

ELECTROLYTIC DEPOSITION OF NICKEL FROM IONIC LIQUID TYPE (II) USING ETHYLENEDIAMINE (EN) AS BRIGHTENERS

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ABSTRACT

Here we study for the first time the electrochemistry and electrolytic deposition of nickel from ionic liquid type II where the metal chloride salt mixed with choline chloride in ratio of 2: 1 respectively. We found that voltammogram is clearly different from type III and aqueous solutions. Also we investigate the deposition morphology and roughness using SEM and AFM which reveal the morphology of nickel is totally different before and after the addition of brightener leads to good agreement with voltammograms. The addition of brighteners like ethylene diamine results a bright metal coating.

Keywords: ethylenediamine, electro deposition, ionic liquid, nickel and cyclic voltammogram.

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INTRODUCTION

Ionic liquids are classified as salts that are liquid at below 100°C¹. Eutectic mixtures have been used extensively for applications of molten salts to reduce the operating temperature and this is where the significant area of ionic liquids developed from i.e. the quest to find aluminium based salt mixtures. While the development of aluminium containing ionic liquids is technologically very important for the field of metal deposition, it is clear that there are many other issues that also need to be addressed and hence methods need to be developed to incorporate a wide range of other metals into ionic liquid formulations. They have been extensively studied primarily for synthetic and electrochemical applications². The majority of investigations have concentrated on imidazolium cations with discrete anions such as BF₄⁻, PF₆⁻ and (F₃CSO₂)₂N⁻. These ionic liquids have large potential windows and exhibit relatively high conductivities and low viscosities. Two recent reviews by Endres^{3,4} cover all aspects of electro deposition from these liquids, Compton and coworkers⁵ have reviewed fundamental aspects of electrochemistry in ionic liquids and Ohno⁶ describes other electrochemical aspects. While ionic liquids with discrete anions show significant potential for the electro deposition of electronegative metals such as aluminium³, issues such as toxicity and availability will limit their practical use for larger scale applications of other metals. An alternative approach to making ionic liquids is to start with a simple quaternary ammonium halide and decrease the freezing point by complexing the anion to effectively delocalise the charge. These eutectic-based ionic liquids can be described by the general formula:

R₁R₂R₃R₄N X: z Y

and we have characterised these materials into three types depending on the complexing agent Y, as follows-

Type I Y = MCl_x, M = Zn, Sn, Fe, Al, Ge

Type II Y = MCl_x, yH₂O

Type III Y = RZ, Z = CONH₂, COOH, OH

The electrochemistry, physical properties and speciation occurring in Types I and II ionic liquids has been reported for a variety of metals^{7,10}. The key advantages of the liquids have become the wide potential

windows, high solubility of metal salts, avoidance of water and metal / water chemistry and high conductivity compared to non-aqueous solvents. Here, the electrolytic deposition and morphologies of metallic Ni coatings from ionic liquids (IL) based on type 2 NiCl₂.6H₂O to 1 ChCl eutectic mix were investigated. Different morphology and composition from the addition of brighteners used in the deposition process have been also investigated. Cyclic voltammetry (CV) and chronocoulometry together with AFM and SEM were used to probe the mechanism of deposition and the structure of the Ni deposits. Electroplated films are determined by the mass loading in the solution. The main mechanism for particulate inclusion is drag onto the electrode surface. The inclusion of suspended particles in the liquid is found to have negligible effect upon the fluid viscosity of the suspension, we propose that this is a consequence of the increased free volume in the fluid component caused by the motion of the suspended particles *i.e.* the particles act as micro stirrers in the liquid.

