

The Electrochemistry of Zn in Deep Eutectic Solvents

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By

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Statement of Originality

The experimental work in this thesis has been carried out by the author in the department of chemistry at the University of Leicester between October 2005 and October 2008. The work has not been submitted, and is not presently submitted, for any other degrees at this or any other university.

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Abstract

Ionic liquids have generated a large amount of interest as possible replacements for aqueous electrolytes in metal and alloy electrodeposition processes. A related class of fluid, the deep eutectic solvents, have recently been shown to have equally interesting electrochemical properties whilst also being more air and moisture stable and economical to produce.

The electrodeposition of Zn from the deep eutectic solvents 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea was investigated. A theory of relative chloride activities was developed and applied to effectively account for differences in the voltammetry, chronoamperometry and morphology of deposits obtained from the two solvents. Additionally the solute concentration was determined to have an effect on the physical properties of the solvent; moreover, this effect was seen to be solvent dependent. The first EXAFS study of metal speciation in deep eutectic solvents was used to elucidate the identity of the dissolved Zn species.

A novel technique, the combined *in-situ* AFM-EQCM, has been designed and applied, in a time resolved manner, to the study of Zn electrodeposition from 1: 2 ChCl: ethylene glycol.

It was shown that the organic additives ethylene diamine and ammonia could be used to modify the Zn deposit morphology. It has been proposed that the additives alter the Zn nucleation and growth mechanism through interaction with the free chloride ions in the electrochemical double layer. The effect of surfactants has also been described and sodium dodecyl sulphate found to be an effective levelling agent.

The feasibility of Zn alloy deposition from choline chloride based deep eutectic solvents has been investigated. Zn-Cu and Zn-Co alloys were successfully deposited from deep eutectic solvents for the first time. In addition the electrochemical quartz crystal microbalance has been used in an original manner to monitor Zn-Sn co-deposit composition.

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This thesis is dedicated to the memory of David John Barron.

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Abbreviations

AFM	Atomic force microscopy
CTAB	Hexacetylammonium bromide
CV	Cyclic voltammetry
DES	Deep eutectic solvent
ED	Ethylene diamine
EQCM	Electrochemical quartz crystal microbalance
EXAFS	Extended X-ray absorption fine structure
IL	Ionic liquid
SEM	Scanning electron microscopy
SDS	Sodium dodecyl sulphate
XRD	X-Ray diffraction spectrometry

Chapter 1: Ionic Liquids as Electrodeposition Media

1. Introduction

1.1 The History of Ionic Liquids

1.2 Ionic Liquid Synthesis

1.3 The Physical Properties of Ionic Liquids

1.4 Electrodeposition From ionic Liquids

1.4.1 Aluminium

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1.4.3 Alloys

1.4.4 Semiconductors

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1.5 Deep Eutectic Solvents

1.5.1 Type I

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1.1 The History of Ionic liquids.

Ionic liquids are a class of fluid which consist of ions and are liquid at temperatures < 100 °C. This arbitrary definition is used to differentiate between ionic liquids and the classical molten salts, which melt at higher temperatures. The first ionic liquid is widely regarded to be that described by Walden in 1914, where the physical properties of ethylammonium nitrate ($[\text{EtNH}_3][\text{NO}_3]$) (m.p. $12\text{--}13$ °C) were described.^[1] Although prompting little interest at the time of publication, Walden's discovery is now considered to be the start of the field of ionic liquid research, a field of research which now encompasses in excess of 1000 publications per annum.

The classical high temperature molten salts, fluid at temperatures around 1000 °C, have been extensively used for the electrowinning of metals such as Li, Na, Ti and Al.^[2-4] Molten salts are wholly ionic and aprotic and as such are excellent electrochemical media with wide potential windows, high conductivities, low viscosities and high solubilities for metal salts. They combine the high solvating power of aqueous solutions while negating many of the reactivity issues, such as the hydrogen evolution reaction. However, the extreme operational requirements are a major limitation, and as such the substrates that can be used for electrodeposition in molten salts are limited. Interest in ionic liquids was reignited by the desire to incorporate the beneficial properties of the well studied molten salts in a material which was liquid at lower temperatures.

The next great advance in ionic liquid research, almost 40 years after the publication of Walden's initial discovery,^[1] resulted from an attempt to develop a lower temperature melt for the electrodeposition of aluminium, which was previously only accessible from high temperature molten salts. The authors found that by altering the composition of LiCl/ KCl/ AlCl_3 mixtures, eutectic melts with freezing points close to 100 °C could be formed.^[5] The lower melting point of this system compared to the pure salts, is due to the formation of bulky chloroaluminate ions (e.g. AlCl_4^- and Al_2Cl_7^-) in the eutectic mixtures. Bulky ions have diffuse charge, which lower the lattice energy and consequently the melting point of the system.^[6]

The principle of reducing the freezing points of molten salts by using bulky asymmetric ions led to seminal research in the 1970s by Osteryoung *et al.* on ionic liquids formed from AlCl_3 and the 1-butylpyridinium cation.^[7] This system was found to be liquid at 20 °C but only over a narrow compositional range, $60\text{--}67$ mol% AlCl_3 .^[7] Additionally, the 1-butylpyridinium cation was found to be easily reduced, restricting the electrochemical applications of this ionic liquid.^[7] Wilkes and Hussey further developed this methodology,

using molecular orbital calculations to predict which organic cations would be most stable to reduction in ionic liquids.^[8] These calculations led to the development of the AlCl₃: 1-ethyl-3-methyl-imidazolium ionic liquid.^[9] This liquid had a much larger liquid range than the 1-butylpyridinium system and is a low viscosity fluid at compositions between 33 and 67 mol% AlCl₃.^[9] The arbitrary definition of ionic liquids being fluids which consist of ions and are liquid at temperatures < 100 °C was first used to describe this class of ionic fluid.^[6] A major limitation of the chloroaluminate ionic liquids is their inherent air and moisture sensitivity, due to the rapid hydrolysis of AlCl₃ upon contact with moisture. The moisture sensitivity of the systems can be somewhat attenuated by the replacement of AlCl₃ with more stable metal halides such as ZnCl₂ to form eutectic based ionic liquids.^[10]

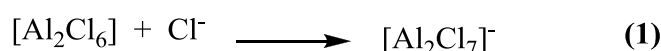


Figure 1.1 The Al speciation equilibria in chloroaluminate eutectic based ionic liquids

The ionic liquids formed from organic cations with AlCl₃ and ZnCl₂ are often termed first generation ionic liquids.^[11] This class of ionic liquids are fluid at low temperatures due to the formation of bulky chloroaluminate or chlorozincate ions at eutectic compositions of the mixture. This reduces the charge density of the ions, which in turn reduces the lattice energy of the system leading to a reduction in the freezing point of the mixture. The metal speciation and hence properties of this class of liquid can be adjusted by altering the composition of the liquid between Lewis-basic, an excess of the organic cation, and Lewis-acidic, an excess of the metal halide.^[12] Neutral liquids, where AlCl₃ and the organic salt are in equimolar amounts, are known but generally require a buffer to maintain neutrality. This is because small changes in the relative concentrations of the two components, *e.g.* during electrodeposition, will result in a shift to acidic or basic conditions.^[13] **Figure 1.1** shows how the Al speciation in the chloroaluminate ionic liquids is altered by changes in the liquid composition. The relative positions of the equilibria depend upon the relative concentration of AlCl₃ in the mixture, with higher order Al ions dominating at low AlCl₃ concentrations. This behaviour lends this class of ionic liquids the name, the eutectic based ionic liquids.

Although their inherent moisture sensitivity has limited their uptake outside of the laboratory, the interesting solvent and physical properties of the eutectic ionic liquids has

ensured that they have become the most widely studied ionic liquids. They have been extensively used in the electrodeposition of a large range of metals and alloys, a full review of which is presented in section 1.4.

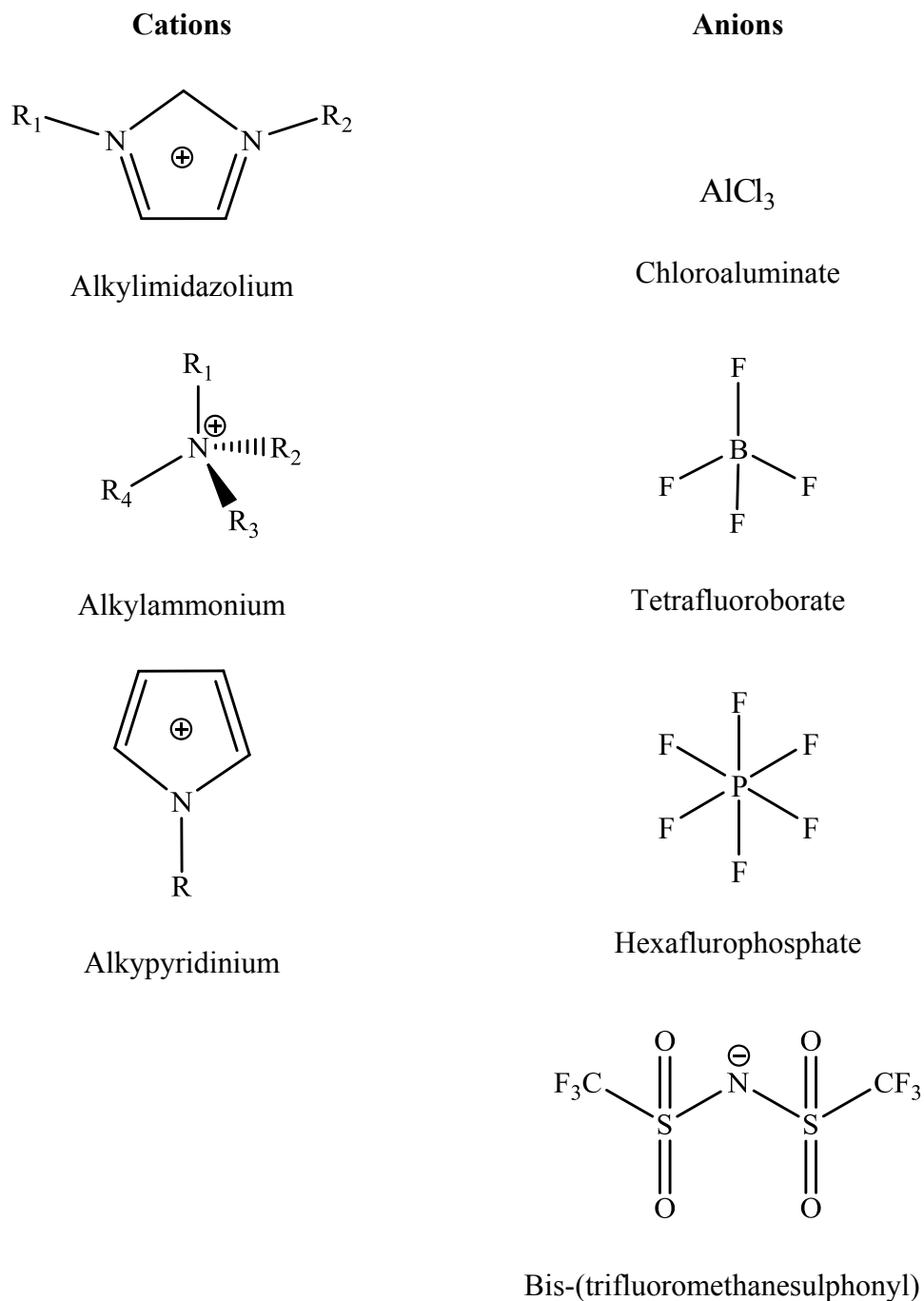


Figure 1.2 A selection of components commonly used in the design and synthesis of ionic liquids

The second generation of ionic liquids are those that are entirely composed of discrete ions, rather than the eutectic mixture of complex ions seen in the first generation ionic liquids. Wilkes and Zaworotko, working with alkyimidazolium salts, discovered that air and moisture stable liquids could be synthesised by replacing the AlCl_3 used in the eutectic ionic liquids with discrete anions such as the tetrafluoroborate and ethanoate moieties.^[14] Although

generally air and moisture stable, some reports have suggested that exposure to moisture affects their chemical and physical properties, with the development of HF as water content increases.^[15] The stability of this class of ionic liquids can be improved by using more hydrophobic anions such as tri-fluoromethanesulphonate (CF_3SO_3^-), bis-(trifluoromethanesulphonyl)imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ and tris-(trifluoromethanesulphonyl)methide $[(\text{CF}_3\text{SO}_2)_3\text{C}]^-$.^[15-17] These systems have the additional benefit of large electrochemical windows, allowing less noble metals, inaccessible from the chloroaluminate liquids, to be electrodeposited from these systems.^[15]

The most widely used ionic liquids can therefore be split into two distinct categories, those formed from eutectic mixtures of metal halides (such as AlCl_3) and organic salts (generally nitrogen based and predominantly with halide anions), and those containing discrete anions such as PF_6^- or bis-(trifluoromethanesulphonyl) imide. Both classes of liquid have a wide range of tuneable properties which have led to different applications.^[18] **Figure 1.2** gives examples of some of the most widely used ions in ionic liquid design. It is estimated that the total number of possible ionic liquids could be in the range of 10^6 distinct systems. Clearly ionic liquids have the potential to be highly versatile solvents, with properties which can be easily tuned for specific uses. However, if ionic liquids are to be successful as viable alternatives to aqueous electrolytes, they must also be simple and economic to synthesise.

1.2 Ionic Liquid Synthesis

Ionic liquids are generally produced by either a metathesis reaction between a halide salt and a group 1, Ag or ammonium salt of the desired anion or *via* acid-base neutralisation reactions.^[11] A general synthetic pathway for the formation of ionic liquids can be seen in **Figure 1.3**

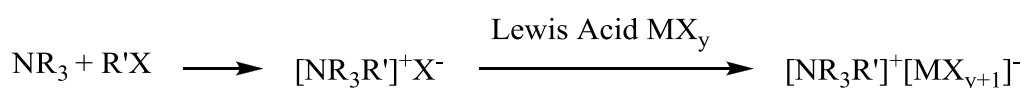


Figure 1.3 A general synthetic pathway for the formation of ionic liquids

The initial step is a quaternisation reaction between an amine (or phosphane) with a halogenated alkyl chain to form the required ammonium or phosphate salt. A number of ionic liquids can be formed directly from quaternisation reactions, *e.g.* the quaternisation reaction between 1-ethyl-3-methylimidazole and methyl triflate to give $[\text{EMIM}(\text{CF}_3\text{SO}_2)]^+$, m.p. -9°C .^[16] The second stage is generally a solid phase synthesis whereby the quaternary salt is mixed with the metal halide. The synthesis of most ionic liquids is therefore

relatively simple, although consideration must be made for the air and moisture sensitive nature of some of the commonly used components.

The non volatile nature of ionic liquids, a feature which makes them particularly attractive as alternative solvents also means that once formed they cannot easily be purified by standard methods such as distillation. It is therefore imperative that the reactants used in chloroaluminate ionic liquid synthesis are pure and that the synthesis is carried out in an air and moisture free environment at as low a temperature as possible.^[19]

1.3 The Physical Properties of Ionic Liquids

The main impetus behind ionic liquid research was initially the desire to obtain highly conducting aprotic electrochemical media, with a high Al concentration, for use in Al electrodeposition. As the field has widened a general set of physical properties, which make ionic liquids suitable as electrodeposition media, have become apparent:

1. Thermal Properties

Ionic liquids are differentiated from classical inorganic salts by their relatively low melting points. Inorganic salts generally have melting points of around 1000 °C, *e.g.* NaCl (m.p. 808 °C) due to the strong electrostatic interactions between the ions and the correspondingly high lattice energy of the salt. By replacing Na⁺ with an organic species such as [EMIM]⁺ or [BMIM]⁺, a large reduction in melting point is observed, to 87 °C and 65 °C respectively.^[9] These large bulky cations have a diffuse charge which results in a reduction of the electrostatic interactions between the ions, which in turn results in a reduction in the melting point of the salt. The principle of reducing the melting point of a salt by using bulky asymmetric cations is central to ionic liquid design and is illustrated by the cationic species most often used in ionic liquid synthesis, shown in **Figure 1.2**. However, the melting point of a salt is not solely governed by the cationic species; melting points can also be modified by altering the anionic species used. The melting points of ionic liquids formed from [EMIM]⁺ and a range of anions are as follows, [Cl]⁻ 89 °C^[20], [Br]⁻ 79 °C^[20], [BF₄]⁻ 15 °C^[21], [CF₃SO₃]⁻ -9 °C^[16], [(CF₃SO₂)₂N]⁻ -15 °C^[22]. It can be seen that the anion effect is similar to that of the cation in that larger anions with larger charge densities have a larger effect on the ionic liquid melting point.

2. Solvent Properties

The ability of ionic liquids to dissolve metal salts is an important property for their application in electrodeposition processes. The solubility of metal salts in the halometalate ionic liquids is generally high, due to the high halide concentration, and the solubilities of a range of metal salts in various halometalate ionic liquids have been reviewed.^[23, 24]

Conversely, ionic liquids containing discrete anions generally have relatively weak coordinating properties. The solvation energy is too small to break the electrostatic interactions between ions in metal salts, and as such this class of ionic liquids generally exhibit poor solubility properties for metal salts, e.g. the solubility of LiCl in 1-butyl-3-methylimidazoliumchloride BF₄ is only 10⁻⁴ wt%.^[25] The solvation strength of the discrete anion ionic liquids can be increased either by introducing halides to the system or by modifying the cation to create task specific ionic liquids (TSIL). In TSIL synthesis the interaction between the ionic liquid and metal salts is increased by the incorporation of functional groups in the cation or anion. For example Davis *et al.* introduced thioether and thiourea groups into the side chain of imidazolium cations. This modification made the extraction of Hg²⁺ and Cd²⁺ ions from an aqueous phase into the ionic liquid phase possible.^[26]

3. *Electrochemical window*

The electrochemical window, *i.e.* the range of potentials over which the electrolyte is neither oxidised nor reduced at an electrode surface, is important when considering electrochemical stability. Aqueous systems have a relatively small potential window, *ca.* 1.2 V, where the cathodic limit is usually due to the hydrogen evolution reaction. In comparison, some ionic liquids have much larger potential windows, up to 4.15 V for [BMIM(PF₆)] at a Pt electrode^[27] and 5.5 V for [BMP(TF₂N)] at a glassy carbon electrode.^[17] This increase in electrochemical stability allows ionic liquids to be used for the electrodeposition of metals and semiconductors which are inaccessible from aqueous systems, such as Al,^[28] Mg,^[29] Ge,^[30] and Si^[31]. However, the direct comparison of electrochemical windows in ionic liquids is confounded by the lack of common consensus on the reference electrode to use.

4. *Mass transport properties*

Although ionic liquids have inherently high charge carrier concentrations, their conductivities are somewhat lower than expected, often less than concentrated aqueous electrolytes at room temperature.^[15] This is due to the fact that the conductivity of any given system is dependent not only upon the charge carrier concentration but also upon the charge carrier mobility, which is generally low in ionic liquids.

The viscosity of ionic liquids is inversely proportional to conductivity, generally being greater than that of common molecular solvents, ranging between 10 to 500 mPa s⁻¹ at 25 °C.^[15] The high viscosities and relatively low conductivities of ionic liquids are due to the low mobility of the species in the liquid. The bulky asymmetric nature of the cations in ionic liquids appears to reduce their mobility and hence bulk conductivity. A theory proposed as

an explanation for the relatively low conductivity of ionic liquids is based upon the availability of holes.^[32] Here it is assumed that as a solid melts, voids of various sizes are formed. The probability of an ion moving through a liquid is therefore dependent upon the presence of an adjacent suitably sized hole. Calculations have shown that the average hole size in ionic liquids is smaller than in aqueous electrolytes whereas the average ion size is larger. This results in a reduced probability of ion movement, an increase in viscosity and a decrease in conductivity. Conductivity values for a range of ionic liquids have been calculated using this model and show a high degree of correlation with the experimentally obtained values.^[32] Additionally, as with most liquids, the fluidity and hence conductivity of ionic liquids increases as a function of temperature.

5. Avoidance of metal/ water chemistry

Hydrogen evolution, which forms the limiting cathodic reaction of aqueous electrodeposition processes, is a major problem in industrial aqueous electrodeposition. The competing evolution of hydrogen at the cathode reduces the current efficiency of electrodeposition, thereby increasing the power consumption and cost of the process. Hydrogen evolution can also lead to the micro-cracking of metal deposits, promoting corrosion and weakening mechanical coatings. This limits the applicability of aqueous solvents for the deposition of less noble metals such as Cr and Al. The aprotic nature of ionic liquids makes it possible to electrodeposit such metals at high current efficiencies and without micro-cracking.

1.4 Electrodeposition from Ionic Liquids

Ionic liquids were first designed as electrochemical media for Al electrodeposition. As the number of systems to be synthesised and studied has increased, the inherent physical properties of ionic liquids, which make them interesting electrolytes have become clear. Consequently, there have been many publications which focus on the electrodeposition of metals from ionic liquids. The scope of this research effort is illustrated in **Table 1.1**. It is worth noting that although there have been many publications in this area; most are limited to simple deposition studies. The relationship between the metal speciation, electrodeposition mechanism and deposit morphology is relatively under explored and will be considered in depth in this thesis.

The majority of electrodeposition studies from ionic liquids have focussed on the first generation ionic liquids. This class of ionic liquids are highly conductive, have wide potential windows and are excellent solvents for many metal salts. However, their uptake outside of the laboratory has been limited due to the moisture sensitive nature of AlCl_3 . The

chloroaluminates are also unsuitable for the electrodeposition of pure reactive metals, such as Si, Ta, Li, the relatively noble nature of Al meaning that these metals can only be obtained as Al co-deposits.

In contrast, electrodeposition from the second generation of ionic liquids, which have low vapour pressures, large electrochemical windows and are air and moisture stable, is relatively understudied. Initially research was hindered by the difficulty of removing impurities, in the form of water and halide ions, from the ionic liquids, making reproducibility problematic. More recently interest has grown in utilising the unique properties of this class of ionic liquids for electrodeposition, particularly of reactive elements and a number of these publications are listed in **Table 1.1**.

Ionic Liquid	Metals
Chloroaluminate	Al, ^[28] Fe, ^[33] Co, ^[34] Ni, ^[34] Cu, ^[35] Zn, ^[36] Ga, ^[37] Pd, ^[38] Au, ^[39] Ag, ^[40] In, ^[41] Sn, ^[42] Sb, ^[43] Te, ^[44] Cr, ^[45] Hg, ^[46] Na, ^[47] Li, ^[48] Tl, ^[44] Pb, ^[49] Bi ^[50]
Chlorozincate	Zn, ^[10] Sn, ^[51] Cd ^[52]
Discrete Anions	Cd, ^[53] Cu, ^[54, 55] Sb, ^[56] Pd, ^[57] Au, ^[58] Ag ^[59, 60] Ge, ^[30, 61, 62] Li, ^[63] Mg, ^[29] Al, ^[64] Si, ^[31, 65] Ta, ^[66] Co, ^[67] La ^[68] , Eu, ^[68] Sm, ^[68] Cs, ^[69] Ga ^[70]
Deep Eutectic Solvents	Ag, ^[71] Cu, Sn, ^[72] Ni, ^[73] Zn ^[72]

Table 1.1 Examples of the range of metals electrodeposited from various ionic liquids/ deep eutectic solvents to date.^[18]

1.4.1 The Electrodeposition of Al from Ionic Liquids

Al coatings are of industrial interest as they are corrosion resistant, due to the ready formation of stable surface oxides, and lightweight. Al coatings are currently obtained through a number of processes including hot dipping, thermal spraying, sputter and vapour depositions and electrodeposition from organic solvents. However, due to the reactive nature of Al and the small electrochemical window of water, Al electrodeposits are inaccessible from aqueous electrolytes.

Al electrodeposition from organic solvents is commercially available as the SIGAL-process.^[74, 75] Deposits obtained through this method are adherent and do not effect the mechanical properties of the substrate. Additionally, the electrodeposition parameters can

be easily altered to control the thickness and quality of the deposits. However, due to the volatility and flammability of the organic solvents used there are some safety issues with the process.

Ionic liquids are highly conducting aprotic media, with high metal ion concentrations, wide electrochemical windows and few of the environmental and safety issues of organic solvents. The electrodeposition of Al from the chloroaluminate ionic liquids was first demonstrated by Osteryoung and Robinson. In a 1980 study, they showed that Al could be electrodeposited from an acidic AlCl_3 : butylpyridinium melt, although this melt was only fluid at temperatures below 100 °C upon the addition of 50 % benzene.^[28] A later study by Osteryoung demonstrated that Al deposits of up to 15 μm thick were obtainable on brass substrates.^[76]

Initial research into Al electrodeposition from imidazolium based liquids was conducted by Lai and Skyllas-Kazacos, who discovered that the Al deposition mechanism was not simply a diffusion controlled process and had complicated kinetics.^[77] The alkyimidazolium research could perhaps be considered the first true Al electrodeposition studies from ionic liquids. The electrodeposition of Al was only possible from the AlCl_3 : butylpyridinium melts when large amounts of organic solvents, generally benzene, were added as diluents. Conversely Al deposits, although dull and poorly adherent, could be obtained directly from the unmodified alkyimidazolium ionic liquids.^[78]

More recently attempts have been made to electrodeposit Al from the air and moisture stable ionic liquids. The ionic liquids $[\text{BMP}]\text{Tf}_2\text{N}$ and $[\text{EMIM}]\text{Tf}_2\text{N}$ were both found to form biphasic mixtures when AlCl_3 was added in the concentration range 1.6-2.5 mol dm^{-3} and 2.5-5 mol dm^{-3} respectively.^[64] The electrodeposition of Al was only possible from the upper phases of both biphasic mixtures with nanocrystalline and microcrystalline Al obtained from $[\text{BMP}]\text{Tf}_2\text{N}$ and $[\text{EMIM}]\text{Tf}_2\text{N}$ respectively.^[64] This apparent cation effect, where $[\text{BMP}]^+$ appears to be acting as a grain refiner highlights the complex nature of electrodeposition from ionic liquids.^[64] Additionally, the experimental difficulties of obtaining speciation data in ionic liquids means that although it is clear that Al electrodeposition is only possible from one phase of these mixtures, a comprehensive understanding of the mechanism is almost completely missing.^[64]

The feasibility of ionic liquid based Al electrodeposition commercialization was investigated in depth by Abbott *et al.* using benzyltrimethylammonium chloride: AlCl_3 . This liquid was shown to be less moisture sensitive, more thermally stable and easier to purify than the 1-methyl-3-ethylimidazolium chloride based systems.^[79] This important

study highlighted the difficulties in taking a laboratory based process to an industrial level, specifically focussing on practical issues such as substrate and current density effects.

Despite over 20 years of concerted research, Al deposition from chloroaluminate ionic liquids remains some distance from being industrialised. The inherent water sensitivity and relatively high cost of the materials used in the production of the ionic liquids has thus far limited their uptake outside of a laboratory environment. However, Al electrodeposition from ionic liquids continues to generate significant amounts of academic interest. Recent publications include those by Endres *et al.* whose wide ranging studies into the growth of nano-materials in ionic liquids have included the electrodeposition of nanocrystalline Al from 1-butyl-3-methyl-imidazolium: AlCl_3 .^[33]

1.4.2 The Electrodeposition of Zn from Ionic Liquids

Zn and its alloys are used as anti-corrosion coatings for ferrous substrates, particularly in the automotive industry.^[80] The electrodeposition of Zn and its alloys is traditionally carried out in aqueous, typically acidic sulphate, electrolyte solutions. However, Zn electrodeposited from traditional aqueous baths suffers from hydrogen embrittlement, whilst low current efficiencies can be an issue in some processes. Zn and its alloys can be obtained in improved quality from ionic liquids.^[80]

Initial research focussed on the well characterised chloroaluminate ionic liquids. In a comprehensive study by Pitner and Hussey, the electrodeposition of Zn from an acidic AlCl_3 : 1-ethyl-3-methyl imidazolium ionic liquid was characterised.^[36] Zn was first introduced to the electrolyte *via* the electrochemical dissolution of a Zn anode. The Zn electrodeposition mechanism was then studied at a range of electrode surfaces including Pt, W, Au and glassy carbon. This study showed that the electrodeposition of Zn proceeded at metallic substrates *via* an underpotential driven deposition mechanism, similar to that observed in aqueous solutions.^[81, 82] Conversely, Zn deposition at glassy carbon required a large overpotential to initiate nucleation, due to the lack of nucleation sites (surface defects) on this well defined surface.^[36] The report also stated that the current efficiency of Zn deposition from the aprotic ionic liquid was an improvement over the aqueous process, the current efficiency of which is generally low due to the competing hydrogen evolution reaction. Current efficiencies of up to 100 % were obtainable at low overpotentials. However, at high overpotentials dendritic growth was observed alongside a corresponding reduction in current efficiency.^[36] Pitner and Hussey's study was the first to comprehensively investigate the electrochemical behaviour of Zn species in the chloroaluminate ionic liquids and the first to demonstrate that Zn could be electrodeposited

from ionic liquids with a high current efficiency and without Al co-deposition, proving the viability of ionic liquids as Zn electrodeposition media.^[36]

Replacing AlCl_3 with ZnCl_2 has previously been shown to both increase the air and water stability of ionic liquids and remove the possibility of Al co-deposition. As the chlorozincates are less susceptible to hydrolysis, they are easier to produce and handle than the corresponding chloroaluminates. The electrochemistry of the chlorozincate ionic liquids is dominated by the relative populations of the complex Zn ions in solution in an analogous manner to the chloroaluminate ionic liquids, **Figure 1.1**.

Hsiu *et al.* investigated the relationship between Lewis acidity and electrodeposition mechanism by studying the potential limits of 1-ethyl-3-methylimidazoliumchloride: ZnCl_2 in the molar ratio range 3:1 to 1:3.^[83] In Lewis acidic compositions (excess ZnCl_2) the negative potential limit was due to the deposition of metallic Zn, whilst the positive potential limit was due to the oxidation of the chlorozincate species.^[83] Conversely, in Lewis basic mixtures the potential window was wider (3 V) and limited by the cathodic reduction of $[\text{EMIM}]^+$ and the anodic oxidation of Cl^- .^[83]

Sun *et al.* have published a series of papers dealing with Zn and Zn alloy deposition from chlorozincate ionic liquids. These studies have chiefly focussed on ZnCl_2 : 1-ethyl-3-methylimidazolium chloride.^[10] An initial paper described the electrochemical behaviour of this system and found that Zn was deposited, at both Ni and glassy carbon electrodes, *via* an overpotential driven 3D instantaneous nucleation mechanism under mixed diffusion and kinetic control.^[10] This is in contrast to the 3D progressive nucleation mechanism observed for Zn electrodeposition in the chloroaluminate ionic liquids,^[36, 84] suggesting that in the chloroaluminate ionic liquids Al species may inhibit Zn from reaching the electrode surface. The Zn was observed to form needle like deposits which were easily dislodged.^[10] However, the addition of 20 % (v/v) of an organic co-solvent, propylene carbonate, resulted in adherent Zn crystal formation; although no change in nucleation mechanism was observed. It was suggested that the formation of Zn needles was due to the relatively high viscosity of the pure ionic liquid.^[10]

In addition to chloride based ionic liquids, Zn electrodeposition has also been studied in Br containing ionic liquids. Electrodeposition of Zn from bromoaluminate ionic liquids such as AlBr_3 : dimethylethylphenylammoniumbromide was possible but it was determined that Zn could only be obtained as an Al co-deposit.^[84, 85] However, by using bromozincates in place of the bromoaluminates, smooth Zn electrodeposits could be obtained. Iwagishi showed

that Zn could be effectively deposited from Lewis basic 1-ethyl-3-methylimidazoliumbromide: ZnCl_2 .^[86] In an extended investigation Iwagishi studied the effect of a range of dihydric alcohols (ethylene glycol, 1,3-propanediol, 1,2-butanediol and 1,3-butanediol) on the Zn electrodeposition process from this ionic liquid.^[85, 86] It was found that the addition of each of the dihydric alcohols improved the current efficiency of the process and the smoothness/ visual aspect of the deposit.^[85, 86] Of the alcohols studied ethylene glycol was found to have the greatest effect and it was proposed that this was due to ethylene glycol acting to promote the disassociation of $[\text{EMIM}]\text{Br}$ to $[\text{EMIM}]^+$ and $[\text{Br}]^-$, and consequently increasing the concentration of ZnBr_4^{2-} .^[85, 86]

More recently Abbott *et al.* have studied the electrodeposition of Zn from 1:2 choline chloride: ZnCl_2 .^[87] Zn electrodeposits obtained from this liquid were found to have a similar morphology to that of Sun at current densities below 5 A m^{-2} . Electrodeposits formed at higher current densities were powdery and non-adherent and it was proposed that this is due to the relatively high viscosity and low conductivity of the liquid.^[87] The current efficiency in this ionic liquid was found to be close to 100 % and the electrodeposition was almost fully reversible.^[87]

1.4.3 Alloy deposition

Alloys are of importance as they often show superior properties to those of single metal deposits such as improved corrosion and wear resistance, better catalytic and magnetic properties and aesthetics. By electrodepositing alloys, a wide number of tuneable variables become accessible, by which the composition, morphology and properties of the alloys can be altered. A number of the physical properties of ionic liquids make them an attractive prospect as alternative alloy electrodeposition media. The large electrochemical window, conductivity and aprotic nature of ionic liquids allows access to metals which aren't readily obtainable from aqueous solutions, which in turn has led to the development of novel alloy systems.

1. Chloroaluminate Ionic Liquids

The majority of research to date has been concerned with the electrodeposition of Al and Zn containing alloys from the chloroaluminate and chlorozincate ionic liquids. As such the majority of alloys formed have been those containing Al or Zn. Binary aluminium alloys including Al-Ti,^[88] Al-Mo,^[89] Al-Zr^[90] and Al-Mg^[91] have all been electrodeposited from 1-ethyl-3-methylimidazoliumchloride: AlCl_3 . A number of groups have also expanded their work to ternary alloys with both Al-Mo-Mn^[92] and Al-Cr-Ni^[93] reported in the literature.

The electrodeposition of alloys from chloroaluminate ionic liquids has been comprehensively reviewed and will not be considered in depth here.^[94]

2. Chlorozincate Ionic Liquids

The development of the chlorozincate ionic liquids has also led to a large amount of research into Zn containing alloys. These systems have the benefit of increased moisture and air stability and also remove the possibility of Al codeposit formation.

Sun *et al.* have comprehensively studied the electrodeposition of Zn alloys from ZnCl_2 : 1-ethyl-3-methylimidazoliumchloride. The first alloy system to be studied in this research, Zn-Cu, is used as both a decorative coating and as a binding layer between rubber and steel.^[95] The aqueous protocol for the electrodeposition of Zn-Cu alloys uses cyanide salts and as such the development of environmentally sound alternative processes is imperative. Cu was first introduced to ZnCl_2 : 1-ethyl-3-methylimidazoliumchloride *via* either the controlled potentiostatic anodization of a Cu wire, or *via* the direct dissolution of anhydrous CuCl, which is highly soluble in liquids with high chloride concentrations.^[96] The deposition of mixed Zn and Cu phases was found to be possible in the Zn underpotential regime, where Cu reduction is under mass transport control. Deposits formed in this regime were found to nucleate *via* a 3D progressive nucleation mechanism whereas depositions at potentials where only Cu reduction occurs, followed a 3D instantaneous nucleation mechanism^[96] (*c.f.* pure ZnCl_2 : 1-methyl-3-ethyl imidazolium chloride^[10]). This behaviour indicates that in the alloy formation range Zn(II) and Cu(II) ions compete for nucleation sites.^[96] XRD analysis indicates that a small amount of both α (which consists of 35 % Zn) and β (corresponding to equimolar Zn and Cu) alloy phases with the intensity of the β phase diffraction line increasing as the deposition potential is made more negative.^[96] This study, the first on Zn-Cu alloy deposition from ionic liquids, showed that Zn-Cu alloy electrodeposition from the chlorozincate systems was feasible and that the composition of the alloy could easily be altered by controlling the electrodeposition parameters.^[96]

Sun *et al.* proceeded to apply the same methodology to a range of Zn alloy and co-deposit systems including Zn-Cd,^[97] Zn-Sn,^[51] Zn-Mg,^[98] and Zn-Pt,^[99] Zn-Co,^[100, 101] Zn-Ni^[102] and Zn-Fe.^[103] Of these systems Zn-Cd and Zn-Sn are best described as co-deposits rather than as homogeneous alloys. Sn and Cd were introduced into ZnCl_2 : 1-methyl-3-ethyl imidazolium chloride by the anodic dissolution of Sn foil and the direct dissolution of CdCl_2 respectively. Co-deposits were obtained *via* potentiostatic electrodeposition and it was found that the Sn/ Cd content of the deposits decreased as the deposition potential was made more negative. In contrast to the Zn-Cu system where true alloy formation was observed,^[96]

in the Cd and Sn containing systems there was no change in nucleation mechanism when the Sn/ Cd was introduced to the system. Nucleation at all potentials studied progressed *via* a 3D instantaneous mechanism for Zn, Sn and Cd. XRD analysis of the Zn-Sn co-deposits confirms that the two metals are present as distinct Zn and Sn phases; this is consistent with the phase diagram of Zn-Sn where only distinct Sn and Zn phases are observed.^[51]

The anomalous co-deposition mechanism dominates in the formation of some Zn alloys in aqueous systems including Zn-Fe,^[104-107] Zn-Ni and Zn-Co.^[108-110] In the anomalous co-deposition mechanism the less noble metal, Zn, is deposited preferentially to the more noble metal, in this case Fe, Ni or Co. Although the mechanisms of this process are not fully understood an oft cited theory is that as hydrogen is evolved at the cathode surface, Zn(OH)₂ precipitates and inhibits the deposition of the more noble metal.^[108] This mechanism means that Zn alloys with high Fe, Ni and Co content can be difficult to produce in aqueous baths. By using the aprotic ionic liquid, 1-ethyl-3-methyl imidazolium, Sun *et al.* were able to obtain Zn-Fe,^[103] Zn-Ni^[102] and Zn-Co^[100] deposits with variable Zn content and it was shown that the deposition occurred *via* a non-anomalous co-deposition mechanism.

3. *Discrete Anion Ionic Liquids*

Before alloy deposition can be carried out from the air and moisture stable ionic liquids it is first necessary to dissolve the metal salts in the ionic liquid. It is often necessary to either add an excess of halide ions to the liquid to form soluble complex metal-halide ions or to electrochemically oxidise the metal in solution.^[111] The range of alloys electrodeposited from air and moisture stable ionic liquids include Pd-Au,^[58] Pd-Ag,^[112] Pd-In,^[57] In-Sn,^[113] Cu-Sn,^[114] and Zn-Mn.^[115]

4. *Surface Dealloying*

The ability of Zn to form surface alloys with some metals has been utilised for the formation of porous metallic materials. Here a surface alloy is formed and the Zn selectively dissolved to leave a porous network of the alloying metal. This process has been used with Zn-Pd,^[116] Zn-Au,^[117] and Zn-Ag. The technique has been used to form high surface area Ag electrodes and these have been shown to have a catalytic effect on the reduction of chloroform.

1.4.4 Semiconductor Electrodeposition

Although still in its infancy, the electrodeposition of semiconductors from ionic liquids is a growing field of interest. The wide thermal range of some systems, combined with large

potential windows has allowed attempts to be made to deposit GaAs,^[118] a system inaccessible from aqueous electrolytes. Although a number of these initial studies showed promise, most electrodeposits to date have been shown to contain both the semiconductor species and the individual elements *e.g.* residual In and Sb in In-Sb deposits from an ionic liquid formed from 1-methyl-3-ethylimidazoliumchloride.^[119]

More recent studies have been more promising. The electrodeposition of Zn-Te has been studied by Lin *et al.*,^[120] here it was demonstrated that Zn-Te could be electrodeposited from basic ZnCl₂: 1-methyl-3-ethylimidazolium chloride. Sun had previously shown that Zn can generally only be plated from acidic ionic liquids^[10] and Te had only previously been electrodeposited effectively from basic melts, due to the formation of tellurium clusters in acidic melts.^[44] To electrodeposit Zn-Te, the melt was therefore modified, first by the addition of propylene carbonate as a co-solvent to reduce the melting point of the melt, and secondly by the addition of 8-quinoline, which acts to shift the reduction of Te(IV) to a more negative potential. This adjustment allowed the underpotential deposition of Zn to occur on Te, at -0.1V. These deposits, when annealed at temperatures between 250 and 400 °C, were found to have an optical band gap of 2.3 eV,^[120] close to the literature values for semiconducting ZnTe.^[121] This study is one of the few to highlight the importance of developing additives for use in ionic liquid electrodeposition processes.

1.4.5 Organic Additives

Few aqueous electrodeposition baths consist of simply the metal salt and solvent. A wide range of additives such as levellers, surfactants and brighteners are generally added to improve the efficiency and characteristics of the deposition process. In aqueous solutions brighteners are generally thought to act in one of two ways, they either complex the metal ions in solution making them more difficult to reduce, or they adhere to the electrode surface, blocking nucleation sites and hindering growth. It is clearly important to investigate how additives function in ionic liquids if they are to become viable replacements for aqueous technologies. However, to date no systematic studies of the effect of brighteners in ionic liquids have appeared in the literature.^[18] The effect of organic additives on the electrodeposition of Zn from deep eutectic solvents is described in detail in **Chapter 4**.

Propylene carbonate has been added to the ZnCl₂: 1-methyl-3-ethyl imidazolium chloride ionic liquid as an organic co-solvent for the electrodeposition of Zn.^[10] This ionic liquid is solid at room temperature and Zn deposits from the pure ionic liquid were found to be needle like and friable.^[10] However, upon the addition of 30 % propylene carbonate the

melting point of the mixture is reduced such that it is liquid at ambient temperatures.^[10] Additionally the Zn deposits obtained in the presence of the co-solvent were adherent, crystalline with increased grain size and with no evidence of needle formation.^[10] Further studies by Sun *et al.* have investigated the effect of propylene carbonate addition on the deposition of Zn-Co alloys from the same ionic liquid.^[100] Here it was seen that no change in morphology was observed upon the addition of 20 % propylene carbonate, the co-solvent simply acting to reduce the viscosity of the melt allowing electrodeposition to be carried out at lower temperatures.^[100]

Hussey *et al.* showed that the quality of Al electrodeposits from acidic AlCl_3 : 1-ethyl-3-methyl imidazolium chloride was improved by the addition of 20 % benzene.^[122] In an analogous study of Ag/ Al alloys in the same melt it was found that benzene inhibited the nucleation of Ag. The addition of benzene to the chlorozincate liquids was also found to inhibit the nucleation of Zn.^[120] These studies highlight the complex nature of additive behaviour in ionic liquids and that a large amount of research is still required to develop a full understanding of their function. It is likely that the suitable additive and concentration will be specific to each metal/ alloy and ionic liquid system.^[18]

1.5 The Development of Deep Eutectic Solvents

1.5.1 Type I Deep Eutectic Solvents

Although a wide range of metals have been electrodeposited from the alkyl ammonium: chloroaluminate ionic liquids, the inherent moisture sensitivity of AlCl_3 has limited their application beyond the laboratory. Recently a new range of ionic fluids has been developed whereby AlCl_3 is replaced by a less reactive metal. Building upon an earlier study where Freeman *et al.* demonstrated that ionic liquids could be formed from FeCl_2 and 1-butyl-3-methylimidazoliumchloride,^[123] initial studies focussed on improving the moisture sensitivity of the alkylammonium: AlCl_3 based ionic liquids, by replacing the chloroaluminate with less reactive metal halides.^[124] In a 2001 study by Abbott *et al.* a range of quaternary ammonium salts were heated with ZnCl_2 and the freezing points of the resulting liquids measured. It was found that the lowest melting point, 23-25 °C, was obtained when choline chloride was used as the ammonium salt.^[124]

This initial study has been extended and Abbot *et al.* have now developed a range of liquids formed from eutectic mixtures of salts and hydrogen bond donors. These liquids are often termed deep eutectic solvents to differentiate them from liquids which contain only discrete anions. The term deep eutectic solvent refers to liquids close to the eutectic composition of

the mixtures and is represented diagrammatically in **Figure 1.4**. The eutectic point of a mixture refers to the molar ratio of the components which gives the lowest melting point.

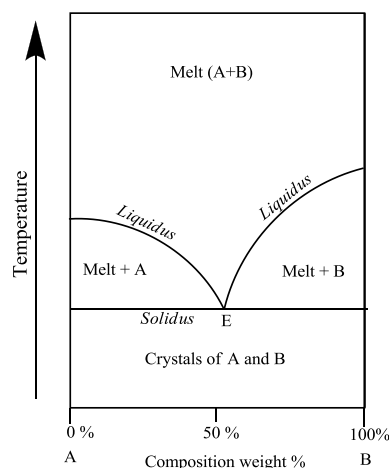


Figure 1.4 Schematic representation of eutectic mixture formation

These liquids can all be described by the general formula $R_1R_2R_3R_4N^+X \cdot zY$ where X is generally a halide ion (often Cl⁻), Y is a complexing agent with z the number of molecules required and $R_1R_2R_3R_4N$ a quaternary ammonium often choline. They are generally separated into three classes:

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

Type II $Y = MCl_x \cdot yH_2O$, $M = Cr,^{[125]} Co, Cu, Ni, Fe$

Type III $Y = RZ$, $Z = CONH_2^{[126]}, COOH,^{[127]} OH$

The ionic liquids formed from $ZnCl_2$ and quaternary ammonium salts, type I, can be considered to be of an analogous type to the well studied metal halide/ imidazolium salt systems. Examples of type I eutectics include the well studied chloroaluminate/ imidazolium salt melts and less common ionic liquids formed with imidazolium salts and various metal halides including $FeCl_2$,^[123] and those featured in Scheffler and Thomson's study with EMIC and the following metal halides $AgCl$, $CuCl$, $LiCl$, $CdCl_2$, $CuCl_2$, $SnCl_2$, $ZnCl_2$, $LaCl_3$, YCl_3 , and $SnCl_4$.^[128]

1.5.2 Type II Deep Eutectic Solvents

The range of non-hydrated metal halides which have a suitably low melting point is limited; however the scope of this class of deep eutectic solvents can be increased by using the hydrated metal halides. Type II eutectics are those formed from hydrated metal halides and choline chloride. This class of liquid has been used to deposit non-microcracked Cr, an

industrially important metal, the aqueous electrodeposition of which is becoming restricted by recent legislation.^[125] Here, a liquid was formed from a 1: 2 molar ratio mixture of choline chloride and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. It was not possible to form the liquid from a mixture of anhydrous CrCl_3 and 6 molar equivalents of water suggesting that the coordination sphere of the Cr is important in the formation of the liquid. It also suggests that this system is not simply a concentrated aqueous solution and in fact is ionic liquid like in character. A further study demonstrated the importance of the cationic species as a grain modifier. Upon the addition of LiCl nanocrystalline black chromium was obtained.^[129] The relatively low cost of many hydrated metal salts coupled with their inherent air/ moisture insensitivity makes their use in large scale industrial processes viable.

1.5.3 Type III Deep Eutectic Solvents

Type III Eutectics, formed from choline chloride and hydrogen bond donors, have been of interest due to their ability to solvate a wide range of transition metal species, including chlorides^[126] and oxides.^[126, 130] A range of hydrogen bond donors have been studied to date, with deep eutectic solvents formed using amides, carboxylic acids and alcohols. These liquids are simple to prepare, relatively unreactive with water, many are biodegradable and are relatively low cost. The wide range of hydrogen bond donors available means that this class of deep eutectic solvents is particularly adaptable. The physical properties of the liquid are dependent upon the hydrogen bond donor and can be easily tailored for specific applications. Although the potential windows are significantly smaller than those for some of the imidazolium salt-discrete anion ionic liquids, they are sufficiently wide to allow the deposition of metals such as Zn with high current efficiencies. A number of publications have demonstrated the applicability of this class of deep eutectic solvents as electrodeposition media for a range of transition metals and alloys including Cu, Ni^[73], Ag^[71], Zn^[131] and Zn-Sn^[72].

