

Electrodeposition of Cu-Ag Alloys Using Ionic Liquid (Ethaline) as Deep Eutectic Solvents

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ABSTRACT

Here we describe the electroless deposition of Cu-Ag alloys in deep eutectic solvents using a variety of electrochemical and surface analysis techniques to determine the mechanism of alloy deposition and composition of deposits. The influence of various conditions on electroless deposition and the morphology of the deposit layers have been investigated by scanning electron microscopy (SEM) with energy dispersive analysis by X-rays (EDX). The electrochemical behaviour of pure copper, pure silver and Cu-Ag alloys was studied at various working electrodes by cyclic voltammetry. The use of (EQCM) electrochemical quartz crystal microbalance is shown to be very dependent upon the concentration of ions in solution. the cathodic current efficiency for the deposition of Cu-Ag alloys is about 99%.

1.INTRODUCTION

Ionic liquids are classed as salts that are liquid at below 100 °C[1]. The electrodeposition of alloys from a solution containing different metal salts is in principle relatively straight forward but in practice very complex. The majority of investigations have been concentrated using ionic liquids with large potential window and low viscosities such as BF_4^- , BF_6^- and $(\text{F}_3\text{CSO}_2)_2\text{N}^-$. Two reviews by Endres [2,3] gives all information of coating from these liquids, Compton and *et al.* [4] have reviewed fundamental aspects of electrochemistry in ionic liquids and a book by Ohno[5] also describes other electrochemical aspects. It has recently been shown that simple eutectic-based ionic liquids can be produced using the quaternary ammonium salts, $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+\text{X}^-$, complexed with hydrogen bond donors, such as acids, amides and alcohols.[6,7]

These so called deep eutectic solvents (DES) have been used for electropolishing[8], polymer synthesis, organic synthesis and metal oxide processing. The previous studies have concentrated on choline chloride as the quaternary ammonium salt, as it is environmentally friendly and is already used as a common constituent of various household and industrial products, such as detergents. The DESs formed with choline chloride and urea, or choline chloride and ethylene glycol, have successfully been employed for the electrodeposition of zinc, tin, zinc-tin and Cu-Sn alloys. This has also shown that the alloy is affected by the choice of hydrogen bond donor and that the electrochemistry of the components in solution, as well as the morphology of the coatings is also affected. A selection of reviewshave discussed the detail of metal deposition by using ionic liquids. [9,10,11] Polletet *al* investigated the electrodeposition of copper from copper(II) chloride in aqueous potassium chloride

and in mixtures of glycerol and choline chloride (2:1) (ionic liquid) (DES) on Pt electrodes, in the potential range for copper deposition and dissolution. In addition, the current density was increased using ultrasound within the two different solvents, when compared with the silent solution.[12]

The electrolytic deposition of copper and copper composites from a solution of the metal chloride salt has been studied in choline chloride based deep eutectic solvents.[13] It was shown that the deposition kinetics and thermodynamics differ from the aqueous processes and that different complexes are formed. EXAFS (Extended X-ray Absorption Fine Structure) showed that the main species formed from the dissolution of CuCl_2 in Deep Eutectic Solvent is $[\text{CuCl}_4]^{2-}$. Bulk electrodeposition in DES results in different deposit morphologies to that encountered in aqueous solutions. The current efficiency of copper deposition in this system is near 100 %.

Abbott *et al.*[13] used an electrochemical quartz crystal microbalance, EQCM, to study the electrodeposition of copper composites. It was possible to calculate the amount of inert particulates (SiC , Al_2O_3 and PTFE) in the copper coatings and it has been shown that material was dragged onto the surface of the copper coating. The amount of micron-size particles of Al_2O_3 and SiC incorporated in the copper deposit is related to the amount of species in the solution. [14]

Cu-Ag alloys are highly used in low power circuits use in electronics due to their higher electrical and thermal conductivity compared to those of pure copper and pure silver. Alloying with copper conserves silver and reduces costs. The electrodeposition of Cu has been shown using 1:2 ChCl /ethylene glycol and the investigation presented here this is extended to study the phase behaviour of Cu-Ag alloys.

