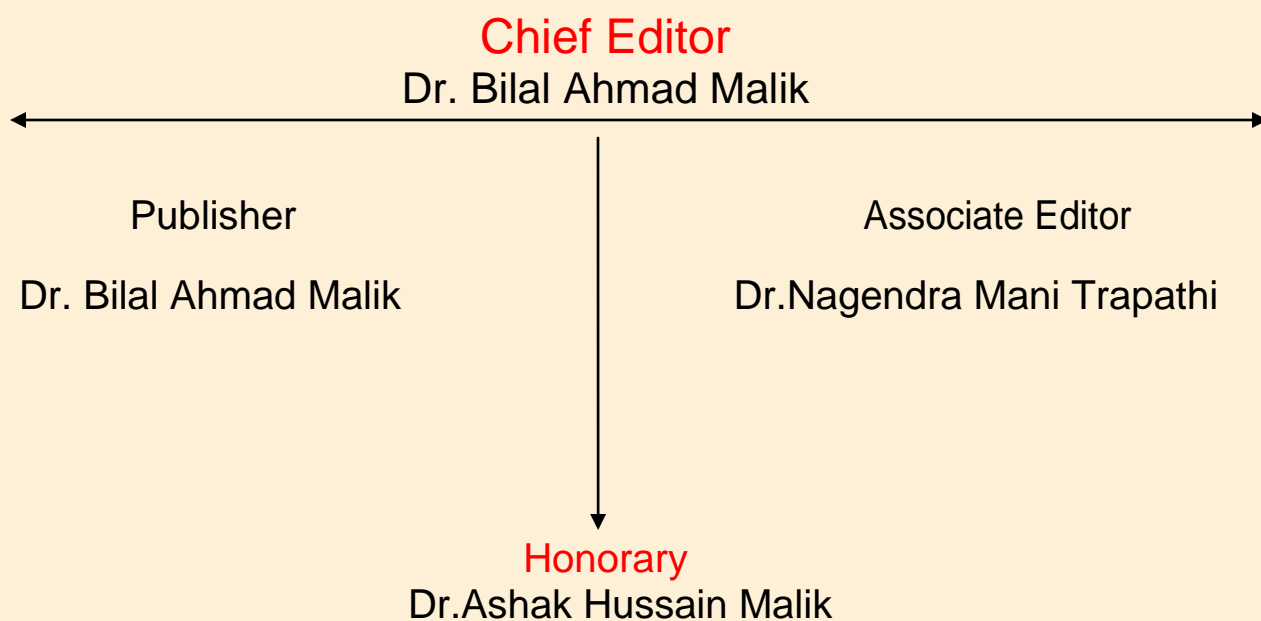


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ISSN NO: 2454 -7514

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THE INFLUENCE OF ACAC ON THE ELECTRODEPOSITION OF NICKEL FROM IONIC LIQUID TYPE (II) SYSTEM AS BRIGHTENER

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ABSTRACT

The addition of acac as brightener to a solution of type II 1: 2 $\text{ChCl}/\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (TypeII) system firstly, the is changed from pale green to dark green solution unlike the addition of ethylenediamine purple colour. Furthermore the investigation shows that uterly dissimilar in voltammogram and the electrodeposition. It is clearly observed that sholders in peak oxidation currents which not seen with added ethylenediamine (symmetrical peaks). In addition the position and the kinetics the thermodynamics of electrodeposition are different from with and without added (en). Also the morphology and the topology of nickel coating were examined by SEM and AFM. Both showed that no microcrack is observed and the nickel coating was evenly deposited.

Keywords: acac, electrodeposition, ionic liquid, nickel and cyclic voltammograms.

INTRODUCTION

Ionic liquids are classified as salts that are liquid at below 100°C^{1-10} . Generally one of the ionic components is organic, most commonly the cation. The ions have a low degree of symmetry. By careful choice of the components it is possible to tune the properties of the liquid. In general ionic liquids;

- 1- Good solvents for organic and inorganic materials.
- 2- Generally considered to be polar yet non-coordinating solvents.
- 3- Immiscible with many organic solvents providing a polar alternative for two-phase systems.
- 4- Have low vapour pressures.

