Electrodeposition from Cationic Cuprous Organic Complexes: Ionic Liquids for High Current Density Electroplating

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The electrochemical behavior of the low-melting copper salts [Cu(MeCN)₄][Tf₂N] and [Cu(PhCN)₄][Tf₂N] (x = 2–4), where MeCN is acetonitrile and PhCN is benzonitrile, is presented. In these compounds, the copper(I) ion is a main component of the ionic liquid cation. Consequently, the copper concentration is the highest achievable for an ionic liquid and this permits to obtain a good mass transport and high current densities for electrodeposition. The cathodic limit of the ionic liquid is the reduction of copper(I) to copper metal instead of the breakdown of the cation as in conventional ionic liquids. It is shown that pure, crack-free copper layers can be deposited from these copper-containing ionic liquids in unstirred solutions at current densities up to 25 A dm⁻².

Ionic liquids are useful solvents for electrochemical applications because of their wide electrochemical window and the presence of intrinsic ionic charge carriers. Examples of such applications are their use as electrolytes in batteries, in photovoltaic devices, and for the electrodeposition of metals. In all of these applications, good mass transfer is needed. However, as the viscosity of most ionic liquids is much higher than that of the most molecular solvents, the mass transport in ionic liquids is rather poor. Moreover, the mass transport is limited even further by the poor solubility of simple metal salts (e.g., chlorides) in most ionic liquids suitable for electrodeposition, except for the dicyanamide ionic liquids. The limited solubility is due to the poor coordinating power of anions such as BF₄⁻, PF₆⁻, or bis(trifluoromethyl-sulfonyl)imide ([Tf₂N]⁻). To increase the solubility, functionalized ionic liquids can be used. These ionic liquids have a built-in coordinating unit such as a nitrile group which can complex the metal ion, thereby increasing its solubility. Another way to improve the solubility of metal ions in ionic liquids is to design ionic liquids with a metal complex as part of their composition. Most ionic liquids of this type contain anionic metal complexes: typical examples of such anionic complexes are [AlCl₄]⁻, [CoCl₂F₂], [ZnCl₂]⁻, and [MnCl₂]⁻. A description of an anionic complex (Co(CO)₉) without chloroligands is given in Ref. 15. In this paper, we present ionic liquids in which the cation is a metal complex and we illustrate their use as medium for the electrodeposition of metals in nonaqueous solutions. Examples of other cationic complexes, based on amine ligands, are already reported in Ref. 16. The complexes under investigation in this paper are tetrakis(acetonitrile) copper(I) bis(trifluoromethylsulfonyl)imide (bistriflimide) [Cu(MeCN)₄][Tf₂N].

In both these complexes the copper ions are in the monovalent oxidation state, as often observed for nonaqueous solvents such as acetonitrile and ionic liquids. The chemical characterization of [Cu(MeCN)₄][Tf₂N] will be presented elsewhere. The electrochemical behavior of copper in organic solvents is already described in Ref. 17-23 and the electrochemistry of copper in ionic liquids in Ref. 7 and 24-28.

Experimental

We have synthesized tetrakis(acetonitrile) copper(I) bis(trifluoromethylsulfonyl)imide, [Cu(MeCN)₄][Tf₂N]. The cation consists of four acetonitrile molecules coordinating to the copper(I) ion in a tetrahedral arrangement. The charge balance is provided by the [Tf₂N]⁻ counter anion. This compound was prepared by reacting copper(II) oxide with bis(trifluoromethylsulfonyl)imidic acid in water to yield copper(II) bistriflimide. Copper metal was then added to a solution of the copper(II) salt in acetonitrile. Because copper(I) is the stable copper species in acetonitrile solutions, a comproportionation reaction between copper metal and the copper(II) ions yielded [Cu(MeCN)₄][Tf₂N]. The reaction sequence is

\[ \text{CuO} + 2\text{H[Tf₂N]} \rightarrow \text{Cu[Tf₂N]}₂ + \text{H}_2\text{O} \]

\[ \text{Cu[Tf₂N]}₂ + \text{Cu + 8CH₄CN} \rightarrow 2\text{[Cu(CH₃CN)]₂[Tf₂N]} \]

It is prepared in an analogous way.

