

Effect of water on the electrodeposition of copper on nickel in deep eutectic solvents

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Abstract

Most studies of metal electrodeposition in ionic liquids dry the electrolyte thoroughly, as water is thought to be detrimental. In some cases, water has a beneficial effect on deposit morphology. The electrodeposition of copper has been studied in 1ChCl: 2EG-water mixtures. It is shown here that the presence of water increases the apparent brightness of the deposit due to changes in the electrodeposit surface feature size, up to a water content of approximately 20 wt%. This study characterises speciation and mass transport in solution, and shows that diffusion can be controlled independently of speciation. It is shown that there is an optimal water content, which is thought to originate from formation of a bicontinuous microemulsion phase in DES-water mixtures. Additionally, the copper species remains in a predominantly ionic medium at low water content but moves to an aqueous environment when water is the main component.

Key words: Deep eutectic solvents, copper, electrodeposition, water.

Introduction

Copper electrodeposition is important for the construction of many electrical devices, including printed circuit boards and silicon chips. There are numerous electrolyte formulations from which copper can be deposited and each produce layers with different properties. Copper electrodeposition can also be applied to the electrowinning of metal from primary and secondary sources, and is routinely carried out in a variety of aqueous media including acid baths, cyanide baths, alkaline non-cyanide baths and pyrophosphate baths. These baths are sensitive to the concentrations of additives required to obtain a good surface finish.¹

An alternative to the use of aqueous media for metal electrodeposition is ionic liquids (ILs) and deep eutectic solvents (DESs). ILs are solvents formed entirely of ions, which are commonly defined as being liquid below 100°C,² whereas DESs are solvents formed from a eutectic mixture of Lewis or Brønsted acids or bases, and can contain a wide variety of cationic and/or anionic species.³ These can have wider potential windows, relatively high conductivity compared to non-aqueous solvents, and high solubility of metals salts, which makes them useful for the electrodeposition of metals.^{4, 5} While the electrodeposition of copper using ionic liquids is not necessarily an important technical advance due to the disparity in the cost of the electrolytes, it is a useful model system as it gives a different deposit morphology when compared to aqueous systems. Mixtures of the two liquids should provide information about the causes of these morphological differences.

Electrodeposition of metals from ILs and DESs has often been investigated in order to avoid oxide/hydroxide chemistry and control metal speciation in solution. The influence of water on the electrochemical window of some ILs and DESs has been studied and it was found that the potential window could be decreased by more than 1 V depending on the anion and amount of water.⁶⁻⁸ This is particularly significant when BF_4^- and PF_6^- anions are present, as these liquids can hydrolyse.⁹ The presence of water in DESs also has the effect of decreasing solution density, viscosity, and surface tension, with a concurrent increase in conductivity. This can be discussed in terms of hole theory, where it is suggested that these changes are due to an increase in average hole size and the size of water compared with the components of the DES.^{10, 11} For the example of Ni-containing DESs, charge transfer is inhibited with increasing water content in 1ChCl:2EG, which is thought to be due to self-limiting growth of Ni by electrolysis of residual water and the formation of Ni-oxide/hydroxide.¹² In some systems, water has a

beneficial effect on the deposition of metal, for example for Cr deposition between 9-12 mole equivalents of water: chromium enables bright, hard chromium to be deposited from a $\text{ChCl}:2\text{CrCl}_3$ mixture.¹³

The main objective of this study it is to quantify and explain some unusual observations with metal electrodeposition that have been seen within the Leicester research group. It has been found that a small amount of water added to a DES has a significant effect on the deposit morphology. It has also been proposed that the anodic reaction in DESs can significantly influence the cathodic reaction. To investigate these parameters, copper was selected as a test metal to electrodeposit from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in DES-water mixtures. The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in DES system has been studied previously,¹⁴ and is of interest as the reversible $\text{Cu}^{\text{II/I}}$ couple can be used to study mass transport. The intention was to investigate if mixing DESs with water alters the morphology of the copper deposit, and to try to quantify the effects of water on mass transport, the double layer structure, and speciation. The effect of added NaCl was also studied, such that the total chloride content in solution remained constant. Finally, the effect of the anode material was investigated by comparing a copper sheet and an iridium oxide-coated titanium mesh.

Experimental

All chemicals in this work were obtained from Sigma-Aldrich, with purity of $\geq 99\%$. The deep eutectic solvents used were made in the usual manner,^{15,16} from choline chloride (ChCl) as the quaternary ammonium salt and ethylene glycol (EG) as the hydrogen bond donor. Copper-containing solutions were made up to a concentration of $0.1 \text{ mol kg}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$. The solvents used were neat 1ChCl: 2EG, and mixtures of 1ChCl: 2EG-water or 1ChCl: 2EG: brine, where the brine contained $5.2 \text{ mol kg}^{-1} \text{ NaCl}$, unless otherwise stated. The water content of 1ChCl: 2EG was measured using a volumetric Karl-Fischer (KF) titrator SNR B727340076, and was determined to be 1.50(4) wt% before experiments, which had increased to about 2 wt% afterwards. All repeat measurements were carried out using fresh DES to reduce the effects of atmospheric water absorption. The viscosities of the 1ChCl: 2EG-water mixtures were measured using a rotational viscometer (Brookfield DV-E+ Pro) instrument. An average of three values were taken for each sample.

Electrochemical measurements were performed using an Autolab PGSTAT20 software-controlled potentiostat, using a three-electrode set-up. A 0.5 mm diameter platinum disc working electrode and a platinum flag counter electrode were employed. As the solvent composition varied throughout these experiments, a normal silver chloride reference electrode could not be used due to the presence of unquantified liquid junction potential effects; therefore a silver wire quasi-reference electrode was used. Bulk deposition was carried out for 1 h at 35°C, with a current density of 50 mA cm⁻². The anodes were either a copper plate (2 cm² surface area) or an iridium oxide-coated titanium mesh (ca. 1-2 cm² surface area), with 1 x 1 cm nickel plates as the cathode. The Ni plates were pre-etched with ammonium persulphate solution, followed by rinsing in deionised water and drying with nitrogen gas. The Cu deposits were rinsed with deionised water and dried with nitrogen.

