

Influence of Additives on Electrodeposition of Metals from Deep Eutectic Solvents

Thesis submitted for the degree of
Doctor of Philosophy
At the University of Leicester

By

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November 2017



Abstract

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In metal electroplating processes, additives are normally added to the plating bath to improve the physical and mechanical properties of the coating such as brightness, roughness, thickness, hardness and resistance to corrosion. The effects of additives on the electrodeposition of metals from aqueous solution have been extensively investigated. However, very few studies have considered the effects of additives on the electrodeposition of metals from ionic liquids (deep eutectic solvents).

This work has shown that ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), sodium iodide (NaI), boric acid (BA) and 5,5-dimethylhydantoin (DMH) as additives can be used to modify the Cu deposit morphology obtained from a 1:2 ChCl: ethylene glycol-based liquid (Ethaline 200) on a mild steel substrate. It was found that NaI significantly influenced the morphology of the Cu deposit, achieving a bright and thick Cu deposition. The effects of nicotinic acid (NA), boric acid (BA) and benzoquinone (BQ) on Zn deposit morphology from Ethaline 200 were also shown, and for the first time a bright zinc coating has been achieved on a copper substrate when NA was used.

The feasibility of Zn-Ni alloy deposition from Ethaline 200-based deep eutectic solvents has been investigated in the absence and presence of boric acid and sodium bromide. It was found for the first time that a successful bright Zn-Ni alloy coating from Ethaline 200 can be produced in the presence of boric acid and NaBr as additives. Moreover, the effects of current density, temperature and concentration of Zn species on electrodeposition of Zn-Ni alloy from Ethaline 200 in the presence of both boric acid and NaBr have been studied.

The last part of this work was to look at the effects of methyl nicotinate (MN) on the electrodeposition of Al from 1-ethyl-3-methylimidazolium chloride/ AlCl_3 and 1-butyl-3-methylimidazolium/ AlCl_3 as classical ionic liquids, and (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide as deep

eutectic solvents. A mirror Al coating has been achieved on a copper substrate from both conventional ionic liquids as a result of using methyl nicotinate as an additive. MN has improved the morphology of Al deposited from (1.5:1) AlCl_3 :acetamide-based liquids and, furthermore, MN has been used to refine the grain size of the Al coating achieved from (1.5:1) AlCl_3 :*N,N*-dimethylacetamide as a deep eutectic solvent.

Conference contributions

(1) Talks:

1. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Effect of Additives on Zinc Electrodeposition from Novel Ionic Liquid Solvent, Midlands Electrochemistry Group (MEG), 22nd June 2015, University of Warwick, Coventry, UK.
2. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Electrodeposition of Zn-Ni Alloy from Deep Eutectic Solvents, Electrochem Conference, 17th -19th August 2016, University of Leicester, Leicester, UK.
3. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Electroplating of Aluminium from Novel Ionic Liquids, Electrochem Conference, 10th -12th September 2017, University of Birmingham, Birmingham, UK.
4. Karl Scott Ryder, Robert Hillman, Emma J.R. Palin, Hasan Al-Esary, Characterisation of Metal Deposition and Metal Dissolution Processes in Deep Eutectic Solvents Using Electrochemical, Gravimetric and Neutron Scattering Methods, 232nd ECS Conference (October 1-6, 2017) National Harbor, Washington, USA.

(2) Posters:

1. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Influence of Nicotinic Acid on Electrodeposition of Zinc from Deep Eutectic Solvents, Department of Chemistry Postgraduate Research Day, 14th April 2015, University of Leicester, Leicester. UK.
2. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Influence of Nicotinic Acid on Electrodeposition of Zinc from Deep Eutectic Solvents, Electrochem Conference, 13th -15th September 2015, Durham University, Durham, UK.
3. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Electrodeposition of Zn-Ni Alloy from Deep Eutectic Solvents, Midlands Electrochemistry Group (MEG), 25nd May 2016, University of Leicester, Leicester. UK.
4. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Electroplating of Aluminium from Novel Ionic Liquids, Midlands Electrochemistry Group (MEG), 26nd April 2017, University of Nottingham, Nottingham. UK.

5. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Electroplating of Aluminium from Novel Ionic Liquids, Electrochem Conference, 10th -12th September 2017, University of Birmingham, Birmingham, UK.
6. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Electrodeposition of bright Zn-Ni Alloy from Deep Eutectic Solvents, EMDoc PGR Conference, 13th September 2017, University of Nottingham, Nottingham. UK.
7. Hasan AL-Esary, K. S. Ryder and A. P. Abbott, Influence of Nicotinic Acid on Electrodeposition of Zinc from Deep Eutectic Solvents, 1st Iraqi Student Conference, 29th September 2017, University of Sheffield, Sheffield, UK

Statement

The work presented in this thesis for the degree of Ph.D. entitled “*Influence of Additives on Electrodeposition of Metals from Deep Eutectic Solvents*”. The experimental work in this thesis has been carried out by the author in the Department of Chemistry at the University of Leicester between September 2013 and September 2016. The work has not been submitted, and is not presently submitted, for any other degrees at this or any other university.

Signed.....

Date.....

Acknowledgements

It is a pleasure to thank the people who have made this dissertation possible. First and foremost I would like to thank my supervisor, Professor Karl Ryder, for his amazing ideas, encouragement, support, guidance and insightful comments throughout my PhD.

I would also like to thank Professor Andy Abbott for giving me useful insights, advice and for his help. It is also a pleasure to thank all the group members, especially Andy Ballantyne, Rob Harris, Rachel and Alex for helping and providing assistance. Thanks also to Virginia for helping and advising me on setting up my experiments, especially in the electrodeposition of Aluminium. I am also thankful to the administrative and workshop staff of the department for their cooperative attitude and assistance. I would like to thank Mr Graham Clark, who helped me to use the scanning electron microscope.

I would like to thank my colleagues and PhD students, some of who have graduated and some are about to graduate. They are: Mohommade Qasem, Hani Ismail, Jalil Kareem Jamil Juma, Shannon Stodd, Wrya Karim, Fikrat and Salih Cihangir. Everyone in the department of chemistry and engineering has helped me at some point or other, so thank you to you all.

Unquestionably, this would have never been possible without the love and patience of my family members especially my parents. I would like to reserve special thanks to my loving wife, Rawaa, for her love, support, and encouragement during times of patience and strength during all these years. I dedicate this thesis to you, my family.

Finally, I would like to thank the Iraqi Ministry of Higher Education and Scientific Research and University of Kerbala, Iraq, for the financial support required to complete this project.

Dedication

I would like to dedicate this thesis to my father, who did not forget me during my studies and pushed me into the way of success, and also I would like to dedicate my thesis to my mother, who did not forget me by supplication to God.

Hasan Fisal AL-Esary
Leicester, 2017

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List of abbreviations

Abbreviations	Full names and unit
ChCl	Choline chloride
EG	Ethylene glycol
DES	Deep eutectic solvent
IL	Ionic liquid
HBD	Hydrogen bond donor
[bmim]Cl	1-Butyl-3-methylimidazolium chloride
[emim]Cl	1-Butyl-3-methylimidazolium chloride
EDTA	ethylenediaminetetraacetic acid disodium salt dihydrate
BA	Boric acid
NA	Nicotinic acid
DMH	5,5-dimethylhydantoin
MN	Methyl nicotinate
BQ	<i>p</i> - benzoquinone
CV	Cyclic voltammetry
WE	working electrode
CE	Counter electrode
RF	Reference electrode
E	Potential / Voltage
E°	Standard electrode potential (V)
E_a	Activation energy for viscous flow (J)
E_{pc}	Cathodic peak potential (V)
E_{pc}	Anodic peak potential (V)
E_η	The activation energy of viscous movement
Q	Charge
ν	Scan rate
F	Faraday
D_0	Diffusion coefficient
UPD	underpotential deposition
QCM	Quartz Crystal Microbalance
f	Frequency (Hz)

f_0	Fundamental frequency of a QCM (Hz)
f_s	Resonant Frequency (Hz)
Δf_q	The observed resonant frequency change
λ	Wavelength (m)
i	Current (A)
i_{pc}	Cathodic peak current (A)
i_{pa}	Anodic peak current (A)
m	Mass (g)
Δm	Mass change
mq	Mass of the quartz crystal (g cm^{-3})
n	Number of electrons
R	Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
R_s	Resistance of solution
R_{ct}	Resistance of charge transfer
t	Time (s)
T	Temperature
Z	Impudence
Z''	Imaginary components of the impedance
Z'	Real components of the impedance
Z_w	Warburg impedance
ω	Angular frequency (radians/s)
SEM	Scanning electron microscopy
EDXS	Energy-dispersive X-ray spectroscopy
AFM	Atomic force microscopy
XRD	X-ray diffraction
EIS	Electrochemical impedance spectroscopy
Ra	Roughness

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1.1 Electroplating

The process of plating materials onto surfaces from solutions of their corresponding species is called electroplating. This process is usually employed to prepare thin layers of materials, including metals, alloys, semiconductors and conductive polymers, in order to change the properties of the objects in terms of, for instance, corrosion resistance, wear resistance, decorative quality, conductivity, etc. A large number of objects such as machines, components, sub-assemblies and tools are normally made from metallic and non-metallic materials. The lifetimes of these materials are often limited due to their operating environments and other external conditions. The interfaces of most of these materials may become damaged because of their atomic structures, and the surfaces of certain materials might contain susceptible sites, which results in them being easily affected by external, for example, environmental, factors. Since most metallic materials are expensive, it is therefore important to protect these materials as much as possible in order to extend their lifetimes. Consequently, electroplating is considered a convenient means of protecting objects from corrosion and increasing thermal stability of object surfaces.¹

Electroplating of metals was carried out for first time in 1805 by Luigi Brugnatelli, who used a Voltaic Pile to deposit gold.² Thereafter, John Wright used a KCN electrolyte in the electroplating of silver and gold, which is similar to the method used today. While this process was initially limited to deposition of decorative metals, Bird, in 1837,³ and Junot de Bussey, in 1848,⁴ were able to deposit the more functional metals of nickel and chromium.

Industrial electroplating of metals is achieved using aqueous solutions. Different types of metals are used in electroplating such as Au, Ag, Zn, Cr, Cu, Ni, Cd and Cu, as well as Zn-based alloys. These metals serve various purposes such as decoration, corrosion resistance, hardness and increasing the thermal stability of surfaces. Plating with Cr, Ni, or Co gives hard coatings, while Zn and Cd can provide coatings with anticorrosion properties, whilst Au and Ag are employed for visual appearance.⁵ Electroplating with these metals is achieved in aqueous solution due to high conductivities, low cost, non-flammability, good throwing power, high metal solubility and high rates of mass transfer. However, there are some disadvantages to using aqueous solutions, such as hydrogen evolution, low current efficiency, narrow potential windows, the requirement to use toxic compounds such as cyanide, passivation of the anode or cathode, and the

significant environmental impact associated with the requirement to treat large volumes of water to remove heavy metals and electrolytes before it can be returned to the water course. Moreover, Cr, Ni and Cd are highly toxic metals, therefore replacement with Al, Ti and W is desirable, where these latter metals are plentiful and are excellent in terms of their resistance to corrosion. However, oxides of these metals are insoluble in aqueous solution.

There are a range of solvents that can be used in the electroplating of metals. These could be ionic or molecular, and polar or non-polar in nature. Some metals, such as Al, have been plated from organic solvents.^{6, 7} These solvents have wide potential uses. However, their disadvantages are that they often have low conductivities, and are highly volatile and flammable. Recently, ionic liquids have been used in the electroplating of metals and their alloys due to the fact that ionic liquids have excellent associated properties, as will be explained in the following sections.

1.2 Ionic liquids

Ionic liquids (ILs) are compounds that are entirely composed of ions and that exist in their liquid state below 100°C, otherwise known as room-temperature ionic liquids (RTILs). Ethylammonium nitrate ([EtNH₃][NO₃]) was the first ionic liquid described in the literature, and was prepared in 1914 by Walden.⁸ At that time, there was little interest in Walden's discovery past that of a being curiosity. However, this liquid is now considered the starting point in the field of ionic liquid research.

At temperatures around 1000°C, a classical molten salts liquid can be prepared and used for the electrowinning of metals such as Li, Na, Ti and Al.^{9, 10} Molten salts are wholly ionic and aprotic, whilst displaying remarkable properties such as high conductivity, wide potential windows, low viscosity and high metal salt solubility. Moreover, molten salts do not suffer from the hydrogen evolution reaction, as can occur in aqueous solutions. However, the substrates one can use for electroplating in molten salts are limited. Therefore, interest in ionic liquids has become significantly greater than that of molten salts.

Almost 40 years after ionic liquids were discovered by Walden, the authors made efforts to prepare a lower temperature melt for the electrodeposition of aluminium, which was previously only accessible from high temperature molten salts. It was found

that eutectic melts with freezing points close to 100°C could be formed when the composition of LiCl/ KCl/ AlCl₃ mixtures were changed.¹¹ The formation of bulky chloroaluminate ions (e.g. AlCl₄⁻ and Al₂Cl₇⁻) in the eutectic mixtures resulted in liquids with low melting points.¹² In the 1970s, Osteryoung *et al.*¹³ prepared ionic liquids by mixing AlCl₃ with the asymmetric 1-butylpyridinium cation, which forms a liquid at 20°C within a narrow compositional range of 60-67 mol% AlCl₃. It was found that the 1-butylpyridinium cation was easy to reduce, where previously this was restricting the electrochemical applications of this ionic liquid. Later, Wilkes and Hussey noted that organic cations can be affected by the stability to reduction of ionic liquids. They prepared an AlCl₃:1-ethyl-3-methyl-imidazolium ionic liquid,¹⁴ whose physical properties, such as low viscosity and good conductivity, were found to be considerably improved over those of the 1-butylpyridinium system.¹⁴ However, applications of the liquids were limited due to their sensitivity to air, principally due to the rapid hydrolysis of AlCl₃ when in contact with moisture. Therefore AlCl₃ was ultimately replaced with ZnCl₂, which is far more stable to hydrolysis.¹⁵

The liquids that were formed from the mixing of organic cations with AlCl₃ and/or ZnCl₂ are often referred to as first generation ionic liquids.¹⁶ These types of liquids are fluid at low temperatures because of the creation of bulky chloroaluminate or chlorozincate ions at eutectic compositions of the mixture. This reduces the ions charge density, which can in turn reduce the lattice energy of the system, causing a reduction in the freezing point of the mixture. In general, delocalisation of charge on the ions reduces lattice energy and, thus, leads to the formation of an ionic liquid. The properties of this generation of ionic liquids are easily affected by changing the composition of the liquid from that of Lewis basic, with an excess of the organic cation, and Lewis-acidic, with an excess of the metal halide.¹⁷ For example, Al speciation in the chloroaluminate ionic liquids can be altered through changing the composition of the liquid. The associated equilibria in these mixtures are ultimately dependent on the relative concentration of AlCl₃, with higher-order Al ions dominating at lower AlCl₃ concentrations (indeed, it is this behaviour that lends this class of ionic liquids the name eutectic-based ionic liquids). Although Al ionic liquids are sensitive to moisture, and this limits their uptake outside the laboratory, they have nevertheless found use in the electroplating of a range of metals and alloys. The formation of these liquids and the speciation as a function of composition have recently been reviewed by Endres *et al.*¹²

The so-called second generation of ionic liquids, rather than being based on eutectic mixtures of complex ions, are entirely composed of discrete ions. Wilkes and Zaworotko suggested that synthesis of stable liquids in the air and moisture can be achieved by replacing the AlCl_3 used in the eutectic ionic liquids with discrete anions such as the tetrafluoroborate and ethanoate moieties.¹⁸ However, it was reported that exposing these more stable ionic liquids to air and moisture can affect their chemical and physical properties, namely via formation of HF with increasing amounts of water from the air.¹⁹ This type of ionic liquids have been optimised in this sense by using more hydrophobic anions, for example with moieties such as trifluoromethanesulphonate, $(\text{CF}_3\text{SO}_3^-)$, bis-(trifluoromethanesulphonyl) imide, $[\text{CF}_3\text{SO}_2]_2\text{N}^-$, and tris-(trifluoromethanesulphonyl) methide, $[(\text{CF}_3\text{SO}_2)\text{C}]^-$.¹⁹⁻²¹ Such classes of liquids have a wide range of potential uses in the deposition of metals that cannot themselves be reduced from the chloroaluminate liquids.¹⁹

Consequently, ionic liquids can be divided into distinct classes, the first of which depends on eutectic systems, which are prepared by mixing metal halides for example, AlCl_3 with organic salts that are normally nitrogen based and predominantly capped with halide anions. The second class of ionic liquid are those that contain discrete anions such as bis-(trifluoromethanesulphonyl) imide or PF_6^- . Each of these generations of ionic liquids have different applications due to their wide range of tuneable properties.²² **Figure 1.1** shows some of the most widely used ions in the synthesis of ionic liquids.

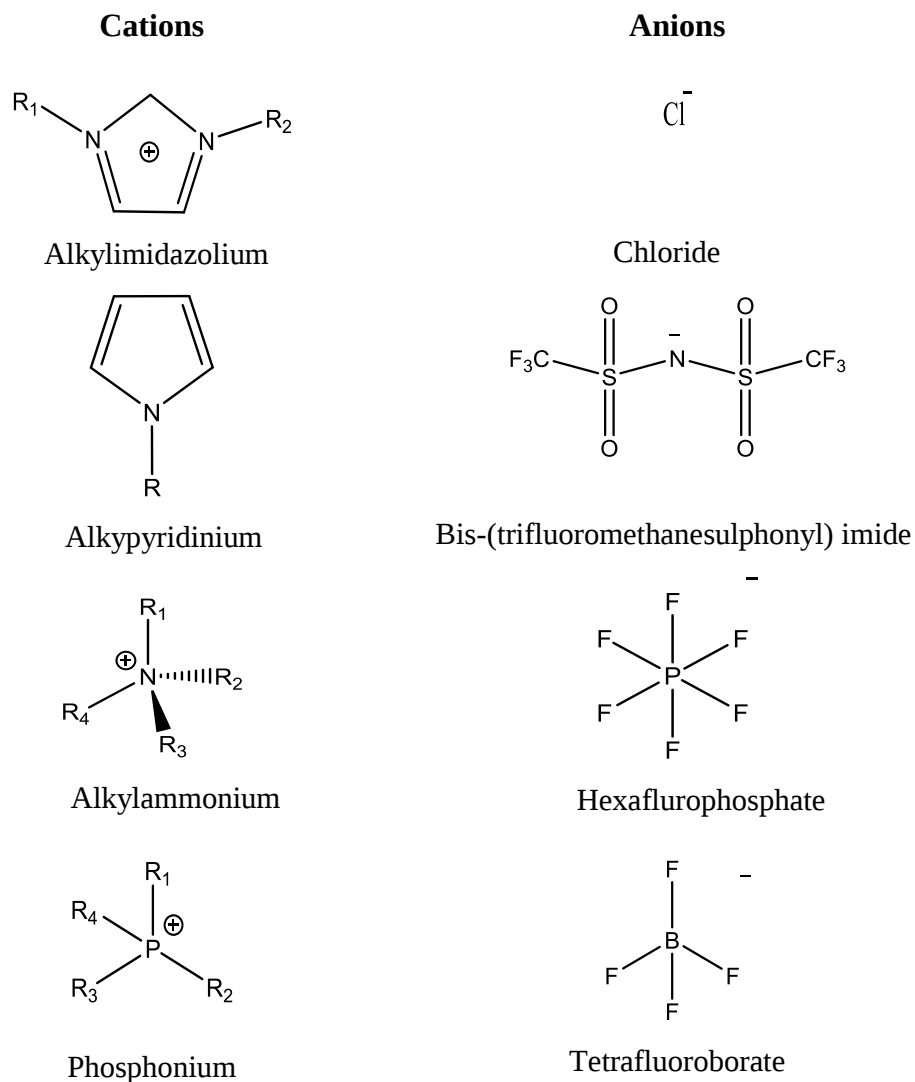


Figure 1.1 A selection of compounds commonly used in the synthesis of ionic liquids.

It has been estimated that the huge number ionic liquids could potentially be in the region of 10^6 distinct systems. General speaking, ionic liquids confer considerable advantages in the electroplating of metals, having a wide potential window which allows for the deposition of metals that cannot otherwise be deposited in aqueous solution, such as Al, as well as the current efficiencies of metals deposited from ionic liquids being higher than those deposited from aqueous solutions.^{12, 23, 24} However, ionic liquids must be simple and economic to synthesise in order to be successful as commercially viable alternatives to aqueous electrolytes.

1.2.1 Synthesis of ionic liquids

Generally, ionic liquids can be prepared by either a metathesis reaction between halide and ammonium salts of the desired anion or via acid-base neutralisation reactions.¹⁶ Synthesis of the majority of ionic liquids is relatively simple. The first step in ionic liquid synthesis is the quaternisation reaction of an imidazole or amine with an alkyl halide to form an imidazolium or ammonium salt.^{14, 16} A large number of ionic liquids can be prepared directly via quaternisation reactions, for example the quaternisation reaction between methyl triflate and 1-ethyl-3-methylimidazole to form [EMIM(CF₃SO₂)], which has a melting point of -9°C.²⁰ However, it is not always possible to directly synthesise the desired anion by such a process, and a further step is often needed. This second stage in the preparation of ionic liquids is generally a solid phase synthesis, which is achieved by mixing a metal halide with the quaternary salt. **Figure 1.2** shows the two possible routes to the synthesis of ionic liquids.

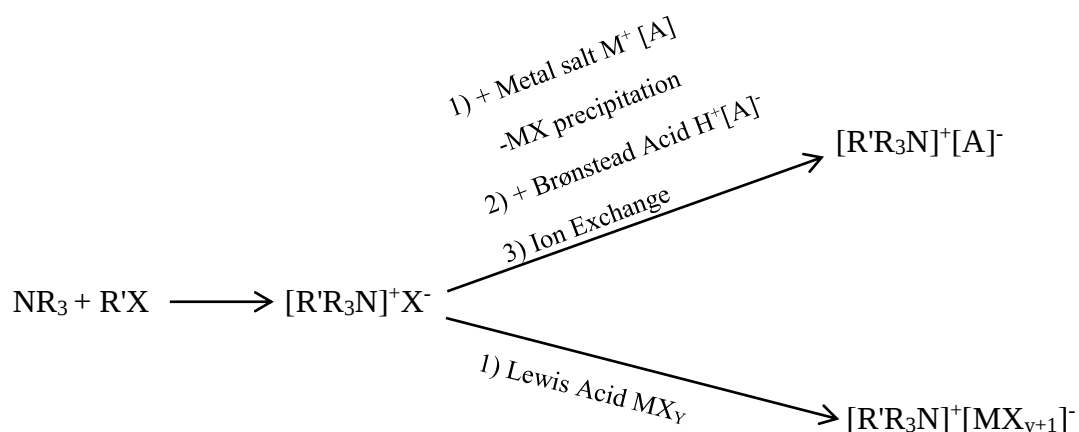
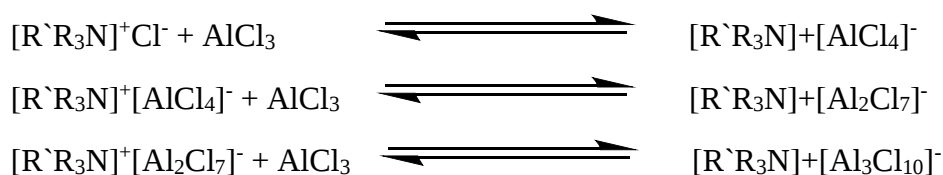


Figure 1.2 Generalised synthetic pathways to the formation of ionic liquids.

Eutectic-based liquids can be synthesised by directly reacting an ammonium halide, $[\text{R}'\text{R}_3\text{N}]^+\text{X}^-$, with a Lewis acid, MX_y , leading to the formation of an ionic liquid, $[\text{R}'\text{R}_3\text{N}]^+[\text{MX}_{y+1}]^-$.²⁵ In this stage, all anionic species are observed in equilibrium, with the ratio of species present being dependent on the ratio of the ammonium halide and Lewis acid.

Chloroaluminate melts could be considered a good example of the effects of changing the ratios of the components of ionic liquids on the species subsequently found to be present. Therefore, changing the ratio of chloride to AlCl_3 in this example will modify the resultant anionic species present. For instance, when the mixture ratio is 1:1 $[\text{EMIM}]\text{Cl}:\text{AlCl}_3$, the predominant anionic species observed is $[\text{AlCl}_4]^-$. However, when the molar fraction of AlCl_3 is at $X(\text{AlCl}_3) > 0.5$, the chloroaluminate anions become multi-nuclear. The various species that can be formed can be seen in the equations below.²⁵



Some ionic liquids need to be synthesised under inert gas, such as 1-ethyl-3-methylimidazolium chloride/ AlCl_3 and 1-butyl-3-methylimidazolium/ AlCl_3 ionic liquids, because AlCl_3 undergoes rapid hydrolysis in air. Chloroaluminates are the most widely known ionic liquids to be synthesised using Lewis acids; it has been reported that ionic liquids can contain SnCl_2 , CuCl_2 , BCl_3 , etc., as the Lewis acid.²⁵

Furthermore, the anion can be modified through the addition of a metal salt, $\text{M}^+[\text{A}]^-$, or by displacing it with a strong acid, $\text{H}^+[\text{A}]^-$. However, this method can result in the presence of impurities from residual halide species. These halide ions could subsequently react with solute materials, and it is therefore necessary to remove them. Unlike conventional solvents, purification cannot be achieved in this instance through distillation, requiring the use of an anion exchange resin.

The nature of ionic liquids is one of non-volatility, a feature which makes them attractive as alternatives to organic solvents, most of which are highly volatile. However, this also means it is not easily to purify ionic liquids by standard methods such as distillation. It is therefore necessary that the materials used in the preparation of chloroaluminate ionic liquid are pure, and the synthesis should proceed under an inert atmosphere (air- and moisture-free) at low temperature.²³

1.2.2 Electrodeposition from ionic liquids

Electroplating has become a popular method of producing various materials, because of its simplicity, cost-efficiency, low energy consumption, and amenability to objects with complex shapes. As mentioned previously, electrodeposition is carried out in aqueous electrolytes because their high conductivities, high solubility to metal salts, good throwing power and low costs are all commercially attractive properties. However, the associated narrow potential window limits the use of aqueous electrolytes, particularly for metals that reduce at highly negative potentials. Moreover, high hydrogen evolution, produced in aqueous solution during the process of metal deposition, leads to a reduction in the current efficiency of the coating. In aqueous solutions, hazardous materials must often be used, such as chromic acid in the electrodeposition of Cr and cyanide in the electrodeposition of Ag and Cu-Zn alloys, as well as strong acids, such as sulphuric acid, which when used in aqueous solution represent extreme environmental hazards.