The deep eutectic solvent, 1: 2 ChCl: ethylene glycol, has also been used to electropolish stainless steel, **Figure 1.5** shows the large reduction in surface roughness of a 316 stainless steel sheet after 25 minutes of electropolishing at 25 mAcm^{-2} in this deep eutectic solvent.^[132] This class of deep eutectic solvents have been shown to be particularly versatile, with a wide range of possible applications investigated including the removal of glycerol from biodiesel,^[133] processing of metal oxides^[130] and the synthesis of cellulose derivatives.^[134]

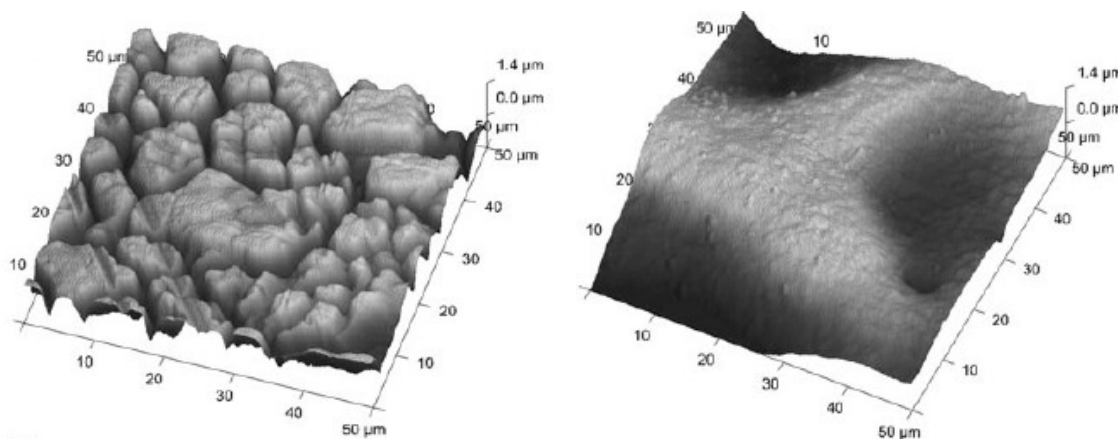


Figure 1.5 Atomic force micrographs of a 316 stainless steel sheet, (a) unpolished and (b) after 25 minutes electropolishing at 25 mA cm^{-2} in 1: 2 ChCl: ethylene glycol. Reprinted with permission.^[132]

1.5.4 Type IV Deep Eutectic Solvents

The majority of ionic liquids which are fluid at ambient temperatures are formed using an organic cation, generally based around ammonium, phosphonium and sulphonium moieties. Inorganic cations generally do not form low melting point eutectics due to their high charge density, however, previous studies have shown that mixtures of metal halides with urea can form eutectics with melting points of $< 150^\circ\text{C}$.^[135, 136] Abbott *et al.* have built upon this work and shown that a range of transition metals can be incorporated into ambient temperature eutectics. It would be expected that these metal salts would not normally ionise in non-aqueous media, however ZnCl_2 has been shown to form eutectics with urea, acetamide, ethylene glycol and 1,6-hexanediol.^[137]

In order to understand the behaviour of the eutectics it is imperative to have an understanding of the metal species present in the system. Preliminary speciation studies using Fast Atom Bombardment Mass Spectrometry, FAB-MS, have suggested that these liquids contain both Zn cations and anions.^[137] This is significant as it would be expected that Zn cations will be present in the electrochemical double layer at cathodic potentials altering the electrodeposition process.^[137]

The physical properties of the eutectics have been described and it was observed that they have similar properties to other classes of ionic liquid and that these can be effectively modelled with hole theory.^[137] This theory dictates that the viscosity of an ionic liquid is controlled by the availability of voids or holes in the system.^[138] When a mixture melts, voids are formed and these are of a random size and orientation. The theory states that an ion can only move through an ionic liquid if the ion is adjacent to a hole of equal or greater size.^[138] The high viscosity of ionic liquids can therefore be considered to be due to a

relatively large ion to hole radius ratio, the radii of the voids can be calculated from the surface tension of the liquid using **Equation 1.1**^[138]

$$4\pi(r^2) = 3.5 \frac{kT}{\gamma} \quad \text{Equation 1.1}$$

Where r is the void radii, k the Boltzmann constant, T the temperature and γ the surface tension. An estimation of the ion radii was then made by modelling the species predicted by the FAB-MS.^[137] If the viscosity of a liquid is limited by the availability of suitably sized holes the activation energy of viscous flow should be proportional to $R_{+/-}/R_h$, the ratio of cation/anion radius and average void radius. **Figure 1.6** demonstrates the good degree of correlation between these quantities for the classical molten salts, a range of molecular and ionic liquids and the type IV deep eutectic solvents.^[137]

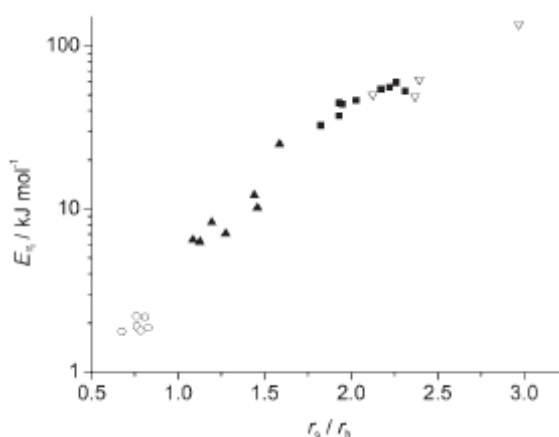


Figure 1.6 Energy of activation for viscous flow as a function for ion to hole radius ratio for molten salts (clear circles), molecular liquids (black triangles), ionic liquids (black squares), type IV deep eutectic solvents (clear triangles).^[137]

It is shown that a characteristic feature of ionic liquids is a large activation energy for viscous flow, E_η , and that this results from the energy required to form and enlarge the voids required for the movement of large bulky asymmetrical ions throughout the liquid.^[137]

The electrochemistry of the urea and ethylene glycol based systems was briefly described and they were shown to have potential windows of around 2.0 V, limited in the cathodic region by Zn deposition and in the anodic region by chlorine evolution.^[137] This is similar to that found for the ZnCl_2 : ChCl eutectic, despite the difference between Zn mole fraction and speciation in the liquids. The main difference between the Zn electrodeposition processes in the type I and type IV eutectics is that the Zn oxidation process is much more reversible in the former. It is proposed that the difference in reversibility is due to a difference in ionic speciation in the electrochemical double layer. In the $\text{ChCl}/\text{ZnCl}_2$

system there will be significantly more free Cl^- ligands available to re-complex the deposited Zn.

The ZnCl_2 / hydrogen bond donor eutectics have been shown to be suitable for bulk Zn electrodeposition and an example of a homogeneous, crystalline Zn deposit from the ZnCl_2 : acetamide eutectic is shown in **Figure 1.7**.^[137]

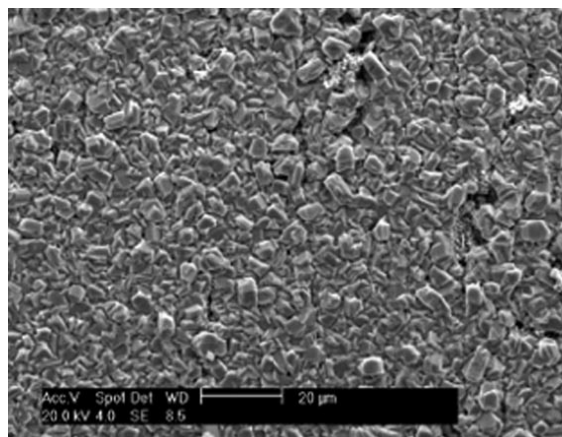


Figure 1.7 Scanning electron micrograph of Zn deposited on Ni from 1: 4 ZnCl_2 : Acetamide at 10 mA cm^{-2} for 20 minutes, reprinted with permission.^[137]

1.6 Industrial and Commercial Applications of Ionic Liquids

In the past decade ionic liquid technologies have begun to move from the laboratory into the industrial world. Perhaps the most well known example is the BASIL process (Biphasic Acid Scavenging utilizing Ionic Liquids), patented in 2002. In this process, the properties of ionic liquids are utilised to improve the efficiency of a reaction. The process is used for the synthesis of alkophenylphosphines, where HCl is formed as an unwanted by-product. Traditionally the HCl is scavenged by a tertiary amine; however, this leads to the formation of a non-stirrable slurry, lowering the yield of the process. By adding the ionic liquid precursor 1-methylimidazole, in place of the tertiary amine, the acid base reaction generates an easily separable ionic liquid phase, 1-methylimidazolium chloride. The productivity of the initial reaction has been shown to have increased by a factor of 8×10^4 , through the incorporation of the ionic liquid forming step.

Although the BASF process was the first ionic liquid process to be commercialised, the first ionic liquid plant was operated by IFP (Institut Français du Pétrole).^[8] Alkenes such as propene and butenes can be dimerised to the more valuable branched hexenes and octenes *via* the Dimerasol process. This process is catalysed using a cationic Ni complex of the form, $[\text{LNiCH}_2\text{R}']$, and is generally conducted without solvent, although the Ni catalyst has been shown to have greater activity when dissolved in aromatic and halogenated

hydrocarbons.^[139] IFP has pioneered the use of chloroaluminate ionic liquids as the solvent in this Ni catalysed reaction. With the addition of the chloroaluminate ionic liquid the reaction proceeds as a biphasic process, at temperatures between -15 °C and 5 °C, the products forming an easily separable second layer whilst the Ni catalyst remains preferentially dissolved in the ionic liquid. This process, when added to the Dimerasol reactor, improves upon the solvent-free and organic solvent containing processes by reducing catalyst waste, increasing dimer selectivity and producing a higher yield even with low concentrations of feedstock.

More recently metal processing technologies have moved closer to becoming industrially viable. The electropolishing of stainless steel is used to improve corrosion resistance and wear. Current aqueous protocols use sulphuric and phosphoric acid mixtures, these solutions are both dangerous to handle and must be neutralised before disposal. Aqueous electropolishing of mild steel is also a highly inefficient process, whereby only between 10 and 20 % of the applied current is utilized for metal dissolution. Electropolishing of mild steel using a type III deep eutectic solvent, 1: 2 ChCl: ethylene glycol, has been reported to be possible with a high current efficiency (> 80 %). The oxidised metal has also been shown to form insoluble complexes in the liquid; these settle at the bottom of the electropolishing bath and can be periodically removed. This process is presently being trialled on a 1200 L scale.

Although at present most electrodeposition protocols from ionic liquids are prohibitively expensive when compared to the equivalent aqueous processes, changes in legislation may make ionic liquids more economically attractive. For example, the electrodeposition of Cr is currently carried out with chromic acid electrolytes containing hexavalent chromium. The toxicity and carcinogenic nature of Cr (VI) has led to a range of legislation limiting its use in the USA and EU. The reduction of Cr (VI) also generally has a low current efficiency, and occurs alongside hydrogen evolution, leading to deposit cracking and embrittlement. The development of a deep eutectic solvent, containing Cr (III) species, which operates with a Cr deposition current efficiency of > 90 %, shows promise as a suitable replacement for aqueous systems. The use of a non-aqueous solvent has the added benefit of reducing the amount of hydrogen evolution, leading to non-microcracked deposits.

1.7 Summary

The field of ionic liquids has developed from a relatively niche field of interest, to one where in excess of 1000 papers are published annually. Zn is an important metal, whose

electrochemical behaviour is well studied in the chloroaluminate and chlorozincate ionic liquids. However few studies have attempted to understand the relationship between metal speciation, the physical properties of the melt, the morphology of the deposits and the electrochemical behaviour of the system. The development of the ChCl based deep eutectic solvent systems represents a real opportunity to develop economically viable replacement electrodeposition technologies for aqueous electrodeposition baths. This thesis will contain the first in-depth study of Zn deposition from ChCl based deep eutectic solvents, demonstrating their viability as electrodeposition media. The relationship between speciation, nucleation mechanism and deposit morphology will be explored. The effect of a range of additives on the Zn electrodeposition process will be investigated and the alloying behaviour of Zn with a series of transition metals will be characterised.

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Chapter 2: Experimental Procedures

2.1 Introduction

2.2 Materials

2.3 Electrochemical Methodology

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2.5 Surface Analysis

2.5.1 AFM

2.5.2 SEM and EDX

2.5.3 XRD

2.5.4 EXAFS

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2.1 Introduction

This chapter contains the standard experimental conditions and protocols used throughout this thesis. The theory underlying standard electrochemical techniques are not described in detail; however a theoretical overview of the less well known technique of Electrochemical Quartz Crystal Microbalance, EQCM, is given.

2.2 Materials

Choline chloride ($\text{HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$) ChCl was recrystallised from absolute ethanol (Aldrich 99%), filtered and dried under vacuum. Ethylene glycol (Aldrich) and urea (Aldrich) were used as received. The deep eutectic solvents were formed by mixing the two components together (in a 1: 2 molar ratio of ChCl: hydrogen bond donor) and heating, with stirring, at 60 °C until a homogeneous colourless liquid was formed.

The metal halide salts ZnCl_2 (Aldrich $\geq 98\%$), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich $\geq 98\%$), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich $\geq 98\%$), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich $\geq 98\%$) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich $\geq 98\%$) were used as obtained. Solutions were generally made up to a metal halide concentration of 0.3 mol dm^{-3} unless otherwise stated.

The organic additives acetonitrile (Fischer Scientific), ethylene diamine (Aldrich), ammonia (30 % aqueous solution, Aldrich) and the surfactants hexacetylammoniumbromide (Aldrich) and sodiumdodecylsulphate (Aldrich) were used as received. Generally, the organic additives were added to the Zn electroplating bath to a concentration of 0.3 mol dm^{-3} .

2.2 Electrochemical Methodology

An Autolab micropotentiostat controlled by GPES2 software was used for electrochemical experiments. The electrochemical experiments were carried out using a three electrode electrochemical cell consisting of a Pt disc (0.5 mm dia.) working electrode, Pt mesh counter electrode and a Ag wire pseudo-reference electrode. Unless otherwise noted all electrochemical experiments were carried out at 50 °C. Additionally, cyclic voltammograms were obtained at 5 mV s^{-1} unless otherwise stated.

Working electrodes were cleaned between each experiment by rinsing with deionised water, polishing with alumina paste, sonicating (5 minutes) in deionised water and drying with N_2

Bulk electrodepositions were generally conducted on mild steel cathodes, which were first manually polished with progressively finer grades of silicon carbide polishing paper, rinsed with water, etched in 30% HCl, rinsed in water, degreased in dichloromethane and dried

with N₂. A dimensionally stable Iridium oxide coated Ti mesh anode was used for bulk electrodeposition unless otherwise stated. All bulk electrodepositions were carried out at 50 °C and at a constant current density of 3 mA cm⁻² except where otherwise noted.

2.4 EQCM

As reduction and oxidation take place during an electrochemical reaction, mass changes may occur at the electrode surface due to deposition or dissolution of a solid phase. These mass changes can be measured using the electrochemical quartz crystal microbalance. The electrochemical quartz crystal microbalance utilizes the piezoelectric nature of quartz crystal to monitor mass changes at the electrode surface.

The application of an electric field to the quartz crystal causes a strain or shear deformation. This strain occurs due to the realignment of dipoles in the crystal structure with the electric field. The application of an alternating electric field, at a characteristic frequency of the quartz, therefore causes the crystal to resonate. The deposition of a mass on the crystal surface shifts the resonant frequency and this can be measured.

Experimentally the change in mass at the crystal surface corresponds to a change in the resonant frequency of the crystal, Δf , from its fundamental value, f_0 . The change in mass, Δm , can therefore be calculated from the change in resonant frequency using the Sauerbrey equation, **Equation 2.1**

$$\Delta f = -\frac{2f_0^2}{\rho v} \Delta m \quad \text{Equation 2.1}^{[1]}$$

where ρ is the density of quartz and v the wave velocity. The Sauerbrey equation can only be used to accurately calculate mass changes if the deposited mass behaves as a rigid resonator. If the deposited mass is non-rigid the frequency shift will be less than that predicted by the Sauerbrey equation and can therefore not be accurately measured.^[2]

Acoustic impedance EQCM experiments were performed using working electrodes consisting of thin Au (without Ti or Cr binding layer) evaporated onto 10 MHz quartz crystals (International Crystal Manufacturing Co., Oklahoma City, USA.). The Au coated quartz crystals were unpolished. The piezoelectric active area of the crystals was 0.23 cm². The crystal impedance spectra were recorded using a Hewlett Packard 87512A transmission/ reflectance unit via a 50 Ω coaxial cable such that the centre of the recorded spectra was close to the resonant frequency, f_0 , of the crystal (*ca.* 10 MHz).

The measured data were fitted to a Lorentzian equivalent circuit model, **Equation 2.2**, incorporating the in-phase impedance, inductance and centre frequency, with an iterative difference method using Microsoft Excel. The fitting procedures used are described in depth in the literature. In order to improve the temporal resolution, network analyser data acquisition was controlled by a computer running HP VEE. This program was capable of recording admittance spectra every 2-3 s. The crystal was placed into a cell such that one face of the crystal was exposed to the solution and one face was exposed to air. The three electrode electrochemical cell was completed with a Pt mesh counter electrode. EQCM experiments were carried out at room temperature (typically 20-23 °C) except where otherwise stated.

$$U(f) = a + ((R)/(R^2 + 16\pi^2 L^2 (f-f_0))) \quad \text{Equation 2.2}$$

Where $U(f)/\Omega^{-1}$ is the measured admittance curve as a function of applied frequency f/Hz (and $U(f) = 1/Z(f)$), R/Ω is the real component of the impedance (Z), L/Henry is the inductance, f_0/Hz is the centre frequency and a/Ω^{-1} is the baseline offset. The latter was used during fitting to compensate for variations in the static calibration of the network analyser.

2.5 Surface Analysis

2.5.1 AFM

Atomic force Micrographs were acquired using a Digital Instruments (DI) Nanoscope IV, Dimension 3100 instrument using resonant tapping or contact mode. A novel application of the AFM, as a combined *in-situ* AFM-EQCM is described in detail in **Chapter 3**.

2.5.2 SEM and EDX

Surface analysis with SEM and elemental analysis by EDX were carried out using a PhillipsXL30 ESEM instrument with an accelerator voltage of between 15 and 20 keV, giving an average beam current of ca. 120 μA . Gold sputtered coating was not required due to the inherently conductive nature of the surfaces studied.

2.5.3 XRD

Powder X-ray diffraction was conducted using a Phillips model PW 1730 X-ray generator, with a PW 1716 diffractometer and PW 1050/25 detector. The X-ray tube was a long fine focus Cu anode with Ni $K\alpha$ filtered radiation. Typical operating conditions were 40 KV, 30

mA scanned between 15 and 110° 2 θ with a step size of 0.02° 2 θ . Angle calibration was carried out using a synthetic Si sintered standard.

2.5.4 EXAFS

EXAFS spectra were obtained at the zinc K edge (nominally at 9659 eV) on station 16.5 of the Synchrotron Radiation Source, Daresbury Laboratory using fluorescence detection by a 30 element solid state detector. The spectra were summed, calibrated and background subtracted using the programs EXCALIB and EXBACK. The EXAFS spectra were then fitted using EXCURV98. This program calculates electron scattering parameters for the atoms in the sample using the Hedin-Lundqvist potential. It provides fitted values of interatomic distances (from the Zn atom) R , coordination numbers N , atomic type and the root mean square variation in interatomic distance σ^2 for the scattering atoms included in the fit. There is also an energy offset E_0 corresponding to the energy between the mean potential in the sample and the energy of the lowest unoccupied molecular orbital (E_0 is always negative as defined in the program). EXCURV98 also provides estimates of the uncertainty in these fitted parameters and an overall goodness of fit.

2.6 Physical properties

Viscosity measurements were obtained using a Brookfield DV-E Viscometer fitted with a thermostatted jacket. Conductivities were obtained using a Jenway 4071 conductivity meter. Surface tension measurements were made using a Kruss K11, fitted with a thermostatted jacket, via the plate method. All physical properties measurements were made at 25 °C, the temperature controlled by a thermostatted water bath.

2.7 References

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Chapter 3: The Electrodeposition of Zn from Deep Eutectic Solvents

3.1 Introduction

3.2 Results and Discussion

3.2.1 Physical Properties

3.2.2 Zinc Speciation

3.2.3 Cyclic Voltammetry

3.2.4 Gravimetric Analysis

3.2.5 Nucleation Mechanism

3.2.6 *In-Situ* AFM-EQCM

3.3 Summary

3.4 References

3.1 Introduction

Zn and its alloys are industrially important materials and are widely used as anticorrosion coatings for ferrous substrates, particularly in the automotive industry. Electrodeposition is a cost-effective method of coating formation with the additional advantage that deposit thickness and morphology can be easily controlled by altering the electrodeposition parameters such as current density, temperature, and electrode geometry. Zn electrodeposition or galvanization is traditionally conducted in either acidic or alkaline aqueous electrolytes, depending upon the cathode material and deposit application.

Alkaline Zn electrodeposition baths are formed from the zinc cyanides such as sodium zinc cyanide. Cast iron and high carbon steels can generally not be deposited from zinc cyanide solutions. Carbon inclusions lower the overvoltage at which hydrogen evolution occurs, leading to hydrogen embrittlement at the negative overpotentials required for Zn deposition. For this reason zinc plating from aqueous solutions of steel pieces used for support or other high strength purposes is restricted by legislation.

Acidic electrodeposition baths are commonly based upon zinc sulphate or zinc chloride. The chloride based baths tend to have current densities close to the theoretical maximum but reduced throwing power. Although aqueous acidic Zn electrodeposition solutions are classical electrolytes it is only relatively recently that the relationship between the electrochemical nature and deposit morphology has been explored.

Ionic liquids offer an interesting alternative to the traditional aqueous electrodeposition solutions. They have intrinsically high metal concentrations, are highly conducting and perhaps most importantly for Zn electrodeposition are usually aprotic. Since the 1980s this intriguing class of fluid has been the subject of an intensive, sustained research effort and their application to metal electrodeposition has recently been reviewed.^[1-4] Further general information concerning the electrodeposition of metals from ionic liquids can be found in **Chapter 1**.

The most widely studied ionic liquid systems are those formed from the chloroaluminates and alkylimidazolium salts. Zn has been electrodeposited from a range of ionic liquids, particularly the zinc based imidazolium systems^[5-8] and solutions of anhydrous ZnCl₂ in chloroaluminate imidazolium melts.^[9, 10] In the most part these

studies have been aimed at the preparation of nano-porous surfaces where zinc deposition and subsequent stripping contributes to surface roughening and alloy formation. Critically, these liquid systems are highly moisture sensitive, require handling under an inert atmosphere and are economically expensive to produce in comparison to their aqueous counterparts.

Although many metals have been deposited from several different ionic liquids it remains the case that relatively little is known about the underlying science, in contrast to the corresponding aqueous systems. In particular little is known about the double layer structure in ionic liquids, how the double layer responds to changes in potential, metal speciation and current density and the detailed mechanisms of nucleation and growth remain unresolved. Here the results of an in depth study on zinc electrodeposition from ionic liquids based on eutectic mixtures of choline chloride (ChCl) with either ethylene glycol or urea are presented.

These liquids, also known as deep eutectic solvents, are comprised of the large, unsymmetrical, choline cation and a complex anion formed between $[Cl]^-$ and a hydrogen bond donor. A wide range of such liquids have been reported using diverse H-bond donors such as amides, alcohols and carboxylic acids.^[11, 12] These liquids differ from more conventional ionic liquids *e.g.* chloroaluminate salts, in that they are both air and moisture stable.^[13] Additionally, some of these liquids have begun to find industrial applications *e.g.* commercial electropolishing, as replacement technologies for aqueous processes that often require strong inorganic acids or toxic co-ligands.^[14] In previous studies Abbott *et. al.* have characterised the physical properties of these liquids, *e.g.* viscosity and conductivity,^[15, 16] and more recently have expanded their research to the characterisation of alloys electrodeposited from mixed systems.^[17] The electrodeposition of metals in this type of ionic liquids has been recently reviewed.^[1]

The focus of this study has been the deposition of zinc coatings, for corrosion protection, from moisture stable ionic liquids aimed at replacement technologies for current aqueous electrolytes (note that the terms ionic liquid and deep eutectic solvents (DES) will be used interchangeably throughout this thesis). The choline chloride based ionic liquids contain a high concentration of $[Cl]^-$ that tends to minimise the role of ambient moisture such that even a relatively high water content (from aerobic absorption) does not noticeably effect the electrolytic deposition process of metals, including zinc. Whilst the liquids were formulated at a temperature of 70 °C the

subsequent ZnCl_2 depositions were carried out at lower temperatures ($50\text{ }^\circ\text{C}$) where water content is $< 3\text{ wt } \%$. These conditions are easily maintained for a commercial or technical zinc deposition process consequently rigorous drying of the ZnCl_2 starting material is not required. This chapter focuses on the fundamental aspects of zinc nucleation and growth under these conditions in choline chloride based ionic liquids using electrochemical methods (cyclic voltammetry, chronoamperometry) together with surface probe microscopy and acoustic impedance spectroscopy using an electrochemical quartz crystal microbalance (EQCM).

3.2 Results and Discussion

Numerous groups have studied the deposition of metals in a wide variety of different ionic liquids. While the majority of the metals in the main block of the Periodic Table have been investigated the studies for most metals are limited to a superficial study of nucleation mechanism without considering aspects such as speciation and mass transport. In a recent review the aspects influencing metal electrodeposition were examined and all of these will be discussed for the first time in this chapter.^[1]

3.2.1 Physical Properties.

In the majority of ionic liquid electrodeposition studies to date, little consideration has been given to the effect the addition of metal salts has upon the physical properties of the solvent. **Figures 3.1 – 3.3** demonstrate that the addition of ZnCl_2 has a clear effect on the viscosity, conductivity and density of the deep eutectic solvents 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol. It is therefore imperative that any discussion of electrodeposition from these systems gives due consideration to the effect on physical properties of the inclusion of a solute.

Figure 3.1 (a) shows the viscosity of 1: 2 ChCl: urea as a function of ZnCl_2 concentration. The corresponding data for the analogous ethylene glycol based eutectic are presented in **Figure 3.1 (b)**. Upon the addition of ZnCl_2 the viscosity of both systems is observed to decrease. However, there is a clear difference in the behaviour of the two solvents. The viscosity of the urea based eutectic rapidly decreases as the concentration of ZnCl_2 is increased. The addition of increasing amounts of solute leads to a significant reduction in viscosity, with a 65 % fall upon the addition of 0.3 mol dm^{-3} ZnCl_2 . Conversely, the viscosity of the ethylene glycol containing eutectic is relatively insensitive to changes in ZnCl_2 concentration.

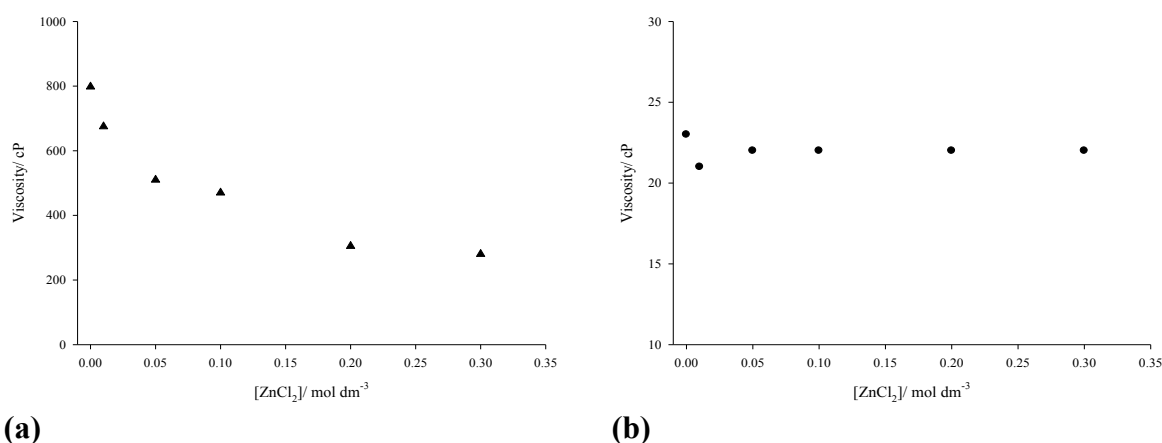


Figure 3.1 The viscosity of (a) 1: 2 ChCl: urea and (b) 1: 2 ChCl: ethylene glycol as a function of ZnCl_2 concentration, at 25 °C

The corresponding change in conductivity with respect to increasing ZnCl_2 concentration is presented in **Figures 3.2 (a)** 1: 2 ChCl: urea and **(b)** 1: 2 ChCl: ethylene glycol. Here, the conductivity of the urea based eutectic gradually increases as a function of ZnCl_2 concentration. However, the conductivity of 1: 2 ChCl: ethylene glycol is, in an analogous manner to the viscosity, relatively insensitive to changes in ZnCl_2 concentration. In aqueous solutions molar conductivity is generally observed to decrease, due to ionic atmosphere and ion pairing effects, as the electrolyte concentration is increased.^[18]

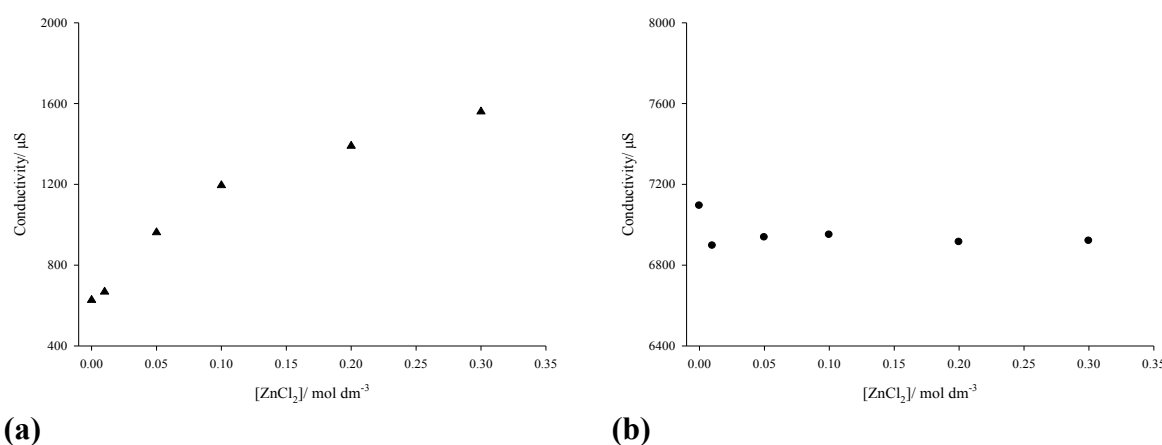


Figure 3.2 The conductivity of (a) 1: 2 ChCl: urea and (b) 1: 2 ChCl: ethylene glycol as a function of ZnCl_2 concentration, at 25 °C

As discussed in **Chapter 1**, the viscosity and conductivity of ionic liquids are bulk physical properties which can be considered to result from the relative mobility of the ionic species present. However, few attempts have been made to accurately model the mass transport properties of ionic liquids at ambient temperatures. Research into this area has been hindered by the complexity of the ionic interactions in ionic liquids. Nevertheless, it has

been shown that the empirical Walden rule, **Equation 3.1**, is applicable to ionic liquids. Where Λ = the molar conductivity and η = the viscosity of the fluid.^[19]

$$\Lambda\eta = \text{Constant} \quad \text{Equation 3.1}$$

A model which has been demonstrated to accurately predict the viscosities and conductivities of ionic liquids and deep eutectic solvents is hole theory.^[15, 16, 20] The central assumption of hole theory is that as a solid melts, voids of random size and orientation are formed. The ability of an ion to move is therefore considered to be dependent upon the presence of an adjacent void of an equal or greater size than the ion. The probability of ion motion can therefore be considered to be a product of the size of the ions in consideration and the relative population of suitably sized holes.

The mass transport properties of a range of ionic liquids and deep eutectic solvents have been calculated using hole theory and show a strong degree of correlation with experimentally obtained values.^[15, 20] This correlation suggests that mass transport in ionic liquids, which contain bulky asymmetric ions, is primarily controlled by the availability of suitably sized holes. This is in contrast to the classical molten salts, which are generally composed of small symmetric ions, where mass transport is principally controlled by the concentration of charge carriers.^[15]

The effect of ZnCl_2 addition on the mass transport properties of the two solvents could be due to either a difference in Zn speciation or a lattice disruption effect. Ethylene glycol is known to be a relatively weak hydrogen bond donor and this is evidenced by the relative fluidity of 1: 2 ChCl: ethylene glycol.^[16] Urea is a much stronger hydrogen bond donor and as such 1: 2 ChCl: urea is around 10 times as viscous as 1: 2 ChCl: ethylene glycol.^[11] The surface tension of 1: 2 ChCl: urea is also known to be higher than that of 1: 2 ChCl: ethylene glycol and this has been ascribed to stronger hydrogen bonding and hence decreased average void size in the urea containing eutectic.^[15] The addition of ZnCl_2 may act to disrupt the hydrogen bonding network in the solvent leading to an increase in average void magnitude and hence an increase in mass transport. Conversely, the relatively weak hydrogen bonding in the ethylene glycol based solvent, which already contains a higher proportion of larger voids, would be less susceptible to disruption upon the addition of a solute.

The density of the two deep eutectic solvents follows the expected trend of increasing as a function of ZnCl_2 concentration and is presented in **Figure 3.3 (a)** 1: 2 ChCl: urea and **(b)** 1: 2 ChCl: ethylene glycol.

An additional point of interest arises if we consider that the addition of ZnCl_2 to 1: 2 ChCl: urea could be viewed as a hybrid of the 1: 2 ChCl: ZnCl_2 and the 4: 1 urea: ZnCl_2 deep eutectic solvents. Given that the viscosities of both of these liquids are over 1000 cP at 25 °C it is interesting to see that the viscosity of the hybrid is considerably lower.^[21]

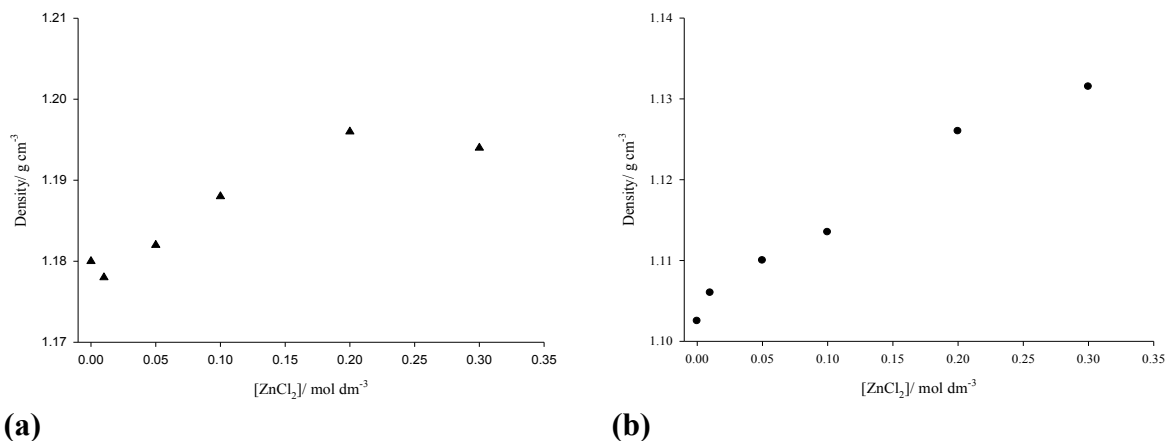


Figure 3.3 The density of (a) 1: 2 ChCl: urea and (b) 1: 2 ChCl: ethylene glycol as a function of ZnCl_2 concentration, at 25 °C

3.2.2 Zinc Speciation

Mass Spectrometry

As discussed in 3.2.1 the physical properties of deep eutectic solvents are dependent upon both the ionic speciation and the internal interactions of the liquid components. However, the speciation of metals dissolved in ionic liquids is comparatively understudied and this oversight has been highlighted in a number of recent reviews.^[22, 23] It is perhaps the difficulty in obtaining unequivocal results in these liquids that has so far limited research in this area.

Mass spectrometry has been used in an attempt to garner Zn speciation data for the dissolution of ZnCl_2 in 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol. The results showed that only anionic Zn species are formed in both solvents. However, the identity of the Zn anions differed between 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol. In the urea based deep eutectic solvent the only zinc containing species present was found to be ZnCl_3^- , whereas in the ethylene glycol based solvent, higher anionic Zn clusters such as Zn_2Cl_5^- and Zn_3Cl_7^- were also detected. In both cases the only cationic species detected by this method was the choline cation, $[\text{Ch}]^+$. The most probable explanation for the observed differences between the Zn species in these two liquids is the difference in ligand strength of the two complexing agents. Urea would be expected to act as a far stronger ligand, stabilising ZnCl_3^-

, whereas the relatively weak ligand ethylene glycol would enable the formation of higher metal clusters to become favourable.

Zinc speciation in the related 2: 1 ChCl: ZnCl₂ and 4: 1 urea: ZnCl₂ has also been investigated using mass spectrometry. It was found that 2: 1 ChCl: ZnCl₂ contained complex zinc anions, including [ZnCl₃]⁻, [Zn₂Cl₅]⁻, [Zn₃Cl₇]⁻ and a number of higher clusters at very low intensities. The only cationic species was found to be [Ch]⁺.

Intriguingly the DES formed from 4: 1 urea: ZnCl₂ was found to contain both Zn anions and cations.^[21] In this system [ZnCl₃]⁻, [Zn₂Cl₅]⁻ and [Zn₃Cl₇]⁻ were detected; ions that were also present in the ChCl: ZnCl₂ eutectic. However, unlike the ChCl based liquid, the mass spectrometry data also suggested the presence of Zn cations. Signals that were characteristic of a Zn isotope-splitting pattern were observed at $m/z = 159, 219$ and 279 and these were determined to be due to the presence of the following [ZnCl]⁺ based cations, [ZnCl(urea)]⁺, [ZnCl(urea)₂]⁺ and [ZnCl(urea)₃]⁺.^[21] It is interesting to note that both these systems will have a lower proportion of free chloride ions than the corresponding ZnCl₂ containing ChCl: hydrogen bond donor deep eutectic solvents. It is therefore logical to conclude that a lack of available free chloride ions will lead to the favourable formation of higher metal clusters.

It must be noted that mass spectrometry is an inherently destructive *ex-situ* technique and as such is not an ideal technique for probing liquid phase structure. Although useful in identifying possible differences between the metal species in various deep eutectic solvents, the technique is perhaps not suitable for accurately identifying the metal species. For example, the higher Zn species observed by this technique may simply be the result of fragmentation artefacts. It is therefore necessary to further probe the speciation of the dissolved ZnCl₂ using a technique which is both *in-situ* and non-destructive.

EXAFS

A few groups have used EXAFS as a technique to determine speciation in ionic liquids and this area of research has recently been reviewed by Hardacre *et al.*^[24] EXAFS appears to be a useful technique for solution phase speciation investigations, allowing metal speciation to be elucidated *in situ* and non-destructively. **Figure 3.4** contains the data from the first study of dissolved metal speciation in this class of deep eutectic solvent.

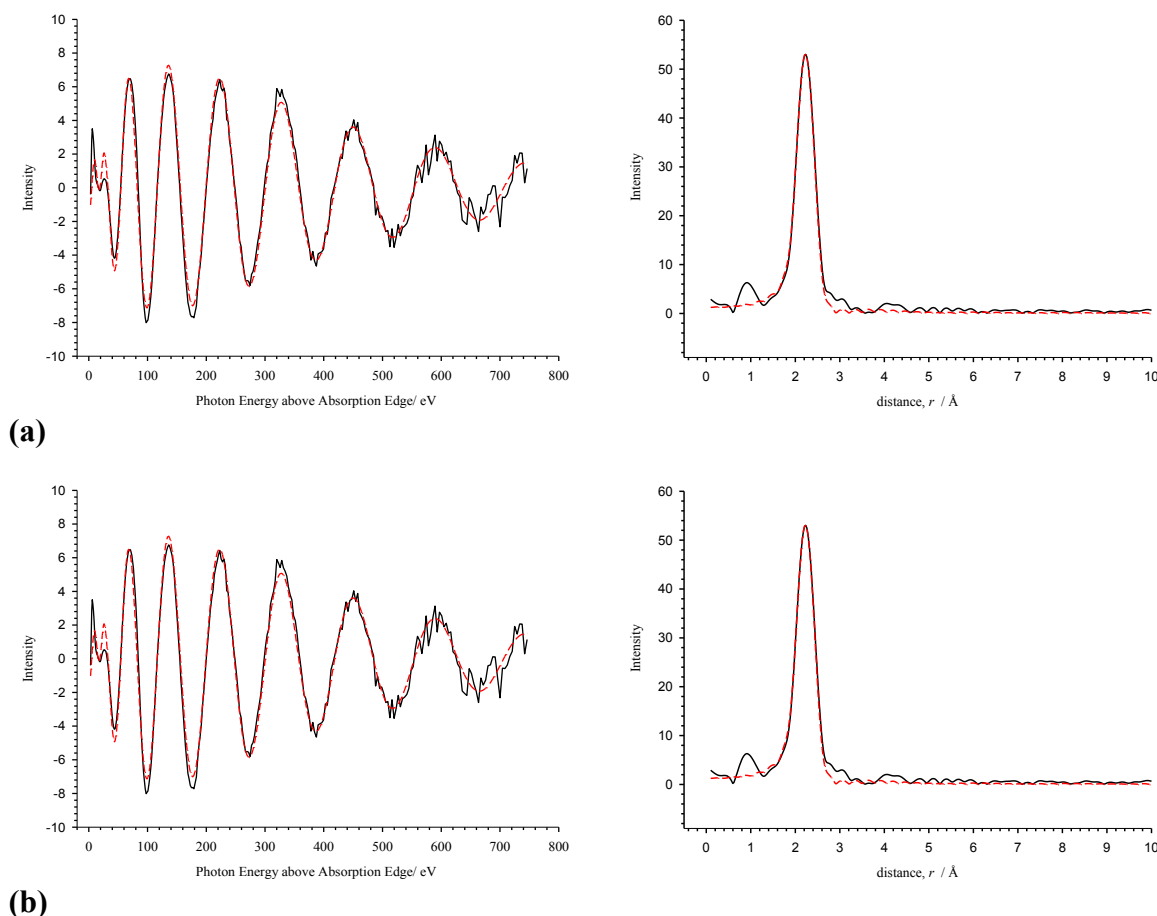


Figure 3.4 EXAFS spectra obtained at the Zn-K-Edge of 0.3 mol dm^{-3} ZnCl_2 in **(a)** 1: 2 ChCl: urea and **(b)** 1: 2 ChCl: ethylene glycol.

Figure 3.4 shows X-ray absorption data obtained at the Zn K edge (9659 eV) for ZnCl_2 dissolved in **(a)** 1: 2 ChCl: urea and **(b)** 1: 2 ChCl: ethylene glycol. The absorption edge has been omitted for clarity. The experimental data is represented by the black trace, the red trace is the calculated best fit used to estimate structural parameters. The EXAFS spectra were fitted using EXCURV98, allowing electron scattering parameters for the atoms in the sample to be calculated using the Hedin-Lundqvist potential. **Table 3.1** shows fitted values of interatomic distances (from the Zn atom) R , coordination numbers N , atomic type and the root mean square variation in interatomic distance σ^2 for the scattering atoms included in the fit. There is also an energy offset, E_0 , corresponding to the energy between the mean potential in the sample and the energy of the lowest unoccupied molecular orbital (E_0 is always negative as defined in the program). EXCURV98 also provides estimates of the uncertainty in these fitted parameters and an overall goodness of fit. It is shown that both samples are best fitted by an environment consisting of four Cl atoms suggesting that the Zn species in both liquids is the same, namely $[\text{ZnCl}_4]^{2-}$. Additionally the calculated interatomic distances of 228 pm is similar to that found in solid state tetrahedral ZnCl_2 (231 pm).

Sample	N	Type	R / pm	σ^2 / pm ²	E ₀ / eV	Fit Index
1: 2 ChCl: ethylene glycol	3.8 ± 0.2	Cl	228 $\pm$ 2	50 $\pm$ 5	-9.8	1.6
1: 2 ChCl: urea	3.9 ± 0.2	Cl	227 $\pm$ 2	55 $\pm$ 5	-9.5	1.8

Table 3.1 Electron scattering parameters for x-ray absorption data shown in **Figure 3.4**, fitted using EXCURV98.

3.2.3 Cyclic Voltammetry

It has been established that 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol represent quite different physical environments for metal deposition in terms of mass transport. For example the urea based liquid is more viscous than the ethylene glycol based liquid by approximately three orders of magnitude.^[1, 11] Interestingly, the solute concentration has been shown to have a contrasting effect on the mass transport properties of the two solvents. Additionally it has been theorised that this difference in behaviour may be due to a speciation or lattice disruption effect. However, the first *in-situ* EXAFS investigation of metal speciation in DESs, proved conclusively that Zn speciation is essentially identical in the both systems. To probe the effect of the DES upon the electrochemical behaviour of $[\text{ZnCl}_4]^{2-}$ the cyclic voltammetry (CV) of ZnCl_2 in both 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol was examined as a function of ZnCl_2 concentration, experimental time scale (potential scan rate) and cathodic overpotential.

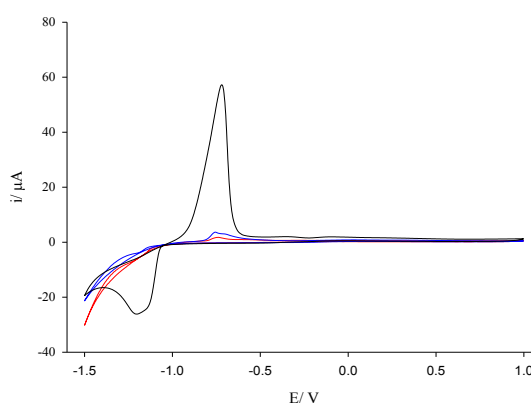


Figure 3.5 Cyclic voltammograms of various concentrations of ZnCl_2 1: 2 ChCl: urea at a Pt disc working electrode (dia. 0.5 mm) vs. a Ag wire pseudo reference electrode ($v = 10 \text{ mV s}^{-1}$). Concentration = 0.3 (black), 0.05 (blue) and 0.01 (red) $\text{mol dm}^{-3} \text{ZnCl}_2$.

The effect of ZnCl_2 concentration on the cyclic voltammetric response of ZnCl_2 dissolved in 1: 2 ChCl: urea is presented in **Figure 3.5**, where it is shown that Zn deposition only occurs when a critical ZnCl_2 concentration is reached. This concentration limit may be due to the structure of the electrochemical double layer at the

electrode surface. As discussed previously, the only Zn species present in solution is $[\text{ZnCl}_4]^{2-}$, a critical concentration of which will be needed at the electrode surface for nuclei formation to occur. However, each of these solvents also contains a much larger concentration of Cl^- anions, which may be preferentially incorporated into the double layer at cathodic potentials, effectively inhibiting the approach of $[\text{ZnCl}_4]^{2-}$ to the electrode surface. A similar effect is observed in 0.3 mol dm⁻³ ZnCl_2 1: 2 ChCl: ethylene glycol.

In the following series of data, **Figures 3.6-3.11**, the ZnCl_2 concentration has been set at 0.3 mol dm⁻³, above the critical limit, removing one variable from the analysis.