The electrochemical experiments were performed in an argon-filled glove box (with O₂ and H₂O concentrations below 1 ppm) because the tested low-melting salts are sensitive to moisture and oxygen and can undergo disproportionation or oxidation of copper(I). Platinum-covered silicon wafers have been used as the substrates for electrodeposition. Before use, these substrates were cleaned by rinsing with acetone and dried. After the deposition of a copper layer, they were rinsed with acetone and ethanol and dried. The solution was contained in a copper crucible, which also served as counter-electrode, and it was not stirred during the experiments. The experiments were done using a Solartron instruments SI 1287 electrochemical interface controlled by a computer with CORKWARE software. All potentials in this paper are relative to a copper wire directly immersed in solution (pseudoreference electrode), unless stated otherwise. If required, the potential values were corrected for the IR drop in real time by using the current interrupt technique or postexperimental using a value for the electrolyte resistance R. This value was determined both experimentally (by electrochemical impedance spectroscopy (EIS) with a Solartron instruments SI 1255 HF frequency response analyzer) and theoretically (by finite element analysis of the experimental setup). During all the electrochemical experiments, the temperature was kept at 90°C, except for the electrogravimetical analysis which was performed at room temperature. Thermogravimetrical analyses (TGAs) were done in an argon atmosphere with a Q 600 instrument from TA Instruments. The viscosity was measured on a Brookfield cone plate viscosimeter (LVDV-II+ programmable viscometer) with a cone spindle CPE-40. The sample holder was purged with dry nitrogen gas and heated to 80°C by a circulating water bath. Morphology and elemental composition of the copper deposits were determined by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) (Philips XL 30 FEG).

Results and Discussion

Characterization.—Both [Cu(MeCN)₄][Tf₂N] and [Cu(PhCN)₄][Tf₂N] are white crystalline solids at room temperature. Upon melting (at 66°C for both [Cu(MeCN)₄][Tf₂N] and
Cu[Tf2N]: 67.7%

Figure 1. Structural formulae of the cations of the copper-containing ionic liquids (a) [Cu(MeCN)4][Tf2N] and (b) [Cu(PhCN)4][Tf2N].

[Cu(PhCN)4][Tf2N] they form colorless liquids. In Fig. 2 and 3, the TGA curves of [Cu(MeCN)4][Tf2N] and [Cu(PhCN)4][Tf2N] are shown, respectively.

Upon heating, the ligands are gradually lost from the complexes, but full dissociation is complete only at temperatures which are higher than the boiling points of MeCN (82°C) and PhCN (188°C). It can also be seen that the decrease in mass starts at higher temperatures for [Cu(PhCN)4][Tf2N] as compared to [Cu(MeCN)4][Tf2N], indicating that the bond between copper(I) and MeCN is thermally more labile than that between copper(I) and PhCN. A possible explanation is the higher molecular mobility of MeCN, which is a much smaller molecule than PhCN with no π-π interactions, that causes its easy removal from the copper(I) ions. To determine the long-term stability of the [Cu(MeCN)4][Tf2N] compound, an electrogravimetrical analysis of the product was performed after it was heated at 90°C for several days. This temperature was chosen because it is the temperature at which the electrochemical experiments have been performed (vide infra). A carefully weighed amount of [Cu(MeCN)4][Tf2N] was dissolved in a 1:1 mixture of demineralized water and concentrated nitric acid. Nitric acid was required to dissolve the metallic copper that resulted after it was heated at 90°C for several days. This temperature was chosen because it is the temperature at which the electrochemical experiments have been performed (vide infra). A platinum gauze electrode was polarized at −0.2 V vs Ag/AgCl overnight until no more copper was deposited. The deposited amount of copper corresponded to 15.3 wt % of the original mass which is close to the theoretical value of 14.9 wt %. Therefore, in the remainder of the paper the copper(I) acetonitrile complex used for electrochemical studies will be denoted by [Cu(MeCN)4][Tf2N]. In an analogous way, the long-term stability

Figure 2. TGA curve of [Cu(MeCN)4][Tf2N]: the temperature was scanned from room temperature to 300°C at 5°C/min. The dashed lines indicate the theoretical mass losses leading to the formation of the different [Cu(MeCN)4][Tf2N] complexes.

Figure 3. TGA curve of [Cu(PhCN)4][Tf2N]: the temperature was scanned from room temperature to 300°C at 5°C/min. The dashed lines indicate the theoretical mass losses leading to the formation of the different [Cu(PhCN)4][Tf2N] complexes.
density of reduction of the metal ion, i.e., electrodeposition. Because the decomposition potential because the cathodic reaction is the liquid itself contains a relatively high amount of cuprous ions. A the ionic liquid there is no need to solubilize a copper salt, the ionic containing cation an advantage over those with a metal-containing by electromigration. This gives liquid metal salts with a metal-

