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Electrochemical study of copper chloride complexes in the RTIL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

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ABSTRACT

The electrochemistry of copper(I) and copper(II) chloride complexes in the RTIL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, $BMPTf_2N$, has been studied with constant current electrolysis and cyclic staircase voltammetry at temperatures between 21.0 and 96.0 °C and in different concentrations of chloride. The chloride concentration was controlled by addition of 1-butyl-1-methylpyrrolidinium chloride, BMPCl. An important finding is the evidence of a three-coordinated complex, $Cu(I)Cl_3{}^{2-}$ which has not been found in organic chloroaluminates without a significant increase in temperature. Two Cu(I) species were found at molar ratios of $[Cl^-]/[Cu] < 4$. The kinetic parameters for the quasi-reversible Cu(I)–Cu(II) electron transfer were obtained with non-linear fitting. Successful fits required that the charge transfer coefficients for the reduction of Cu(II) (α) and oxidation of Cu(I) (β) did not sum up to unity, i.e. $\alpha + \beta \neq 1$. This result was interpreted using Tsallis non-extensive thermostatistics.

1. Introduction

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, $BMPTf_2N$, is an air and moisture stable hydrophobic room temperature ionic liquid, RTIL. It was first investigated by MacFarlane et al. [1] for its physical properties, including phase transition temperature, viscosity, density and conductivity. Also, the electrochemistry and deposition of Si [2,3], Al [4,5], Ta [6], Se, In and Cu [7] in $BMPTf_2N$ has been reported. In these cases, chloride salts were used without additives as the source of metal ions with the exception of Ta, where the experiments were carried out in the presence and absence of LiF as an additive. Metal salts with inorganic anions have limited solubility in RTILs based on fluorinated anions. Two different approaches to improve their solubility have been reported in the literature: addition of a complexing agent with components common to both the RTIL and the inorganic salt [8], or using a salt which has a common anion with the RTIL [9].

The electrochemistry of copper(I) and copper(II) chloride complexes has been thoroughly investigated in the chloroaluminate ionic liquids. Hussey et al. [10] reported that the reduction of Cu(II) is reversible, and that the reduction of Cu(I) to metallic Cu proceeds through instantaneous three-dimensional nucleation in the acidic $AlCl_3{}^-$ butylpyridinium chloride IL. Also nernstian slopes were obtained by varying the ratio of [Cu(II)] to [Cu(I)], suggesting that these cations are not complexed with chloride ions in acidic compositions. Nanjundiah and Osteryoung [11] utilized both the Lewis acidic and Lewis basic regimes of the same IL, and found evidence of $Cu(I)Cl_4{}^{3-}$ and $Cu(II)Cl_6{}^{4-}$ in the Lewis basic regime using potentiometric measurements. Laher and Hussey [12] reported the equilibrium between $Cu(I)Cl_2{}^-$, $Cu(I)Cl_3{}^{2-}$, and $Cu(I)Cl_4{}^{3-}$ in the Lewis basic $AlCl_3{}^-$ 1-ethyl-3-methylimidazolium chloride IL. They found that 2 and 4 coordinated complexes would dominate at 40 °C, but the equilibrium shifts toward a 3 coordinated complex when the temperature is raised.

Our previous research on the Cu^{2+} electrochemistry [13] has shown that there could be two species present in homogenous equilibrium in $BMPTf_2N$ with added BMPCl. At relatively low concentrations of chloride, approximately 1:1 molar ratio of BMPCl and $Cu(II)Cl_2$, cyclic voltammetry would show two separate Cu^{2+} reduction waves at potentials positive to Cu deposition on Pt. Raising the temperature did not change the relative magnitudes of these waves, but the shape of the wave at the lower potential was changed drastically. As the chloride content was increased, the wave at the higher potential, which showed no change with respect to temperature apart from obvious effects, would vanish, leaving just the wave at the lower potential. The same behavior will be seen further in this paper, as the redox processes are measured by oxidation of Cu(I).

Electrochemical measurements in $Cu(II)Cl_2$ solutions with minimal added chloride are quite hard to quantify because $Cu(II)Cl_2$ can

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Table 1
Prepared electrolyte solutions. The copper mass fraction was determined by AAS analysis (Varian 240, air–acetylene flame, λ = 324.8 nm). The total chloride content was determined by mass assuming a weighing accuracy of 1 mg. A density of 1.41 g/cm^3 for BMPTf$_2$N [1] was used to calculate the concentrations.

Solution	Concentration (mM)	mg(Cu)/mg	
	total [Cl$^-$]	[Cu(II)]	[Cu(I)]
Cl$^-$ a	77 ± 2		
Cl$^-$ b	184 ± 2		
Stock Cu(II)	397 ± 3	46 ± 1	2.07 ± 0.04
Low Cu(II)	397 ± 3	51 ± 1	2.32 ± 0.02
Low Cu(I)	399 ± 3	45 ± 2	2.05 ± 0.07
High Cu(I) a	392 ± 2	92 ± 2	4.17 ± 0.08
High Cu(I) b	435 ± 2	92 ± 2	4.15 ± 0.09
High Cu(I) c	480 ± 2	93 ± 2	4.21 ± 0.08

be dissolved only by complexation with chloride. Such solutions are turbid, thus the concentration of the electroactive species is unknown. The electrochemical study presented in this paper starts from the Cu(I) species which, at the chloride contents considered, do not have the same solubility problems as Cu(II)Cl$_2$.