Data for the cyclic voltammetry of ZnCl_2 in both 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol, as a function of potential scan rate, are presented in **Figure 3.6**. The CV data for 1: 2 ChCl: ethylene glycol are presented in **Figure 3.6 (b)**; where the cathodic portion of the scans shows no well defined reduction peak, indicating that the relative nucleation rate is slow. This is most evident at faster scan rates where no clear nucleation loop is observed. At slow scan rates cross-over of the current traces is observed at cathodic potentials as evidence of nucleation and subsequent growth. The difference in experimental time scale between the slow (5 mV s⁻¹) and faster (20 mV s⁻¹) scans presented here indicates that in the potential range between -1.25 V and -1.50 V nucleation is occurring over a time period of approximately 10 and 50 seconds. This is in clear contrast to the voltammograms of ZnCl_2 in 1: 2 ChCl: urea shown in **Figure 3.6(a)**. Here a well defined reduction wave and cathodic current cross-over is observed at all three potential scan rates, indicating that nucleation is fast even at short experimental time scales. This could be thought to be a consequence either of the speciation of Zn^{2+} close to the electrode surface or of the mobility of ionic species close to the cathode (*i.e.* slower diffusion may encourage nucleation) although in previous studies on Zn/Sn alloys in the same liquids it is noted that only part of the observed differences in the CV response is due to the relative viscosity.^[17]

Results presented in this thesis suggest that the bulk Zn speciation is the same in both 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol. This implies that differences in the cyclic voltammetry are due to either local changes in speciation at the electrode surface or the differing Cl^- activity of the two systems. In 1: 2 ChCl: ethylene glycol, the hydrogen bond donor, ethylene glycol, is a relatively weak ligand. As a consequence, the free Cl^- activity in this liquid will be high. Conversely, 1: 2 ChCl: urea contains a stronger

ligand, urea, and as such the free Cl^- activity would be expected to be much lower. In 1: 2 ChCl the Cl^- ions will rapidly diffuse to the electrode surface, preferentially to the bulkier $[\text{ZnCl}_4]^{2-}$ anions, this will in effect reduce the concentration of Zn species in the electrochemical double layer and hence the rate of Zn nucleation. In 1: 2 ChCl: urea the free Cl^- activity is much lower, therefore the Zn concentration in the double layer will be higher and nucleation will be faster.

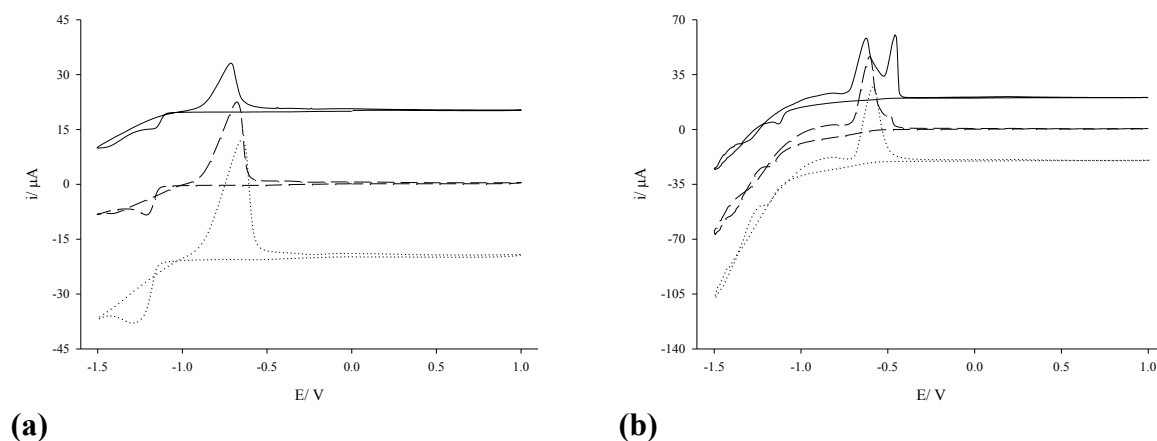


Figure 3.6 Cyclic voltammograms of $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in both; **(a)** 1: 2 ChCl: urea and **(b)** 1: 2 ChCl: ethylene glycol at a Pt disk working electrode (dia. 0.5 mm) using a silver wire pseudo reference electrode. Potential scan rates, v , were (i) 5 (solid) (ii) 10 (dashed) and (iii) 20 mV s^{-1} (dotted) respectively (voltammograms are offset for clarity).

The anodic portions of the CV scans for ZnCl_2 in the two liquids are also very different. In 1: 2 ChCl: ethylene glycol two stripping peaks are observed; $E_p^1 = -0.45 \text{ V}$ and $E_p^2 = -0.62 \text{ V}$ (vs. Ag wire), **Figure 3.6 (b)**. This strongly suggests the presence of two separate Zn phases. However, in contrast only a single stripping peak is observed in the voltammogram of the urea based liquid, **Figure 3.6 (a)**, at $E_p = -0.72 \text{ V}$ (vs. Ag wire) indicating a single phase growth mechanism. Interestingly, this single anodic stripping process corresponds much more closely in potential with the most cathodic of the two stripping processes for 1: 2 ChCl: ethylene glycol. In addition to these effects it is also clear from the voltammograms in **Figure 3.6** that the magnitude of currents is much smaller in 1: 2 ChCl: urea than in 1: 2 ChCl: ethylene glycol (e.g. cathodic currents are smaller by a factor of *ca.* 5); this is a consequence of slow mass transport in the urea based liquid due to its relatively high viscosity.

In an attempt to discover the cause of the two phase stripping response of Zn in 1: 2 ChCl: ethylene glycol, potential dependant atomic force microscopy (AFM) imaging techniques have been used. The results of a typical experiment are presented in **Figure 3.7**. Zinc was initially electrodeposited on a Pt electrode from 1: 2 ChCl: ethylene glycol at a potential of -1.50 V for 500 s. The electrode was then removed from

solution, dried with nitrogen, and imaged with the AFM, **Figure 3.7 (a)**. The unmodified electrode was then returned to the liquid at the same potential and a linear anodic scan was initiated from -1.50 V up to a potential of -0.53 V at a scan rate of 5 mV s⁻¹. [The value of applied potential, $E_{App.} = -0.53$ V, corresponds to the point on the potential scale that lies mid-way between the two anodic stripping peaks, see **Figure 3.6 (a)**]. The electrode was once more removed from the electrolyte, dried with nitrogen and the AFM image of the surface recorded once more, **Figure 3.7 (b)**. To ensure that the AFM images were representative of the entire surface 5 images were obtained of different parts of the surface for each set of sample conditions. The representative images in **Figure 3.7** are presented on the same scales for clarity of comparison and exhibit very different morphologies. The initial image, **Figure 3.7 (a)**, shows both small surface crystallites, 100-200 nm, as well as larger scale, 400-1000 nm features. After completion of the first anodic stripping process the small scale features are no longer present, **Figure 3.7 (b)**. Consequently the cathodic stripping peak, E_p^2 , is assigned to removal of the small scale, *nano*, growth whereas the anodic peak, E_p^1 , is assigned to removal of bulk phase growth. This analysis is consistent with the previous observations that nucleation is slow in the ethylene glycol liquid but relatively fast in the urea liquid; consequently we see only *nano* growth (resulting from fast nucleation) in the stripping voltammogram where urea is the H-bond donor whereas we see both *nano* and bulk growth when ethylene glycol is present. It is interesting that the peak height of the *nano* stripping peak, as shown in **Figure 3.6 (b)**, is only weakly dependant on scan rate (rather than a linear dependence as would normally be expected for a surface process). This may indicate that in the ethylene glycol based liquid other kinetic factors are controlling the rate of dissolution from the surface. Another interesting feature of the AFM images presented in **Figure 3.7** is that the average size of the larger-scale features is greater in **Figure 3.7 (b)** than in **Figure 3.7 (a)** *i.e.* after anodic stripping of the small crystallites. This could be caused by a coalescence phenomenon, however closer examination of several areas of the same surface reveals that this is probably due to local variations in size distribution of the crystal features.

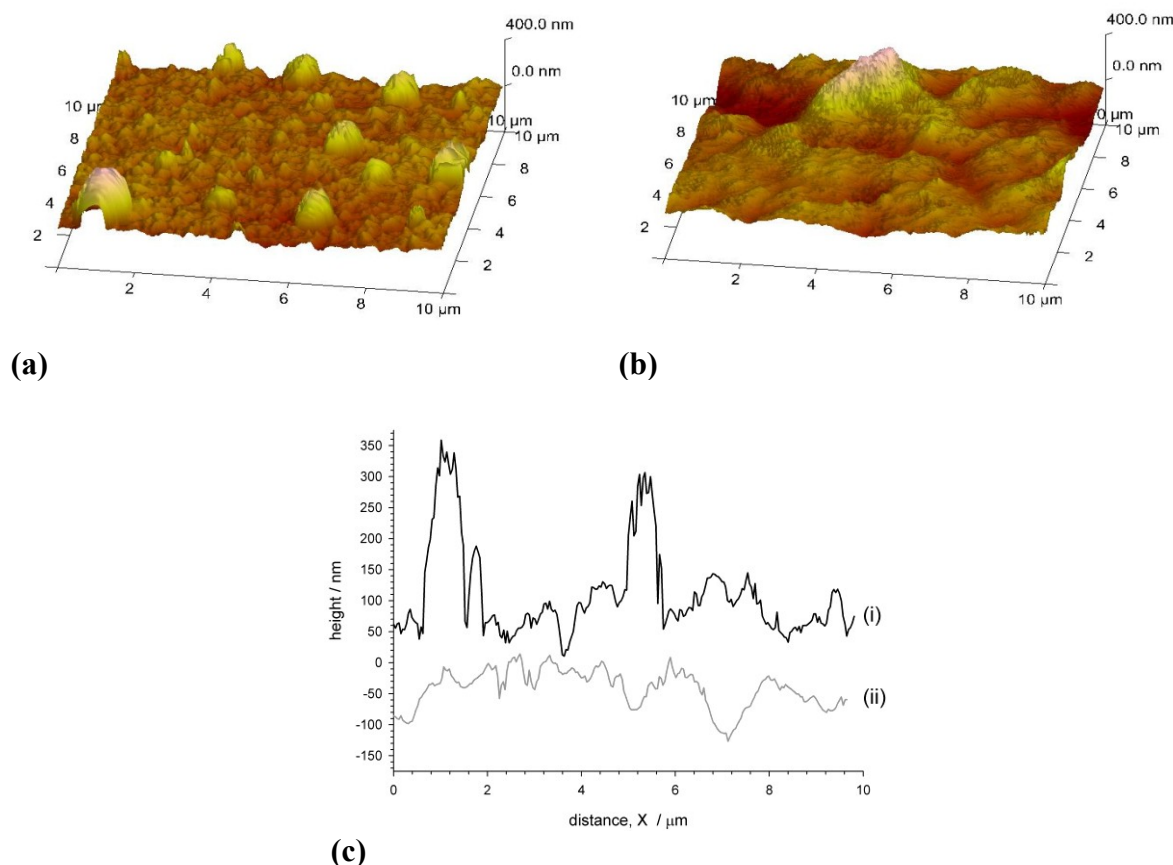


Figure 3.7 Atomic Force Microscopy images of a Zn deposit on a Pt disc (0.5 mm); **(a)** after deposition at -1.5 V for 500 s in $0.3\text{ mol dm}^{-3}\text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol at $50\text{ }^\circ\text{C}$, **(b)** then swept anodically to -0.53 V (scan rate of 5 mV s^{-1}), **(c)** representative line scans for the images in part **(a)**, (i) and **(b)**, (ii) offset for clarity.

Another representative set of voltammetric data are presented in **Figure 3.8**; here the potential scan rate was fixed at a value of 5 mV s^{-1} , whilst the cathodic limit of the scan was progressively increased (cathodically). Increasing the cathodic limit of the scan has two effects on the experiment, *i*) it increases the thermodynamic driving force and *ii*) it increases the time spent in the electrodeposition regime. In **Figure 3.8 (b)**, for 1: 2 ChCl: ethylene glycol, we can see that increasing (-ve) the cathodic limit from an initial value of -1.2 V to -1.5 V has very little effect on the *nano* stripping response; consistent with a slow nucleation process. However, the more anodic *bulk* stripping response, whilst all but absent from the initial voltammogram (where the cathodic limit is set at a value of -1.2 V) is much larger when the cathodic limit is increased to a value of -1.5 V . This is consistent with an increase in bulk growth as a consequence of the larger (-ve) overpotential and the increased time (an additional 120 s) spent in the cathodic deposition regime. Once again this is in contrast to the behaviour of ZnCl_2 in 1: 2 ChCl: urea.

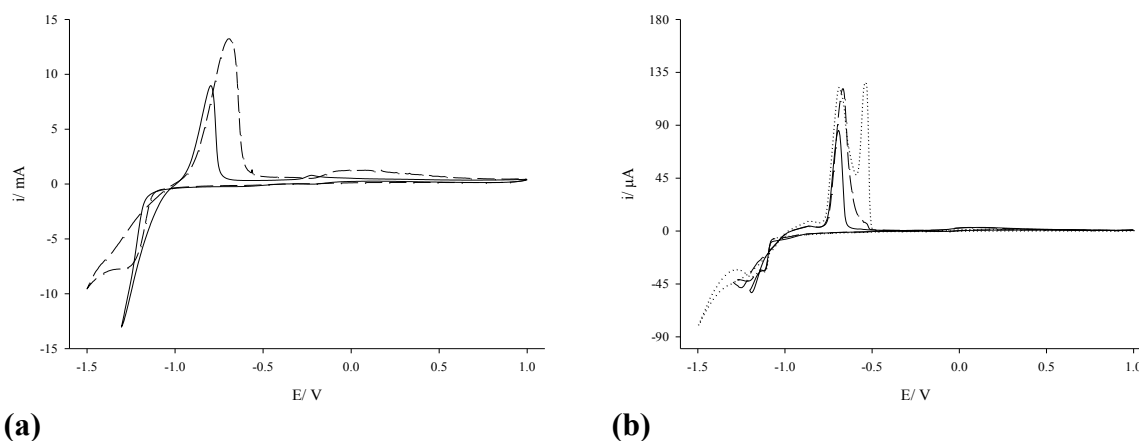


Figure 3.8 Cyclic voltammograms of ZnCl_2 (0.3 M) in **(a)** 1: 2 ChCl: urea with a cathodic potential limit of -1.30 V (solid) and -1.50 V (dashed); **(b)** 1: 2 ChCl: ethylene glycol with a cathodic potential limit of -1.20 V (solid), -1.30 V (dashed) and -1.50 V (dotted); at a Pt disk working electrode (dia. 1 mm) using a silver wire pseudo reference electrode at a potential scan rate, v , of 5 mV s^{-1} . In all voltammograms the anodic potential limit was fixed at a value of +1.00 V.

Voltammetric data presented in **Figure 3.8 (a)**, suggests that in 1: 2 ChCl: urea only *nano* growth occurs as a consequence of rapid nucleation. This nucleation/ growth rate is sensitive to the change in cathodic potential from -1.2 V to -1.3 V (evidenced by the increase in stripping peak) but after this nucleation rates become mass-transfer limited and so little change is observed between cathodic potentials of -1.3 V and -1.5 V.

The interdependence of the relative amounts of *nano* and *bulk* phases observed from Zn deposition in 1: 2 ChCl: ethylene glycol was investigated in a separate experiment; here the electrode potential of the Pt cathode was stepped to a value of -1.5 V and held there for a period of time, t_d (t_d = dwelling time). After the dwelling time had elapsed the electrode potential was then scanned anodically up to a value of +1.0 V. This linear scanning voltammetry (LSV) experiment was carried out using dwelling times, t_d = 50 s, 100 s and 500 s, and the results of these experiments are presented in **Figure 3.9**.

Here the ratio of *bulk* to *nano* scale growth is dramatically increased in favour of *bulk* as the dwelling time is increased. This is again consistent with slow nucleation and a mechanism of growth that favours the spreading and growth of established nuclei over formation of new nucleation sites. This type of mechanism can lead to optically bright (reflective) surfaces because large (relatively flat) crystal surface domains are formed.

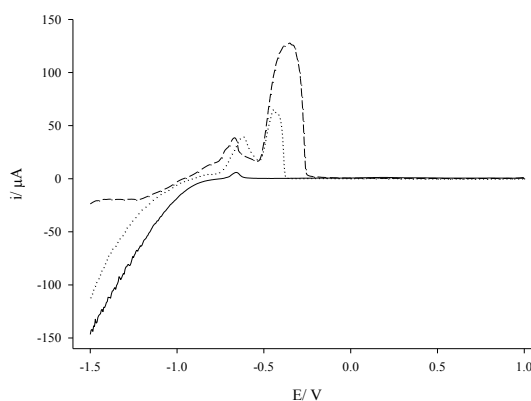


Fig. 3.9 Linear sweep voltammograms of $0.3\text{ mol dm}^{-3}\text{ ZnCl}_2$ in 1: 2 ChCl: ethylene glycol at a Pt disk working electrode (dia. 1 mm) at a potential scan rate, ν , of 5 mV s^{-1} and dwelling times, $t_d = 50\text{ s}$ (solid) 100 s (dotted) and 500 s (dashed).

During this investigation a Pt disk working electrode has been used as an inert cathode substrate. However, it remains the case that the cathode substrate is an integral part of the electroplating interface and in order to exclude the possible formation of surface alloys involving Pt (for example as an explanation for a two-phase stripping response) the cyclic voltammetric response for ZnCl_2 in both the ethylene glycol and urea based liquids was studied using a glassy carbon (GC) electrode. The results of a typical experiment in 1: 2 ChCl: ethylene glycol are shown in **Figure 3.10**. Here the two phase stripping response is still clearly visible, corresponding to the separate growth phases of the Zn metal deposit. This is unequivocal since there is no possibility of surface alloy formation at the GC surface. It is also clear from these data that nucleation is sensitive to cathodic overpotential. This latter observation is not surprising because the relatively smooth and amorphous surface interface present at the GC surface offers very few nucleation sites in comparison to a crystalline metal (e.g. Pt).

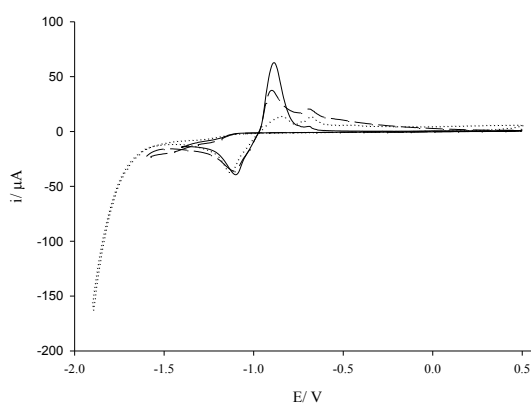


Fig. 3.10 Cyclic voltammograms of $0.3\text{ mol dm}^{-3}\text{ ZnCl}_2$ in 1: 2 ChCl: ethylene glycol at a GC disk working electrode (dia. 3.0 mm) using a silver wire pseudo reference electrode at a potential scan rate, ν , of 5 mV s^{-1} . Cathodic potential limits of each scan were -1.40 V (solid) (ii) -1.60 V (dashed) (iii) -1.90 V (dotted) with the anodic potential limit fixed at a value of $+0.50\text{ V}$.

3.2.4 Gravimetric Investigation

The hydrogen bond donor has been shown to have a marked effect on the physical properties and cyclic voltammetric response of ZnCl_2 containing ChCl based DESs. Conversely, Zn speciation has been determined to be relatively independent of the hydrogen bond donor, rather it is dominated by the common presence of free chloride anions in both solvents. In addition to electrochemical methods, the growth behaviour of Zn has been studied using tandem electrochemical acoustic impedance spectroscopy, in gravimetric mode (Electrochemical Quartz Crystal Microbalance, EQCM), in order to monitor mass changes at the surface of a cathode during deposition. This technique is described in detail in **Chapter 2** but in summary a resonant quartz crystal, coated with a Au electrode substrate, is positioned in contact with the DES and used as a mass probe for the electrolytic deposition of Zn metal.^[25-27] The experimental cell design is shown schematically in **Figure 3.11**; one face of the Au coated crystal is in contact with the liquid interface whilst the other is in contact with air. Here the resonant frequency of the quartz crystal was correlated to the mass of material deposited under potential control. In a typical experiment the potential of the Au electrode was controlled at a value of -1.1 V (vs. Ag wire) and the frequency/admittance, $U(f)$ (where $U = 1/Z$, and Z is the real part of the impedance), response of the quartz crystal resonance was monitored as a function of time. The $U(f,t)$ data were then converted to $\Delta m(t)$ using established methods.^[28]

In order to accurately measure mass changes at the quartz crystal the deposited film is assumed to act as a rigid resonator. This assumption is only valid when the Q factor, which is related to the width of the impedance peak, varies by less than 10 % during the experiment. A larger shift in Q factor indicates that the surface has become rough and can no longer be assumed to act as a rigid resonator. Throughout each experiment the Q factor of the resonant crystal did not change by more than 8 %.

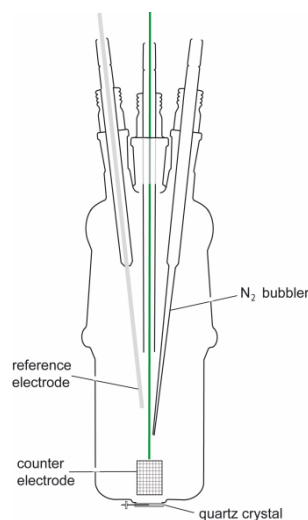


Figure 3.11 Schematic representation of the cell used in electrochemical acoustic impedance spectroscopy (EQCM) experiments showing the three electrode arrangement over the top of the working surface of the quartz crystal electrode. The cell was also equipped with an N_2 gas bubbler.

Earlier in this chapter, in section 3.2.2, CV data showing electrolytic deposition and stripping of Zn metal were presented. Determination of current efficiency from such experiments by integration of the $i(t)$ traces can often be misleading and inaccurate either because of the time scales involved, or if crystallites of metal are lost from the electrode as metallic Zn (*i.e.* crystals fall off the electrode). This can happen easily if the deposit is friable or if the active electrochemical surface is not the outer most interface. Here the current efficiency is determined using EQCM. Metallic Zn was deposited on a Au coated resonant quartz crystal under constant potential from both urea and glycol based liquids. The data presented in **Figure 3.12** show the mass of Zn deposited plotted vs. the charge passed during deposition in 1: 2 ChCl: ethylene glycol. The theoretical slope for this plot is equal to, $3.389 \times 10^{-4} \text{ g C}^{-1}$, defined by Faraday's law according to **Equation 3.2**.

$$\frac{d(\Delta m)}{dq} = \frac{rmm}{2F} = \frac{65.4}{1.93 \times 10^5} \quad \text{Equation 3.2}$$

Where, Δm is the change in mass, dq the change in charge, rmm the relative molecular mass of Zn and F the Faraday constant. The measured slope of the data, **Figure 7**, was determined as $2.90 \times 10^{-4} \text{ g C}^{-1}$, giving a current efficiency of 87 %. The good linear fit of these data even at long time scales (here 1600 s) shows that current efficiency is not a function of deposition time. Similar data were acquired for the urea based liquid showing that Zn deposition is essentially quantitative.

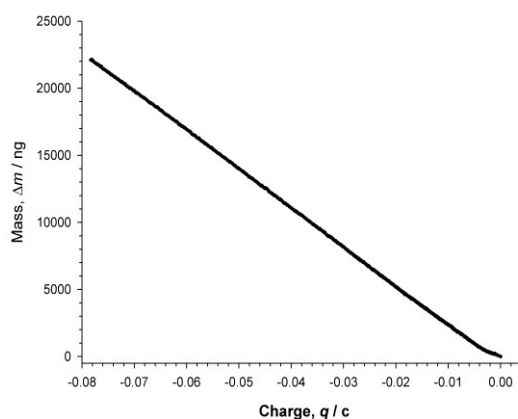


Figure 3.12 Gravimetric deposition of Zn metal from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol on a Au coated EQCM crystal at an applied potential of -1.1 V (versus Ag wire) for a period of 1600 s.

The results of two gravimetric EQCM experiments carried out with different ZnCl_2 concentrations in both 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol are shown in **Figure 3.13 (a)** and **Figure 3.13 (b)** respectively.

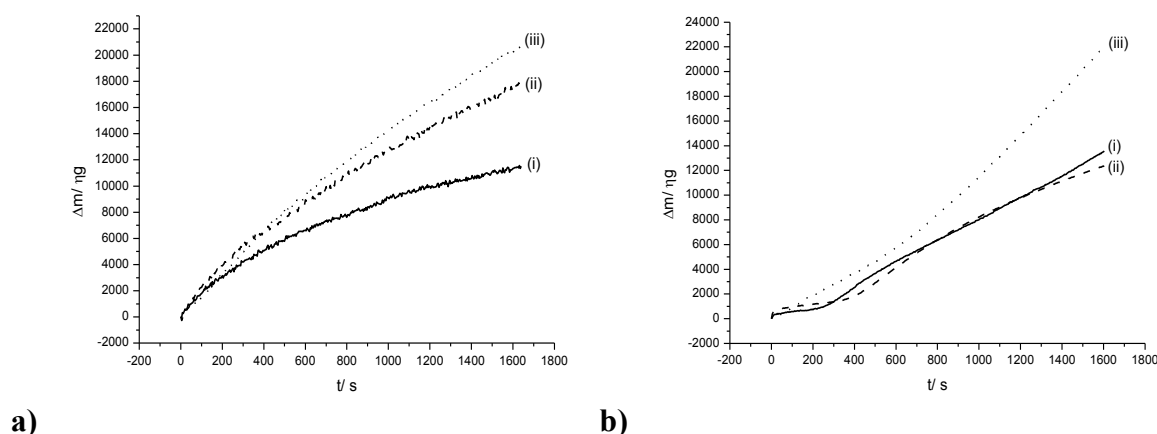


Figure 3.13 Gravimetric EQCM traces for Zn metal deposition at a Au coated quartz crystal (10 MHz) surface in **(a)** 1: 2 ChCl urea **(b)** 1: 2 ChCl: ethylene glycol. The concentration of ZnCl_2 was (i) 0.1 (ii) 0.2 and (iii) 0.3 mol dm^{-3} . During the deposition experiment the potential of the working electrode surface (geometric area 0.23 cm^2) was potentiostatically controlled at a value of -1.1 V (versus Ag wire).

The mass trace, $\Delta m(t)$, for the experiment performed in 1: 2 ChCl: urea, **Figure 3.13(a)**, shows that at long times, $t > 1000 \text{ s}$, the rate of deposition ($d\Delta m/dt$) is a function of concentration with the highest deposition rates occurring at largest concentrations. This is not surprising since this growth phase is likely to be mass-transfer limited. However, at short times, $t < 200 \text{ s}$, the rates of deposition are very similar and apparently concentration independent. This is typical of a fast nucleation process; in fact there is a clear turn over in rate between nucleation and growth phases that occurs at around $t = 200$ to 300 s . This turnover in rate corresponds to a deposition mass of around 2000 –

4000 ng over the crystal surface (0.23 cm^2) giving an average distribution of between $8.7 - 17.4 \text{ } \mu\text{g cm}^{-2}$. Assuming an average bulk density for Zn metal ($\rho = 7.14 \text{ g cm}^{-3}$) this corresponds to a thickness of between 12 – 24 nm, or 80 - 160 atomic layers (using 0.15 nm for the atomic radius of Zn). Once this critical surface coverage is reached, through rapid nucleation, then bulk growth, which is limited by the diffusion of $[\text{ZnCl}_4]^{2-}$ to the electrode surface and hence slower by comparison, becomes dominant.

In contrast, the mass trace, $\Delta m(t)$, for the experiment performed in 1: 2 ChCl: ethylene glycol, **Figure 3.13 (b)**, shows that at short time scales $t < 400 \text{ s}$, the rate of deposition is very slow but nevertheless quite sensitive to concentration. In this case the turnover in deposition rate occurs at a surface coverage of between 1000 - 3000 ng corresponding to $4.3 - 13.1 \text{ } \mu\text{g cm}^{-2}$ or a thickness of 6 – 18 nm. This critical surface coverage is similar in magnitude to that observed in 1: 2 ChCl: urea, but it is achieved over a longer period. Subsequent bulk growth in 1: 2 ChCl: ethylene glycol is now rapid in comparison as the viscosity is relatively low.

The trends observed in the gravimetric analysis are consistent with the theory proposed in relation to the difference in electrochemical and physical properties between the two solvents. In 1: 2 ChCl: ethylene glycol, the activity of the free $[\text{Cl}]^-$ will be relatively high, consequently $[\text{Cl}]^-$ will readily migrate to the electrode surface, preferentially to the bulkier $[\text{ZnCl}_4]^{4-}$ anions. The prevalence of $[\text{Cl}]^-$ in the electrochemical double layer and diffusion layer may slow the rate at which Zn reaches its critical nucleation concentration adjacent to the electrode surface accounting for the slow initial growth rates in **Figure 3.13 (b)**. This behaviour will clearly be affected by ZnCl_2 concentration and this relationship is apparent in the gravimetric data presented in **Figure 3.13 (b)**. Contrastingly, in 1: 2 ChCl: urea, the stronger hydrogen bond donor may more effectively complex the free $[\text{Cl}]^-$, reducing the chloride activity in this solvent. This will in effect reduce the inhibiting effect of $[\text{Cl}]^-$ on Zn electrodeposition and is observed as a relatively high initial rate of Zn deposition in 1: 2 ChCl: urea, **Figure 3.13 (a)**. If the assumption is made that by reducing the activity of $[\text{Cl}]^-$ in the solvent the concentration of Zn species in the double layer and diffusion layer would be increased, it is logical to assume that the initial stages of deposition (prior to mass transport control, where the rate of diffusion of $[\text{ZnCl}_4]^{2-}$ from the bulk solution dominates) will be relatively independent of the bulk ZnCl_2 concentration. Consequently these data show an independent but self-consistent picture to that observed from analysis of the

electrochemical data presented earlier.

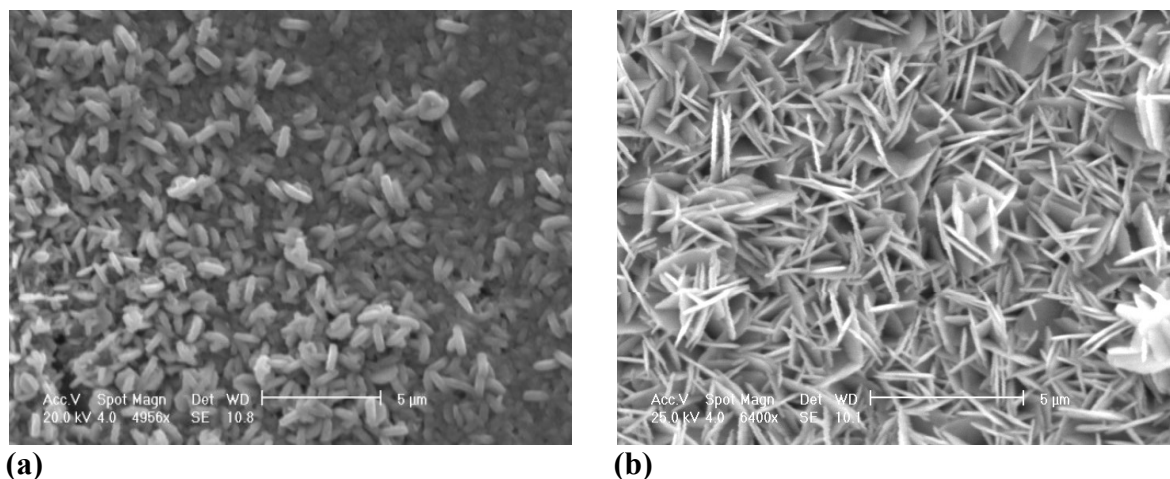


Figure 3.14 SEM images of Zn deposits obtained from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in **(a)** 1: 2 ChCl: urea **(b)** 1: 2 ChCl: ethylene glycol at 5°C , on mild steel at $J = 3 \text{ mA cm}^{-2}$.

In **Figure 3.14** a representative pair of scanning electron micrographs of Zn deposited on mild steel from 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol are shown. The Zn deposited from 1: 2 ChCl: urea has a “rice-grain” morphology, with homogeneously sized crystallites, this is consistent with the rapid nucleation mechanism, predicted by the cyclic voltammetry. A very different Zn morphology occurs when 1: 2 ChCl: ethylene glycol is used as the electrolyte. Here a needle like structure is observed; similar morphologies have been observed in Zn deposits obtained from other high $[\text{Cl}]^-$ concentration ionic liquids, such as the acidic ZnCl_2 : 1-ethyl-3-methyl-imidazolium melt.^[29] It is clear that the growth of the Zn crystallites is inhibited in the X-Y plane. This morphology could be caused by the preferential absorption of $[\text{Cl}]^-$ at particular crystal faces. Although not well understood in the growth of bulk metals, specific chloride adsorption has been used to control the dimensional growth of metal nano-wires.^[30] The specific adsorption of $[\text{Cl}]^-$ at both Cu,^[30] at the (001) face, and ZnO ^[31] has been utilised to restrict growth in particular planes for nano-wire growth.^[30, 31] It is interesting to note that this morphology is not obtained from Zn deposited from the 2: 1 ZnCl_2 : ChCl and 1: 4 ZnCl_2 : acetamide DESs (*c.f.* **Chapter 1, Sections 1.5.1 and 1.5.4**) where the free chloride concentration is much lower.^[21]

3.2.5 Nucleation Mechanism

Although the data presented above strongly suggests that there is a difference in the nucleation mechanism of Zn in 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol, it remains the case that no attempt has thus far been made to determine nucleation mechanisms in this type of DES.

The most widely used theoretical model for the nucleation of metals from both aqueous and ionic liquid electrolytes is that proposed by Scharifker and Hills^[32]. This model assumes that nucleation occurs at certain specific sites on the surface, and describes the nucleation mechanism as being either instantaneous or progressive. If the rate of nucleation is rapid in comparison with the resultant rate of growth, subsequent nuclei are formed at all possible growth sites within very short times and nucleation is considered as instantaneous. However, if the rate of nucleation is slow, nucleation will continue to take place at the surface whilst previous nucleation centres continue to grow, and nucleation is termed progressive.

In order to distinguish between an instantaneous or progressive nucleation process, the experimental chronoamperometric data are represented in a dimensionless plot of I^2/I_m^2 versus t/t_m and compared with theoretical plots derived from Scharifker and Hills equations.^[33] The Scharifker and Hills^[33] model for instantaneous nucleation followed by 3D diffusion-limited growth, assuming hemi-spherical nuclei, is defined as:

$$\frac{I_m}{I_m^2} = \frac{1.9542}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-1.2654 \left(\frac{t}{t_m} \right) \right] \right\}^2 \quad \text{Equation 3.3}$$

Equally the Scharifker and Hills model for the progressive nucleation followed by 3D diffusion-limited growth of hemi-spherical nuclei is defined as:

$$\frac{I_m}{I_m^2} = \frac{1.2254}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_m} \right) \right]^2 \right\}^2 \quad \text{Equation 3.4}$$

Where t is time, I is current density, I_m is the maximum current density and t_m is the time at which the maximum current occurs.

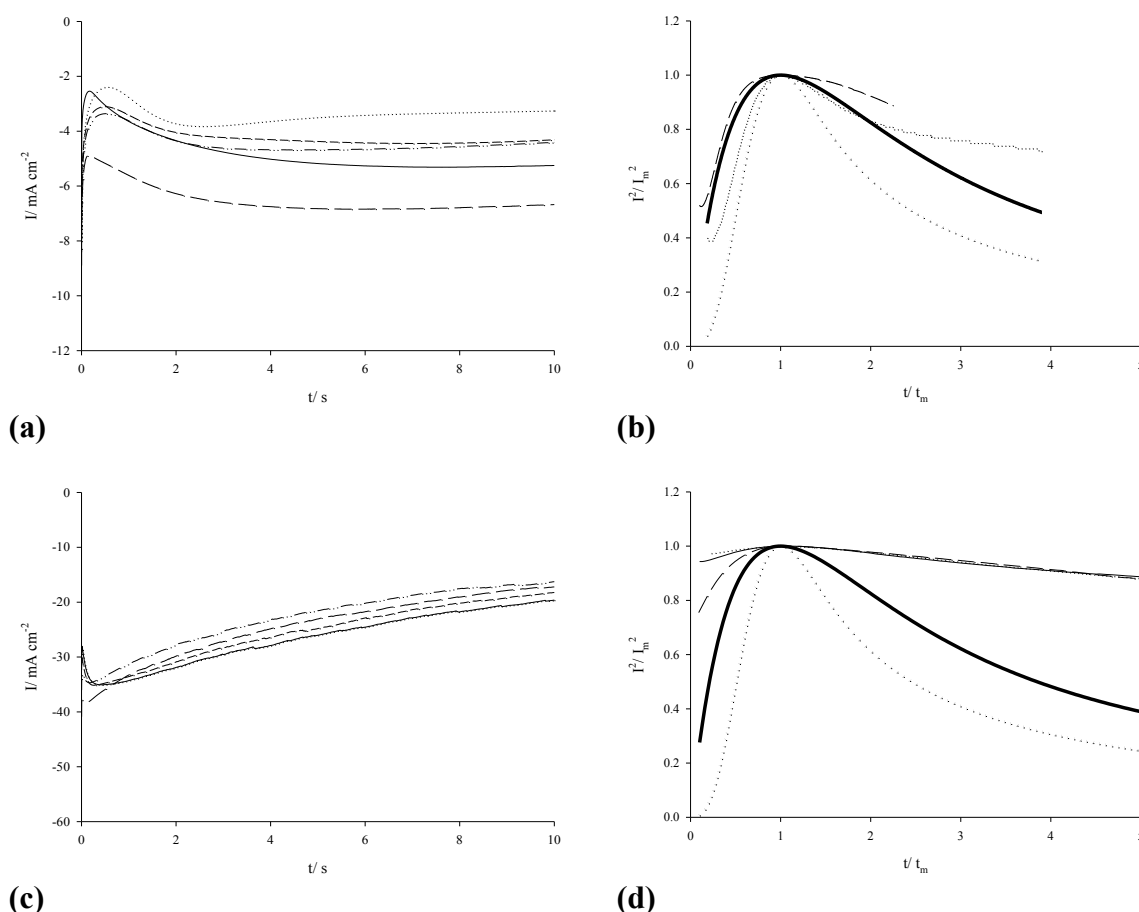


Figure 3.15 The experimental I - t data for the electrodeposition of Zn from (a) 1: 2 ChCl: urea and (c) 1: 2 ChCl: ethylene glycol. Here the potential was stepped from open circuit potential, o.c.p, to a cathodic potential where Zn nucleation was known to occur (here between -1.20 and 1.30 V, vs. Ag wire). The data is also shown fitted to the theoretical limiting 3D instantaneous (bold, black trace) and 3D progressive (bold, dotted trace) nucleation mechanisms proposed by Scharifker and Hills for (b) 1: 2 ChCl: urea and (d) 1: 2 ChCl: ethylene glycol.

A comparison of the experimental I - t curves with the theoretical models for 3D instantaneous and progressive nucleation for Zn deposition from 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol is presented in **Figure 3.15**. At first appearances the I - t traces, **Figure 3.15 (a)** and **(c)**, appear to follow the standard behaviour predicted for a metal nucleation process. As an overpotential is applied, the current first rises sharply due to double layer charging (this current spike is omitted from **Figure 3.15** for clarity), followed by a relaxation in current. A rise in current to a current maximum, which is indicative of a nucleation process, is then observed. This current increase is proposed by Scharifker and Hills to be due to the formation and growth of nuclei. As the individual nuclei growth zones begin to overlap, the current begins to fall towards a diffusion limited level. The nucleation of Zn from 1: 2 ChCl: urea, **Figure 3.15 (a)** follows this predicted behaviour and fits most closely to a 3D instantaneous nucleation mechanism, **Figure 3.15 (b)**. The

chronoamperometry therefore provides a self-consistent explanation of the behaviour noted in the cyclic voltammetry.

However, it is here that the I-t data for 0.3 mol dm^{-3} in 1: 2 ChCl: ethylene glycol diverges from the predicted behaviour. In **Figure 3.15 (c)**, it is clear that at long times the j-t traces do not converge to a diffusion limited level, in fact the limiting current is overpotential dependent. Additionally, the experimental data for Zn nucleation shows a very poor fit for the theoretical models proposed by Scharifker and Hills, **Figure 3.15 (d)**. This poor fit is difficult to explain, however, it may show that the assumption that nuclei are hemispherical may not be applicable to nucleation mechanisms which result in needle like morphologies as seen in **Figure 3.14 (b)**. Alternatively, secondary processes occurring at the electrode surface may account for a proportion of the measured current, making accurate fitting of the data problematic. Despite the difficulty in fully resolving the nucleation mechanism of Zn from 1: 2 ChCl: ethylene glycol, the chronoamperometric data provide further evidence of the difference in Zn growth processes in the two DESs. The nucleation of Zn from 1: 2 ChCl: ethylene glycol is further discussed in **Chapter 4**, including a quantitative analysis of the chronoamperometric data.

In order to resolve these issues and elucidate a mechanism for Zn nucleation in 1: 2 ChCl: ethylene glycol, a novel combination of analytical techniques was used. The result obtained by concurrently observing morphological changes with variations in electrochemical and gravimetric response using a combined liquid phase AFM and EQCM are presented **3.2.6**.

3.2.6 An *in-situ* AFM-EQCM study of Zn deposition from 1: 2 ChCl: ethylene glycol.

Atomic Force Microscopy (AFM) is a surface probe technique which can be used to determine the structure of conducting and insulating surfaces both in air and liquid environments. When combined with electrochemical techniques it is a useful tool for the investigation of electrochemical reactions at surfaces^[34-36] during metal deposition,^[37, 38] passivation, pitting and electrochemical dissolution.^[39, 40] Previously in this chapter AFM has been utilised, alongside Scanning Electron Microscopy (SEM), to illustrate the clear difference in the morphology of Zn electrodeposited from 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol. Evidence obtained from cyclic voltammetry, chronoamperometry and gravimetric analysis strongly suggests that this change in morphology is due to a difference in the initial nucleation and growth mechanisms of Zn in the two solvents. However, each of these experiments was conducted independently and the resulting morphological studies performed *ex-situ*. In order to form a true understanding of the electrodeposition processes one would ideally wish to observe the development of the electrodeposit morphology

alongside changes in the electrochemical and gravimetric responses, concurrently and *in-situ*.

To this purpose attempts have been made to combine AFM and EQCM,^[41-43] however, the technique is not commonly used due to the non-trivial nature of the experiment and the need for high cost specialist equipment. Whilst metal deposition processes have been widely studied using the two techniques, the topographical and morphological studies are generally conducted *ex-situ* and in air.^[41-43] The results presented in this thesis represent the first application of the combined AFM-EQCM to concurrently monitor, in a time-resolved manner, electrodeposition processes in an ionic liquid/ DES morphologically, electrochemically and gravimetrically.

Liquid phase AFM experiments in DESs are further complicated by the relatively high viscosity of the liquids. The technique was successfully applied to Zn deposition from 1: 2 ChCl: ethylene glycol, however, 1: 2 ChCl: urea was observed to be too viscous, 800 cP at 25 °C, to allow AFM images to be obtained with acceptable levels of piezo-electric drift. The results presented below are therefore restricted to Zn electrodeposition from 1: 2 ChCl: ethylene glycol.

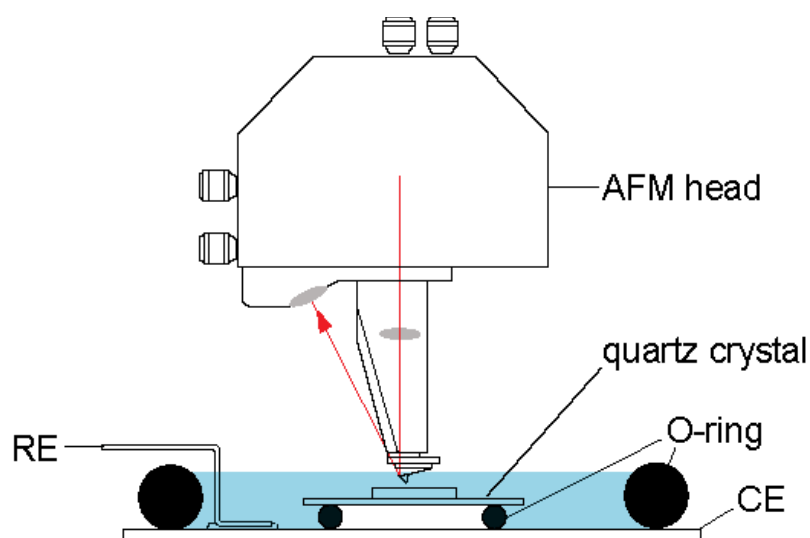


Figure 3.16 Schematic of the liquid phase AFM-EQCM cell, designed to allow a resonating gold coated quartz crystal under potentiostatic control to be placed under the AFM head and be submerged in liquid. The cell consists of a gold coated quartz crystal working electrode, a Ag wire pseudo reference electrode and a Zn foil counter electrode.

An illustrative diagram of the electrochemical cell used for the AFM-EQCM experiments is shown in **Figure 3.16**. The liquid reservoir was formed by attaching two suitably sized ‘O-rings’, to a Zn foil base which also acted as the counter electrode (CE). The Ag wire reference electrode (RE) was then attached to the Zn base with insulating epoxy resin. A

polished Au coated quartz crystal was used as the working electrode (WE) allowing the changes in Zn morphology to be monitored without being obscured by substrate defects which would be present on an unpolished substrate. The AFM, EQCM and 3 electrode cell were controlled as described in **Chapter 2**.

Preliminary experiments were conducted in order to establish that the surface-tip interaction did not interfere with crystal resonance and that the RF output of the network analyser did not disturb the scanning control electronics of the AFM head. A Au coated crystal mounted onto the experimental cell was positioned under the AFM head and submerged in fresh 1: 2 ChCl: ethylene glycol. For the purposes of this initial experiment no ZnCl_2 was added to the solvent. A tapping mode AFM image was then recorded with and without the crystal resonating at approximately 10 MHz. No differences were observed in the recorded AFM images and the overlaid acoustic spectra remained unaltered when the AFM was scanning. This is consistent with the findings of Friedt *et al.* who reported that when used in combination with an AFM, the QCM did not visibly modify the image shape because of its oscillation and that the out-of-plane oscillation of the quartz crystal did not affect the resolution of the AFM for typical measurements in aqueous solvents.^[42]

The following results describe the results of a single combined AFM-EQCM experiment following the electrodeposition of Zn from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol, highlighting the wealth of information obtained from such an experiment. By comparing the AFM images and the simultaneously recorded current transient, it is possible to obtain unique and detailed information concerning the electrodeposition of Zn from 1: 2 ChCl: ethylene glycol.

The following experiment was conducted using the cell design featured in **Figure 3.16**. The experiment was conducted under ambient conditions and the cathodic potential applied to initiate electrodeposition was -1.30 V (vs. Ag wire). Samples of the time-resolved AFM images are illustrated in **Figure 3.17**. **Figure 3.17 (a)** is an image of the bare polished gold-coated quartz crystal taken in the deposition liquid, $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol, immediately before the application of the overpotential used to initiate Zn deposition. This has been included to allow comparison of the roughness of the substrate with the surface features observed during the deposition. As the experiment was conducted on a polished Au-coated quartz crystal, the substrate surface is free from the mechanical scratches and pits that may be seen when using a pure metal substrate and as a result any surface features that result from the electrodeposition process are not obscured.