2.EXPERIMENTAL

Choline chloride [$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$] (ChCl) (Aldrich 99%) was recrystallised from absolute ethanol, filtered and dried under vacuum. 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, colourless liquid formed. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and AgNO_3 were used as received (both Aldrich $\geq 99\%$). Electrochemical investigations of cyclic voltammetry were undertaken using an Echo Chemie Autolab PGSTAT12 potentiostat controlled with GPES (v 4.9) software, Ivium CompactStat and Gamry Reference 600 Potentiostat/Galvanostat. In each case a three-electrode system was used consisting of a platinum working electrode (1- or 2-mm diameter, made in-house) and a platinum counter electrode. The working electrode was polished with $0.3\text{-}\mu\text{m}$ alumina paste, rinsed and dried prior to all measurements. All voltammograms were recorded at ambient temperature ($20 \pm 2^\circ\text{C}$) over a range of potential scan rates. A silver wire quasi-reference electrode was used in all electrochemical experiments.

The authors have previously demonstrated that this approach gives a stable reference potential in chloride-based eutectics.[15] The potential window limits of EG-based DESs have been reported previously and are outside the electrochemical regions discussed in this work.[16] Acoustic impedance EQCM experiments were carried out using electrodes consisting of thin Au films (no Ti or Cr binding layer was used) evaporated on 10-MHz AT cut quartz crystals (International Crystal Manufacturing Co., Oklahoma City, USA); the surface finish of these crystals was unpolished. The piezoelectric active electrode area was 0.23 cm^2 . Crystal impedance spectra were recorded using a Hewlett Packard HP8751A network analyser, connected to a HP87512A transmission/reflection unit via 50-W coaxial cable (or an Agilent ENA E5061A network analyser) such that

the centre of the spectrum was near the centre of resonance f_0 (10 MHz), with a typical sweep width of 20–200 kHz depending on the interface. Peak frequency/mass, Q factor and viscosity data were extracted from the acoustic impedance spectra by fitting to a Lorentzian line shape using methods described elsewhere. In addition a Gamry EQCM module (Reference 600) was used in conjunction with the Gamrypotentiostat. SEM and EDX elemental analysis were carried out under vacuum using a Philips XL30 ESEM instrument with voltage between 15 and 20 keV giving an average beam current of ca. 120 μA . X-ray diffraction patterns of alloy phases were measured using a Phillips model PW 1730 X-ray generator, with a PW 1716 diffractometer and PW 1050/25 detector. The copper tube used as the anode filtered Cu- $K\alpha$ radiation at a wavelength of 0.1540 nm. The running conditions for the X-ray tube were 40 kV and 40 mA, scanned between 20° and $85^\circ 2\theta$ with a step size of $0.02^\circ 2\theta$. Angle calibration was carried out using a synthetic Si sintered standard.

3.RESULTS AND DISCUSSION

Figure 1a and **b** show the cyclic voltammograms of pure $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and AgNO_3 in 1:2 CHCl_3/EG (Ethaline). The hydrated metal salts were chosen for study here although the authors have previously shown that the water content of the salts at these concentrations does not affect the speciation of the metals in solution.[17]

The voltammogram shown in **Figure 1b** recorded in Ethaline shows only a single reduction peak, arising from the reduction of Ag^+ to Ag metal and a single oxidation peak arising from the metal being oxidised back to Ag^+ . The peak potentials for these two processes are at around -0.1 and 0.0V respectively.