EXPERIMENTAL

Choline chloride [HOC₂H₄N(CH₃)₃Cl] (ChCl) (Aldrich 99%) was, when necessary, recrystallised from absolute ethanol, filtered and dried under vacuum. Urea (Aldrich > 99%) was dried under vacuum prior to use. Ethylene glycol (EG) (Aldrich 99+ %), was used as received. The mixtures were formed by stirring the two components together, in the stated proportions, at 50 °C until a homogeneous, colorless liquid formed. The liquids, once formulated, were kept in a thermostatic oven at 50 °C prior to use. Cyclic voltammetry and other electrochemical measurements were carried out in a sealed cell to minimize water ingress but the liquids were not degassed and no attempt was made to remove dissolved oxygen. Particulate suspensions were formed by mixing either Al₂O₃ (0.05 μm or 1.0 μm, Aldrich), or silicon carbide (1-3 μm, hexagonal phase, Aldrich) with the appropriate ionic liquid (1 ChCl: 2 EG, or 1 ChCl: 2 urea) in wt. /wt. % ratio.

Electrochemical investigations including potential step chronoamperometry, chronocoulometry and cyclic voltammetry were carried out using Echo ChemieAutolab PGSTAT12 and μ-Autolab III, potentiostats controlled with GPES (v 4.9) software. A three-electrode system was used consisting of a platinum working electrode (1 mm or 2 mm diameter, made in-house), a platinum counter electrode and a silver wire quasi-reference electrode. The working electrode was polished with 0.3 μm alumina paste, rinsed and dried prior to all measurements. All voltammograms were performed at ambient temperature (20 ± 2 °C) and at various scan rates from 2–20 mVs⁻¹. Chronometric deposition experiments were carried out under diffusion control at applied potentials of either -0.80 V or -1.00 V. A silver wire quasi-reference electrode was used in all electrochemical experiments which has been shown to have a stable reference potential in chloride based eutectics.¹¹ The potential windows of both urea and ethylene glycol based DESs have been reported previously and are outside the electrochemical regions discussed in this work.^{1,9}

RESULTS AND DISCUSSION

Effect of Ionic Liquid

Cyclic voltammograms (CVs) were recorded at a polished 1.0 mm Pt disc electrode immersed in a solution of type II 1 : 2 ChCl/NiCl₂.6H₂O at scan rate 20mV/s (Fig.-1). This voltammogram shows the shape of the oxidation is different from type III (ChCl : 2 EG and ChCl :2 urea IL) as well in aqueous solutions. Furthermore the cyclic voltammogram is quite different from the cyclic voltammogram of type II 1 : 2 ChCl / CrCl₃.6H₂O where no oxidation peak current is observed but in case of type II 1 : 2 ChCl/NiCl₂.6H₂O the presence of the anodic processes with maximum peak current at about 5.5 × 10⁻⁴A / 0.5 V and beside a shoulder is clearly visible at 0.1 V it proposed, that may due to under potential deposition. The reduction process that is initiated at approximately 0.00 V is most probably due to the reduction of Ni²⁺ to Ni⁰ at 1.00 V. Probably the most interesting observation is that no reduction current for the decomposition of water is observed. This suggests that the water molecules are highly coordinated and since the medium acts as a poor base, the protons on the water are less acidic than in aqueous solution.

The shape of the Ni stripping peaks depends upon sweep rate in both liquids showing that the processes were kinetically slow. It is interesting to note that the current on the anodic sweep is slow to return to zero, inferring that some material is strongly bound to the electrode surface.

Figure-2 shows that AFM images of Ni deposited from type II 1 : 2 ChCl / NiCl₂.6H₂O at an applied potential of 2.5 V (in a two electrode cell) for 120 minutes. The surface topology of the Ni-deposited samples relatively dense and compact with roughness.

