Electrochemical behaviour of Cu(II)/Cu(I) redox couple in 1-hexyl-3-methylimidazolium chloride ionic liquid

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Abstract. The electrochemical behaviour of Cu(II)/Cu(I) redox couple in 1-hexyl-3-methylimidazolium chloride (C₆mimCl) ionic liquid was studied using glassy carbon electrode at 375 K by cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. In this electrochemical study, we have made an attempt to avoid the problem of water contamination in hygroscopic C₆mimCl ionic liquid by setting the temperature at 375 K without glove box. This high temperature cyclic voltammetric study revealed two-step one electron reductions of Cu(II) to Cu(I) followed by Cu(I) to Cu metal. The reduction of Cu(II) to Cu(I) was found to be quasi-reversible at 375 K. The diffusion coefficients of Cu(II) and Cu(I), and the charge transfer rate constant of Cu(II) in C₆mimCl were estimated by Randles-Ševčík equation and Nicholson's method, respectively, and found to be consistent with the quasi-reversible process. Further, constant potential electrodeposition of metallic copper was carried out on a stainless steel electrode at 375 K and the deposit was characterised by X-ray diffraction and electron microscopy.

Keywords. Copper; ionic liquid; electrodeposition; quasi-reversible; diffusion coefficient.

1. Introduction

Ionic liquids (ILs) are being employed for electrodeposition of metals and alloys since they offer wider electrochemical windows with extended cathodic stability.^{1–8} ILs are liquids below 373 K that contain exclusively ions and exhibit intrinsic ionic conductivity.^{9–11} Room temperature ionic liquids (RTILs) have melting point at or below 298 K. The key properties of RTILs which allow them for electrochemical applications are the ionic conductivity and electrochemical stability.¹¹ The ionic conductivity of RTILs depends essentially on the availability of individual ions and viscosity. Generally, RTILs are more viscous than other type of electrolytes, but they contain more charge carriers, and viscosity can be reduced significantly by increasing the temperature. This can also bring down the solution resistance in ionic liquids. The electrochemical stability of RTILs is expressed in terms of electrochemical window. RTILs can have electrochemical window as high as 7 V with cathodic stability up to –3.3 V.^{4,12} In addition to these two properties, RTILs also exhibit insignificant vapour pressure,¹³ high thermal stability,¹⁴ which are essential for various other applications.^{12,15–17}

The electrodeposition of copper and its alloys is an important area of research as these materials are employed in electrocatalysis and related applications.^{18–21} There are a number of reports on the electrochemistry and electrodeposition of copper in RTIL media.^{22–27} The Cu(II)/Cu(I) couple shows reversible behaviour in aluminium chloride-N-methylpyridinium chloride acidic RTIL²² while it exhibits quasi-reversible behaviour in butylpyridinium chloride-aluminium chloride²³ and in 1-ethyl-3-methylimidazolium tetrafluoroborate RTIL containing excess 1-ethyl-3-methylimidazolium chloride.²⁴ However, the Cu(II)/Cu(I) redox couple is reported to show irreversible behaviour in the binary mixture of tri-n-octylmethylammoniumchloride (TOMAC) and chloroform.²⁵ Anodic dissolution of copper metal has been employed to introduce cuprous ions into 1-butyl-3-methylimidazolium salicylate IL and then the deposition of copper was carried out on iron substrates.²⁶ It is clear that these studies reported different redox behaviours of Cu(II)/Cu(I) couple in various ILs. However, most ILs do not dissolve copper salts easily. Hence, copper ions are forced into ILs by anodic dissolution of copper metal.^{24,27}

In the present study, 1-hexyl-3-methylimidazolium chloride (C₆mimCl) IL is used as electrolyte, which provides working electrochemical window of about 2.6 V (–1.7V to 0.9V) where copper has its redox

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Figure 1. CuCl_2 dissolved C_6mimCl ionic liquid (a) at RT (b) below 373 K (c) above 373 K.