UV-Vis spectroscopy was performed using A Shimadzu Model UV-1601 Spectrophotometer in order to monitor changes in copper speciation. Due to strong colour of samples, a 0.1 mm cuvette was used.

The morphology of the copper deposits were examined using an FEI SIRION SEM scanning electron microscope (SEM), whilst the composition of the deposited Cu layer was analysed via X-ray diffraction (XRD) using a Phillips model PW 1730 X-ray generator.

Results and discussion

Effect of water on the electrochemical window of 1ChCl: 2EG

In the present study, the effect of water on the electrochemical window of the DES 1ChCl: 2EG was investigated. **Figure 1** shows that the cathodic current increases with the addition of water, potentially indicating that the choline cation dominates the double-layer structure at the working electrode surface. With the addition of 10 wt% water, the anodic current initially decreases, then increases again after the addition of 20 wt% water or greater. The extra current is likely due to oxidation of water which is easier than that of EG. Several recent studies using atomic force microscopy showed that ILs and DESs form ordered layers at the electrode solution interface.¹⁷⁻¹⁹ The addition of up to 20 wt % water increased the layer structure at the electrode/ DES interface confirming the importance of choline in the interfacial structure.¹⁹

Cyclic voltammetry (CV) experiments were carried out in solutions of 0.1 mol kg⁻¹ CuCl₂·2H₂O in solutions of 1ChCl: 2EG, with 0, 10, 20, and 100 wt% water. The addition of water both reduces viscosity,²⁰ and provides the opportunity for different copper species to be formed, such as mixed chloride/aquo complexes. In low-chloride aqueous solutions where [Cu(H₂O)₆]²⁺ forms, disproportionation occurs between Cu^{II} and Cu metal due to the difference in standard aqueous redox potentials (+0.52 V for the Cu^{+/0} redox couple versus +0.16 V for the Cu^{II/I} redox couple).²¹ However, it has been shown that [CuCl₄]²⁻ is the main species that forms in 1ChCl: 2EG,²² and that Cu^I species are also stable over a wide potential range.²¹

The electrochemical behaviour of copper chloride in 1ChCl: 2EG as a function of water content is shown in **Figure 2**. In these systems, the electrochemical behaviours of the copper species present are similar to that of copper chloride in 1ChCl: 2EG, in that both Cu^{II/I} and Cu^{I/0} couples are accessible.^{23, 24} The electrode potential for the Cu^{II/I} couple remains roughly constant with respect to the quasi-reference, whereas the onset potential for reduction to the metal becomes less negative as water is added to the solution (**Table 1**). This decrease in deposition overpotential is important, as it would tend to indicate that the copper species present has a lower stability constant than the copper tetrachloride DES species, such as a mixed chloro/aquo complex, the presence of which will be discussed further below. Similar behaviour has been observed in aqueous medium, with the addition of NaCl resulting in an increase in deposition overpotential.²⁵ Additionally, the current density associated with the Cu^{I/0} redox couple increases with increasing water content due to the associated decrease in viscosity,²⁰ and hence increase in conductivity, as the availability of holes for the species to move into becomes greater.²⁶

The addition of water will naturally change the relative concentration of ligands in solution as the amount of water is increased (**Table 1**). This can be circumvented by adding 5.2 mol kg⁻¹ NaCl in water which maintains the chloride concentration at a roughly constant value. In these DES: brine mixtures, the Cu^{II/I} and Cu^{I/0} redox couples are both observed, (**Figure 2**) similarly to the water-free DES system, however, the potential difference between the Cu^{II/I} and Cu^{I/0} couples decreases as water is added indicating that different copper complexes are formed. This results in the copper complex in brine being a green colour, i.e. not the tetrachloride complex present in the DES. Whilst the Cu^{II/I} couple in the NaCl brine solution is relatively unchanged in potential compared to the brine-free DES system, the onset potential for the Cu^{I/0} couple

was shifted by up to 0.2 V in a positive direction, similar to aqueous chloride systems, where with increasing chloride content the $\text{Cu}^{\text{I/0}}$ couple shifts approximately 0.2 V to negative potentials,²⁷ showing that a mixed ligand complex with more H_2O is easier to reduce than $[\text{CuCl}_4]^{2-}$, as could reasonably be expected from comparison of aqueous stability constants.²⁸ The shape of the copper stripping peak changes with different amounts of brine splitting in two in the pure brine system. This behaviour has been seen previously and has been shown to be due to the deposition and stripping of metal in different morphologies (nanodeposits at lower overpotentials and micro at larger overpotentials).²⁹

Copper speciation with the addition of water

The changes in current with water content could result from changes in mass transport or speciation. Complexes with higher stability constants are more difficult to reduce than those with lower stability constants. In 1ChCl: 2EG, copper is known to form $[\text{CuCl}_4]^{2-}$ and $[\text{CuCl}_2]^-$,^{22, 30, 31} whereas in chloride-free water, only the hexaaqua complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ should be present.