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\text{Figure 4. Cyclic voltammograms of (a) } [\text{Cu(PhCN)}_2][\text{Tf}_2\text{N}] \text{ and (b) } [\text{Cu(PtCN)}_2][\text{Tf}_2\text{N}] \text{ on a Pt working electrode at } 90^\circ\text{C. The scan rate was } 50 \text{ mV s}^{-1}.
\]

of \([\text{Cu(PhCN)}_4][\text{Tf}_2\text{N}]\) was determined. The electrogammetric analysis indicates a copper content of 11.0 wt % in between the values for \(x = 2\) and \(x = 3\) (11.6 and 9.74 wt %, respectively). Because the measured value is closer to \(x = 2\) than \(x = 3\), the compound will be denoted by \([\text{Cu(PhCN)}_3][\text{Tf}_2\text{N}]\).

Voltammetry.— Because the cuprous ion is a part of the cation it will move toward the cathode during electrodeposition experiments by electromigration. This gives liquid metal salts with a metal-containing cation an advantage over those with a metal-containing anion. Furthermore, because the cuprous ion is an integral part of the ionic liquid there is no need to solubilize a copper salt, the ionic liquid itself contains a relatively high amount of cuprous ions. A third advantage is that such ionic liquids do not have a cathodic decomposition potential because the cathodic reaction is the reduction of the metal ion, i.e., electrodeposition. Because the density of \([\text{Cu(PhCN)}_4][\text{Tf}_2\text{N}]\) is \(1.59 \times 10^3 \text{ g dm}^{-3}\) at room temperature (based on crystallographic data), the concentration \(c\) of copper(II) ions is \(1.59 \times 10^3 \text{ g dm}^{-3} \times (507.89 \text{ g mol}^{-1})^{-1} = 3.1 \text{ mol dm}^{-3}\). No data are available for \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\) at room temperature.

Figures 4a and b show the cyclic voltammograms of \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\) and \([\text{Cu(PhCN)}_2][\text{Tf}_2\text{N}]\), respectively. The overall appearance of these cyclic voltammograms is typical for an electrode reaction involving the electrodeposition and stripping of bulk metal.

From a comparison of these figures, one can see that the electrochemical behavior of \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\) distinctly differs from \([\text{Cu(PhCN)}_2][\text{Tf}_2\text{N}]\). At first, the current density in \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\) is remarkably higher and, second, the voltammogram for \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\) does not have a peak on the cathodic side, which would indicate a diffusion-limited process. One possibility is that the higher electrochemical activity of the acetonitrile complex is linked to the weaker bond between the cuprous ions and the acetonitrile ligands. This means that copper can be extracted more easily from the acetonitrile complex and be reduced because the electrodeposition process requires that the bonds between the cuprous ions and the ligands are broken.

To test this hypothesis, linear potential scans were measured versus a common reference electrode, so that the potential values could be compared between the different solutions. The reference electrode consisted of a glass tube with a ceramic frit. This tube could be compared between the different solutions. The reference versus a common reference electrode, so that the potential values 

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\text{Figure 5. Potential scan vs a home-made reference electrode (see text) on a Pt working electrode at } 90^\circ\text{C for } [\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}] \text{ and } [\text{Cu(PhCN)}_2][\text{Tf}_2\text{N}] \text{. The scan rate was } 50 \text{ mV s}^{-1}.
\]

It is evident that the reduction of copper(II) in \([\text{Cu(PhCN)}_2][\text{Tf}_2\text{N}]\) shifts toward more negative potentials than is the case for \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\), indicating the higher stability of the former complex. The difference in reduction potential is 0.25 V. Based on the formula \(\Delta G = nF\Delta E\), in which \(n\) is the number of exchanged electrons and \(F\) is the Faraday constant, the difference in free energy of both low-melting salts \(\Delta G = 24.1 \text{ kJ mol}^{-1}\). A copper deposit from \([\text{Cu(PhCN)}_2][\text{Tf}_2\text{N}]\) with a thickness of 1 \(\mu\)m on a Pt working electrode is shown in Fig. 6. The deposition potential was \(-0.25 \text{ V}\). The total time required to achieve a thickness of 1 \(\mu\)m was 4 min, much longer than for deposits made from \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\) (vide infra).