Ionic liquids have solved various issues relating to the electrodeposition of metals from aqueous solution. For the last two decades, ILs have been extensively used in the fields of catalysis, separation, material chemistry, electrochemistry, analytical chemistry, biomass treatment, and so forth.²⁶⁻³³ Because they have many attractive properties, they were used in electrodeposition of metals because: 1) they have wide electrochemical windows (EW), such that one is able to deposit metals with highly negative potentials before decomposition of the liquid; 2) they allow for high-temperature deposition of certain materials to be achieved due to ILs having low vapor pressures and good thermal stability; and 3) they have tunable physicochemical properties, which can be adjusted through the strategic choice or appropriate modification of the constituent cations and anions, thus making the control of redox potentials and, therefore, the deposition of novel alloys, entirely possible. Thus, ILs are widely used in the electrodeposition of various types of metals. A number of books and reviews^{5, 12, 22, 33-36} have been published regarding electrodeposition of metals and their alloys from ILs.

The first metal deposited from an ionic liquid was Al, which was achieved due to the attractive properties of ionic liquids mentioned above, the demonstration of which has led to their widespread use in the electrodeposition of many ‘problem’ metals. The scope of this research effort is illustrated in **Table 1.1**.

Table 1.1 List of metals commonly deposited from ionic liquids.

Ionic liquid	Metals
Chloroaluminate	Al, ³⁷ Fe, ³⁸ Co, ³⁹ Cr, ⁴⁰ Ni, ³⁹ Cu, ⁴¹ Zn, ⁴² Pd, ⁴³ Ga, ⁴⁴ Au, ⁴⁵ Ag, ⁴⁶ Tl, ⁴⁷ In, ⁴⁸ Sn, ⁴⁹ Sb, ⁵⁰ Te, ⁴⁷ Hg, ⁵¹ Li, ⁵² Na, ⁵³ Pb, ⁵⁴ Bi ⁵⁵
Chlorozincate	Zn, ¹⁵ Sn, ⁵⁶ Cd ⁵⁷
Discrete Anions	Cd, ⁵⁸ Co, ⁵⁹ Cu, ^{60, 61} Pd, ⁶² Sb, ⁶³ Au, ⁶⁴ Ag, ^{65, 66} Ge, ⁶⁷⁻⁶⁹ Li, ⁷⁰ Al, ⁷¹ Mg, ⁷² Si, ^{73, 74} Ta, ⁷⁵ Eu, ⁷⁶ La, ⁷⁶ Ga ⁷⁷ Sm, ⁷⁶ Cs, ⁷⁸
Deep Eutectic Solvents	Ni, ^{79, 80} Cu, ⁸¹ Zn, ⁸²⁻⁸⁵ Cr, ⁸⁶ Ag, ⁸⁷ Sn ⁸²

This thesis deals with the electrodeposition of Cu, Zn, Zn/Ni and Al from DESs. These have been studied by several groups and a more in-depth review of the topic is contained in the recent book edited by Endres *et al.*¹² Although there are several publications in this field, most are limited to simple deposition studies. Physical and mechanical properties (such as brightness, roughness and thickness) of the metal coatings still need to be improved, the approach to which is through empirical studies as to the effects of different types of additives on the electrodeposition of metals from ionic liquids.

Commonly, electrodeposition studies were achieved using first generation ionic liquids because this class has wide potential windows, good conductivity and represent excellent solvents for dissolution of various metal salts. However, their sensitivity to air and moisture, due to the nature of AlCl₃, has limited their commercial application. Unfortunately, chloroaluminates are also unsuitable for the electrodeposition of pure reactive metals, such as Si, Ta and Li, as the relatively ‘noble’ nature of Al means they can only be obtained as Al co-deposits.

Thus, the second generation of ionic liquids were preferred in commercial use due to their stability in air and moisture, low vapour pressures and large electrochemical windows. However, there are still a number of problems associated with the use of this class of ionic liquids, one of which is that of impurities. The impurities can be halide ions and water, which make reproducibility problematic. Recently, a new type of ionic liquid, deep eutectic solvents, has been developed, and a number of metals have already

been electrodeposited from this class. Appropriate publications regarding the deposition of metals from deep eutectic solvents are also listed in **Table 1.1**.

1.3 Deep eutectic solvents (DESs)

In 2003, Abbott *et al.*⁸⁸ synthesised a new type of ionic liquid that are now known as deep eutectic solvents (DESs), and are named thus to distinguish them from ionic liquids, which contain only discrete anions. They are usually prepared by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD), mixing two types of solid compounds that have high melting points. This leads to the production of a liquid with a lower melting point than its individual compounds, a DES. The first type of DES was prepared by mixing choline chloride (ChCl) with urea in a 1:2 ratio, respectively. The melting point of ChCl is about 302 °C, whilst the melting point of urea is 133 °C; however, the mix of the two in this ratio can remain a liquid at temperatures of less than 12 °C due to the interaction between the halide anion and the hydrogen bond donor (HBD). Thus, the melting point of such mixtures (DESs) are highly dependent on the ratio of the constituent species. DESs contain large, non-symmetric ions that have low lattice energies and hence have low melting points. The charge delocalisation across their hydrogen bonding networks (between, for example, halide ions and hydrogen-donor moieties) is the cause of the extreme decreases in the melting points of these mixtures in comparison to the melting points of the individual components.⁸⁸ In 2001, Abbott *et al.* studied the reaction between a range of quaternary ammonium salts with ZnCl₂, and further measured the freezing points of the resultant liquids. They found that when choline chloride was used as the ammonium salt, extremely low melting points, of the range 23-25 °C, could be obtained.⁸⁸ The authors then extended this study, synthesising a range of liquids from eutectic mixtures of salts and hydrogen-bond donors.

The general formula $\text{Cat}^+\text{X}^-\text{zY}$ can be used to describe deep eutectic solvents in a stoichiometric sense, where Cat^+ is, in principle, any ammonium, phosphonium, or sulfonium cation, X is a Lewis base, generally a halide anion, and Y is a Brønsted acid, which is a metal salt or hydrogen bond donor (HBD), whilst z refers to the number of Y molecules interacting with the anion. The reaction between X^- with either a Lewis or Brønsted acid, Y, leads to the formation of the complex anionic species. Choline chloride, $[\text{ChCl}, \text{HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3\text{Cl}^-]$, however, is a more practical cation to use than quaternary ammonium and imidazolium cations. DESs have been divided into four

subtypes, depending on the nature of the complexing agent used. This is summarised in **Table 1.2**.

Table 1.2 General Formula for the classification of DESs

Type	General Formula	Terms
Type I	$\text{Cat}^+ \text{X}^- z\text{MCl}_x$	$\text{M} = \text{Zn},^{15, 89, 90} \text{Sn},^{91} \text{Fe}, \text{Al},^{92} \text{Ga},^{93} \text{In}^{94}$
Type I	$\text{Cat}^+ \text{X}^- z\text{MCl}_x \cdot y\text{H}_2\text{O}$	$\text{M} = \text{Cr},^{95} \text{Co}, \text{Cu}, \text{Ni}, \text{Fe}$
Type III	$\text{Cat}^+ \text{X}^- z\text{RZ}$	$\text{Z} = \text{CONH}_2,^{88} \text{COOH},^{96} \text{OH}^{97}$
Type IV	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+ \cdot \text{RZ} + \text{MCl}_{x+1}^-$	$\text{M} = \text{Al}, \text{Zn}$ and $\text{Z} = \text{CONH}_2, \text{OH}$

1.3.1 Properties of deep eutectic solvents

Conventional ionic liquids and deep eutectic solvents have different chemical properties. However, they have similar physical properties, in particular the potential for use as tunable solvents that can be customised to a particular type of chemistry; they also have low vapour pressures, relatively wide potential windows, and are non-flammable. DESs have excellent properties compared to conventional ILs, such as low cost, lower toxicity, lower sensitivity to water than transitional ILs and increased ease of preparation.⁹⁸ DESs can be produced through the straightforward combination of two compounds with moderate heating. This means DES production incurs low overheads compared to conventional ionic liquids, permitting large-scale application. In terms of toxicity, DESs are also preferable to conventional ILs; the individual components of DESs tend to be well characterised in a toxicological sense. That said, there is very little information available as to the toxicology of the eutectic solvents themselves. It is clear that this area of DESs is in need of further investigation by the scientific community.

1.3.1.1 Phase behaviour

It has been reported that the melting point of DESs are based on the reaction between their individual components.^{88, 96, 98} At the eutectic composition of a binary mixture, A + B, the change in freezing point corresponds to the degree of interaction between A and B. Therefore, the maximum interaction between the individual components of DESs causes an increase in ΔT_f , as shown in **Figure 1.3**.

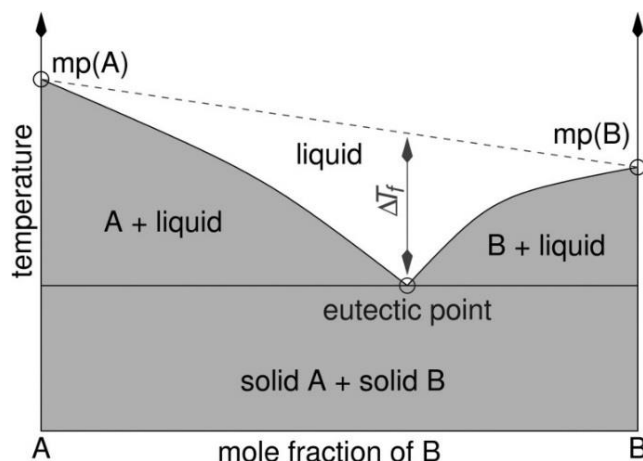


Figure 1.3 Schematic representation of a eutectic point on a two-component phase diagram.⁹⁸

In type I DESs, the interactions between different metal halides and the halide anion from the quaternary ammonium salt can form a similar halometallate species with similar enthalpies of formation, and one might suggest that values for ΔT_f should be between 200 and 300°C. It has been observed that metal halides must have melting points of approximately 300°C or less to form a eutectic at around ambient temperature. Hence, metal halides such as AlCl_3 (mp = 193°C),⁹⁹ ZnCl_2 (290°C),¹⁰⁰ FeCl_3 (308°C),¹⁰¹ InCl_3 (586°C),¹⁰² SnCl_2 (247°C),¹⁰⁰ CuCl (423°C),¹⁰³ and GaCl_3 (78°C)¹⁰⁴ can form ambient temperature eutectics. Metal salts such as SbCl_3 (mp = 73°C), BeCl_2 (415°C), BiCl_3 (315°C), PbBr_2 (371°C), HgCl_2 (277°C), and TeCl_2 have remained unstudied to date, but it is anticipated that they should also produce ambient temperature eutectics. Quaternary ammonium salts also show similar properties; less symmetrical cations generally show lower melting points, and can therefore be used to produce lower melting point eutectics. Hence, imidazolium halides, C_2mimCl (mp = 87°C) and C_4mimCl (65°C), show superior phase behaviour and mass transport properties in comparison to ChCl (301°C).

After numerous attempts, a new subtype of DESs were developed, type II DESs, using metal halide hydrates. It was found that metal halide hydrates have low compared to their anhydrous salts. The waters of hydration can decrease the melting point of metal salts as their presence can decrease the lattice energy; as can be seen in **Figure 1.3**, a small depression in freezing point, ΔT_f , can be produced when the pure metal salt is used. This correlation between the freezing temperature and the depression of freezing

point for metal salts and amides can be seen in **Figure 1.4**. Data for Figure 1.4 is reported in the literature (see **Table 1.3**).⁹⁸

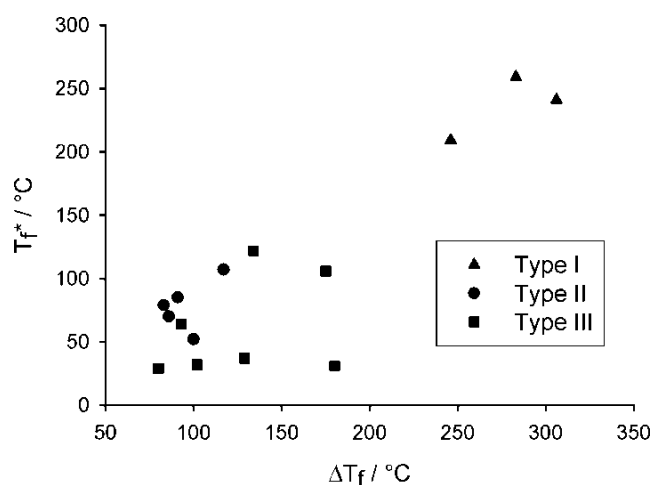


Figure 1.4 Correlation between freezing temperature and depression of freezing point for metal salts and amides when mixed with choline chloride in a 2:1 ratio, where the individual points represent different mixtures.⁹⁸

Similar phase diagrams to that shown in **Figure 1.3** have been found for most of the systems that have been studied in the literature. Two eutectic points have been found in a small number of systems containing AlCl_3 , FeCl_3 , and SnCl_2 when mixed with imidazolium chlorides at approximately 33% to 66% metal halide.

The formation of hydrogen bonds between the halide anion of the salt and the HBD play a significant role in type III DESs; where these HBDs are multifunctional, the eutectic point tends to be found around a 1:1 molar ratio of salt and HBD.^{96, 98} In these same studies, it was found that the depression in freezing point was related to the mass fraction of HBD in the mixture.

1.3.1.2 Density, viscosity and conductivity

The densities of the different types of DESs have been measured using the method suggested by Mjalli *et al.*¹⁰⁵ Average relative percentage errors (ARPE) for density values of DESs are about 1.9%. The effects of the salt:HBD molar ratio on ARPE in terms of predicted DES densities have also been investigated. The formation of DESs through reacting phosphonium-based salts with different hydrogen-bond donors was further demonstrated by this same research group.¹⁰⁶ Melting temperature, density, viscosity, pH, conductivity, and dissolved oxygen content were all measured as functions of temperature. The author also found that the molar ratio of salt:HBD and the

types of these components can significantly affect DESs in terms of such physical properties as density, viscosity, conductivity, and surface tension.

Physical properties of different types of DESs, ionic liquids with discrete anions and a number of molecular solvents at 298 K are reported in **Table 1.3**.

Table 1.3 Physical properties of various types of DES at 298 K.

salt (mol equiv.)	HBD (mol equiv.)	Viscosity / cP	Conductivity / mS cm ⁻¹	Density / g cm ⁻³
ChCl (1)	urea	632	0.75	1.24
ChCl (1)	ethylene glycol	36	7.61	1.12
ChCl (1)	glycerol	376	1.05	1.18
ChCl (1)	malonic acid	721	0.55	1.33
C ₄ mimCl	AlCl ₃	19	9.2	1.14
ChCl (1)	CrCl ₃ ·6H ₂ O	2346	0.37	1.43

From the values in **Table 1.3**, it can be seen that DESs have high viscosities and low conductivities compared to ionic liquids and molecular solvents. This is due to the size of the ions being large and free volumes being small.

It was reported that there is a good correlation between the molar conductivity, Λ , and the viscosity, η , of ionic liquids.^{98, 107} The same observation has been made for DESs. This is attributed to the validity of the Walden rule, which states that $\Lambda\eta = \text{constant}$ for a given electrolyte at infinite dilution in a range of solvents. As a consequence of hole theory, Abbott and co-workers were able to show that charge transport is limited by the holes (which are at infinite dilution), rather than being due to ions.⁹⁸ It was shown that the Nernst-Einstein equation is valid within the bounds of this model. The refractive indices of choline chloride-based liquids with the hydrogen-bond donors glycerol, ethylene glycol, and 1,4-butanediol were measured and compared to predicted values using an atomic contribution method. It was concluded that the refractive indexes of these liquids can be predicted using the method chosen, and it was found that these values lay between the extremes represented by the refractive indices of the salt and the HBD.^{98, 108} The interesting thing here was that the electrical conductivity of DESs was found to be temperature dependent.¹⁰⁹

1.3.1.3 Hole theory

The greatest differences between DESs and aqueous electrolytes are those of viscosity and conductivity. In some cases, the use of DESs becomes limited due to their high viscosity and low conductivity compared to aqueous electrolytes. A few studies have attempted to understand the properties of traditional ionic liquids and deep eutectic solvents. However, given that liquid and free volumes both increase as a consequence of melting, a number of models have been used in the attempt to describe the motion of ions in high temperature ionic liquids (molten salts). Hole Theory has been used in an attempt to rationalise the motion of ions in DESs. In the melt state, Hole Theory supposes that an ionic material contains empty spaces that arise from thermally generated fluctuations in local density.¹¹⁰⁻¹¹³ These holes are of random size and location, and are in constant flux. The radius of the average-sized void, r , is related to the surface tension of the liquid, γ , by **Equation 1.1**:

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

where k is the Boltzmann constant and T the absolute temperature.

In molten salts, the average hole size is of similar dimensions to that of the corresponding ion, therefore it is relatively easy for a small ion to move into a vacant site, which means that the liquid viscosity is consequently low. At low temperatures, the viscosity of a liquid will be higher due to small hole sizes compared to a larger ion size such that ion movement is more restricted, leading to an increase in viscosity and decrease in conductivity.

1.3.2 Electrodeposition from deep eutectic solvents

Recently, the use of metal electrodeposition has increased due to its utility in numerous fields of industrial application such as aerospace, sensors, optics, automotive and electronics. As mentioned earlier, electrodeposition of metals was previously undertaken in aqueous solution. However, the disadvantages of aqueous solutions limited the deposition of metals. DESs are used, as a form of ionic liquid, in the electrodeposition of metals to solve the various problems associated with electrodeposition from aqueous and non-aqueous solutions. Generally, the electrolyte used in electroplating should show high solubility to metal salts, high conductivity, low cost, good throwing power, non-flammability, low ohmic loss, high rates of mass transport, and high electrochemical stability. Aqueous electrolytes suffered in particular

from issues such as their electrochemical stability, limited potential windows (resulting in gas evolution leading to hydrogen embrittlement), and passivation of substrates, electrodes, and deposits. The main advantage of DESs over aqueous and organic solvents is their high solubility to metal salts, metal oxides and hydroxides. One of the major problems in the formation of the passivation layer in aqueous solution is that these layers are normally formed from non-soluble oxides and/or hydroxides that appear on the electrode surface, inhibiting metal deposition and leading to the production of a thin-film metal coating. Passivation layer effects are not generally observed in the deposition of metals from DESs because DESs show high solubility to metal oxides and hydroxides, which can allow for the production of a thicker layer than could otherwise be achieved in aqueous solution. In aqueous solution, hazardous complexing agents such as cyanide compounds must often be used; these compounds are, of course, very toxic and not particularly economical to deal with. Water is not inherently a green solvent; although it is non-toxic, all solutes must be removed before it can be returned to the watercourse.¹¹⁴

Since DESs have excellent properties such as low cost, reduced toxicities, high metal solubility and a reduced sensitivity to water compared to ionic liquids. They can provide suitable media for many of the technological goals of industry.^{5, 98} DESs have been used in the deposition of corrosion-resistant metals such as Al, Ti and W.^{22, 115, 116} Moreover, DES systems are used as replacements to environmentally toxic metal coatings and, further, can be used in the deposition of novel new alloys and semiconductors.

The reduction processes of a range of metals have been investigated in DES systems including Cr,⁹⁵ Ni,⁷⁹ Cu,^{81, 117} Zn,⁸³ Sn,⁸² Ag,¹¹⁸ Co,¹¹⁹ Al¹²⁰ and Sm.¹¹⁹ In aqueous solution, electrodeposition of metals can be achieved under constant current or constant voltage, and current density often significantly affects the morphology and adhesion of the coating. In DESs, the morphology of metal deposits can be effected by varying the composition of the DES and by using additives. Electrodeposition of Cr, Al, Cu, Ni, Co and Zn have been achieved from DESs. In addition to the use of DESs in the electrodeposition of metals, they are also used in various industrial applications such as electropolishing,^{97, 121} metal oxide processing,^{122, 123} purification of materials, drug solubilisation and catalysis.

1.3.2.1 Copper plating

The electrodeposition of copper has increased considerably due to its high electrical conductivity and excellent electrical migration resistance. Recently, aluminium has been replaced by copper as the metal used for interconnects in the electronics industry. Copper is particularly beneficial as a pre-coating for soft-soldered work or for the zinc alloy die-castings used by the automotive industry because it can be easily coated and electroplated with other metals. Therefore, Cu layers can be used as a protective layer to allow additional coatings to be applied at some later point.^{124, 125} Usually, electrodeposition of Cu is achieved from aqueous solutions which show high solubility to metal salts and electrolytes, resulting in highly conducting solutions. Lately, new liquids have been suggested as alternative plating solutions, and these could offer a less environmentally hazardous option. Many types of ionic liquids have been used in the electroplating of Cu, and the study of these systems has been dominated by chloroaluminate ionic liquids in the 1960s and 1970s.^{41, 126, 127} In the 1990s, electrodeposition of Cu became more easily achieved from discrete anion ionic liquids such as $[\text{BF}_4]^-$, and $[\text{F}_3\text{CSO}_2)_2\text{N}]^-$ ($[\text{Tf}_2\text{N}]^-$).^{60, 61} Certain issues have been associated with electrodeposition of Cu from traditional ionic liquids, however, such as toxicity, availability and high cost.

Recently, it has been found that simple eutectic-based ionic liquids can be prepared by mixing quaternary ammonium salts $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ with hydrogen-bond donors such as acids, amides, alcohols, and the deep eutectic solvents (DES) discussed previously. DESs are widely used in various fields such as electrodeposition, electropolishing, polymer synthesis, electroless (immersion) deposition and metal oxide processing due to their excellent properties compared to classical ionic liquids (non-toxic, low cost, ease of preparation).

A few years ago, Popescu *et al.*¹²⁸ studied the electrodeposition of Cu through the dissolution of CuCl_2 in ChCl combined with various hydrogen-bond donors, namely urea, malonic acid, oxalic acid, and ethylene glycol. It was found that fine, homogeneous, and adherent Cu deposits were obtained when the deposition was achieved from ChCl :oxalic acid and ChCl :ethylene glycol-based liquids. The electron transfer kinetics of the $\text{Cu}^+/\text{Cu}^{2+}$ redox couple have been studied by Murtomaki *et al.*¹²⁹ using cyclic voltammetry, and impedance spectroscopy in ChCl :ethylene glycol-based liquids. The author found that the reaction was quasi-reversible, and also suggested that Cu species in the ChCl :ethylene glycol-based liquid are those of $[\text{CuCl}_3]^{2-}$ and $[\text{CuCl}_4]^{2-}$.

The effects of ultrasound at different powers and frequencies on Cu electroplating from CuCl_2 in both ChCl:glycerol-based liquid and aqueous solution were investigated by Pollet *et al.*¹³⁰ Abbott *et al.*⁸¹ studied the electrodeposition of Cu in two DESs, 1:2 ChCl:ethylene glycol and 1:2 ChCl:urea, and found that Cu can be deposited from these liquids with high current efficiency. The researchers concluded that Cu deposition in both solvents was affected by the use of ultrasound, observing a five-fold increase in current in ChCl:glycerol compared to when ‘silent’ conditions, i.e., without ultrasound, were used.

In the electrodeposition of metals from either aqueous solution and/ or traditional ionic liquids, additives were introduced into the plating bath to optimise the physical properties of the coating such as brightness, roughness, thickness and hardness. There are many types of organic and inorganic additives used in ion electrodeposition of metals. For example thiourea,¹³¹⁻¹³⁶ gelatine,^{132, 136} polyacrylamide,^{136, 137} polyethylene glycol,¹³⁸ 3-mercapto-2-propanesulphonic acid,¹³⁹ ethylenediaminetetraacetic acid (EDTA),¹⁴⁰ ethylenediamine,¹⁴⁰ triethanolamine¹⁴⁰; various mixtures of additives are often used as brightening and levelling agents in the electrodeposition of Cu. Even though additives are used in the electrodeposition of Cu from aqueous solution, this kind of system still suffers from the issues previously mentioned. Relatively few studies have been undertaken as to the effects of additives on the mechanism of nucleation of metal electrodeposition from traditional ionic liquids.¹⁴¹⁻¹⁴³ There is nothing in the literature on the effects of additives on the electrodeposition of Cu from DESs. Since DESs have much-improved properties compared to classic ionic liquids and aqueous solutions, it should be very interesting to study the influence of additives of the nucleation mechanism of Cu electrodeposition from DESs.

1.3.2.2 Zinc plating

Zinc is an excellent and widely used surface coating. It is widely used for the protection of steel from corrosion, even if scratched or damaged, due to it having a more negative standard potential (-0.76 V vs. standard hydrogen electrode SHE) than iron (-0.44 V vs. SHE).¹⁴⁴⁻¹⁴⁷ Furthermore, Zn has excellent properties such as being a low cost, non-toxic recyclable, where such properties have led to its widespread use in various industrial fields.^{148, 149} According to the International Zinc Association, more than 5 million tonnes of Zn are used every year to protect steel against corrosion worldwide.¹⁴⁸

Excellent Zn coatings have been produced from aqueous systems. However, ten years ago, DESs were suggested as alternatives to aqueous and traditional ionic liquids.^{149, 150} The electrodeposition of Zn on a copper substrate from ChCl:ethylene glycol and ChCl:urea as DESs was achieved for the first time by Ryder *et al.*¹⁵¹ Zn metal deposited from DESs tends to have a compact microcrystalline structure, whereas in aqueous electrolytes a more dendritic structure is observed in the absence of strong bases within the bath. Usually, in aqueous solution, additives are introduced into the plating bath to improve the physical and mechanical properties of the metals coatings. In 1907, Snowden studied the effects of adding formaldehyde as an organic compound to the aqueous zinc bath.¹⁵² He found that adding small amounts of formaldehyde led to a reduced grain size in the Zn deposits. Several types of organic additives have been used in the electrodeposition of Zn. The purposes of additives can be categorised as: **a)** to improve the properties of the coatings such as the brightness, roughness and stress of the coating; and **b)** to improve the operating performance of the plating bath, such as the current efficiency, anodic depolarisation and throwing power. Organic additives such as aromatic amides, quinone derivatives and polyvinyl alcohol have been used in the electrodeposition of Zn from acid and cyanide baths.¹⁵³

Only a few years ago, the effects of acetonitrile, ethylene diamine and ammonia on the electrodeposition of Zn from 1:2 ChCl:ethylene glycol and 1:2 ChCl:urea as DESs were studied by Abbott *et al.*⁸³ for the first time. They found that bright Zn deposits were obtained when ethylene diamine and ammonia were added to the plating bath.

1.3.2.3 Nickel plating

Ni is important in engineering and has attracted considerable attention due to its high hardness and good corrosion resistance.³³ It is widely used in the fabrication of printed electronic circuitry and also in decorative applications.^{80, 154, 155} Recently, electrodeposition of Ni has been studied in ChCl:ethylene glycol and ChCl:urea-based liquids.⁷⁹ It was found that the deposition thermodynamics and kinetics were different to those in aqueous solution as a result of a difference in the morphologies of the coatings. Brightener additives such as nicotinic acid (na) ethylenediamine (en) and acetylacetonate (acac) were used in the electrodeposition of metals which led to the production of bright deposits. Guo *et al.*¹⁵⁵ studied the effects of nicotinic acid on the electrodeposition of Ni on a Cu substrate from a ChCl:urea mixture as DES. It was

found that nicotinic acid can inhibit the deposition of Ni. The use of nicotinic acid led to the production of a bright, smooth and highly uniform Ni deposition. Recently, our group⁸⁰ have studied the effects of temperature on Ni species in ChCl:ethylene glycol-based liquids where it was found that the colour of the Ni solution was strongly dependent on temperature; the colour of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in DES (ChCl:ethylene glycol) changed from pale green (room temperature), to spring green ($\sim 70^\circ\text{C}$), to blue ($\sim 120^\circ\text{C}$). Gu *et al.*¹⁵⁶ also studied thermochromism of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in ChCl:ethylene glycol and ChCl:urea DESs, where they found that the colour to which Ni solutions changed with increasing temperature corresponded to the change in Ni ion species.

