



Effects of ultrasound and temperature on copper electro reduction in Deep Eutectic Solvents (DES)



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ABSTRACT

This paper concerns a preliminary study for a new copper recovery process from ionic solvent. The aim of this work is to study the reduction of copper in Deep Eutectic Solvent (choline chloride–ethylene glycol) and to compare the influence of temperature and the ultrasound effects on kinetic parameters. Solutions were prepared by dissolution of chloride copper salt CuCl_2 (to obtain Copper in oxidation degree II) or CuCl (to obtain Copper in oxidation degree I) and by leaching metallic copper directly in DES. The spectrophotometry UV–visible analysis of the leached solution showed that the copper soluble form obtained is at oxidation degree I (Copper I). Both cyclic voltammetry and linear voltammetry were performed in the three solutions at three temperatures (25, 50 and 80 °C) and under ultrasonic conditions ($F = 20$ kHz, $PT = 5.8$ W) to calculate the mass transfer diffusion coefficient kD and the standard rate coefficient k° . These parameters are used to determine that copper reduction is carried out via a mixed kinetic-diffusion control process. Temperature and ultrasound have the same effect on mass transfer for reduction of $\text{Cu}^{II}/\text{Cu}^I$. On the other hand, temperature is more beneficial than ultrasound for mass transfer of Cu^I/Cu . Standard rate constant improvement due to temperature increase is of the same order as that obtained with ultrasound. But, by combining higher temperature and ultrasound ($F = 20$ kHz, $PT = 5.6$ W at 50 °C), reduction limiting current is increased by a factor of 10 compared to initial conditions ($T = 25$ °C, silent), because ultrasonic stirring is more efficient in lower viscosity fluid. These values can be considered as key-parameters in the design of copper recovery in global processes using ultrasound.

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1. Introduction

In electrochemistry, Room Temperature Ionic liquids (RTILs) are considered as alternative solvents for electrodeposition of metals [1–5]. These molten salts, composed of organic cations and inorganic/organic anions, have a melting point below 100 °C. Their advantages for electrodeposition processes are their wide potential window, their negligible vapor pressure and non-flammability, the high solubility of metal salts, their good conductivity compared to non aqueous solvents, and the avoidance of water. However, most RTILs are unstable if exposed to water and air and are expensive, meaning they are economically non-competitive compared to conventional plating processes. Nevertheless, they continue to be the only means of carrying out electrodeposition of metals with low redox potential such as Al or Ti, which cannot be achieved in the other solvents [6–9].

In the last decade, Deep Eutectic Solvents (DES) have emerged as a new class of Ionic liquids [10,11]. They have most of the RTILs properties, but exhibit smaller potential windows. These ambient temperature molten salts are formed by mixing quaternary ammonium salts (chloride choline) with hydrogen-bond donors (amines, carboxylic acids or alcohols). They have economical and ecological advantages since they are easier to elaborate, stable to water and to air, cheaper, less toxic, and, in some cases, readily biodegradable. Thus their use is of interest in the field of electrochemistry, and particularly in electropolishing [12], and electrolytic deposition of several metals and metal alloys [13–19].

The rather high viscosity of DESs, which is sometimes a drawback in electrochemistry [20,21], can be overcome by a temperature increase [22] or by ultrasound stirring [23,24]. The advantage of coupling electrochemistry processes to ultrasound is now well known [25–28]. All works in a variety of areas such as electrodeposition [29,30], corrosion [28,31] or fundamental studies [32–34] have shown that sonication leads to an increase in limiting current, when kinetics is under mass transfer control, and keeps the electrode surface activated by the elimination of

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surface oxides through mechanical stirring. These phenomena are ascribed to the cavitation activity induced by ultrasound propagation in the liquid media. Indeed, at the electrode surface, cavitation bubbles grow and collapse in an asymmetric manner that liberates high amounts of energy and induces high speed microjets [35]. Thus, use of ultrasound in DES media can be an alternative solution for reducing the drawback of their high viscosity.

The aim of this paper is to study the electrochemical behavior of copper(I) and copper(II) in a DES at two different temperatures and to determine the positive contribution of ultrasound on the mass transfer and electrochemical kinetics. All experiments were conducted in the mixture synthesized from choline chloride (ChCl), associated with ethylene glycol (EG) in a 1:2 M ratio.

2. Experimental

2.1. Reagents and solutions

All chemical reagents, choline chloride (ChCl) (Aldrich, $\geq 98\%$), ethylene glycol (EG) (Acros, 99 + %), copper(II) chloride anhydrous (Acros, 99%) and copper(I) chloride anhydrous (Acros 99%), were used as received without further purification.

The eutectic mixture was obtained by mixing choline chloride (a quaternary ammonium salt, $C_5H_{14}NOCl$) with ethylene glycol (hydrogen bond donor specie) in a 1:2 M ratio. The mixture was stirred and heated at 100 °C until a homogenous colorless liquid was formed, and then air-cooled at room temperature. Chloride concentration is 4.53 mol L^{-1} , considering that the density of the mixture was measured at 1.11 g mL^{-1} .