potentials. Unlike the other ILs, C_6mimCl dissolves CuCl_2 completely. The CuCl_2 dissolved in C_6mimCl IL at room temperature is blue in colour due to $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, as shown in figure 1. The equilibrium $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$ can exist between copper aquo and chloro complexes.²⁸ This equilibrium shifts towards $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ species at room temperature in the presence of water showing blue colour. This species is primarily responsible for the blue colour of the C_6mimCl ionic liquid solution containing Cu^{2+} . As the temperature increases to 373 K, the water content in the ionic liquid decreases and solution turns gradually green due to the mixture of aquo and chloro complexes. Above 373 K, the solution colour changes to yellow due to the shift in equilibrium towards $[\text{CuCl}_4]^{2-}$ species. We therefore sought to study the $[\text{CuCl}_4]^{2-}$ species in ionic liquid medium by shifting the equilibrium towards chloro complex at 375 K. At this temperature the amount of water is negligible and the ionic liquid solution predominantly contains $[\text{CuCl}_4]^{2-}$ species. This study shows a way to overcome the hygroscopic nature and high viscosity of C_6mimCl ionic liquid by maintaining the electrochemical cell at 375 K during the measurements.

2. Experimental

2.1 Chemicals

Analytical grade 1-methylimidazole and 1-chlorohexane (Sigma Aldrich, Bangalore), and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (CDH, New Delhi) were used. 1-methylimidazole and 1-chlorohexane were distilled over anhydrous KOH before use. The colourless C_6mimCl IL was prepared by the procedure as reported elsewhere.²⁹

2.2 Characterization and electrochemical analysis

The X-ray diffraction pattern of Cu films on stainless steel substrates were recorded using Bruker AXS D8 Advance diffractometer and at a scan rate of $0.05^\circ \text{ s}^{-1}$, using $\text{Cu } K_\alpha (\lambda = 1.5414 \text{ \AA})$ radiation generated at 40 kV, 30 mA. The surface morphology and elemental analysis of the copper metal deposit were studied using

a FEI Quanta 200 Scanning electron microscope (SEM) coupled with EDS.

Electrochemical studies were carried out using a three electrode single compartment quartz cell maintained at a particular temperature by placing in a silicon oil bath. The C_6mimCl IL was heated at the specified temperature for 2–3 h to eliminate water and the same is used to prepare 50mM Cu(II) solution by adding required amount of dehydrated CuCl_2 for electrochemical measurements. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ can be dehydrated by keeping the salt in oven at 100°C for 15 min. The dehydrated CuCl_2 can be identified by change in colour from bluish green to brown. A 3 mm diameter glassy carbon (GC) disc electrode with exposed area of 0.071 cm^2 (CH Instruments, Inc. USA) was used as working electrode. 0.2 mm thick Pt plate and 0.2 mm diameter Pt wire were used as counter and quasi-reference electrodes, respectively. For electrodeposition studies, a $2 \times 2 \text{ cm}^2$ stainless steel (SS) plate of 0.3 mm thickness was used as a working electrode. The electrochemical measurements were carried out using Electrochemical Workstation, CH Instruments, USA. All the voltammetry measurements were recorded with internal resistance (IR) compensation.

3. Results and Discussion

3.1 Cyclic voltammetry study of Cu(II)/Cu(I) in C_6mimCl IL

The cyclic voltammograms of pure C_6mimCl and 50mM Cu(II) in C_6mimCl recorded using glassy carbon (GC) and stainless steel(SS) electrodes at 375 K are shown in figure 2. The cyclic voltammogram recorded at GC consists of two cathodic peaks $E_{p,c}^1$ and $E_{p,c}^2$ correspond to the reduction of Cu(II) to Cu(I) and Cu(I) to metallic Cu deposition, respectively. Similarly, in the reverse sweep, two anodic peaks $E_{p,a}^2$ and $E_{p,a}^1$ corresponding to the oxidation of Cu(0) to Cu(I) and oxidation of Cu(I) to Cu(II) , respectively, are observed. Similar redox behaviour is also seen at SS electrode with small shifts in the peak potentials, and that the reduction of copper, $E_{p,c}^2$, at SS electrode occurs at less negative potential than at GC electrode. The role of ionic liquid on the redox potential and electrode kinetics would be very complex as the solution could contain a variety of copper chloride species including the network of Cu species attached to the imidazolium ion ring by hydrogen bonding as shown in figure S1 (supporting information). The effect of these species on the redox potentials of copper would be difficult to determine when we use quasi-reference electrode such as 0.2 mm diameter Pt wire. Figure S2 shows the cyclic