The mechanism by which brighteners function is extremely complex. They can work by either affecting speciation, mass transport or by adsorption at the electrode solution interface. Juma studied methylnicktinoate, nicotininc acid, 5,5-dimethylhandetoin and boric acid and concluded that the additives functioned by adsorption on the electrode surface. This could be through the aromatic ring of the first 3 brighteners or by specific interaction with the functional groups. The work did not conclude which of these was the more likely method of interaction.¹⁵⁷

1.3.2.4 Aluminium plating

In several applications, such as for automobiles, aviation, household appliances, containers and electronic devices, aluminium has been used.¹⁵⁸⁻¹⁶⁰ This due to Al having many excellent properties such as good electrical and thermal conductivities, low density, high ductility, and good corrosion resistance. Al is able to form a thin natural oxide layer on its surface in a wide variety of media,¹⁶¹⁻¹⁶⁶ where it has been reported that the oxide film has high resistance to corrosion.¹⁶⁷⁻¹⁷⁰ The stability of the oxide film on the Al surface makes it difficult to extract from minerals and apply as a surface coating.

Al electrodeposition cannot be achieved in aqueous solution due to the extensive evolution of hydrogen at the electrode before Al can even be deposited; the second reason is the stability of the oxide film on the Al surface. Therefore, electroplating of Al is carried out commercially in organic solvents such as toluene. However, the high flammability and pyrophoric nature of these solvents has limited their use in the electroplating of Al. Therefore, considerable study has been undertaken on the deposition of Al from conventional ionic liquids. These conventional liquids are

normally prepared by mixing organic chloride salts such as 1-ethyl-3-methylimidazolium chloride or 1-butyl-3-methylimidazolium chloride with AlCl_3 . The only Al species found in these liquids is the $[\text{Al}_2\text{Cl}_7]^-$ anion, which is responsible for the deposition itself, but due to the high cost of quaternary ammonium halide salts and the hygroscopic nature of these liquids, their use has been delayed.¹⁹ Recently, Abbott *et al.*¹²⁰ have prepared Al liquids by mixing simple amides with AlCl_3 , where these liquids are considered to be types of deep eutectic solvents. They used acetamide or urea as the hydrogen bond donor and the liquids that were formed were, relatively speaking, less sensitive to water. These liquids contained both anionic and cationic Al species, $[\text{AlCl}_2\cdot\text{urea}]^+$ and $[\text{AlCl}_4]^-$, and the authors found these liquids are suitable media for both Al electrodeposition and the acetylation of ferrocene.^{120, 171} Abbott liquids are about 10 times less costly than conventional ionic liquids due to the fact that simple amides are cheaper and less sensitive to air than the quaternary ammonium salts used to synthesise conventional ionic liquids. However, these types of liquids have low conductivities and high viscosities compared to the imidazolium chloroaluminate systems.

Very recently, Liu *et al.*¹⁷² have investigated the synthesis of several amide- AlCl_3 -based ionic liquids. They have used different structured amides as donor molecules. These molecules were acetamide, *N*-methylacetamide and *N,N*-dimethylacetamide. They found that each amide has a different coordination with the AlCl_3 . It was found that electrodeposition of Al from conventional ionic liquids still needs to be improved; therefore, additives have been suggested for the Al plating bath in order to optimise the electrodeposition of the Al coating. Endres *et al.*³⁸ studied the effect of nicotinic acid on the electrodeposition of Al from an $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ system, where a nanoscale Al deposit was produced with an average particle size of around 14 nm. Subsequently, Ryder *et al.*¹⁴¹ studied the effects of toluene and lithium chloride (LiCl) upon Al electrodeposition from chloroaluminate-based ionic liquids. They found that Al mirror coatings can be produced when 30 wt% toluene is added to the Al plating bath. The addition of LiCl , however caused the production of a dark grey Al deposit. These effects were found to be due to changes in speciation. Recently, Zhang *et al.*¹⁷³ studied the effects of methyl nicotinate, nicotinic acid and 3-methylpyridine on Al electrodeposition from $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$, where they found a uniform, mirror Al deposit was achieved when methyl nicotinate and nicotinic acid were used as additives. However, as has been mentioned previously, traditional Al liquids such as 1-ethyl-3-

methylimidazolium aluminium chloride, [Emim]Cl/AlCl₃, and 1-butyl-3-methylimidazolium aluminium chloride, [Bmim]Cl/AlCl₃, are expensive and more sensitive to air. The electrodepositions of Al from DESs (Al-acetamide and Al-urea eutectic solvents) was achieved by Abbott *et al.*¹²⁰ However, further study is still required. The same group studied the effect of toluene on the electrodeposition of Al from a 1.5:1 AlCl₃:urea eutectic solvent, finding that toluene has little effect upon the morphology of the Al deposit.¹⁷¹ Therefore, it should be very interesting to study the effect of additives on electrodeposition of Al from DESs. In this project, the effects of methyl nicotinate on electrodeposition of Al from acetamide-AlCl₃, *N*-methyleacetamide-AlCl₃ and *N,N*-dimethyleacetamide-AlCl₃-based ionic liquids will be studied for the first time.

1.3.3 Alloy plating

Although much effort has been expended on metal electrodeposition from air- and water-stable ILs, alloy electroplating from ILs has rarely been studied. Deposition of alloys is particularly difficult due to the separation in reduction potentials between the two elements. In aqueous solution, it is hard to co-deposit two elements that have well-separated reduction potentials. The wide potential window that can be achieved with air- and water-stable ILs, however, makes such deposition a viable proposition. There are various different types of alloy that have been produced from ionic liquids such as Cu-Mn,¹⁷⁴ Cu-Li,^{175, 176} Fe-Al,¹⁷⁷ Fe-Si,¹⁷⁸ Cu-Zn¹⁷⁹ and Cu-Zn-Al¹⁷⁹. The properties of electrodeposited metal alloys can be controlled by varying the operating conditions, such as concentration of metals in the solution, current density, deposition potential and temperature. Pd-Ni¹⁸⁰ and Pd-Sn¹⁸¹ alloys coatings were produced from traditional ILs by adjusting the deposition potential and solution composition.

A few studies have examined the electrodeposition of alloys from DESs. Therefore, it would be very interesting to study electrodeposition of alloys from DESs under different conditions. It is possible to deposit a variety of alloy coatings from DESs. For example, Abbott and co-workers have studied the electrodeposition of Zn-Sn alloy on mild steel from choline chloride and ethylene glycol or urea as DESs.⁸² Additionally, DESs have been used in the deposition of Ni-Co,¹⁸² Ni-Zn,¹⁸³ Co-Sm¹¹⁹ and Co-Pt¹⁸⁴ alloys.

1.3.3.1 Zn alloys

Technologically, Zn deposition is relatively simple, but Zn alloy deposition is particularly difficult in aqueous solutions due to the differences in redox potentials of the alloying elements.⁹⁸ Zn and its alloys have been widely used for imparting corrosion resistance to active metal substrates used within aggressive, corrosive environments.¹⁸³ Zn-based alloy deposits from ionic liquids could be used to replace or improve a variety of coatings including the following: a high amount of Zn can be deposited in the Zn-Sn alloy, considerably less hydrogen evolution occurs at the cathode surface in the electrodeposition of Zn-Ni alloys, a relatively high amount of Fe in Zn-Fe alloy can be achieved in DESs compared to aqueous electrolytes, and deposition of Zn-Co alloys with higher amounts of Co can be produced in DESs.¹⁸⁵ In addition, deposition from aqueous systems is currently limited due to the strong acids and alkalis or toxic complexants that are currently used in aqueous electrolytes.

The Zn-Ni alloy coating has attracted considerable attention due to its high corrosion resistance and improved mechanical characteristics when compared with other zinc alloys.¹⁸⁶ Recently, Zn-Ni alloy deposits have been the subjects of intense interest in many applications due to their various advantageous characteristics such as high resistance to corrosion, greater hardness and better wear resistance than pure Zn films.¹⁸⁷⁻¹⁹¹ Moreover, Zn-Ni alloys are used in the automotive and aerospace industries as replacements for Cd and Cd alloy coatings due to the high toxicity of Cd.^{192, 193}

Electrodeposition of Zn-Ni alloys from acid baths have been successfully achieved.^{194, 195} However, poor throwing power is observed in most acid baths. Bright Zn-Ni alloy deposits have been produced from alkaline cyanide baths, but the highly toxic nature of cyanide to both humans and the environment has limited the use of these baths in the electrodeposition of Zn-Ni alloys. Alkaline non-cyanide baths were used in the electrodeposition of the Zn-Ni alloy coating, where a number of complexing agents have been added to the plating bath, such as sodium acetate,^{196, 197} amine,¹⁹⁸ tartrate,¹⁹⁹ ethylenediamine,²⁰⁰ glycinate,^{201, 202} triethanolamine, citrate and urea.²⁰³ However, these baths suffer from relatively low current efficiencies. To solve this problem, DESs have been successfully used in the electrodeposition of Zn-Ni. Recently, bright Zn-Ni alloy coatings have been produced from alkaline baths containing 5,5-dimethylhydantoin (DMH) as the complexing agent, where this was achieved using coumarin (CA) and vanillin (VL) as additives.²⁰³ However, aqueous systems still suffer from the

considerable disadvantages discussed earlier, such as low current efficiency due to high hydrogen evolution, a narrow potential window, and toxicity.

Recent developments in the field of room temperature ionic liquids and/or eutectic-based ionic liquids have directed the attention of researchers toward the development of alternative formulations for metal electrodeposition based on this new class of solvents. Ionic liquids are considered ‘green’ solvents and as being viable alternatives to the toxic baths used to date.²⁰⁴ The key advantages of these types of liquids are the high solubility they show to metal salts, their wide electrochemical potential windows, good conductivities and non-toxicity compared to aqueous solutions.²⁰⁴

A few studies can be found in the literature on the electrodeposition of Zn-Ni alloys from a DES based on a mixture of choline chloride and urea.^{183, 205} Yang *et al.*¹⁸³ have studied the electrodeposition of Zn-Ni alloy coatings from a 1:2 ChCl: urea-based liquid, where it was found that the Zn-Ni electrodeposition was not the anomalous co-deposition normally observed in aqueous electrolytes. Co-deposition of Zn-Ni was produced through the deposition of Zn upon (deposited) Ni, always resulting in a Zn content lower than 50 at.%. The Zn-Ni deposits that were achieved from the ZnCl₂:1-ethyl-3-methylimidazolium chloride ionic liquid were rough and formed from nodules.²⁰⁶ The morphologies of Zn-Ni films obtained from DESs/ILs are not satisfactory and need considerable optimisation.

Adding additives to the plating bath is the method which is usually used to improve the morphology of the coating. Additives can affect the properties of the electrodeposited coatings such as grain size, brightness, thickness, hardness and corrosion resistance.²⁰⁷ There are several studies in the literature which explain the effects of additives on the properties and mechanisms of metal coatings; this subject will be discussed in detail later in this chapter. In the electrodeposition of Zn-Ni alloy from aqueous solutions, boric acid,²⁰⁸ gelatin²⁰⁹, ethylenediaminetetraacetic acid (EDTA),^{210, 211} ammonium chloride (NH₄Cl),²¹⁰ polyvinyl alcohol,²¹² piperonal²¹² a phenolic polyoxyethilenate derivative,¹⁸⁷ *p*-aminobenzoic acid (PABA)²¹¹ and cetyltrimethylammoniumbromide (CTAB) have been used.²¹¹ A very few studies have focused on the influence of additives on the electrodeposits of Zn-Ni from DESs. Very recently, Nuno *et al.*¹⁹² studied the effects of ethylamine and ethylenediamine on the electrodeposition of the morphologies of Zn-Ni coatings from a choline chloride:ethylene glycol eutectic-based ionic liquid at 40°C. Chapter 5 of this thesis will examine the electrodeposition of Zn-Ni alloy from 1:2 choline chloride:ethylene glycol eutectic-based ionic liquid as

influenced by different physical parameters (temperature, current density and metal concentration). Moreover, in the same chapter the influence of boric acid and sodium bromide on the electrodeposition of Zn-Ni alloy from a 1:2 choline chloride:ethylene glycol eutectic-based ionic liquid will be investigated.

1.4 Role of additives on electrodeposition of metals

Considerable effort has been made to optimise the physical and mechanical properties of the electrodeposition of metals; this has been achieved by changing the conditions of the plating bath such as current density, temperature, concentration of metal salts and deposition time. However, the properties of metal deposits still need to be optimised. A wide range of additives have been used in the electroplating of metals to improve the efficiency and properties of the electroplated metals such as brightness, roughness, thickness, hardness and resistance of the coating to corrosion.^{153, 213}

There are different types of additives which can be used in electroplating processes. Normally, the choice of the additive depends on the nature of the metal that is to be deposited, as well as the temperature and pH of the electrolyte.²¹⁴

In aqueous solutions, the additives generally act as complexing agents, which can be reacted with the metal ions in solution and make them more difficult to reduce, or they can adsorb on electrode surfaces, blocking nucleation sites and hindering growth. The additives that have been used in the electrodeposition of metals are classified in **Table**

1.4

Table 1.4 Classification of additives used in the electrodeposition of metals.²¹⁵

properties	Classification
Chemical nature	Organic compounds Inorganic compounds
Interfacial activity	Surfactants: a) Anionic b) Cationic c) Non-ionic Tensioinactive substances
Dimensions of particles	Molecular solutions Colloids
Mechanism of adsorption on the cathode. ²¹⁵	Rapid adsorption-desorption Class I Brighteners (Carriers, Control agents) Specific adsorption Class II Brighteners (Levellers, Polarizers)
Effect on the deposit	Levelling agents Brightening agents

1.4.1 Effects of additives on cathodic deposits

1.4.1.1 Grain refinement of the deposit

In order to achieve a bright and smooth coating, it is necessary to refine the grain size of the metal deposited. In terms of crystal size, the deposit is found to be relatively refined in all cases of levelling and brightening. There are two factors that can affect the grain size of a metal deposition. The first is current density, where high current densities can lead to a high degree of supersaturation of the surface by adatoms. The second is impurities or additives, where the impurities/additives can adsorb on the electrode surface and inhibit surface diffusion of adatoms towards growth, or can otherwise create disorder through the incorporation of adatoms into the lattice. The additives can be strong complexing compounds that can be reacted with the metal ions in solution, which can lead to a reduction in grain growth of the deposited metals. These factors can occur simultaneously or separately. For example, Na-ligninsulphonate has been used to refine grain quality in the electrodeposition of Pb from aqueous solution, supposedly because it inhibits the growth of individual crystals, thus increasing the rate of nucleation of lead from the lead crystallites. However, it was found that the presence

of ligninsulphonate alone is not enough to refine the grain size of the metal deposition or to produce a coating with high levelling. Therefore, another agent, such as animal glue or flavonoid compounds, should be present in the plating bath.^{213, 216, 217}

1.4.1.2 The polarization of the cathode

Numerous additives increase the polarization of the cathode when they were used in the electrodeposition of metals. The additives reduce the current density obtained at a given electrode potential. Roth and Leidheiser²¹⁸ measured cathodic polarization in nickel plating baths in the presence of various additives. Moreover, Watson and Edwards²¹⁹ have studied cathodic polarization in nickel plating baths in the presence of coumarin, thiourea and saccharin. They found that coumarin and thiourea increased cathodic polarization compared to a system without additives, but found that saccharin had little effect.

It was observed that the increase in cathode polarization can help refine grain size in Pb deposition.^{216, 217} It was also observed that cathode polarization can decrease with increasing temperature, stirring rate and concentration of lead in the electrolyte. The limiting currents are sensitive to stirring rate, if the reaction is controlled by the diffusion of the additive.^{213, 220} The change of electrode polarization in the presence of additives can be used in the determination of the concentration of additives in electroplating baths where the rotating disc electrode technique has been used to measure polyethyleneglycol (PEG) and polypropyleneglycol (PPG) concentrations in acid copper plating baths.²¹³ It can also be used to measure the difference in voltage between the copper-plated cathode and a reference electrode when a constant electric current is passed through the plating cell. Different concentrations of PEG were used, and the equilibrium cathode potential measured. This value was plotted against the known amount of additive so as to provide a standard curve for determining unknown amounts of the same additive. The electrosorption of additives at the electrode surface causes changes in the cathode potential, increasing the effective current density and thus increasing the overvoltage as a result of surface coverage of the electrode with molecules of the additive.²²¹

Weiner and Klein^{213, 222} reported that there are some additives that can decrease cathodic polarization in cyanide plating baths. Thiourea was used as a brightening agent in a Wattstype nickel plating bath, where it was reported that the thiourea decreased

cathode polarization when a concentration of less than 0.001 M was used in the plating bath.²¹⁹ Sometimes, when more than one type of additive is added to the plating bath, if one of these additives acts as a polarizing agent and the other as a depolarizing agent, the cathodic potential will be unaffected.^{213, 223}

1.4.1.3 Incorporation of additives in the deposit

During the electrodeposition of a metal, the additives can be consumed; therefore, the concentration of additives in the plating bath must be maintained during the process. The consumption of additives is achieved through their incorporation in the deposit (co-deposition).²¹³

There are several techniques that can be used in the determination of the rate of additive consumption during the deposition process. These are methods such as mass spectrometry and use of radiotracers, which are considered direct methods, while indirect methods are those such as determination of the bulk concentration and determination of deposit resistivity. The radiotracer is considered a highly successful technique in the determination of the rate of additive consumption, and is often employed when the brightening or levelling agent is a compound of known structure where one of its constituent atoms has a radioactive isotope with which it can be replaced. Bedcom and Riley^{213, 224} have used this method to show that sodium allylsulphonate, when presented as a levelling agent in a nickel plating bath, is preferentially deposited at the high points of a rough surface. Sodium allylsulphonate was added to the plating electrolyte in the form of a radioactive material containing the ³⁵S radioactive isotope.

As mentioned previously, the radiotracer (levelling agent) can be adsorbed on the active sites or high points of an electrode surface; at these high points, the thickness of the diffusion layer is less than that in the recesses, thus organic molecules will be transported faster. Consequently, adsorption of organic molecules in the recesses will be much lower. Therefore, the metals tend to deposit in the recesses of the electrode surface.^{153, 213, 225} Rogers *et al.*²²⁶ arrived at this same conclusion in their studies of the addition of thiourea to a nickel plating bath. They also reported that thiourea can not only be adsorbed at high peaks on the electrode but that the incorporation of thiourea depends on the stirring rate and current density. It was shown that the diffusion

of thiourea through the boundary layer at the metal-solution interface had a strong influence on brightening and incorporation.

There are several theories about the incorporation of additives during the electrodeposition of metals. Some researchers have demonstrated that certain additives can be co-deposited with the metal in an unchanged or unreduced form,²¹⁹ while other investigators have confirmed that additives have been reduced on the cathode.²²⁷ If the reduction products are less adsorbable, it will be easier for them to return to the bulk solution, which could in part explain why a significant difference between additive consumption and incorporation rates has been observed in some instances. In some cases, however, reduction or dimerization products of additives are responsible for levelling the cathodic deposit. Loshkarev *et al.*²²⁸ reported the reduction of cotarnine as a brightening agent affecting the levelling in Zn deposition.

As mentioned, mass spectrometry can be used to study the co-deposition of additives during metal electrodeposition. The concentration of organic matter in the deposit is compared to a reference concentration obtained for a clean electrodeposit. The behaviour of *p*-toluenesulphonamide and coumarin as additives in the electrodeposition of Pt on Ir and W from sulphate-dinitroplatinous acid were investigated using mass spectrometry.^{229, 230}

1.4.1.4 The change of orientation of crystals in the deposit

In the coating, the orientation of the metal crystals varies according to several factors such as plating conditions and bath composition. Additives can also change the orientation of crystals; in the presence of additives, the crystals may adopt a preferred orientation that can be investigated using X-ray diffraction. The change in the crystals' orientation corresponds to the difference in the rates of growth, which can lead to the formation of different crystal faces. This difference in growth rate is increased by preferential adsorption of additives molecules.²³¹

If there is a relationship between crystal orientation and coating brightness, it has not yet been found. However, a number of investigators have reported that the nickel deposit fibre axis corresponds to the structural type observed (for example platelet, equiaxed crystallite, or spiral-type) and the additive agents in the plating bath.²³² It has been suggested that the brightness depends on the plane of the crystals forming the metal deposit. The principle of the brightness of a metal coating is that it not only

corresponds to a small grain size in the metal deposit, but also that the orientation of the crystals plays a significant role. Non-bright metals deposits have been obtained even though they have very small grain sizes, due to the type of growth resulting in crystals which have no light-reflecting plane parallel to the surface. Consequently, some organic additives can be adsorbed on the electrode surface that allow the metal crystals to grow in the same face, for example using thiourea as an additive in the electrodeposition of Cu from an acid plating bath.²³³ The interference operates on the growth of crystals on the (111) and (100) faces of the single crystals, limiting their growth.

A strong preference for the (101) plane was seen in the electrodeposition of zinc from acidic baths in the presence of animal glue,²³⁴ where the type of orientation was attributed to the additive preferentially increasing the overpotential along particular crystalline faces; this has the effect of increasing nucleation rate and reducing the size of the resultant zinc grains.

1.4.2 Mechanisms of levelling and brightening

1.4.2.1 Levelling

Smooth coatings can be obtained by adding suitable agents to the plating bath. For example, using polyvinyl alcohol as a levelling agent in the electrodeposition of Zn and butyne-diol added to the Ni baths. The theory of “diffusional” levelling has been explained by Kardos,²²³ where the organic additive can be adsorbed on the electrode surface, or “blocking surface”. Thus, the deposition of metal cannot take place on sites occupied by organic molecules. The levelling molecules will be adsorbed on the active sites or on the high points of the electrode surface, whereas at these high points the thickness of the diffusion layer is less than that in the recesses; thus, organic molecules will be transported faster. Consequently, adsorption of organic molecules in the recesses will be much lower. Therefore, the metals tend to deposit in the recesses of the electrode surface, as shown in **Figure 1.5**. A typical microprofile is of such dimensions that the electrode potential does not vary over the microprofile, but the thickness of the diffusion layer will allow for such variation.

For example, a typical groove depth of 60 pm and enclosed angle of 90° would satisfy these criteria. Another criterion which should be satisfied is that the metal ions that need to be deposited should not depend on diffusion control.

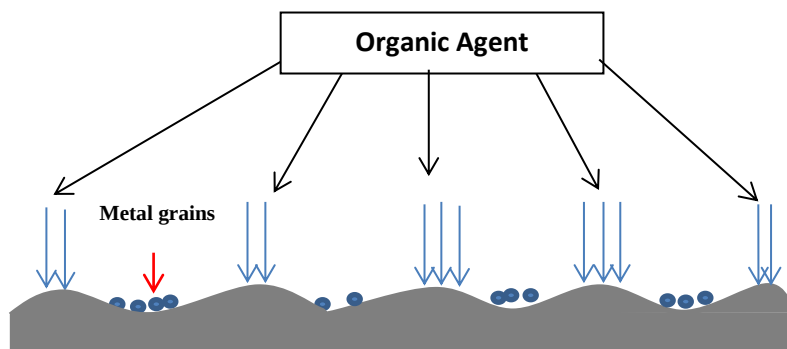


Figure 1.5 Adsorption of organic agent on the high points of the surface of an electrode.

Leidheiser²³⁵ reported that the beneficial effects of agitation on the levelling action no doubt provided the groundwork for the formulation of this theory. Kruglikov *et al.*,²³⁶ Rogers and Taylor²³⁷ and Kardos and co-workers²²³ have all presented support for this theory. The theory has provided a good scientific basis to elucidate the phenomenon of levelling, but it is still only semi-quantitative in nature.

1.4.2.2 Brightening

Brightness is related to the smoothness of a surface that is able to reflect visible light, where surface roughness should be less than 400 nm. Brightening can be defined as the ability of a solution to deposit crystals that have size smaller than the wavelength of visible light, i.e., crystals should normally be smaller than 400 nm.²¹³ Small crystals are essential for brightness, but this cannot in itself be a satisfactory condition. Some studies have found that brightness depends on the orientation of crystallites that are deposited on the surface in the same plane.²¹³ Generally the additives can be worked as levellers or brighteners. Some organic compounds can be correlated with the metal forming complexes, and this refines the metal crystals. These compounds usually have a sulphur atom bonded directly to a carbon atom or contain a $\text{-C}\equiv\text{C-}$ triple bond.²¹³

Edwards and co-workers have studied the effects of organic additives on the brightness of Ni deposits. They found that the addition of succinimide and quinoline methiodide to the Ni plating bath causes an enhancement of the adsorption of each species. Some researchers have studied the effects of sulphur compounds and thiourea on the electrodeposition of Ni and Cu from acid baths.^{131, 238} They found that these compounds

can be strongly adsorbed on the electrode and then decomposed, leading to the incorporation of fairly large amounts of sulphide in the deposit. Kruglikov *et al.*¹³¹ found that more than 5 wt% sulphide was found in electrodeposited copper and nickel obtained in the presence of these compounds. Turner and Johnson postulated that (for copper) the formation of copper sulphide modifies the normal crystal growth of the plate.

Raub *et al.*²³⁹ studied the influence of different types of compounds containing acetylenic and sulphur on the electrodeposition of Ni, which the study achieved using different methods such as polarization, (*i-E*) curves, and the rise-time of initial current transients. They reported that both levelling and brightening agents impede the deposition of metals on the cathode, and that the levelling action is controlled by diffusion. However, brighteners do not necessarily show this diffusional behaviour. They also used compounds that work as brightening and levelling agents. They observed, perhaps rather unintuitively, that bright deposits do not necessarily have more ordered crystal structures than dull deposits; similarly, mirror brightness was observed in deposits with both random crystal orientations and more ordered structures. Moreover, similar orientations may be observed in both matte and bright deposits.

1.5 Electrocrystallisation

Electrodeposition of metal occurs at electrode/electrolyte interfaces when an electric field is applied. Metal deposition processes that proceed electrochemically are called electrocrystallisation. This process has attracted much attention from both scientists and engineers. Electrocrystallisation is the process in which mass transfer is accompanied by a charge transfer.²⁴⁰ The formation of a new phase requires that the system is in a metastable phase. Supersaturation is obtained by disturbing the equilibrium, either through the applied potential or changing the temperature and the electrolyte bath composition. The applied potential plays a significant role in controlling the deposition, and also affects the crystallisation process through the following two means:

- a) The direct effect of the potential, which can determine the type of nucleation and the growth kinetics for the metal electrodeposition.
- b) The indirect influence that occurs due to side reactions such as solvent decomposition. This can change the local reaction environment around the

electrode, which thus alters the nature of the reaction product. For example, evolution of hydrogen in unbuffered electrolytes may result in co-deposition of metal oxides/ hydroxides in addition to the metal deposition itself.