Since even tiny amounts of atmospheric oxygen or moisture change the behavior of the system, i.e. introduce additional reaction mechanisms and complex equilibria, the measurements are preferably carried out in an inert atmosphere of a glove box. When metals are to be deposited electrochemically from RTILs, the reduction potential may also depend on the complex speciation. The purpose of this work is to study further the different copper chloride complexes and elucidate the kinetics of the prevailing reactions.

2. Experimental

2.1. Reagents and solutions

The chemicals used were Cu(II) chloride (Alfa Aesar, 99.995%, ultra dry, sealed ampoule), 1-butyl-1-methylpyrrolidinium chloride (Fluka, ≥99.0%) (BMPCl), 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide (Fluka, ≥98.5%) (BMPTf$_2$N). Three sets of solutions were prepared in a glove box (Vacuum Atmospheres Company) under argon atmosphere which was circulated through a gas purifier. An opened jar of P$_2$O$_5$ was kept inside the glove box to further remove water from the inert gas. The oxygen and water contents were both found to remain below 2 ppm. First, for the study of chloride only, two solutions containing 77 ± 2 mM and 184 ± 2 mM BMPCl in BMPTf$_2$N were prepared by mixing after several hours with a magnetic stirrer, yielding clear solutions.

For the electrochemical study of copper chloride complexes, a second set of solutions with a molar ratio of ca. 8 of total chloride to total copper, and a third set with three different molar ratios of 4–5 of total chloride to Cu(I), were prepared from a stock solution of Cu(II) that was made by mixing BMPTf$_2$N, BMPCl and Cu(II)Cl$_2$. The stock solution was mixed vigorously for several hours, during which it turned yellow. Cu(I) electrolytes were prepared from a portion of the stock solution by the addition of 5 mm long, 5 mm diameter Cu slugs lathed from a 9 mm diameter copper rod (Koch-Light, ≥99.95%). The solution turned colorless during ca. 24 h under vigorous mixing. The final Cu(I) concentration is assumed to be a result of complete comproportionation,

$$Cu^{2+} + Cu \rightarrow 2Cu^{+} \quad (1)$$

that is, twice the starting Cu(II) concentration. The stock solution had the concentration ratio of Cl$^-$ to total Cu of ca. 8. The comproportionation reaction obviously brought this ratio down to ca. 4 by doubling the Cu concentration (see Table 1). Thus, in order to make a Cu(I) electrolyte with similar molar ratio of Cl$^-$ to total Cu as the stock solution, a portion of the comproportionated solution was diluted with a mixture of BMPCl and BMPTf$_2$N. This solution is referred to as the “Low Cu(I) solution”. The rest of the comproportionated solution was divided in three portions, to which two of them BMPCl was added to modify the chloride content. As the Cu(I) concentration was not reduced by dilution for these solutions, they are referred to as the “High Cu(I) solutions”.

The stock solution was used in the first experiments, but it was found that Cu(II) was gradually reduced to Cu(I). The Cu(I) solutions did not exhibit the same behavior. Thus, a fresh Cu(II) solution was made in the same way as the stock solution. The new Cu(II) solution is referred to as the “Low Cu(II) solution”. Table 1 holds a summary of the electrolytes described above.

2.2. Apparatus

The electrochemical experiments were carried out in the same glove box where the electrolytes were prepared. A three-electrode setup was mainly used, and modifications to this setup will be clarified in the corresponding experimental sections. A (1.00 ± 0.01) mm diameter Pt disc was used as a working electrode. The diameter was measured with a microscope. Some of the experiments utilize a reference electrode consisting of a 0.7 mm diameter Cu wire inside a glass capillary that has a narrow opening separating the reference electrolyte from the bulk electrolyte. However, due to its high impedance, this capillary electrode was not utilized in most of the measurements, but it was used to calibrate a wire reference electrode in direct contact with the electrolyte.

Galvanostatic experiments in all Cu(I) electrolyte solutions and potentiostatic experiments in the High Cu(I) solutions were conducted with the Autolab PGSTAT302N controlled with GPES software. The cyclic staircase voltammetry (CSV) responses in the Low Cu(I) and Low Cu(II) solutions were measured at different temperatures using a Princeton Applied Research Model 263A potentiostat. The *iR* drop was compensated for by positive feedback. In order to determine the solution resistance, a EG&G Princeton Applied Research Model 5208 Dual Lock-In Amplifier was attached to the PAR 263A potentiostat, and a 10 kHz sine wave of 10 mV(RMS) amplitude was applied to the cell. The real part of the impedance was assumed to be a sufficient approximation of the solution resistance, and it was compensated for at least 75%, current range permitting.

The temperature was controlled with a Supercool PR-59 Peltier controller attached to a specially constructed heating–cooling-module. The module utilized a 60 W Peltier element, which was sandwiched between an aluminum CPU cooler (cold side) and a block of copper (hot side). An aluminum cylinder attached to the hot side with a heat-conducting adhesive worked as a mantle for the glass vial containing the electrolyte. A glass-bead 10 kΩ NTC resistor inside the copper block on the hot side was used for the Peltier controller feedback circuitry, but the actual temperature inside the electrolyte vial was measured with a J-type thermocouple inside a glass sheath. The thermocouple voltage was amplified using an AD594 monolithic thermocouple amplifier IC with internal cold junction compensation.

3. Results and discussion

3.1. Cu(I) oxidation in the High Cu(I) solutions

The CSV responses in the High Cu(I) electrolytes were measured using a Cu wire as a reference electrode and a copper coil as an auxiliary electrode. The copper wire reference potential was corrected against the capillary reference filled with the High Cu(I) a electrolyte. The correction was 3 mV against the High Cu(I) a electrolyte (itself), and 15 mV against the High Cu(I) b and c electrolytes.