Figure 2. Cyclic voltammograms of (a) C_6mimCl ionic liquid, (b) $50mMCu(II)$ in C_6mimCl at glassy carbon and (c) stainless steel electrodes at 375 K.

voltammograms of Cu(II) at SS electrode recorded at 348 K and 398 K. At 348 K, H_2 evolution at SS electrode was observed around the reduction potential $E_{p,c}^2$, indicating the presence of water in IL medium. However, no gas evolution occurred at 375 K and 398 K where IL is almost free of water and we chose to work at 375 K for all electrochemical studies. This is further verified by TGA experiments presented in figure S3. In the case of IL with 50% water content, the TGA weight loss of water is about 36.1% above 373 K. The loss of water from IL with dissolved $CuCl_2$ at room temperature and 375 K respectively is 4.2 and 2.8%. This shows that the amount of water present in 50 mM Cu(II) in C_6mimCl solution used in our experiments at 375 K would be negligible.

3.2 The quasi-reversibility of Cu(II)/Cu(I) in C_6mimCl

Figure 3 shows the cyclic voltammograms of the Cu(II) to Cu(I) redox couple at GC electrode recorded at different scan rates at 375 K. As seen from the figure, the reduction peak potential shifts towards more negative side and the cathodic peak current increases with increase in the scan rate. The value of $|E_p - E_{p/2}|$ is slightly larger (85 mV at 375 K) than the expected value for a reversible redox couple, where $E_{p/2,c}$ is the half-wave potential as indicated in figure 3. For a reversible redox system, the anodic to cathodic peak separation should be about 74 mV at 375 K for a one electron transfer process³⁰ and also be independent of

Figure 3. Cyclic voltammograms of $50mMCu(II)$ in C_6mimCl ionic liquid at glassy carbon electrode recorded at various scan rates at 375 K.

the scan rate. However, in the present case, the peak separation ($E_{p,a}^1 - E_{p,c}^1$) is found to be 127 mV for a scan rate of $0.01 V s^{-1}$ and increases with increasing scan rate. The average peak potential $(E_{p,c}^1 + E_{p,a}^1)/2$, remains constant at all scan rates. Table 1 summarizes the peak potentials at different scan rates determined from figure 3. It is observed that the reduction and oxidation peak potentials marginally shift towards more cathodic (negative) and more anodic (positive) potentials, respectively. These observations clearly indicate that the Cu(II) to Cu(I) reduction in C_6mimCl IL medium at glassy carbon electrode is not a reversible process but quasi-reversible in nature³⁰ which is controlled by both diffusion and charge transfer processes.

The diffusion coefficient of Cu(II) species can be determined by irreversible Randles-Ševčík equation (1) which relates the cathodic peak current and the scan rate at a particular temperature for a soluble-soluble irreversible redox couple such as Cu(II)/Cu(I).^{30,31} The equation (1) is applicable to quasi-reversible systems as well,^{32–34}

$$i_{p,c}^1 = 0.496nFC_{Cu(II)}AD_{Cu(II)}^{1/2} \left(\frac{\alpha n_\alpha Fv}{RT} \right)^{1/2} \quad (1)$$

where A is the electrode area ($0.071 cm^2$), $C_{Cu(II)}$ is the concentration of Cu(II) ion in $mol cm^{-3}$, $D_{Cu(II)}$ is the diffusion coefficient in $cm^2 s^{-1}$, F is the Faraday constant, n is the number of exchanged electrons, v is the scan rate in $V s^{-1}$, α is the charge transfer coefficient, n_α is the number of electrons transferred in the rate determining step and T is the absolute temperature. The

Table 1. Analysis of cyclic voltammograms of Cu(II)/Cu(I) reversible couple in C₆mimCl ionic liquid at glassy carbon electrode at 375 K.