Because we are interested in compounds which permit a large mass transport during electrodeposition, the remainder of the discussion will mainly focus on \([\text{Cu(MeCN)}_2][\text{Tf}_2\text{N}]\).
Detailed experiments on $[\text{Cu(MeCN)}_2\text{][Tf}_2\text{N}]$—As it seemed that high current densities could be reached in $[\text{Cu(MeCN)}_2\text{][Tf}_2\text{N}]$, this system was pushed to find the maximum achievable current density. The outcome of these initial experiments gave the impression that an astonishingly high current density of 170 A dm$^{-2}$ could be applied (Fig. 7a). A closer look of the resulting deposit showed a rough, strongly dendritic morphology (Fig. 7b). Therefore, the real current density had to be much lower than the value, calculated on the basis of the geometrical size of the electrode, and these results indicate that one cannot rely solely on voltammetry data. To be able to control the real current density, the experimental setup was adjusted.

If disk electrodes are used, the high current density on the edges of the disk leads to an uncontrollable surface area because the deposit grows radially and a rough morphology arises due to dendritic growth. To decrease the tendency for dendritic growth, a cell was built in which a cylindrical channel made out of PTFE was placed in front of the disk electrode. The cell is schematically shown in Fig. 8. Of course, this configuration increased the $iR$ drop. Where possible the $iR$ drop was corrected for during the measurement by the current interrupt technique. Otherwise, the measured $j$ vs $E$ curves were corrected postexperimentally.

Figure 6. Copper deposit from $[\text{Cu(PhCN)}_2\text{][Tf}_2\text{N}]$ on a Pt working electrode at 90°C. The deposition potential was −0.25 V and it was applied until a thickness of 1 μm was reached.

Figure 7. Preliminary experiment on $[\text{Cu(MeCN)}_2\text{][Tf}_2\text{N}]$ on a Pt working electrode at 90°C: (a) linear potential scan at 50 mV s$^{-1}$ and (b) dendritic copper deposit from $[\text{Cu(MeCN)}_2\text{][Tf}_2\text{N}]$.

Figure 8. Schematic of the electrochemical cell: (a) overview of the electrochemical cell and (b) cross-section of the electrochemical cell with isopotential lines.
Using a constant electrolyte resistance $R$. In a first approximation, $R$ consists of two parts: $R = R_1 + R_2$. $R_1$ is the resistance of infinity to the entrance of the channel and is approximately equal to $R_1 = (4\pi l)^{-1}$, as calculated by Newman. $R_2$ is the resistance in the channel, modeled as a straight conductor whose resistance is equal to $R_2 = l(1/(\pi r^2)\sigma)^{1}$, in which $l$ is the length of the channel, $r$ is the radius of the channel, and $\sigma$ is the solution’s conductivity (1.62 $\Omega^{-1}$ m$^{-1}$). The total value for the resistance $R$ is therefore 627 $\Omega$. This value was also found by the finite-element model and experimentally by EIS. The exact EIS value was determined by extrapolating the high frequency end of the measured curve to the real axis (Fig. 9).

A cyclic voltammogram of $\text{[Cu(MeCN)₄][Tf₂N]}$, not corrected for $iR$ drop, is shown in Fig. 10a; the corrected voltammogram (by a current interrupt technique) can be seen in Fig. 10b.

One can immediately notice the much lower current densities and inclination versus the baseline in the uncorrected CV. At negative potentials versus Cu, the copper(I) ion can be extracted from the cation and reduced to copper metal. This metallic copper layer can be stripped at positive potentials. It is clear that even for small overpotentials, a remarkably high current density could be achieved. When the system was pushed to higher overpotentials, current densities up to 25 A dm$^{-2}$ could be reached (Fig. 11).

This potential scan could only be corrected for $iR$ drop postexperimentally as the current interrupt method becomes unstable at higher current densities. The low overpotential region of the potential scan should be compared to the cyclic voltammogram in Fig. 10b. It is clear that at the start of the measurement the resemblance is satisfactory.

**Copper deposition.**—As mentioned in Ref. 15, one should realize that the electrochemical experiments are performed in a pure ionic liquid that acts as both the supporting electrolyte and the electrochemically active species, which is therefore present in a high concentration. It also follows that migrational processes might occur. In contrast with other ionic liquids that often contain negatively charged electroactive species, in our ionic liquids the migrational flux helps to increase the mass transport due to the positively charged copper complex. Based on the information obtained by voltammetry, deposition experiments were performed for three different current densities: 1, 5, and 25 A dm$^{-2}$. The SEM micrographs of these deposits are shown in Fig. 12. All layers have a theoretical thickness of 1 $\mu$m (135 C dm$^{-2}$).