For the electrochemical studies, solutions were prepared by dissolving in the eutectic mixture either $15 \cdot 10^{-3} \text{ mol L}^{-1}$ of $CuCl_2$ or $15 \cdot 10^{-3} \text{ mol L}^{-1}$ of $CuCl$. Another way to prepare a solution with $15 \cdot 10^{-3} \text{ mol L}^{-1}$ of copper at oxidation degree I (99.997%), is the chemical dissolution of 653.1 mg of copper chips in ChCl-EG for 48 h. Copper base metal composition is given in Table 1.

2.2. Electrochemical characterization

All electrochemical measurements were conducted with a classical three-electrode setup connected to a potentiostat (OrigaStat100 – Origalys, France) monitored with OrigaMaster 5 software. The reference electrode is a homemade AgCl/Ag electrode obtained by anodization of a silver wire in a 1 M hydrochloric acid solution. This electrode is inserted in a 3 mm PTFE tube filled with a saturated solution of KCl gelified with agar-agar, and sealed at the end with a Vycor glass separator. A platinum wire is used as a counter-electrode. The working electrode is a rotating disc electrode (Radiometer) made of platinum ($r = 0.1 \text{ cm}$). Before each experiment, the electrode tips were polished to a mirror finish using diamond suspensions of decreasing size, down to $0.25 \mu\text{m}$. The electrochemical cell (Fig. 1) is a double-jacketed reactor (cell

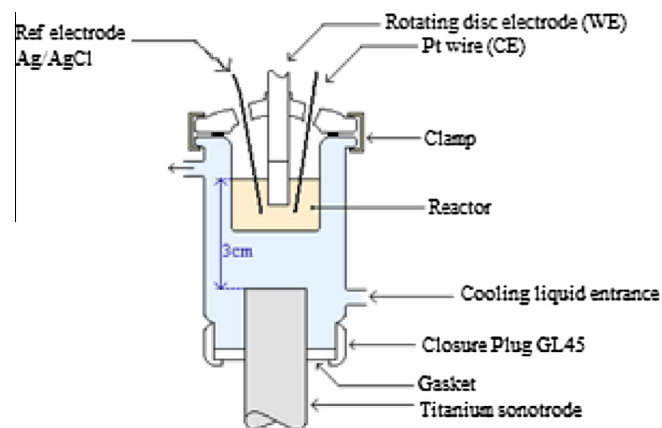


Fig. 1. Diagram showing the experimental setup.

volume = 7 ml) allowing work under ultrasound (20 kHz). The transducer horn closes the bottom of the reactor. The ultrasonic device used is a NEXUS 198 apparatus (SINAPTEC Society, France). The cooling fluid circulating in the jacket maintains a constant temperature in the cell (25, 50 or 80 °C). The top of the reactor consists of a glass lid equipped with three holes to accommodate the electrode system.

The electrochemical behaviors of copper(I) and (II) have been investigated by cyclic and stationary voltammetries in the ChCl + EG mixture.

Experiments without ultrasound were firstly undertaken to determine the kinetic parameters and evaluate the influence of temperature and the nature of the solution.

3. Results and discussion

3.1. UV-visible spectrophotometry analysis

After preparation, the solutions were analyzed by UV-visible spectrophotometry (Uviline 9400 spectrophotometer, SECOMAM). The speciation of copper complexes in choline chloride and water mixtures have been previously studied [36]. The color of aqueous Cu(II) solutions changed gradually from pale blue to yellow with the increase concentrations of choline chloride. The solution obtained with the Cu(II) salt is yellow in color, but the presence of H-bond donor (ethylene glycol) induces certainly a blue shift effect. Its spectrum (Fig. 2a) shows one intense peak at 289 nm and two other peaks at 238 and 406 nm, respectively, corresponding to the spectra of cupric chloro-complex $CuCl_2^-$ with a square or planar tetrahedral structure [37–39]. The solution containing Cu(I) species is green in color, and its UV-visible spectrum (Fig. 2b) only shows a singular peak at 269 nm. According to the literature [40,41], this indicates the presence of the cuprous chloro-complex $CuCl_3^-$. The solution, obtained by chemical dissolution (copper leaching), presents the same green color and the same UV-visible spectrum (Fig. 2c) as the Cu(I) solution. The presence of the Cu(I) form can be explained by the high chloride concentration in the solution (around 4.5 mol L^{-1}), which seems to stabilize the Cu(I) species in DES. Indeed, in ChCl-EG, the standard onset potential of Cu^{II}/Cu^I is more positive than the standard onset potential of Cu^I/Cu^0 , so that, in the absence of any dismutation reaction, both the Cu^{II} and Cu^I species are stable in this media [42]. A new UV-visible spectrum was performed for this last solution after 4 months' ageing. The new spectrum reveals the emergence of two new peaks at 238 and 406 nm, indicating that Cu(I) tends to be partially oxidized into Cu(II) (Fig. 2d).

Table 1
Copper base metal composition as a percentage.

Metals	Percentage (%)
Copper	99.997
Silver	0.001
Zinc	<0.001
Iron	0.001
Nickel	<0.001
Cobalt	<0.001
Tin	<0.001
Lead	<0.001
Gold	<0.001
Platine	<0.001
Arsenic	<0.001

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