With the addition of 10 wt% water to a solution of $0.1 \text{ mol kg}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1ChCl: 2EG, the colour only changes slightly from the yellow tetrachloride species (**Figure 3a**), indicating that the speciation remains mostly unchanged. After the addition of 20 wt% water, the solution develops a green colour due to the presence of mixed chloride-aquo complexes. UV-vis spectroscopy of these samples showed only a slight shift of the absorbance bands between the water-free and 20 wt% water systems, indicating that chloride is the main coordinating ligand. Upon the addition of 50 wt% water, the absorbance bands indicate that a significantly different complex is present. In ChCl: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ systems, a water content above 39 wt% was required before a significant proportion of the water ligands become incorporated into the first coordination shell of the Cu^{II} ion.³² A water content of greater than 95 wt% was required before most of the chloride ligands were excluded. For $[\text{C}_2\text{mim}][\text{Cl}]$:water systems, a similar water content (40 wt%) was also required before mixed chloride-aquo coordination became observable.³³ By comparing these literature spectra to those obtained for the 1ChCl: 2EG: water systems, it appears that the addition of 10 wt% and 20 wt % water to 1ChCl: 2EG has a similar effect to the addition of 27-39 wt% and 49 wt% in ChCl: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ systems, respectively. From neutron total scattering experiments,³⁴ it has been identified that the DES nanostructure in DES: water mixtures was retained up to approx. 42 wt% water, whereas above 51 wt% water, water-water and DES-water interactions began to dominate. As the copper ions are only

expected to form the tetrachloride species in DES domains, this could therefore explain why the speciation is retained up to 40 wt% water in Ethaline.

As the speciation in these 1ChCl: 2EG: water mixtures could be changing due to the increasing concentration of water ligands or the dilution of the chloride content, samples were made where the water was replaced by an aqueous 5.2 mol kg⁻¹ NaCl solution. This ensures a similar solution density to Ethaline (1.12 g cm⁻³) and is comparable with other aqueous brine studies.^{35, 36} **Figure 3b** shows that the copper in the DES-free solution forms a pale green complex rather than the blue hexaaqua species, indicating either the presence of a mixture of species or a mixed-ligand complex. Therefore, whilst the chloride content remains high in these DES: brine systems, water ligands can still be found coordinating to the copper cation. It is therefore more likely that this change in speciation behaviour is due to the change in the H₂O: Cl ratio as shown in **Table 1**. Brugger et al. investigated the complexation behaviour of copper in LiCl brines.³⁵ At 25°C and 5 mol kg⁻¹ LiCl, copper(II) ions were present as 10% Cu^{II}, 40% CuCl^I, 40% [CuCl₂]⁰, and 10% [CuCl₃]⁻. No [CuCl₄]²⁻ was predicted to be present. Additionally, EXAFS measurements of copper chloride in NaCl brines showed that at 5 mol dm⁻³ NaCl, the copper ion was coordinated to an average of 1.0 x O-donors and 2.1 x Cl⁻.³⁶ Other studies using up to 3 mol dm⁻³ NaCl determined an average coordination of 2 x Cl⁻ and 4 x O-donor ligands.³⁷ In both of these cases, the tetrachloride species was not indicated, in agreement with the spectra in **Figure 3**.

Bulk copper electrodeposition

To demonstrate the effect of water on the electrodeposition of copper in mixed 1ChCl: 2EG-water systems, bulk electrolysis was carried out in the systems used above. All experiments were performed for 1 h at 35°C and at a current density of 50 mA cm⁻² on a Ni substrate. The increased water content has a significant effect on both the appearance and morphology of the copper deposits, as can be seen in **Figure 4**. In the absence of water, a dull, red-orange deposit is obtained, which increases in apparent brightness up to 20 wt% water, but becomes dull brown when 100 wt% water is used with ChCl. The SEM images show that the copper electrodeposit surface features increase in size with increasing water content. However, it was observed that there is minimal change in the structure of these features between the addition of 10 wt% and 20 wt% water. This could be due to changes in speciation, mass transport or double layer

properties. It is assumed that in the DES: water mixtures the anodic reaction is the oxidation of water.

Morphology is dependent on a number of factors, including mass transport rates, reduction kinetics, nucleation mechanism, and the underlying structure and defects of the substrate, amongst others. Speciation has a strong effect on mass transport and complex stability, but reduction kinetics are also impacted by the double-layer structure at the cathode surface. It was proposed above that choline adsorbs to the electrode surface at low potentials, even when a high concentration of water ligands are present. To examine the effect of water on how the Cu deposit develops, XRD was carried out on the electrodeposited copper samples, as can be seen in **Figure 5**. The crystallographic texture of the deposits change with the amount of water, and with changes in relative amounts of crystal orientation. The texture coefficients calculated for the Cu deposits obtained from the various systems are listed in **Table 2** and have been normalised to the relative intensity of the Cu[111] reflection. In all systems, the Cu[111] reflection was the most intense, followed by the Cu[200] and Cu[220] reflections. As water content increases, the relative intensities of the Cu[200] and Cu[220] reflections both increase with respect to the Cu[111] reflection, suggesting that the double-layer structure formed at the cathode favours a particular orientation of crystal growth, or that the speciation has an effect on the crystal growth kinetics of these different orientations. Ghosh et al. carried out copper deposition in 1ChCl:2EG onto low carbon steel at a low current density of 4.7 mA cm^{-2} .²⁴ This deposit showed the presence of Cu[111], Cu[200] and Cu[220] reflections in a ratio of 100:12:21, with an average surface feature size of approximately 66 nm. The deposit obtained in the present study showed reflection ratios of 100:45:27, indicating that a 10x higher current density (50 mA cm^{-2}) is more favourable towards formation of the Cu[200] crystal orientation.

In the aqueous 0.1 mol kg^{-1} NaCl solution, reflections at 2θ values of 28° , 33° , 47° , and 56° were present. This is most likely to be solid CuCl that precipitates out of solution, as Cu^{I} is known to be destabilised in aqueous solution compared to in DES systems. In aqueous systems, the presence of the chloride ions in copper plating baths can induce formation of CuCl precipitate at the cathode surface, leading to a high charge-transfer resistance for reduction of Cu^{II} ions at the cathode surface.³⁸ The absence of these reflections in the DES: water systems is due to the enhanced stability of Cu^{I} species therein. As the intensity of the Cu reflections relative to those for Ni is low, it is likely that the Cu deposit is fairly thin. Deposition onto

stainless steel at -0.4 V vs quasi-ref has a different effect on morphology, with brighter deposits of a more nodular morphology forming, with diameters of up to 1 μm .³⁹

With the addition of water to DES solution, the copper species present are known to change. To differentiate speciation effects from double layer effects, the total molality of chloride was kept constant in solution by adding a 5.2 mol kg^{-1} aqueous solution instead of pure water (**Figure 6**). This had the effect of changing the copper deposit to a more yellow/brown colour. It is, however, notable that the brightest deposit is again obtained with 20 wt% water added. The deposit morphology also changes to much smaller surface feature sizes.