In most deposition processes, both the affects above are observed.

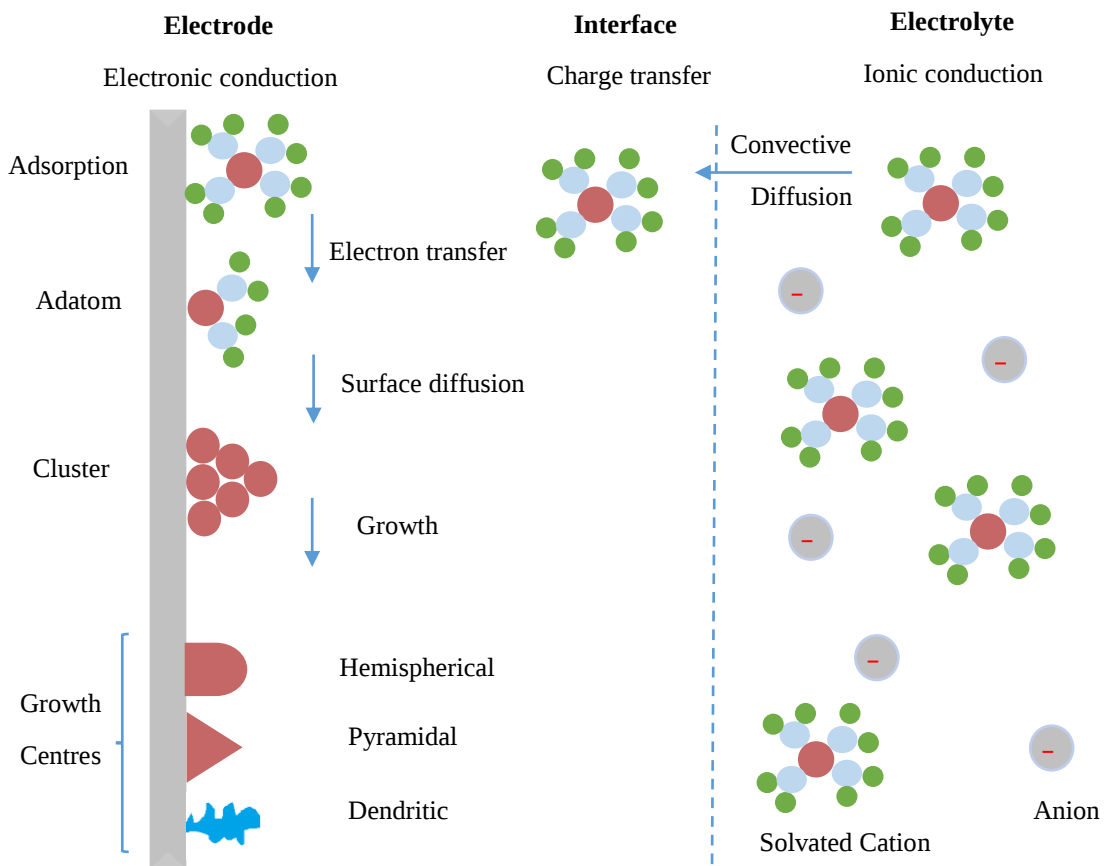


Figure 1.6 A simplified diagram showing metal electrocrystallisation onto an electrode surface.

The reaction between the electrode surface and an ionic conductor is a heterogeneous charge transfer reaction. This reaction occurs through the process demonstrated in **Figure 1.6**. The electrocrystallisation process could play a role in the following processes:

- cathodic, anodic or cell reactions;
- chemical and electrochemical steps;
- ions and uncharged species, including the solvent;
- disappearance, appearance or transformation of a solid phase; and

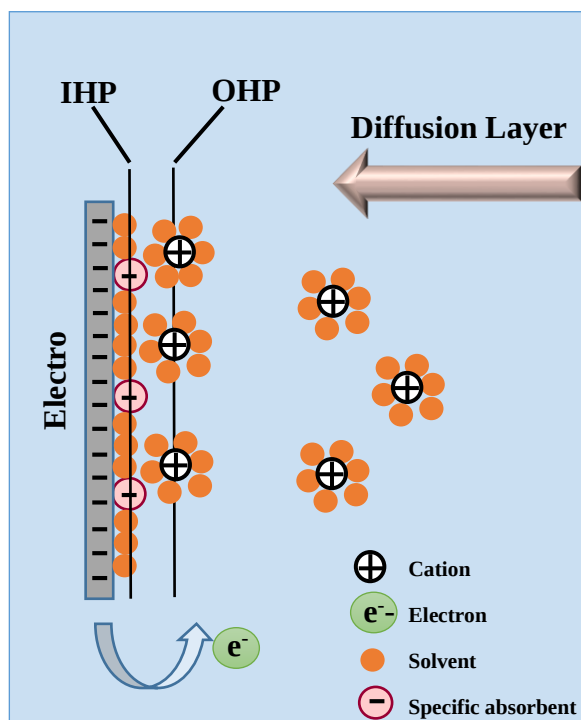
- e) phases which remain on the electrode or which reside in the electrolyte.

Changing the interfacial layers near the electrode interface can influence the electrocrystallisation processes. The interface region is divided into the following three zones: the Electrical Double Layer, the Concentration Profile Layer and the Fluid Velocity Layer.

1.5.1 Electrical double layer

The electrochemical reaction between an electrode and solution is called a heterogeneous reaction, which depends on transfer from an electrode (metal or semiconductor) to a chemical species in solution, or vice versa. Phenomena relating to the electrical double layer can occur at the electrode interface. The electrical double layer is formed due to charge separation, resulting in a distribution of potential near the surface in contact with the solution.²⁴¹ The double layer has been studied in most detail for a mercury electrode immersed in aqueous solution.²⁴² The Helmholtz compact double-layer model is the simplest model of the structure of the metal-solution interphase. This model is based on a single layer, and supposes that solvated ions arrange along the surface of the electrode, but do not actually come into contact with it due to the spatial ‘buffering effect’ of the molecules in their solvation spheres.

There are several layers of the solution in contact with the electrode, as suggested by the Gouy-Chapman-Stern model.^{243, 244} The charge on the electrode, q_M , can be negative or positive depending on the potential applied; this charge can be formed in a layer with a thickness of about $0.1 \text{ \AA}$ close to the electrode surface. This layer, called the internal layer, is largely composed of solvent molecules and in a small part by molecules or anions of other species. A new model was proposed by Gouy, Chapman and Stern, where they supposed that the interactions between the electrode surface and the ions are based on the equilibrium between their chemical interaction with the substrate and the heat of solvation. The ions interact with the electrode surface through electrostatic forces, but only where this is non-specifically adsorbed, and this reaction forms the outer Helmholtz plane (OHP). A pictorial description of the double layer is shown in **Figure 1.7**.



Figures 1.7 A detailed picture of the electrode/solution double layer

The specific adsorption of other species can occur on the electrode surface, as shown in **Figure 1.7**. The distance between the metallic electrode and the nucleus of the species that is specifically adsorbed is referred to as the Internal Helmholtz Plane (IHP). The ions oppositely charged to the electrode, which are obviously solvated, can approach the electrode at up to twice the distance of the above, which is defined as the Outer Helmholtz Plane (OHP).

1.5.2 Concentration profile layer

The concentration profile layer normally arises from the depletion of species in the electrolyte near the interface of the electrode due to convective diffusion.^{240, 245} At the limiting current, the reaction is under mass transport control, and the surface concentration will reach zero. By assuming a (fictitious) linear diffusion profile, The Nernstian diffusion layer thickness can be defined using **Equation 1.2**:

$$K_L = \frac{D}{\delta N} \quad \text{Equation 1.2}$$

where K_L is the mass transport co-efficient, and D is the diffusion coefficient.

1.5.3 Fluid velocity layer

The fluid velocity layer arises due to localised differences in electrolyte convection due to both fluid shear and the manner in which the flow develops. Bulk velocity is increasingly retarded as proximity to the electrode increases. At the surface itself, the fluid is stationary relative to the electrode. The Prandtl (hydrodynamic) boundary layer thickness, δ_{pt} , can be obtained by assuming a linear profile in the above.

1.6 Formation of metal phase

1.6.1 Nucleation

The electrodeposition of metal on the foreign substrate is achieved through the fundamental processes of nucleation and crystal growth. The granularity and morphology of the deposit can be determined by the rates of these processes. A finer-grained crystal deposit can be formed when the rate of nucleation is high. Nucleation, the initial stage of metal deposition, is kinetically limited by the Gibbs formation energy, which is linked to an increase of the Gibbs energy of the system. It has been found that the dimensionality of the active sites plays a significant role in the transfer of ions from the electrolyte to the substrate surface. The probability of the deposition of metal ions is high on rough, high-indexed surfaces or on stepped vicinal or planes with a high density of kink sites²⁴⁶ (**Figure 1.8**). Active sites can also be formed through oxidation/ reduction of a surface, ad/desorption of anions, reconstruction processes, or solvent molecules. Reconstruction is the displacements of the surface atoms, where it can be happened with many metals have less stable surfaces.

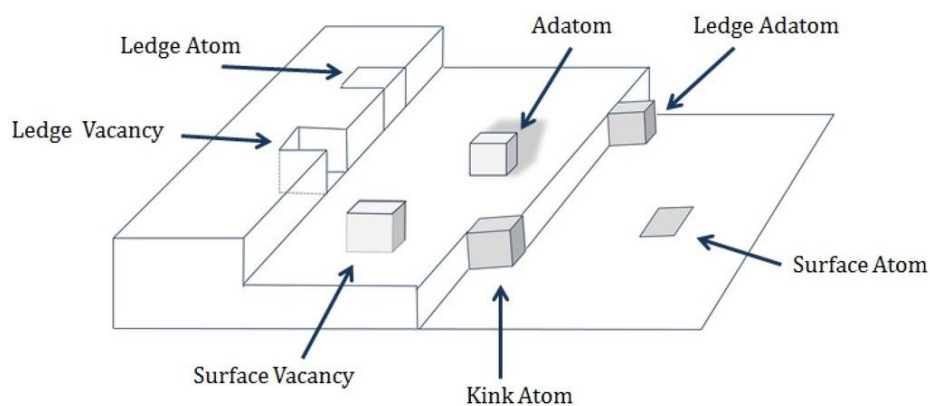


Figure 1.8 Different types of surface imperfections.²⁴⁷

The Au (111) reconstruction has been studied, and it was found that the reconstructed surface has a 4% higher atom density than the unreconstructed surface. As a result of a potential that is positively charged, the reconstruction is lifted and the atoms relax back into the positions on the truncated three-dimensional lattice to form a hexagonal structure. The crystallography of the Au (111) electrode is significantly influenced by adsorption of anions (particularly halides), which can cause the removal of a reconstructed surface.²⁴⁸ The degree of roughness may alter the electrochemical behaviour of the electrode and can cause the excess 4% reconstructed atoms.

1.6.2 Growth

Growth is the expansion of a supercritical nucleus through continued incorporation of monomers. The film morphology and structural properties such as the perfection, flatness and interface abruptness of the layers can be determined by the growth mode, which can be controlled by the kinetics of the transport and diffusion processes on the surface.²⁴⁰ The different atomistic processes taking place on the surface during new phase formation are shown in **Figure 1.9**.

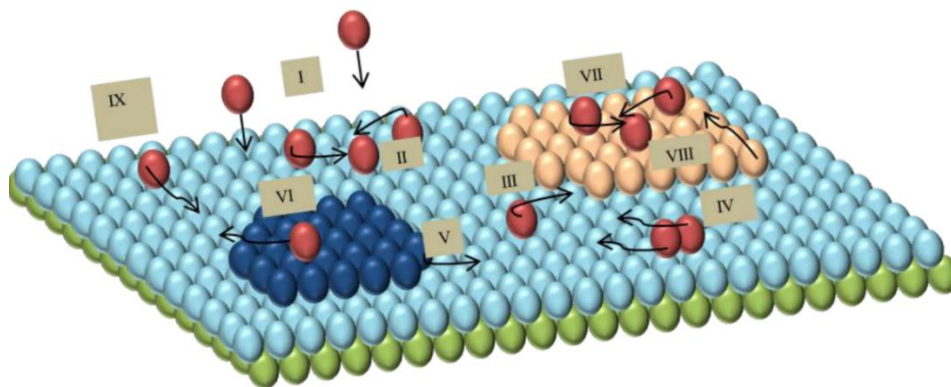


Figure 1.9 Schematic diagram of nucleation and growth, (I) arrival (II) nucleation on island (III) attachment to island (IV) diffusion of dimer (V) detachment from an island (VI) diffusion to lower terrace (VII) binding and nucleation on second layer (VIII) diffusion along step edge (IX) diffusion on terrace.²⁴⁰

There are three basic regimes of growth. An applied potential and/or the difference in surface energy strongly affects the rates of nucleation and growth. Therefore, growth can be divided into mononucleation, polynucleation and oligonucleation.

1.7 Aim of this project

Electroplating is the most widely used method of surface finishing. Electroplating of metals is normally achieved from aqueous electrolytes, though as discussed previously such solutions have a number of drawbacks. Recently, ionic liquids have been used as alternatives to aqueous electrolytes in the electrodeposition of metals, where they are considered more environmentally compatible deposition systems. Ionic liquids, especially deep eutectic solvents, offer some opportunities to circumvent some of the issues associated with using aqueous solutions for electroplating. Amongst the most important of these is the use of other metal salts which circumvent REACH regulations and the ability to deposit metals that cannot be deposited from aqueous solutions e.g. aluminium.

While the electrodeposition of metals from DESs has been studied by several groups the main issue preventing their application on a large scale is the morphology of the deposit. In aqueous solution additives have been developed to produce bright adherent coatings. The use of additives has not been studied to any great extent in ionic liquids or deep eutectic solvents. Recent work within our group has shown that some additives used in aqueous solutions also work with nickel deposition in DESs. The main aim of this thesis is to determine whether the same additives are universal and function for a range of other metals or whether the additives are metal specific or specific only to aqueous solutions.

In the first chapter, (EDTA), sodium iodide (NaI), boric acid (BA) and 5,5-dimethylhydantoin (DMH) will be used to examine their influence on Cu deposition from Ethaline 200. In the second chapter, the effects of nicotinic acid (NA), boric acid (BA) and benzoquinone (BQ) on Zn deposition from Ethaline 200 will be investigated. In the third chapter, the electrodeposition of a Zn-Ni coating from Ethaline 200 will be studied by varying different physical parameters (current density, temperature and concentration of metal salts). In addition, the effects of boric acid (BA) and sodium bromide (NaBr) on the electrodeposition of the Zn-Ni coating will be examined. The final results chapter investigates the electrodeposition of Al from conventional ionic liquids (1-ethyl-3-methylimidazolium chloride/ AlCl_3 and 1-butyl-3-methylimidazolium/ AlCl_3) and DESs, namely (1.5:1) acetamide- AlCl_3 , (1.5:1) *N*-methylacetamide- AlCl_3 and (1.5:1) *N,N*-dimethylacetamide/ AlCl_3 -based liquids.

Moreover, the influence of methyl nicotinate (MN) on the electrodeposition of Al from these liquids will also be studied.

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2 Introduction

This chapter is split into two parts; the first part forms an introduction to electrochemistry, mechanisms of electrode reactions and the principles behind the main techniques that were used in this project. The second part will discuss the standard experimental conditions and protocols used throughout this thesis.

2.1 Part I (Electrochemistry and principle of techniques)

2.1.1 Electrochemistry

Electrochemistry is a branch of chemistry based on oxidation and reduction reactions in which electrons can be transferred from one reactant to another, or from an electrode to a reactant, and vice versa. Oxidation and reduction reactions can be started by mixing reactants in a suitable container, or can otherwise be achieved in an electrochemical cell. Electrochemical cells are classified as being of two types: galvanic cells and electrolytic cells. The galvanic cell works by generating current from a chemical reaction, such as in batteries, where in this type of cell the reaction happens spontaneously. In an electrolytic cell, the chemical reactions occur when an external voltage is applied to the cell, such as with the electroplating of metals using a power supply where the oxidation/ reduction of metals takes place when an external voltage is applied.¹ Electrochemistry plays a significant role in many fields such as electrophoresis, electroplating and technologies. Since this research is about electroplating, it is important that one first understands the principle behind electrochemical reactions.

2.1.1.1 Electrode reactions and mechanisms of electron transfer

The transfer of electrons between an electrode and reactant molecules in solution is dynamic electrochemistry. There are various factors that can affect the dynamics of an electrode reaction, including the electrode potential and the nature of the electrode surface, the mass transport of the various species involved and the nature of the species in the solution. An electrode reaction is a charge transfer between an electrode and an ion or molecules in the solution. Applying a voltage (potential) is the driving force for starting an electrode reaction. Voltage means energy, which causes the movement of charges from the electrode to the molecules. For example, Fe^{3+} ions in solution are

reduced to Fe^{2+} when a potential is applied to the electrode; the Fe^{2+} ions can then be oxidised through the loss of an electron, as shown in **Equation 2.1**.²



Therefore, an electrode reaction can be summarised as one where molecules or ions move to the electrode surface, electrons are transferred from the electrode surface to molecules, and the molecules can then lose electrons back to the electrode.

Electron transfer from the electrode to the reactant can be understood according to the Fermi-level. It is clear from **Figure 2.1** that the Fermi-level depends on the energy level of the electron in the metal (electrode). On the left side, the electron energy in the metal (electrode) is less than the energy of the lowest unoccupied molecular orbital (LUMO) of the molecules in the solution; therefore, electrons are unable to transfer from the electrode surface to the reactant. On the right side, the electron energy (Fermi-level) of the electrode metal is greater than the LUMO energy of the reactant; thus, electrons can transfer to the species and result in reduction.²

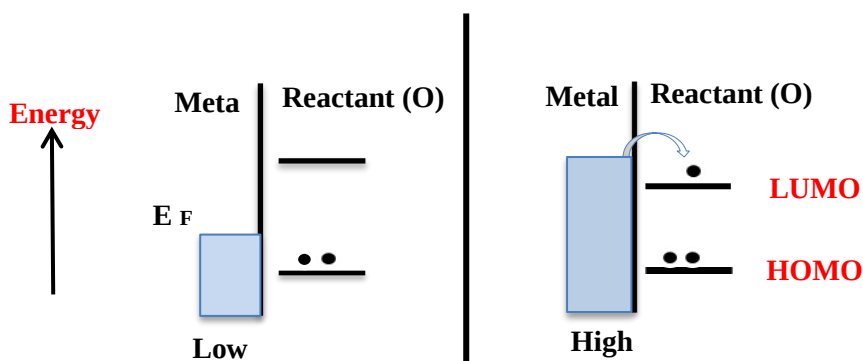


Figure 2.1 Fermi-level in a metal and the reduction of a reactant species.

2.1.1.2 Cyclic voltammetry

Cyclic voltammetry is an electrochemical analytical method, and is useful for studying redox reactions. It is usually used for acquiring qualitative information such as identifying the type of metal in solution by elucidating its oxidation and reduction voltages. It is based on a reaction that occurs at an electrode surface or on the

thermodynamics of redox reactions and kinetics of heterogeneous electron transfer reactions.³

Figure 2.2 (a) shows the variation of applied potential as a function of time in a cyclic voltammetry experiment, where a triangular potential waveform is applied to the working electrode. The potential swept from E_1 (initial) to E_2 (final) and then reversed to E_1 . During this sweep, the current is measured. A plot of the current versus potential is called a voltammogram; one such is illustrated in **Figure 2.2 (b)**. This figure shows a cyclic voltammogram for a reversible redox process.³

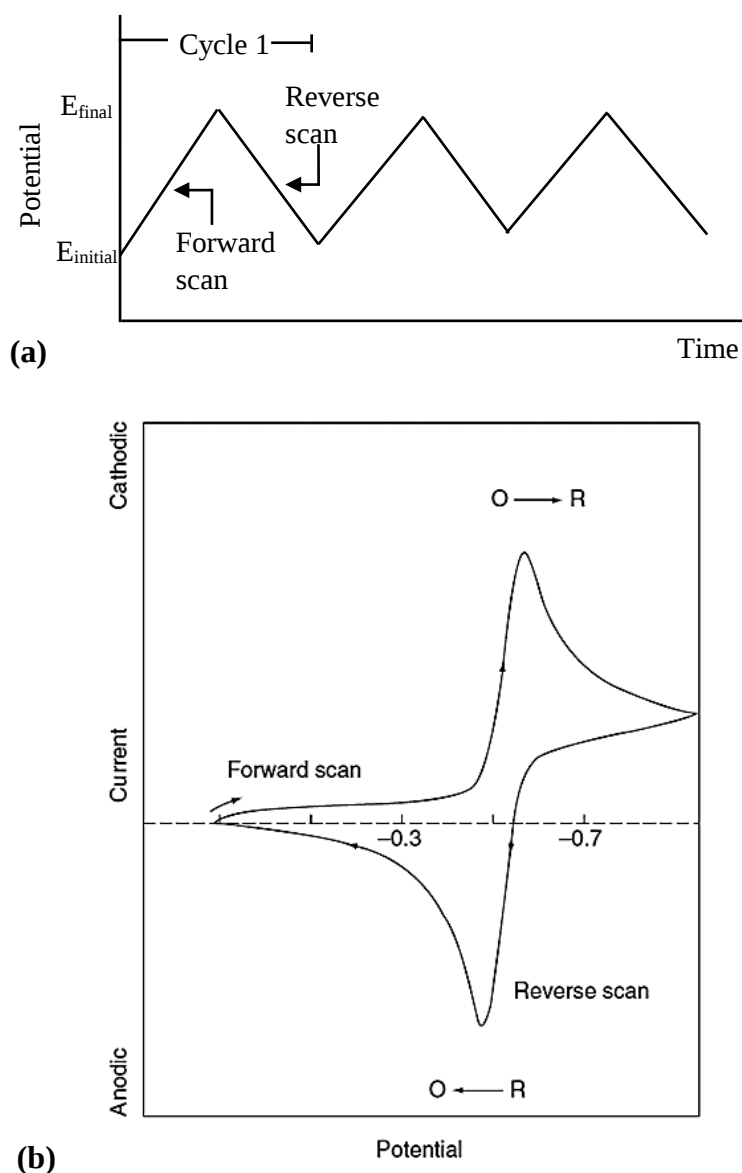


Figure 2.2 (a) Variation of applied potential as a function of time in a cyclic voltammetry experiment. **(b)** Typical cyclic voltammogram for a reversible redox process.³

In general, the redox processes in electrochemical reactions at an electrode surface can be characterised by the following reaction, **Equation 2.2**.



where O and R represent the oxidised and the reduced forms, respectively. When the potential is applied to the working electrode, reactant O starts to reduce to form R, and the cathodic current increases (the reduction process); the potential is then reversed. This will lead R to back to O by the loss of an electron (the oxidation process), resulting in an anode peak. Consequently, current can be measured as a function of the potential applied to the working electrode.³

The cyclic voltammetry method provides both qualitative and quantitative information about the analyte in the solution. The value of the potential gives information about the type of analyte, and peak current gives us information about the concentration of the analyte in the solution.¹

The concentration of analyte for a reversible system at 25 °C can be calculated using the Randles-Sevcik equation:

$$i_p = 2.69 \times 10^5 \text{ A } C^\circ n^{3/2} D^{1/2} \nu^{1/2} \quad \text{Equation 2.3}$$

where n is the number of electrons, A is the area of the electrode, D is the diffusion coefficient, C° is the concentration of the species of interest and ν is the scan rate.¹

2.1.2 Mass transport

In electrochemical reactions, reactants can be transported from solution to the electrode surface via three mechanisms, which are diffusion, migration and convection.^{1, 2}

1. Diffusion: if we have two regions in the solution with different concentrations, molecules or ions will move from the high concentration region to the low concentration region. This process is called diffusion. This process depends on the variation in the concentration of the reactants at the electrode surface and the bulk solution; this variation generates a concentration gradient which in turn results in the diffusion of reactant ions from the bulk solution to the electrode surface.¹
2. Migration: in this type of mass transport, anions move to the positive electrode, while cations move to the negative electrode. Normally, this type of transport is undesirable. Thus, to reduce migration of cations and anions to the positive and negative electrode, it is necessary to add a supporting electrolyte to the electrochemical cell. The supporting electrolyte can be an inert electrolyte at a high concentration. In addition, the supporting electrolyte works to reduce the IR drop (cell resistance).¹
3. Convection: reactants can be transported to or from an electrode surface under the influence of an external mechanical force such as stirring or agitation of the solution. The mechanical force causes a decrease in the thickness of the diffused layer, and thus concentration polarization will be decreased. There are two types of convection; the first is natural convection, which depends on temperature or on a difference in density within the solution. When the reaction occurs at the electrode, the new products will be generated near the electrode surface; the products have different densities from the reactants in the solution. The second type is forced convection. Here, the reactants can be moved by external forces such as pumping, stirring or bubbling gas through the solution.^{1, 2}

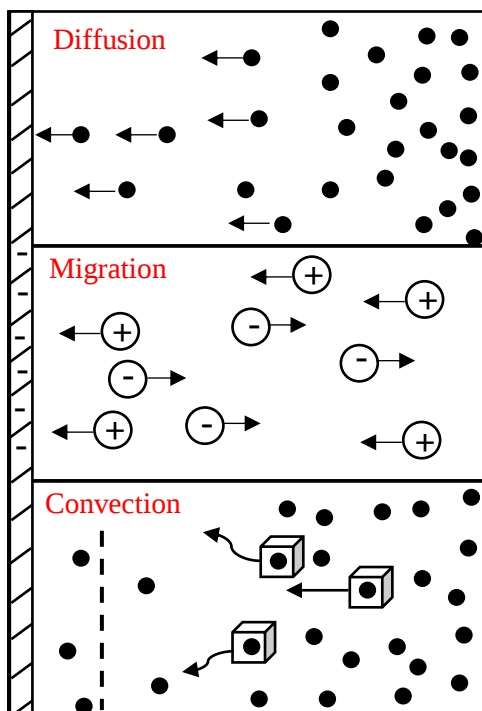


Figure 2.3 Types of Mass Transport

2.1.3 Quartz crystal microbalance QCM

During an electrochemical reaction, a reduction and an oxidation will take place. On the electrode surface, mass may change due to the deposition or dissolution of a solid phase. This change in mass can be measured using an electrochemical quartz crystal microbalance (EQCM). The electrochemical quartz crystal microbalance utilizes the piezoelectric nature of a quartz crystal to monitor the changes in mass at the surface of the electrode. In this technique, whilst a quartz crystal is used, there are different types of quartz crystal available depending on experimental necessity and circumstance. Some are coated with gold on both sides, whilst some are coated with gold on one side and platinum on the other. An example of such a quartz crystal is shown in **Figure 2.4 (a)**.