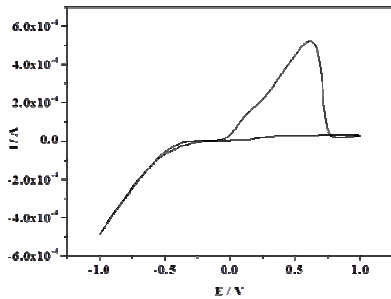


Fig.-1: The cyclic voltammograms for the reduction of type II Ni chol.chloride eutectic mixture at 20°C on a Pt electrode with scan rate

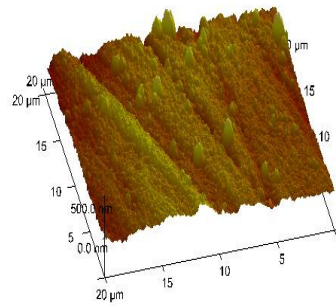


Fig.-2 AFM image of deposits obtained from electrolysis of type II 1:2ChCl/CrCl₃.6H₂O containing 60°C at applied potential of 2.0 V for 60min.

Addition of ethylene diamine (en) as brightener

Brighteners are commonly used in aqueous electrodeposition to avoid black coating and very good adhesion to the surface to be coated and tend to function by one of the three methods; adsorbing at the electrode, solution interface and altering viscosity or changing speciation.

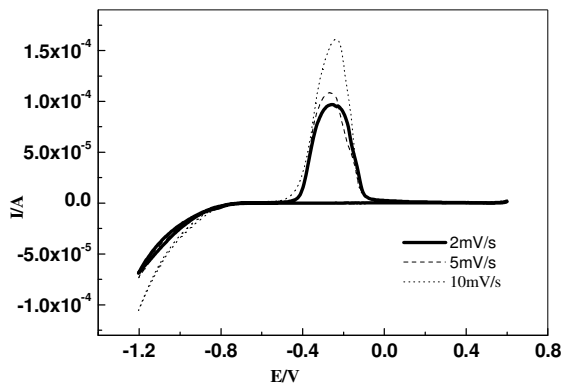


Fig.-3: Cyclic voltammogram for the reduction of 1ChCl : 2NiCl₂ .6H₂O ionic liquids and subsequent addition of EG as diluent and 10%(V/V) en at 20°C on Pt electrode as a function of sweep rate.

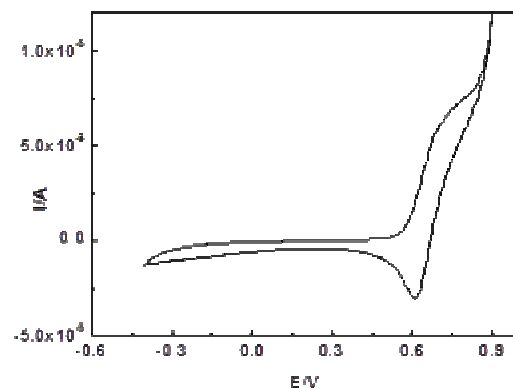


Fig.-4: Corresponds to under potential deposition (UPD) and anodic regions of scan (5mV/s) in Figure 3.

The presence of brightener (en) at 60 °C on a Pt microelectrode as a function of sweep rate 2, 5 and 10 mV/s Furthermore the green colour of Ni(II) ionic liquid is changed to purple when ethylene diamine is added, the purple colour due to chelation between the nickel ion and the ethylene diamine . The clear application of an ionic liquid containing nickel is for the study of nickel electrodeposition is shown in Figure 3 the cyclic voltammogram for the 1:2 ChCl/ NiCl₂.6H₂O system brightener is added to obtain bright finish coating.

It has been observed the current oxidation peak increases as scan rates increase around -0.20V. The electrochemical response in the two ionic liquids is clearly different from type III ionic liquid and significantly the response of 1:2 ChCl/NiCl₂.6H₂O without added brightener as shown in fig.-1.