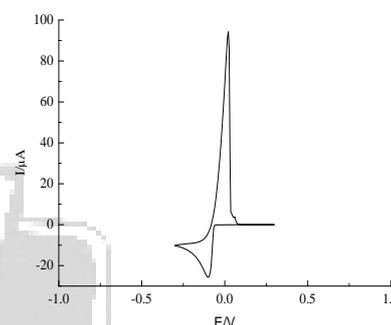
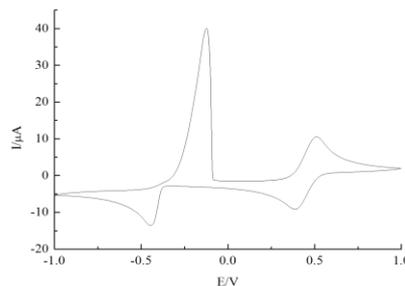


Figure 1 Voltammogram scan rate 5mVs^{-1} for Pt as a working electrode ($r = 0.5\text{ mm}$) using silver wire pseudo reference immersed in Ethaline containing (a) $0.1\text{ mol dm}^{-3}\text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ and (b) $0.1\text{ mol dm}^{-3}\text{ AgNO}_3$

The voltammograms of copper in **Figure 1a** show four waves in Ethaline or assigned to $\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu redox couples. To probe the effect of solution composition upon kinetics of the Cu–Ag deposit during growth, three different mixed metal chloride compositions have been examined in addition to the pure $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and AgNO_3 solutions. This approach was used to ensure that the metal concentration was constant through all experiments. The three mixed metal compositions having Cu : Ag molar ratios of 1:1, 1:3 and 3:1, respectively, dissolved in Ethaline are presented in

In Ethaline, the redox potentials of the two pure metal salts are very close as evidenced by comparison of **Figure 1a** with **Figure 1b**.

This is in contrast to the standard aqueous redox potentials for the Cu^{2+}/Cu and Ag^+/Ag couples which are 0.35 and 0.10 V, respectively. Compression of the range of redox potentials or metal salts is a known effect of DES electrolytes. Cyclic voltammograms for the three Cu–Ag mixtures recorded on a Pt wire in Ethaline are presented in **Figure 2a, b and c**.

The relative amounts of Cu and Ag ions are expressed both as a ratio and in terms of their molar concentrations. **Figure 2a** shows the cyclic voltammetry of an equimolar mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and AgNO_3 in the EG-based liquid. Three distinct redox processes are clearly visible. The most cathodic of these at -0.42 V, shows the deposition and stripping response of a Cu rich phase. Similarly, the second process at $+0.05$ V, corresponds to the deposition and stripping response of an Ag rich phase. Finally at $+0.32$ V, a reversible 1 electron process corresponds to the reversible $\text{Cu}^{2+}/\text{Cu}^+$ couple.

The CV was obtained using a Pt disc electrode in the DES containing 3:1 AgNO_3 : $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline, which is shown in **Figure 2b** and, as expected, the current response for the silver rich phase increases with respect to that for copper. Abbott *et al.*[18] have recently studied the effect of concentration upon the redox potential of the Ag/Ag^+ couple and the $\text{Cu}^{2+}/\text{Cu}^+$ couples.

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{\text{ox}}}{a_{\text{red}}} \right) =$$

$$E^0 + \frac{RT}{nF} \ln \left(\frac{m_{\text{ox}}}{m_{\text{red}}} \right) + \frac{RT}{nF} \ln \left(\frac{\gamma_{\text{ox}}^{\pm}}{\gamma_{\text{red}}^{\pm}} \right) \quad (1)$$

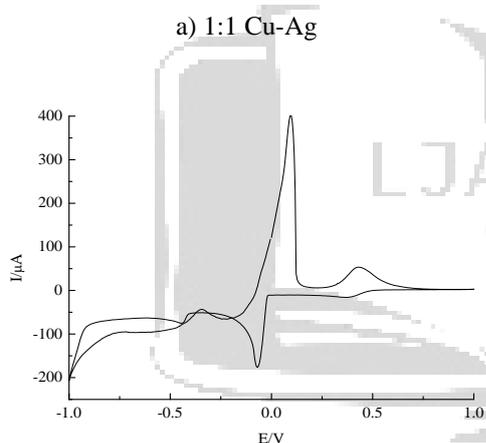
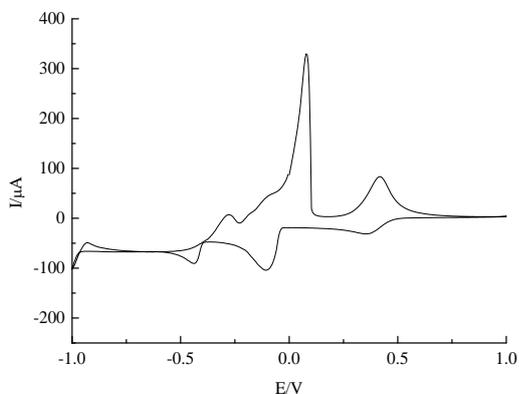
It was found that up to a concentration of 1 mol kg^{-1} , the redox potentials changed in a **Nernstian** manner i.e. they obeyed the **Nernst equation (1)**;