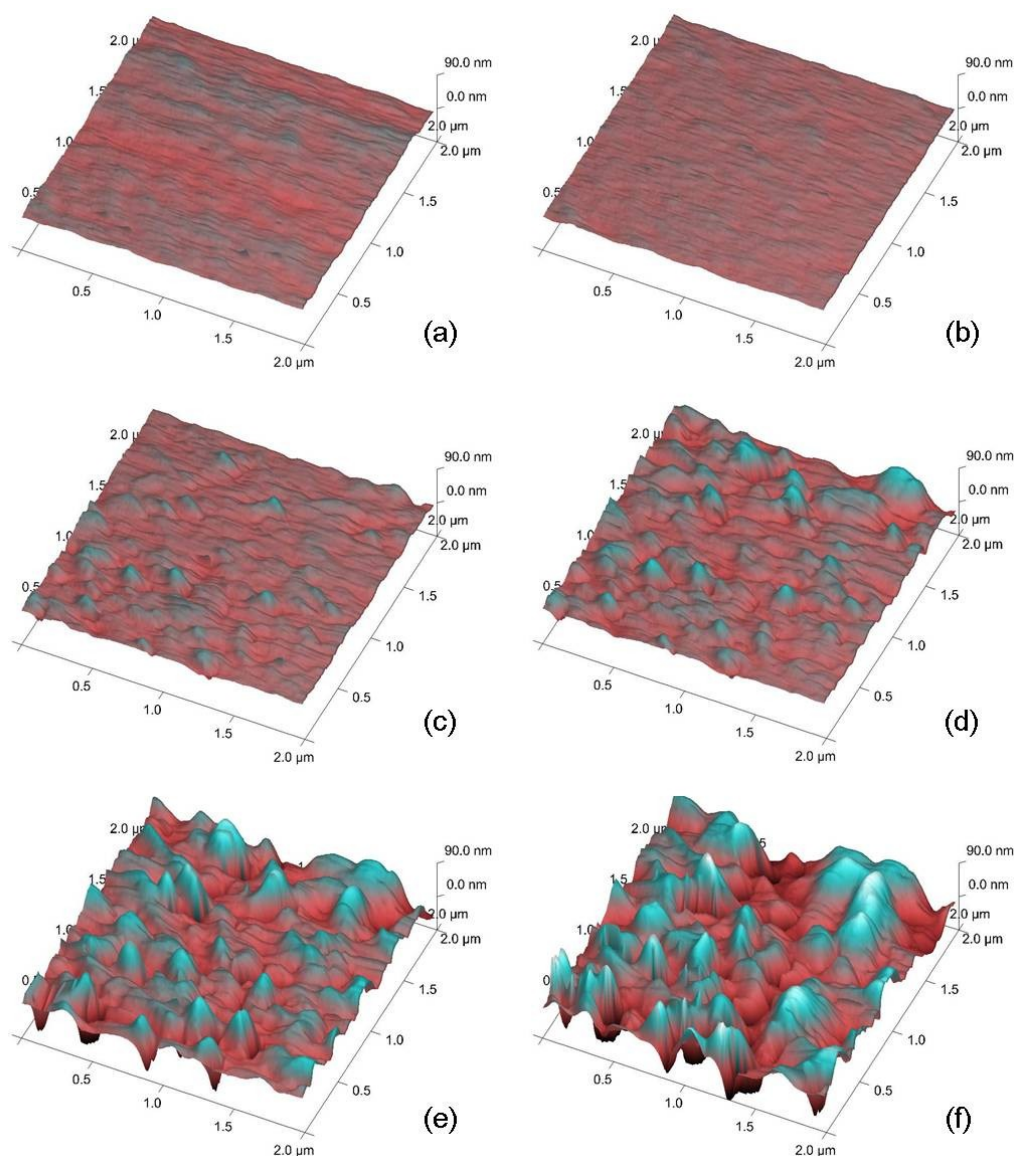


Figure 3.17 Tapping mode, liquid, AFM images recorded in $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in 1: 2 ChCl: ethylene glycol, of an Au coated resonating quartz crystal under electrochemical control (-1.1 V versus Ag wire). Images show Zn deposition at times (a) $t = 0$, (b) $t = 2$, (c) $t = 4$, (d) $t = 6$, (e) $t = 8$, (f) $t = 10$ minutes. Each image was exported as a 3D height plot from the Nanoscope v6.13 software and comprises 128×128 data points.

Upon the application of a cathodic overpotential (-1.30 V vs. Ag wire) the electrodeposition of Zn was initiated and the change in morphology followed using the continuously scanning AFM. **Figures 3.17 (b-f)** clearly show the successive formation of small Zn nucleation sites, followed by the growth of these nuclei in terms of both their size and shape. A small amount of piezo-electric drift by the scanning head was observed, nevertheless, the same features are clearly identifiable in each image. During the experiment a compromise was made between image resolution and acquisition rate. On average an AFM image was obtained every 60 s, whilst the electrochemical and gravimetric data was collected continuously. It is therefore important to note that there will also be a degree of time-

resolution within each individual image. Nevertheless, the shape of the Zn crystallites was regular and well defined and it is clear that there are crystallites of varying size present at each snapshot of the deposition. As has been discussed previously, the nucleation mechanism of Zn in 1: 2 ChCl: ethylene glycol was difficult to determine using chronoamperometry alone as the experimental I-t traces did not fit any of the limiting theoretical models, **Figure 3.15**. However, the presence of differently sized crystallites is indicative of a progressive nucleation mechanism, where nucleation events are continually occurring at different times. Images are only presented here for the first 10 minutes of the experiment, though the total length of the experiment was 20 minutes. At a time-scale greater than 700 seconds the crystallites became less well-defined and the Zn appears to coalesce, this is consistent with the findings in the chronoamperometric data which are presented in **Figure 3.18**

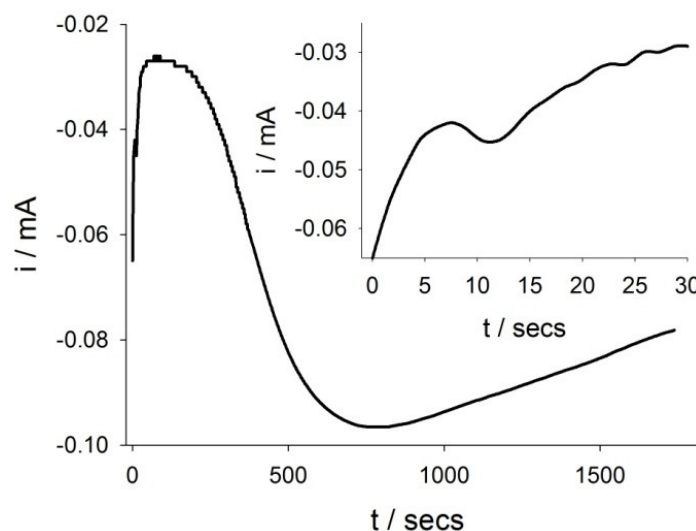


Figure 3.18 Chronoamperometric data acquired simultaneously alongside the AFM images presented in **Figure 3.17**. The insert contains magnification of the initial 30 s of experiment, highlighting data used for modelling in **Figure 3.19**.

A nucleation peak was observed in the chronoamperometric data at a short time scale ($t = 12$ s) and is presented as an insert in **Figure 3.18**. This early nucleation peak was followed by a steady decrease in current associated with diffusion-limited growth. An interesting feature of the chronoamperomogram is the large increase in current apparent between 250 and 750 s. By comparing the data in **Figure 3.18** with the concurrently obtained AFM images in **Figure 3.17** it is clear that this is an effect of the surface roughness of the deposit. As the Zn crystallites grow they effectively increase the active surface area of the electrode, resulting in an increase in current. However, at times greater than 700 s, the Zn crystallites first begin to overlap and then coalesce, resulting in a reduction in the relative surface area

and hence current. The AFM images and chronoamperometric data independently present mutually supportive information on the Zn growth mechanism.

The data presented in **Figure 3.18** has been fitted to the limiting nucleation mechanisms proposed by Scharifker and Hills.^[33] The experimental data exhibits a reasonably good fit to the 3D progressive model in **Figure 3.19**; hence, both the qualitative AFM images, and the quantitative chronoamperometric data have independently provided evidence of the same nucleation mechanism. It is worth noting that the models for the chronoamperometric data are only valid for the initial point in time when nucleation occurs, in this experiment the initial 15 s of the experiment. Conversely, the AFM results cover the time-scale of the complete experiment with images being acquired constantly, approximately once every minute. A different experimental set-up would therefore be required to specifically look at the short time-period of the initial nucleation events. Having said this, the AFM images still agree with the results of the modelling, and consequently it is reasonable to state that the initial mechanism of nucleation is progressive and that this progressive mechanism continues throughout the time period of the experiment.

Resonant QCM was used as a mass probe to investigate the rate of deposition of Zn during the experiment. Most commercial QCM instruments use a derivative technique that locks and tracks the peak frequency of the crystal resonance as a function of time. However, this does not work well with ionic liquids and DESs, as one of their common properties is high viscosity, which attenuates the crystal resonance. By using acoustic impedance spectroscopy, the full resonance spectrum of the crystal can be recorded. Later, curve fitting allows the calculation of the peak frequency and the real component of the impedance for the crystal circuit. Subsequently the electrical impedance of the crystal is coupled to mechanical losses at the crystal/liquid interface, giving quantitative information about surface roughness and density.

The mechanical losses or the broadness of the resonance curve can be measured empirically using the Q factor, Q , of the admittance resonance curve, given by **Equation 3.5**

$$Q = f_0/w \quad \text{Equation 3.5}$$

Where f_0 is the frequency value at the centre of resonance and w is the Full Width of the peak at Half Height (FWHH).

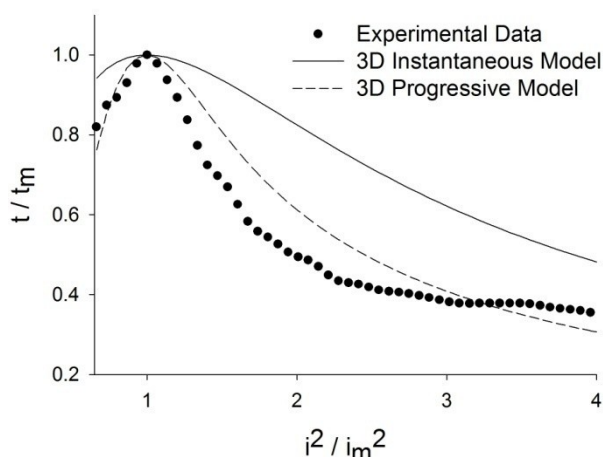


Figure 3.19 Normalised plot of chronoamperometric data at short time-scale for nucleation analysis. 3D-progressive model (dotted line), 3D-instantaneous model (solid line) and experimental data (dots) from **Figure 3.18** insert.

Acoustic impedance (admittance) plots recorded for the quartz crystal before and after Zn deposition were very similar in shape and intensity. Q factor calculations ($Q_{\text{(after)}}/Q_{\text{(before)}} = 0.914$) confirmed that the resonance peak shape was relatively unchanged by the deposition of Zn. The lack of viscoelastic losses during the experiment suggests that a rigid Zn metal deposit was formed during the deposition, allowing the Sauerbrey equation to be used to calculate the deposited mass. The plot of deposited mass versus charge can be seen in **Figure 3.20** with the total mass of Zn deposited during the experiment calculated as being approx. 42000 ng. The mean slope of the linear regression for the plot was $3.128 \times 10^{-4} \text{ g C}^{-1}$ which, when compared to the theoretical value of $3.389 \times 10^{-4} \text{ g C}^{-1}$ for Zn, gave a mean current efficiency of 92 % for the deposition process.

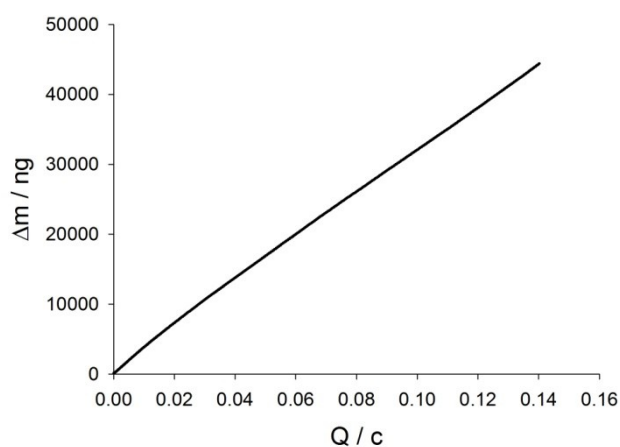


Figure 3.20 Deposited mass, Δm , versus charge passed, Q , acquired simultaneously with the $i(t)$ trace and AFM images during deposition from a $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ solution in 1: 2 ChCl: ethylene glycol.

The combination of AFM, EQCM and electrochemical measurements has been shown to be a novel method for obtaining a wealth of information on electrodeposition mechanisms. The technique has been applied for the first time to a DES, the individual techniques providing mutually supportive evidence for the progressive nucleation mechanism of Zn from 1: 2 ChCl: ethylene glycol.

3.3 Summary

The DESs 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol have been shown to be suitable media for the electrodeposition of Zn.

For the first time solute concentration has been shown to not only have an important effect on the physical properties of this class of solvent but that this effect is quite different from that observed in aqueous electrolytes and is also dependent upon the hydrogen bond donor. It is therefore imperative that future studies of electrodeposition from this class of solvent take into account solvent concentration effects.

In-situ EXAFS has been effectively applied for the first time to elucidate dissolved metal structure in a ChCl based DES. The structure of dissolved ZnCl_2 , until now only poorly understood through destructive *ex-situ* measurements such as mass spectrometry, has thus been conclusively determined to be $[\text{ZnCl}_4]^{2-}$ in both 1: 2 ChCl: urea and 1: 2 ethylene glycol.

Electrochemical experiments including cyclic voltammetry and chronoamperometry have established that there is a clear difference in Zn electrodeposition processes in the two solvents. Zn deposition has been shown to occur *via* a 3D instantaneous nucleation mechanism in 1: 2 ChCl: urea, yielding a homogeneous morphology. Conversely, the nucleation of Zn from 1: 2 ChCl: ethylene glycol has been hypothesized to be inhibited by the high chloride activity in the solvent. The resulting morphological studies show a very different needle like Zn structure. It has been proposed that this structure is common in high chloride concentration ionic liquids and may be due to the specific adsorption of chloride ions. Cyclic voltammetry experiments have independently predicted this difference in Zn morphology and provide self consistent evidence, alongside gravimetric analysis, for the different mechanisms.

A novel technique, the combined time-resolved *in-situ* AFM-EQCM has been applied to elucidate the nucleation mechanism of Zn electrodeposition from 1: 2 ChCl: ethylene

glycol. This method has enabled, through concurrent monitoring of I-t, gravimetric and morphological variations, the elucidation of a 3D progressive nucleation for Zn electrodeposition from 1: 2 ChCl: ethylene glycol. These results represent the very first application of the combined *in-situ* EQCM-AFM technique to metal phase growth in ionic liquids. The results obtained using this method are consistent with those obtained from individual experiments and as such provide a distinct yet self-consistent validation of the applicability of the technique.

In the following chapter this study will be extended to provide the first in-depth investigation of the effect of organic additives on Zn electrodeposition mechanisms from deep eutectic solvents.

3.4 References

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Chapter 4: The Effect of Organic Additives on Zn Electrodeposition from Deep Eutectic Solvents

4.1 Introduction

4.2 Results and Discussion

4.2.1 Organic Additives: Cyclic Voltammetry

4.2.2 Organic Additives: Nucleation Mechanisms

4.2.3 Organic Additives: Gravimetric Analysis

4.2.4 Organic Additives: Speciation and Morphology

4.2.4 The effect of Surfactants on Zn Deposition from Deep Eutectic Solvents

4.3 Summary

4.4 References

4.1 Introduction

In **Chapter 3** the electrodeposition of Zn from the deep eutectic solvents 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea was investigated. Clear differences were observed in the cyclic voltammetry, chronoamperometry and gravimetric data obtained during the deposition of Zn from the two solvents. Additionally, the bulk Zn deposit morphology was strongly dependent on the deep eutectic solvent.

The formation of this class of deep eutectic solvents occurs through the complexation of the $[\text{Cl}]^-$ anion, from choline chloride, by a hydrogen bond donor. The chloride activity in the solvent is therefore dependent upon the relative strength of the hydrogen bonding between the hydrogen bond donor and $[\text{Cl}]^-$. The differences in the Zn electrodeposition processes were therefore proposed to result from the difference in the relative chloride activity in 1: 2 ChCl: urea and 1: 2 ethylene glycol. In 1: 2 ChCl: ethylene glycol, where the hydrogen bond donor is relatively weak, the $[\text{Cl}]^-$ activity is higher. This was proposed to lead to both a lower concentration of Zn in the electrochemical double layer, reducing the rate of electrodeposition, and specific chloride adsorption, altering the morphology of the Zn deposit. Conversely, 1: 2 ChCl: urea contains a stronger hydrogen bond donor, urea, resulting in a lower $[\text{Cl}]^-$ activity. This reduction in chloride activity was evidenced by an increased initial rate of Zn deposition, a clear 3D instantaneous nucleation mechanism and homogeneous deposit morphology.

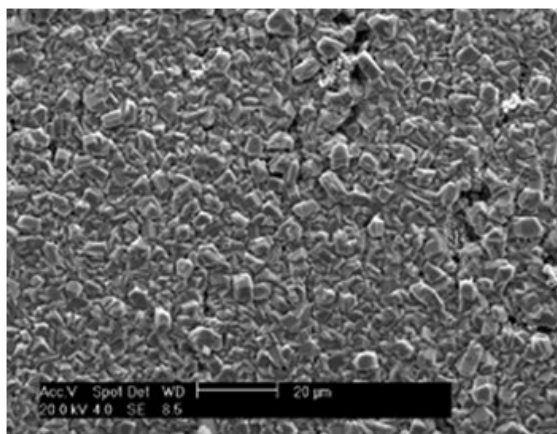


Figure 4.1 Representative scanning electron micrograph showing the typical Zn electrodeposit morphology obtained from constant current density electrodeposition from 1: 4 (molar ratio) ZnCl_2 : acetamide.^[1]

The theory of morphology modification by the specific adsorption of chloride ions is additionally supported by examining the Zn electrodeposition processes in two related deep eutectic solvents, ChCl: ZnCl_2 and ZnCl_2 : acetamide.^[1] In these solvents the free chloride concentration is much lower than in the ChCl: hydrogen bond donor electrolytes and

consequently Zn electrodeposition proceeds with no evidence of chloride adsorption, yielding homogeneous crystalline Zn, **Figure 4.1**.

The aqueous electrodeposition of Zn is most often conducted in acidic sulphate baths. Electrolytes with high chloride concentrations are usually avoided as they tend to yield black, friable deposits. This behaviour is thought to be due to the ease of nucleation in halide media which leads to a large number of nuclei forming at the electrode surface. In order to obtain bright deposits in chloride electrolytes it is considered to be necessary to control the rate of nucleation while encouraging the growth of existing nuclei. This is often achieved in aqueous electrolytes through the introduction of organic additives and surfactants.

In industrial Zn electrodeposition processes, where the use of high purity feedstock is often economically unfeasible, the presence of metallic impurities, often Ni or Sb, can be highly problematic. Although their behaviour is complex, metallic impurities are known to reduce current efficiency, lower the quality of Zn deposits and consequently increase power usage during Zn electrodeposition. In consequence, additives are often added to aqueous electrolytes to specifically ligate metallic impurities and hence increase the cathodic overpotential of reduction.

Organic additives are therefore added to aqueous Zn electrodeposition baths to solve two distinct problems. They can be used to directly affect the Zn electrodeposition mechanism, in order to improve deposit morphology and physical characteristics; or alternatively they can be used to inhibit the reduction of impurities in the electrodeposition solution.

The additives most commonly used in aqueous electrolytes can therefore be considered to function in one of two ways:

- i) They act to ligate the metal species, forming a complex which is more difficult to reduce.
- ii) They are adsorbed at the electrode surface, altering the electrochemical double layer and inhibiting metal nucleation.

It is therefore imperative to consider both metal speciation and electrochemical double layer structure if an understanding of how additives effect metal deposition is to be obtained.

Organic additives are often added to electroplating solutions as complexing agents, i.e. as ligands, which change the metal speciation in the solution, consequently altering the deposition characteristics of the metal. The effect of complexing agents on Zn is somewhat

understudied. This is perhaps not surprising when one considers that Zn is a relatively non-reactive d^{10} metal. Nevertheless, examples of Zn complexation in aqueous chloride electrodeposition baths do appear in the literature. The addition of NH_3 to a ZnCl_2 containing aqueous electrolyte led to a cathodic increase in the Zn reduction potential. This was attributed to the formation of $[\text{Zn}(\text{NH}_3)_4]^{2+}$, a thermodynamically more stable ion, which required a greater cathodic overpotential to reduce.^[2]

Organic additives can also be added to the electrodeposition bath to directly affect the Zn electrodeposition mechanism at the electrode surface. A group of organic materials added to aqueous electrolytes to alter electrodeposition characteristics are the surfactants. It has been shown that surfactants such as cetyltrimethylammonium bromide (CTAB) act as effective levelling agents whilst also improving the current efficiency of Zn deposition from acidic sulphate plating baths.^[3] More recent investigations by Gomes *et al.* have determined that changing the charge of the surfactant head group has an effect on the electrodeposition mechanism. It was found that cationic surfactants such as CTAB reduce the crystallinity and grain size of the Zn, whereas anionic surfactants such as sodiumdodecylsulphate (SDS) increase grain size and crystallinity.^[4, 5] It is probable that these surfactants are specifically adsorbed at the electrode surface and act to alter the structure of the electrochemical double layer.

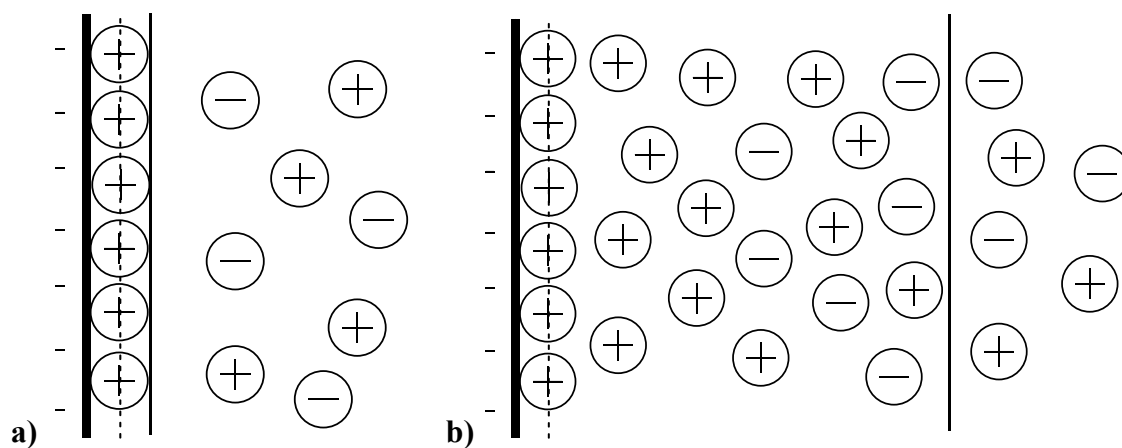


Figure 4.1 The Helmholtz **(a)** and Gouy-Chapman-Stern **(b)** models for the double layer structure in dilute aqueous electrolytes. The inner Helmholtz plane is represented by ----- and the interphase-solution boundary is represented by a solid line. Here the structure of the solvating water molecules is omitted for clarity.^[6]

The most widely accepted model for double layer structure in dilute aqueous electrolytes is the Gouy-Chapman-Stern model (modified by Grahame to take the solvation sheath of ions into account).^[6] This model builds upon the earlier Helmholtz model, **Figure 4.1 (a)**, where the excess charge on the electrode is simply assumed to be neutralised by a monomolecular layer of ions of opposite charge, a “double layer”.^[6] The Gouy-Chapman model, adds an

extra degree of sophistication by taking into account the freedom of ions to move in the solution due to thermal motion.^[6] Here the theory of the coulombic metal electrode-counter ion interaction (the Helmholtz double layer) is retained, but the random motion of ions is accounted for by a diffuse double layer in which the counter ion concentration is greatest closest to the electrode and progressively decreases to the homogeneous ion distribution in the bulk electrolyte.^[6] The Stern modification, Gouy-Chapman-Stern, **Figure 4.1 (b)**, introduces the concept of ion size to the approximation.^[6]

It is important to note that the traditional models of double layer structure are derived from the Deybe-Huckel theory of dilute electrolytes, an assumption which is clearly not valid for ionic liquids. To date there have been relatively few studies of the structure of the electrochemical double layer in ionic liquids. Additionally, the majority of publications have focussed on the alkyimidazolium: discrete anion ionic liquids and have assumed that the electrochemical double layer will behave in the same manner as in a dilute aqueous electrolyte. More recently theoretical studies by Kornyshev^[7, 8] and Federov^[8] have shown that this approach may be invalid. Two assumptions of the traditional models are particularly difficult to justify for ionic liquids

- i) The ionic species are treated as hard spheres. This is unlikely to be a sound principle for ionic liquids, which generally contain bulky asymmetric ions. Some evidence has already been cited that the orientation of 1-ethyl-3-methylimidazolium ions at the electrode interface in an ionic liquid is sensitive to the applied potential and may have an effect on electrodeposition.^[9]
- ii) The models assume a dilute solution of ions, whereas ionic liquids are by their very nature concentrated ionic media.

Initial studies into the double layer structure in imidazolium: $[(F_3CSO_2)_2N]^-$ and $[BF_4]^-$ ionic liquids have shown that a double layer model based on alternating cation and anion layers may be more applicable.^[10, 11] Furthermore, the double layer capacitance of ionic liquids is smaller than that predicted for a perfect Helmholtz layer, suggesting that ion-pairs are present at the electrode surface at all potentials.^[12]

Recently Baldelli has demonstrated that the orientation of imidazolium cations at a charged interface is sensitive to the applied potential, adding a further layer of complexity to the double layer structure.^[9] Additionally, Baldelli has shown that the double layer is one ion layer thick using sum frequency generation spectroscopy and electrochemistry to probe the electric field at the ionic liquid/ electrode interface.^[13]

The bulky nature of the cations present in ionic liquids may also influence double layer structure. In aqueous solutions the metal ion radii are generally in the order of 1-2 Å. In the absence of neutral moieties the concentration of anions and cations at the interface will be potential dependent, moreover the cationic radii of ionic liquid components are often in the order of 3-5 Å.^[12] The electrode interface could therefore be considered to be coated with a layer of ions up to 6 Å thick. As the majority of metals which dissolve in ionic liquids yield anionic species, the concentration of metal ions at the electrode surface will decrease at more negative applied potentials. The reduction of more noble metals may therefore be difficult in ionic liquids. At the negative potentials required for electrodeposition, the cationic layer may inhibit the approach of the metal anions to the electrode surface, maintaining the metal anion concentration in the double layer below that required for nucleation. Although not well understood this mechanism may partially account for the behaviour demonstrated in **Chapter 3**, where the electrodeposition of Zn from 1: 2 ChCl ethylene glycol and 1: 2 ChCl: urea required a relatively high critical ZnCl₂ concentration. It may be that the incorporation of [Ch]⁺ in the electrochemical double layer inhibits the approach of [ZnCl₄]²⁻ to the electrode surface. Recently the first study of double layer structure in ChCl based deep eutectic solvents has been published and here it was demonstrated that the differential capacitance of the deep eutectic solvent/ electrode interface was similar to those calculated for the traditional ionic liquids.^[14]

As the interest in the use of ionic liquids as electrodeposition media continues to grow, relatively few studies have systematically approached the topic of additive effects. The majority of studies which have touched upon this crucial area are often limited to the addition of organic solvents as diluents, to reduce the melting points and viscosities of the ionic liquids. The addition of large volumes of diluents, often of between 20- 50 weight % of the ionic liquid, raises the question of whether these liquids can still be truly classed as ionic liquids, or are more accurately described as co-solvents. Sun *et al.* have used polypropylene carbonate as a co-solvent in the electrodeposition of Zn^[15] and Zn-Co^[16] from the acidic ZnCl₂-1-ethyl-3-methylimidazolium chloride ionic liquid. In both studies the addition of propylene carbonate acted to reduce the melting point of the fluid, allowing electrodepositions to be carried out at lower temperatures.^[15, 16] The morphology of Zn deposits was also significantly altered by the presence of the organic co-solvent, being more crystalline and with increased grain size when compared to the needle like deposits obtained from unmodified liquid.^[15] Benzene has also been investigated as a possible co-solvent for Zn electrodeposition from AlCl₃-1-methyl-3-ethylimidazoliumchloride, although little explanation was given a clear alteration in surface morphology was observed.^[17]

A wide range of metals have been electrodeposited from ionic liquids and deep eutectic solvents. However, these studies are generally limited to determining the possibility of electrodeposition; few are as thoroughly studied as the corresponding aqueous systems. The purpose of this thesis is to take a single system and to systematically study the individual factors affecting the electrodeposition process. In the previous chapter the electrodeposition of Zn from ChCl based deep eutectic solvents was shown to be sensitive to both the hydrogen bond donor and ZnCl_2 concentration. It was shown that adherent but dull Zn deposits could be obtained from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol and $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: urea. The majority of aqueous electrodeposition processes incorporate a number of organic additives in the electrodeposition bath, as brighteners and levellers, yet this area is almost unstudied in ionic liquids. In this chapter the first systematic study of the effect of a range of organic additives and surfactants on the electrodeposition mechanism of Zn from 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea is presented. The relationship between the electrodeposition mechanism and the resulting deposit morphology is described. In addition the importance of an increased understanding of the double layer structure in ionic liquids and deep eutectic solvents will be highlighted.

4.2 Results and Discussion

The organic additives acetonitrile, ethylene diamine and ammonia were added to 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea and their effect on Zn electrodeposition investigated. Ammonia was initially chosen as previous studies have determined that Zn is effectively complexed by this ligand in aqueous sulphate electrolytes.^[2] Acetonitrile and ethylene diamine were chosen to represent a weaker and a stronger nitrogen containing ligand respectively. This is the first in depth study of the effect of organic brighteners on the Zn electrodeposition mechanism from deep eutectic solvents.

4.2.1 Voltammetry

Figure 4.3 compares the cyclic voltammetric response of a solution of $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in 1: 2 ChCl: ethylene glycol in the absence **(a)** and presence of equimolar quantities of the organic additives acetonitrile **(b)** ethylene diamine **(c)** and ammonia **(d)**.

As described in the **Chapter 3**, with a representative voltammogram reproduced in **Figure 4.3 (a)**, the onset of Zn reduction (vs. Ag) in 1: 2 ChCl: ethylene occurs at $E = -1.080 \text{ V}$ and the oxidation of Zn occurs via a two stage process, with two oxidation peaks at $E = -0.680 \text{ V}$ and $E = -0.554 \text{ V}$. This two phase stripping process was determined to be due to the presence of two energetically different phases of Zn. It is clear from **Figures 4.3 (b)-(d)**

that the presence of the organic additive causes significant changes in the shape and position of the voltammograms. This indicates that the presence of the organic additives alters both the Zn deposition and stripping processes.

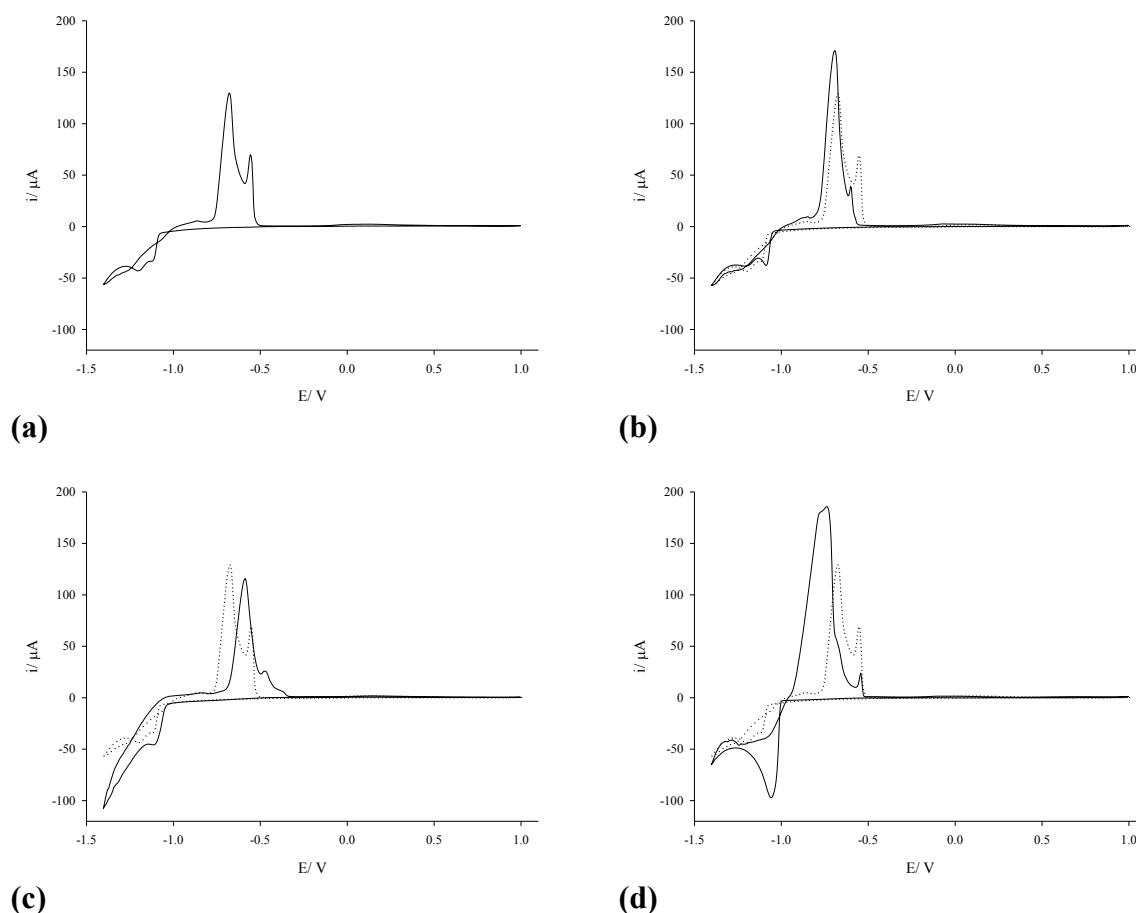


Figure 4.3 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) at 50 °C at 5 mV s^{-1} for (a) $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in 1: 2 ChCl: ethylene glycol and with the following organic additives (b) 0.3 mol dm^{-3} acetonitrile (c) 0.3 mol dm^{-3} ethylene diamine and (d) 0.3 mol dm^{-3} ammonia (from 30 % solution). The dashed lines in (b) (c) and (d) represent the voltammogram obtained in the absence of organic additives (a).

Figure 4.3 (b) contains a representative voltammogram for $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in 1: 2 ChCl: ethylene glycol upon the addition of 0.3 mol dm^{-3} acetonitrile. Here the onset of the Zn reduction potential is unchanged from that of the unmodified solution with $E = -1.080 \text{ V}$. A two phase oxidation process is apparent with stripping peaks at $E = -0.680 \text{ V}$ and $E = -0.554 \text{ V}$, analogous to that in the additive free solution. However, it is clear that the relative charge passed through each of the oxidative processes is different. This may be due to increased mass transport in the acetonitrile containing solution, which would act to promote the diffusion of $[\text{ZnCl}_4]^{2-}$ to the electrode surface, encouraging bulk growth.

The addition of 0.3 mol dm^{-3} ethylene diamine to $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol has a marked effect on the cyclic voltammetry, **Figure 4.3 (c)**. Here, the onset of

reduction is shifted anodically by almost 50 mV to $E = -1.034$ V, suggesting that the presence of ethylene diamine acts to promote the reduction of Zn. This implies that the ethylene diamine does not ligate the Zn species in solution. The replacement of chloride by ethylene diamine, a stronger ligand, would be expected to make the solution phase Zn species more stable and hence more difficult to reduce. Equally, the adsorption of ethylene diamine at the electrode surface would also be expected to inhibit Zn reduction. It is therefore clear that ethylene diamine is not behaving in a similar manner to organic brighteners in aqueous electrolytes as described in 4.1. Nevertheless, preliminary Zn deposition studies have shown that the addition of ethylene diamine to 0.3 mol dm⁻³ ZnCl₂ 1: 2 ChCl: ethylene glycol leads to brighter Zn deposits. Moreover, the position of the cathodic stripping peaks is markedly different to that seen in the additive free solution. In **Chapter 3** it was proposed that Zn electrodeposition is inhibited in 1: 2 ChCl: ethylene glycol by the incorporation of chloride ions in the electrochemical double layer. Ethylene diamine, a stronger hydrogen bond donor than ethylene glycol, may act to reduce the activity of free chloride ions close to the electrode surface. This would in turn act to promote Zn reduction, as the relative concentration of $[\text{ZnCl}_4]^{2-}$ close to the electrode surface would increase as the $[\text{Cl}]^-$ activity and hence chloride mobility is decreased. As $[\text{Cl}]^-$ ions are required to re-complex Zn^0 during oxidation, a reduction in chloride activity would also account for the anodically shifted Zn stripping peaks in **Figure 4.3 (c)**.

The addition of 0.3 mol dm⁻³ ammonia (from 30 % ammonia solution) **Figure 4.3 (d)**, has the largest effect on the voltammetric response. Here the onset of Zn reduction is shifted anodically by 92 mV to $E = -0.991$ V, suggesting that ammonia promotes Zn reduction. The addition of ammonia leads to a reversible reduction peak which shows a clear current crossover, indicative of a nucleation driven process. It is interesting to note that the major stripping peak occurs at a more anodic potential, $E = -0.740$ V, than Zn oxidation in **Figures 4.3 (a)-(c)**. This may indicate that Zn deposited from the ammonia containing solution exists as a different phase (morphology) to that obtained from the additive free, acetonitrile and ethylene diamine containing systems. Additionally it should be noted that the charge passed during Zn oxidation and reduction is greatly increased relative to the additive free solution, however, this is likely to simply be an effect of increased mass transport due to the addition of NH_3 in aqueous solution form.

The corresponding data for 0.3 mol dm⁻³ ZnCl₂ 1: 2 ChCl: urea are presented in **Figure 4.4**. **Figure 4.4 (a)**, contains a representative voltammogram for 0.3 mol dm⁻³ ZnCl₂ in 1: 2 ChCl: urea. As previously discussed, Zn reduction in 1: 2 ChCl: urea occurs *via* a single step reduction with a reduction onset of $E = -1.080$ V. The single oxidation peak, $E = -0.630$

V_r is broad as a consequence of the relatively high viscosity of this liquid. The reduction process shows a clear current cross over loop indicative of a nucleation process. In **Chapter 3** Zn deposition from 1: 2 ChCl: urea was shown to be mass transport controlled. Chloride adsorption was proposed to be less important in this solvent as the chloride activity is thought to be considerably lower than in the equivalent 1: 2 ChCl: ethylene glycol.

The addition of acetonitrile to this solution, **Figure 4.4 (b)**, has a more pronounced effect than in 1: 2 ChCl: ethylene glycol deep eutectic solvent, **Figure 4.3 (b)**. Here the oxidation process is both sharper and more cathodic at $E = -0.775$ V, although this may be a product of increased mass transport in the solution.

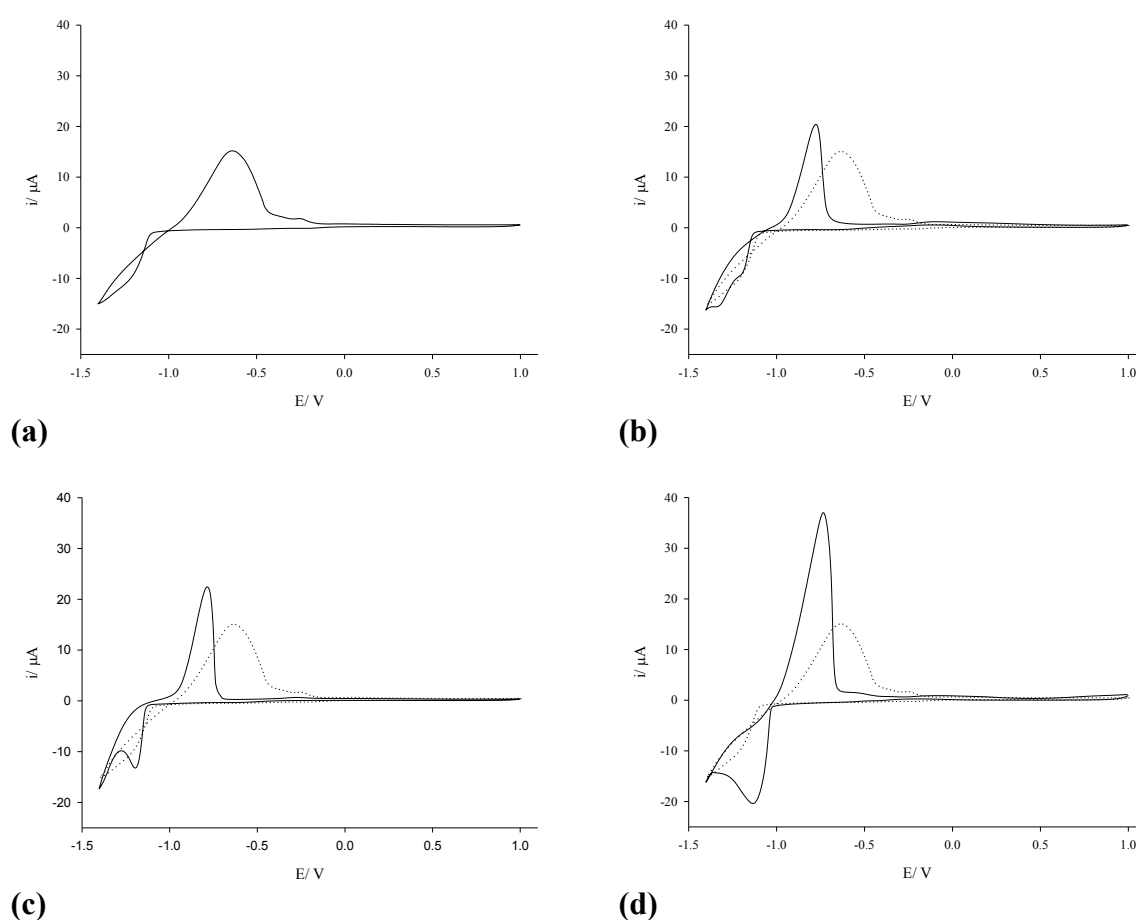


Figure 4.4 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) at 50°C at 5 mV s^{-1} for (a) $0.3\text{ mol dm}^{-3}\text{ ZnCl}_2$ in 1:2 ChCl: urea and with the following organic additives (b) 0.3 mol dm^{-3} acetonitrile (c) 0.3 mol dm^{-3} ethylene diamine and (d) $0.3\text{ mol dm}^{-3}\text{ NH}_3$ (from 30 % aqueous solution). The dashed lines in (b) (c) and (d) represent the voltammogram obtained in the absence of organic additives (a).

Upon the introduction of 0.3 mol dm^{-3} ethylene diamine, **Figure 4.4 (c)**, to 0.3 mol dm^{-3} 1: 2 ChCl: urea, the reduction wave becomes well defined. In addition the onset of reduction is shifted 40 mV cathodically to $E = -1.12$ V, suggesting that in this system the ethylene

diamine inhibits the initiation of Zn nucleation. This behaviour is contrary to that observed in 1: 2 ChCl: ethylene glycol, where ethylene diamine appeared to promote Zn reduction.

Figure 4.4 (d) shows the effect of the addition of 0.3 mol dm^{-3} ammonia (from 30 % ammonia solution) to 0.3 mol dm^{-3} ZnCl₂ 1: 2 ChCl: urea. As with 1: 2 ChCl: ethylene glycol, the reduction of Zn appears to be promoted by ammonia, with a shift of reduction onset potential to $E = -1.020 \text{ V}$.

The cyclic voltammetric data presented above suggests that whilst acetonitrile has a limited effect on Zn reduction and oxidation, ethylene diamine and ammonia fundamentally alter the Zn electrodeposition process. Furthermore it is clear that the behaviour of the organic additives is very different in 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea. In **Chapter 3** it was determined that Zn deposition in 1: 2 ChCl: urea is primarily mass transport controlled. Conversely, Zn electrodeposition from 1: 2 ChCl: ethylene glycol was proposed to be limited by the high chloride activity of the solvent. The difference in effect of the organic additives in the two solvents may be a result of competition between these two limiting factors. The ability of the organic additives to hydrogen bond to free chloride ions increases in the order acetonitrile < NH₃ < ethylene diamine. In 1: 2 ChCl: ethylene glycol the strength of the hydrogen bond donor will have the greatest effect on Zn reduction and this trend is observed in the cyclic voltammetry, where NH₃ and ethylene diamine are shown to encourage Zn reduction. On the contrary, the reduction in mass transport upon the addition of the additives will be the dominant effect in 1: 2 ChCl: urea. It is also important to acknowledge that all of these studies assume that the reference potential remains unchanged by the additive.

4.2.2 Nucleation Mechanisms

In order to further probe the possible change in Zn reduction mechanism, the nucleation mechanism must be studied. **Figure 4.5** contains the I-t transients for 0.3 mol dm^{-3} ZnCl₂ in 1: 2 ChCl: ethylene glycol **(a)** and with the addition of 0.3 mol dm^{-3} acetonitrile **(b)** 0.3 mol dm^{-3} ethylene diamine **(c)** and 0.3 mol dm^{-3} NH₃ **(d)**.

In each of the following experiments the initial rise in current due to double layer charging at potential switching has been omitted for clarity. All four systems display an increase in current at short time scales which is related to Zn nucleation. In each system a current density maximum, I_m , is reached and followed by a falling current. This behaviour is indicative of a nucleation/ growth type mechanism. However, the addition of organic additives significantly alters the position of the maximum current density and time of

maximum current density, t_m , coordinates and in the case of NH_3 the shape of the I-t transients.

The I-t transients obtained for $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol are reproduced in **Figure 4.5 (a)**, where a broad current peak is observed suggesting that the initial stages of Zn formation from this liquid are relatively slow as discussed in the **Chapter 3**. Although the I-t transients appear to decay to a mass transport controlled limit, it is clear that at different applied overpotentials, the transients do not decay to a single current, as would be expected for a system which is solely under Cottrell type diffusion control.

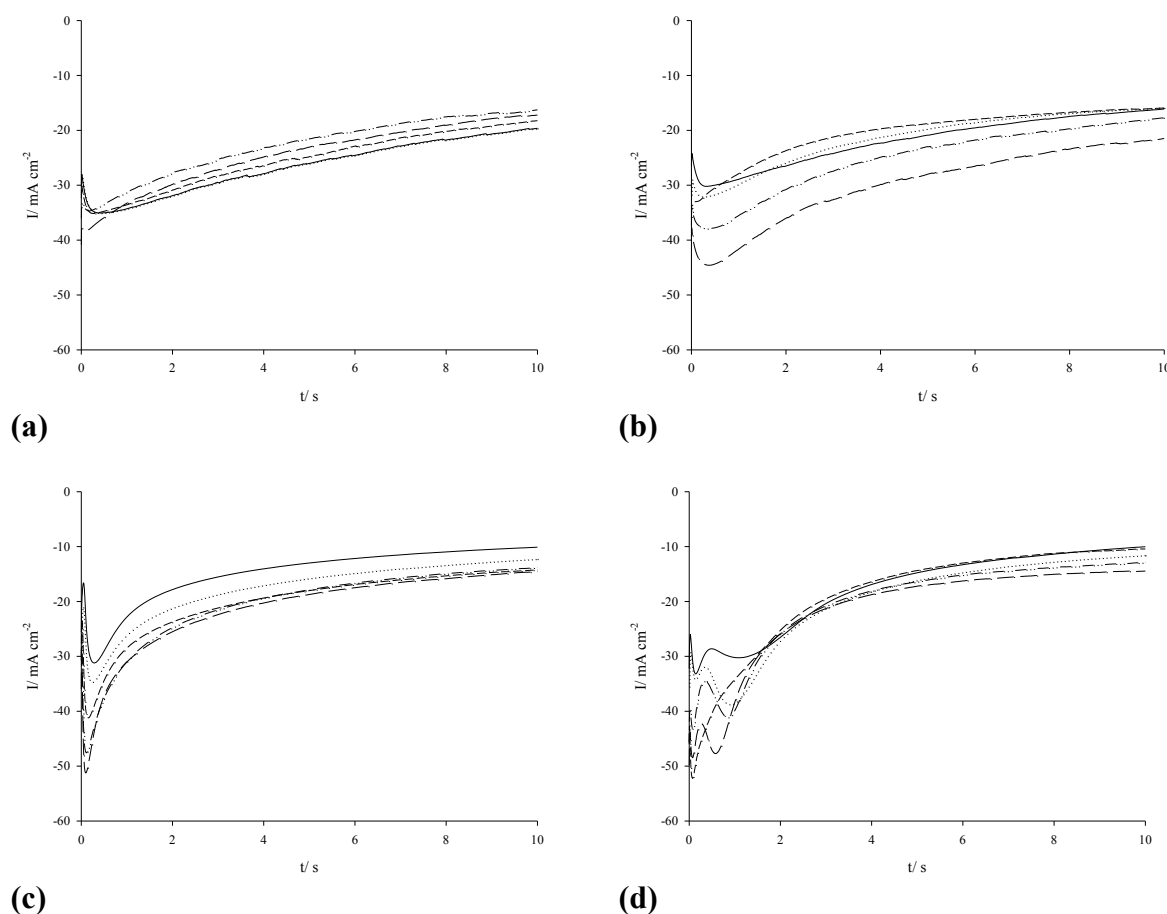


Figure 4.5 Chronoamperograms obtained at a Pt disc (0.5 mm dia.) at 50 °C vs. a Ag wire pseudo reference electrode for (a) $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol and with the following organic additives (b) 0.3 mol dm^{-3} acetonitrile (c) 0.3 mol dm^{-3} ethylene diamine and (d) 0.3 mol dm^{-3} ammonia. Applied potentials range from -1.20 V (solid black line) to -1.28 V (dashed black line) with steps of 20 mV. An initial preconditioning potential of -0.80 V was applied for 10 s in all experiments.

