

Sono-electrodeposition (20 and 850 kHz) of copper in aqueous and deep eutectic solvents

Bruno G. Pollet^{a,*}, Jean-Yves Hihn^b, Timothy J. Mason^c

^a Fuel Cells Group, Chemical Engineering Department, The University of Birmingham, Edgbaston Road, Birmingham B15 2TT, UK

^b Equipe Sonochimie et Réactivité des Surfaces, Institut UTINAM UMR CNRS 6213, Université de Franche-Comté, 30, Avenue de l'Observatoire, 25009 Besançon, France

^c Faculty of Health and Life Sciences, Coventry University, Priory Street, Coventry CV1 5FB, UK

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Abstract

This paper reports the effects of ultrasound at different frequencies and powers upon the electrodeposition of copper(II) chloride in aqueous potassium chloride and in glyceline 200 (a deep eutectic solvent – DES) on Pt electrodes in the potential range for copper deposition and dissolution. It is shown that the deposition of copper in both solvents is greatly affected by ultrasound at the two frequencies of 20 and 850 kHz employed. Limiting current densities were obtained in both solvents under sonication at 20 and 850 kHz and a 10-fold and 5-fold increase in currents in aqueous potassium chloride and glyceline 200 compared to silent conditions was observed respectively. The difference in viscosity of water (KCl) and glyceline 200 was found to be a crucial parameter in the evaluation of limiting current densities.

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1. Introduction

Many electrochemical processes such as the electrodeposition of copper in aqueous solvents [1–5] are limited by reactions that control the potential window, i.e. those involving the oxidation and reduction of the solvent. Non-aqueous solvents include acetonitrile, DMF, DMSO, THF, methylene chloride and propylene carbonate are considered suitable as they exhibit a potential window that are 1.5–2.5 times wider than that of aqueous acid electrolytes. A wide range of salts can be used for aqueous electrolyte solutions, however, salts for non-aqueous electrolyte solutions are more restricted and typically consist of large cations (e.g., tetraalkylammonium cations) and anions (e.g., hexafluorophosphate, tetrafluoroborate, and perchlorate) to ensure full dissociation.

In the last decade, room temperature ionic liquids (RTILs) have attracted considerable interest for use as non-aqueous

solvents [6–14]. As their name implies, they are compounds made up of ions rather than molecular species, by combinations of organic and/or inorganic cations and anions [12]. Three recent reviews by Compton and co-workers [12], Endres [13] and Lewandowski and co-workers [14] cover the fundamental aspects of electrochemistry and electrodeposition from ionic liquids based upon the imidazolium cation and $(F_3CSO_2)_2N^-$, BF_4^- and PF_6^- discrete anions. These ionic liquids present many advantages such as (i) wide electrochemical windows of up to 4 V which allows the electrodeposition of a number of metals that cannot be achieved in aqueous solutions, (ii) relatively high conductivities and (iii) low viscosities.

For example, the electrodeposition of copper in RTILs has been widely studied [15–21]. It was found that the reduction of Cu^{2+} to metallic Cu occurs in two one-electron steps: in the first step Cu^+ is formed and in the second step the metal is deposited [15,16]. Endres et al. [17,18] have shown, using in situ STM, that the bulk deposition of copper from acidic chloroaluminate liquids on gold is preceded by three processes. Furthermore, the electrode potential for the redox $Cu(I)/Cu(II)$ is more positive than the surface oxidation of gold in that liquid. The electrodeposition of copper in chloroaluminate ionic

* Corresponding author. Tel.: +44 7814952112; fax: +44 121 414 5377.

E-mail address: b.g.pollet@bham.ac.uk (B.G. Pollet).

¹ ISE member.

liquids [19], a basic 1-ethyl-3-methylimidazolium tetrafluoroborate and a Lewis acidic ZnCl_2 -1-ethyl-3-methylimidazolium chloride RTIL has been recently investigated [20,21].

However, the use of this type of ionic liquids have several disadvantages such as toxicity and cost making them somewhat impractical for larger industrial applications such as metal electroplating and electrodeposition.

An alternative to the above non-aqueous solvents are deep eutectic solvents (DES), which are a type of ionic solvent with special properties composed of a mixture forming a eutectic with a melting point much lower than either of the individual components [22]. Compared to ionic liquids, they share many characteristics, but are only ionic mixtures and not ionic compounds, and are known to be less-toxic, air and moisture stable, biodegradable and economically viable to large-scale processes [22]. DESs are either urea or ethylene glycol and choline chloride based ionic compounds [22]. Abbott et al. [22,23] were the first to produce ‘type 3’ eutectic-based ionic solvents: $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+$. RZ and use simply amides ($\text{Z} = \text{CONH}_2$), acids ($\text{Z} = \text{COOH}$) and alcohols ($\text{Z} = \text{OH}$) as complexing agents, thus making the ionic liquids more versatile. They have shown that DESs can be successfully employed in electropolishing [24], electroplating and metal oxide processing [25]. Recently, they have also shown that choline chloride (as the quaternary ammonium salt) and either urea or ethylene glycol (as hydrogen bond donors) based DES can be employed in the electrodeposition of zinc, tin and zinc–tin alloys but the electrochemical reactions are rather slow due to the high viscosity of the electrolytes. This, in turn, reduces the mass transfer of the electro-analyte due to low diffusion coefficients [26].