where E^0 is the standard cell potential, R is the gas constant, T is absolute temperature, F is the Faraday constant, n is the number of electrons, $\gamma_{\pm}^2 = \gamma_+ \gamma_-$ is the mean activity coefficient and a and m are the activity and molality of the solute, respectively.

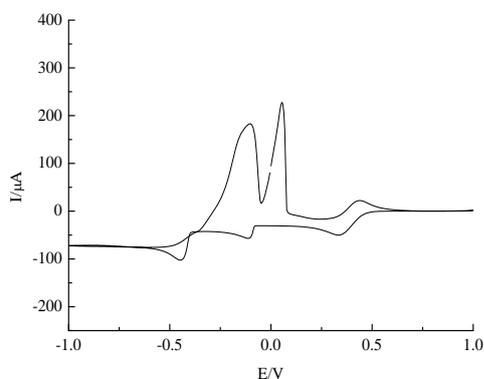
It was shown that the high ionic strength shielded the metal ions from each other and the third term in the **Nernst eq.** could be ignored, as the activity coefficients of the reduced and oxidised species were both unity. It follows from this that the $\text{Cu}^{2+}/\text{Cu}^+$ and Ag/Ag^+ signals should overlap at high silver concentrations and the Cu^+/Cu and Ag/Ag^+ signals should overlap at high copper concentrations, which is what is observed in **Figures 2b and d**.

From the CV scans of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and AgNO_3 , it has been found that copper and silver have reduction peaks at different positions, as mentioned above in **Figure 2a, b and c** for using Ethaline as ionic liquids. When both metals are together in the same solution, a broadening and negative shift of the peaks are observed.

However, the charge for the copper rich phase increases with copper content in the alloy and the area under the current peak of silver species increases with increasing silver content. Changing the Ag^+ concentration from 0.05 to 0.15 mol dm^{-3} will cause the potential to shift by only 28 mV. It is notable that the copper rich solution leads to two peaks. This could be due to the different phases, pure copper and a copper/silver solid solution, or because the materials are deposited with different morphologies.



b) 1: 3 Cu: Ag



c) 3: 1 Cu: Ag

Figure 2 Cyclic voltammograms of (a) 1:1, (b)1:3 and (c) 3:1 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ in Ethaline at a Pt disk working electrode (dia. 0.5mm) using a silver wire pseudo reference electrode.

3-1 Analysis of Cu-Ag deposit using EQCM

An electrochemical acoustic impedance quartz crystal microbalance, EQCM, has previously been used to determine the current efficiency of metal deposition and Abbott and co-worker have recently shown that it can be used for the deposition of composites to determine the loading of neutral particulates. [13] It has also been used to study the electrodeposition of alloys [19,20] and Mallett *et al.*[21] showed that the data for copper- platinum alloys could be deconvoluted to determine elemental composition. In the current study EQCM data were gathered for the deposition of pure metal phases together with those from the three different mixtures. The raw and processed data for pure Cu and pure Ag deposition at a fixed potential of -0.55V are shown in Figure 3a and b. The centre frequency of the admittance spectra (admittance is the reciprocal of impedance) (**Figure 3c and d**) moves to a lower value as Cu or Ag is deposited. This is indicative of increased mass. In the case of Cu deposition (**Figure 3c**), and in the early time period of Ag deposition (**Figure 3d**), the shape and intensity of the spectrum remains mostly unchanged. Under these circumstances the frequency change can be converted to an equivalent mass Δm using the Sauerbrey equation.[22] A plot of deposited mass Δm vs. Faradaic charge Q for Cu and Ag passed during electrolysis is presented in **Figure 3a** and b. Comparing the slope (linear regression) of these data with the Faradaic ratio, $\text{ramCu}/2F$, gives a current efficiency of 99.9% for Cu deposition. Consequently Cu behaves as a model metal under these circumstances. Deposition of pure Ag also yielded