Scan rate (ν)/V s ⁻¹	$E_{p,c}^1$ /V	$E_{p,a}^1$ /V	$(E_{p,a}^1 - E_{p,c}^1)/V$	$\left(\frac{(E_{p,c}^1 + E_{p,a}^1)}{2}\right)/V$
0.01	-0.120	0.007	0.127	-0.057
0.02	-0.132	0.021	0.153	-0.056
0.04	-0.144	0.034	0.178	-0.055
0.06	-0.153	0.042	0.195	-0.056
0.08	-0.159	0.048	0.207	-0.056
0.10	-0.166	0.052	0.218	-0.057

value of αn_α can be obtained from equation (2) where $E_{p/2,c}^1$ is the cathodic half-peak potential,^{31,32}

$$E_{p,c}^1 - E_{p/2,c}^1 = -\frac{1.857RT}{\alpha n_\alpha F} \quad (2)$$

Using this expression we obtained average value of αn_α as 0.62.

Now the linear dependence of cathodic peak current $i_{p,c}^1$, is plotted against the scan rate $\sqrt{\nu}$, in figure 4 which yields the diffusion coefficient of Cu(II) in the IL medium. The diffusion coefficient of Cu(II) in C₆mimCl has been determined to be $6.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 375 K. Using this procedure we have obtained the value of $D_{Cu(I)}$ from cyclic voltammetry data in figure 3. The $D_{Cu(I)}$ value is found to be $4.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ which is of the same order as that of $D_{Cu(II)}$ at 375 K. $D_{Cu(II)}$ and $D_{Cu(I)}$ are expected to be different in C₆mimCl ionic liquid due to the charge difference.³⁴ Accordingly, Cu(II) ion shows slightly lesser value of the diffusion coefficient compared to Cu(I) ion in C₆mimCl ionic liquid at 375 K.

The diffusion coefficient of Cu(II) in C₆mimCl is also determined by assuming reversible hypothesis using Randles-Ševčík reversible equation³¹ and the $D_{Cu(II)}$

Figure 4. The plot of $i_{p,c}^1$ versus $\nu^{1/2}$.

value calculated is $5.22 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 375 K. This value is of the same order of the value obtained by invoking the irreversible hypothesis above and slightly higher than the values reported in the literature (table 2). Therefore the diffusion coefficient of Cu(II) ion in C₆mimCl IL under quasi-reversible redox conditions can be estimated by both reversible and irreversible kinetic limits.

The heterogeneous charge transfer rate constant, k_s , is determined by the Nicholson's method for quasireversible reactions studied by cyclic voltammetry.^{30,35,36} The expression is given by

$$\psi_T = \frac{k_s \left(\frac{D_{Cu(II)}}{D_{Cu(I)}}\right)^{\alpha/2}}{\sqrt{\pi D_{Cu(II)}} (nF\nu/RT)} \quad (3)$$

where $D_{Cu(II)}$ and $D_{Cu(I)}$ are the diffusion coefficients of Cu(II) and Cu(I) in C₆mimCl IL n is number of electrons transferred, T is the experimental temperature in K and ψ is the Nicholson dimensionless parameter. Based on the value of k_s , the redox process can be classified as reversible process when $k_s \geq 0.3\nu^{1/2} \text{ cm s}^{-1}$, quasi-reversible when $0.3\nu^{1/2} \text{ cm.s}^{-1} \geq k_s \geq 2 \times 10^{-5} \nu^{1/2} \text{ cm s}^{-1}$, and irreversible when $k_s \leq 2 \times 10^{-5} \nu^{1/2} \text{ cm s}^{-1}$.²⁹ The ψ can be obtained from the theoretical plot of the peak separation $(E_{p,a}^1 - E_{p,c}^1)$ and ψ as proposed by Nicholson.³⁵ The theoretical plot of ψ versus $\Delta E_p = (E_{p,a}^1 - E_{p,c}^1)$ given by Nicholson is assumed to be valid for 298 K. However, in the present study, the experiments are carried out at 375 K. Hence it is required to convert the ΔE_p^{375K} values to ΔE_p^{298K} using equation (4) and the corresponding conversion of ψ^{298K} to ψ^{375K} using equation (5).^{6,33,34}