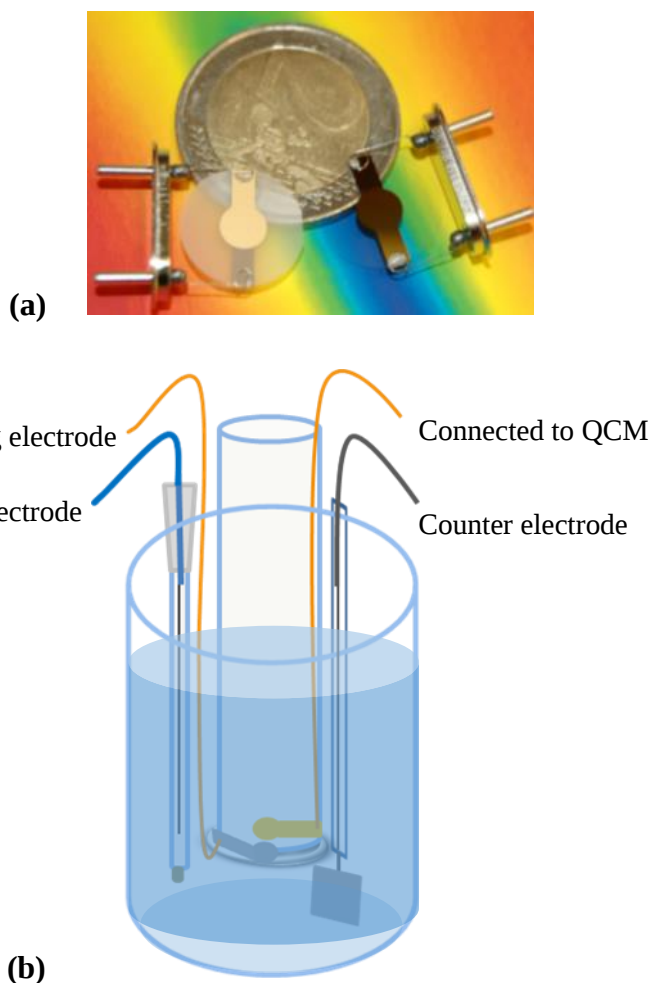


Figure 2.4 (a) sample of a quartz crystal and **(b)** schematic representation of the cell used in electrochemical gravimetric analysis experiments, showing the three electrodes, the quartz crystal as the working electrode, the platinum flag as the counter-electrode and Ag/AgCl as the reference electrode.

The experimental cell design is shown schematically in **Figure 2.4 (b)**. This cell was immersed in the plating solution in order to be used as a mass probe for electrolytic deposition of the metal. The Pt face of the crystal was left in contact with the liquid interface, whilst the Au face was left exposed to air. The quartz crystal is resonant when an electric field is applied; the deposition of mass on the crystal surface shifts the resonant frequency, and this shift can be measured. The consequent change in resonant frequency of the quartz crystal, Δf , corresponds to the mass of metal deposited.

From the fundamental frequency value, f_0 , the change in mass, Δm , can consequently be calculated from the change in resonant frequency using the Sauerbrey equation,⁶

$$\Delta f = -2 \frac{f_0^2}{pv} \Delta m \quad \text{Equation 2.4}$$

where ρ is the density of quartz and v the wave velocity. The Sauerbrey equation is only valid in the instance where the deposited mass behaves in the manner of a rigid resonator. If it behaves non-rigidly, the frequency shift will be less, to an unknown degree, than would be otherwise predicted by the Sauerbrey equation which, therefore, prevents accurate measurement.⁷

2.1.4 Surface analysis techniques

2.1.4.1 Scanning electron microscopy (SEM)

Scanning electron microscopic analysis is considered a particularly influential instrument in the determination of micro- and nano-morphological patterns of materials. The basic principle of this technique is the use of an electron beam to scan the sample, and the secondary electrons given off from each point of the surface are collected by a suitable detector. Contrast in the micrograph results primarily from variations in surface topography; consequently, a direct image of surface structure can be achieved via SEM.⁸ **Figure 2.5** shows a schematic of the scanning electron microscopic technique.

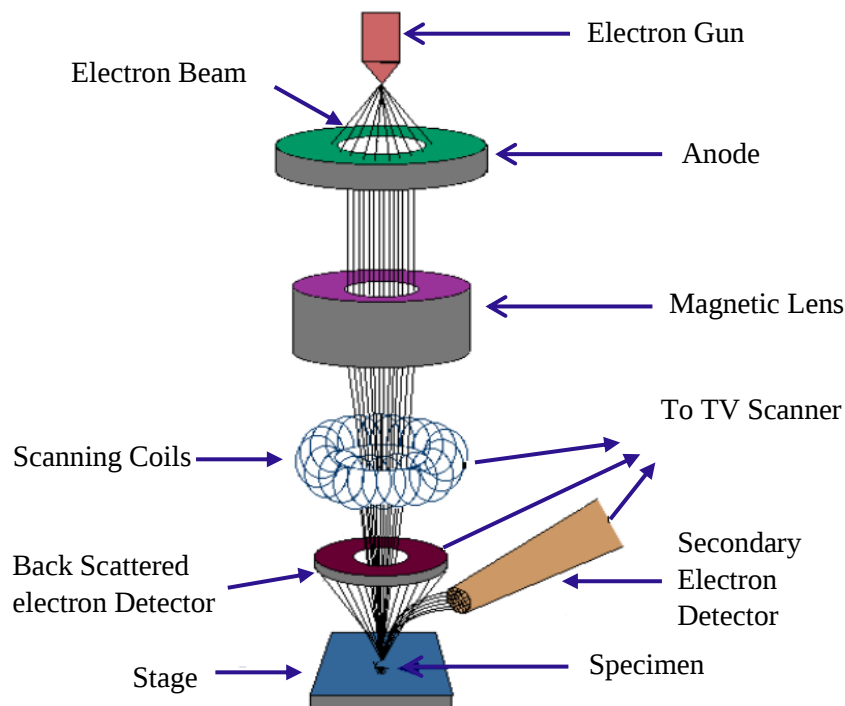


Figure 2.5 Schematic of the scanning electron microscopic technique.

2.1.4.2 Atomic force spectroscopy (AFM)

AFM is one of the techniques used in this project. It is a very high-resolution form of scanning probe microscopy (SPM). This technique can be used to determine the nanometre morphological patterns of materials. The principle of this technique is that the specimen surface can be monitored by a cantilever with a sharp tip (the probe). Monitoring the position of the probe employs the deflection of a laser beam, with differences in sample height causing the cantilever to deflect up or down. In contact mode, the tip probes the repulsive regime of the interaction force. Contact mode can be destructive as the tip is dragged across the surface of the sample, producing strong lateral forces. In non-contact mode, the probe is held a small distance above the sample. Attractive van der Waals forces acting between the tip and the sample are detected. In non-contact mode, however, the probe is frequently drawn to the sample surface, resulting in unusable data and sample damage. A large range of topographies and many kinds of materials can be imaged using AFM such as atomic terraces, carbon nanotubes, colloidal particles, DVD textures up to micro lens textures, fractured surfaces, and complex multi-phase polymers. **Figure 2.6** shows a simple diagram illustrating the AFM technique

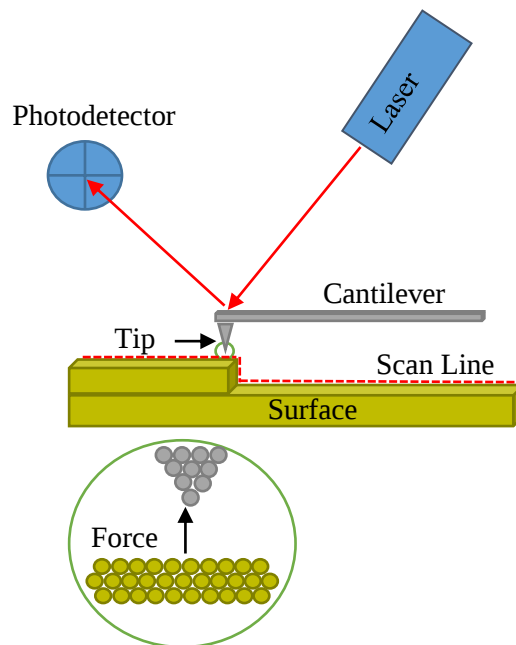


Figure 2.6 Schematic representation of the AFM technique.

2.1.4.3 X-Ray diffraction (XRD)

The XRD technique is used to determine the atomic and molecular structure of a crystalline structure. The principle of this technique is electron bombardment of the sample, which removes an electron from the inner shell of an atom. The electron returns to its normal state by transferring an electron from some outer shell to the inner shell with the consequent emission of energy as X-rays; that is, photons of high energy and short wavelength (0.154 nm for Cu K α radiation) can be used to detect of the emission characteristics of particular elements in the samples. This technique illuminates the surface of a sample with a monochromatic beam of X-rays, which is subsequently rotated to allow data to be recorded over a wide range of angles of incidence and diffraction. The angles of the diffraction peaks in an X-ray diffraction pattern can be directly related to atomic separations. The atoms, and/or molecules, in a powder, can be considered to form different sets of lattice planes in the crystal of inter-plane distance, d , where d can be measured using **Equation 2.5**

$$d = \lambda / 2 \cdot \sin \theta$$

Equation 2.5

where θ is the diffraction angle and λ is the X-ray wavelength. Peak positions, intensities, widths and shapes all provide information regarding the structure and morphology of the material.

2.2 Part II (experimental)

2.2.1 Materials

Table 2.1 List of compounds used in this project. All the chemicals were used as obtained without further purification.

Compound	Abbreviation	Molecular Weight g/mol	Purity
Choline Chloride (ChCl)	$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)^+\text{Cl}^-$	139.63	Aldrich 99%
Ethylene Glycol (EG)	$\text{C}_2\text{H}_4(\text{OH})_2$	62.07	Aldrich 99%
Copper Chloride Dihydrate	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	170.48	Aldrich 99.9%
Zinc Chloride	ZnCl_2	136.30	Aldrich $\geq 98\%$
Nickel Chloride Hexahydrate	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	237.69	Aldrich $\geq 98\%$
Aluminium Chloride	AlCl_3	133.34	Alfa 99 %
Silver Chloride	AgCl	143.32	Aldrich 99.9 %
Ethylenediaminetetraacetic Acid Disodium Salt Dihydrate (EDTA)	$\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$	372.24	Sigma $\geq 99\%$
Sodium Iodide	NaI	149.89	Aldrich 99.9 %
Boric Acid (BA)	H_3BO_3	61.83	Analar 99.8%
5,5-Dimethylhydantoin (DMH)	$\text{C}_5\text{H}_8\text{N}_2\text{O}_2$	128.13	Sigma $\geq 99.5\%$
Nicotinic Acid (NA)	$\text{C}_6\text{H}_5\text{NO}_2$	123.11	Sigma 99.5 %
<i>p</i> -Benzoquinone (BQ)	$\text{C}_6\text{H}_4(=\text{O})_2$	108.9	Aldrich 98 %
Sodium Bromide	NaBr	102.89	Sigma $\geq 99.9\%$
Methyl Nicotinate	$\text{C}_7\text{H}_7\text{NO}_2$	137.14	Aldrich 97%
1-Butyl-3-methylimidazolium chloride	$\text{C}_8\text{H}_{15}\text{ClN}_2$	174.67	Aldrich $\geq 98\%$

Compound	Abbreviation	Molecular Weight g/mol	Purity
Ethyl-3-methylimidazolium chloride	$C_6H_{11}ClN_2$	146.62	Aldrich 98%
Acetamide	CH_3CONH_2	59.07	Alfa 99%
<i>N</i> -Methylacetamide	$CH_3CONHCH_3$	73.09	Aldrich $\geq 99\%$
<i>N, N</i> Dimethylacetamide	$CH_3CON(CH_3)_2$	87.12	Fisher $\geq 99\%$
Sodium Nitrate	$NaNO_3$	84.99	Hogg laboratory supplies
Decane anhydrous	$CH_3(CH_2)_8CH_3$	142.28	$\geq 99\%$
Ammonium persulfate	$(NH_4)_2S_2O_8$	228.20	Sigma $\geq 98\%$

2.2.2 Preparation of solutions

2.2.2.1 Deep eutectic solvents

The ionic liquid used in chapters 3, 4 and 5 was 1:2 ChCl:EG (Ethaline 200). Here, ethylene glycol (EG) is considered to be a hydrogen-bond donor. The deep eutectic mixture was prepared by continuous stirring of the two components at 70°C until a homogeneous, colourless liquid was formed.

2.2.2.2 Metal salts solutions

Copper chloride dihydrate, $CuCl_2 \cdot 2H_2O$, was used in **Chapter 3** of this study. The concentration of $CuCl_2 \cdot 2H_2O$ in ethaline solution was 0.2 M. In **Chapter 4**, zinc chloride, $ZnCl_2$, was used at a concentration of 0.4 M. **Chapter 5** of this project was the electrodeposition of Zn-Ni alloy from Ethaline 200, for which different concentrations of Ni and Zn salts were used, 0.1 M of $NiCl_2 \cdot 2H_2O$ with, variously, 0.5 M, 0.6 M, 0.7 M, 0.8 M, and 0.9 M $ZnCl_2$. In **Chapter 6**, five types of Al liquid were synthesised, two of them classical liquids (1:2 1-ethyl 3-methylimidazolium chloride/ $AlCl_3$ and 1:2 1-butyl-3-methylimidazolium chloride/ $AlCl_3$), whilst the others were deep eutectic solvents (1.5:1 acetamide- $AlCl_3$ -, 1.5:1 *N*-methylacetamide/ $AlCl_3$ -and 1.5:1 *N,N*-dimethylacetamide- $AlCl_3$ -based liquids).

2.2.2.3 Additive solutions

The concentrations of additives used in the electrodeposition of Cu from Ethaline 200 were 0.03 M ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), 0.1 M sodium iodide (NaI), 0.2 M Boric Acid (BA) and 0.2 M 5,5-dimethylhydantoin (DMH), while the concentrations of additives used in the electrodeposition of Zn were 0.05 M nicotinic acid (NA), 0.03 M benzoquinone (BQ) and 0.2 M boric acid. The concentrations of additives used in the electrodeposition of Zn-Ni alloy from Ethaline 200 were 0.2 M Boric Acid (BA) and 0.1 M NaBr. Only the effects of methyl nicotinate on the electrodeposition of Al were studied, at a concentration of 0.01 M.

2.2.3 Physical properties

2.2.3.1 Viscosity measurements

The physical properties (viscosity and conductivity) of the Cu and Zn plating solutions in the presence and absence of the various additives were measured. The viscosities were measured using a Brookfield DV-E Viscometer fitted with a thermostated jacket. The readings were recorded at different temperatures, ranging from 30 to 90°C at 5°C increments, with the measurements conducted using the S61.

2.2.3.2 Conductivity measurements

The conductivities of the Cu and Zn solutions in the presence and absence of additives were measured using a Jenway 4510 conductivity meter fitted with an inherent temperature probe (cell constant = 1.01 cm⁻¹). The conductivity values were measured at temperatures ranging from 30 to 90°C in 5°C increments. Readings were recorded after shaking the beaker containing the solution before each reading to ensure that temperature was at equilibration throughout the plating bath.

2.2.4 UV-Vis spectrophotometer

The UV-vis spectrophotometer used in this project was a Shimadzu model uv-1601; the cell used was a quartz cuvette with a cell path length equal to 10 mm. Values for λ_{max} were determined using the spectrophotometer's built-in peak-pick feature, using the UV-probe software. The Cu experiments were carried out at 80 °C, while spectrum of Ni was examined at a range of temperatures from 30 °C to 90 °C. Temperature control was achieved using thermocouple (SCI 196).

2.2.5 Electrochemical measurements

2.2.5.1 Cyclic voltammetry

Electrochemical methods such as cyclic voltammetry and chronoamperometry were performed using an Autolab PGSTAT12 potentiostat controlled by the GPES2 software (version 4.9). The electrochemical cell consisted of three electrodes: a Pt disc (1 mm dia.) working electrode, a Pt flag counter electrode and an Ag/AgCl reference electrode. These electrodes have been used in all the electrochemical experiments in this thesis except for the Al systems, where different types of electrodes were used (for example, Pt and Cu were used as a working electrodes, Pt and Al flag electrodes as counter electrodes, and Ag and Al wire were used as pseudo-reference electrodes). The cyclic voltammetric study of Cu was performed using a potential window of +1.0 to -1.0 V, while cyclic voltammograms were recorded for Zn using a potential window of 0.0 to 1.5 V. The potential for the cyclic voltammetry for the Zn-Ni deposition was chosen to be +0.5 to -1.5 V. Cyclic voltammetry of Al was achieved over different potential window depending on the type of Al liquid used.

The cyclic voltammetry experiments were carried out at different temperatures and at different scan rates. In all experiments, the working electrode was polished between each experiment with alumina paste, washed with deionised water and dried with nitrogen.

2.2.5.2 Chronoamperometry

Chronoamperometric data were obtained using three electrodes: a Pt disc (1 mm dia.) working electrode, a Pt flag counter electrode and an Ag/AgCl reference electrode. The potential stepping has been chosen according to the deposition potential of the metals; for example, the applied potential was -0.4 V for Cu deposition and -1.25 V for Zn deposition. The applied potential for the Zn-Ni deposition in chronoamperometry experiments was -1.3 V. All chronoamperometric data were achieved under the same cyclic voltammetry conditions (same temperature, concentration and same electrodes). Here, also, the working electrode was polished with alumina paste and washed with deionised water before drying with nitrogen between each experiment.

2.2.5.3 Electrochemical quartz crystal microbalance (EQCM)

The data from the Quartz Crystal Microbalance (QCM) technique 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). To improve temporal resolution, the network analyser data acquisition was controlled using a computer running the HP VEE software. This program is capable of recording admittance spectra every 2-3 s.

In this work, a 10 MHz AT-cut polished (flat mirror) finish quartz crystal with a platinum film thickness of 900 Å, deposited in a keyhole shape on both sides with central disc active area of 0.23 cm², was used (International Crystal Manufacturing Co., Oklahoma City, USA.). The crystal was placed in a Teflon 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 flag counter electrode and an Ag/ AgCl reference electrode. EQCM experiments were carried out at the same temperature as the plating (typically 80°C). The measurements were performed at -0.4 V for the Cu deposition and at -1.25 V for Zn deposition over a period of 30 minutes.

2.2.6 Reference electrode

The reference electrode used in this project, and in particular in the electrochemical methods (cyclic voltammetry, chronoamperometry and quartz crystal microbalance), is Ag/AgCl. The electrode that was prepared does not contain the aqueous solution; it contains the ionic liquid. It was prepared by the researcher himself. The reference electrode was prepared by putting a silver wire in strong HCl for 24 h and then washing the wire with water and acetone before drying in nitrogen, after which the wire was immersed in a glass tube containing 0.1 M AgCl prepared in Ethaline 200. **Figure 2.7** shows a simple schematic of the Ag/AgCl reference electrode prepared in the laboratory.

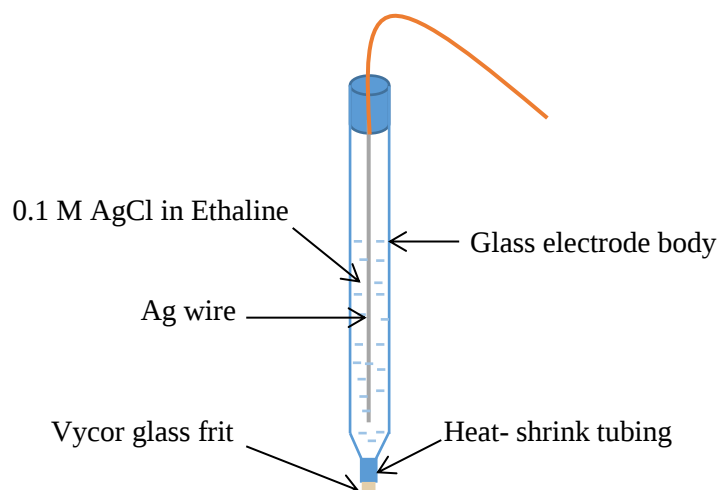


Figure 2.7 Schematic diagram of the Ag/AgCl in Ethaline 200 reference electrode

2.2.7 Bulk electrodepositions

2.2.7.1 Electrodeposition of Cu

Electrodeposition of Cu from Ethaline 200 containing 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the presence and absence of additives was achieved on mild steel cathodes. The mild steel substrates were first manually polished with progressively finer grades of silicon carbide polishing paper, washed with water, etched in strong HCl, washed again in water and then dried with nitrogen. The anode was Ti mesh, which is iridium oxide coated Ti. The electrodepositions were performed at 80°C and at a current density of 2.5 mA cm^{-2} for 1 h.

2.2.7.2 Electrodeposition of Zn

Electrodeposition of Zn from Ethaline 200 containing 0.4 M ZnCl_2 in the presence and absence of additives were achieved on a Cu substrate. The cathode substrate was, firstly, etched in ammonium persulfate solution, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, washed with water and then dried with nitrogen. The anode was Ti mesh, and the electrodepositions were performed at 80°C and a current density of 3.3 mA cm^{-2} for 2 h.

2.2.7.3 Electrodeposition of Zn-Ni alloy

Electrodeposition of Zn-Ni alloys has been carried out from Ethaline 200 under different conditions (temperature, series concentration of ZnCl_2 , and different current density). Boric acid and sodium bromide have been used as additives. All Zn-Ni coatings were achieved on Cu substrate over 1 h. In this project, electrodeposition of the Zn-Ni alloy has been divided into four parts:

- 1- Electrodeposition of Zn-Ni alloy achieved from Ethaline 200 containing 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.5 M ZnCl_2 , 0.2 M boric acid and 0.1 M NaBr at 80°C and different current densities (4, 6, 8, 10, 12 mA cm^{-2}).
- 2- Electrodeposition of Zn-Ni alloy achieved from Ethaline 200 containing 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.5 M ZnCl_2 , 0.2 M boric acid and 0.1 M NaBr at a current density of 8 mA cm^{-2} and at different temperatures (50, 60, 70, 80, 90°C).
- 3- Electrodeposition of Zn-Ni alloy achieved from Ethaline 200 containing 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, with different concentrations of ZnCl_2 (0.5, 0.6, 0.7, 0.8, 0.9 M), 0.2 M boric acid and 0.1 M NaBr at a current density of 8 mA cm^{-2} and at 80°C.
- 4- Electrodeposition of bright Zn-Ni alloy achieved from 0.05 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.8 M ZnCl_2 , 0.2 M boric acid and 0.05 M NaBr at 80°C at different current densities (5 mA cm^{-2}).

Here also, the Cu substrate was first etched in ammonium persulfate solution, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and then washed with water and dried with nitrogen. In all experiments, the samples that were produced were washed with water and then dried.

2.2.7.4 Electrodeposition of Al

Electrodeposition of Al has been achieved from five types of Al liquids prepared specifically this work, two of which were traditional ion liquids, 1-ethyl-3-methylimidazolium chloride/ AlCl_3 and 1-butyl-3-methylimidazolium/ AlCl_3 , whilst the others were deep eutectic solvents, (1.5:1) acetamide- AlCl_3 , (1.5:1) *N*-methylacetamide- AlCl_3 and (1.5:1) *N,N*-dimethylacetamide/ AlCl_3 -based liquids. All Al depositions were achieved on a Cu substrate at 30°C for 1 h and in the absence and the presence of 0.01 M methyl nicotinate. The anode was Al with an area three times bigger than that of the cathode. The distance between the cathode and anode was 2 cm.

The anode was cleaned by dipping into 1% HNO_3 , 65% H_3PO_4 , 5% acetic acid and water for 5 min, and was then washed with deionised water and acetone. After the deposition, all samples were washed using propan-2-ol and then rinsed with deionised water and acetone. Due to the fact that the Al liquids used in this project are sensitive to air and water, decane was used, which forms as a layer above the Al liquids to prevent contact between the liquid and air, as illustrated in **Figure 2.8**.



Figure 2.8 Photograph of the phase behaviour of decane with acetamide- AlCl_3 liquid

This due to the fact that decane is inert and does not mix with the Al liquids, its density is low enough that it can be floated on the surface of the liquid. The advantage of using this decane layer is this that cathode substrate and Al anode plate can be simply immersed through the decane layer and direct plating can occur without the need to purge the environment surrounding the plating bath.

2.2.8 Surface analysis

2.2.8.1 Scanning electron microscopy and energy dispersive x-ray analysis

Surface analysis with SEM and elemental analysis by EDAX were carried out using a Phillips XL30 ESEM instrument with an accelerator voltage of 20 keV, giving an average beam current of ca. 120 μA .

2.2.8.2 Atomic force microscope (AFM)

Atomic force micrographs were acquired using a Digital Instruments Nanoscope IV Dimension 300 (Veeco) atomic force microscope with a 100 mm scanning head was used in both contact and tapping (resonant) modes. The controlling software was Nanoscope version 6.13. Images were acquired in air.

2.2.8.3 X-Ray diffraction (XRD)

Powder X-ray diffraction was performed 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 α -filtered radiation of wave. It was typical operated at 40 kV, 30 mA, and 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.

2.2.8.4 Cross-section

Cross-section microstructure: The Cu, Zn and Zn-Ni alloys films were mounted in a resin using a Struers LaboPress 3. The samples were then polished first with 240 grit silicon carbide paper to make them flat, then with diamond abrasives of successively 9 μ m and 3 μ m size and finally with a 0.05 μ m colloidal silica.

2.2.9 Hardness

In this project, a Mitutoyo model MVK-G25 hardness meter was used to measure the hardness of some of the electrodeposited samples, such as the Zn-Ni alloy's resistance to indentation, in the form of force of indentation and depth of indentation. The Vickers number is the number obtained by dividing the kg-force load by the square of the area of indentation of a standard probe. The measurements were achieved by taking the average of five readings. The thickness of the film was in all cases > 2.5 times the indentation depth. The force applied was always 25 g and the measurement was carried out on the surface of the sample.

2.2.10 Corrosion studies by electrochemical measurements

The corrosion resistance of Zn, Ni and Zn-Ni alloy deposits were determined via Tafel curves and electrochemical impedance spectra (EIS). These measurements were performed using a three-electrode cell with a Pt foil as the counter electrode with area close to the area of working electrode (0.875 cm^2) and an Ag/AgCl reference electrode. The experiments were achieved using an Autolab PGSTAT20 potentiostat (Ecochemie, Holland) controlled by GPES software. The deposits were immersed in 0.1 M NaNO_3 solution. Tafel curves were then recorded in the range -0.25 to 0.25 V with respect to the open circuit potential (OCP). The experiments were recorded at a scan rate of 10 mV s^{-1} at 25°C .

The electrochemical impedance spectra EIS was performed under the same conditions as the Tafel curve experiments (0.1 M NaNO_3 , 10 mV s^{-1} , potential range -0.25 to +0.25 V and at 25°C). The impedance spectra were measured at OCP in the frequency range between 10^5 Hz and 10^{-2} Hz with an amplitude of 5 mV.