A similar behaviour is observed when 0.3 mol dm^{-3} acetonitrile is added to the additive free solution, **Figure 4.5 (b)**. A broad current density peak is reached followed by decay to a current density which is dependent on applied potential. Furthermore, the addition of

acetonitrile causes an increase in the current density maximum alongside a decrease in the time of current maximum.

The addition of 0.3 mol dm^{-3} ethylene diamine, **Figure 4.5 (c)**, yields a typical I-t transient for a nucleation/ growth process, where I_m increases with applied cathodic overpotential while t_m decreases. It is clear that ethylene diamine acts to promote Zn nucleation, and this is consistent with the voltammetric data presented in **Figure 4.3 (c)**, where it was observed that ethylene diamine caused the onset of Zn reduction to be shifted 50 mV anodically.

Figure 4.5 (d) shows the effect of the addition of 0.3 mol dm^{-3} ammonia. Here an initial nucleation related current increase is followed by a second current peak before the system relaxes to mass transport control. This indicates the existence of a second nucleation process at the electrode surface after the initial nucleation of Zn; ammonia clearly promotes Zn nucleation, over the growth of existing nuclei.

The current transients obtained for $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in 1: 2 ChCl: urea, with each of the additives, at a range of potentials, are presented in **Figure 4.6**.

When no additive is present, **Figure 4.6 (a)**, a broad shallow nucleation peak is observed. The magnitude of the coordinates, I_m and t_m , differ by approximately a factor of 5 to those obtained from 1: 2 ChCl: ethylene glycol. This is an effect of the differing mass transport properties of the two liquids, these being at 25°C , 22 cP and 240 cP for $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol and $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1:2 ChCl: urea respectively.

The addition of acetonitrile, **Figure 4.6 (b)**, leads to an increase in the current passed and an increase in the time taken to reach I_m . This effect may be due to acetonitrile acting as a diluent, reducing the viscosity of 1: 2 ChCl: urea.

Upon the addition of 0.3 mol dm^{-3} ethylene diamine, the current transients show characteristic nucleation related peak formation, followed by a current decay to a mass transport related limit, **Figure 4.6 (c)**. It is interesting to note that while the chronoamperometric data suggests ethylene diamine promotes Zn nucleation, the cyclic voltammetry, **Figure 4.4 (c)**, indicated an inhibitory effect.

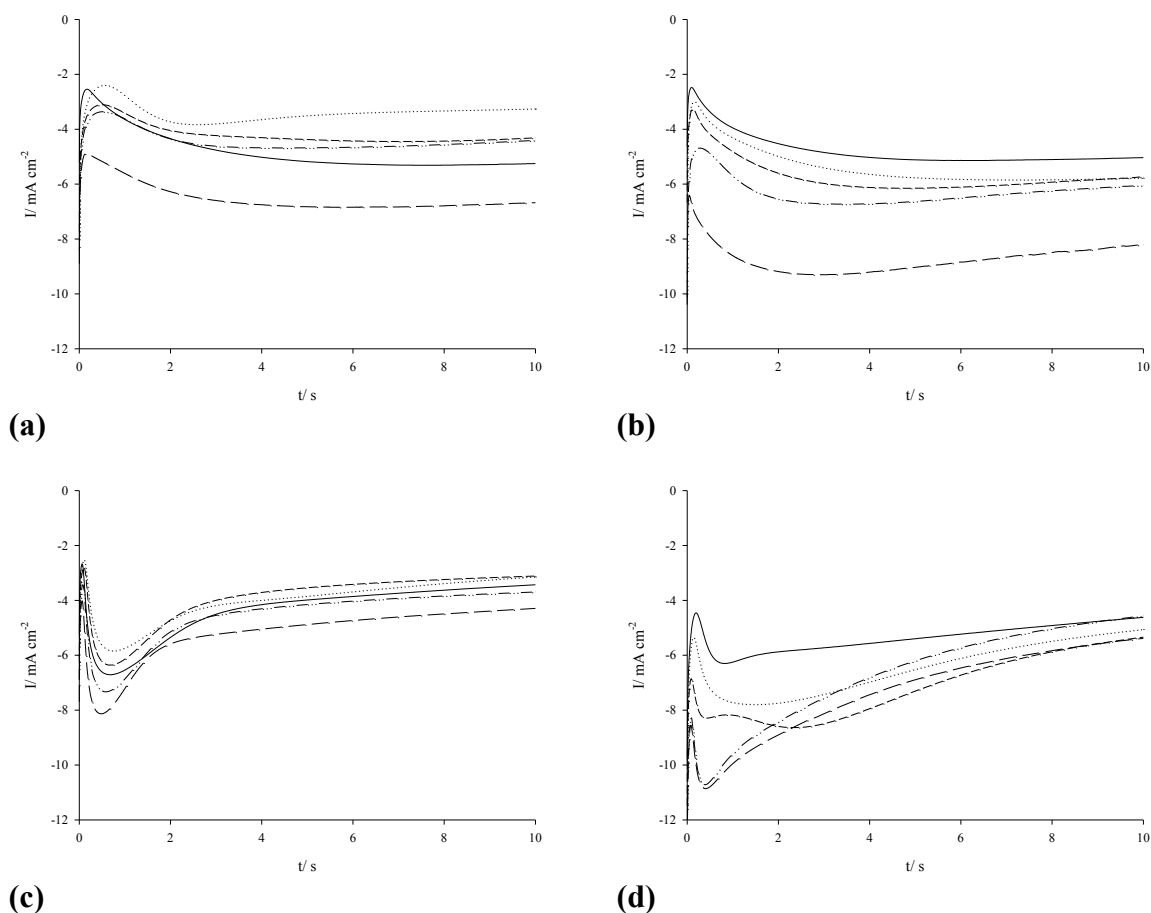


Figure 4.6 Chronoamperograms obtained at a Pt disc (0.5 mm dia.) at 50 °C vs. a Ag wire pseudo reference electrode for (a) 0.3 mol dm⁻³ ZnCl₂ 1: 2 ChCl: urea and with the following organic additives (b) 0.3 mol dm⁻³ acetonitrile (c) 0.3 mol dm⁻³ ethylene diamine and (d) 0.3 mol dm⁻³ ammonia. Applied potentials range from -1.20 V (solid black line) to -1.28 V (dashed black line) with steps of 20 mV. An initial preconditioning potential of -0.80 V was applied for 10 s in all experiments.

A clear nucleation maximum is seen when ammonia is introduced to the additive free solution, **Figure 4.6 (d)**. It is evident that ammonia acts to promote Zn nucleation and this is supported by the cyclic voltammetric data discussed in **4.2.1**. As with 1: 2 ChCl: ethylene glycol, the limiting current in each of the above experiments is strongly overpotential dependent, suggesting that the systems studied are not simply under diffusion control.

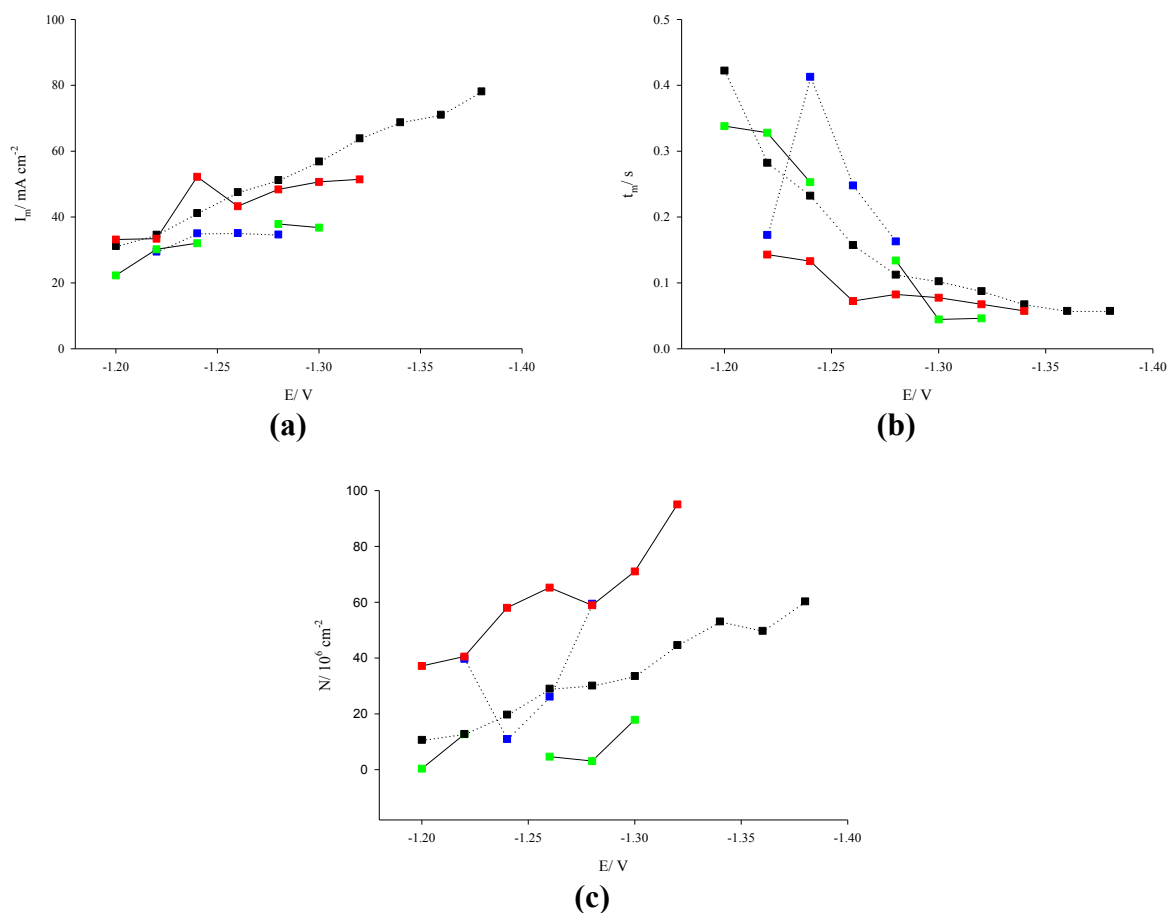


Figure 4.7 Plots showing the relationship between cathodic overpotential and (a) I_m , (b) t_m and (c) N for $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in 1: 2 ethylene glycol (blue squares) with 0.3 mol dm^{-3} acetonitrile (green squares), 0.3 mol dm^{-3} ethylene diamine (black squares) and 0.3 mol dm^{-3} ammonia (red squares). These values are calculated from the chronoamperometric data presented in **Figure 4.4**.

The relationship between the nucleation parameters I_m , t_m and N (nuclear number density) and cathodic overpotential, in 1: 2 ChCl: ethylene glycol, is presented in **Figure 4.7**. As the cathodic overpotential is increased, I_m increases linearly and t_m decreases for the systems containing ethylene diamine and ammonia. However, when the deep eutectic solvent contains acetonitrile or is without additives there is less correlation. It is clear that the I_m of nucleation, at low overpotentials, is similar in each of the systems. However, I_m is reached at different rates in the order ammonia > ethylene diamine > acetonitrile > unmodified liquid. This suggests that the presence of ethylene diamine and ammonia acts to promote the nucleation of Zn at the Pt surface. The behaviour observed in the falling part of the I vs. t trace is controlled by diffusion to the planar electrode and can be quantitatively described by the Cottrell equation, **Equation 4.1**

$$I(t) = \frac{nFD^{\frac{1}{2}}C_0}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}} \quad \text{Equation 4.1}$$

Where $I(t)$ is the current density as a function of time, t , n the number of moles of electrons involved in the electrodeposition (in the case of Zn^{2+} reduction, 2), F is the Faraday constant, D is the diffusion coefficient and C_0 the bulk Zn concentration. A number of methods have been devised to determine nucleation mechanisms and parameters, the most widely used being the model developed by Scharifker and Hills.^[18] This model allows chronoamperometric data to be assigned to one of two limiting nucleation mechanisms, instantaneous or progressive. Instantaneous nucleation, where the slow growth of nuclei at a small number of concurrently activated active sites is the dominant mechanism, is defined by **Equation 4.2**:

$$\frac{I_m}{I_m^2} = \frac{1.9542}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-1.2654 \left(\frac{t}{t_m} \right) \right] \right\}^2 \quad \text{Equation 4.2}$$

Progressive nucleation, where the rapid growth of a large number of active sites activated throughout the reduction dominates is defined by **Equation 4.3**:

$$\frac{I_m}{I_m^2} = \frac{1.2254}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_m} \right) \right]^2 \right\}^2 \quad \text{Equation 4.3}$$

Where I_m and t_m are the current and time at the peak coordinate of maximum current. **Figures 4.8** and **4.9** contain experimental current transients plotted as reduced current and time alongside the limiting theoretical cases of 3D instantaneous and 3D progressive nucleation.

In **Figure 4.8 (a)** it is seen that the experimental chronoamperometry data for 0.3 mol dm^{-3} ZnCl_2 1: 2 ChCl : ethylene glycol shows a poor fit to the 3D models proposed by Scharifker and Hills. The data also fits poorly to the 2D limiting cases (not shown). This behaviour remains when 0.3 mol dm^{-3} of acetonitrile is added to the system, **Figure 4.8 (b)**, consistent with the voltammetric results where this additive was shown to have a limited effect, **Figure 4.3 (b)**. Although at longer time scales the general shape of the experimental transient is similar to the theoretically proposed models, the magnitudes of the reduced currents are much higher than the theoretical. This suggests that the experimental current is not solely due to the nucleation of Zn and so can not be easily modelled by the Scharifker-Hills method.

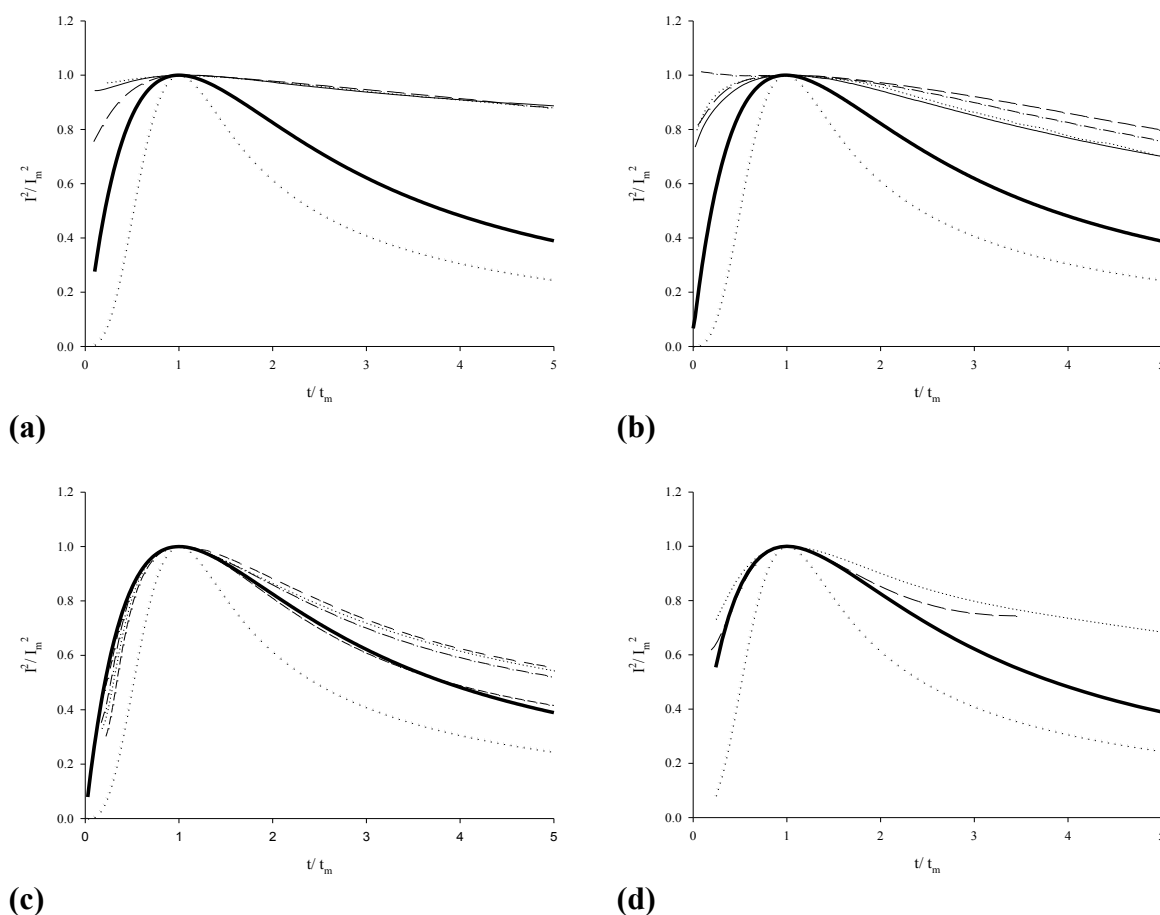


Figure 4.8 Reduced t vs. reduced I plots for a representative selection of the chronoamperometric data presented in **Figure 4.5**, where (a) $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol and with the following organic additives (b) 0.3 mol dm^{-3} acetonitrile (c) 0.3 mol dm^{-3} ethylene diamine and (d) 0.3 mol dm^{-3} ammonia.

The experimental data for the addition of 0.3 mol dm^{-3} ethylene diamine, **Figure 4.8 (c)**, fits well to the limiting 3D instantaneous nucleation mechanism, although at times greater than t_m the fit decreases.

Upon the addition of 0.3 mol dm^{-3} ammonia to $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol, **Figure 4.8 (d)**, the nucleation process is more complex. The experimental I - t transients, **Figure 4.5 (d)**, display two current maxima. The current initially rises to a maximum, begins to fall towards the mass transport controlled level before rising a second time to a second maximum. This behaviour suggests that a second nucleation process is preferential to the growth of existing nuclei at short time scales. In fitting the two current peaks separately to the Scharifker-Hills model it becomes clear that the two processes fit the two limiting models; the initial I - t peak adheres well to the 3D instantaneous case, whereas the broader second I - t peak fits the theoretical trace for a 3D progressive nucleation mechanism.

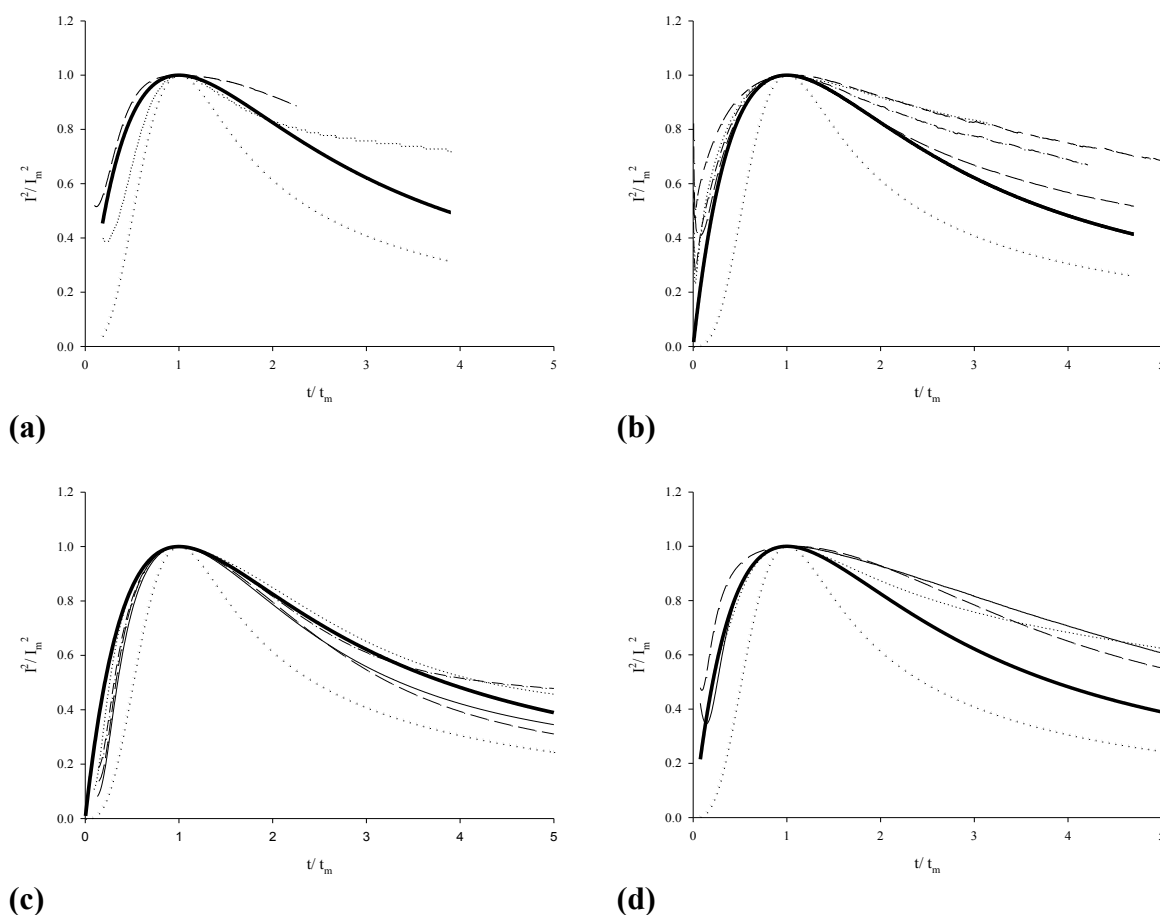


Figure 4.9 Reduced t vs. reduced I plots for a representative selection of the chronoamperometric data presented in **Figure 4.6**, where (a) $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: urea and with the following organic additives (b) 0.3 mol dm^{-3} acetonitrile (c) 0.3 mol dm^{-3} ethylene diamine and (d) 0.3 mol dm^{-3} ammonia.

The nucleation mechanism of Zn in the presence of organic additives in 1: 2 ChCl: urea modelled using the Scharifker-Hills model is shown in **Figure 4.9**. The effect of each of the additives on the Zn nucleation mechanism is shown to be similar to the behaviour in 1: 2 ChCl: ethylene glycol. The chronoamperometric data for the unmodified ZnCl_2 containing solvent fits poorly to the limiting 3D, **Figure 4.9 (a)**, and 2D (not shown) nucleation models. Equally, the solution containing 0.3 mol dm^{-3} acetonitrile, **Figure 4.9 (b)**, also shows a poor degree of fit to the limiting mechanisms.

The addition of 0.3 mol dm^{-3} ethylene diamine leads to the development of a clear current maximum which fits well to a 3D instantaneous mechanism, **Figure 4.9 (c)**. The addition of $0.3 \text{ mol dm}^{-3} \text{ NH}_3$ does not lead to a two stage Zn nucleation mechanism in 1: 2 ChCl: urea, **Figure 4.9 (d)**, a single nucleation process is observed which fits well to a 3D instantaneous mechanism at times less than t_m .

As the reduced plots in **Figures 4.8** and **4.9** suggest a 3D instantaneous mechanism, diffusion coefficients, D , can be calculated from the $I_m^2 t_m$ product suggested by Scharifker, **Equation 4.4**:

$$I_m^2 t_m = 0.163 (nFC^\infty)^2 D \quad \text{Equation 4.4}$$

Where I_m is the maximum current density, t_m the time at which the maximum current density occurs, n the number of moles of electrons involved in the electrodeposition (in the case of Zn^{2+} reduction, 2), F is the Faraday constant and C the bulk Zn concentration. Diffusion coefficients calculated for the data presented in **Figures 4.5** and **4.6** using **Equation 4.4** are presented in **Table 4.1**.

Diffusion Coefficients $\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$	No Additive	Ethylene Diamine	NH_3	Acetonitrile
1:2 ChCl: EG	4.76	5.13	3.07	5.50
1:2 ChCl: Urea	1.43	0.454	0.587	3.29

Table 4.1 Mean diffusion coefficients, D , calculated from the chronoamperograms presented in **Figures 4.5** and **4.6**

The data in **Table 4.1** represents the effect of organic additives on the diffusion coefficient, calculated from the chronoamperometric presented in **Figures 4.5** and **4.6**. However, it is important to note that as the I - t traces do not decay to a mass transport limited level *via* Cottrell type decay, the diffusion coefficients can only be treated as a relative measure.

4.2.3 Gravimetric Analysis

The rate of Zn deposition has been analysed using EQCM, the data for both 0.3 mol dm^{-3} ZnCl_2 in 1: 2 ChCl: ethylene glycol and 0.3 mol dm^{-3} 1: 2 ChCl: urea have been presented in the previous chapter. **Figure 4.10 (a)** shows the effect of the addition of 0.3 mol dm^{-3} acetonitrile, 0.3 mol dm^{-3} ethylene diamine and 0.3 mol dm^{-3} NH_3 , on the growth rate of Zn from 1: 2 ChCl: ethylene glycol. The data is consistent with that derived from the cyclic voltammetry and chronoamperometry. The addition of acetonitrile is shown to have little effect on the growth rate of the Zn deposit. As in the additive free solution, the deposition process is retarded at short time scales, less than 300 s, before a turn over point in growth rate is reached. Ethylene diamine and ammonia both act to increase the rate of Zn deposition from 1: 2 ChCl: ethylene glycol, the initial stages of the mass-time trace are no longer very slow. From the electrochemical data previously discussed it has been shown

that it is unlikely that ethylene diamine and ammonia have acted to complex the Zn species in solution, rather that they must interact with the free $[\text{Cl}]^-$ in solution. Ethylene diamine and ammonia are both strong hydrogen bond donors and may act to reduce the activity of the chloride anions close to the electrode surface. This in turn will reduce the rate of $[\text{Cl}]^-$ diffusion to the electrode surface, effectively reducing the hypothesised $[\text{Cl}]^-$ adsorption effect observed in the absence of additives and with acetonitrile.

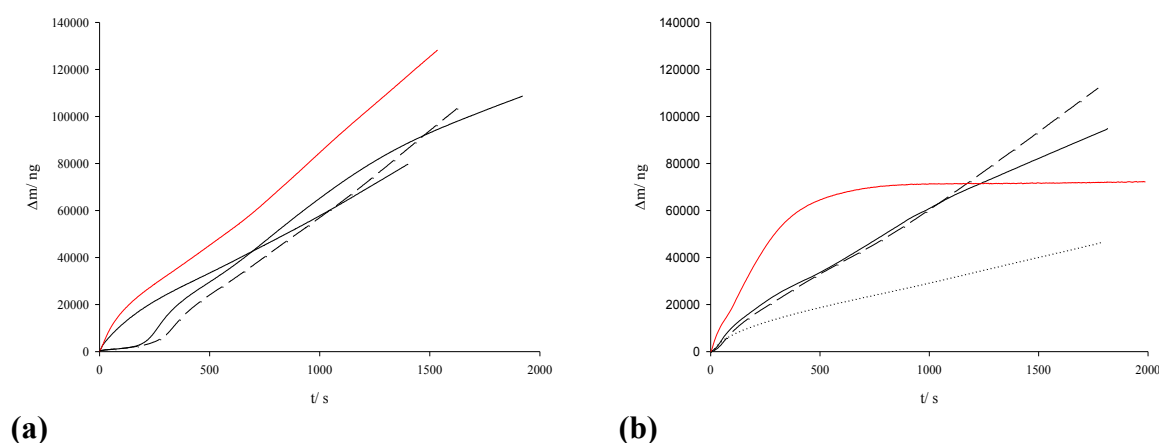


Figure 4.10 Mass-Time traces for the potentiostatic electrodeposition of Zn from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in (a) 1: 2 ChCl: ethylene glycol and (b) 1: 2 ChCl: urea (solid black line) and with the following organic additives 0.3 mol dm^{-3} acetonitrile (dashed black line) 0.3 mol dm^{-3} ethylene diamine (dotted black line) and 0.3 mol dm^{-3} ammonia (solid red line). In each experiment the applied potential was switched from the o.c.p. to -1.30 V (vs. Ag wire).

The corresponding data for $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: urea are presented in **Figure 4.10 (b)**. Acetonitrile is once more observed to have a minimal effect on the Zn deposition process. However, the behaviour of the solutions containing 0.3 mol dm^{-3} ethylene diamine and 0.3 mol dm^{-3} ammonia is very different to that observed in the ethylene glycol based liquid. When 0.3 mol dm^{-3} ethylene diamine is added to 0.3 mol dm^{-3} 1: 2 ChCl: urea, the rate of growth is reduced, in comparison to the ethylene glycol based liquid where an increase in deposition rate was observed. This suggests that in the urea based liquid ethylene diamine is inhibiting Zn growth, consistent with the cyclic voltammetry data presented in **Figure 4.4 (c)**. Conversely the addition of ammonia promotes Zn reduction, however, it is clear that a rough deposit is obtained, as at times $> 500 \text{ s}$ the deposit clearly no longer acts as a rigid mass. Analysis of the mass-charge transient from the same experiment, **Figure 4.11**, confirms that at long time scales the Zn deposit from the ammonia containing liquid is no longer acting as a rigid resonator, after 500 s the charge continues to increase with no consequent increase in mass.

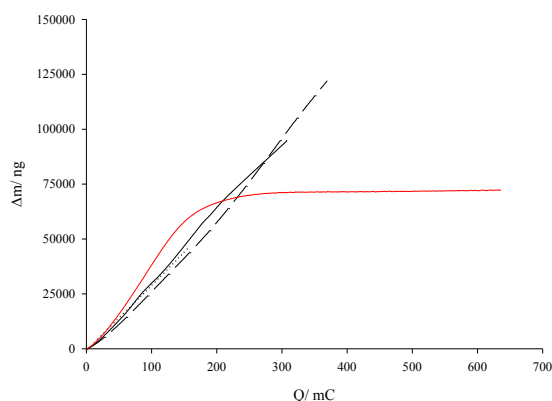


Figure 4.11 Mass-Charge traces for the potentiostatic electrodeposition of Zn from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: urea (solid black line) and the following organic additives 0.3 mol dm^{-3} acetonitrile (dashed black line) 0.3 mol dm^{-3} ethylene diamine (dotted black line) and 0.3 mol dm^{-3} ammonia (solid red line). In each experiment the applied potential was switched from the o.c.p. to -1.30 V (vs. Ag wire).

4.2.4 Deposit Morphology and Ionic Liquid Speciation

Figure 4.12 contains representative SEM images of Zn electrodeposited from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol **(a)** and $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol with 0.3 mol dm^{-3} acetonitrile **(b)**, 0.3 mol dm^{-3} ethylene diamine **(c)** and $0.3 \text{ mol dm}^{-3} \text{ NH}_3$ **(d)**. The Zn electrodeposits were prepared under identical conditions and are representative of the standard results obtained from a larger range of electrodeposition studies (*ca.* 10 electrodeposits were made under these conditions for each additive). As such the images can be treated as representative of the Zn morphologies obtained in the presence of the organic additives. It is important to consider that the morphological studies have been performed on a different substrate to the electrochemical studies (mild steel rather than platinum) making direct comparisons difficult. However, sample SEM images have been taken of the Pt electrode surfaces after Zn deposition, and the Zn morphology appears to be identical to that obtained on mild steel.

In the absence of any organic additives, **Figure 4.12 (a)**, Zn electrodeposits from 1: 2 ChCl: ethylene glycol appear to have a two dimensional morphology, perpendicular to the substrate. The crystallites retain the hexagonal structure usually found for Zn deposits; however, growth appears to be inhibited at specific crystal faces, leading to the morphology shown. In the previous chapter it was suggested that this morphology may be caused by specific chloride adsorption at the growing Zn surface. The only Zn species in this liquid has been shown to be $[\text{ZnCl}_4]^{2-}$, when this species is reduced at the electrode surface chloride will be discharged. It is proposed that this chloride adsorbs to the growing Zn surface inhibiting the adsorption of further $[\text{ZnCl}_4]^{2-}$ anions to the electrode surface.

Furthermore, the degree of chloride adsorption will be related to the chloride activity in the liquid. Ethylene glycol is a relatively weak hydrogen bond donor, and as such the chloride activity in 1: 2 ChCl: ethylene glycol will be high, leading to large amounts of chloride adsorption.

The addition of 0.3 mol dm^{-3} acetonitrile, **Figure 4.12 (b)**, results in a change in morphology. The Zn crystallites now have a homogeneous hexagonal structure; however, the growth of the crystals still appears to be restricted to certain crystal faces. This 2D growth mechanism may account for the poor fit of the chronoamperometric data, **Figures 4.5 and 4.8 (b)**. The limiting nucleation models proposed by Scharifker and Hills, which assume that hemispherical nuclei grow *via* either 3D growth or 2D growth in the x and y axes, may be insufficient to describe this form of nucleation where growth is 2D in the x(y) and z axes.

The Zn morphology is further modified upon the introduction of 0.3 mol dm^{-3} ethylene diamine to the solution, **Figure 4.12 (c)**. Here, the underlying Zn morphology obtained is similar to that shown in previous Zn electrodeposition studies from both ionic liquids and aqueous systems.^[1, 15] However, at longer time scales/ higher current densities large plates are formed and these lead to dispersive bright Zn deposits. Ethylene diamine is a relatively strong hydrogen bond donor and will effectively coordinate to the chloride anions in solution and as such may act to reduce the hypothesised chloride adsorption at the growing Zn surface. This would lead to the morphology observed in **Figure 4.12 (b)**, whereby the growth of existing Zn crystallites is more favourable than the formation of new nuclei.

Conversely, the addition of 0.3 mol dm^{-3} ammonia, **Figure 4.12 (d)**, results in a Zn deposition mechanism whereby nucleation is favoured over growth. This behaviour can be seen in the SEM image presented above, where the underlying Zn structure is clearly similar to that obtained with ethylene diamine, **Figure 4.12 (c)**, however, in this system secondary nucleation events have led to the development of large Zn crystallites which grow perpendicular to the electrode surface. Additionally, the development of further Zn crystallites can be seen upon these large Zn crystallites. This morphology is consistent with chronoamperometric data presented in **Figures 4.5 and 4.8 (d)** where the addition of ammonia lead to a I-t trace with two distinct current maxima, the earliest of which fits well to the 3D instantaneous whereas the second nucleation process fits well to the 3D progressive mechanism. This may be due to the presence of $[\text{NH}_4]^+$ in the double layer, which may change the mechanism of growth. It has recently been shown by Endres^[19] and Abbott^[20] that the cation has a significant affect upon the nucleation mechanism for

aluminium. Endres *et al.* studied the difference between ethyl-methyl-imidazolium and pyrrolidinium cations whereas Abbott *et al.* investigated the addition of LiCl to an imidazolium-based ionic liquid. Both studies saw changes in morphology from nano-crystalline to micro-crystalline but neither drew conclusive evidence to show the double layer effect that caused this change.

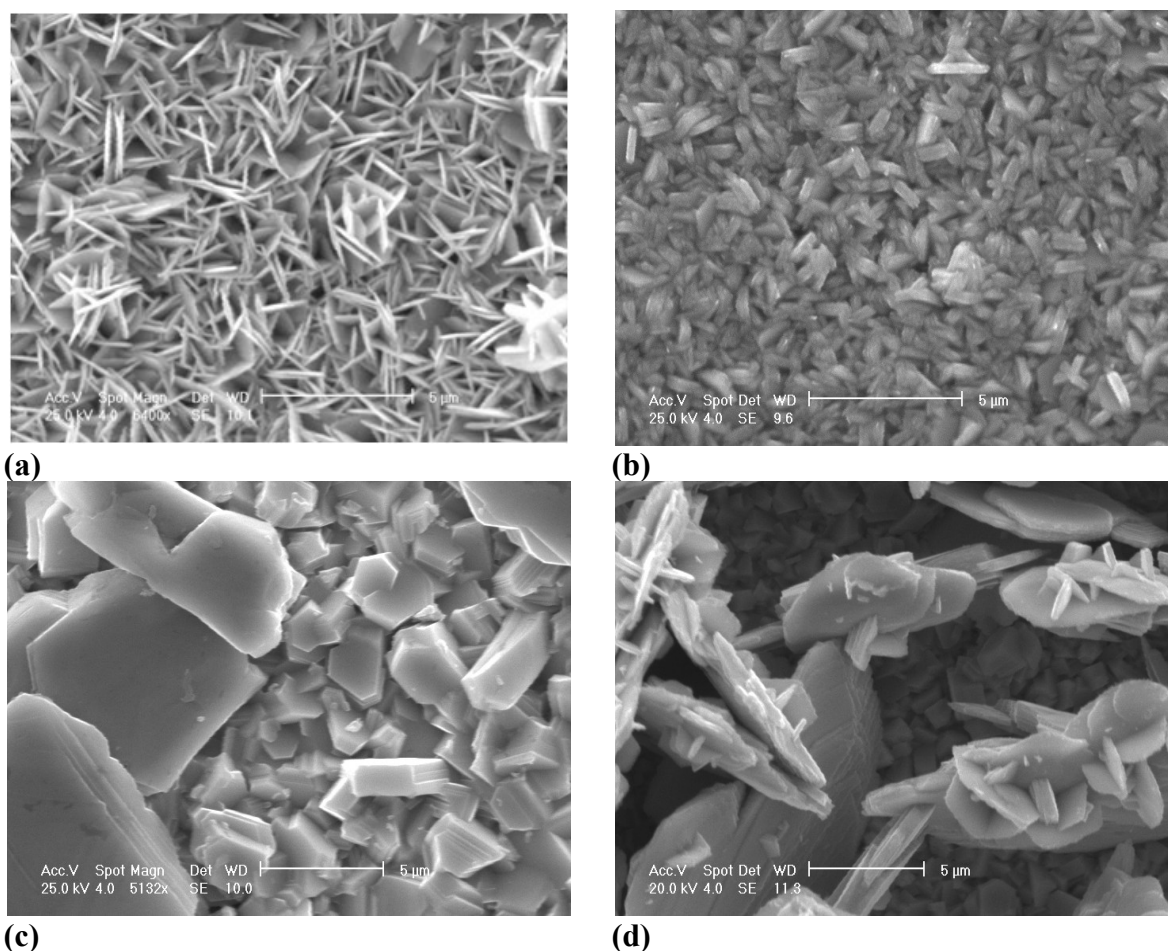


Figure 4.12 Representative scanning electron micrographs of Zn electrodeposited from (a) 0.3 mol dm^{-3} 1: 2 ChCl: ethylene glycol with (b) 0.3 mol dm^{-3} acetonitrile (c) 0.3 mol dm^{-3} ethylene diamine and (d) 0.3 mol dm^{-3} ammonia. All electrodepositions were carried out on mild steel plates, at 50°C and at a constant current density of 2.5 mA cm^{-2} for 30 minutes.

The analogous data set for Zn electrodepositions from 0.3 mol dm^{-3} ZnCl_2 1: 2 ChCl: urea is presented in **Figure 4.13**. As with **Figure 4.12** the SEM images are samples taken from a larger set of reproducible deposition studies and as such can be considered as representative of the Zn morphologies obtained from 0.3 mol dm^{-3} ZnCl_2 1: 2 ChCl: urea (a) and 0.3 mol dm^{-3} ZnCl_2 1: 2 ChCl: urea with 0.3 mol dm^{-3} acetonitrile (b) 0.3 mol dm^{-3} ethylene diamine (c) and 0.3 mol dm^{-3} ammonia (d) under the stated conditions.

In the absence of additives, **Figure 4.13 (a)**, the Zn deposit appears to have a homogeneous rice-grain like deposit, very different to that obtained in 1: 2 ChCl: ethylene glycol, **Figure 4.12 (a)**. It has been shown in **Chapter 3** that the Zn speciation in the two ionic liquids is

identical; therefore the difference in morphology cannot be a metal speciation effect. The cationic species in both ionic liquids is also thought to be identical, the choline cation, and as such the cation effect can also be eliminated. The difference in morphology can therefore only be due to either the difference in viscosity (1: 2 ChCl: urea is *ca.* 10 times more viscous than 1: 2 ChCl: ethylene glycol), or the relative chloride activity in the liquids. Urea is a stronger hydrogen bond donor than ethylene glycol and as such will readily complex free chlorides in the solution, preventing chloride adsorption at the electrode surface (within the electrochemical double layer). This may account for the much clearer Zn reduction wave observed in voltammetric experiments in 1: 2 ChCl: urea, **Figure 4.4**. This morphology is also consistent with the chronoamperometric data in **Figures 4.6 and 4.9 (a)**, where a 3D instantaneous nucleation mechanism was predicted. In a 3D instantaneous nucleation mechanism a large number of nuclei form instantaneously and grow at the same rate, leading to a homogenous distribution of crystallite sizes as seen in **Figure 4.13 (a)**.

The addition of acetonitrile, **Figure 4.13 (b)**, results in a change in the Zn morphology whereby the deposit is less homogeneous than the rice-grain structure observed in the absence of additives. Here, it is clear that some crystallites are larger than others and that growth of existing Zn crystallites is being promoted. This is consistent with the cyclic voltammetric data, **Figure 4.4 (b)**, where the addition of acetonitrile was shown to increase the reduction potential of Zn. A comparison of the chronoamperometric data, **Figure 4.6 (b)**, also shows that acetonitrile impedes Zn nucleation, in that the time taken to reach the current density maximum is increased.

In contrast to Zn electrodeposition from 1: 2 ChCl: ethylene glycol, the Zn morphologies obtained from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: urea upon the addition of 0.3 mol dm^{-3} ethylene diamine, **Figure 4.13 (c)**, and 0.3 mol dm^{-3} ammonia, **Figure 4.13 (d)**, are very similar. In this deep eutectic solvent, the chloride activity will be much lower than in the analogous ethylene glycol containing solvent. Here, the dominant effect may be the reduction in mass transport which will promote the growth of existing nuclei over the formation of new nucleation site.

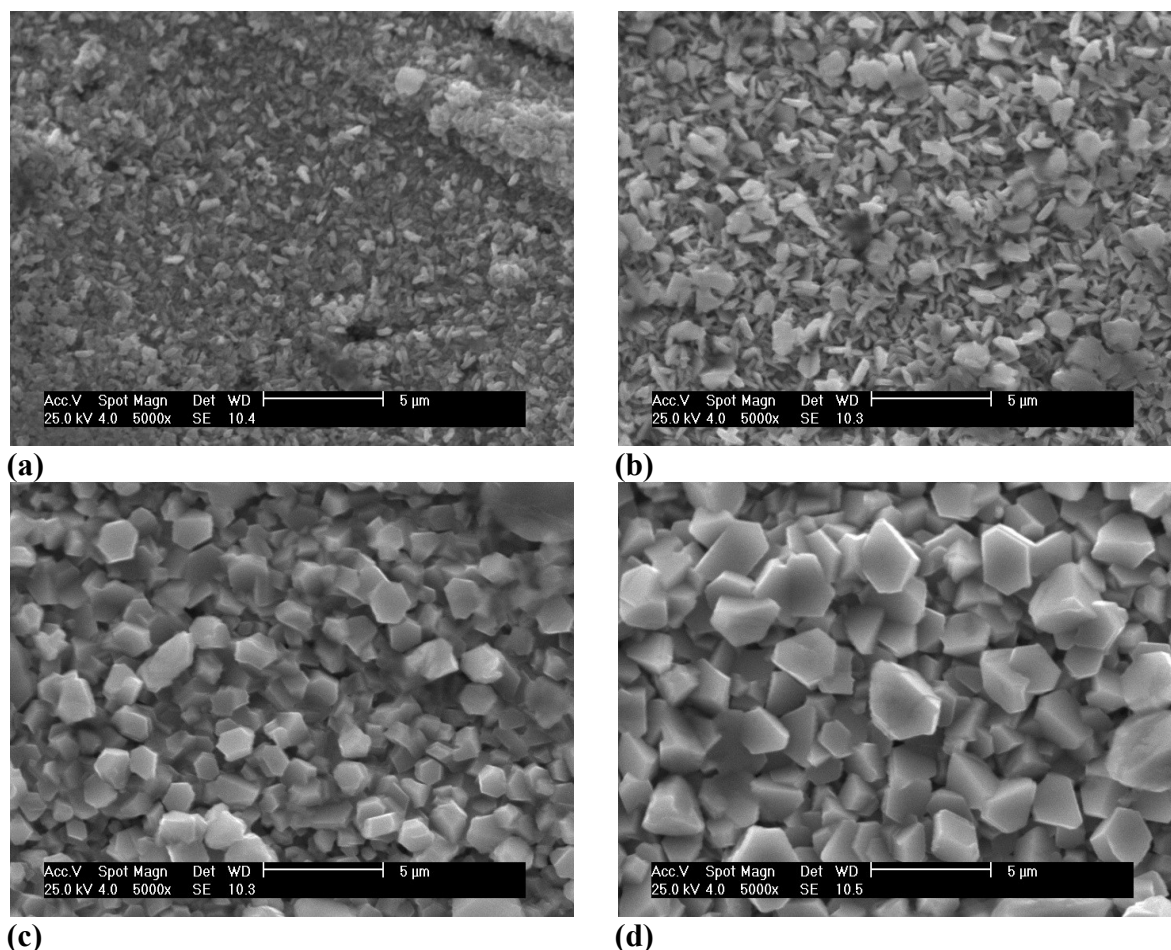


Figure 4.13 Representative scanning electron micrographs of Zn electrodeposited from (a) 0.3 mol dm^{-3} 1: 2 ChCl: urea with (b) 0.3 mol dm^{-3} acetonitrile (c) 0.3 mol dm^{-3} ethylene diamine and (d) 0.3 mol dm^{-3} ammonia. All electrodepositions were carried out on mild steel plates, at 50°C and at a constant current density of 2.5 mA cm^{-2} for 30 minutes.