essentially quantitative current efficiencies but only over smaller time scales. For example at an applied potential of -0.75 V for 246 s the current efficiency (from the plot of Δm vs. Q) was determined as 94.5% as shown in **Figure 3c**. At longer time scales, however, the Δm (Q) plots were no longer linear. **Figure 3 b** shows the change in mass as a function of the charge passed for the deposition of pure Ag at a fixed potential of -0.55 V for a time of 1805 s. The slope of the graph in **Figure 3b** is $1.118 \times 10^{-3} \text{ g C}^{-1}$, which is the same as that calculated from Faraday's law (i.e., $r.a.m / nF$) showing that the current efficiency of Ag deposition is $\approx 100\%$. In addition, the mole fraction of Cu in Cu-Ag alloy can be calculated from the slope of the Δm vs. Q plots using Faraday's law by using this **equation 2**.

$$\frac{dm}{dQ} = \frac{X_{Cu} \cdot ram_{Cu} + (1 - X_{Cu}) \cdot ram_{Ag}}{F(X_{Cu} + 1)} \quad (2)$$

Where X_{Cu} is the mole fraction of Cu, and X_{Ag} is the mole fraction of Ag. The relative atomic masses for Cu and Ag are 63.5 g mol^{-1} and $107.87 \text{ g mol}^{-1}$ respectively. **Figure 4** shows the Δm vs. Q plots for the three mixed metal systems. The slope of the linear best fit for the 3: 1 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ is $4.52 \times 10^{-3} \text{ g C}^{-1}$. It follows that the experimental slope, $\frac{d(\Delta m)}{dQ}$, of the Δm vs. Q plots is a measure of the average composition according to **Equation 3**.

$$X_{Cu} = \frac{ram_{Ag} - \left(\frac{d(\Delta m)}{dQ}\right) \cdot F}{\left(\frac{d(\Delta m)}{dQ}\right) \cdot F - ram_{Cu} + ram_{Ag}} \quad (3)$$

As copper is depleted from the solution the silver content increases and then reverts as the silver is depleted. The solution containing predominantly silver starts with a high silver content and then reverts to all copper. This suggests that silver in copper forms a

solid solution whereas copper in silver forms a two phases alloy. As will be seen below in **Table 1**, the results from the average mole fraction calculated using EQCM were very close with the metal ratios determined using EDAX