Effect of using a soluble anode

Soluble anodes are often used to maintain the metal ion concentration in plating baths and prevent undesirable side reactions such as solvent breakdown. Solvent decomposition in DES media is of concern, as several undesirable decomposition products have been reported.⁴⁰ However, anode passivation may contribute to an increase in cell resistance and decrease deposit quality. Studies in aqueous media have shown the formation of a brown/ black passive layer on the surface of the anode.⁴¹ This layer is likely to be copper oxide which has a relatively small band gap of 1.3 - 2.1 eV.⁴² In DES media, chloride salts have been shown to form at the anode surface,⁴³ which increase resistivity.⁴⁴ At a Cu anode, the main electrochemical process is likely to be oxidation of Cu metal, whereas at the iridium oxide-coated titanium mesh anode the process must involve the breakdown of the electrolyte. In DESs the small but significant water content (typically 0.5 to 1 wt %) water acts as a sacrificial reagent, although this can lead to local pH changes. Use of an insoluble anode can affect the morphology, chemical composition, electrochemistry and apparent brightness of any subsequent copper deposition.⁴⁵

Repeating the above experiments with a soluble copper anode under the same electroplating conditions produces deposits with a more reddish-orange colour than when the iridium oxide-coated Ti mesh anode was used (**Figure 7**). The morphology of the deposit is also altered; with 10 wt% water, small nodular deposits are obtained, with a small amount of dendritic material on top. When pure water was used, the copper electrodeposits are embedded in an amorphous layer which EDX and XRD diffractograms confirm is likely to be CuCl precipitated onto the electrode surface. The SEM images for the corresponding brine solutions are shown in **Figure 8**. These deposits are generally brighter than the brine-free aqueous systems. With the addition

of 20 wt% brine the morphology is dendritic, and in the DES-free system large nodules are present, but with no CuCl on the surface. Deposition of copper from aqueous sulphuric acid solution with 5.82 mM HCl produces similar morphological behaviour to the 100% brine solution studied here, despite the change in acidity.⁴⁶

The copper anode etches for all electrolytes, but the appearance of the anode is very different in each case. When 10 wt% water is added some areas of the copper anode appear to be bright, as if polishing occurs. Electropolishing of metals has previously been studied in 1ChCl: 2EG and it was found that small amounts of water (< 10 %) had a beneficial effect on the quality of the polish obtained.⁴⁷ Most metals which polish in 1ChCl: 2EG form an insoluble film on the electrode surface under anodic polarisation.⁴³ For some of the metals, this layer was identified as being due to metal halides, with a thickness for the latter of up to 3.75 µm formed on copper in 1ChCl: 2EG. While metal halides are generally very soluble in DESs due to the formation of negatively charged species, it was found that the high viscosity and low mobility of the ligands meant neutral species were formed, i.e. for the anodic dissolution of Cu, CuCl₂ was formed instead of [CuCl₄]²⁻. The presence of a more resistive film on the anode will affect the total applied cell potential for a given applied current density and result in different potential profiles at both the anode and cathode surfaces affecting the deposit morphology. This is the first time that the anodic process has been shown to change the deposit morphology in ionic media.

Diffusion coefficient in copper-water system.

From CV measurements, it is possible to calculate the diffusion coefficient for the Cu^{II} species using the Randles-Sevcik equation (**Equation 1**); where j_p is peak current density (A cm⁻²), c is concentration of redox-active species (mol cm⁻³), F is the Faraday constant (C mol⁻¹), n is number of electrons, D is the diffusion coefficient (cm² s⁻¹), v is sweep rate (V s⁻¹), R is the gas constant (J mol⁻¹ K⁻¹), and T is absolute temperature (K). CVs at scan rates from 5 to 50 mV s⁻¹ were measured, the peak current potentials plotted against inverse scan rate (**Figure 9**), and the calculated diffusion coefficients are presented in **Table 3**. As the brine content increases, some deviations from linearity occur for the 50 mV s⁻¹ scan rate.

$$|j_p| = 0.446c \sqrt{\frac{F^3 n^3 D v}{RT}} \quad 1$$

Across the DES: brine series, the ratio of i_{pa}/i_{pc} (where i_{pa} and i_{pc} are peak anodic and cathodic currents, respectively) is very close to 1, indicating reversibility of the electron transfer reaction. This indicates that the Cu^{I} species is stable during the experimental time scales, even in the 100% aqueous NaCl brine system. $E_{pa}-E_{pc}$ is consistently 90-100 mV (where E_{pa} and E_{pc} are peak anodic and cathodic potentials, respectively), which has been seen for quasi-reversible couples in more viscous ionic liquids.⁴⁸

For a species of radius r , diffusing in a homogeneous medium of viscosity η , the diffusion coefficient is given by the Stokes Einstein equation (**Equation 2**).

$$D = \frac{kT}{6\pi r\eta} \quad 2$$

Plotting the diffusion coefficient as a function of fluidity (η^{-1}) should yield a straight line if the speciation of the diffusing species remains constant. **Figure 10** shows that as the fluidity increases, i.e. as more water is added, the diffusion coefficient is linear when the water content is < 50 %. In brine solution with no DES, the diffusion coefficient is lower than would be predicted from an extrapolation of the DES-water mixture data. This can only really be explained by a model in which the liquid is non-homogeneous, which has already been shown to be the case for water-DES mixtures.⁴⁹ The change in the diffusion coefficient would then be caused by the copper changing its environment from a primarily ionic phase to a water dominated phase and accordingly the speciation change (**Figure 3**) produces a species with a different apparent radius.

