected as the the current was limited by DcMFc.

In the SWV measurements, as in the CVs the concentration ratio of Cu$^{2+}$ and DcMFc had a great effect on the shape of the current curves: two reduction waves could be at the same Cu$^{2+}$ concentration regime in which the nucleation loop could be detected in the CVs. At macroscopic electrodes these reactions are not as clearly distinguishable in CVs (e.g. [9,45,46]). The peak potential of the first wave corresponded well to the expected value based on the standard redox potential of the reaction while the subsequent reversible step took place at a lower...
The simulations provided an estimation for the kinetic reaction rate constant for the first step of the reduction which was in the quasi-reversible regime. The value is at the same magnitude as the reaction rate constant derived for tetracyanoquinodimethane anion mediated Cu$^{2+}$ reduction in our previous work [29]. Further data on kinetics of electron transfer to Cu$^{2+}$ at ITIES is scarce, while kinetic studies for Cu$^{2+}$ reduction at solid electrodes in deep eutectic solvents have been reported [49, 50].

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

Research Article