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Chapter 3: Effect of Additives on Electrodeposition of Copper from Deep Eutectic Solvents

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3.1 Introduction

Recently, the electrodeposition of Cu has become an important process in the field of technology, especially for the fabrication of printed circuit boards, due to copper's high electrical conductivity, excellent electrical migration resistance, lower cost and, recently, because Cu has replaced with Al in microelectronic interconnections.¹⁻⁴ Since Cu and its alloys are important in electronic applications, optics, electric motors and aerospace,⁵ it is thus desirable to improve the properties of Cu coatings. A great deal of effort has been expended in optimising these properties; this has been achieved by changing the conditions of the plating bath, such as temperature, current density, metal concentration and coating time. Furthermore, organic and inorganic additives have been used in electroplating applications to enhance the characteristics of electroplated metals, such as brightness, roughness of coating, enhanced resistance to corrosion and hardness.^{6, 7}

Routinely, Cu electroplating is carried out using acidic sulphate baths. Usually, aqueous solutions with high concentrations of chloride are avoided because they tend to produce a black and friable film. This is due to presence of a halide in the electrolyte increasing the number of nuclei at the surface of the electrode. To yield a bright Cu deposit from a chloride electrolyte it is necessary to control the rate of nucleation and increase the growth of nuclei, which usually occurs in aqueous solution by adding organic additives and a surfactant. In aqueous Cu electrodeposition electrolytes, the organic additives are often included to improve the morphology and physical properties of the deposit; also, some additives can impede the reduction of impurities in the electroplating electrolyte. The additives that are normally used in the electrodeposition of metals from aqueous solution function in one of two ways:

- i) They work as ligands and form complexes with metal ions, which makes the metal ions difficult to reduce.
- ii) They adsorb on the surface of the electrode and inhibit nucleation of the metal, or they alter the electrochemical double layer.

Different types of additives, such as 8-hydroxy-7-iodo-5-quinoline sulphonic acid (HIQSA), 8-hydroxyquinoline (HQ), 2-iodo-3-pyridinol (IP), ethylenediaminetetraacetic acid (EDTA), thiourea, gelatine, animal glue and polyacrylamide have been used in the electrodeposition of Cu from aqueous plating baths.⁸⁻¹¹

Generally, Cu electroplating is carried out in aqueous solutions which show high solubility to metal salts and have high conductivities. They can be used to easily create highly uniform coatings on complex shapes, and on shapes with internal surfaces (a *high throwing power*).¹² However, there are disadvantages to using aqueous solutions such as extensive hydrogen evolution that results in a reduction in the current efficiency of the coating and a narrow positional window. In most Cu plating solutions, acids, bases and cyanide compounds are used; these have various drawbacks, such as toxic effluent, air pollution and high energy consumption.¹³ The morphology and composition of the metal deposits are strongly affected by the type of solvent. Recently, ionic liquids have been employed as alternatives for metal plating from aqueous solutions, with the aim of providing a less environmentally hazardous alternative.⁵ In the 1960s and 1970s, the electrodeposition of Cu was performed using different types of chloroaluminate ionic liquids.^{12, 14-16} In the 1990s, discrete anions such as $[\text{BF}_4]^-$, and $[\text{F}_3\text{CSO}_2)_2\text{N}]^-$ ($[\text{Tf}_2\text{N}]^-$) were introduced, improving the ease by which the electrodeposition of Cu could be performed.^{12, 17, 18} Endres and co-workers demonstrated that electrodeposits of Cu could be obtained from [butylmethylpyrrolidinium][Tf_2N] at various temperatures. However, the solubility of Cu compounds was limited in this system, and Cu cations were introduced into the liquid through the dissolution of the anodic Cu electrode.^{12, 19} Ionic liquids with discrete anions have issues such as high cost, toxicity, and availability, and clearly these issues will reduce their industrial utility.

Solvents are of particular importance in the field of green chemistry, where new types of ionic liquids (ILs) have been produced by forming complexes between quaternary ammonium salts $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+\text{X}^-$ and hydrogen bond donors such as acids, amides and alcohols.^{20, 21} These liquids are called deep eutectic solvents (DESs). Compared to other types of ionic liquids, DESs have significant physiochemical advantages such as availability, non-toxicity, biodegradability, recyclability, flammability, and low cost.^{5, 20, 22-25} As DESs are relatively cheap and environmentally clean compared to the fabrication and use of ionic liquids, they represent a much more attractive alternative to ionic liquids from various perspectives. DESs can be used on an industrial scale in electropolishing,^{12, 26-28} electroplating,^{4, 21, 29, 30} metal oxide processing^{31, 32} and polymer synthesis.³³ Choline chloride is the quaternary ammonium salt that has been most used in previous studies, because it is non-toxic, biodegradable and can be produced easily and cheaply. Ethaline 200 is the commercial name for the eutectic mixture formed by

mixing choline chloride with ethylene glycol as a hydrogen bond donor in a 1:2 molar ratio, respectively. This type of deep eutectic solvent has been used in the electrodeposition of several types of metal such as nickel,³⁴ copper,²¹ zinc,³⁵ tin³⁶ and zinc–tin alloys.³⁶

There is clearly a large literature on the use of brighteners in metal deposition and there are a wide range of compounds which have been studied. In this study a selection of brighteners were chosen which are known to function with the metals used in this study. It was shown by Juma³⁷ that aqueous additives also work in the same way in DESs. Boric acid is used in electrodeposition of nickel from aqueous solution and the author found that this enhances the Ni nucleation process.³⁸ Moreover, Hepel *et al.* studied the effect of boric acid on the electrodeposition of Co-Zn alloys, where they observed smooth and bright Co-Zn alloy coatings produced as a result of adding boric acid to the plating bath.³⁹ It was mentioned in the literature review that some additives such as ethylenediaminetetraacetic acid EDTA, boric acid, nicotinic acid and 5,5 dimethylhydantoin acted as a very effective brightener, producing highly uniform and smooth metal deposits.⁴⁰⁻⁴⁶ Supicova *et al.* studied the influence of boric acid on the electrochemical deposition of Ni. They found that boric acid inhibited Ni deposition and improved the brightness of the Ni layer.⁴¹ 5,5 dimethylhydantoin (DMH) was used as a complexing agent to produce bright gold coatings.⁴⁶ Recently, Pereira *et al.*⁴⁷ investigated the effects of EDTA on the electrodeposition of Zn-Sn alloy from Ethaline and Reline. They observed an increase in the current efficiency of the coating as a result of using EDTA as an additive. Juma *et al.*, studied the effect of nicotinic acid, methylnicotinate boric acid and 5,5-dimethylhydantoin on the electrodeposition of Ni-Cu from Ethaline.⁴⁸ They found bright Ni coatings were obtained when these additives were used. Therefore, it was suggested that the effects of these types of additives on the electrodeposition of different metals such as Zn, Co, Cu, Al and their alloys should be studied.

In this chapter, the electrodeposition of Cu from Ethaline 200 has been achieved at 80°C in the absence and presence of different types of additives. The novelty of this work consists of using ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), sodium iodide (NaI), boric acid (BA) and 5,5-dimethylhydantoin (DMH) as additives for the electrodeposition of Cu from Ethaline 200 (1:2 ChCl:EG-based liquid). Species of CuCl₂·2H₂O in Ethaline 200 with and without those additives have been investigated

using UV-Vis spectroscopy, and it has been shown that new Cu species were formed when EDTA and NaI were added to the Cu solution. Also, the physical properties (viscosity and conductivity) of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution in the absence and presence of these additives were studied; it was found that some of these additives affected the viscosity and conductivity of the Cu electrolyte. Moreover, the electrochemical properties of the Cu electrolyte have been studied using cyclic voltammetry (CV) and a quartz crystal microbalance (QCM). Clear differences were observed in the cyclic voltammetry of Cu in the presence of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ and NaI; furthermore, it has been shown that these additives increase the rate of Cu deposition, particularly NaI. The morphologies of Cu films have been examined using scanning electron microscopy (SEM). The nucleation mechanism of Cu deposits was investigated using chronoamperometry and atomic force microscopy (AFM) techniques. In addition, X-ray diffraction (XRD) was employed to identify the structure of the Cu films.

3.2 Aims and objectives of the work

Many researchers have studied the effects of additives electrodeposition of Cu from aqueous solutions. However, few studies have considered the role of additives in the electrodeposition of Cu from deep eutectic solvents. The research will study electrodeposition of Cu from Ethaline 200 at elevated temperatures using additives which function for copper in water e.g. ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) and boric acid (BA). These effect of these additives will be contrasted with two additives that work with Ni in DES; sodium iodide (NaI), and 5,5-dimethylhydantoin (DMH). The initial objective was to understand which additives are active in DESs, how they affect the physical properties of the solution and the mechanism by which they brighten the surface. Finally the properties of the copper film with different additives was characterised.

3.3 Results and discussion

3.3.1 Speciation

Commercial aqueous Cu plating solutions are generally operated by adding organic or inorganic additives to the plating bath; this can affect the speciation of the metal ion. This effect is especially relevant to Cu electrochemistry due to ligand exchange processes for Cu^{2+} . Here, UV-Vis spectroscopy has been used to identify species of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 in the absence and presence of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, NaI, BA and DMH. The UV-Vis spectra of 0.4 mM solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 in the absence and presence of different concentrations of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ (0.05, 0.10, 0.15, 0.20, 0.25 mM) were measured at 80°C, as shown in **Figure 3.1 (a)**. The colour of 0.40 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 was yellow in the absence of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$. However, the colour was observed to change gradually from yellow to yellowish green, and then green to blue, with increasing concentrations of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, as shown in **Figure 3.1 (b)**. The yellow colour indicates the presence of $[\text{CuCl}_4]^{2-}$ complexes in the solution.⁴⁹ The yellowish green and green colours could be assigned to a mixed of $[\text{Cu}(\text{EDTA})]^{2-}$ and $[\text{CuCl}_4]^{2-}$.^{49, 50} It is clear from **Figure 3.1 (a)** that the absorption spectra are active in two regions, the ultraviolet at ~300 nm, and the visible at ~410 nm. More specifically, in the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution without $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, two absorption maxima can be observed at 406 and 291 nm. These bands corresponded to the formation of $[\text{CuCl}_4]^{2-}$, which was subsequently established using EXAFS.^{21, 51} The intensity of the band that appeared at 406 nm gradually decreased with an increasing amount of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, which means that the concentration of $[\text{CuCl}_4]^{2-}$ species is steadily reduced.⁴⁹

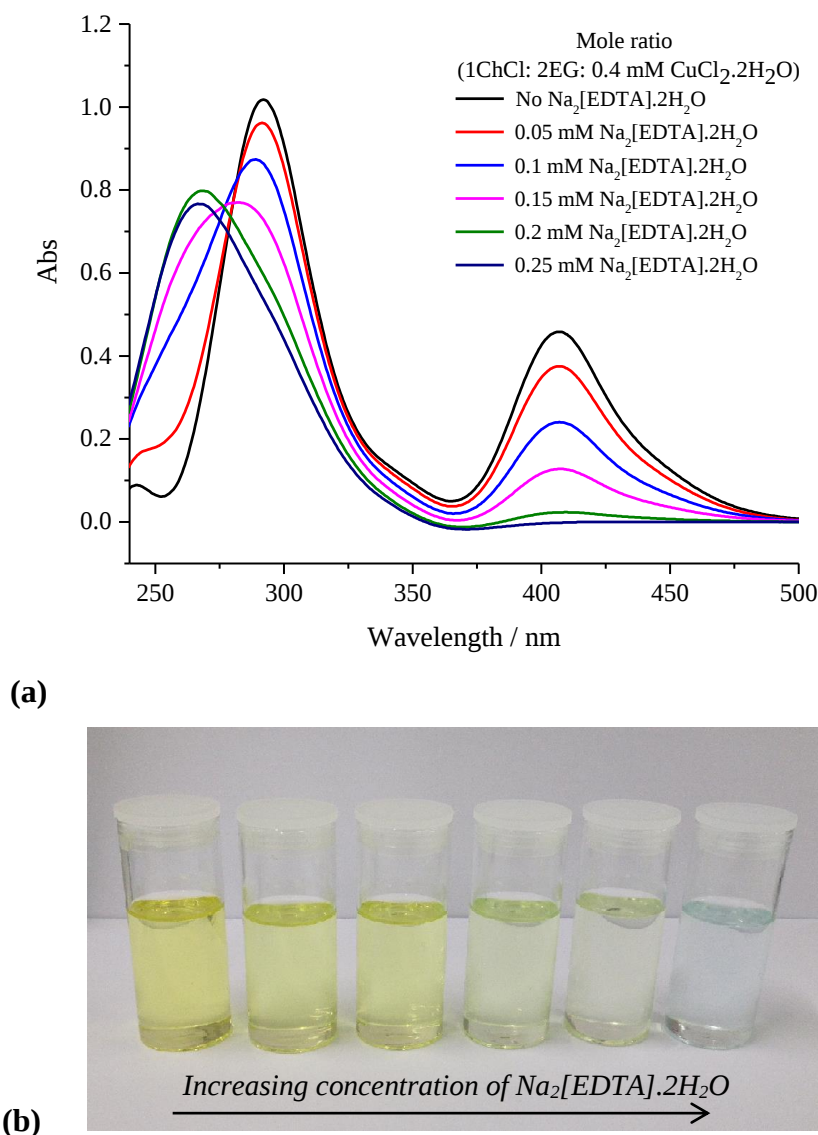


Figure 3.1(a) UV-Vis spectra of a 0.4 mM solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 with different concentrations of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ measured at 80°C ; **(b)** photographic images of the same solutions showing the concentration of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ dependant colour changes.

The intensity of the absorption band at 291 nm shifts towards the blue with an increasing concentration of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, with an attendant reduction in intensity. This can be interpreted as a reduction in the concentration of $[\text{CuCl}_4]^{2-}$ species as they react with EDTA. No isosbestic point can be seen in the UV-Vis spectrum. This means that it is unlikely there is a simple mechanism that transforms one complex directly to another.

Figure 3.2 shows the UV-Vis absorption spectra for 0.40 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 recorded in the absence and presence of different concentrations of NaI (1, 2, 3, 4, 5 mM). The absorption bands at 406 and 291 nm seen in **Figure 3.2** are due to the

$[\text{CuCl}_4]^{2-}$ species, as explained previously. When NaI was added to the Cu electrolyte, a new band appeared at 357 nm, associated with the formation of triiodide ions, I_3^- , in solution.^{52, 53} Cu^{II} is oxidising some of the I^- to form I_2 which is forming I_3^- (and/or I_2Cl^-).⁵³⁻⁵⁶ This band became clearer with increasing concentrations of NaI. The presence of I_3^- in the electrolyte produced two bands at 350 nm and at 288 nm^{52, 53}, as can be clearly seen in **Figure 3.2 (b)**.

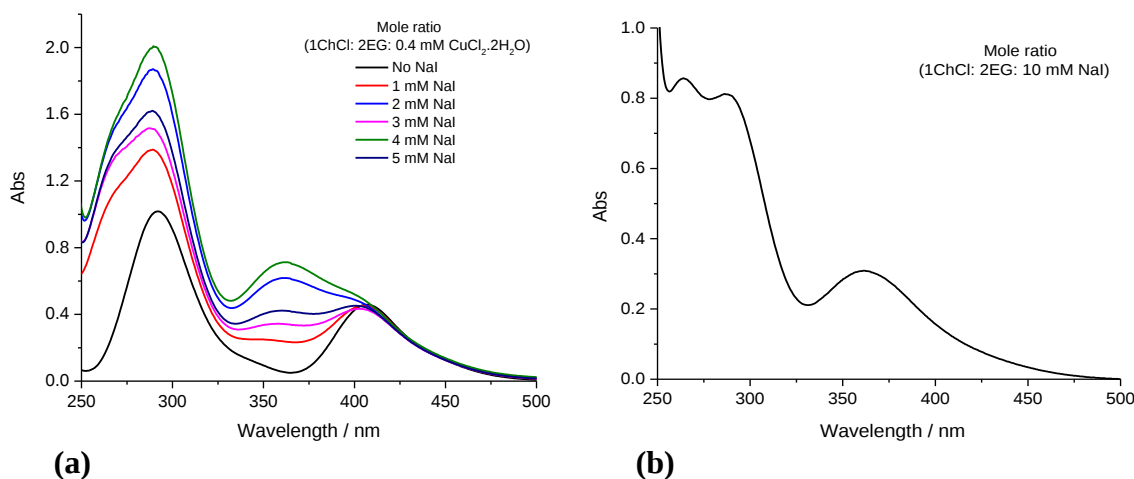


Figure 3.2 (a) UV-Vis spectra for 0.40 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 with different concentrations of NaI measured at 80°C; **(b)** UV-Vis spectra for 10 mM NaI in Ethaline 200 measured at 80°C.

The absorption spectra of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, NaI, BA, and DMH are shown in **Figure 3.3 (a)**. Two absorption bands can be seen in **Figure 3.3 (a)** for 0.40 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 at 406 and 291 nm. The colour of the solution is a good indication of metal ion speciation. No change in the colour of the Cu electrolyte was observed when BA and DMH were added. In addition, from **Figure 3.3 (a)**, it can be seen that there was no remarkable change in the absorption spectra of Cu when using BA and DMH. This indicates that these additives do not react with the Cu species present in Ethaline 200. As mentioned earlier, the absorption band at 406 nm disappeared when $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ was added to the Cu solution. A new band appeared at 357 nm as NaI was added, which corresponded to the formation of triiodide ions in solution.⁵³ Again, no isosbestic points can be seen in **Figure 3.2 (a)** or **Figure 3.3 (a)**. As will be discussed below, this could be due to the formation of secondary products that prevent the appearance of the isosbestic points.

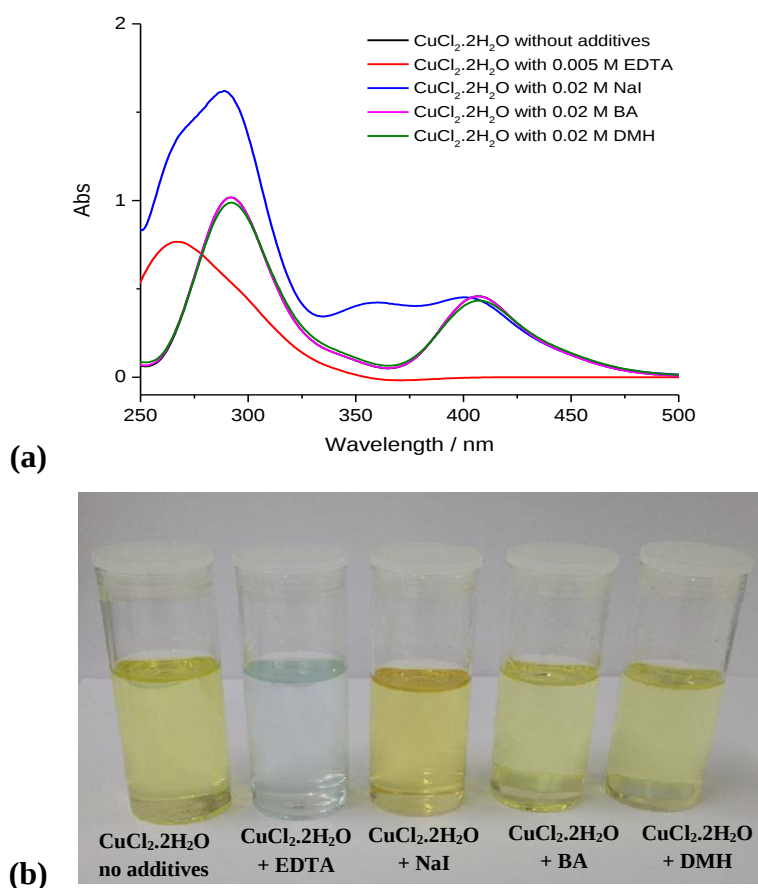


Figure 3.3(a) UV-Vis spectra for 0.40 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 with the following additives: $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, NaI, BA and DMH, all at 80°C; **(b)** photographic image of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 with different additives.

3.3.2 Physical properties

3.3.2.1 Viscosity

In the majority of ionic liquid electrodeposition studies to date, little attention has been given to the effects of addition of organic and inorganic compounds upon the physical properties of Ethaline 200. In the electroplating process, mass transport of the reactive material to the electrode surface can be directly affected by the viscosity of liquid. In this section, the viscosity of Cu in Ethaline 200 with and without additives has been investigated. The viscosities were measured using a Brookfield DV-E Viscometer fitted with a thermostatted jacket, where all measurements were achieved between 25-90 °C. A thermocouple was used to help control the temperature of the bath. **Figure 3.4** shows the viscosity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 as a function of temperature and the addition of different organic and inorganic additives. The additives were $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, NaI, BA and DMH.

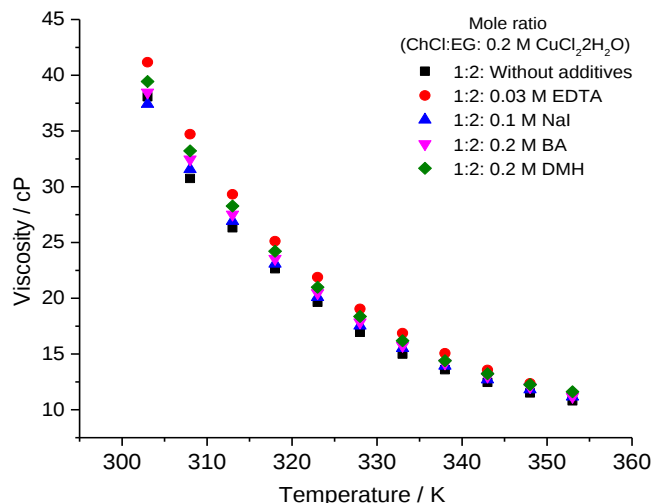


Figure 3.4 a) The viscosity of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 as a function of temperature and different additives

From **Figure 3.4**, it can be noticed that the additives have marginally increased the viscosity of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200. $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, BA and DMH can be considered to be hydrogen bond donors. The same trends were observed by Barron and Juma.^{37, 57}

3.3.2.2 Conductivity

In the electrodeposition of metals from ionic liquids, the conductivity of the plating electrolyte has a significant effect on coating properties, so it is important to study the conductivity of the coating electrolyte. **Figure 3.5** shows the conductivity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 as a function of temperature in the presence of the following additives: $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, NaI, BA and DMH. Here, the conductivity of the Cu solution was found to decrease in the presence of each of the additives with the exception of NaI, where a clear increase in the conductivity of the Cu electrolyte was observed. The same trends were observed by Barron and Juma. It should be noted that the additives do not significantly change mass transport in the DES so this method of brightening can be ignored.

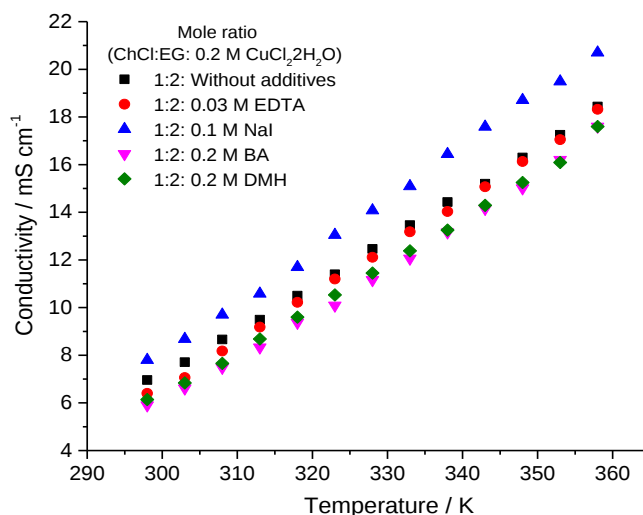


Figure 3.5 The conductivity of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 as a function of temperature and different additives;

3.3.3 Electrochemical properties

3.3.3.1 Voltammetry

Figure 3.6 shows the cyclic voltammograms recorded for 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 as a function of scan rate, where the voltammograms were recorded at 80°C using a 1.0 mm Pt disc electrode, a Pt flag counter-electrode and Ag/AgCl as the reference electrode. The cyclic voltammetry was performed from 1.0 V toward the negative direction to -1.0 V, and then reversed to the starting point. It is clear from the voltammograms that there are two distinct reduction processes, corresponding to the reversible Cu^{2+} to Cu^+ couple at +0.51 V, and the second process relating to the reduction of Cu^+ to Cu^0 at -0.33 V, in the process of which metallic copper is deposited on the electrode surface.^{58, 59} The reverse scan of the voltammogram shows two anodic stripping peaks at -0.3 V which are related to Cu dissolution (from Cu^0 to Cu^+) and the second oxidation peak, appearing at 0.38 V, corresponding to the reversible Cu^+ to Cu^{2+} .

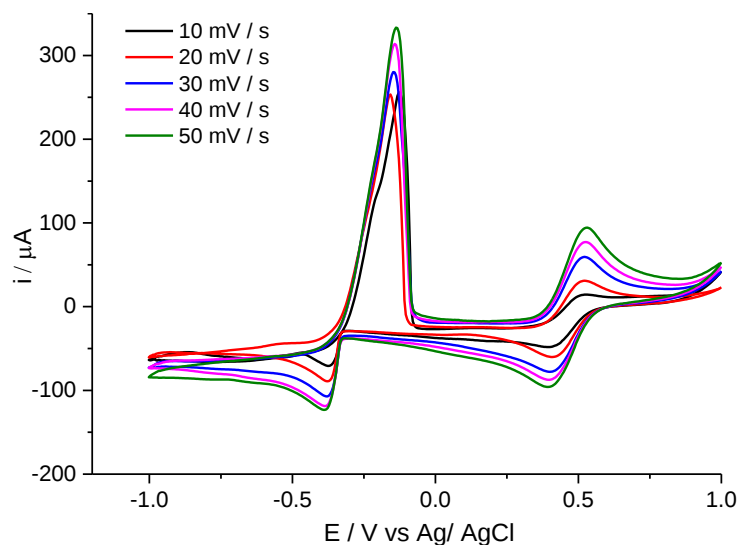


Figure 3.6 Cyclic voltammograms of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 as a function of sweep rate, at 80°C , using a Pt disc (1 mm diameter) electrode; a Pt flag was used as the counter-electrode, and Ag/AgCl as the reference electrode.

The data presented in **Figure 3.6** shows that the potential peak separation values of $\Delta E_p = 110$ mV are larger than might be expected for a one-electron Nernstian process, although the stripping and deposition peak current ratios are fundamentally independent of scan rate. However, the theoretical value of the deferent between the oxidation and reduction potentials (ΔE_p) at $T = 298$ K is 59 mV. The high value obtained for our system is due to resistive organic electrolytes, and it should be noted that the data shown in **Figure 3.6** did not measure the resistance of the solution.

The $\text{Cu}^{2+}/\text{Cu}^+$ couple seems reversible at a scan rate of 10 mV s^{-1} , where it was found that the ratio of anodic and cathodic currents for this redox couple (calculated from the data presented in **Figure 3.6**) is close to 1:1. This indicates that redox of Cu^{2+} to Cu^+ is reversible, and the electrode surfaces have remained free of any irreversibly-adhered materials, either by adsorption or under-potential deposition (upd).

Cyclic voltammetry was performed to investigate the electrochemical behavior of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at ambient and elevated temperatures. **Figure 3.7** demonstrates voltammograms of Cu solution at 80°C and at room temperature. There is an obvious decrease in the oxidation–reduction current peak when cyclic voltammetry is performed at room temperature. The viscosity and conductivity of the plating liquid are key parameters that affect the electrochemical processes, and these are mainly influenced by temperature. The viscosity of the IL depends on the free volume; therefore, high

temperature increases these volumes and this results in the increased movement of cations and anions in the liquid.^{4, 60} Thus, high temperature can accelerate the oxidation-reduction processes through increased mass transport towards the electrode surfaces.