$$\Delta E_p^{298} = \Delta E_p^T \left(\frac{298}{T(K)} \right) \quad (4)$$

$$\psi_T = \psi_{298} \left(\frac{T(K)}{298} \right)^{1/2} \quad (5)$$

Table 2. Diffusion coefficients of Cu(II) in various ionic liquids.

Ionic liquid medium	Electrochemical process	Temperature /K	Electrode	Diffusion coefficient / cm^2s^{-1}	Ref.
AlCl_3 -N-methylpyridinium chloride	Reversible	298	RDE (GC)	2.9×10^{-7}	22
AlCl_3 (excess)-BuPyCl	quasi-reversible	300	RDE (GC)	1.37×10^{-7}	23
AlCl_3 -BuPyCl(excess)	Reversible	300	RDE (GC)	3.67×10^{-7}	23
EMI-C-BF ₄	quasi-reversible	303	RDE (W)	1.5×10^{-7}	24
TOMAC/ CHCl_3	Irreversible	298	GC	7.12×10^{-9}	25
1-hexyl-3-methylimidazolium chloride	quasi-reversible	375	GC	6.8×10^{-7}	This work

The k_s values and other parameters obtained by this method are given in table 3. The k_s values are found to be within the range of quasi-reversible system. It is therefore established that the reduction of Cu(II) to Cu(I) at glassy carbon electrode in C_6mimCl IL at 375 K is a quasi-reversible kinetic process.

Generally, the rate of the electron transfer kinetics is assessed by k_s , while the rate of mass transport is assessed by the mass transport coefficient (m_T) which is given by the equation (6) for a cyclic voltammetric experiment³⁷

$$m_T \approx \sqrt{\frac{D_{\text{Cu(II)}}}{(RT/Fv)}} \quad (6)$$

Using equation (6) we have obtained the value of mass transport coefficient of Cu(II) ion in C_6mimCl IL as $4.59 \times 10^{-4} \text{ cm s}^{-1}$ at a scan rate of 0.01 V s^{-1} . For a reversible process, $k_s \gg m_T$ for a quasi-reversible process, $k_s \sim m_T$ and for an irreversible process, $k_s \ll m_T$.³⁷ However, in the present case we obtained $k_s \sim m_T$ which indicates that the reduction of Cu(II) to Cu(I) is controlled to an equal extent by both diffusion and charge transfer kinetics. Hence, the reduction of Cu(II) in C_6mimCl at glassy carbon electrode is further confirmed as a quasi-reversible process.

Table 3. The kinetic parameters, k_s and ψ at different scan rates for the reduction of Cu(II) in C_6mimCl ionic liquid at glassy carbon electrode at 375 K.

Scan rate (v)/ V s^{-1}	$\Delta E_p^{375\text{K}}$ /V	$\Delta E_p^{298\text{K}}$ /V	$\psi^{298\text{K}}$	$\psi^{375\text{K}}$	$k_s \times 10^4$ / cm s^{-1}
0.01	0.127	0.101	0.593	0.665	5.41
0.02	0.153	0.122	0.341	0.383	4.40
0.04	0.178	0.141	0.252	0.283	4.60
0.06	0.195	0.155	0.221	0.248	4.94
0.08	0.207	0.164	0.2	0.224	5.16
0.1	0.218	0.173	0.179	0.201	5.16