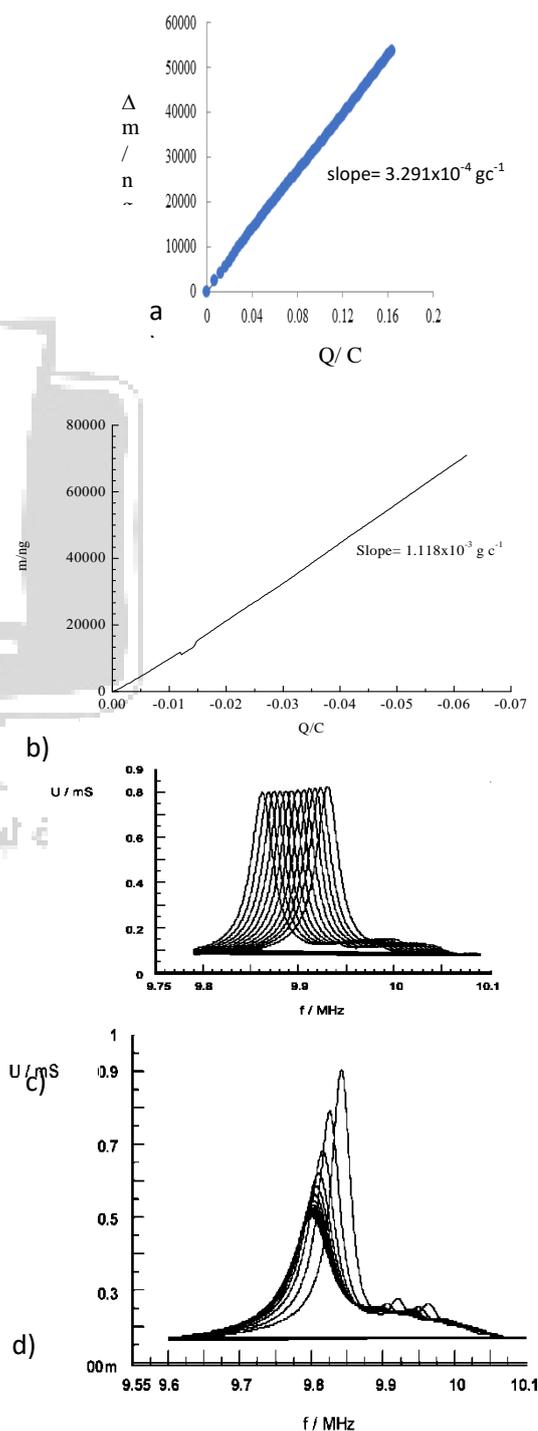


Figure 3 EQCM data for Cu and Ag deposition on a

Au-coated quartz crystal over a time period of 560 and 1805 s, respectively, a and b peak frequency data displayed as deposited mass vs. charge(Q) c and d raw admittance spectra every twentieth spectrum is shown.

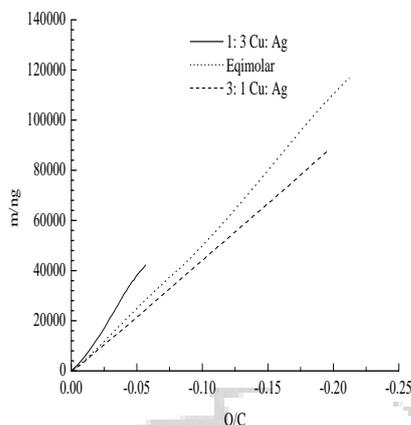


Figure 4 Mass versus charge plots for Cu/Ag alloy deposition using EQCM; The electrolyte contained $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ in different mole ratios. The potential was stepped from O.C.P and held at -0.75 V , using Ag/AgCl as a reference electrode.

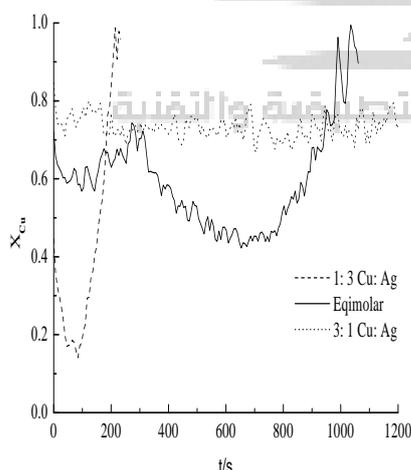


Figure 5 The mole fraction vs time plot for Cu in three metal mixtures 1:1 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$, 1: 3 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ (dash line), (solid), and 3: 1 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ (dot line) from Ethaline. The potential was stepped from O.C.P and held at -0.75 V

The relative compositions of the deposits obtained during this experimental investigation were also analysed using EDAX and SEM.

Table 1 Cu mole fractions of the deposits obtained by deposition at -0.75 V from the EQCM technique compared with EDAX analysis of the same deposits.