The addition of organic brighteners has been shown to have a significant effect on the morphology of Zn deposited from deep eutectic solvents. Parallel studies by Abbott *et al.* on the electrodeposition of Cu and Ni from the deep eutectic solvents studied in this thesis, in the presence of organic additives, have demonstrated that ethylene diamine alters the Cu/Ni species present in the liquid, evidenced by a clear change in the UV-Vis absorption spectra.^[21] Although the coordination chemistry of d_{10} Zn is very different to that of Cu and Ni, it remains essential to determine whether the changes in Zn morphology and electrochemical response are due to coordination with the organic additives. It has been demonstrated in the previous chapter of this thesis that *in-situ* EXAFS is a useful technique for probing metal speciation in deep eutectic solvents. EXAFS showed that the only Zn species present in the 0.3 mol dm^{-3} ZnCl_2 1: 2 ChCl: ethylene glycol and 0.3 mol dm^{-3} ZnCl_2 1: 2 ChCl: urea liquids is the $[\text{ZnCl}_4]^{2-}$ anion. Here EXAFS is used to probe the bulk Zn speciation in 1: 2 ChCl: ethylene glycol upon the addition of ethylene diamine and ammonia. **Figure 4.13** shows X-ray absorption data obtained at the Zn K edge (9659 eV) for (a) 0.3 mol dm^{-3} ZnCl_2 1:2 ChCl: ethylene glycol with (b) 0.3 mol dm^{-3} ammonia and (c)

0.3 mol dm⁻³ ethylene diamine. The EXAFS spectra were fitted using EXCURV98, allowing electron scattering parameters for the atoms in the sample to be calculated using the Hedin-Lundqvist potential. **Table 4.2** shows fitted values of interatomic distances (from the Zn atom) R, coordination numbers N, atomic type and the root mean square variation in interatomic distance σ^2 for the scattering atoms included in the fit. There is also an energy offset E_0 corresponding to the energy between the mean potential in the sample and the energy of the lowest unoccupied molecular orbital (E_0 is always negative as defined in the program). EXCURV98 also provides estimates of the uncertainty in these fitted parameters and an overall goodness of fit. It is clear that the three spectra are essentially identical and that each of the three samples are best fitted by an environment consisting of four Cl atoms suggesting that the Zn species in both liquids is the same, namely $[\text{ZnCl}_4]^{2-}$, i.e. proving unequivocally that there is no coordination between the Zn and ethylene diamine or ammonia. Additionally the calculated interatomic distances of 228 pm is similar to that found in solid state tetrahedral ZnCl_2 (231 pm). Although no data was obtained for the addition of 0.3 mol dm⁻³ acetonitrile it is clear from the voltammetric and chronoamperometric response that acetonitrile has less of an effect on the electrochemistry of the solution and therefore is unlikely to be coordinated to Zn.

The results presented in **Figure 4.13** and **Table 4.2** are unusual as they prove that the organic additives ammonia and ethylene diamine are not acting to complex the Zn species in 1: 2 ChCl: ethylene glycol. However, it is clear from the data presented in this chapter that the additives do have an effect on the Zn nucleation mechanism and deposit morphology. It has been hypothesised that this alteration of Zn reduction mechanism may be due to solvent inclusion, anion activity or cation adsorption. To further probe the effect of organic additives on Zn deposition from ChCl: hydrogen bond donor deep eutectic solvents, the study has been extended to investigate cations and anions which are known to specifically adsorb at interfaces, surfactants. The anionic surfactant, sodium dodecyl sulphate (SDS), and the cationic surfactant, hexacetylammonium bromide (CTAB), were selected as their activity in aqueous Zn electrodeposition baths has been well characterised.^[4, 5, 22]

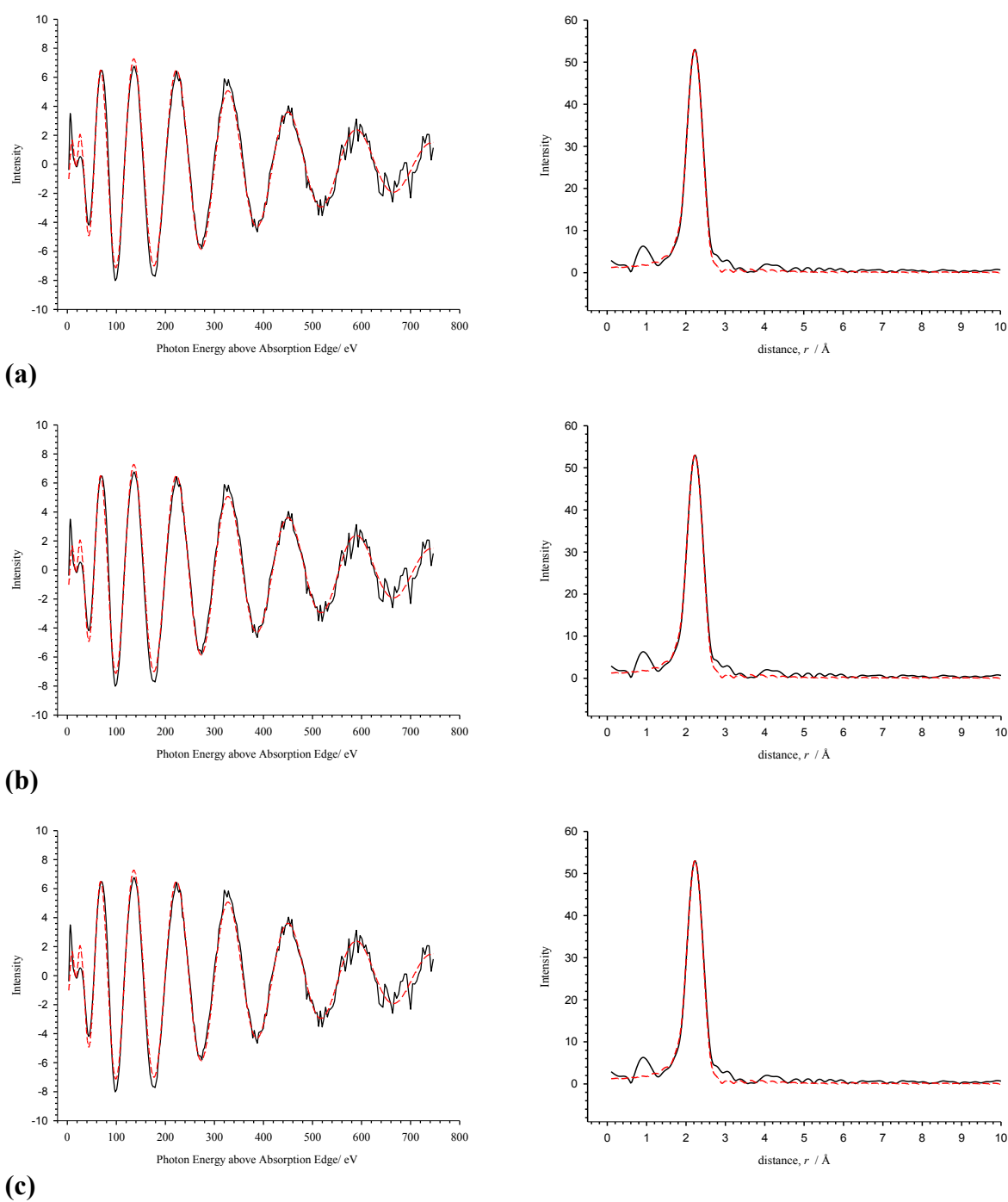


Figure 4.13 EXAFS spectra obtained at the Zn-K-Edge of $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in 1: 2 ChCl: ethylene glycol with (a) no additives (b) 0.3 mol dm^{-3} ammonia and (c) 0.3 mol dm^{-3} ethylene diamine.

0.3M ZnCl ₂ in 1: 2 ChCl: Ethylene Glycol	N	Type	R pm	σ^2 (pm) ²	E ₀ eV	Fit Index
No Additives	3.8±0.2	Cl	228±2	50±5	-9.8	1.6
0.3M NH ₃	3.8±0.2	Cl	228±2	50±5	-9.6	1.9
0.3M Ethylene Diamine	3.9±0.2	Cl	227±2	55±5	-9.5	1.8

Table 4.2 Electron scattering parameters for x-ray absorption data shown in **Figure 4.13**, fitted using EXCURV98.

4.2.4 The Effect of Surfactants on Zn Deposition from Deep Eutectic Solvents

Cationic and anionic surfactants have been added to acidic aqueous Zn plating baths to act as levelling agents.^[3] CTAB and SDS have both been shown to affect Zn crystallinity and grain size,^[4, 5, 22] whilst it has also been suggested that CTAB increases the current efficiency of the Zn deposition process in acidic sulphate baths.^[3] The effect of surfactant addition to Zn deposition from ionic liquids is yet to be comprehensively studied. Here, a preliminary investigation into the effect of ionic surfactants on Zn electrodeposition in deep eutectic solvents is presented.

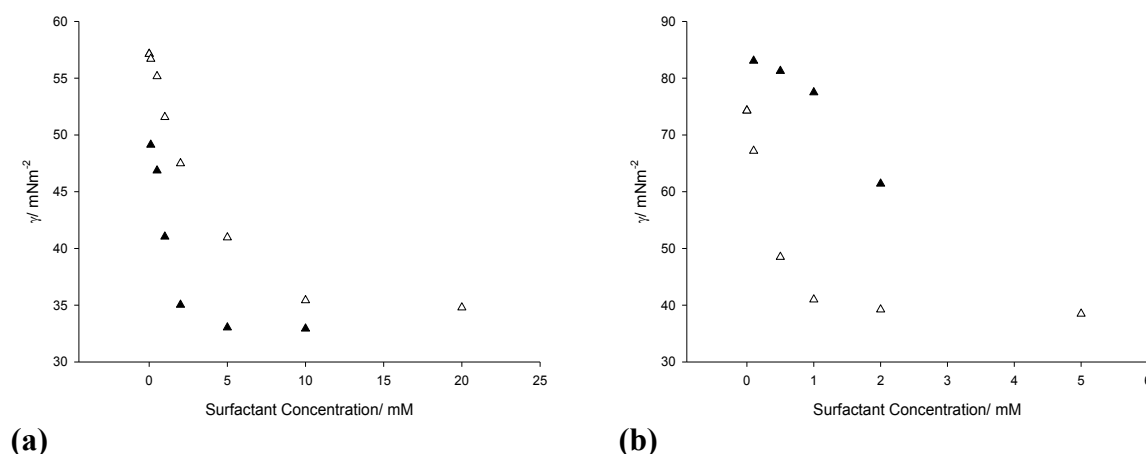


Figure 4.14 Surface tension of 0.3 mol dm^{-3} ZnCl₂ in (a) 1: 2 ChCl: ethylene glycol and (b) 1: 2 ChCl: urea as a function of CTAB (black triangles) and SDS (clear triangles) concentration.

It is well known that surfactants work by forming micelles and that the adsorption of these micelles at active sites can effect metal nucleation mechanisms.^[4, 5, 22] However, a critical concentration of surfactant, the critical micellar concentration (c.m.c.) is required for micelle formation. The c.m.c can be estimated by measuring the surface tension of the solvent as a function of surfactant concentration, **Figure 4.14**. The critical micellar

concentrations of CTAB and SDS in 1: 2 ChCl: ethylene glycol have thus been determined to be 3 mmol dm^{-3} and 6 mmol dm^{-3} respectively. In contrast, the critical micellar concentrations of CTAB and SDS were found to be 2 mmol dm^{-3} and 1 mmol dm^{-3} respectively in 1: 2 ChCl: urea. Additionally, the introduction of the surfactants to the deep eutectic solvents results in a general increase in the density of the systems, **Figure 4.15**.

The surfactants CTAB and SDS have been shown to have a marked effect on the surface tension and density of the deep eutectic solvents. The following sections will focus on Zn electrodeposition from 1: 2 ChCl: ethylene glycol; which as the least viscous and most conductive of the two deep eutectic solvents is the more interesting solvent from a commercial viewpoint.

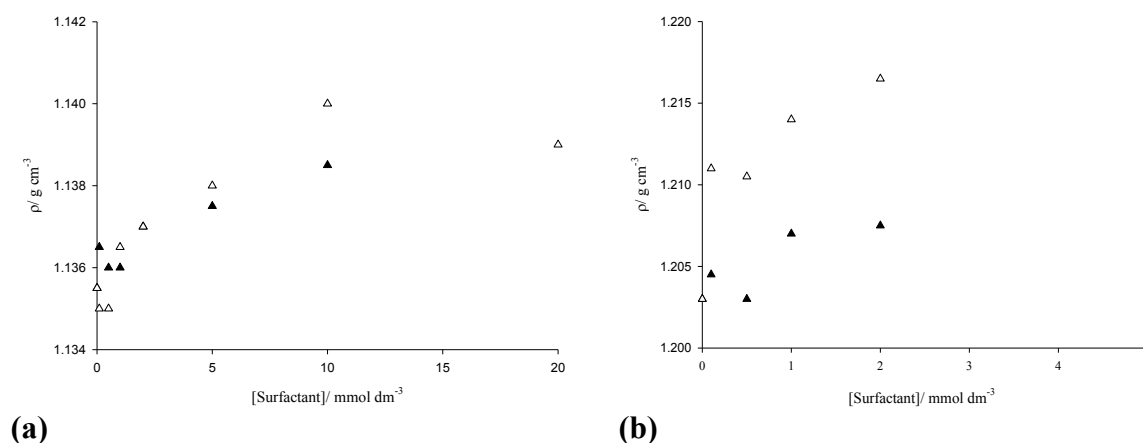


Figure 4.15 Density of $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ in (a) 1: 2 ChCl: ethylene glycol and (b) 1: 2 ChCl: urea as a function of CTAB (black triangles) and SDS (clear triangles) concentration.

The introduction of SDS to $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol has a clear effect on the cyclic voltammetry. The Zn reduction wave is increasingly suppressed with increasing surfactant concentration, **Figure 4.16 (a)**, an effect not observed in Zn deposition from aqueous electrolytes, where the anionic SDS was shown to solely inhibit Zn oxidation having no effect on the Zn reduction process.^[4] This may be explained by a preferential orientation of the anionic surfactant head group within the electrochemical double layer at the cathode, which in turn restricts the approach of $[\text{ZnCl}_4]^{2-}$. At higher cathodic overpotentials, **Figure 4.16 (c)**, a clear suppression of Zn oxidation is apparent, with the anodic oxidation charge falling with increased SDS concentration. It is also clear that the introduction of SDS inhibits the 2nd anodic oxidation process present in the voltammogram without surfactant, which is discussed in detail in **Chapter 3**. This indicates that the surfactant may alter the morphology of the electrodeposited Zn.

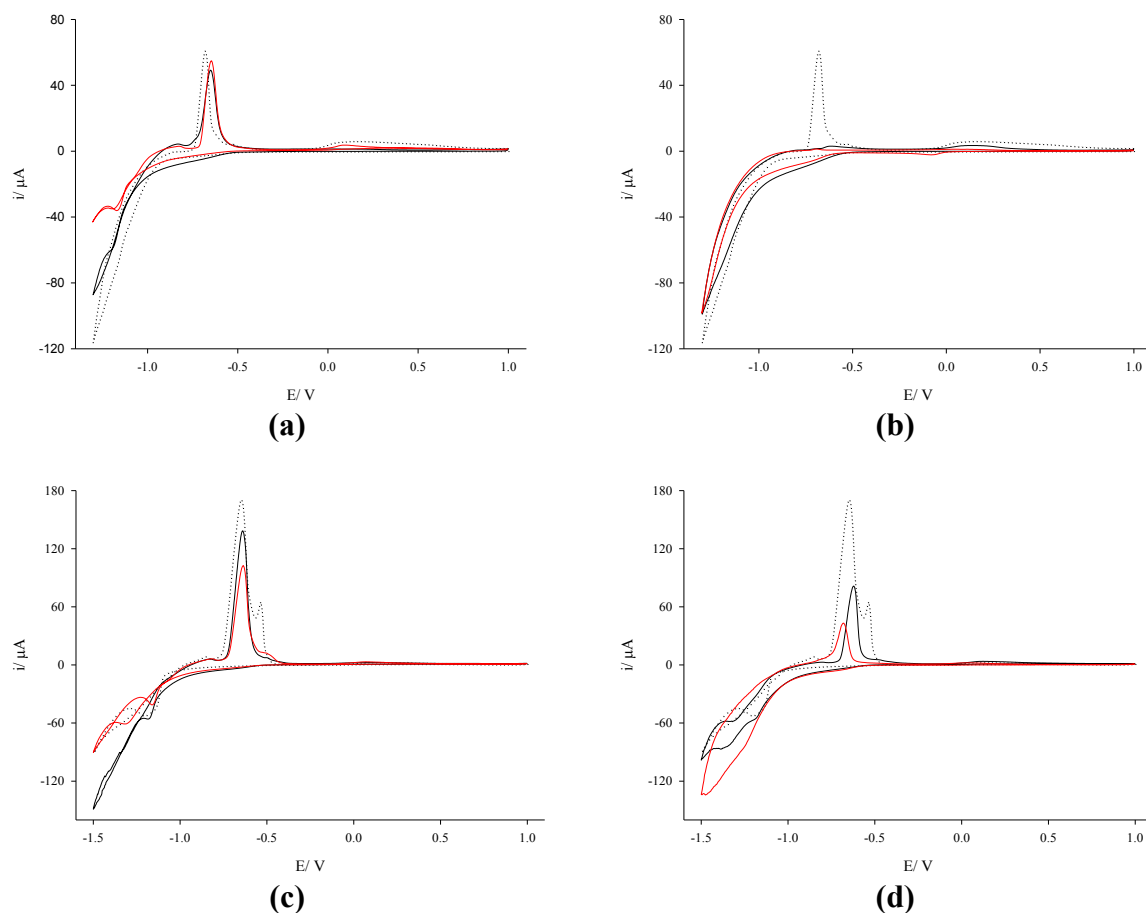


Figure 4.16 Representative cyclic voltammograms showing the effect of the addition of sodium dodecyl sulphate (**a, c**) and hexacetylammmonium bromide (**b, d**) to $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol. The plots are presented as a function of surfactant concentration, no surfactant (dotted line), 2 mmol dm^{-3} surfactant (solid black line) and 10 mmol dm^{-3} surfactant (solid red line). Voltammograms were obtained at 10 mV s^{-1} .

The cathodic surfactant, CTAB, also alters the voltammetric response of $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol. In **Figure 4.16 (b)**, the oxidation of Zn is fully inhibited upon the addition of 2 mmol dm^{-3} CTAB, whilst the reduction wave is significantly broadened. When the cathodic limit of the experiment is extended to -1.50 V , **Figure 4.16 (d)**, the reduction wave becomes broad and ill defined, the corresponding Zn oxidation peak reducing in size with increasing CTAB concentration. It is also clear that as CTAB concentration increases the current cross over indicative of nucleation is obscured. This, alongside the increase in cathodic current suggests that the cathodic surfactant is adsorbing to the electrode surface, inhibiting Zn nucleation.

The addition of ammonia and ethylene diamine to the deep eutectic solvents was previously shown to modify the Zn deposit morphology. Differences in the cyclic voltammetry were proposed to be the product of the formation of various Zn phases. The cyclic voltammograms in **Figure 4.16** suggest that as surfactant concentration is increased the number of Zn phases is reduced. This in turn implies that bulk Zn deposits obtained in the

presence of high concentrations of surfactant will have a more homogeneous morphology than those formed in the absence of surfactants.

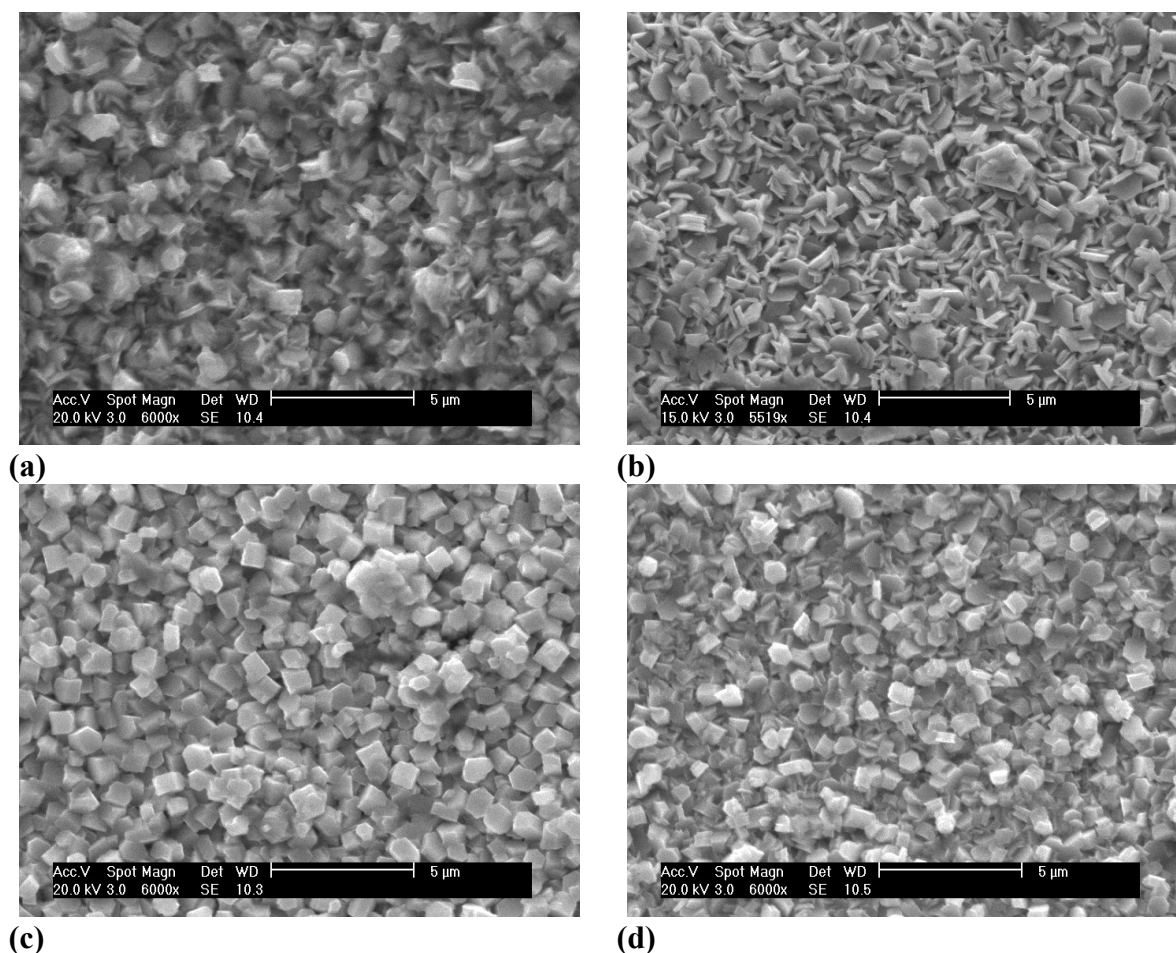


Figure 4.17 Scanning electron micrographs of Zn electrodeposits obtained from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol with (a) SDS 0.1 mmol dm^{-3} and (c) 5 mmol dm^{-3} and (b) CTAB 0.1 mmol dm^{-3} and (d) 5 mmol dm^{-3} . Electrodeposits were carried out at 50°C and a constant current density of 3 mA cm^{-2} .

As predicted by the cyclic voltammetry, the addition of surfactants does indeed alter the Zn morphology, **Figure 4.17**. Without surfactant, as seen in **Figure 4.12 (a)**, Zn electrodeposition from 1: 2 ChCl: ethylene glycol leads to irregularly arranged crystallites with a needle like appearance. Upon the addition of SDS there is an apparent change in the preferred orientation of the Zn crystallites, **Figure 4.17 (a)**. Here, a more regular homogeneous deposit of hexagonal Zn crystallites is obtained. As the SDS concentration is increased above the c.m.c., **Figure 4.17 (c)**, homogeneous hexagonal Zn crystallites dominate. The deposits are visibly less friable and granular than those obtained in the absence of SDS. This single phase morphology is consistent with the voltammetric data presented in **Figure 4.16**. SDS appears to act as a surface modifier, reducing the chloride adsorption effect observed in the absence of surfactant. It is probable that the anionic

surfactant is preferentially incorporated in the electrochemical double layer, restricting the approach of $[\text{Cl}]^-$ and controlling the deposition of Zn.

CTAB is a much less effective grain modifier than SDS. Zn deposits obtained with CTAB concentrations below the c.m.c., **Figure 4.17 (b)** had a similar morphology to those obtained in the absence of surfactant, albeit with a lower average crystallite size. Additionally, increasing the CTAB concentration above the c.m.c did not lead to a homogeneous Zn morphology, **Figure 4.17 (d)**. CTAB is a cationic surfactant and as such will have less of an effect on the high concentration of chloride ions incorporated in the electrochemical double layer, inhibiting Zn growth as described in **Chapter 3**. Rather, the cyclic voltammetry and morphology data suggest that CTAB is adsorbed at the growing Zn surface and inhibits bulk growth.

The addition of ionic surfactants to 1: 2 ChCl: ethylene glycol has a clear effect on the cyclic voltammetry and the deposit morphology. To further investigate the Zn nucleation mechanism in the presence of surfactants, an illustrative pair of chronoamperometric experiments is presented in **Figures 4.18**.

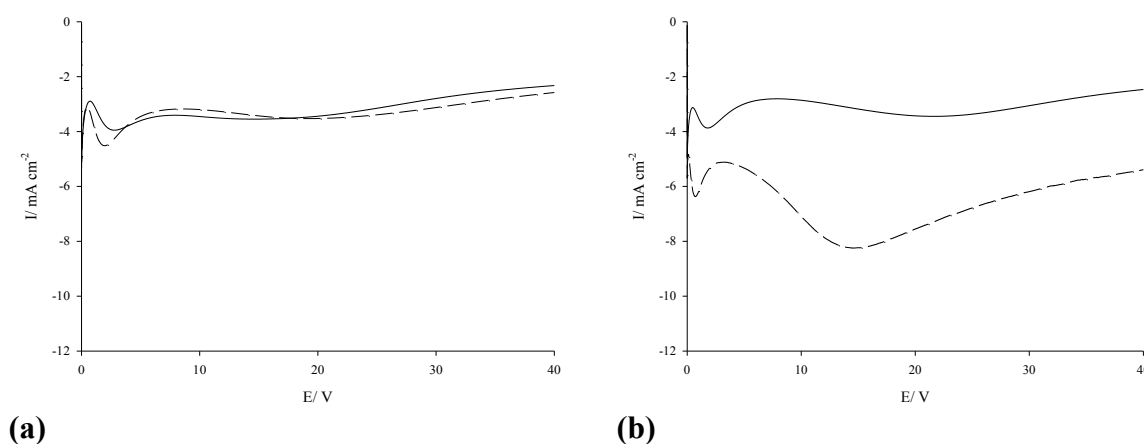


Figure 4.18 Chronoamperograms obtained at a Pt disc (0.5 mm dia.) at 50 °C vs. a Ag wire pseudo reference electrode, with an applied potential of -1.30 V, for 0.3 mol dm⁻³ ZnCl₂ 1: 2 ChCl: ethylene glycol with the organic surfactants **(a)** SDS and **(b)** CTAB at 1 mmol dm⁻³ (solid line) and 5 mmol dm⁻³ (dashed line) concentrations. An initial preconditioning potential of -0.80 V was applied for 10 s in all experiments.

Figure 4.18 (a) contains I-t data for the potentiostatic deposition of Zn in the presence of SDS at concentrations above and below the c.m.c (intermediate concentrations are omitted for clarity). As the SDS concentration is increased a clear I-t maximum is observed, unlike the I-t trace in the absence of surfactant. However, the I-t transient is relatively similar at all SDS concentrations. Additionally at each concentration the I-t trace decays to the same

mass transport related current density. As the concentration of SDS is increased past the c.m.c., the magnitude of the current maximum shows a slight increase as the time to reach the maximum current falls. This is consistent with cyclic voltammetry where SDS was seen to have little effect on the Zn reduction current at this potential (although at higher cathodic overpotentials the surfactant concentration becomes significant, **Figure 4.16 (c)**). However, this behaviour is in contrast to the expected behaviour of surfactants in aqueous electrolytes, where the surfactant is adsorbed at the electrode surface, blocking nucleation sites and hence causing a net decrease in current.

Conversely, the I-t behaviour is highly sensitive to CTAB concentration. As the concentration of CTAB is increased, the maximum current passed also rises. Again this is consistent with the voltammetric data where an increase in cathodic current was observed with increasing CTAB concentration. At longer time scales it is also clear that the CTAB containing solution does not directly relax to mass transport control, there is a second broad current density maximum. As with the addition of ammonia, this behaviour suggests a nucleation mechanism where nucleation is favoured over growth, consistent with the irregularly sized Zn crystallites observed in the bulk deposit, **Figure 4.17 (b) and (d)**.

By fitting the chronamperograms to the Scharifker and Hills nucleation models, **Figure 4.19**, it is clear that both SDS and CTAB have differing effects on the nucleation mechanism. I-t traces obtained in the presence of SDS show a poor fit to both 3D instantaneous and progressive nucleation mechanisms. Additionally increasing the concentration of SDS has little effect on the nucleation mechanism.

In contrast, increasing the CTAB concentration shifts the Zn nucleation mechanism from 3D instantaneous to a 3D progressive mechanism. Once more this is consistent with a model where the cationic CTAB adsorbs preferentially to active sites, inhibiting the Zn nucleation. A similar effect was observed in aqueous Zinc sulphate electrodeposition baths where SDS was determined to have little effect on the nucleation mechanism whereas CTAB caused a shift in the nucleation mechanism from 3D instantaneous to 3D progressive.^[5]

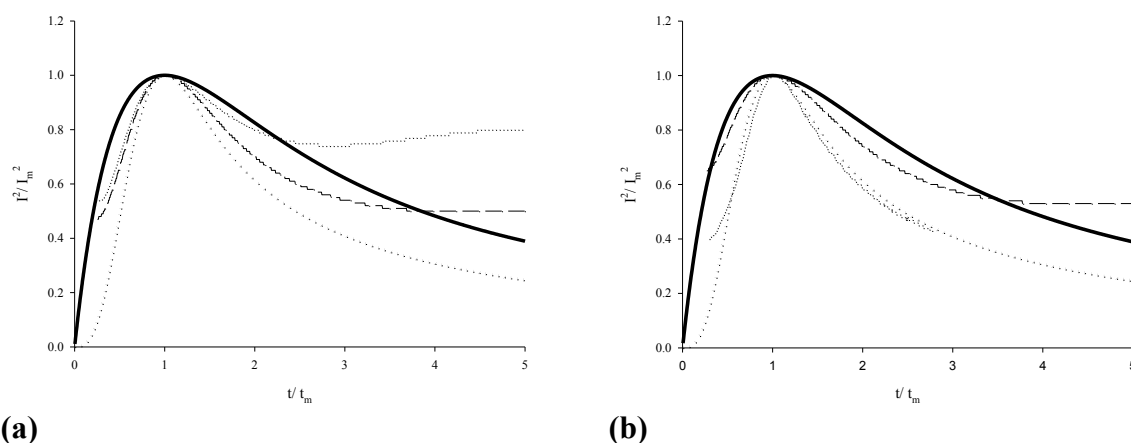


Figure 4.19 Theoretical and experimental dimensionless I_m/I_m^2 vs. t/t_m for Zn deposition from $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$ 1: 2 ChCl: ethylene glycol in the presence of SDS (a) and CTAB (b).

The introduction of surfactants to the electrodeposition bath, at concentrations greater than the critical micellular concentration, has a significant effect on the Zn electrodeposition mechanism and deposit morphology. In the previous chapter the growth of Zn films over long time scales was monitored using EQCM. This technique has also been applied to further probe the electrodeposition mechanism of Zn in the presence of the surfactants, SDS and CTAB.

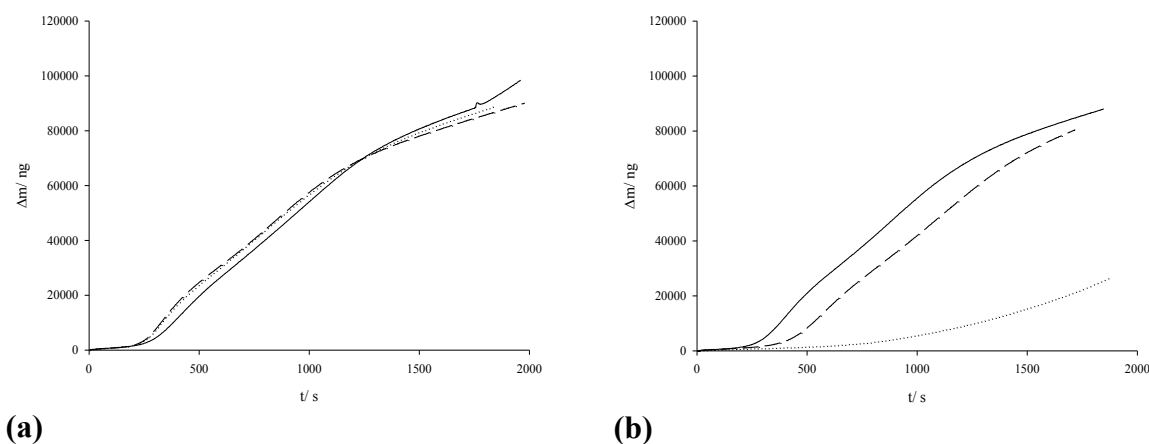


Figure 4.20 Mass-time traces for the electrodeposition of Zn from 1: 2 ChCl: ethylene containing (a) SDS and (b) CTAB. Surfactant concentrations used are 0 mmol dm^{-3} (solid line) 5 mmol dm^{-3} (dashed line) and 10 mmol dm^{-3} (dotted line).

Unlike the addition of ethylene diamine and ammonia, the addition of SDS and CTAB do not significantly alter the shape of the mass-time trace, **Figure 4.20**. The mass time traces shown above indicate that at the concentration ranges studied SDS has little effect on the rate of Zn deposition from 1: 2 ChCl: ethylene glycol, **Figure 4.20 (a)**. The profile is similar to that in the absence of surfactant; the initial stages of growth are slow, before the process becomes mass transport controlled. Conversely, at concentrations of 5-10 mmol

dm^{-3} the cationic surfactant CTAB strongly inhibits the deposition of Zn, **Figure 4.20 (b)**. The gravimetric analysis therefore provides independent mutually supportive evidence for the adsorption of CTAB inhibiting the growth of Zn at the electrode surface.

4.3 Summary

Organic additives are often added to aqueous electrodeposition baths as levellers and brighteners. However, little is known about the action of such additives in ionic liquid electrolytes.

In this thesis the first full investigation into the effect of additive addition on the Zn electrodeposition process in ChCl: ethylene glycol and ChCl: urea has been presented. The additives studied, acetonitrile, ammonia and ethylene diamine were shown to have varying effects on the Zn deposition mechanism. Ammonia and ethylene diamine were demonstrated to be effective brighteners for Zn deposition, however, EXAFS was used to conclusively prove that this was not due to ligatation of the Zn ions in solution. Rather, changes in the cyclic voltammetry, chronoamperometry and morphology were determined to be due to the differing hydrogen bond strengths of the additives. An extension of the chloride activity/ adsorption model proposed in **Chapter 3** has been effectively applied to explain the unexpected behaviour of acetonitrile, ammonia and ethylene diamine in ChCl based deep eutectic solvents.

The study has been further extended to consider the effect of ionic additives, the surfactants CTAB and SDS. The anionic surfactant, SDS, was determined to be an effective levelling agent for Zn deposits and proposed to replace the free chloride ions in the electrochemical double layer. However, cationic CTAB was proposed to specifically adsorb at the electrode surface at cathodic potentials, inhibiting Zn nucleation.

It is clear that the addition of additives to ionic liquids is an important area of study; any industrialised process is certainly unlikely to consist of electrolyte and metal salt alone. However, it is also apparent that the mode of action of organic additives in ionic liquids is very different to that in aqueous systems. As such it is probable that brightener and leveller systems will be unique to each ionic liquid/ metal system studied.

In **Chapter 5** the possibility of Zn alloy formation with the first row transition metals from ChCl based deep eutectic solvents will be described.

4.4 References

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Chapter 5: The Electrodeposition of Zn Alloys from ChCl based Deep Eutectic Solvents

5.1 Introduction

5.2 The Electrodeposition of Zn-Cu Alloys

5.3 A Gravimetric Analysis of Zn-Sn Co-Deposit Composition

5.4 The Electrodeposition of Zn-Co Alloys

5.5 The Electrodeposition of Zn-Ni Co-Deposits

5.6 Summary

5.7 References

5. 1 Introduction

The electrodeposition of alloys is an important subject as alloys often have improved properties over single metal deposits. Zn alloys have been used for a variety of applications from the aesthetic such as brass, to the functional such as Zn-Sn anticorrosion coatings.

Zn alloys are currently electrodeposited from aqueous electrolyte solutions; however, there are a number of issues with such systems including the toxicity of cyanide containing electrolytes and hydrogen embrittlement of the substrate due to low current efficiencies.

Ionic liquids are currently being studied as aprotic alternatives for the electrodeposition of a wide range of alloys. The advantages of such systems for alloy electrodeposition include their high conductivity, wide electrochemical windows and the negation of hydrogen embrittlement. These properties mean that large numbers of alloy systems are open to study including a number inaccessible in aqueous electrolytes. The majority of Zn alloy research to date has focussed on the chlorozincate: alkylimidazolium ionic liquids. Sun *et al* have demonstrated that Zn-Cu,^[1] Zn-Cd^[2] and Zn-Sn^[3] could be deposited from equimolar 1-ethyl-3-methylimidazolium: ZnCl₂ and that the composition of the deposits could be controlled by deposition potential, alloying metal concentrations and temperature.

Several Zn alloys including Zn-Fe, Zn-Co and Zn-Ni are electrodeposited *via* an anomalous co-deposition mechanism. In this process the more noble metal, Zn, is deposited preferentially to the less noble metal. Alloys with a low Zn content can therefore not be obtained from aqueous solutions. Ionic liquids may be particularly suitable for the electrodeposition of this kind of alloy. Indeed, it has been demonstrated that Zn-Fe,^[4] Zn-Co^[5, 6] and Zn-Ni^[7] alloys can be electrodeposited via a normal co-deposition mechanism in the chlorozincate ionic liquids, allowing access to both Zn and Fe/Co/Ni rich coatings, inaccessible from aqueous systems. A general introduction to Zn alloy deposition from ionic liquids can be found in **Chapter 1**. Additionally, the alloy systems Zn-Cu, Zn-Sn, Zn-Co and Zn-Ni are considered in depth below.

Here, the first attempt to study the electrodeposition of a range of Zn alloys from the deep eutectic solvents 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea will be presented. The morphology and composition of the deposits will be analysed as a function of relative metal concentration in the solution, cathodic overpotential and current density using SEM and EDAX. The first application of *in-situ* EQCM to estimate the composition of binary Zn alloys will be developed and demonstrated.

5.2 The Electrodeposition of Zn-Cu Alloys

The primary applications of Zn-Cu alloys are as decorative coatings^[8] and as binding layers to improve the adhesion of rubber to steel.^[9] The electrodeposition of brass (typically Zn: Cu in a 70: 30 % ratio) has traditionally been carried out in aqueous cyanide containing electrolytes. A wide range of alternative electrolytes and additives have been studied as environmentally compatible alternative media for the electrodeposition of Cu-Zn including pyrophosphates,^[10, 11] glycerol and D-mannitol.^[12] However, all of these systems suffer from the problem common to the aqueous electrodeposition of most Zn containing coatings, *i.e.* hydrogen evolution and resulting deposit embrittlement. Ionic liquids are a promising alternative for Zn-Cu electrodeposition, as they are generally aprotic, have relatively high conductivities and wide potentials. Recently, Sun *et al.* have demonstrated that Zn-Cu alloys can be electrodeposited from 50: 50 mol% ZnCl₂: 1-ethyl-3-methylimidazolium chloride.^[13] Here an attempt is made to electrodeposit Zn-Cu from the deep eutectic solvents 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea.

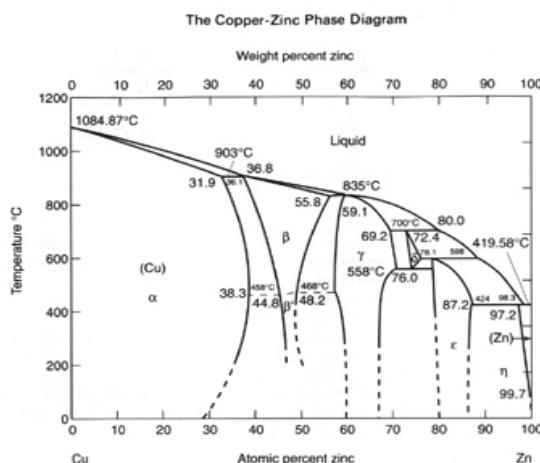


Figure 5.1 The binary Zn-Cu equilibrium alloy phase diagram.^[14]

It is first important to have an understanding of the equilibrium phase diagram of the binary system to be studied. The equilibrium phase diagram for Zn-Cu is shown in **Figure 5.1**, it is clear that a number of Zn-Cu phases can be obtained at ambient temperatures. The copper rich phase (≥ 28 %), consists of an α -Cu-Zn phase, *i.e.* a solid solution of Zn in Cu. This phase has a face centred cubic structure (f.c.c) in common with bulk Cu. As the proportion of Zn in the alloy is increased, Zn-Cu exists as a body centred cubic β phase. This β phase dominates at Zn atom % up to 58.2 % at ambient temperatures. At temperatures below 400 °C the γ phase of Zn-Cu is present at compositions between 58 and 66 at% Zn. This phase is also known as the gamma brass structure, has a cubic crystal structure and an ideal stoichiometry of Cu₅Zn₈. At a composition of 80-87.2 % Zn the ϵ alloy phase has a

hexagonal structure similar to bulk Zn. Finally, when the Cu at% is less than 2.72 % a solid solution of Cu in Zn is obtained, the η phase. It is therefore clear that the equilibrium phase diagram of Zn-Cu is complicated with a number of distinct phases. As such the morphology of Zn-Cu deposits of varying compositions would be expected to be markedly different. The electrodeposition of Zn-Cu has previously been demonstrated in 50 % - 50 % ZnCl_2 : 1-ethyl-3-methylimidazolium and here a mixture of α and β phase Zn-Cu was seen to form.^[1]

As the Zn: Cu ratio has a pronounced effect upon the structure and physical properties of electrodeposited Zn-Cu alloys, it is imperative to understand the effect of altering the composition of the deposition electrolyte. To this effect, cyclic voltammograms of various molar ratios of ZnCl_2 and $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 1: 2 ChCl: ethylene glycol are presented in **Figure 5.2**.

A selection of typical staircase cyclic voltammograms for 1:2 ChCl: ethylene glycol containing 0.3 mol dm^{-3} , 50-50 mol % ZnCl_2 - CuCl_2 are presented in **Figure 5.2 (a)**. The reduction of Cu occurs in a two stage process, a reversible 1 electron charge transfer at $E_p = 0.40 \text{ V}$ due to the reduction of Cu^{2+} to Cu^+ and a second 1 electron process at $E_p = -0.43 \text{ V}$, the reduction of Cu^+ to Cu^0 . The corresponding oxidation processes occur at $E_p = -0.15 \text{ V}$, and $E_p = 0.44 \text{ V}$. As the overpotential is increased a current crossover is observed indicating that Zn nucleation is occurring, however, there is no well-developed reduction or oxidation peak. This suggests that at 50 mol % Cu the reduction of Zn is somewhat inhibited.

As the relative mol % of ZnCl_2 in the solution is increased to 70 mol %, **Figure 5.2 (b)** and 90 mol %, **Figure 5.2 (c)**, reduction waves ascribed to the reduction of solution phase Zn^{2+} to bulk Zn metal develop. A broad, complex peak is present in the region where the oxidation of Zn is observed in the absence of Cu. Although some of the peak broadening will be due to the fact that the Zn has been deposited on a Cu surface (*c.f.* Pt surface in the absence of Cu) the current response appears to be composed of two processes at $E_p = -0.80 \text{ V}$ and $E_p = -0.63 \text{ V}$, the more anodic of these corresponding well to the oxidation of bulk Zn, $E_p = -0.62 \text{ V}$. Additionally, as the relative concentration of Zn in the solution is further increased a third oxidation process develops, initially as a shoulder on $E_p = -0.15 \text{ V}$, becoming a defined peak at high overpotentials and Zn concentrations. It is clear that this process, $E_p = -0.26 \text{ V}$, is both more anodic than the oxidation of bulk Zn and more cathodic than the oxidation of bulk copper (it is worth noting that a two phase stripping response analogous to that observed in Zn oxidation in 1: 2 ChCl: ethylene glycol is not observed for Cu oxidation in the absence of Zn)^[15] suggesting that this process could be due to the oxidation of a Cu rich Zn-Cu mixed phase.

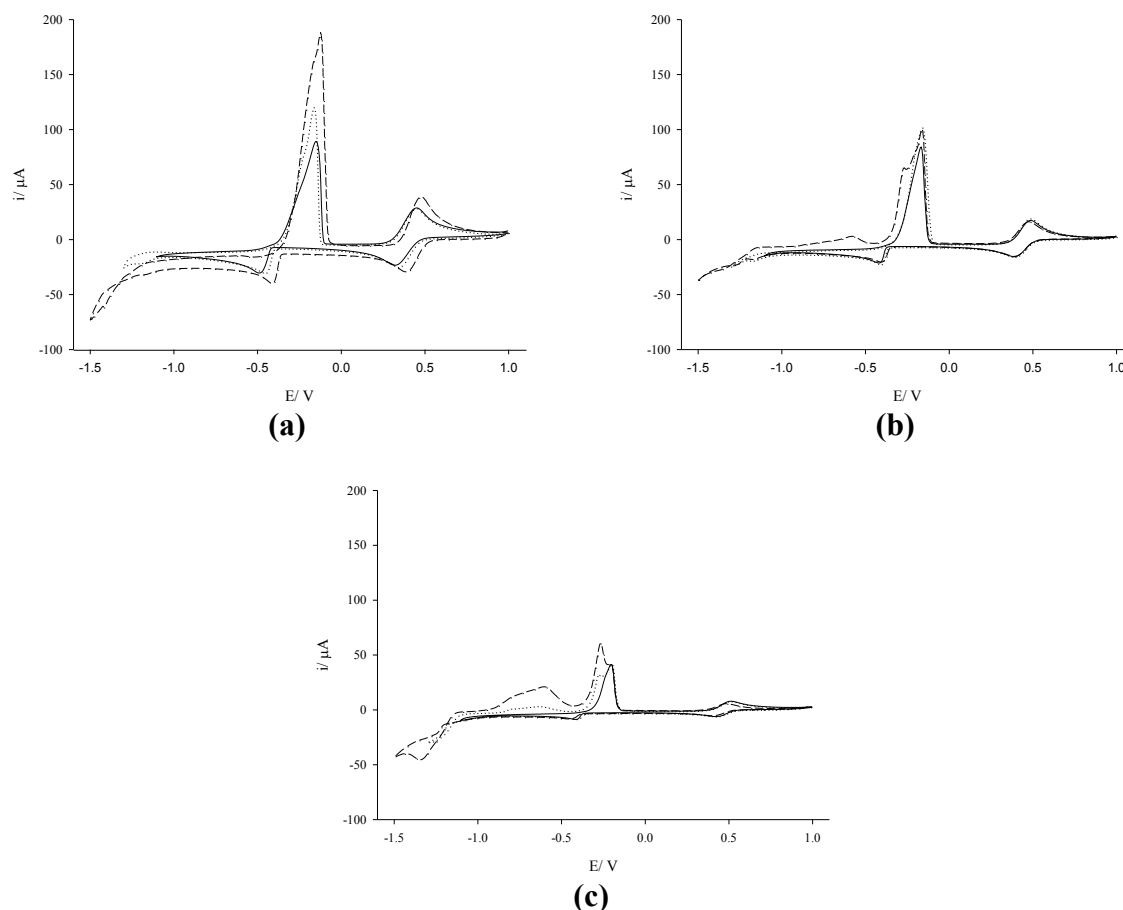


Figure 5.2 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) at 50 °C for (a) 0.3 mol dm⁻³ 1: 1 ZnCl₂: CuCl₂·2H₂O (b) 0.3 mol dm⁻³ 7: 3 ZnCl₂: CuCl₂·2H₂O (c) 0.3 mol dm⁻³ 9: 1 ZnCl₂: CuCl₂·2H₂O in 1: 2 ChCl: ethylene glycol. Data are presented as a function of cathodic overpotential.