For a current density of 1 A dm$^{-2}$, the morphology of the deposit was rough and nodular. The grain size exceeded 1 $\mu$m. Based on
the formula $N = (\pi d^2)^{-1}$, in which $N$ represents the nucleation density and $d$ is the deposit’s thickness, and the fact that the substrate is not fully covered with deposited copper, $N$ is lower than $3 \times 10^{11}$ m$^{-2}$. The higher the current density, the higher the nucleation density and the smoother the layers become: for 5 A dm$^{-2}$ the layer had a fine cauliflower like morphology, whereas for 25 A dm$^{-2}$ the surface was wavy yet uniform. No cracks were visible, indicating the absence of large internal stresses. The value for the nucleation density was not determined for the higher current densities but based on the smooth appearance it is considerably higher than $3 \times 10^{11}$ m$^{-2}$.

Figure 13 displays the EDX analysis of the deposit made at 25 A dm$^{-2}$ from [Cu(MeCN)$_2$][Tf$_2$N] at 90°C: (a) linear potential scans at 5 mV s$^{-1}$ and (b) steady-state current $j_L$ as a function of $\nu^2/\nu_0$.

![Figure 13](image-url)  
**Figure 12.** Copper deposits from [Cu(MeCN)$_2$][Tf$_2$N] on a Pt working electrode at 90°C for (a) 1 A dm$^{-2}$, (b) 5 A dm$^{-2}$, and (c) 25 A dm$^{-2}$. The theoretical thickness is 1 µm.

Because the solution was contained in a copper crucible that also served as counter-electrode, the anodic reaction was the dissolution of copper. In a recent paper, it was reported that the [Tf$_2$N]$^-$ anion can be decomposed during the anodic dissolution of copper, leading to the formation of CuF$_2$ which remains in the ionic liquid as a white suspension. During our experiments, the solution kept its clear appearance, so we believe that no significant decomposition occurred. A first possible explanation for this discrepancy is the large ratio of anode area to cathode area so that the current density and overpotential at the anode are kept small. Second, the deposition time to reach 1 µm thickness is 135, 27, and 5.4 s for 1, 5, and 25 A dm$^{-2}$, respectively, which is much shorter than the 2 hours of continuous anodization reported in Ref. 31.

**Diffusion coefficient.**—The diffusion coefficient for Cu$^+$ was measured by using a rotating disk electrode and the well known Levich equation:

$$j_L = 0.62 nF D^{1/2} \nu^{-1/6} c^{1/2} \sqrt{\omega}$$  

[3]

In this equation $j_L$ (A dm$^{-2}$) is the limiting current density, $D$ is the diffusivity (dm$^2$ s$^{-1}$), $\nu$ is the kinematic viscosity ($5.7 \times 10^{-6}$ dm$^2$ s$^{-1}$), $c$ is the concentration (mol dm$^{-3}$), and $\omega$ is the angular frequency of rotation (rad s$^{-1}$). To circumvent the interference of the electrodeposition reaction and possible change in the electrode’s surface area, Cu$^+$ was oxidized to CuF$_2$ instead of being reduced to metallic copper. Linear potential scans at 5 mV s$^{-1}$ for different rotational speeds are plotted in Fig. 14a, while Fig. 14b shows $j_L$ as a function of $\nu^2/\nu_0$.

A straight line is fitted through the data points. The diffusion coefficient $D$ can calculated from the slope of this fit and its value is $4.9 \times 10^{-10}$ dm$^2$ s$^{-1}$. The value for $D$ is rather low. In the authors’
opinion, the oxidative reaction of Cu⁺ is quite different from the reduction to copper metal. In the latter case ligand bonds need to be broken and the liberated acetonitrile molecules can influence complex formation by Cu⁺ and attribute a migrational component into the transport of Cu⁺ ions.

Conclusion

The electrochemical behavior of the liquid copper salts \([\text{Cu(MeCN)}_2\text{TF}_2\text{N}]\) and \([\text{Cu(PhCN)}_2\text{TF}_2\text{N}]\) \((x = 2-4)\) is presented. For electrodeposition purposes, low-melting salts with a cationic complex are preferred over anionic complexes. The \([\text{Cu(MeCN)}_2\text{TF}_2\text{N}]\) complex is the easiest to be reduced to copper and current densities up to 25 A dm⁻² in unstirred solutions could be achieved. The resulting copper deposits from \([\text{Cu(MeCN)}_2\text{TF}_2\text{N}]\) had a smooth appearance, did not show cracks, and were free from incorporated species. Due to stronger ligand interaction, \([\text{Cu(PhCN)}_2\text{TF}_2\text{N}]\) did not show the same behavior. We believe that the much better mass transport in this system is due to the high metal concentration and the favorable electrostatic interactions between the cationic electroactive species and the cathode. This makes the use of liquid metal salts with electrochemically active cationic complexes interesting for electrochemical applications where mass transport is important.

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