	Solution composition		
	$X_{\text{Cu}} = 0.5$	$X_{\text{Cu}} = 0.25$	$X_{\text{Cu}} = 0.75$
X_{Cu} by EDAX	0.46	0.23	0.71
X_{Cu} by EQCM	0.54	0.24	0.73

A comparison between the copper content of the deposits estimated using **Equation 3** and the copper content measured by EDAX is presented in **Table 1**. The alloy composition analysis using both experimental EQCM and EDAX produce consistent values. However, it is clear from the SEM image in **Figure 6** that at 1:3 Cu: Ag deposition formation gives a rough surface. The clear change in deposit morphology as Ag content is increased is illustrated in **Figure 6**.

In the Ag rich solution, the deposit obtained has a crystalline appearance with branched structures of almost pure silver on the surfaces. Nodules with relatively constant dimensions of approximately $1 \mu\text{m}$ are produced from a solution of equimolar metal salt concentration. The deposit obtained from the Cu rich solution was similar in appearance to that obtained from the equimolar solution, with a very similar grain size. This is consistent with the data obtained from EDAX and EQCM as discussed later. The phase composition of the Cu-Ag alloys deposited from Ethaline was determined using

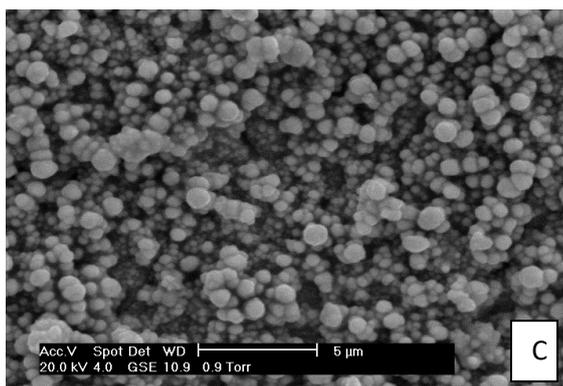
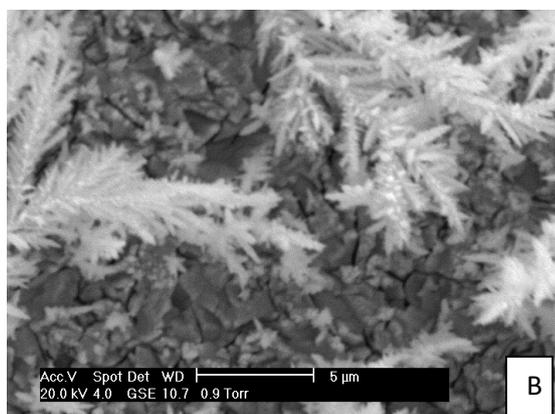
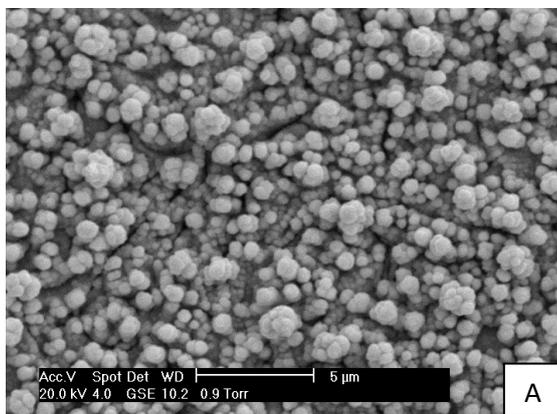


Figure 6 Representative scanning electron micrographs of Cu-Ag alloys electrodeposited from (a) 1:1 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ (b) 1:3 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ (c) 3:1 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ in Ethaline. Deposits are made on a gold covered quartz crystal. The potential was stepped from

O.C.P and held at -0.75 V

EDAX and was found to be strongly affected by the current density. An increase in the current density leads to an increase in the ratio of Cu:Ag in the deposited layer as shown in **Figure 7**. The current density at different positions across the Hull cell was calculated using **Equation 4**.

$$C = i(5.1 - 5.24 \log_{10} X) \quad (4)$$

Where C is a current density, i current applied and X = distance from high current density end of the panel.