Conclusion

The electrodeposition of copper from a choline chloride-ethylene glycol-based DES was investigated as a function of water content. The addition of water was seen to significantly change the deposit morphology. Most notably, the colour and hue of the copper deposit changed when water was added to the DES.

The addition of water was found to affect the copper speciation, mass transport, double layer structure at the cathode, and film formation on the anode. The most important finding was that the copper changes its solvation from a chloride to a water dominated environment. Bright copper is obtained when the Cu^{II} species remains in a predominantly ionic environment, but mass transport is higher due to the reduced viscosity that results from having significant water domains. The fact that the Cu^{II} species is the anionic $[\text{CuCl}_4]^{2-}$ species, rather than cationic

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex could also result in a difference in reactivity and double layer structure. This is shown when concentrated brines are used and a morphology more similar to that obtained in a DES is observed.

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Figures and Tables

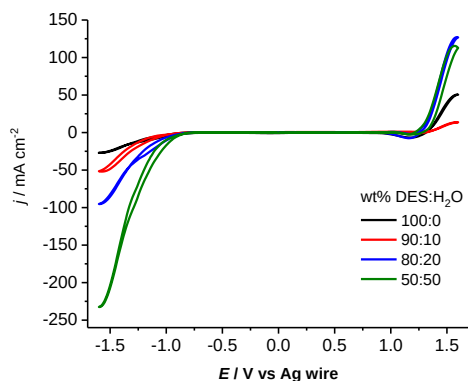


Figure 1: CVs of a Pt-working electrode in different 1ChCl: 2EG-water mixtures. Scans measured at 5 mVs^{-1} .

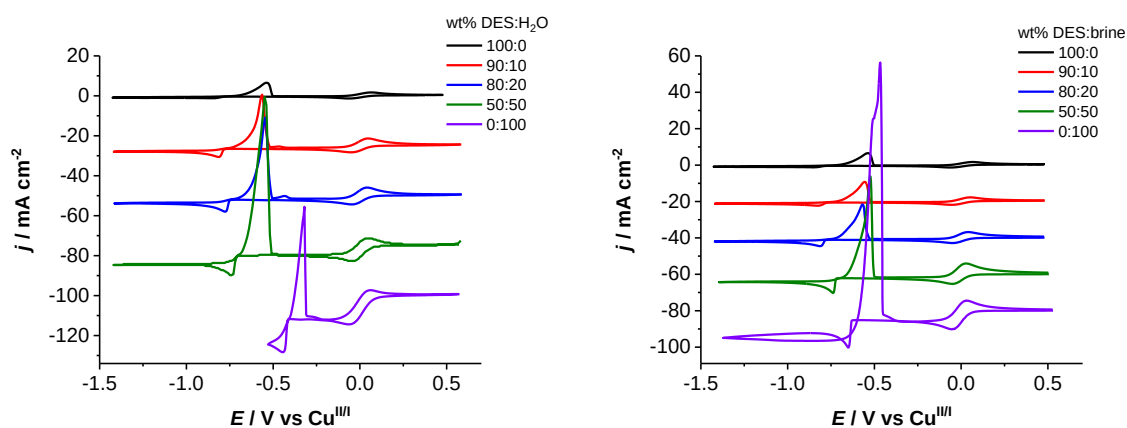


Figure 2: CVs of a Pt working electrode in solutions containing $0.1 \text{ mol kg}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ in mixtures of 1ChCl: 2EG with varying amounts of water (left), and in mixtures of 1ChCl: 2EG with varying amounts of $5.2 \text{ mol kg}^{-1} \text{ NaCl}$ brine (right). Scans measured at 20 mVs^{-1} .