The addition of en suppresses the under potential deposition (UPD) of Ni as shown in Figure-4. It has previously been shown for Zn that the amount of UPD material increases the amount of microcrystalline material and suppresses the growth of nanocrystallites.^{12,13}

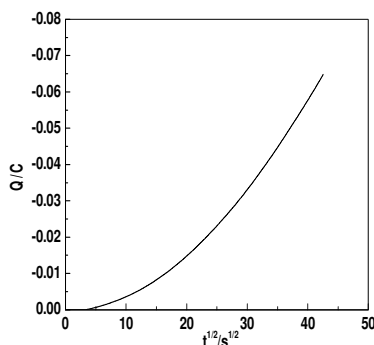


Fig.-5: Charge/time transient for Pt electrode immersed in ChCl : 2 NiCl₂.6H₂O type II IL system containing for potential step from +1 V (held for 10 s) to -1 V for 30 minutes.

The study of charge versus under the root square time for a Pt electrode immersed in Ni type II ionic liquid system for a potential step from +1 V (held for 10 s) to -1 V for 30 minutes is shown in Figure-5. The charge/time transients are considerably linear which leads to the current efficiency is not 100% so the deposition is mass transport limited.

Bulk deposition of Ni from type(II) IL

The deposit of Ni on copper substrate was obtained from type (II) liquid using ethylene diamine as brightener by holding at 2.00 V for half an hour. The coating was bright, silvery and distributed evenly on the surface of copper substrate.

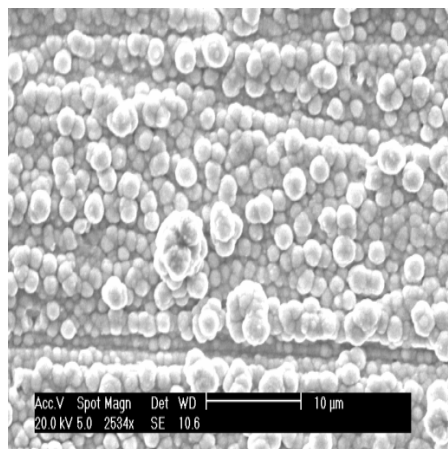


Fig.-6: SEM image of Ni deposit on copper plate from Ni type II) system in the presence of ethylene diamine as brightener.

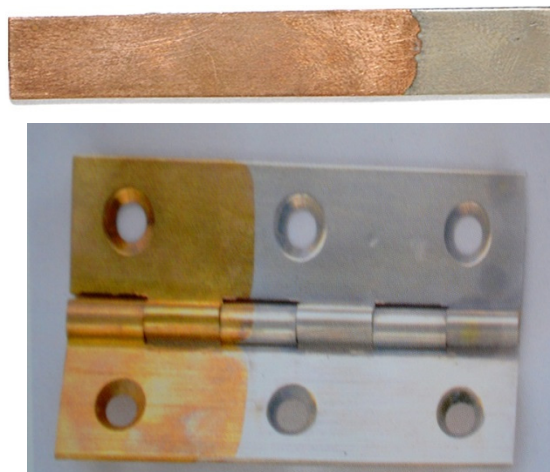


Fig.-7: A photograph of Ni deposits on different substrates following electrolysis of Nickel type(II) ionic liquid system

The nickel coating shows a very good adhesion and promising to use this protocol on industrial scale.

Figure- 6 shows the image of scanning electron microscope (SEM) of deposit nickel obtained by electrolysis of the solution in figure-6 SEM can show clearly no micro-cracked that can lead to pitting corrosion in the substrate material. Figure-7 show bulk deposition in the bright silver and even surface finish onto two different substrates copper and brass showing the consistency of obtaining bright silvery coating.^{14,15}

CONCLUSION

The work shows that ionic liquids based on eutectic mixture of choline chloride and nickel (II) chloride hexa hydrate classified as type (II) ionic liquid has electrochemistry remarkably different from the electrochemistry of ionic liquid type (I) system. the addition of ethylene diamine brightener shows great influence on the morphology of the coating obtained. The presence of ethylene diamine leads very encouraging results to look for new method in industrial scale The addition of ethylene diamine to Ni type (II) ionic liquid system produces shiny bright smooth finish Ni coating furthermore sem images showed no sign of cracking.

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