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 aluminum 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 applications ¹¹. The majority of investigations have concentrated on imidazolium cations with discrete anions such as BF_4^- , PF_6^- and $(F_3CSO_2)_2N^-$. These ionic liquids have large potential windows and exhibit relatively high conductivities and low viscosities. Two recent reviews by Endres ^{12, 13} cover all aspects of electrodeposition from these liquids, Compton and coworkers ¹⁴ have reviewed fundamental aspects of electrochemistry in ionic liquids and Ohno ¹⁵ describes other electrochemical aspects. While ionic liquids with discrete anions show significant potential for the electrodeposition of electronegative metals such as aluminium ³, 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:



And we have characterised these materials into three types depending on the complexing agent Y;

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

Type II $Y = MCl_x, yH_2O$

Type III $Y = RZ$, $Z = CONH_2, COOH, OH$

Type IV Metal chloride hydrate + hydrogen bond donor

It has recently been shown that eutectics can also be formed between a metal salt (hydrate) and a simple amide or alcohol to form a metal containing solution composed of cations and anions via disproportionation processes e.g.



These so-called **Type IV** eutectics are useful as they produce cationic metal complexes, ensuring that the double layer close to the electrode surface has a high metal ion concentration. The electrochemistry, physical properties and speciation occurring in Types I and II ionic liquids has been reported for a variety of metals ^{8,11}. 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 $NiCl_2 \cdot 6H_2O$ 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.

EXPERIMENTAL

Choline chloride [$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$] (ChCl) (Aldrich 99%) was, when necessary, recrystallised from absolute ethanol, filtered and dried under vacuum. The metal halide $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$ Aldrich) was used as obtained. The additive acetyl acetone (**acac**) Aldrich were used as sodium salt. The mixtures were formed by stirring the two components Choline chloride with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ together, in the stated proportions, at 50°C until a homogeneous liquid was 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 minimise water ingress but the liquids were not degassed and no attempt was made to removed dissolved oxygen.

Electrochemical investigations including potential step chronoamperometry, chronocoulometry and cyclic voltammetry were carried out using Echo Chemie Autolab PGSTAT12 and \square -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 $0.3 \mu\text{m}$ alumina paste, rinsed and dried prior to all measurements. All voltammograms were performed at ambient temperature ($20 \pm 2^\circ\text{C}$) and at various scan rates from $2\text{--}20 \text{ mVs}^{-1}$. 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.¹² 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.^{1,16}

RESULT 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/ $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at scan rate 20 mV/s , **Figure 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. 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 Ni^{2+} to Ni^0 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.

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. Also it is very interesting to find that surface morphology is quietly different from the type (II) 1: 2 ChCl / NiCl₂.6H₂O with added acac where we are going to investigate.

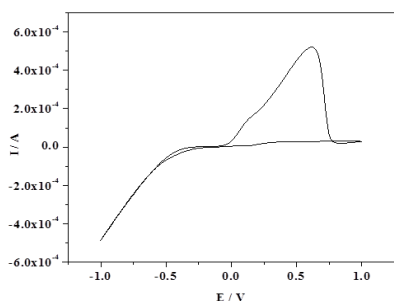


Figure 1 shows the cyclic voltammograms for the reduction of type II Ni chol. chloride eutectic mixture at 20°C on a Pt electrode with scan rate

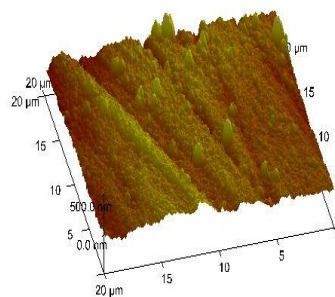


Figure 2 AFM image of deposits obtained from electrolysis of type II 1:2ChCl/CrCl₃.6H₂O containing 60°C at applied potential of 2.0 V for 60 min.

Addition of acetylacetonate (acac) as brightener

Brighteners are vital additives which commonly used in electrodeposition of metals or alloys 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.

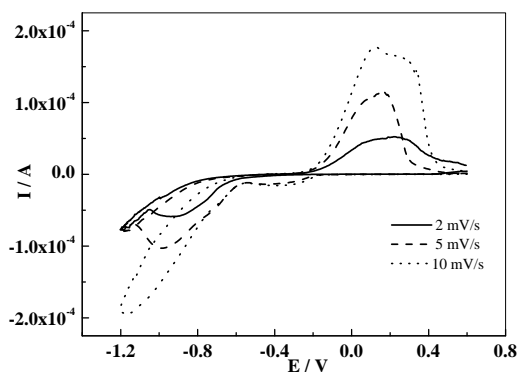


Figure 3 Cyclic voltammogram for the reduction of 1ChCl : 2NiCl₂ .6H₂O ionic liquids and subsequent addition of acac at 20°C on Pt electrode as a function of sweep rate.