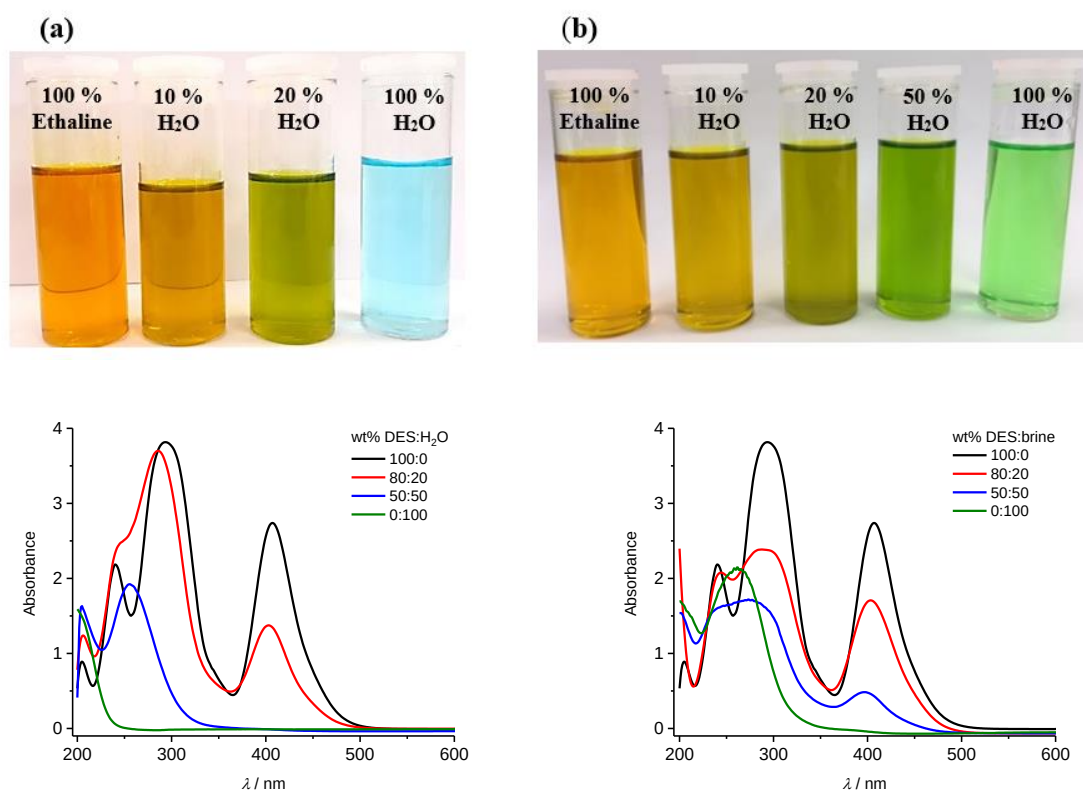


Figure 3: Solutions of 0.1 mol kg⁻¹ CuCl₂·2H₂O (a) different DES-water mixtures, (b) in different DES-brine mixtures with 5.2 mol kg⁻¹ NaCl, with their corresponding UV-vis spectra.

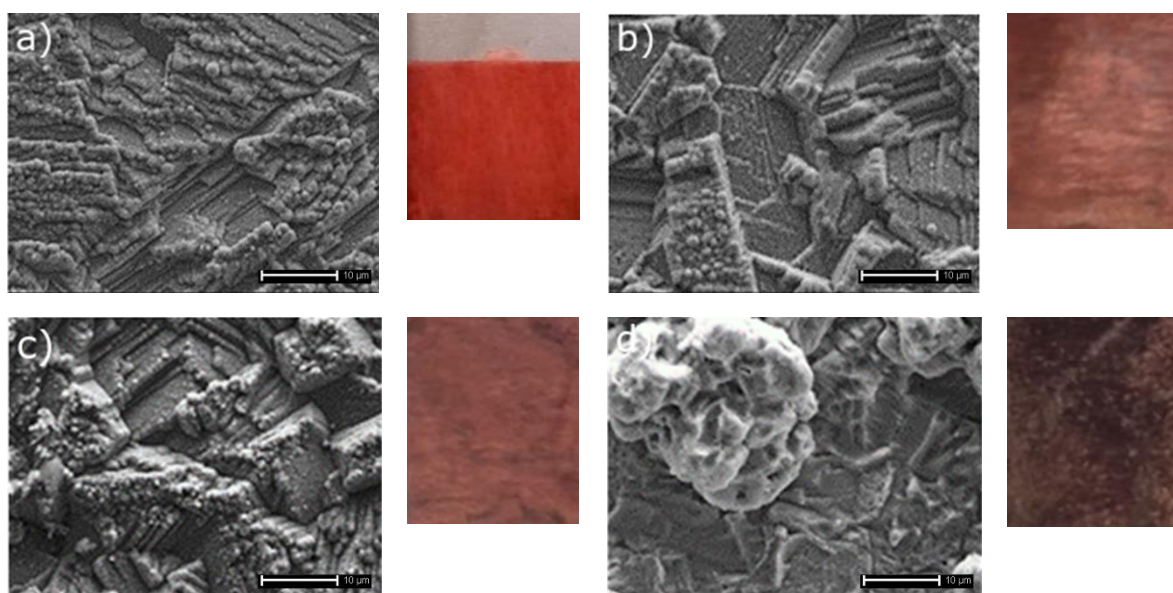


Figure 4: SEM and optical images of copper electrodeposited from 0.1 mol kg⁻¹ CuCl₂·2H₂O in 1ChCl: 2EG: water mixtures, using a Ni-cathode and an iridium oxide-coated Ti mesh anode. DES: water content was a) 100:0, b) 90:10, c) 80:20, and d) 0:100 wt%.

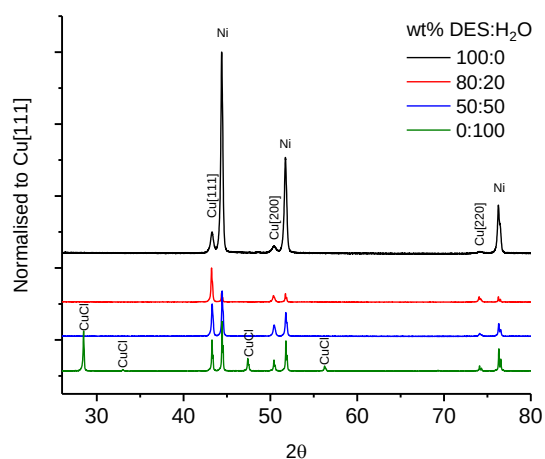


Figure 5: XRD patterns for Cu electrodeposits onto nickel obtained from 1ChCl: 2EG: water mixtures. Patterns are offset for ease of comparison.