To probe the identity of the process leading to peak, $E_P = -0.26$ V, it is possible to calculate the charge passed due to Cu deposition. As the deposition of Cu continues past the peak current into the Zn deposition region, the amount of charge due to Cu deposition must be determined before an estimation of the current due to Zn-Cu co-deposition can be made. If it is assumed that copper deposition continues to the cathodic potential limit under Cottrell type control, the Cu reduction current in the Zn deposition region can be estimated. The amount of charge passed can then be calculated simply by integrating this estimated current. For the cyclic voltammetric data presented in **Figure 5.2 (c)**, where the cathodic overpotential limit is -1.50 V, the total charge passed due to the reduction of Cu is estimated at 740 μC and that calculated for the two oxidation processes $E_P^{50} = -0.26$ V and $E_P^{20} = -0.15$ V is 717 μC . The cathodic and anodic charges are almost equal suggesting that the two oxidation processes are both due to the oxidation of Cu. This could be explained by the oxidation of Cu⁰ from two different substrates, that from the Pt electrode surface and that from Cu which is electrodeposited on underpotential deposited Zn.

Figure 5.3 contains an analogous set of data for $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1: 2 ChCl: urea. As in 1: 2 ChCl: ethylene glycol the reduction of the Cu species in solution occurs via a 2 step reduction, Cu^{2+} to Cu^+ , $E_p = +0.40 \text{ V}$ and Cu^+ to Cu^0 , $E_p = -0.44 \text{ V}$. The large difference in equilibrium potentials between the two reductions, greater than 1.00 V , indicates that the Cu^+ species is very stable in this high chloride environment. Additionally, the current passed during the experiments is less when 1: 2 ChCl: urea is the solvent; this is due to the relatively high viscosity of the urea containing eutectic.

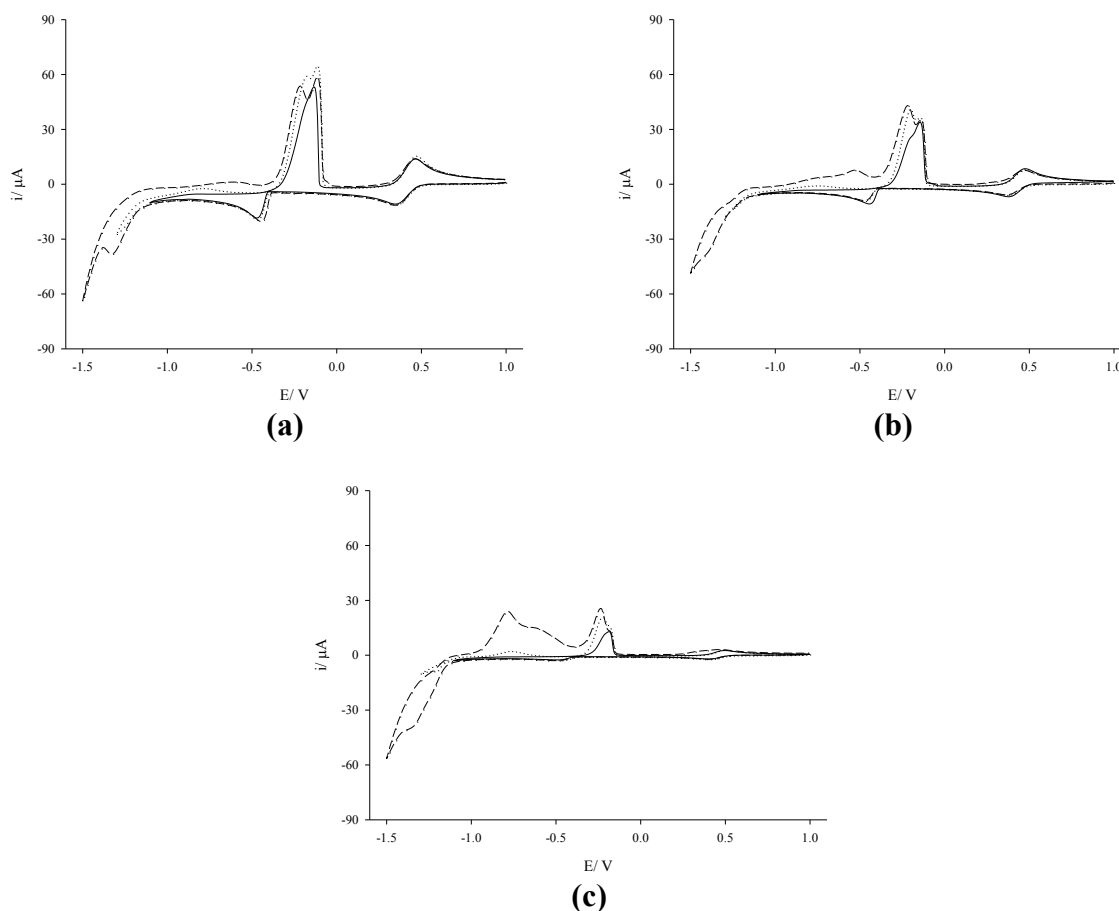


Figure 5.3 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) at 50°C for (a) 0.3 mol dm^{-3} 1: 1 ZnCl_2 : $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (b) 7: 3 ZnCl_2 : $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (c) 9: 1 ZnCl_2 : $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1: 2 ChCl: urea. All data are presented as a function of cathodic overpotential.

Unlike **Figure 5.2 (a)** where 1: 2 ChCl: ethylene glycol was used as the electrolyte, a Zn related oxidation process is evident in 1: 2 ChCl: urea even at high $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ concentrations (0.15 mol dm^{-3} , **Figure 5.3 (a)**). As proposed in **Chapter 3** this may be due to the relative hydrogen bond donor strengths of ethylene glycol and urea and the respective difference in chloride activity in the two solvents. At lower concentrations of ZnCl_2 (0.15 mol dm^{-3} , **Figure 5.4 (a)**) the high activity of the free chloride in 1: 2 ChCl: ethylene glycol effectively inhibits the reduction of Zn. In 1: 2 ChCl: urea the activity of the free chloride is lower, the critical Zn concentration required for nucleation to occur is thereby reduced,

hence Zn reduction occurs even at a concentration of 0.15 mol dm^{-3} , **Figure 5.3 (a)**. It is interesting to note that the current passed during Zn reduction is much higher than that which occurred in the absence of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (*c.f.* Zn reduction in 1: 2 ChCl: urea, **Chapter 3, Figure 3.6**). This additional current may be accounted for if we consider that there will be a current contribution due to the mass transport limited reduction of Cu^+ . Alternatively, some bubbling was observed at the cathode during Zn-Cu deposition in 1: 2 ChCl: urea, this may indicate that hydrogen evolution occurs in the system, leading to an increase in the current passed in the Zn reduction region.

The oxidative processes appear to be similar to those observed in 1: 2 ChCl: ethylene glycol. The waves due to Cu^0 to Cu^+ and Cu^+ to Cu^{2+} oxidation are apparent at $E_p = -0.15 \text{ V}$ and $E_p = -0.45 \text{ V}$ respectively. A cathodic shoulder can be seen to develop as the ZnCl_2 concentration is increased at $E_p = -0.24 \text{ V}$, this may indicate the formation of a Cu rich Zn-Cu phase. The Zn oxidation process is broad and consists of two peaks at $E_p = -0.79 \text{ V}$ and $E_p = -0.60 \text{ V}$, the more anodic of which may indicate the presence of a Zn rich Zn-Cu phase.

In **Chapter 4** it was shown that the addition of ethylene diamine to a ZnCl_2 containing deep eutectic solvent affects the nucleation mechanism and morphology of the Zn deposit. An analogous, unpublished, study has shown that ethylene diamine also functions as a brightener in Cu containing deep eutectic solvents, although in this case the ethylene diamine clearly acts to complex the Cu species in solution (a clear colour change of the solution from yellow to blue is observed upon the addition of ethylene diamine). The addition of ethylene diamine to a mixed Zn-Cu system would therefore be expected to have an effect on the deposition mechanism of the mixed phase.

In **Figure 5.4 (a)** it can be seen that the addition of ethylene diamine alters the Cu reduction process, the reduction wave attributed to the reversible $\text{Cu}^{2+} / \text{Cu}^+$ ($E_p = 0.40 \text{ V}$) couple is no longer present. This is probably due to the relative stabilities of the chloro- and ethylene diamine copper complexes. The ethylene diamine containing Cu^{2+} complex will be a more stable ion and as such the formation of a Cu^+ species will be less thermodynamically favourable than with the corresponding chloro-complexes. The reduction of Cu^{2+} therefore occurs via a single reduction process, $E_p = -0.40 \text{ V}$. **Figure 5.4 (c)** contains a complicated series of reduction waves in the Zn deposition region at $E_p = -1.05 \text{ V}$ and $E_p = -1.28 \text{ V}$. Moreover, the Zn oxidation wave is smaller than would be expected, suggesting that the majority of Zn is deposited with the copper and is stripped as a Zn-Cu phase. The oxidation waves at only to develop when the cathodic switching potential is beyond the onset potential of Zn deposition. As the cathodic overpotential is increased the relative magnitude of the

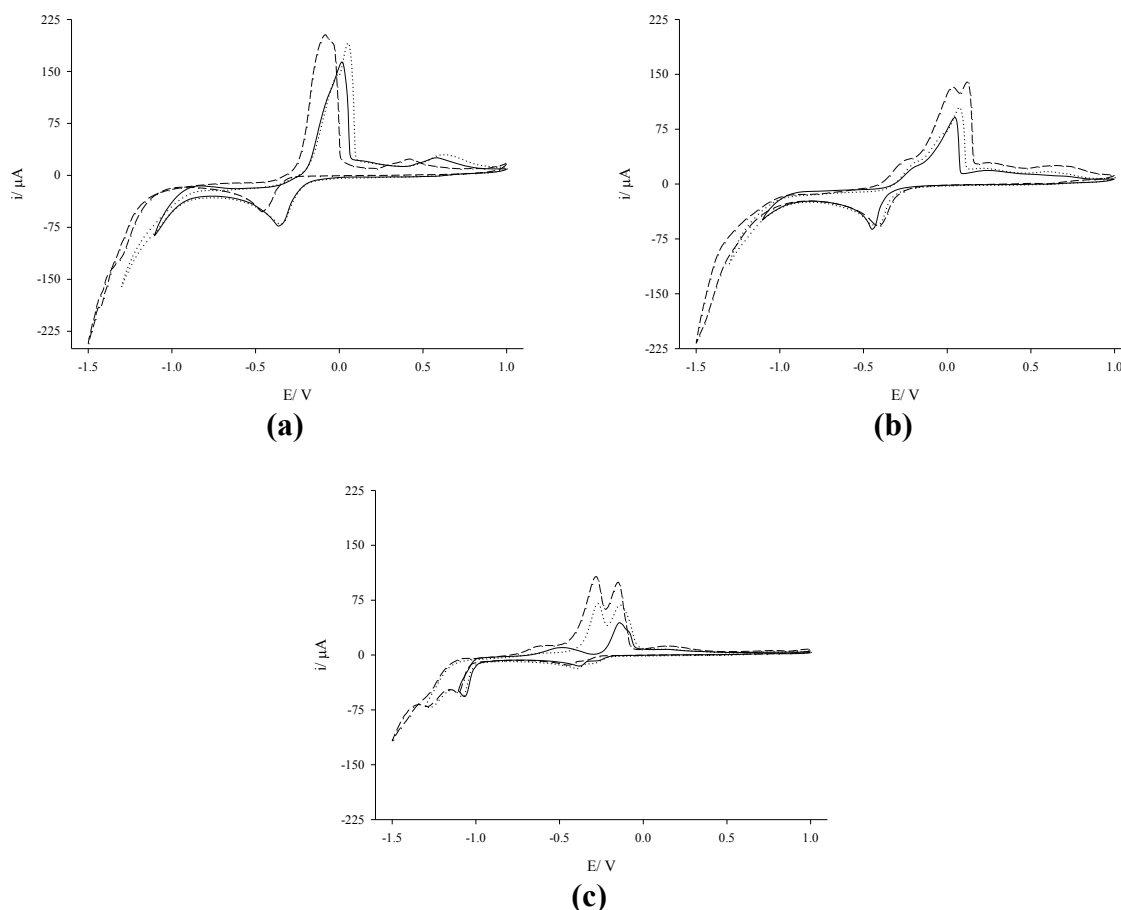
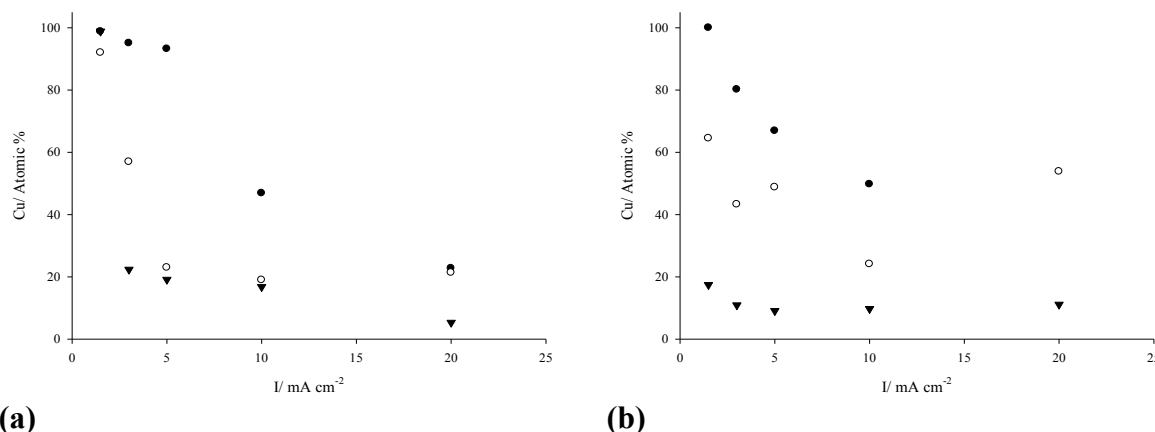


Figure 5.4 Cyclic voltammograms obtained at aPt disc (0.5 mm dia.) at 50 °C for **(a)** 0.3 mol dm⁻³ 1: 1 ZnCl₂: CuCl₂·2H₂O **(b)** 7: 3 ZnCl₂: CuCl₂·2H₂O **(c)** 9: 1 ZnCl₂: CuCl₂·2H₂O in 1: 2 ChCl: ethylene glycol + 0.3 mol dm⁻³ ethylene diamine. All data are presented as a function of cathodic overpotential.

Bulk deposits were prepared from 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol, however, those deposited from 1: 2 ChCl: urea were friable and non-adherent. This may be due to the presence of hydrogen evolution at cathodic overpotentials. This solvent was therefore considered to be unsuitable for Zn-Cu electrodeposition.

Figure 5.5 only considers the relative composition of Zn-Cu deposits prepared from 1: 2 ChCl: ethylene glycol in the absence of **(a)** and presence of **(b)** 0.3 mol dm⁻³ ethylene diamine. It can be seen that the amount of Cu present in the deposits can be controlled by both applied current density and the relative concentrations of metal salts dissolved in the deep eutectic solvent, consistent with previously published results.^[1] Clearly, an increase in the copper content of the liquids leads to an increase in the Cu atomic % in the deposit. A reduction of the Cu atom % in the coatings can be seen as the current density is increased. The copper content of the deposit can be varied from between 100 and 10 % by altering the deposition parameters and metal concentrations. A wide range of Zn-Cu compositions is therefore obtainable from 1: 2 ChCl: ethylene glycol. As predicted from the binary phase

diagram, **Figure**, the morphology of these phases is very different and is shown in **Figures 5.6 and 5.7**.



(a) **(b)**
Figure 5.5 The Cu at % in deposits obtained from **(a)** 1: 2 ChCl: ethylene glycol and **(b)** 1: 2 ChCl: ethylene glycol + 0.3 mol dm⁻³ ethylene diamine containing 0.3 mol dm⁻³ 1: 1 ZnCl₂: CuCl₂·2H₂O (black circles), 7: 3 ZnCl₂: CuCl₂·2H₂O (clear circles), 9: 1 ZnCl₂: CuCl₂·2H₂O (black triangles). All deposits are on a Ni substrate and were conducted at 50 °C.

The bulk electrodeposit morphology was found to be independent of the electrolyte composition but strongly dependent on the relative composition of the deposit. Representative images of the bulk morphology of Zn-Cu deposits with varying Cu content electrodeposited from 1: 2 ChCl: ethylene glycol are presented in **Figure 5.6**. The colour of the electrodeposits changed from a red to a yellow-brown to a grey-brown as the Cu content fell from 95 to 62 to 42 atomic %. The change in the visible aspect of the coatings is mirrored by a change in the deposit morphology. At high Cu concentrations **(a)** the deposit morphology is very similar to that obtained from CuCl₂·6H₂O 1: 2 ChCl: ethylene glycol in the absence of ZnCl₂, indicating the presence of α Zn-Cu. As the Cu at% decreases the deposit morphology dramatically changes, at the compositions estimated by EDX, the deposit in **Figures 5.6 (a) and (c)** would be expected to consist of β and γ Zn-Cu phases. Additionally it was observed that at current densities greater than 5 mA cm⁻² dendrites are formed and that these have a higher Cu content than the underlying homogeneous crystalline surface.

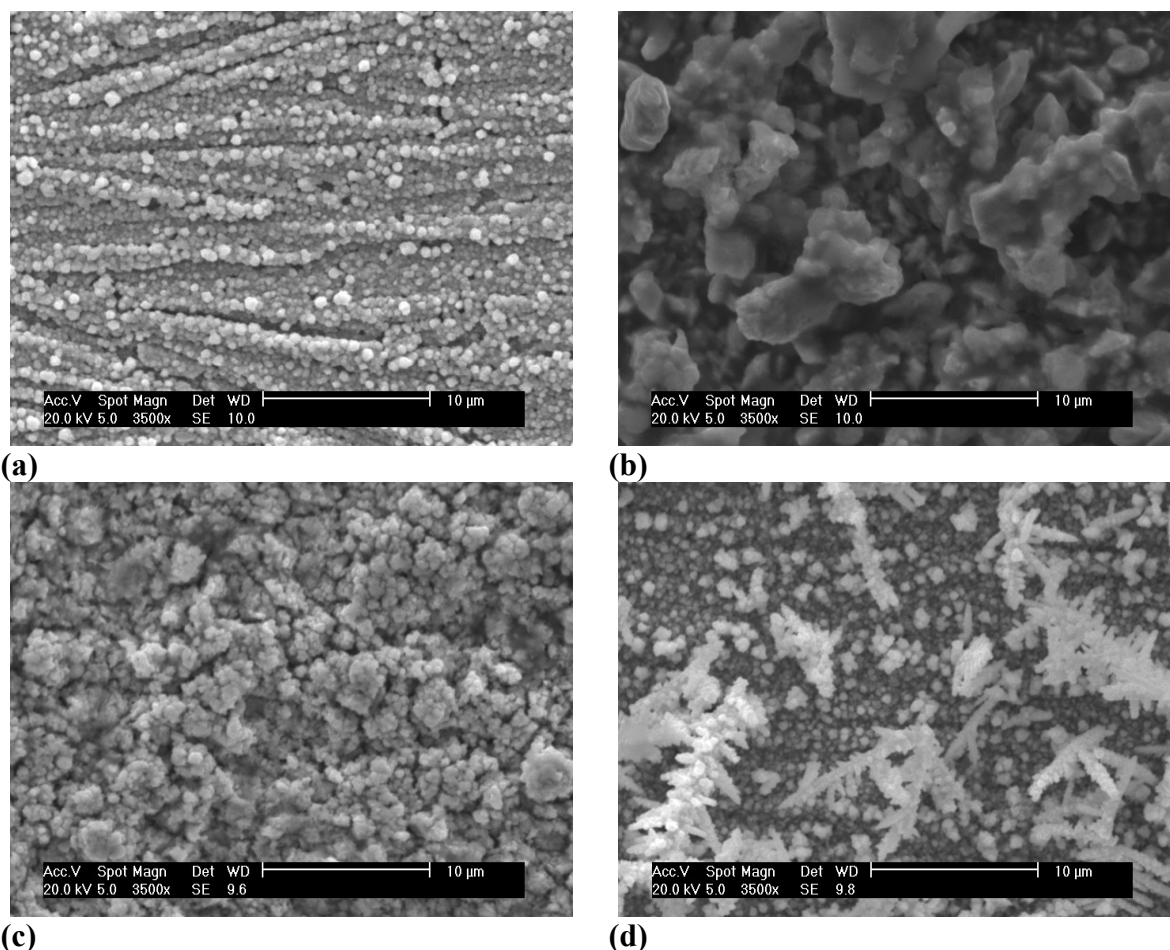


Figure 5.6 Representative SEM micrographs of the deposits obtained from 1: 2 ethylene glycol and $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2 \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ containing (a) 95, (b) 62, (c) 43 and (d) 10 at% Cu. Depositions shown were obtained at $I = 3 \text{ mA cm}^{-2}$.

The SEM micrographs presented in **Figure 5.7** clearly demonstrate the change in morphology of the Zn-Cu co-deposits as the mol % Cu is decreased. The deposit containing 95 % Cu has a very similar morphology to that of pure copper obtained from this deep eutectic solvent. At 62% Cu the deposit is formed from aggregated crystallite clusters. As the Cu content continues to fall, a mixed morphology is present, **Figure 5.7 (c)** with distinct Zn and Cu (from point EDAX analysis) rich crystallites. At Cu concentrations of 10% and below the needle like morphology previously observed for bulk Zn deposits dominates. Furthermore it is clear that the deposits obtained in the presence of ethylene diamine are more crystalline than those obtained in its absence.

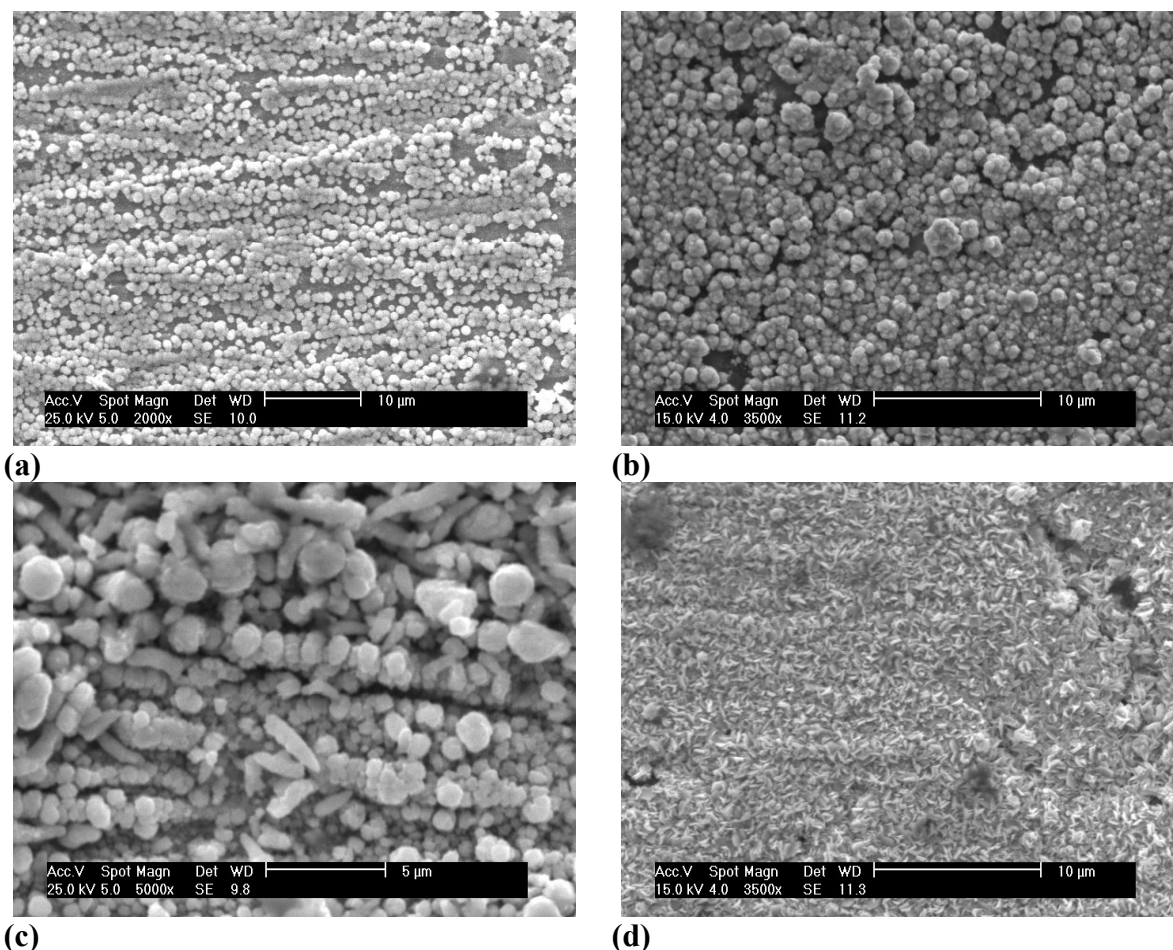


Figure 5.7 Representative SEM micrographs of the deposits obtained from 1: 2 ethylene glycol containing 0.3 mol dm^{-3} ethylene diamine and $0.3 \text{ M ZnCl}_2 \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ containing (a) 95, (b) 62, (c) 43 and (d) 8 at % Cu. Depositions shown were obtained at $I = 3 \text{ mA cm}^{-2}$.

An XRD analysis of representative Zn-Cu deposits is presented in **Figure 5.8**. The electrodeposits obtained from 1: 2 ChCl: ethylene glycol were generally thin, as such the XRD spectra is dominated by Ni substrate peaks at $2\theta = 44.28$ and 52.13 . However, Zn peaks are observed at 2θ . The presence of both γ and β phase Zn-Cu alloys are indicated by peaks at $2\theta = 37.98$ and 42.04 respectively.^[12] The intensity of the γ phase peak increases when a larger current density was applied (blue trace) whilst the intensity of the β phase peak decreases. This is consistent with both the binary phase diagram, **Figure 5.1**, and the cyclic voltammetry/ morphological studies where a more cathodic overpotential lead to the development of Zn rich phases.

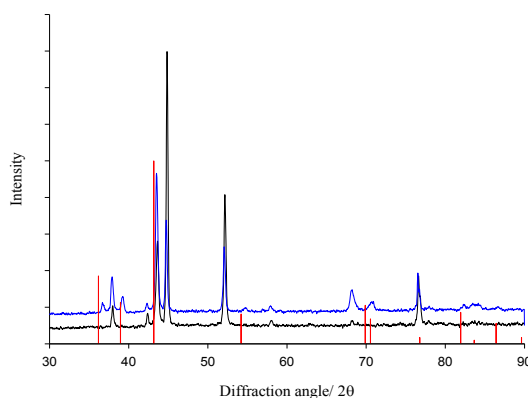


Figure 5.8 XRD patterns of Zn-Cu electrodeposited from 1: 2 ChCl: ethylene glycol + 0.3 mol dm⁻³ ethylene diamine at 1.5 mA cm⁻² (black) and 5 mA cm⁻² (blue). The red lines represent the XRD pattern obtained for Zn electrodeposits from this solution.

5.3 A Gravimetric Analysis of Zn-Sn Co-Deposit Composition

Zn-Sn co-deposits are used as corrosion resistant coatings for ferrous substrates, providing greater protection than Zn alone, particularly in high humidity environments and being less environmentally problematic than the alternative Zn-Cd alloys.^[16] Zn and Sn are known to have low mutual solubilities, their phase diagram showing a simple eutectic mixture of the distinct Zn and Sn phases. However, a number of studies have been published concerning the electrodeposition of Zn-Sn co-deposits from aqueous electrolytes,^[17, 18] ionic liquids^[3] and deep eutectic solvents.^[16] Additionally, the large difference in molecular mass of Zn and Sn make this system an ideal candidate for the novel application of the EQCM to monitor alloy composition during electrodeposition. In this section this technique will be used for the first time to examine the development

The electrodeposition of Zn-Sn co-deposits from 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea has been published by Abbot *et al.*^[16] This study highlighted the differences in co-deposit formation in the two deep eutectic solvents. Sn solubility was shown to be extremely low in 1: 2 ChCl: urea, however, it was proposed that a single phase Zn-Sn alloy could be deposited from this electrolyte.^[16] Conversely, it was determined that distinct Sn and Zn phases were deposited from 1: 2 ChCl: ethylene glycol, consistent with the known low mutual solubility of the two metals. Cyclic voltammetric data for a solution of 0.15 mol dm⁻³ SnCl₂ 1: 2 ChCl: ethylene glycol is presented in **Figure 5.9 (a)**. Two distinct oxidation peaks are present in the voltammogram, $E_p = -0.08$ V and $E_p = 0.04$ V. The more anodic of these processes has previously been ascribed to the formation of a Sn rich Zn-Sn phase in coatings electrodeposited from ZnCl₂: SnCl₂·2H₂O mixtures in 1: 2 ChCl: Ethylene.^[16] However, the presence of this oxidative process in the Zn free solution proves that this

cannot be the case. In order to further probe the nature of this oxidation, a series of linear sweep voltammograms are presented in **Figure 5.9 (b)**. Here, the cathodic overpotential was held at -0.55 V for different dwell times, t_d , of 60 s 180 s and 300 s, before the potential was swept to 1.00 V. It is clear that the size of the more cathodic oxidation process is relatively independent of deposition time (within the range applied); whereas the more anodic oxidation process increases as the dwell time is increased. A similar relationship is observed between potential scan rate and the oxidation process. When a lower potential scan rate is applied the more anodic oxidation process becomes dominant.

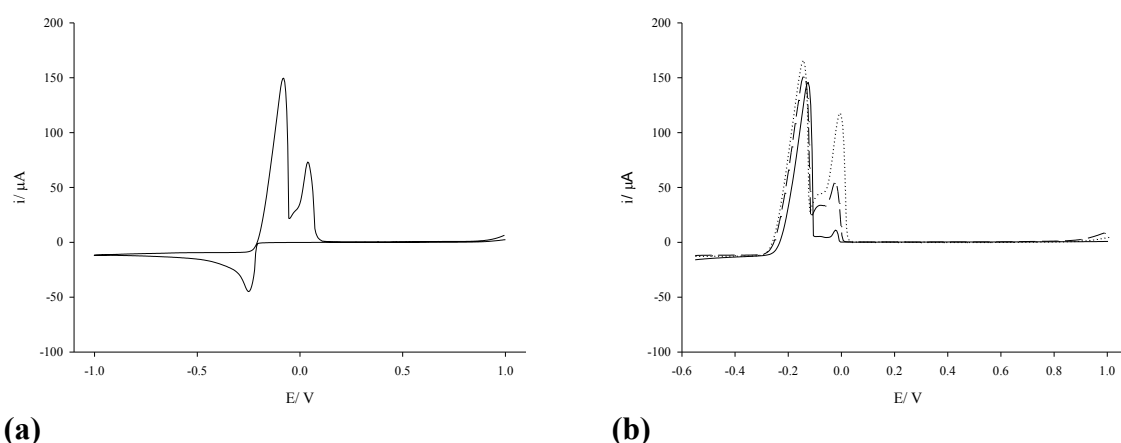


Figure 5.9 Voltammetric data for $0.15 \text{ mol dm}^{-3} \text{ SnCl}_2 \cdot 2\text{H}_2\text{O}$ 1: 2ChCl: ethylene glycol **(a)** cyclic voltammogram, obtained at 5 mV s^{-1} and **(b)** linear sweep voltammograms following an applied static potential of -0.55 V for 60 s (solid), 180 (dashed) and 300 s (dotted).

At large deposition time scales and high cathodic overpotentials, Sn is known to form dendrites in this class of deep eutectic solvent. It is proposed that the more cathodic Sn oxidation process is due to the stripping of crystalline Sn; whereas the more anodic oxidation process is due to the stripping of dendritic Sn formed at longer time scales.

In order to further probe the identity of this process the EQCM was used to monitor the mass flux during a potential sweep experiment. A representative data set is presented in **Figure 5.10** where Sn was initially deposited from a solution of $0.15 \text{ mol dm}^{-3} \text{ SnCl}_2 \cdot 2\text{H}_2\text{O}$ 1: 2 ChCl: ethylene glycol onto a Au coated quartz crystal at a constant potential of -0.55 V for 300 s. The electrolyte was then replaced with pure 1: 2 ChCl: ethylene glycol (without metal salts) and the potential swept at 1 mV s^{-1} to 1.00 V. A slow scan rate was used to ensure the resolution of the voltammetric and gravimetric data was similar. The mass flux was observed to follow the voltammogram closely until a point between the two oxidation processes. Here, the mass flux was seen to fall sharply, *i.e.* the crystal experienced a sudden increase in mass. This may be due to the low solubility of SnCl_2 in 1: 2 ethylene glycol. As Sn is removed from the electrode surface the diffusion layer may rapidly become saturated,

resulting in the precipitation of insoluble Sn. The precipitated material will then settle on the electrode surface causing a sharp increase in observed mass.

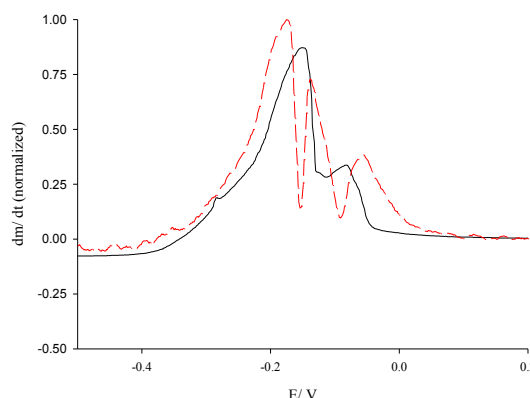


Figure 5.10 The oxidation behaviour of a Sn deposit in 1: 2 ChCl: ethylene glycol. The normalised voltammetric data (black) is presented alongside the normalised mass flux, dm/dt (red, dashed)

The mass detected at the electrode surface begins to fall once more, the Sn saturation point is reached and a second sharp fall in mass flux observed. The second oxidation process then occurs with the expected fall in mass flux.

The electrochemical behaviour of SnCl_2 in 1: 2 ChCl: ethylene glycol is clearly complicated by the low solubility of Sn species in this solvent. Consequently, the previously analysed ZnCl_2 : $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 1: 2 ChCl: ethylene glycol system has been revisited.^[16] The effect of the ZnCl_2 : $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration ratio on the cyclic voltammetry is presented in **Figure 5.11**.

Here it is evident that Zn and Sn are electrodeposited as two distinct phases with distinct reduction peaks occurring at $E_p = -1.01$ V and $E_p = -0.380$ V. It is interesting to note that Sn reduction occurs at a more cathodic potential in the presence of Zn, this may indicate that Zn inhibits the reduction of Sn. The oxidative processes are also similar to those found in the voltammograms of the individual metals, with Zn stripping occurring at $E_p = -0.80$ V and Sn at $E_p = -0.18$ V. Furthermore, it is clear that the secondary oxidation process at $E_p = -0.04$ V is dependent upon the amount of SnCl_2 in solution, increasing in dominance as the SnCl_2 concentration is increased from 0.03 mol dm^{-3} , **Figure 5.11 (c)**, to 0.9 mol dm^{-3} and 0.15 mol dm^{-3} , **Figures 5.11 (b) and (a)**.

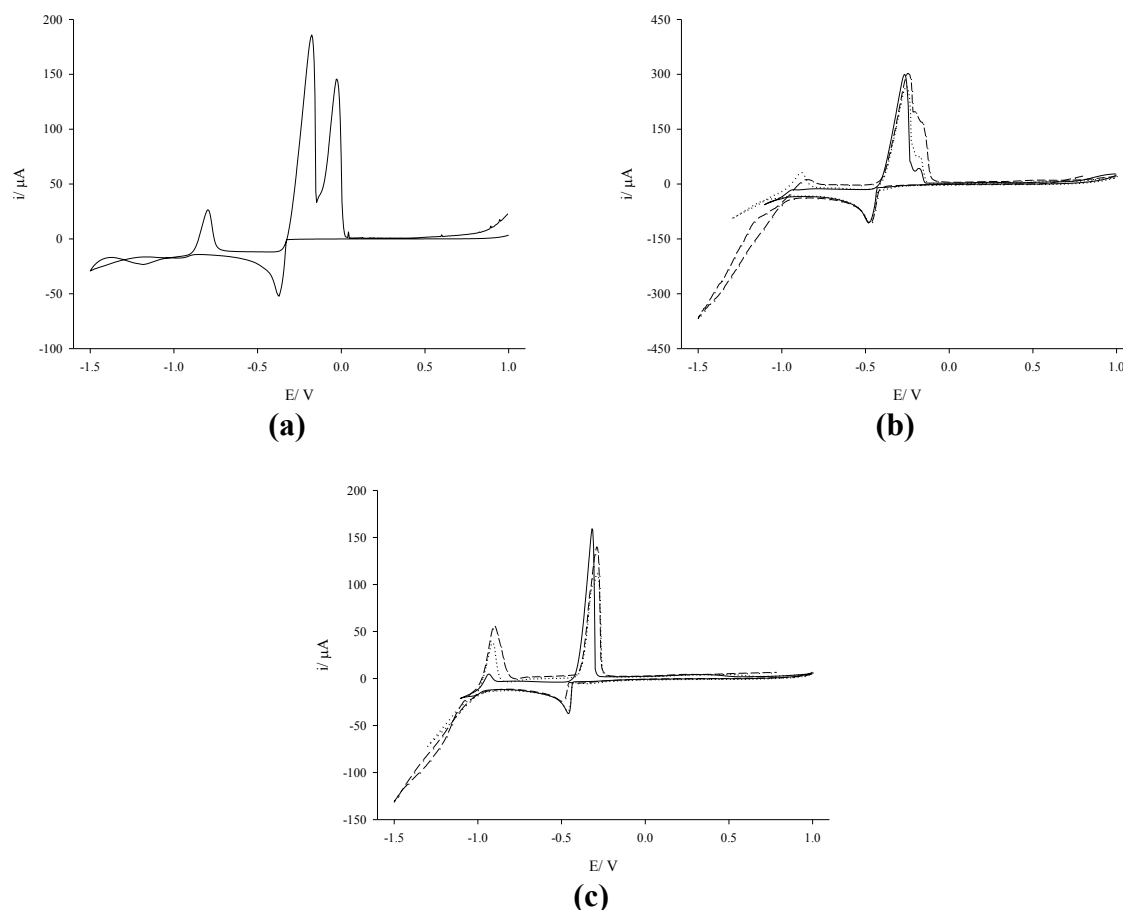


Figure 5.11 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) at 50 °C for 0.3 mol dm^{-3} (a) 1: 1 $\text{ZnCl}_2:\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (b) 7: 3 $\text{ZnCl}_2:\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and (c) 9: 1 $\text{ZnCl}_2:\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1: 2 $\text{ChCl}:\text{ethylene glycol}$. All data are presented as a function of cathodic overpotential.

Figure 5.12 shows the $\Delta m/Q$ plots for 1: 2 $\text{ChCl}:\text{ethylene glycol}$ containing 0.3 mol dm^{-3} 50-50 mol% $\text{ZnCl}_2:\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The data for three different constant potential deposition experiments are shown and it can be seen that at potentials of -1.30 V and -1.50 V a quasi-linear response is obtained; at these potentials both Sn and Zn electrodeposition will be under diffusion control. At -1.10 V only the electrodeposition of Sn is under mass transport control and would be expected to be the dominant process; in this case at the start of the experiment $\Delta m/Q$ gives a linear response; however, as the deposition progresses the charge continues to increase with no corresponding increase in mass. Sn is known to form dendrites when electrodeposited from 1: 2 $\text{ChCl}:\text{ethylene glycol}$ in the presence and absence of ZnCl_2 .^[16] The electrochemical quartz crystal microbalance only functions as an accurate balance when the deposit acts as a rigid thin film, rough or dendritic growths cannot be measured accurately. An empirical measure of the roughening of the surface can be obtained through the Q factor, a measure of the mechanical losses at the crystal surface, **Equation 5.1**

$$Q = \frac{f_0}{w} \quad \text{Equation 5.1}$$

Where f_0 is the frequency value at the centre of the resonance and w is the full width of the peak at half height. As a general rule the EQCM is considered to function as an accurate mass balance only where the change in Q factor throughout the timescale of the experiment is less than 10 %. When the potential is held at -1.100 V there is a rapid reduction in Q factor (35%) corresponding to a large amount of surface roughening, therefore under these conditions the EQCM no longer functions as an accurate mass balance. As the mol% of ZnCl_2 in the solution is increased the $\Delta m/Q$ response at each of the studied potentials becomes more linear, suggesting that these coatings are predominantly Zn, which has previously been shown to form adherent crystalline deposits.

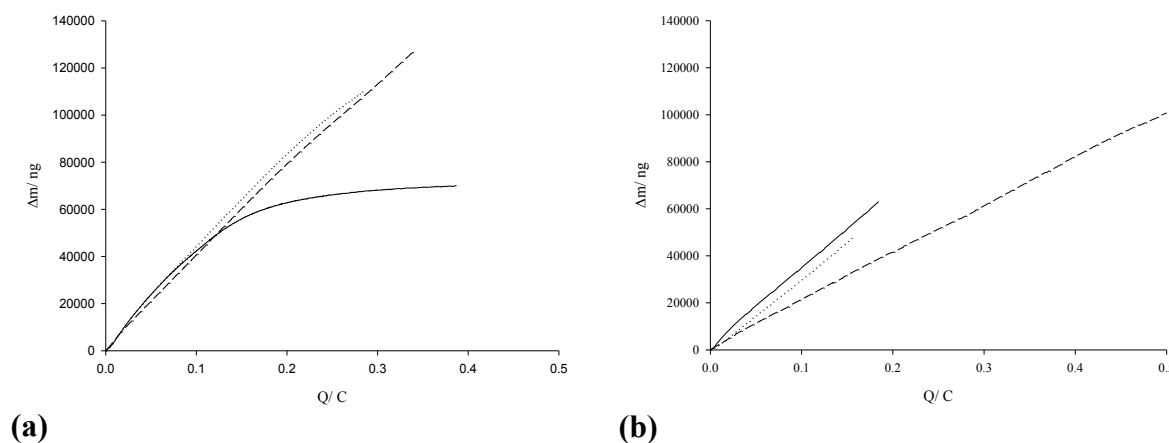


Figure 5.12 $\Delta m/Q$ plots for (a) 0.3 mol dm^{-3} 1: 1 ZnCl_2 : $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and (b) 0.3 mol dm^{-3} 7: 3 ZnCl_2 : $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1: 2 ChCl : ethylene glycol. The potential was stepped from O.C.P and held at -1.10 V (solid), -1.30 V (dotted) and -1.50 V (dashed) for 1800s at 23 °C.

The EQCM is an effective tool for measuring electrochemical and gravimetric changes at an electrode surface. Previously in this thesis the EQCM was combined with liquid phase AFM in a novel experiment to monitor the growth of Zn deposits in a time resolved manner. Here, the EQCM is used for the first time to monitor changes in co-deposit composition as an electrodeposition progresses. This approach will have the greatest sensitivity when there is a large difference in the molecular weights of the two components of the alloy. The relative atomic masses of Zn and Sn are 65.38 and 118.7 g mol^{-1} respectively. Additionally, the electrodeposition of both metals from 1: 2 ChCl : ethylene glycol is known to occur with a high current efficiency, > 90 %, at short time scales. This system is therefore a useful candidate for determining the validity of the EQCM composition monitoring technique.

When the current efficiencies of electrodeposition of the individual metals are close to 100 %, the assumption can be made, as a consequence of Faraday's law, that for the co-

deposition of two metals the slope of $\Delta m/Q$ will be a linear combination of contributions from the metals present in the solution. Equally, for a binary alloy/ co-deposit the total mass of alloy can also be expressed as a mole fraction of the two deposit components, **Equation 5.2**

$$\chi_{Zn} = 1 - \chi_{Sn} \quad \text{Equation 5.2}$$

Where χ_{Sn} is the mole fraction of Sn and χ_{Zn} the mole fraction of Zn. Therefore the mass of one mole of the alloy will be a linear combination of the mass of Zn and the mass of Sn deposited; this can be calculated from the mole fractions of the two metals and their respective molecular weights, **Equation 5.3**

$$m = \chi_{Zn} \cdot rmm_{Zn} + \chi_{Sn} \cdot rmm_{Sn} \quad \text{Equation 5.3}$$

If the reasonable assumption is made that Sn is in the 2^+ oxidation state and we now apply the assumption of linear contributions to the slope of $\Delta m/Q$, from Faraday's law we arrive at **Equation 5.4**

$$\frac{dm}{dQ} = \frac{\chi_{Sn} \cdot rmm_{Sn} + (1 - \chi_{Sn}) \cdot rmm_{Zn}}{2F} \quad \text{Equation 5.4}$$

It follows that **Equation 5.4** can be rearranged to show that the experimental slope is a measure of the alloy composition, **Equation 5.5**.

$$\chi_{Sn} = \frac{\left(\left(\frac{d(\Delta m)}{dQ} \right) \cdot 2F - rmm_{Zn} \right)}{(rmm_{Sn} - rmm_{Zn})} \quad \text{Equation 5.5}$$

Figure 5.13 shows the calculated Sn mole fraction of Zn-Sn deposits as a function of the experimental timescale for the deposits obtained at -1.300 V for 3 molar ratios of $ZnCl_2$ - $SnCl_2 \cdot 2H_2O$ 1:1, 7:3 and 9:1 in 1: 2 ChCl: ethylene glycol. Under these controlled conditions a good linear fit is obtained for each of the solutions, although the plots are noisy (a common issue with differential plots) the data suggest relatively constant values of around 20, 10 and 2-4 % Sn in the deposits obtained from the liquids containing 1:1, 7:3 and 9:1 $ZnCl_2$: $SnCl_2 \cdot 2H_2O$ respectively. However, as the $ZnCl_2$ content of the electrodeposition solution is decreased the model ceases to function

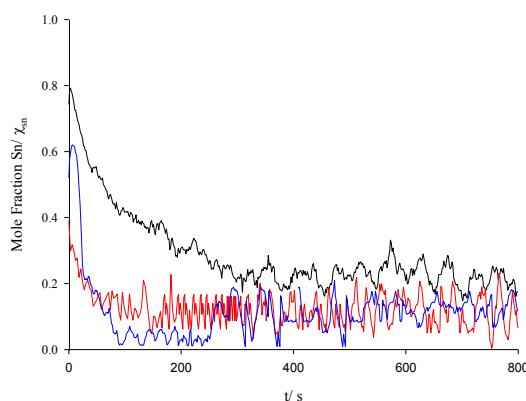


Figure 5.13 The calculated mole fraction of Sn in Zn-Sn deposits obtained from 1: 1(black) 7: 3(red) and 9: 1(blue) ZnCl_2 : $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1: 2 ChCl : ethylene glycol plotted as a function of potential time scale. The depositions were carried out at a constant potential of -1.300 V (vs. Ag wire) at 23°C .

The relative compositions of the deposits obtained during the EQCM experiments were also analysed using EDAX. A comparison between the Sn content of the deposits estimated using **Equation 5.6** and the Sn content measured by EDAX is presented in **Table 5.1**. The co-deposit compositions monitored using the EQCM are quite close to the values obtained by EDX analysis. However, it is clear that at 1:1 ZnCl_2 : $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ the model ceases to function. This is undoubtedly a result of surface roughening due to the formation of Sn dendrites.

	Solution composition		
	1:1 Zn:Sn	7:3 Zn:Sn	9:1 Zn:Sn
% Sn by EDAX	42	13	8
% Sn by EQCM	22-26	15	9-13

Table 5.1 Sn mole fractions of the deposits obtained by deposition at -1.3 V from the EQCM technique compared with EDAX analysis of the same deposits.

The use of EQCM to monitor alloy composition is a novel technique and has been shown to work effectively. However there are two major limitations,

- 1) The molecular weights of the alloy components must be significantly different
- 2) The electrodeposition must be close to 100 % current efficient and result in a compact, rigid coating.