3.3 Chronopotentiometric analysis

The potential-time transients of Cu(II) in C_6mimCl IL at glassy carbon electrode at different applied constant currents are shown in figure S4. The transition time (τ) shown in the figure S4 is a measure of the time after application of the constant current when the potential transition occurs. In other words, it is the time between the beginning of the reduction to the end of the reduction process where the concentration of Cu(II) species reaches zero at the GC electrode. The relation between applied current and the obtained transition time is given by Sand's equation 7.³⁰

$$i\tau^{1/2} = \frac{nFA(D_{\text{Cu(II)}}\pi)^{1/2}C_{\text{Cu(II)}}}{2} \quad (7)$$

According to this equation $i\tau^{1/2}$ is constant at different applied currents as given in table 4. The applicability of Sand's expression is tested by plotting i versus $1/\tau^{1/2}$ as shown in figure 5. The linearity of the plot indicates the applicability of the Sand's expression and slope gives the diffusion coefficient of Cu(II) in IL medium. The diffusion coefficients of Cu(II) in C_6mimCl determined at different applied currents are given in table 4. The diffusion coefficient values of Cu(II) obtained by this method are in agreement with the diffusion

Table 4. Estimated diffusion coefficients of Cu(II) in C_6mimCl ionic liquid by Sand's equation at glassy carbon electrode at 375 K.

Cathodic current, i/A	$\tau/\text{s}^\#$	$i\tau^{1/2}/\text{A s}$	$D_{\text{Cu(II)}} \times 10^7/\text{cm}^2 \text{s}^{-1}$
6.2×10^{-5}	13.8	-2.30×10^{-4}	5.76
-6.4×10^{-5}	13.0	-2.31×10^{-4}	5.78
-6.6×10^{-5}	12.8	-2.36×10^{-4}	6.05
-6.8×10^{-5}	12.0	-2.36×10^{-4}	6.02
-7.0×10^{-5}	11.5	-2.37×10^{-4}	6.12

[#]obtained from chronopotentiometry data in figure S4

Figure 5. The plot of i versus $1/\tau^{1/2}$.

coefficient value obtained by cyclic voltammetry experiment earlier.

3.4 Electrochemical impedance spectroscopy studies

Figure 6 shows the plot of real versus imaginary parts of impedance (Nyquist plot) of Cu(II) in C_6mimCl IL recorded using glassy carbon electrode in the frequency range of 0.1 Hz–100 kHz with an applied amplitude of 10 mV and at the reduction potential -0.056 V of Cu(II)). The plot consists of a semi-circle in the higher frequency range, and a straight line at angle of 45° to the real axis in the lower frequency range. The semi-circle in the Nyquist plot confirms the parallel combination of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). The straight line at 45° confirms the

Figure 6. Nyquist plot of Cu(II) in C_6mimCl ionic liquid obtained at glassy carbon electrode at a potential of -0.56 V. Inset: Randles equivalent circuit model.

semi-infinite linear diffusion of ions from and to the glassy carbon electrode.³¹

The experimental data is fitted to the Randles equivalent circuit model as shown in the inset of figure 6 where R_s is the solution resistance, C_{dl} is the double layer capacitance, R_{ct} is the charge transfer resistance and W is the Warburg impedance, which is generally associated with diffusion of charged particles within the electrolyte.³⁸ The data is reasonably fit to the proposed Randles model. It confirms that the redox process of Cu(II)/Cu(I) at glassy carbon electrode is controlled by the diffusion as well as the charge transfer processes. This observation once again corroborates the quasi-reversible nature of Cu(II) reduction at glassy carbon electrode. The values of R_s , C_{dl} , R_{ct} and W obtained by fitting the experimental data, respectively, are 249.2 ohm, 2.164 μF , 28.39 ohm and 0.00192 ohm. Various simulations have been done in order to get better fitting of the impedance curve shown in figure 6. But the values of the elements in the equivalent circuit do not vary much (figure S5). The high solution resistance values obtained from impedance fitting in figure 6 and figure S5 can be attributed to the viscous nature of ionic liquid medium. Viscosity of ionic liquid has direct role to play in conductivity and self-diffusion processes. Conductivity is inversely related to the viscosity of ionic liquid. At room temperature the conductivities of ionic liquids fall in the range of 0.1–18 mS cm^{-1} which is much lower than the conductivity of aqueous electrolyte solutions.⁷ In the present study, we have tried to decrease the viscosity and increase the conductivity as much as possible by increasing the temperature to 375 K.