It was, however, found that the morphology of the surface layer was dependent on the current density

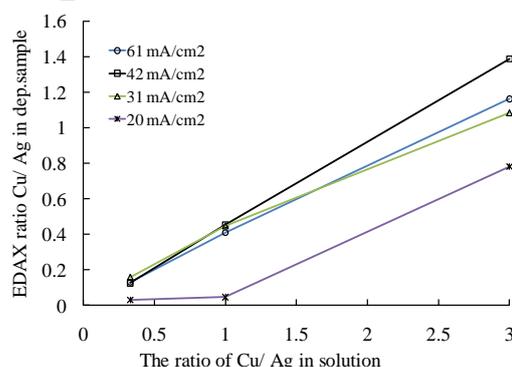


Figure 7 EDAX result for the deposits using a Hull cell, obtained at three different concentrations (equimolar, 1: 3 and 3: 1) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{AgNO}_3$ from Ethaline as ionic liquid

3-2 Phase formation XRD

For determination of the phases that appeared in the alloys, XRD analysis was carried out. **Figure 8** shows the profiles of XRD patterns for the Cu-Ag alloys deposited from Ethaline ionic liquid on Ni substrate at (A) position. As illustrated in **Figure 8**, the pure Cu disappears upon the formation of Cu-Ag alloy, and the characteristic 2θ of the Cu-Ag alloys varied with increasing Cu percentage in the electrodeposited alloys. The peak intensity of Ag decreases with an increase in Cu concentration. The characteristic signal of pure Cu and Ag disappeared upon the

formation of Cu-Ag alloys, with increasing of Cu percentage in the electrodeposited alloys.

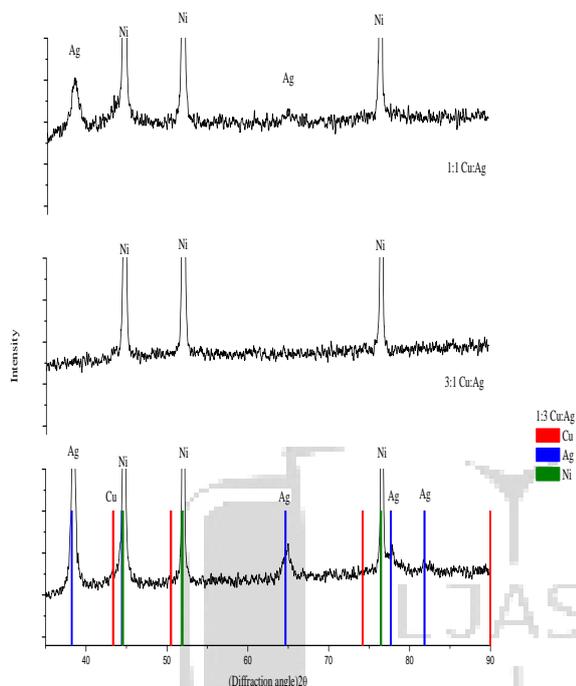


Figure 8 XRD results of the Cu-Ag samples deposited on nickel substrate from 1ChCl : 2 EG ionic liquid at different concentrations a) 1: 1 CuCl₂·2H₂O: AgNO₃, b) 1: 3 CuCl₂·2H₂O: AgNO₃, and c) 3: 1 CuCl₂·2H₂O: AgNO₃

4-CONCLSION

This study shows the successful electrodeposition of Cu-Ag alloys from Ethaline DESs at room temperature. A real-time in situ method for probing the mass composition of mixed metal electrolytic deposits in Ethaline is demonstrated. The suite of analytical techniques employed including cyclic voltammetry, EQCM, XRD, SEM and EDX have shown that there are significant differences between the responses for multiphase alloys than those for simple solid solutions although these are not as

simple to analyse due to the complexity of the phases formed.

As would be expected, the concentration of Cu²⁺ ions in solution is a very important factor which influences the composition of the Cu-Ag alloy deposition and the properties of the film. Acoustic impedance EQCM has also been successfully applied to characterising the formation of a Cu-rich and Ag-rich Cu-Ag alloys and has been partially validated by SEM (EDX) analysis. EQCM showed that the alloy composition is not homogeneous throughout the alloy layer.

5-REFRANCES

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