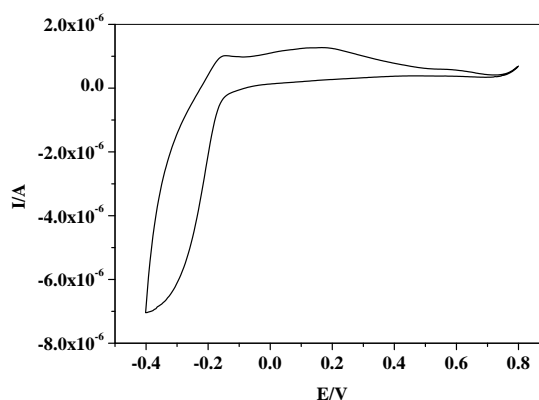


Figure 4 corresponds to under potential deposition(UPD) and anodic regions of scan (5mV/s) in Figure 3.

When the brightener (acac) the green colour of Ni(II) ionic liquid is changed to dark green colour, the dark green colour due to chelation between the nickel ion and the acetyl acetonate sodium salt. 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 with added brightener at scan rate 2, 5 and 10 mV/s as shown in figure 3. It is clearly obvious that as scan increases the peak oxidation current increases and the shape of the peak oxidation current for every scan is different from the other two scans which could be due to different deposition rate and how strongly adsorbed to electrode surface. At scan rate 5 and 10 mV/s peak oxidation current both show shoulder with opposite position suggesting different morphology of deposit nickel metal¹⁷.

It has been observed the current oxidation peak increases as scan rates increase around -0.60V. The electrochemical response in the two ionic liquids with and without added brightener is clearly different from type III ionic liquid and significantly the response of 1:2 ChCl/NiCl₂.6H₂O without added brightener as shown in figure 1. Figure 4 shows the voltammetry of oxidative sweep rate between -0.4 to +1V. A one oxidation corresponds to conversion of Ni⁺² to Ni⁺¹ can be seen at 0.6V on sweep anodic rate.

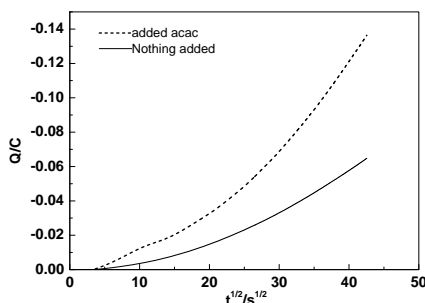


Figure 5 Charge/time transient for Pt electrode immersed in 1ChCl : 2 NiCl₂.6H₂O type II IL system with and without acac containing for potential step from +1 V (held for 10 s) to -1 V for 30 minutes.

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.

SEM and AFM of Ni coating 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.

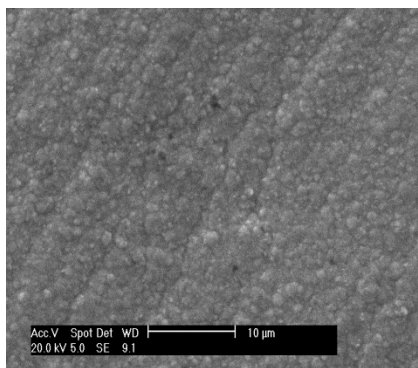


Figure 6 shows SEM image of Ni deposit on copper plate from Ni type II) system in the presence of acac as brightener.

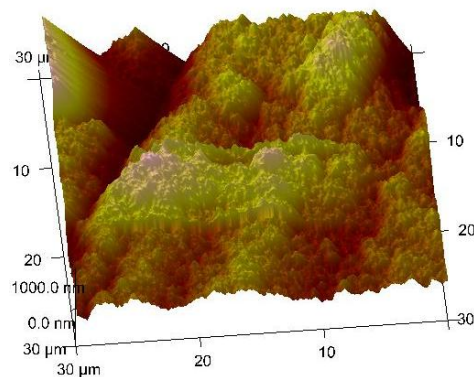


Figure 7 AFM image of the deposit formed following the electrolysis of the 1:2 $\text{ChCl/NiCl}_2 \cdot 6\text{H}_2\text{O}$ system with added acac at 25°C for onto a copper plate.

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 dull gray and even surface finish onto copper substrates showing the consistency of obtaining even thick layer coating.^{18,19}

CONCLUSION

It has been shown the formation of ionic liquid between choline chloride and different hydrated metal salts and can be used for electrodeposition of variety metal coatings. The size of deposited particles, the morphology, adhesion and more properties can be controlled by many parameters such as temperature and the type of brightener which was investigated in this work. It has been found that the addition of acac can be used as brightener for the electrodeposition of nickel and the nickel coating formed was thick, adherent and crack-free. Also it has been demonstrated the hydrated water molecules in the metal salts are highly coordinated in the ionic liquid are not significantly within the potential window of the ionic liquid type(II) system. This could offer an efficient and environmentally more acceptable process by which to electrodeposit nickel than aqueous system.

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