3.5 Electrodeposition of copper

The electrodeposition of Cu from 50mM of Cu(II) in C_6mimCl IL (figure 1c) has been carried out on SS electrode by constant potential electrolysis at -1.5 V for about 3 h and 5 h at 375 K under ambient atmosphere. We observed the formation of a very thin layer of Cu deposit within few minutes of electrolysis in the ionic liquid medium. However, the electrodeposition on SS electrode was carried out for 3 h and 5 h to allow complete grain formation. After the electrolysis, the electrodes were washed with distilled water followed by acetone to remove the adhered IL and finally dried in air. The XRD pattern of the film deposit on SS substrate is shown in figure S6 which confirms the deposition of copper metal (PCPDF No.85-1326). The SEM images of the surface morphologies of deposits are shown in figure 7. The SEM images clearly show copper metal grain growth, particularly in

Figure 7. SEM micrographs of copper metal deposited on SS electrode from 50 mM of Cu(II) in C₆mimCl without glove box at an applied potential of -1.5 V; 3 h deposit, (a) 1000×magnification, (b) 3000×magnification; 5 h deposit, (c) 1000×magnification (d) 3000×magnification.

the case of 5 h deposit (figure 7c and 7d) the formation of secondary growth of nuclei of copper is observed all over the dense deposit of copper. The formation of two distinct particle sizes with longer deposition time seems to be due to the effect of interaction between the cations and Cu species present in the ionic liquid medium (figure S1). The EDS pattern of copper metal deposit obtained on SS plate is given in figure S7, which confirms the presence of copper with slight amount of Fe from SS electrode. The growth of copper islands and porous copper alloys phases under the ionic liquid media without glove box and their morphologies as well as activity are being investigated further.

4. Conclusions

The electrochemical behaviour of copper (II) in C₆mimCl IL at glassy carbon electrode has been studied. The aim of conducting the electrochemical experiments in C₆mimCl IL medium at high temperature is to eliminate water and also reduce the viscosity of the medium. The experiments carried out above 373 K without glove box show that there is no significant effect of moisture on the electrochemical behaviour of Cu(II)/Cu(I) in C₆mimCl. Under these experimental conditions, the

redox process is found to be quasi-reversible for which diffusion coefficient for Cu(II) and charge transfer rate constants are estimated as $6.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $4.94 \times 10^{-4} \text{ cm s}^{-1}$, respectively. The diffusion coefficient for Cu(I) is estimated to be $4.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The results reveal two-step, one electron reductions of Cu(II) to Cu(I) and Cu(I) to Cu(0) at 375 K. Electrochemical impedance analysis revealed both the charge transfer at the electrode/electrolyte interface, and Warburg diffusion of Cu(II) species towards the electrode indicated by the semi-circle and a straight line at an angle of 45°. Uniform growth of Cu islands has been achieved under the experimental conditions employed in this study.

Supplementary Information

The electronic supporting information can be seen at www.ias.ac.in/chemsci.