One of the many approaches to increase mass transfer in such processes is to employ efficient stirring or forced convection in the form of ultrasound. The effect of ultrasound on electrochemical systems was first reviewed in 1990 [27] and continues to be an active and exciting research area [28,29]. Extensive work has been carried out in which high power ultrasound (20 kHz–2 MHz) was applied to various electrochemical processes leading to several industrial applications and many publications over a wide range of subject areas including electrodeposition, electroplating, electrochemical dissolution and corrosion testing [30–33]. It has been shown that the effects of high intensity ultrasonic irradiation on electrochemical processes leads to both chemical and physical effects, for example, mass-transport enhancement, surface cleaning and radical formation.

The work of Coury et al. [34–36] and Compton et al. [37] have shown that sonication lead to decrease the diffusion layer thickness (δ) thereby giving a substantial increase in limiting current (I_{lim}), which can be attributed to effects of cavitation and/or micro and macro-streaming. It has also been shown that ultrasonic irradiation is more effective than traditional hydrodynamic methods e.g. rotating disc electrode (RDE) in reducing δ and thus both cavitation and acoustic streaming effects contribute significantly to the increase in observed experimental currents [38,39]. The experimental decrease in the diffusion layer thickness is also thought to be due to asymmetrical collapse of cavitation bubbles at the electrode surface leading to the

formation of high velocity jets of liquid being directed toward its surface. This jetting, together with acoustic streaming, can lead to random puncture and disruption of the mass transfer boundary layer at the electrode surface.

For high viscosity liquids, being the case in emergent non-aqueous solvents, the use of ultrasound can be an excellent method to ensure an efficient stirring close to the electrode surface, but up to now, only a few papers are available in the literature and only concerns ionic liquids [40]. In this paper, we report for the first time the use of ultrasound for the electrodeposition of copper(II) in a deep eutectic solvent at room temperature, at atmospheric pressure and at two ultrasonic frequencies (20 and 850 kHz).

2. Experimental

All experiments were carried out potentiostatically using a Radiometer PGP201 potentiostat connected to a PC for data acquisition and control. Electrochemical experiments were performed using either a 50 cm³ or a 100 cm³ jacketed cooling cells. A glass cooling coil was also placed in the cell to provide better control and regulation of the electro-analyte temperature. Both the jacketed cooling cell and the glass cooling coil were linked to two Grant thermostatted baths operating at pre-set temperatures. The temperature of the electro-analyte was measured with a Fluke 51 digital thermometer fitted to a K-type thermocouple. The electrochemical cell was placed in a Faraday cage. The working electrodes were either a platinum rotating disc ($\varnothing = 0.2$ cm, area = 0.0314 cm²) or a platinum wire (area = 0.322 cm²). A platinum flag was used as the counter electrode (area = 1.0 cm²). For the 20 kHz sono-electrochemical experiments, the distance between the ultrasonic probe (20 kHz, $A = 1.33$ cm²) and the working electrode was $d = 2 \pm 0.1$ mm (Fig. 1). For the 850 kHz sono-electrochemical experiments, the 850 kHz ultrasonic bath was employed as the electrochemical cell and the distance between the ultrasonic transducer ($A = 10.24$ cm²) and the working electrode was $d' = 3 \pm 1$ mm (Fig. 2). All platinum electrodes were electrochemically cleaned by cycling in sulphuric acid (1.0 mol dm⁻³) for 10 min prior

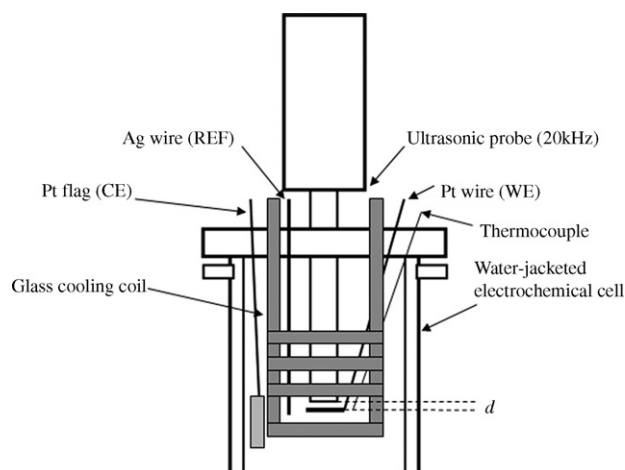


Fig. 1. Sono-electrochemical (20 kHz) set-up employed in this study.

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