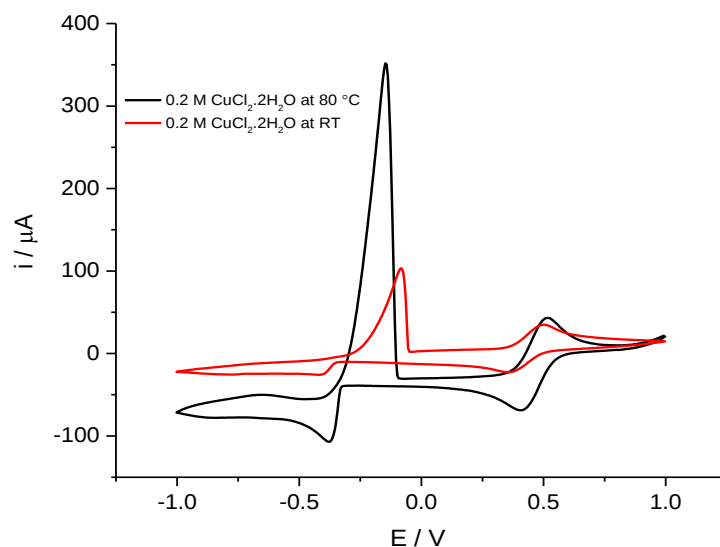


Figure 3.7 Cyclic voltammograms of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 at 80°C (black line) and at room temperature (red line), using a Pt disc (1 mm diameter) electrode; a Pt flag was used as the counter-electrode and Ag/AgCl as the reference electrode.

In addition, Cu reduction peaks were shifted anodically, as shown in **Figure 3.7**, when the process was run at 80°C. This could be due to the decrease in viscosity and IR ohmic drop due to increasing the temperature, causing the Cu^{2+} to deposit at a lower potential^{61, 62}, Cu electrodeposition could be inhibited in Ethaline 200 by the incorporation of chloride ions in the electrochemical double layer. High temperatures may work to reduce the specific adsorption of free chloride ions on the electrode surface and promoting the process of Cu reduction, where the concentration of $[\text{CuCl}_4]^{-2}$ will be increased at the electrode surface as the activity and mobility of chloride ions, Cl^- , is decreased.³⁵ Therefore, high temperature could result in reduced adsorption of choline cations on the electrode surface, and thus the rate of Cu deposition will increase.

3.3.3.2 Diffusion coefficients

Figure 3.8 (a) shows the CVs obtained for 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 using a Pt working electrode at room temperature and at different scan rates. The anodic and cathodic peaks' potentials did not change despite increasing the scan rate. The diffusion coefficient was calculated by plotting the reduction peak currents from the reversible $\text{Cu}^{2+}/\text{Cu}^+$ couple against the square root of scan rate, as shown in **Figure 3.8 (b)**. For a reversible electrode reaction, the diffusion coefficient D_0 of Cu^{2+} can be calculated using the Randles-Sevcik equation, **Equation 3.1**:

$$i_p = Kn^{\frac{3}{2}} AC D^{\frac{1}{2}} \nu^{\frac{1}{2}} \quad \text{Equation 3.1}$$

where:

$$K = 0.4463 \sqrt{\frac{F^3}{RT}}$$

I_p is the peak current in A, n is number of electrons, A is the area of electrode in cm^2 , C is the bulk concentration in mol cm^{-3} , D_0 is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, ν is the scan rate in V s^{-1} , F is the Faraday Constant in C mol^{-1} , R is the gas constant in $\text{J mol}^{-1} \text{K}^{-1}$, and T is the absolute temperature in K.⁶³ The slope has been calculated from **Figure 3.8 (b)** and, by applying the Randles-Sevcik equation (**Equation 3.1**), that D_0 for $\text{Cu}^{2+}/\text{Cu}^+$ in Ethaline 200 at room temperature was $3.73 \times 10^{-8} \text{ cm}^2 \text{s}^{-1}$. The value of D_0 was increased when the reversible $\text{Cu}^{2+}/\text{Cu}^+$ was performed at 80°C , being found at $1.66 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ (data taken from **Figure 3.8 (d)**). The value of D_0 calculated at 80°C is significantly larger than that determined at room temperature. The huge increase in D_0 at high temperature is not surprising due to the decrease in the viscosity of the Cu solution and the increased mobility of the charged species (i.e., an increased mass transport).

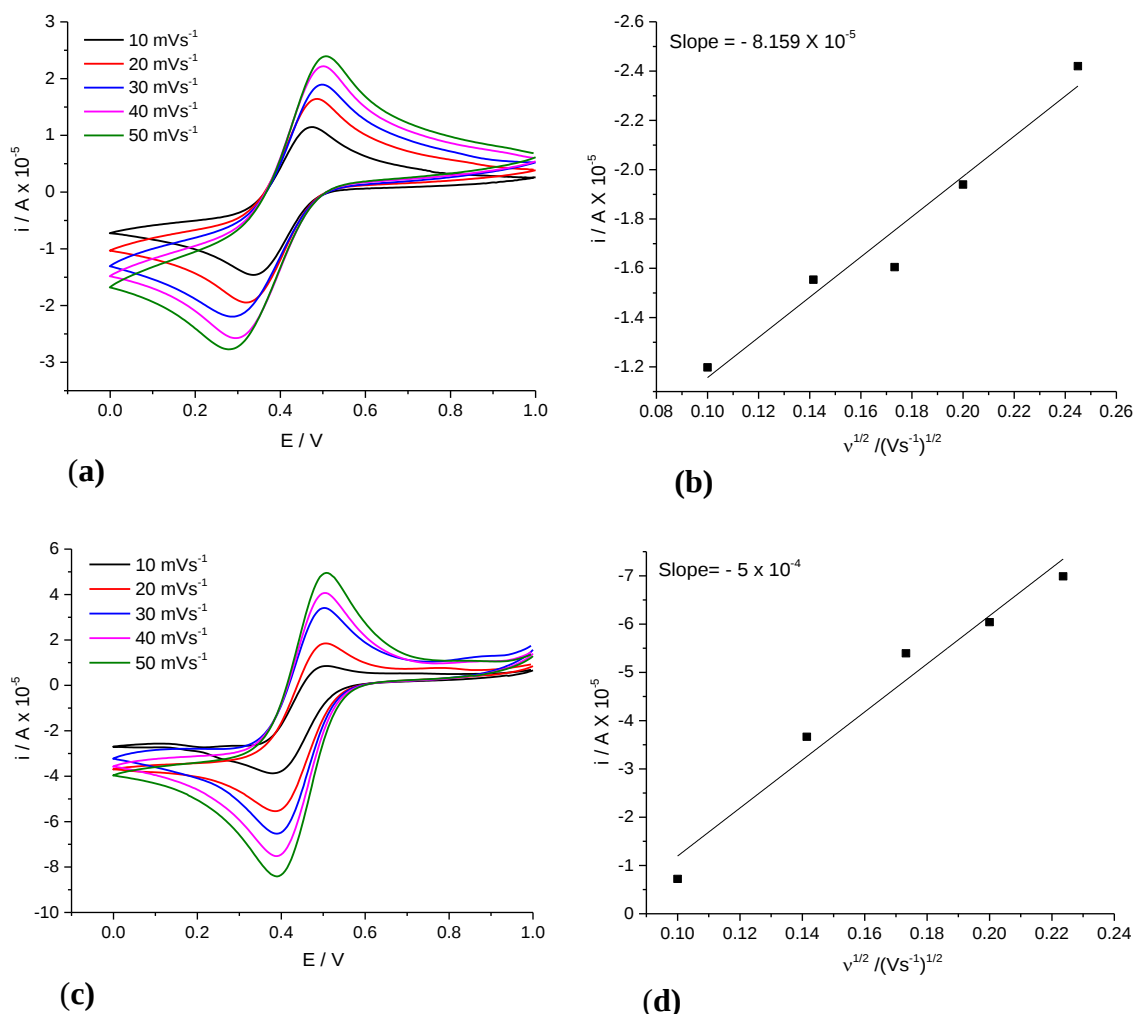


Figure 3.8 (a) and (c) Cyclic voltammograms of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 at room temperature and 80°C, respectively, (b) and (d) reduction current peaks for 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 as a function of the square root of scan rate at room temperature and 80°C, respectively. All experiments were achieved using a Pt electrode (1mm), with a Pt flag electrode as counter-electrode and an Ag/AgCl reference electrode.

3.3.3.3 Electrochemical of additives in Ethaline 200

Figure 3.9 shows the cyclic voltammetry of Ethaline 200 in the absence and presence of EDTA, NaI, BA and DMH at 80°C. It is clear that these additives have different electrochemical effects. The associated voltammograms have been recorded using a Pt disk electrode (vs. an Ag/AgCl reference) cycled from 1.2 V in the negative direction to -1.2 V, and then reversed to the positive potential.

In Figure 3.9 (a), the reduction peak that was obtained at about -0.9 V corresponds to the reduction of cationic species (Cat^+) in the Ethaline 200, while the oxidation peak

obtained at +1.1 V corresponds to the oxidation of chloride ions (anions) to molecular/gaseous chlorine,⁶⁴ as shown in the following reaction:



Furthermore, a small reduction wave can be seen at 0.0 V in the cyclic voltammogram of Ethaline 200, **Figure 3.9 (a)**, which corresponds to the reduction of H^+ cations to H_2 . The electrochemical potential window of ILs is mainly dependent on the resistance of the cation to reduction and the anion to oxidation. ILs normally have a potential window of more than 2.0 V. However, this window might be limited by the side reaction between the ILs and any impurities. For instance, water can decrease both the cathodic and the anodic potential windows.⁶⁵ **Figure 3.9 (b)** demonstrates the cyclic voltammetry of various concentrations of EDTA in Ethaline 200 on a Pt disk electrode at 80°C. Here, a peak is observed to start at -0.7 V, which can be attributed to the reduction of water contained in the EDTA salt; indeed, this peak was seen to increase in intensity with an increasing amount of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ in the Ethaline 200. The electrochemical behaviour of NaI in Ethaline 200 at 80°C was studied, and is shown in **Figure 3.9 (c)**. Cyclic voltammetry was performed from 0.0 V toward the positive direction until 0.7 V, and then reversed to the starting point (0.0 V). Two oxidation waves can be seen in the cyclic voltammograms of the NaI electrolyte. The first oxidation wave was observed at about 0.44 V, and corresponds to the oxidation of iodide to triiodide (**Equation 3.4**), while the second oxidation wave can be assigned to the dissociation of triiodide to iodine at 0.61 V (**Equation 3.5**).⁶⁶⁻⁶⁸



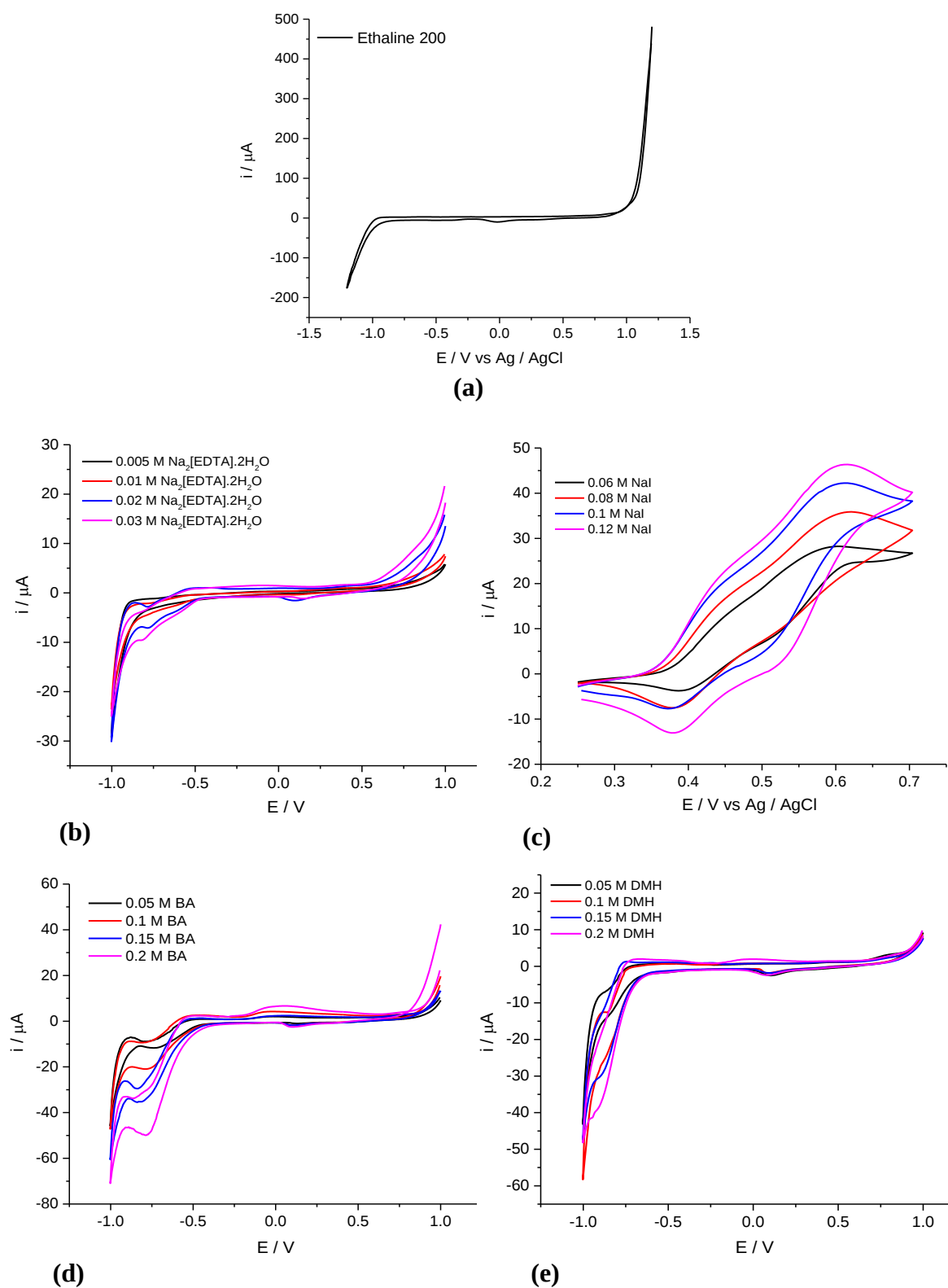


Figure 3.9 Cyclic voltammograms of organic / inorganic additives in Ethaline 200 measured at 80°C ; (a) Ethaline 200 without additives; (b) EDTA; (c) NaI; (d) BA; and (e) DMH.

Two reduction waves observed in the cyclic voltammograms of the NaI electrolyte, the wave at 0.53 V can be allocated to the reduction of iodine to triiodide, followed by reduction of the triiodide anion to iodide at 0.37 V.^{66, 68}

Cyclic voltammograms of BA in Ethaline 200 at 80°C are shown in **Figure 3.9 (d)**. The presence of BA in Ethaline 200 leads to free protons in solution, which is of particular relevance around the cathodic diffusion layer when potentials are of a magnitude where the reduction of water is possible. Therefore, for BA the range of potentials over which proton discharge is possible extends towards more negative potentials than one might normally expect.⁶⁹ As BA was introduced into the Ethaline 200, the onset potential for the cathode reaction with the BH was observed at -0.55 V, which corresponds to the dissociation of BA supplying an excess of protons. It is also clear that the current of this peak has been enhanced as a result of increasing the concentration of BA. Moreover, a shift in the BA dissociation peak was obtained with its increasing concentration; this was attributed to the adsorption of BA species on the electrode surfaces impeding the ability of other species to be reduced.

Figure 3.9 (e) demonstrates the influence of the addition of DMH on cyclic voltammograms of Ethaline. It can be observed that a clear change in the cathodic current and the onset potential of the cathodic reaction in Ethaline is -0.9 V, and this increases to -0.65 V with increasing amounts of DMH. It can be suggested that the DMH that could be adsorbing on the surface of cathode could then affect the nucleation mechanism and improve the morphology and brightness, as well as the adhesion, of the Cu deposition. This may be due to the modification to the double layer structures. The ionisation of DMH proceeds as follows:⁷⁰



Equation 3.6

3.3.3.4 Cyclic voltammetry of Cu²⁺ in the presence of additives

Figure 3.10 compares the cyclic voltammetric response of a solution of 0.2 M CuCl₂·2H₂O in Ethaline 200 at 80°C in the absence and presence of the following additives: (a) Na₂[EDTA]·2H₂O, (b) NaI, (c) BA and (d) DMH. **Figure 3.10 (a)** shows the cyclic voltammograms of 0.2 M CuCl₂·2H₂O in the absence and presence of 0.03 M Na₂[EDTA]·2H₂O at 80°C.

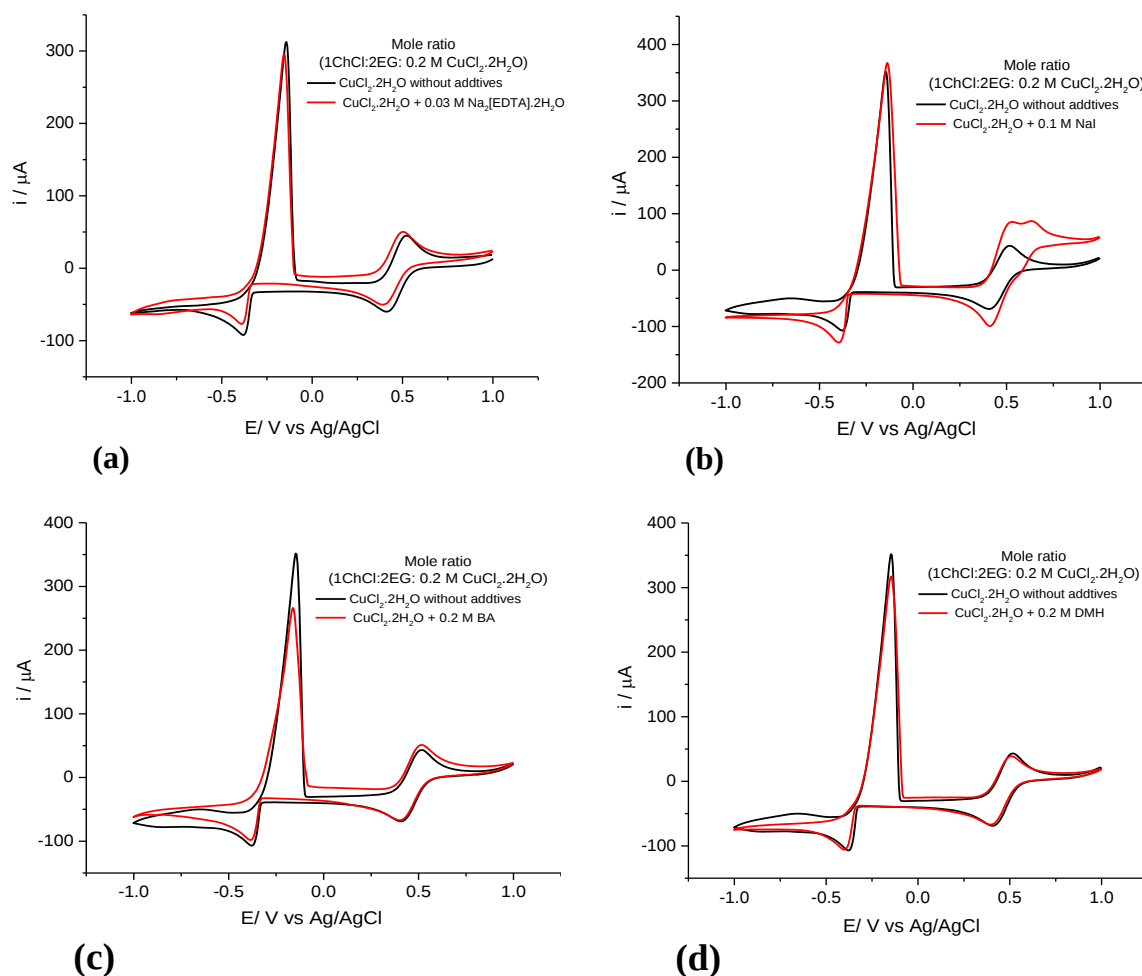


Figure 3.10 Cyclic voltammograms obtained for 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 with the following additives: **(a)** 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$; **(b)** 0.1M NaI; **(c)** 0.2 M BA; and **(d)** 0.2 M DMH. All experiments were performed using a Pt disk electrode (1mm), a Pt flag electrode as the counter-electrode and Ag/AgCl the reference electrode at 80°C and a scan rate of 30 mV s^{-1} .

The cyclic voltammetry was performed from 1.0 V towards the negative direction to -1.0 V, and then reversed to the starting point. As mentioned previously for **Figure 3.6**, the reduction that occurred at the positive potential was interrupted by the reduction of Cu^{2+} to Cu^+ , whilst the reduction observed at the negative potential corresponded to the electrodeposition of Cu^+ to Cu^0 . There is a clear lessening in the reduction current peaks of Cu when $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ is added to the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution, as shown in **Figure 3.10 (a)**. This type of additive can be presented as a complexing agent (ligand) that complexes to the Cu ions. The colour of the Cu electrolyte is changed from yellow-brown to dark green when this compound is added. From **Figure 3.10 (a)**, Cu deposition peaks were decreased and shifted cathodically when $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ is used because the Cu^{2+} is chelated by the EDTA. This results in the formation of a strong

complex of copper in solution, which was investigated by UV-Vis spectroscopy, as shown in **Figure 3.1**. As mentioned previously, $[\text{CuCl}_4]^{2-}$ is formed as a result of dissolution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200.⁵¹ However, the chloride ions can be replaced by $[\text{EDTA}]^{2-}$ when EDTA is added to the Cu electrolyte, which makes the Cu species more stable, and hence requires more energy to reduce. Consequently, the formation of this complex inhibits Cu electrodeposition and slows the associated reaction kinetics.^{71, 72} The morphology of the Cu deposit is also changed by this chelate, as will be discussed later.

Figure 3.10 (b) compares the cyclic voltammograms of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 at 80°C in both the absence and presence of 0.1 M of NaI. The shape of the voltammogram obtained in the presence of NaI was modified compared to the voltammogram recorded in its absence. The colour of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 was changed to a very dark red-brown colour when NaI was added, where this colour could be attributed to the formation of the triiodide ion.⁷³ **Figure 3.10 (b)** shows one oxidising peak is observed for Cu^{2+} at the positive potential in the system without additives, where this peak originates from the reduction of Cu^{2+} to Cu^+ . However, this peak is increased in intensity and a new peak appears at about 0.62 V when NaI is added to the Cu electrolyte. The increase in current peak may be due to the oxidation of both iodide to the triiodide ion and Cu^+ to Cu^{2+} at nearly same potential, while the new peak corresponds to the formation of iodine through the oxidation of the triiodide anion. Moreover, increases in the reduction peak of Cu^{2+} to Cu^+ have been obtained when NaI was used. This increase could also correspond to the reduction of triiodide and Cu^{2+} at the same potential.

It is clear from **Figure 3.10 (b)** that the reduction current peak of Cu that took place at a negative potential increased in the presence of NaI. Iodine can be produced by adding NaI to the Cu solution (as previously explained in **Figure 3.2**), where I_2 or the triiodide ion forms as a monolayer on the electrode surface. This layer prevents a passivation layer of Cu oxide from forming on the electrode surface.⁷⁴ In addition to surface passivation, iodine layers may have an additional benefit with respect to Cu electrodeposition, by acting as a surfactant to enhance conformal Cu growth.⁷⁴

Cyclic voltammograms of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with and without 0.2 M BA are shown in **Figure 3.10 (c)**. There is a slight decrease in the Cu deposition peak that occurs at negative potential in the presence of BA, where this decrease is due to the adsorption of BA onto the electrode surface, inhibiting Cu deposition.^{75, 76} **Figure 3.10 (c)** also shows

that the anodic process for Cu that occurred at negative potential was reduced by 100 μA in the presence of BA. This indicates that, as a consequence of adsorption of BA onto the surface of the electrode, the nucleation of the metal growth mechanisms is affected, which hinders the stripping peak.

The last type of additive used in electrodeposition of Cu in this project was DMH, for which there was no significant change that could be observed in the shape and position of the Cu redox peaks, as per **Figure 3.10 (d)** which illustrates the effects of addition of 0.2 M DMH to the Cu solution. However, the Cu reduction peak (Cu^+ to Cu^0) is shifted cathodically by 25 mV. It was concluded from the UV-Vis spectra (**Figure 3.3**) that DMH did not complex with the Cu ion. Therefore, one might suggest that DMH adsorbs on the on the active sites of the electrode surfaces and impedes the deposition of Cu. DMH and BA can be adsorbed on the electrode surface through their ion pair formation; furthermore, molecules of these compounds can be adsorbed in different orientations, as shown in **Figure 3.11**, depending on the concentrations of the additives.

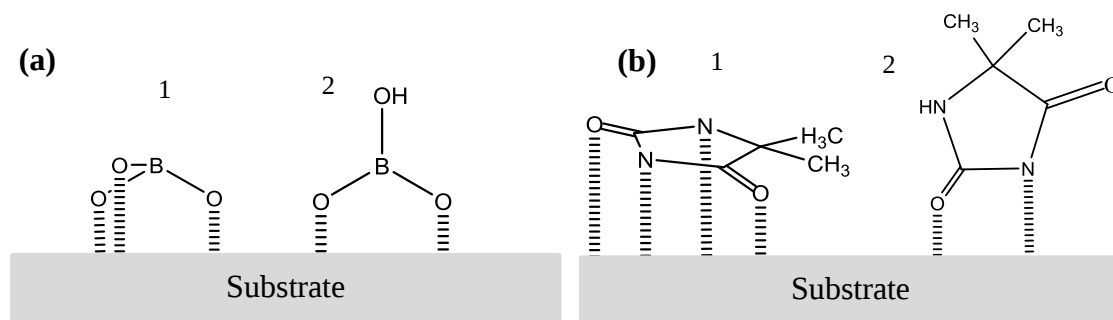


Figure 3.11 The orientation and probability of molecular adsorption of **(a)** BA; and **(b)** DMH on the metal surface by ion pair formation.