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References

- Galinski M, Lewandowski A and Stepniak I 2006 *Electrochim. Acta* **51** 5567
- Abbott A P and McKenzie K 2006 *J. Phys. Chem. Chem. Phys.* **8** 4265
- Endres F, Mac Farlane D and Abbott A P (eds.) 2008 *Electrodeposition from Ionic Liquids* (Germany: Wiley ACH)
- Venkatesan K A, Rao C J, Nagarajan K and Rao P R V 2012 *Int. J. Electrochem.* Article ID 841456, 12 pages, doi: [10.1155/2012/841456](https://doi.org/10.1155/2012/841456)
- Katayama Y 2011 In *Electrochemical aspects of ionic liquids* 2nd ed. H Ohno (Ed.) (New Jersey: John Wiley)
- Rao C J, Venkatesan K A, Nagarajan K, Srinivasan T G and Rao P R V 2009 *Electrochim. Acta* **54** 4718
- Simka W, Puszczczyk D and Nawrat G 2009 *Electrochim. Acta* **54** 5307
- Endres F 2002 *ChemPhysChem* **3** 144
- Welton T 1999 *Chem. Rev.* **99** 2071
- Earle M J and Seddon K R 2000 *Pure Appl. Chem.* **72** 1391
- Freemantle M 2010 In *An introduction to Ionic Liquids* (Cambridge: RSC Publishing)
- Plechkova N V and Seddon K R 2008 *Chem. Soc. Rev.* **37** 123
- Earle M J, Esperanc J M S S, Gilea M A, Lopes J N C, Rebelo L P N, Magee J W, Seddon K R and Widegren J A 2006 *Nature* **439** 831
- Ngo H L, Compte K L, Hargens L and McEwen A B 2000 *Thermochim. Acta* **357** 97
- Pandey S 2006 *Anal. Chim. Acta* **556** 38
- Rao P R V, Venkatesan K A and Srinivasan T G 2008 *Prog. Nucl. Energy* **50** 449
- Sakaebe H, Matsumoto H and Tatsumi K 2007 *Electrochim. Acta* **53** 1048
- Hu C, Guo Y, Wang J, Yang L, Yang Z, Bai Z, Zhang J, Wang K and Jiang K 2012 *ACS Appl. Mater. Interfaces* **4** 4461
- Yang C, Kumar A S, Kuo M, Chien S and Zena J 2005 *Analytica Chimica Acta* **554** 66
- Reyter D, Belanger D and Roue L 2009 *J. Phys. Chem. C* **113** 290
- Tang W, Zhang L and Henkelman G 2011 *J. Phys. Chem. Lett.* **2** 1328
- Hussey C L, King L A and Carpio R A 1979 *J. Electrochem. Soc.: Solid-state Science and Technology* 1029
- Nanjundiah C and Osteryoung R A 1983 *J. Electrochem. Soc.: Electrochemical Science and Technology* **130** 1312
- Chen P Y and Sun I W 1999 *Electrochim. Acta* **45** 441
- Assaker I B and Dhahbi M 2011 *J. Mol. Liq.* **161** 13
- Chen P Y and Chang Y 2012 *Electrochim. Acta* **75** 339
- El Abedin S Z, Saad A Y, Farag H K, Borisenko N, Liu Q X and Endres F 2007 *Electrochim. Acta* **52** 2746
- Moeller T 1944 *J. Phys. Chem.* **48** 111
- Huddleston J G, Visser A E, Reichert W M, Willauer H D, Broker G A and Rogers R D 2001 *Green Chem.* **3** 156
- Bard A J and Faulkner L R 2001 In *Electrochemical Methods: Fundamentals and Applications* 2nd ed. (New York: John Wiley)
- Scholz F (Ed.) 2010 In *Electroanalytical Methods* 2nd ed. (Berlin: Springer-Verlag)
- Nagaishi R, Arisaka M, Kimura T and Kitatsuji Y 2007 *J. Alloys Compd.* **431** 221
- Kuznetsov S A, Hayashi H, Minato K and Escard M G 2005 *J. Electrochem. Soc.* **152** C203
- Kuznetsov S A and Escard M G 2006 *J. Electroanal. Chem.* **595** 11
- Nicholson R S 1965 *Anal. Chem.* **37** 1351
- Ramamurthy A C and Rangarajan S K 1981 *Electrochim. Acta* **26** 111
- Compton R G and Banks C E 2011 In *Understanding Voltammetry* 2nd ed. (London: Imperial College Press)
- Barsoukov E and Macdonald J R (Eds.) 2005 In *Impedance Spectroscopy* 2nd ed. (New Jersey: John Wiley)