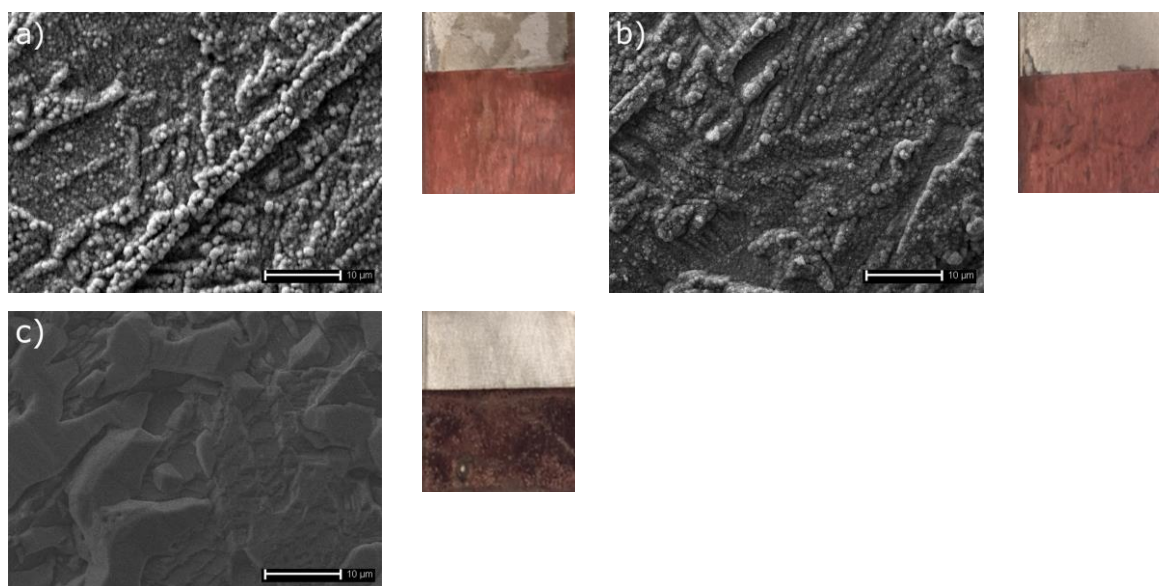


Figure 6: SEM images of copper electrodeposited from $0.1 \text{ mol kg}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1ChCl: 2EG: brine mixtures, using a Ni-cathode and an iridium oxide-coated Ti mesh anode. DES: brine content was a) 90:10, b) 80:20, and c) 0:100 wt%.

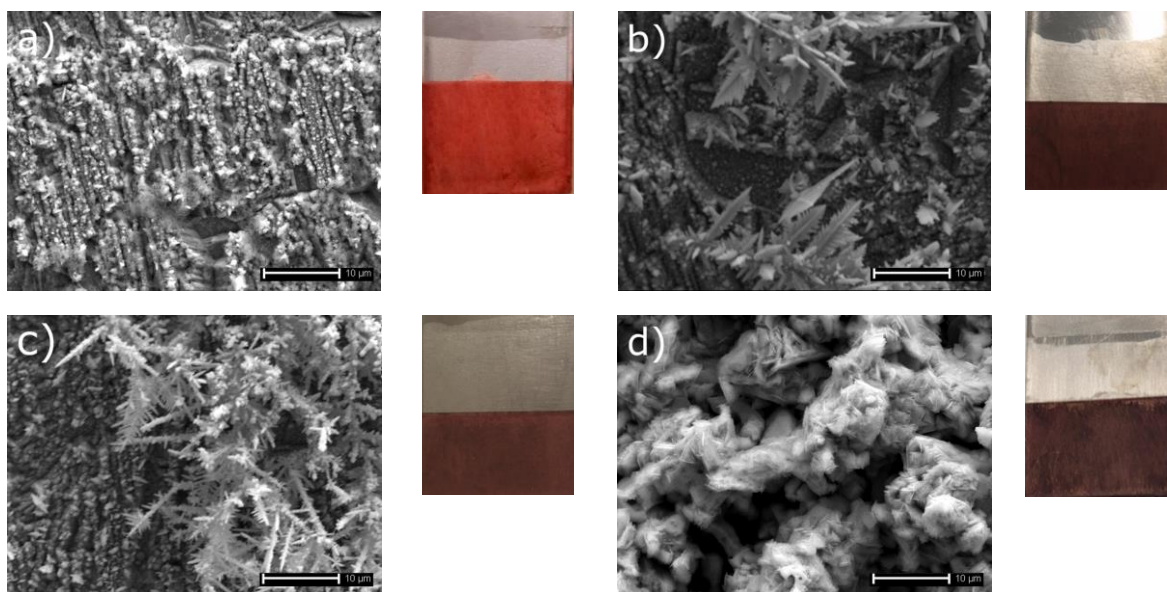


Figure 7: SEM images of copper electrodeposited onto nickel from $0.1 \text{ mol kg}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1ChCl: 2EG: water mixtures, using a copper anode. DES: water content was a) 100:0, b) 90:10, c) 80:20, and d) 0:100 wt%.

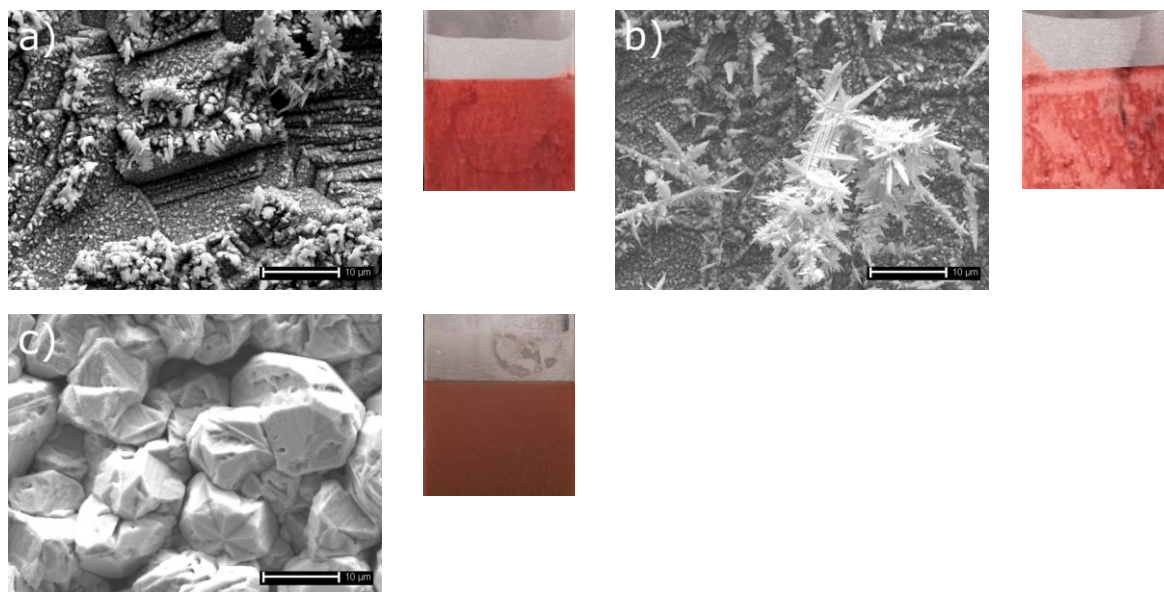


Figure 8: SEM images of copper electrodeposited onto nickel from $0.1 \text{ mol kg}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1ChCl: 2EG: brine mixtures, using a copper anode. DES: brine content was a) 90:10, b) 80:20, and c) 0:100 wt%.