5.4 The electrodeposition of Zn-Co Alloys

The electrodeposition of Co from aqueous systems is generally carried out in sulphate electrolytes. Chloride baths have the disadvantage that the gas evolved at the anode, chlorine, must be collected. Additionally some studies have suggested that chloride inclusion during the electrodeposition increases the stress of the Co deposit.^[19] However, chloride electrolytes do have advantages over sulphate electrolytes including higher electrical conductivity, a lower overpotential for Co deposition and generally higher cathodic current efficiencies.^[20] The effect of the electrodeposition parameters on Co electrodeposition from chloride^[20-22] and sulphate^[23, 24] acid electrolytes has been well documented in the literature. It is generally observed that the current efficiency of Co electrodeposition increases with current density and pH.^[20] This is due to the competing hydrogen evolution reaction which is suppressed as current density and pH are increased.^[20]

The incorporation of small amounts of Co into Zn electrodeposits is known to give coatings with increased corrosion resistance. As with cobalt metal, early Zn-Co electrodepositions were carried out in aqueous acid sulphate electrolytes, although more recent studies have focussed on chloride electrolytes.^[25] The electrodeposition of Zn-Co alloys from both aqueous acid sulphate^[26] and chloride baths was found to occur *via* an anomalous co-deposition mechanism. In an anomalous co-deposition the less noble metal, Zn, is deposited preferentially to the more noble metal, Co. Due to this process the amount of Co in Zn-Co electrodeposits is generally much lower than the Co concentration in the solution, e.g. a maximum of 15.2 wt.% Co content was obtained in Zn-Co alloys electrodeposited from an aqueous acid chloride bath containing 81.9 wt.% Co.^[25] The anomalous co-deposition of Zn-Co alloys is generally considered to occur due to the formation of insoluble Zn(OH)₂ at the electrode surface, inhibiting the nucleation of the more noble metal, Co.^[26] The electrodeposition of Zn-Co alloys from aqueous electrolytes is an economically and industrially viable process which gives electrodeposits with improved ductility, weldability, hardness and paintability over the individual metals.^[5] The corrosion resistance of the Zn-Co alloys is higher than that of standard galvanised Zn at low cobalt concentrations.^[27] However, the electrodeposition current efficiency is limited by the competing hydrogen evolution reaction and the anomalous co-deposition mechanism means that studies of alloys with a high Co content are minimal.

The aprotic nature of ionic liquids gives access to high Co content Zn-Co alloys, inaccessible from aqueous baths. The first ionic liquid to be used for Zn-Co alloy deposition was the CoCl₂-ZnCl₂-1-butylpyridinium molten salt.^[6] Zn-Co alloys were

obtained from both acidic and basic melts, however the viscosity of the acidic melt was high even at elevated temperatures, resulting in a low current efficiency and needle like deposits.^[6] A number of organic solvents were added to the melt in order to reduce the viscosity, resulting in an electrolyte mixture containing up to 67 % (volume), from which a 43 % Co, Zn-Co amorphous alloy phase was electrodeposited. This study demonstrated that the electrodeposition of high Co content Zn-Co alloys from ionic liquids was feasible, albeit in this case only upon the addition of a large amount of organic co-solvent.^[6] Additionally, it was shown that the Co content of the alloy could be easily controlled by varying the electrodeposition parameters.^[6]

More recently ZnCl_2 : 1-ethyl-3-methylimidazoliumchloride has been used as an electrodeposition media for Zn-Co alloys.^[5] This ionic liquid has the advantage of a lower viscosity and higher conductivity than the previously studied CoCl_2 - ZnCl_2 -1-butylpyridinium, although it is solid at 25 °C and electrodeposits were obtained at 80 °C.^[5] Sun *et al.* have shown that Zn-Co alloys can be deposited from this ionic liquid *via* a non-anomalous co-deposition mechanism, allowing the alloy composition to be varied between Zn and Co rich.^[5]

Zn-Co alloys are therefore of interest as corrosion resistant coatings for ferrous substrates and have been electrodeposited from a range of aqueous electrolytes and ionic liquids. The ChCl based deep eutectic solvents represent another class of electrolytes which may be advantageous as Zn-Co electrodeposition media. They offer many of the advantages of classical ionic liquids whilst remaining economically viable due to the low cost of their components. Additionally, the relatively low viscosity of 1: 2 ChCl: ethylene glycol allows the electrodeposition to be carried out at lower temperatures than ZnCl_2 : 1-ethyl-3-methylimidazoliumchloride^[5] and CoCl_2 - ZnCl_2 -1-butylpyridinium.^[6]

The binary Zn-Co alloy phase diagram is shown in **Figure 5.14**, pure cobalt generally has a cubic close packed structure, although Co electrodeposits are often amorphous. At ambient temperatures the major Zn-Co alloy phases known to form are β phase Zn-Co (at compositions of between 53 and 53.8 % Zn) and γ phase Zn-Co, at compositions of 75.2 and 85.4 % Zn. Additionally, γ_2 and γ_3 Zn-Co phases at narrow compositional ranges above 88 % Zn. It would therefore be expected that high Zn content Zn-Co alloys will be attained through electrodeposition from the deep eutectic solvents.

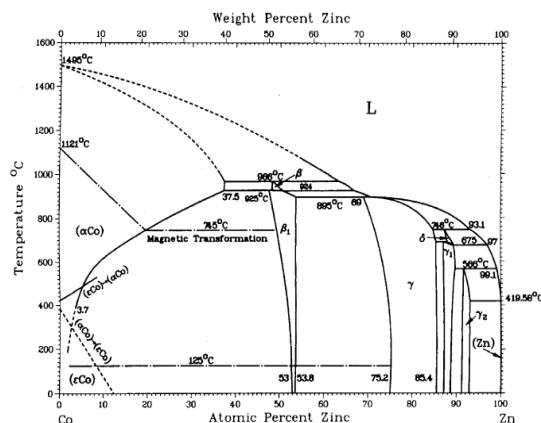


Figure 5.14 The Zn-Co binary alloy equilibrium phase diagram.^[28]

To understand the deposition of Zn-Co alloys it is first imperative to investigate the deposition of Co from the liquids to be studied. The electrochemical behaviour of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 1: 2ChCl: urea and 1: 2 ChCl: ethylene glycol is described here. The dissolution of 0.15 mol dm^{-3} $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 1: 2 ChCl: urea gives a navy blue solution; **Figure 5.15 (a)** contains cyclic voltammograms obtained in this solution at different cathodic overpotentials. During the forward scan, a single reduction wave is observed at $E_p = -1.02 \text{ V}$; this is assigned to the deposition of bulk Co. During the reverse scan, a single anodic process is observed at $E_p = 0.014 \text{ V}$, related to the oxidation of bulk Co. It is clear that Co deposition in 1: 2 ChCl: urea is quasi-reversible with 960 mV between the onset potentials of Co reduction and oxidation.

The reduction of Co in 1: 2 ChCl: urea occurs at around the same potential as Zn overpotential deposition and such there is the possibility of co-deposit formation. When equimolar amounts of ZnCl_2 and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are introduced to the system, **Figure 5.15 (b)**, the reduction wave due to Co at -1.02 V is suppressed; whilst the corresponding Co oxidation peak is also absent. The actual $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ concentration, 0.15 mol dm^{-3} , is identical to the solution shown in **Figure 5.15 (a)**, suggesting that the presence of ZnCl_2 inhibits Co reduction. The oxidation processes are also altered by the presence of ZnCl_2 , two broad oxidation waves are now apparent at $E_p = -0.25 \text{ V}$ and $E_p = -0.680 \text{ V}$. The more cathodic of the peaks is in a similar position to that of the oxidation of pure Zn in 1: 2 ChCl: urea, $E_p = -0.65 \text{ V}$, and as such may represent the oxidation of bulk Zn. The more anodic oxidation wave is not present in the cyclic voltammograms for either pure Zn or Co in this solvent. When an alloy film is anodically polarized from an electrode surface the components will dissolve at various potentials depending upon their kinetic and equilibrium properties.^[25] Different alloy phases will therefore be expected to form separate current peaks in an anodic polarization curve.^[25]

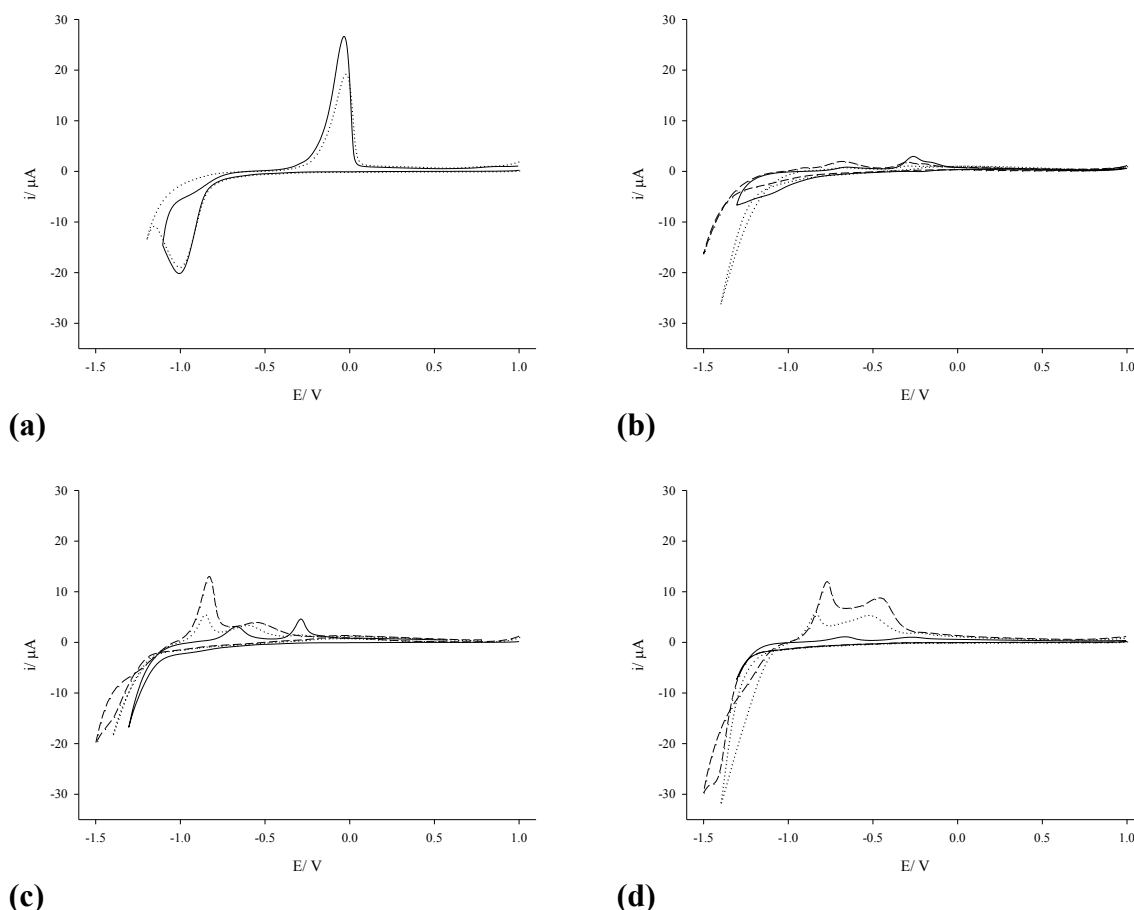


Figure 5.15 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) at 50 °C for (a) $0.15 \text{ mol dm}^{-3} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$ (b) $0.3 \text{ mol dm}^{-3} 1:1 \text{ ZnCl}_2: \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (c) $7:3 \text{ ZnCl}_2: \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and (d) $9:1 \text{ ZnCl}_2: \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in $1:2 \text{ ChCl: urea}$. Data are presented as a function of cathodic overpotential.

Previous studies in aqueous electrolytes have determined that different Zn-Co alloy phases can be detected by the appearance of intermediate current peaks in the anodic polarization trace of the Zn-Co deposit.^[25] The oxidation wave at $E_p = -0.25 \text{ V}$ may therefore be due to a Zn-Co phase with a high Co content. When the Co concentration in the bath is reduced to 0.9 mol dm^{-3} (with a Zn concentration of 0.21 mol dm^{-3}), **Figure 5.15 (c)**, there is a clear change in both the position and shape of the reduction and oxidation waves. There is still no clear reduction process in the cobalt reduction region, the onset of reduction being shifted cathodically in comparison to the equimolar Zn-Co solution. When the cathodic switching potential is set at -1.30 V two clear oxidation processes are seen and these correspond well to the two processes which occur in the equimolar Zn-Co solution, $E_p = -0.250 \text{ V}$ for a Co rich Zn-Co alloy phase and $E_p = -0.680 \text{ V}$ for the dissolution of bulk Zn. When the scan is reversed at a more cathodic limit, -1.40 V , a third oxidation process develops at $E_p = -0.850 \text{ V}$, more cathodic than the oxidation of bulk Zn from this liquid, $E_p = -0.630 \text{ V}$. Increasing the cathodic limit still further to -1.50 V results in an increase in the

relative size of the oxidation peaks at -0.630 V and -0.850 V, confirming that these two oxidation processes involve Zn. Further decreasing the Co concentration in solution, ($0.03 \text{ mol dm}^{-3} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$, $0.27 \text{ mol dm}^{-3} \text{ ZnCl}_2$) **Figure 5.15 (d)**, leads to an increase in the reduction current. It is clear that the deposited metal phases are strongly dependent upon the composition of the electrodeposition solution. Additional studies, where the peak shapes were shown to be sensitive to potential scan rate, suggest that the Zn-Co oxidation processes are charge transfer limited.

As with 1: 2 ChCl: urea, the dissolution of $0.15 \text{ mol dm}^{-3} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 1: 2 ChCl: ethylene glycol yields a navy blue solution. However, the cyclic voltammetry obtained in the two deep eutectic solvents is clearly very different, **Figure 5.16**. The overlay plots in **Figure 5.16 (a)** show the difference in onset potential of Co reduction in 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea. Co reduction occurs at $E_p = -0.70$ V in 1: 2 ChCl: ethylene glycol; whereas in 1: 2 ChCl: urea Co reduction occurs at $E_p = -1.01$ V. This suggests that there is a difference in the stability of the Co complexes in the two liquids. Although no data has yet been obtained on metal speciation in mixed metal deep eutectic solvent solutions, the navy blue colouration and known high chloride concentration of the solvents strongly suggests that Co is present as a chloro-complex in both liquids. The chloride activity in 1: 2 ChCl: urea and 1: 2 ChCl: ethylene glycol is thought to be different due to the relative hydrogen bond donor strength of urea and ethylene glycol and this has been discussed in **Chapters 3 and 4**.

The introduction of an equimolar quantity of ZnCl_2 to the $0.15 \text{ mol dm}^{-3} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$ 1: 2 ChCl: ethylene glycol solution alters the cyclic voltammetry, **Figure 5.16 (b)**. In contrast to 1: 2 ChCl: urea two clear reduction waves are observed, prior to a large increase in current which may be due to hydrogen evolution, **Figure 5.16 (b)**. The more anodic reduction process at $E_p = -0.684$ V corresponds well to the reduction wave in the solution without ZnCl_2 , **Figure 5.16 (a)**, indicating that this reduction wave is due to the reduction of Co^{2+} to Co metal. The more cathodic reduction wave at $E_p = -0.876$ V is intermediate to the onset of Co reduction and the onset of Zn reduction (in a Co free solution). The reduction process is evidently irreversible, with no clear oxidation peaks observed. When the ZnCl_2 concentration is increased to 0.21 mol dm^{-3} (with $0.09 \text{ mol dm}^{-3} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$), **Figure 5.16 (c)**, two oxidation processes develop. The more anodic oxidation process, $E_p = -0.223$ V is more cathodic than the oxidation of bulk Co, indicative of a Co rich Zn-Co alloy phase. This is further evidenced in **Figure 5.16 (d)**, where the ZnCl_2 concentration is increased to 0.27 mol dm^{-3} . Here, the charge passed during both oxidation waves is increased with increasing Zn concentration, indicating that both oxidation processes involve Zn.

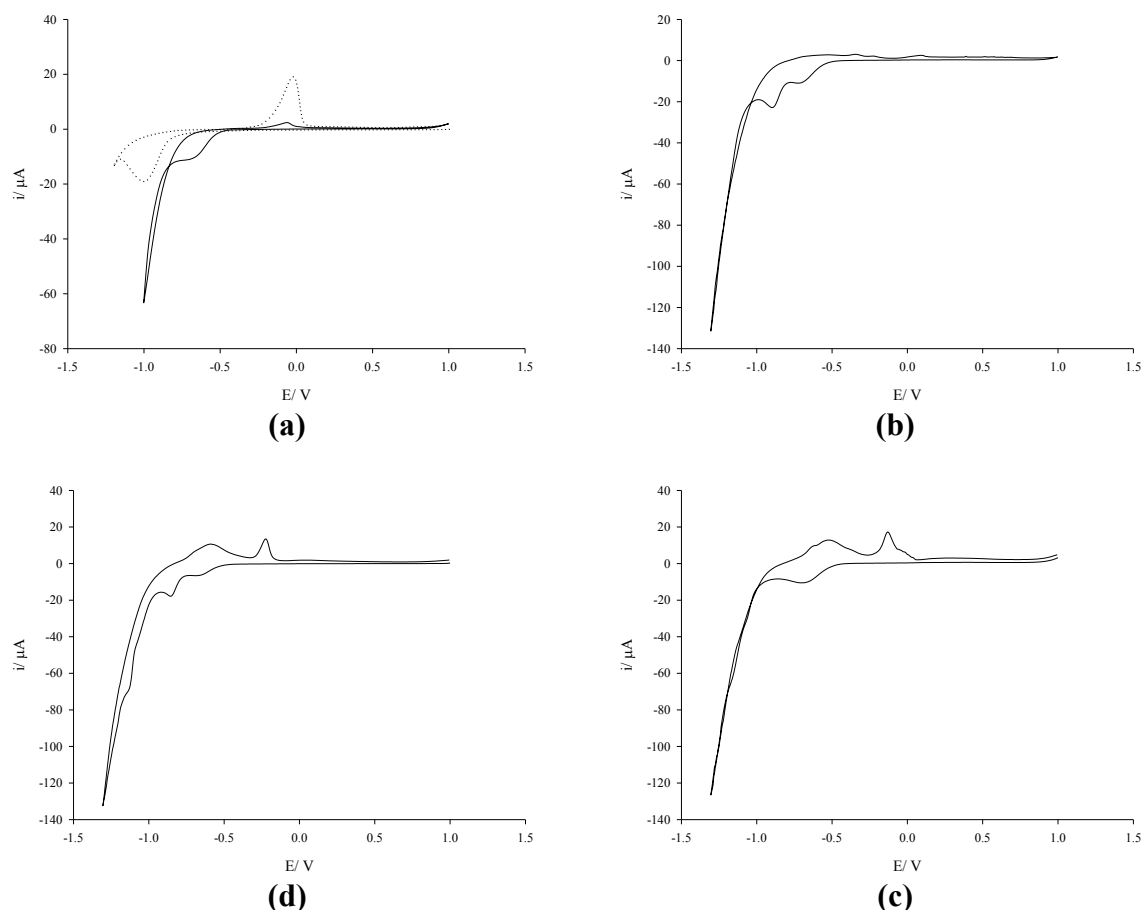


Figure 5.16 Cyclic voltammograms obtained at Pt disc (0.5 mm dia.) at 50 °C for (a) 0.15 mol dm⁻³ CoCl₂·6H₂O (b) 0.3 mol dm⁻³ 1:1 ZnCl₂:CoCl₂·6H₂O (c) 7:3 ZnCl₂:CoCl₂·6H₂O and (d) 9:1 ZnCl₂:CoCl₂·6H₂O in 1: 2 ChCl: ethylene glycol. The overlay plot (---) in 5.6 (a) represents a cyclic voltammogram of 0.15M CoCl₂·6H₂O in 1: 2 ChCl: urea obtained under the same conditions.

Bulk Zn-Co electrodeposits were obtained from 1 both 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea. However, Zn-Co coatings electrodeposited from 1: 2 ChCl: urea were generally powdery and friable and as such are not fully considered in the following discussion.

Figure 5.17 shows the relative atomic % of Co in Zn-Co co-deposits prepared from 0.3 mol dm⁻³ ZnCl₂: CoCl₂·6H₂O dissolved 1: 2 ChCl: ethylene glycol. It is clear that in all molar ratios studied, the amount of Zn in the deposit increases with increasing current density. When equimolar amounts of Zn and Co are present in the liquids, Co is preferentially deposited, making up 70-90 atomic % of the deposits. When the amount of cobalt is reduced to between 30 and 10 molar %, at a current density of 0.5 mA cm⁻², the deposit contains atomic % of Zn and Co comparable to those found in the bulk solution. It is clear that in this system the deposition of Zn-Co occurs via a non-anomalous mechanism. At current densities in excess of 1 mA cm⁻² anomalous co-deposition dominates, where the more noble metal, Co is present in lower quantities in the deposit than in the solution. This suggests that hydrogen evolution is a problem in Zn-Co electrodeposition in this class of

deep eutectic solvent. Visual examination of the cathode surface during electrodeposition did detect gassing and the formation of bubbles appeared to qualitatively increase as the amount of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was increased. It is proposed that H_2O is liberated during Co reduction and that this is then reduced to H_2 during the reduction of Zn.

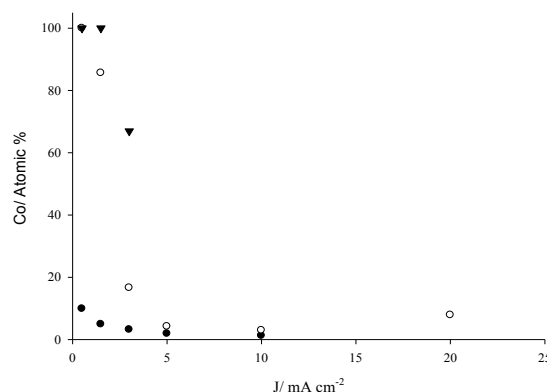


Figure 5.17 The relative atomic % of Co in deposits prepared from 0.3 mol dm^{-3} 9: 1 ZnCl_2 : $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (filled circles) 7: 3 ZnCl_2 : $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (clear circles) and 1: 1 ZnCl_2 : $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (filled triangles) 1: 2 ChCl : ethylene glycol.

The clear change in deposit morphology as Co content is increased is illustrated in **Figure 5.18**. At 3 at% Co, the deposit has a crystalline appearance with grains of a homogeneous size and shape. As the Co content is increased the grains become smaller and the overall aspect of the deposit becomes more amorphous. When the deposit is 74 at% Co, the deposit is amorphous in appearance and is additionally substantially cracked. Similar deposit morphologies have been observed in Zn-Co deposits obtained from alkaline glycine solutions^[29] and it is suggested that the presence of Co in the deposit promotes hydrogen evolution. This is consistent with the voltammetric and visual analysis discussed above. *I.e.* As Co is deposited, water molecules are released from the coordination shell of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ leading to an increase in free H_2O in the system, which in turn may lead to an increase in hydrogen evolution and deposit micro-cracking.

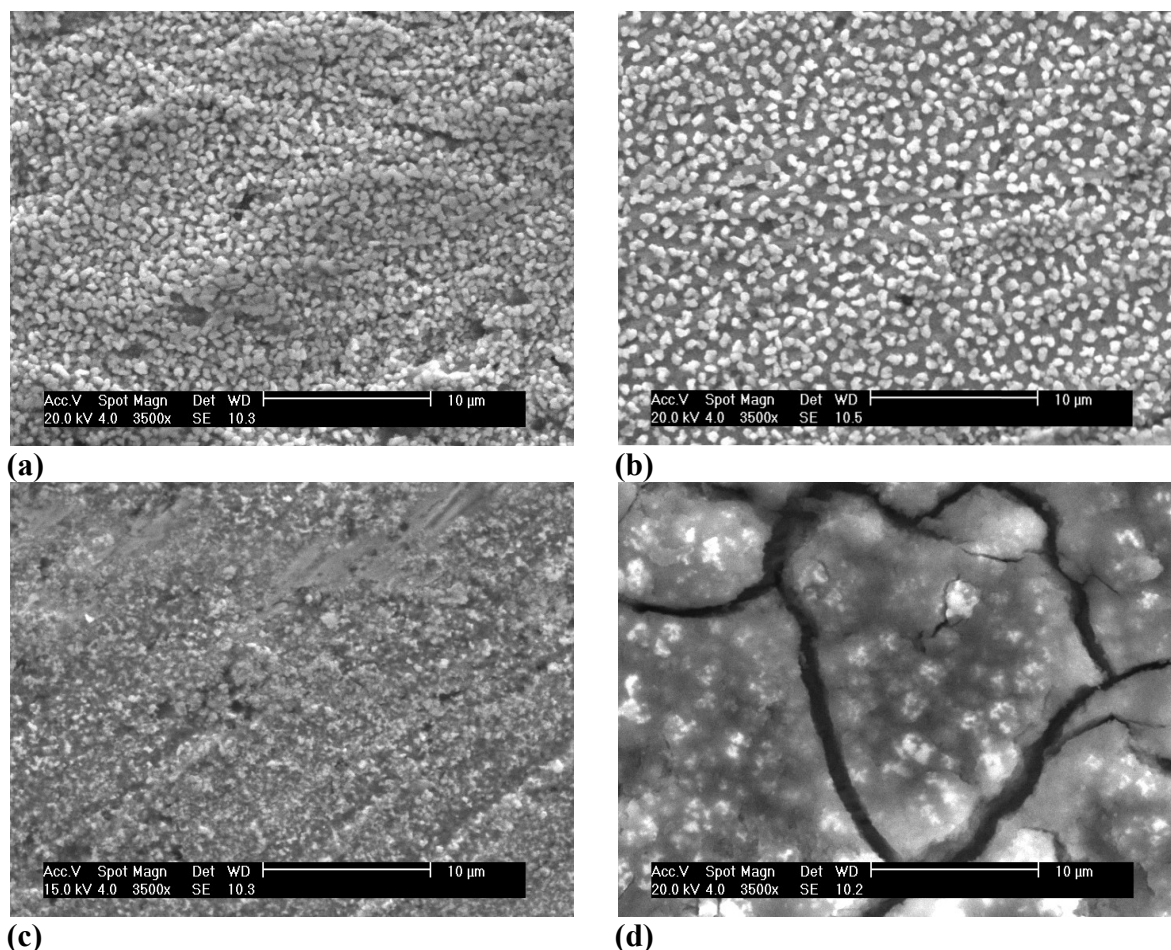


Figure 5.18 Representative SEM micrographs of the deposits obtained from 1: 2 ethylene glycol and various molar ratios of $0.3 \text{ mol dm}^{-3} \text{ ZnCl}_2$: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ containing (a) 3, (b) 8, (c) 28 and (d) 74 % Co. Depositions shown were obtained at $I = 3 \text{ mA cm}^{-3}$

The X-ray diffraction patterns for a selection of the Zn-Co electrodeposits are presented in **Figure 5.19**. These bulk deposits were prepared by galvanostatic deposition at 50°C on a Ni substrate. The data presented is for electrodeposits obtained from a solution of $0.27 \text{ mol dm}^{-3} \text{ ZnCl}_2$ and $0.03 \text{ mol dm}^{-3} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 1: 2 ChCl : ethylene glycol. The deposits were generally quite thin and as such Ni substrate peaks dominate the majority of the graphs at $2\theta = 44.80^\circ$ and 52.13° . However, there are clear Zn peaks represented by the red lines in **Figure 5.19**. The amorphous nature of the high Co % deposits means that it is difficult to detect these phases using XRD. However, as the applied current density and hence Zn content in the alloy phase increases, a corresponding increase in the crystallinity of the phase is observed. A broad peak at $2\theta = 42.7^\circ$ suggests an amorphous/ less crystalline and this signal has previously been determined to be due to a mixed Zn-Co phase of the type $\text{Co}_5\text{Zn}_{21}$. The Zn-Co phase diagram supports the existence of this mixed phase at ambient temperature and pressure, where Zn-Co deposits containing 15 % Co exist as a γ_2 alloy phase. Additionally, as the % of Co in the deposits decreases, the signal at 42.7° decreases indicating that this phase does contain Co.

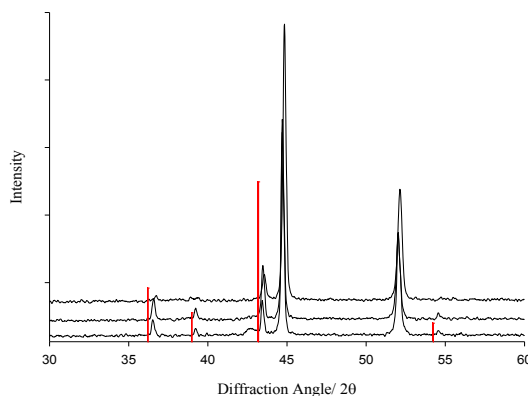


Figure 5.19 XRD patterns of Zn-Co electrodeposited from 0.3 mol dm⁻³ (7: 3) ZnCl₂: Co.Cl₂.6H₂O in 1: 2 ChCl: ethylene glycol at 1.5 mA cm⁻², 3 mA cm⁻² and 5 mA cm⁻². The red lines represent the XRD pattern obtained for Zn deposits from this solution

5.5 The Electrodeposition of Zn-Ni Co-Deposits

As with Zn-Co alloys, the closely allied Zn-Ni alloys are principally of interest as sacrificial anticorrosion coatings for ferrous substrates and electro-catalytic materials. Their electrodeposition from aqueous electrolytes occurs via the anomalous co-deposition mechanism, whereby the less noble metal, Zn, is preferentially deposited. It has been suggested that this mechanism is caused by the hydrogen evolution mechanism. In the presence of hydrogen, Zn hydroxide precipitates at the electrode surface inhibiting Ni nucleation. Ionic liquids have been suggested as an aprotic alternative for the deposition of Zn-Ni alloys, a number of studies have used the chloroaluminates and more recently the more air and moisture stable ZnCl₂-1-ethyl-3-methylimidazolium chloride.^[30] The deep eutectic solvents used here present a similarly high chloride environment with the advantage that they are relatively simple and economical to prepare.

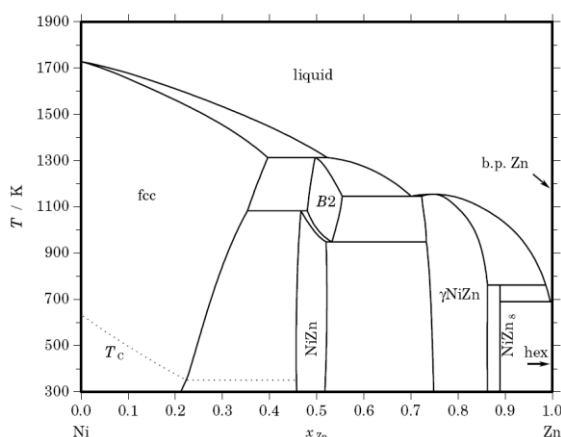


Figure 5.20 The Binary Zn-Ni equilibrium alloy phase diagram.^[28]

The binary Zn-Ni phase diagram, **Figure 5.20**, is quite similar to the Zn-Co phase diagram at low temperatures ($< 500\text{ }^{\circ}\text{C}$). This is unsurprising as both Co and Ni have a cubic close packed crystal structure and are similarly sized and so would be expected to have similar degrees of lattice matching with Zn. Zn-Ni alloys containing 46-52 % Zn are present as the β phase, generally of the stoichiometry NiZn. At higher compositions of 75-85 % the γ phase dominates and at compositions greater than 88 % Zn a hexagonally close packed structure, similar to pure Zn is the predominant phase.

Here the electrodeposition of Zn-Ni co-deposits from 1: 2 ChCl: urea is described. In a contrasting manner to the Zn-Cu and Zn-Ni co-deposits, Zn-Ni could not be effectively electrodeposited from 1: 2 ChCl: ethylene glycol, therefore this solvent is not considered in the following discussion.

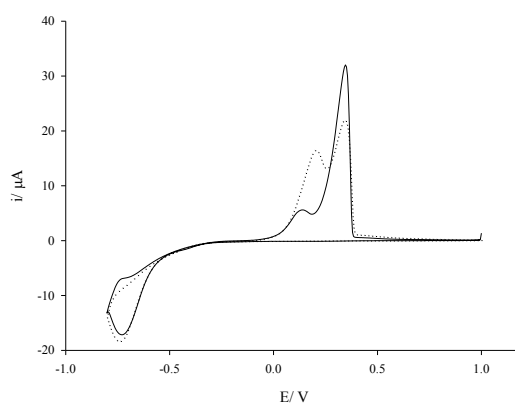


Figure 5.21 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) for 0.15 mol dm^{-3} $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 1: 2 ChCl: ethylene urea 1st scan (solid) and 2nd scan (dashed).

In **Figure 5.21** it can be seen that Ni deposition from 1: 2 ChCl: urea occurs via a quasi reversible deposition process, with a single reduction wave at $E_p = -0.72\text{ V}$. Two corresponding oxidation processes, the relative area of which change with successive scans, are observed in the reverse scan. With each additional scan the more cathodic oxidation process increases in dominance, inferring that this oxidation process is due to the oxidation of bulk Ni, whereas the more anodic oxidation process is due to oxidation of Ni from the Pt electrode surface. It has previously been reported that the Ni oxidation process is kinetically slow, with the oxidation peak shape changing with potential scan rate.^[31]

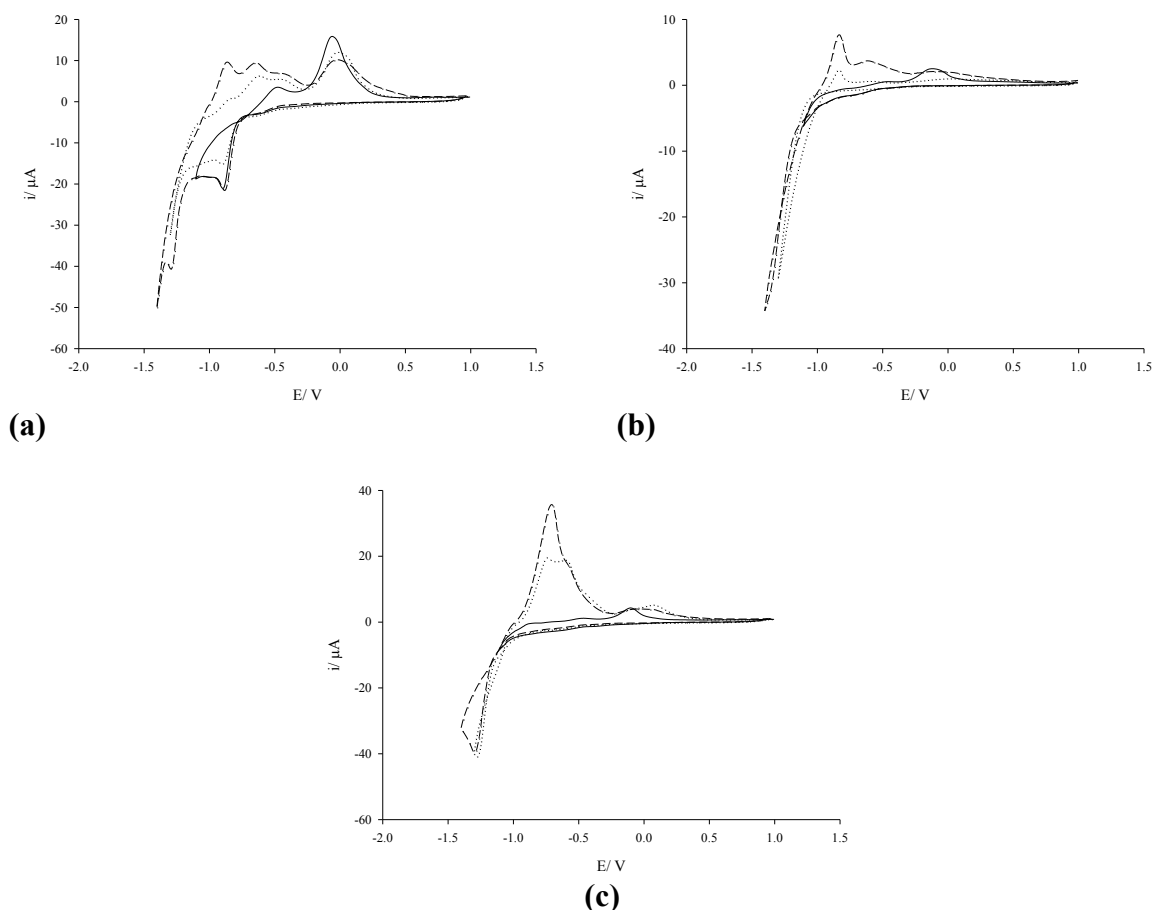


Figure 5.22 Cyclic voltammograms obtained at a Pt disc (0.5 mm dia.) at 50°C for (a) 0.3 mol dm⁻³ 1: 1 ZnCl₂: NiCl₂·6H₂O (b) 7: 3 ZnCl₂: NiCl₂·6H₂O (c) 9: 1 ZnCl₂: NiCl₂·2H₂O in 1: 2 ChCl: urea. All data are presented as a function of cathodic overpotential

A reduction wave due to reduction of Ni²⁺ to Ni⁰ is present at $E_P = -0.88$ V. On the reverse scan a complex series of oxidation processes occur. Four oxidation waves are present, those at $E_P = -0.05$ V and $E_P = -0.48$ V are attributed to the oxidation of Ni species. In the absence of NiCl₂·6H₂O, Zn is oxidised at $E_P = -0.72$ V in 1:2 ChCl: urea. When ChCl: urea contains equimolar amounts of ZnCl₂ and NiCl₂·6H₂O, **Figure 5.22 (a)**, there is no equivalent Zn oxidation peak. However, there are two additional oxidation processes at $E_P = -0.63$ V and $E_P = -0.86$ V, which are not present in the cyclic voltammograms of either ZnCl₂ or NiCl₂·6H₂O in 1: 2 ChCl: urea. In this system the reduction of Ni is occurring within the underpotential deposition regime of Zn, therefore it is possible that the two oxidation processes are due to the stripping of Zn rich and Ni rich Zn-Ni co-deposits respectively. When the relative molar % of ZnCl₂ in the solution is increased to 70 %, the Ni reduction wave is no longer clear and the charge due to Ni oxidation is reduced. When the relative molar concentration of ZnCl₂ is increased to 90 %, the cyclic voltammogram is similar to that observed in the absence of NiCl₂·6H₂O. The Zn oxidation wave is broad and this may be a consequence of Zn being deposited on a rough Ni surface as opposed to the Pt

electrode. A broad oxidation wave is present at $E_p = -0.08$ V and this may be due to a Ni rich Zn-Ni phase.

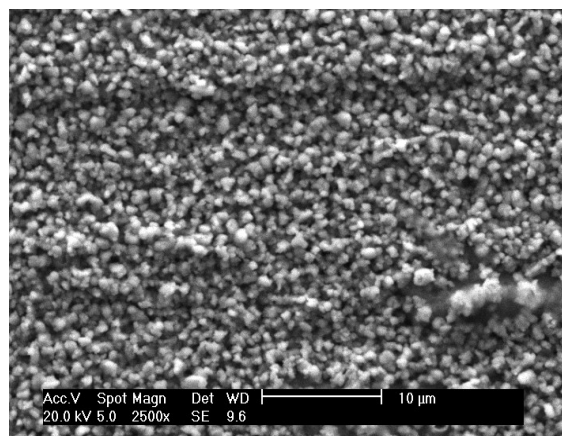


Figure 5.23 A representative SEM of Zn-Ni, containing 88 % Zn, electrodeposited on Cu from 0.3 mol dm^{-3} (7:3) ZnCl_2 : $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 50°C for 30 minutes.

Bulk deposits were prepared from various molar ratios of 0.3 mol dm^{-3} ZnCl_2 : $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 1: 2 ChCl: urea. Unlike Zn-Cu and Zn-Co the morphologies and composition of these deposits was relatively insensitive to the applied current density and electrolyte composition. A representative SEM image of a Zn-Ni deposit, containing 88 % Zn (from EDX analysis), is shown in **Figure 5.23**. Additionally XRD spectra contained no evidence of Zn-Ni alloy phases and were dominated by Zn patterns. It is therefore proposed that the Zn-Ni deposits obtained from 1: 2 ChCl: urea exist as distinct Zn and Ni phases.

Summary

For the first time it has been demonstrated that Zn-Cu, Zn-Co, and Zn-Ni co-deposits can be electrodeposited from 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea. Zn-Cu and Zn-Co were found to be most effectively electrodeposited from 1: 2 ChCl: ethylene glycol and the composition of the deposits could be controlled by altering the deposition potential, current density or the relative metal concentrations in the liquid. XRD analysis of selected Zn-Cu and Zn-Co deposits contained evidence of alloy phases, the first alloy electrodeposits from this class of deep eutectic solvent.

Zn-Ni was successfully electrodeposited from 1: 2 ChCl: urea, electrodeposition from 1: 2 ChCl: ethylene glycol led to the formation of non-adherent and powdery deposits. However, no evidence was found for the existence of Zn-Ni alloy phase and it was proposed that the deposits consisted of distinct phases of Zn and Ni.

The electrochemical quartz crystal microbalance has been used for the first time to probe Zn co-deposit composition in deep eutectic solvents and it has proved possible to estimate the

mole fractions of the components of binary co-deposits. However, the sensitivity of the technique is limited by the difference in the molecular weights of the two components. As such, Zn-Sn co-deposition was chosen as a model system to assess the applicability of this novel technique. The validity of this technique was verified by comparison to EDX analysis of the deposits; both techniques provided mutually supportive results.

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Chapter 6: Summary and Future Directions

6.1 Summary

6.1.1 Zn Electrodeposition from Deep Eutectic Solvents

6.1.2 The Effect of Organic Additives

6.1.3 Zn Alloy Electrodeposition from Deep Eutectic Solvents

6.2 Future Directions

6.3 References

6.1 Summary

The aim of this thesis was to take a single metal, Zn, and to develop an understanding of the electrodeposition mechanism in 1: 2 ChCl: ethylene glycol and 1: 2 ChCl: urea. The results contained within this report represent the first comprehensive study of metal deposition from ChCl: hydrogen bond donor deep eutectic solvents.

6.1.1 Zn Electrodeposition from Deep Eutectic Solvents

The physical properties, concentration effects, electrochemical behaviour and morphology of Zn deposits obtained from these two ostensibly similar solvents were found to be very different. A single phase of Zn was proposed to be deposited in 1: 2 ChCl: urea, whereas a two phase Zn deposit was obtained from 1: 2 ChCl: ethylene glycol. Analysis of cyclic voltammetry, chronoamperometry and electrogravimetry conducted in the two solutions indicated that the difference in morphology was due to a difference in the Zn nucleation and growth mechanism.

A theory involving the activity of free chloride ions and their specific adsorption at growing Zn crystal faces was proposed as a possible explanation for this divergence in behaviour. Zn growth was determined to be limited in ChCl: urea by the high viscosity of the fluid. Conversely, Zn deposition in 1: 2 ChCl: ethylene glycol was proposed to be principally controlled by the inclusion of active free chloride ions in the electrochemical double layer.

A novel combined technique, the *in-situ* liquid phase AFM-EQCM was applied for the first time to a metal deposition process in an ionic liquid. This technique allowed the Zn nucleation mechanism in 1: 2 ChCl: ethylene to be elucidated whilst providing independent and mutually supportive evidence for the behaviour observed in distinct experiments.

6.1.2 The Effect of Organic Additives

The investigation was extended to determine the effect of organic additives on the Zn electrodeposition mechanism. Few aqueous electrodeposition protocols consist of electrolyte and metal salt alone; a wide range of additives are usually introduced to the electroplating solution as levellers, brighteners and complexing agents. However, little consideration has been given to the effect of additives in ionic liquid/ deep eutectic solvent electroplating protocols.

In this thesis it has been shown that the organic additives acetonitrile, ethylene diamine and ammonia have a profound effect on the Zn electrodeposition mechanism in ChCl: hydrogen bond donor deep eutectic solvents.

Ethylene diamine and ammonia were shown to significantly alter the deposited Zn morphology. Corresponding changes in the cyclic voltammetry and chronoamperometry were indicative of a change in the Zn electrodeposition mechanism.

Brighteners are thought to act in one of two ways in aqueous electrolytes:

- 1) They act to complex the metal in solution making it harder to reduce
- 2) They are adsorbed at the electrode surface, inhibiting nucleation.

EXAFS was applied for the first time to this class of solvent to identify the metal species present in solution. This technique conclusively proved that Zn was present as $[\text{ZnCl}_4]^{2-}$ in ZnCl_2 containing 1: 2 ChCl : ethylene glycol in the presence of both 0.3 mol dm^{-3} ethylene diamine and 0.3 mol dm^{-3} ammonia, *i.e.* the additives were not acting to complex the metal ions in solution. The chloride activity model described previously was expanded to successfully explain the effect of the additives as being due to their relative hydrogen bond donor strength.

The effect of additive charge was then considered through the addition of the ionic surfactant sodium dodecylsulphate and Hexacetylammoniumbromide to the electrolyte. It was therefore proposed that the differences in electrochemical behaviour and deposit morphology were due to the relative hydrogen bond donor strength of the additives.

The effect of additive charge was then studied through the addition of anionic sodium dodecylsulphate and cationic hexacetylammonium bromide to the electrolytes. The anionic surfactant was proposed to preferentially adsorb at the electrode surface and acted as an effective levelling agent for Zn deposition. The cationic surfactant acted to inhibit Zn nucleation and this was proposed to be due to a specific adsorption of the surfactant at the electrode surface at cathodic potentials.

6.1.3 Zn Alloy Electrodeposition from Deep Eutectic Solvents

Finally the applicability of this class of solvent to Zn alloy electrodeposition was explored. Zn-Cu, Zn-Co and Zn-Ni co-deposits were electrodeposited from ChCl based deep eutectic solvents for the first time. The composition of the co-deposits could be controlled by altering the electrolyte composition or the electrodeposition parameters. Evidence was obtained for alloy phase formation in the Zn-Co and Zn-Cu systems.

Finally the co-deposition of Zn-Sn was revisited to highlight the validity of a novel technique for monitoring co-deposit formation using the electrochemical quartz crystal

microbalance. Results obtained using this technique were independently verified by EDX analysis of the resulting deposits.

6.2 Future Directions

This thesis has highlighted the complexity of electrodeposition processes in ionic liquids/deep eutectic solvents. It is clear that the electrodeposition mechanism is strongly dependent on the solvent used and the concentration of solute. Additionally it has been shown that while organic additives can be used as brighteners in these systems, their mode of action is very different to that in aqueous systems and is also solvent dependent. As such it is likely that unique brightener systems will need to be developed for each deep eutectic solvent. This is a research area, which to date has been rather under represented. The adsorption of cations on metal surfaces has been studied by Endres using STM.^[1] It would be useful to apply this technique to this system as it would also provide information about the magnitude of the adsorption energy. This could then provide evidence for the change from progressive to instantaneous nucleation.

Data presented in this thesis suggests that the changes in Zn deposition, both between the two electrolytes studied and upon the addition of organic additives, is due to a difference in Cl⁻ activity and the structure of the electrochemical double layer. However, little is known about the structure of the double layer in this class of deep eutectic solvent. This thesis highlights the importance of further investigations into double layer structure, to allow a more quantitative understanding of electrodeposition processes at the electrode interface to be gained. This would also allow substantiation of the possible adsorption of neutrals to be obtained.

The new technique of digital holographic microscopy could be used to image the early stages of nucleation in real time. This technique allows reflective surfaces to be imaged with a depth resolution of 10 nm and a time resolution of 20 μ s. This will permit a dynamic view of the nucleation process and will allow species to be added to the solution and their effect monitored in real time.

Chapter 4 has opened up the very interesting area of colloidal dispersions in ionic liquids. It would be interesting to determine the dimensions any structures formed and whether these can be used to template morphologies as has been achieved in aqueous systems. Preliminary data suggests that the viscosity of the solution decreases when surfactants are added to an ionic liquid. The causes underlying this would be interesting to study. The most probable cause of this phenomenon is an increase in free volume caused by the micelles breaking up

the ionic liquid structure. This could be studied by simple density measurements and corroborated using NMR diffusion measurements.

6.3 References

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