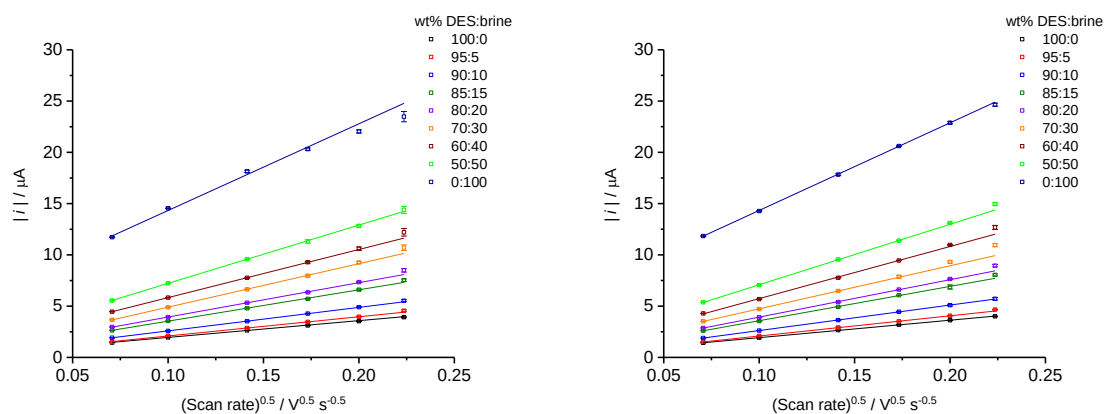


Figure 9: Randles-Sevcik plots for 0.1 mol kg⁻¹ CuCl₂·2H₂O in DES: NaCl-brine mixtures. Cathodic peak currents (left), anodic peak currents (right).

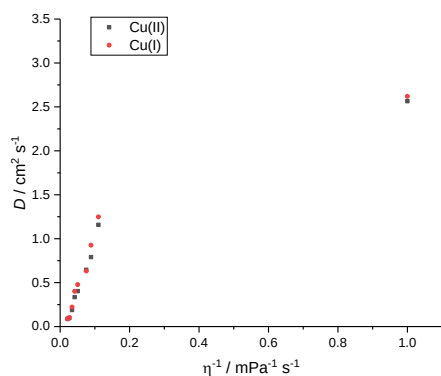


Figure 10: Plot of diffusion coefficient vs. fluidity for the Cu^{II/I} couple in the 1ChCl: 2EG: brine systems.

Tables

Table 1: Electrode potentials for the $\text{Cu}^{\text{I/0}}$ couple at a Pt-working electrode in solutions of 1ChCl: 2EG containing different amounts of water (left) and 5.2 mol kg^{-1} NaCl brine (right). Potentials taken for the 20 mVs^{-1} scan rate and referenced to the $\text{Cu}^{\text{II/I}}$ couple.

Water wt%	Molar Water:Cl	$E_{1/2} \text{Cu}^{\text{I/0}}$ (water) / V	$E_{1/2} \text{Cu}^{\text{I/0}}$ (brine) / V
0	0.223:1 ^a	-0.735(2)	-0.735(2)
5	3.66:1		-0.733(9)
10	1.63:1	-0.738(2)	-0.736(9)
15			-0.727(6)
20	3.66:1	-0.706(1)	-0.739(4)
30		-0.673(3)	-0.717(4)
40			-0.6875(6)
50	14.7:1	-0.568(5)	-0.681(6)
100	186:1	-0.410(5)	-0.61(1)

^a assuming background water content

Table 2: Texture coefficients of the Cu deposits onto nickel prepared from different DES: water mixtures, containing 0.1 mol kg^{-1} $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Intensities are relative to the [111] reflection.

Wt% DES:H ₂ O	[111]	[200]	[220]
100:0	100	45	27
90:10	100	48	34
80:20	100	51	34
0:100	100	64	43

Table 3: Viscosity and diffusion coefficients of $\text{Cu}^{\text{II/I}}$ in DES: NaCl brine systems at 35°C.

Wt% DES:brine	η / mPa s	$D (\text{Cu}^{\text{I}})$ / $\text{cm}^2 \text{s}^{-1}$	$D (\text{Cu}^{\text{II}})$ / $\text{cm}^2 \text{s}^{-1}$
100:0	41 [†]	8.57×10^{-8}	8.90×10^{-8}
95:5	37.73(7)	1.18×10^{-7}	1.14×10^{-7}
90:10	29.09(6)	1.87×10^{-7}	1.65×10^{-7}
85:15	23.87(5)	3.20×10^{-7}	2.91×10^{-7}
80:20	19.8(1)	4.02×10^{-7}	3.31×10^{-7}
70:30	13.31(3)	5.80×10^{-7}	5.56×10^{-7}
60:40	11.24(5)	8.38×10^{-7}	7.08×10^{-7}
50:50	9.07(5)	1.25×10^{-6}	1.16×10^{-6}
0:100	1.0	2.62×10^{-6}	2.56×10^{-6}

Where: η is viscosity, and D is diffusion coefficient.

[†] Value for T = 25 °C, taken from ref ²⁰

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