3.3.3.5 Chronoamperometry

Chronoamperometry is one of a number of methods that have been used to study the nucleation mechanism that leads to the electrodeposition of metals. Nucleation mechanisms of Cu electrodeposition from 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 have been investigated by using the chronoamperometry method; deposition was achieved at 80°C and on a polished Pt disk. This study achieved the electrodeposition of Cu in both the absence and presence of organic and inorganic additives, with the aim of examining the influence of these additives on the nucleation of Cu from Ethaline 200 as a deep eutectic solvent. The additives that were used were the same as those discussed in the previous

section ($\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$, NaI, DMH and BA). The applied potential for the nucleation study was -0.4 V, where this potential is the highest current voltage which was observed for reduction of Cu^+ to Cu^0 (which was taken from data shown in **Figure 3.10**). Scharifker and Hills have suggested a theoretical model to investigate nucleation of metals from both aqueous solution and ionic liquids.⁷⁷ This model assumes that nucleation can take place at certain sites on the surface. Chronoamperometric data were analysed by plotting current and time for three-dimensional nucleation, and nucleation mechanism have been classified as *instantaneous* or *progressive*.⁷⁸ According to the Scharifker and Hills model, instantaneous nucleation follows **Equation 3.7** and progressive nucleation follows **Equation 3.8**⁷⁸

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.9542}{\frac{t}{t_m}} \left\{1 - \exp\left[-1.2654 \left(\frac{t}{t_m}\right)\right]\right\}^2 \quad \text{Equation 3.7 (Instantaneous)}$$

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.2254}{\frac{t}{t_m}} \left\{1 - \exp\left[-2.3367 \left(\frac{t}{t_m}\right)\right]\right\}^2 \quad \text{Equation 3.8 (Progressive)}$$

Here, i is current, t is time, i_m is the maximum current and t_m is the time at which the maximum current occurs. The $i(m)$ and $t(m)$ values refer to the current and time coordinates of the nucleation feature in the current-time trace, where these points are shown in **Figure 3.12 (c)**.

When the nucleation rate is fast compared to the resultant rate of growth, the nuclei at all sites on the surface form over a short timescale, in which case the nucleation is referred to as instantaneous. However, if the rate of nucleation is slower than the growth rate, nucleation will occur at the surface while prior nucleation centres continue to grow, in which case the nucleation is referred to as being progressive.⁷⁷

Figure 3.12 shows the experimental i - t curves with the theoretical models for three-dimensional instantaneous and progressive nucleation for Cu deposited from Ethaline 200 at 80°C (a) without additives and (b) with $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$, (c) with NaI, (d) with BA and (e) with DMH.

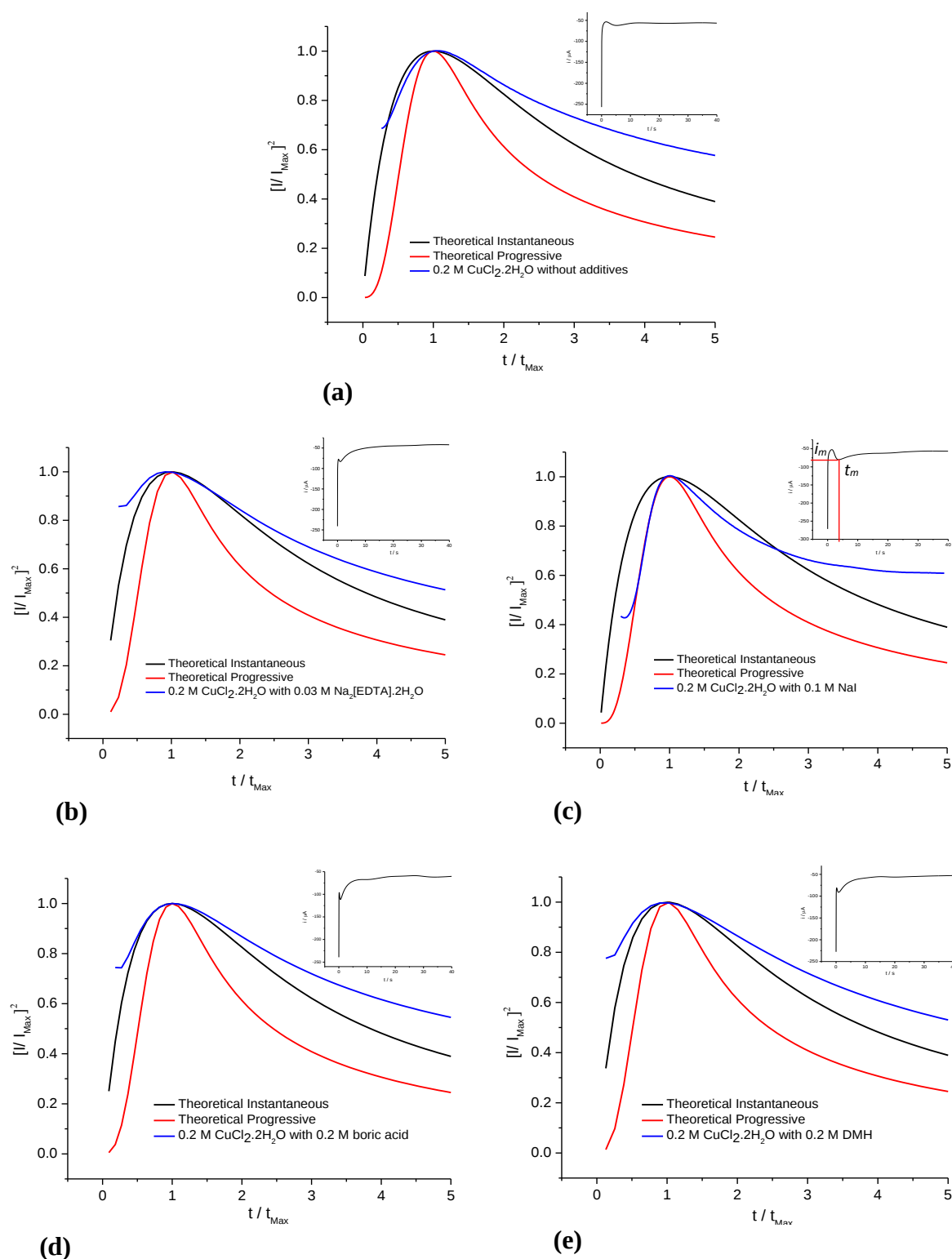


Figure 3.12 The experimental i - t data for electrodeposition of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ from Ethaline 200 on a Pt disc (1 mm dia.) at 80°C vs. an Ag/AgCl reference electrode for (a) 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 in the absence of additives; (b) 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, (c) 0.1 M NaI, (d) 0.2 M BA and (e) 0.2 M DMH. The applied potential was -0.4 V for all experiments.

Figure 3.12 (a) shows the experimental chronoamperometry data for 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 without additives. As a potential is applied, the current raises to a current maximum, and then the nucleation process was observed. The increase in current is indicative of the formation and growth of nuclei. It was found that the nucleation mechanism of Cu deposition from an additive-free electrolyte is fitted to the three-dimensional instantaneous nucleation mechanism.

The results presented in the cyclic voltammetry section suggest that there is a difference in the nucleation mechanism of Cu from Ethaline 200 in the presence of these additives. However, no change can be seen in the nucleation mechanism of Cu deposition from Ethaline 200 in the presence of $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, BA and DMH. The nucleation mechanisms of Cu deposition with these additives fitted well to the three-dimensional instantaneous nucleation mechanism, as shown in **Figures 3.12 (b), (d) and (e)**. However, the nucleation mechanism of the Cu deposition was more in accord with the three-dimensional progressive mechanism when NaI was added to the system, as shown by **Figure 3.12 (c)**. It can be seen that in the presence of 0.1 M NaI, nucleation was initially fitted to the progressive mechanism; however, the nucleation of the Cu subsequently changed to better fit the instantaneous mechanism. This may be as per the explanation given in the cyclic voltammetry section in **Figure 3.10 (b)**, in that adding NaI to the Cu electrolyte leads to the production of the triiodide ion, I_3^- , in solution, and a monolayer of iodine or triiodide ion may form on the electrode surface, and in acting as a surfactant it may then enhance Cu growth.⁷⁴ This is possible because of an increase in Cu deposition rate and thus an increase in the thickness of the coating. Where this happens, the rate of Cu deposition will be significantly increased, which will be demonstrated later in the gravimetric analysis section when using the QCM technique. Moreover, the thickness of the Cu deposit was increased when NaI is used in the electrodeposition of Cu; this will also be explained later.

3.3.3.6 Gravimetric analysis

Sodium iodine and $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$ as additives have been shown to have a marked effect on the speciation, physical properties and cyclic voltammetric response of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ containing Ethaline 200 DESs. In addition to electrochemical methods (cyclic voltammetry and chronoamperometry), the Electrochemical Quartz Crystal Microbalance (EQCM) technique can be used to study the effect of these additives on

the rate of Cu deposition from Ethaline 200. This technique was described in detail in **Chapter 2**, but in summary uses a resonant quartz crystal, coated with gold on one side and platinum on the other. The experimental cell design is shown schematically in **Figure 3.13**.

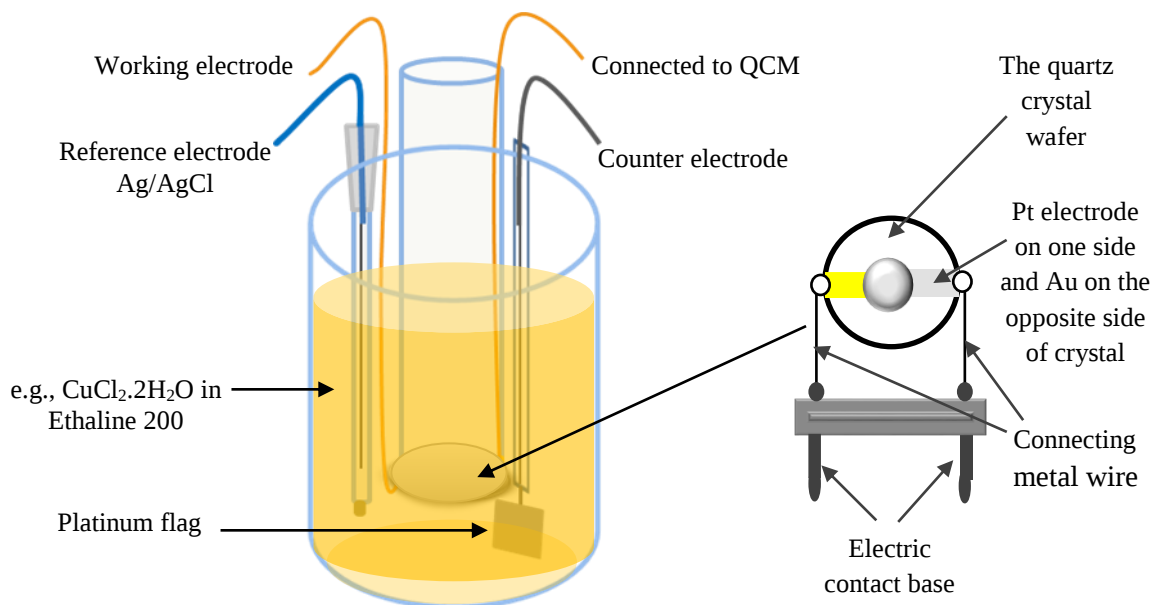


Figure 3.13 Schematic representation of the cell used in electrochemical gravimetric analysis experiments showing the three electrodes, the quartz crystal as a working electrode, the platinum flag as a counter-electrode and Ag/AgCl as the reference electrode.

This cell was immersed in the Cu solution in order to be used as a mass probe for electrolytic deposition of the Cu.^{79, 80} The Pt face of the crystal was left in contact with the liquid interface whilst the Au face was left exposed to air. The consequent change in resonant frequency of the quartz crystal corresponds to the mass of Cu deposited. The change in the resonance frequency of the quartz crystal is linearly related to the mass change, as shown by the Sauerbrey equation (**Equation 3.9**).⁸¹

$$\Delta f = \frac{-2f_0^2}{A\sqrt{\rho_0\mu_0}} \Delta m \quad \text{Equation 3.9}$$

where Δf is the frequency change in Hz, f_0 is the resonant frequency in Hz, A is the piezoelectrically active surface area in cm^2 , ρ_0 is the density of quartz in g cm^{-3} , μ_0 is the shear modulus of quartz for an AT-cut quartz crystal in $\text{g cm}^{-1} \text{s}^{-2}$ and Δm is the change

in mass in ng. For a 10 MHz AT-cut quartz crystal, the Sauerbrey equation simplifies to give $\Delta f = -1.1\Delta m$.⁸¹

The experiment was run by first measuring the resonance of the dry crystal, followed by immersing the quartz crystal as the working electrode, a Pt flag as the counter electrode, and Ag/AgCl reference electrodes in the Cu plating solution.

Figure 3.14 shows the mass-charge plot for the Cu electrolyte with different concentrations of additives at -0.4 V (which is the same potential that was selected for the chronoamperometric experiments shown in **Figure 3.12**). It can be seen that NaI has a significant effect upon the electrodeposition of Cu, as shown in **Figure 3.14**. The deposition of Cu was enhanced by adding NaI to the plating bath. It was discussed earlier that adding NaI to the Cu system caused a change in the speciation of Cu and caused iodine to be formed in solution. Iodine has the ability to prevent the formation of a passivation layer on electrode surface. Thus leading to an increased rate of Cu deposition. Furthermore, the presence of iodine in the solution can enhance the rate of Cu deposition.⁷⁴

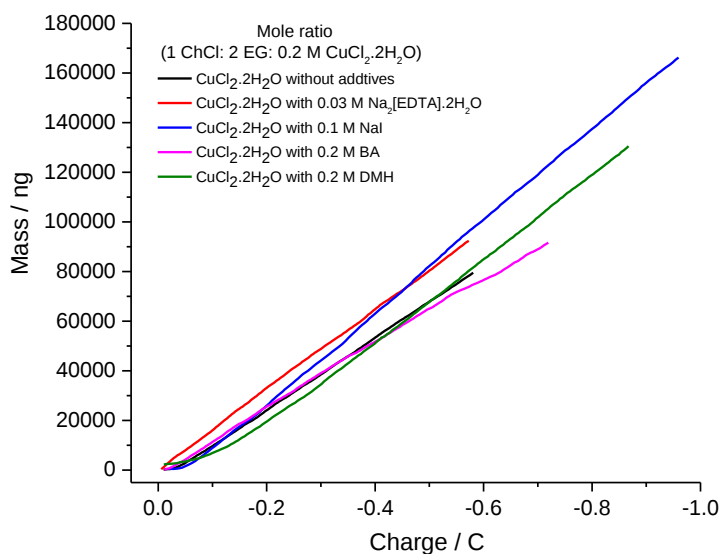


Figure 3.14 Mass-Charge traces for the potentiostatic electrodeposition of Cu from 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 with the following organic additives: 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, 0.1M NaI, 0.2 M BA and 0.2 M DMH. In each experiment, the applied potential was -0.4 V (vs. Ag /AgCl) at 80°C.

No significant change was observed in the amount of Cu deposited when BA was added to the Cu liquid. However, the surprising thing was the increase in the mass of Cu deposited when EDTA was added to the plating bath, as shown in **Figure 3.14**, whereas

according to the cyclic voltammetry of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with EDTA, **Figure 3.10 (a)**, deposition of Cu is reduced, and is slower, than deposition in the system without additives. Therefore, the increase in the mass of Cu deposition using EDTA as an additive could correspond to the incorporation of EDTA molecules with the deposition of Cu. This leads to an increased rate of mass deposition on the resonating crystal, which then causes a change to its resonant frequency. In addition, co-deposition of EDTA with Cu can increase the thickness of the Cu coating, as will be explained in the next section by measuring the thickness of the Cu deposit using SEM. The mass of Cu deposited has also been enhanced as a result of adding DMH to the Cu bath; here also, the increase in Cu mass corresponds to the co-deposition of DMH with Cu.

Furthermore, the mass-time plot for Cu deposition is shown in **Figure 3.15**. Gravimetric EQCM experiments were carried out on $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 in both the absence and presence of the same four organic and inorganic additives at 80°C and applying a potential of -0.4 V vs. Ag/AgCl . There is no significant change in the results shown in **Figure 3.15** compared with those of **Figure 3.14**. As explained above, the rate of Cu deposition was increased by adding these additives separately to the Cu liquid. NaI as an additive caused a significant increase in the rate of Cu deposition, as seen in **Figure 3.15**, for the reasons explained previously.

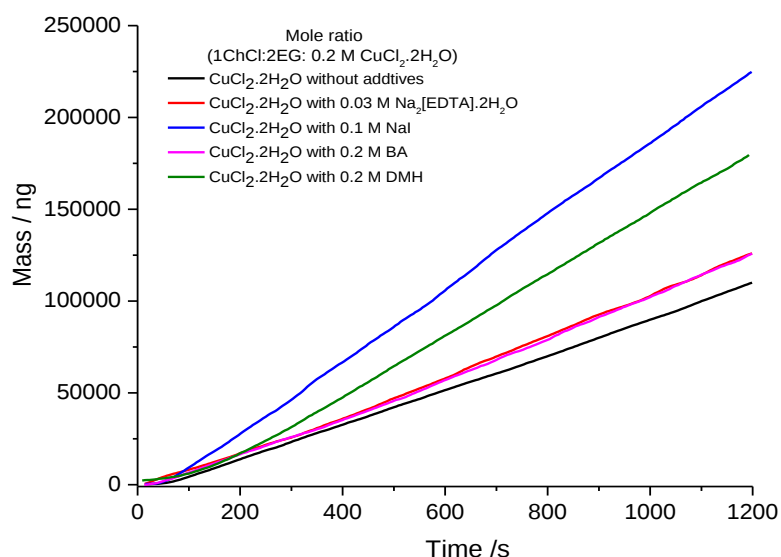


Figure 3.15 Mass-Time traces for the potentiostatic electrodeposition of Cu from 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a $1:2$ $\text{ChCl}:\text{EG}$ -based liquid with the following organic and inorganic additives: 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, 0.1 M NaI , 0.2 M BA and 0.2 M DMH . In each experiment the applied potential was -0.4 V (vs. Ag/AgCl) at 80°C .

DMH has the effect on the mass of Cu deposited as illustrated in **Figure 3.15**, where the use of DMH increased the rate of Cu deposition from Ethaline 200. DMH did not complex the Cu ion, as shown in the speciation panel of **Figure 3.3**, thus it can be said that DMH adsorbs on the electrode surface and incorporates with the deposition of Cu, leading to an increased rate of deposition and thickness of coating. This type of additive can be adsorbed on the surface of the electrode by electron pair formation, which blocks the active site of the electrode surface and then either incorporates into the Cu deposition or increases the current density of the Cu deposition. In the electrodeposition process, some additives can be adsorbed on the high points of the electrode surface and then block these points.⁸² Thus, the deposition of the metal cannot take place on the points occupied by molecules of the additives. At these points, the thickness of the diffusion layer is less than in the recesses, and thus additive molecules will be transported faster. Consequently, adsorption of additives in the recesses will be reduced. Therefore, the metals tend to deposit in the recesses of the electrode surface because the current density at these points is higher than the current density at the peaks; **Figure 3.16** may be considered a simple illustration for processing the adsorption of DMH on the electrode surface. Therefore, adsorption of additives on the cathode surface leads to an increase in the rate of metal deposition.^{83, 84}

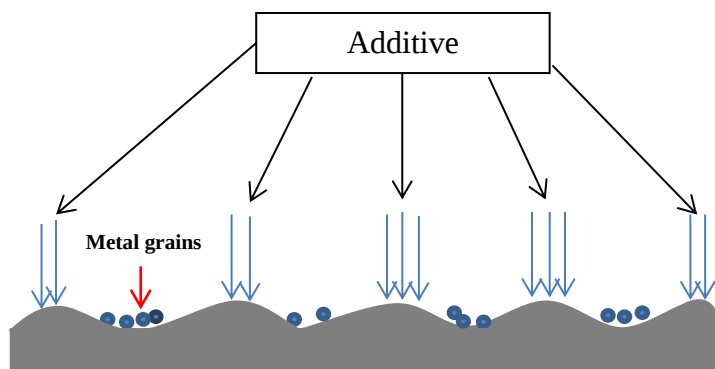


Figure 3.16 Adsorption of organic agents (additives) at active sites on the surface of the electrode.

The same occurred when BA was added to the Cu plating bath. BA can also be adsorbed on the electrode surface since it does not change species or form a complex with the Cu^{2+} ions. Therefore, BA could also increase the current density of Cu deposition and incorporate into the Cu deposition, consequently enhancing the rate of Cu deposition observed. However, the increase in mass of Cu when using BA was less

than the mass of Cu that was deposited using DMH. This is due to the structural differences between BA and DMH, as per **Figure 3.17**. For example, the molecular size of DMH is greater than that of BA, so adsorption of DMH on the electrode surface will result in a larger change in the frequency of the quartz crystal than that due to the adsorption of BA. In addition, incorporation of DMH with Cu deposition may increase the thickness of the Cu deposit more than that of BA.^{83, 85, 86} Rogers *et al.*⁸⁶ studied the electrodeposition of Ni using thiourea as an additive, where they reported that the thiourea can be adsorbed on the electrode and incorporated with the Ni deposit. A number of investigators have confirmed that additives have indeed been reduced on the cathode.⁸⁷

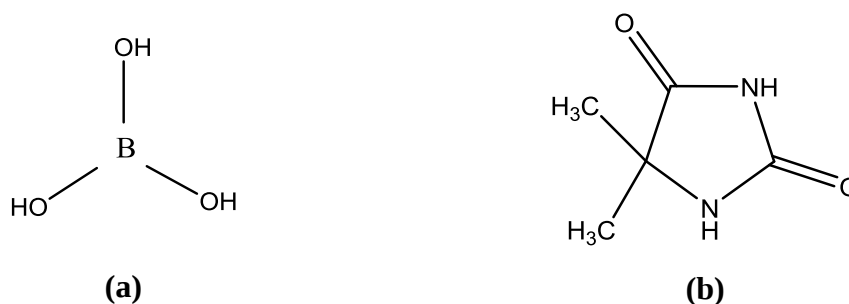


Figure 3.17 (a) Structures of boric acid (BA) and **(b)** 5,5-dimethylhydantoin (DMH).

3.3.4 Surface analysis

3.3.4.1 Morphology of Cu deposits achieved at low and high temperatures

The morphology of metal deposits has been investigated by the scanning electron microscopy (SEM) technique. **Figure 3.18** shows the comparison between the morphologies of Cu film deposited from Ethaline 200 containing 0.2 M CuCl₂·2H₂O at room temperature and at 80°C, where both electrodepositions were achieved on a mild steel substrate for 1 h and at a current density of 2.5 mA cm⁻². Cracks can be seen in the morphology of the Cu deposit when the electrodeposition is performed at room temperature, which are clear in **Figure 3.18 (a)**; also, the colour of the Cu coating was dark compared to the colour of the Cu deposit achieved at 80°C. This is the result of several factors: firstly, the high viscosity of the plating liquid at room temperature obstructs the movement of species toward the cathode, leading to the production of hydrogen bubbles on the cathode surface; these bubbles play a key role in the formation of cracks in the deposit. Secondly, the larger concentrations of Cl⁻ anions in the solution

may result in its specially preferential adsorption on the electrode surface at room temperature, effectively inhibiting the approach of $[\text{CuCl}_4]^{-2}$ to the electrode surface, leading to a decreased rate of Cu deposition and thus decreasing the current efficiency.³⁵

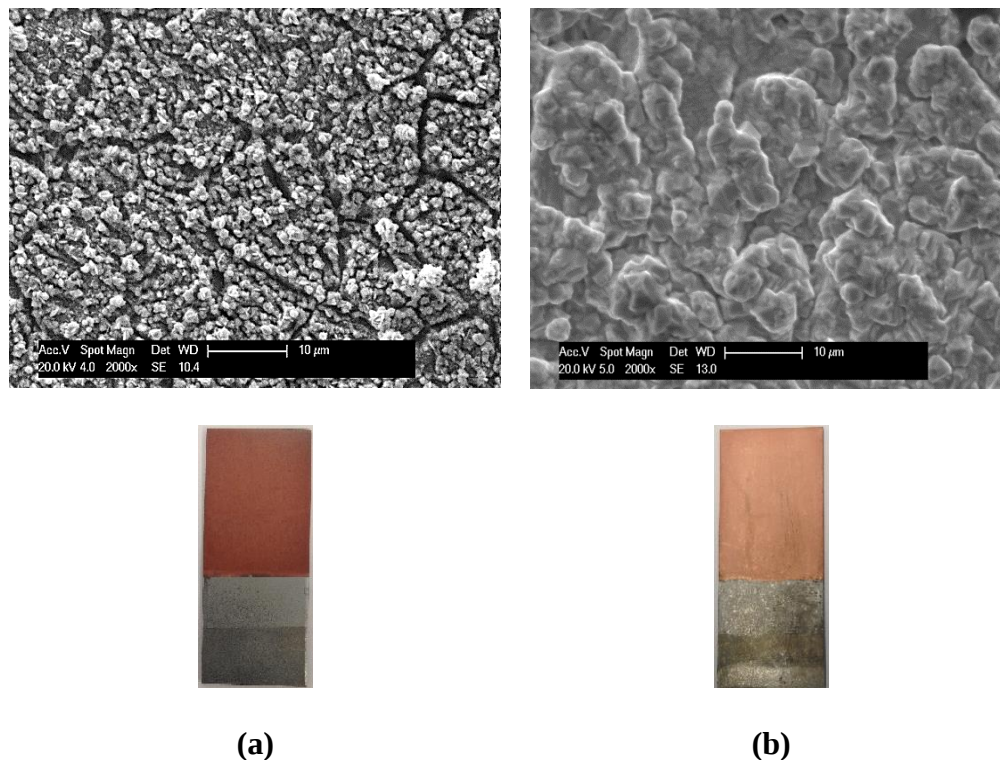


Figure 3.18 SEM images for samples electrodeposited from 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 systems **(a)** at room temperature and **(b)** at 80 °C (both samples were achieved on a mild steel electrode and at an applied current density of 2.5 mA cm^{-2} for 1 h (sample width 2 cm)).

As discussed previously, higher temperatures strongly affect the physical properties of the plating electrolyte (i.e., viscosity and conductivity; see **Figure 3.4** and **Figure 3.5**). Increasing the temperature of the Cu plating bath results in a decrease in the viscosity of the electrolyte, increasing the diffusion rate/mass transport of Cu species toward the electrode surface (see **Figure 3.8**), where this consequently enhances the rate of Cu deposition. In addition, electrodeposition of Cu from Ethaline 200 at high temperature may reduce the preferential incorporation of Cl^- into the double layer at the cathodic potentials, leading to an increase in concentration of $[\text{CuCl}_4]^{-2}$ at the cathode. This results in an increase in deposition of Cu and improves the morphology that can be obtained.

3.3.4.2 Effect of additives on the morphology of the Cu deposit

Figure 3.19 demonstrates the SEM, cross-sectional and optical images for electrodeposition of 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ from Ethaline 200 at 80°C using various types of organic/inorganic additives. The experiments with additives used a mild steel substrate at current a density of 2.5 mA cm^{-2} for 1 h. The four additives used were: 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, 0.1 M NaI, 0.2 M BA and 0.2 M DMH. From **Figure 3.19**, extreme changes in the morphology of the Cu deposit were observed when additives were included in the Cu plating bath.

Morphologies of Cu deposits obtained from the Cu bath without additive and from a bath containing EDTA are shown in **Figures 3.19 (a)** and **(b)**, respectively. No obvious changes can be seen in the nucleation mechanisms of Cu electrodeposition from the systems with and without additives (as shown previously in **Figure 3.12 (a)** and **(b)** by using the chronoamperometry method). However, considerable changes occurred to the morphology of the Cu deposit as a result of adding EDTA to the Cu electrolyte, as can be clearly seen in **Figure 3.19 (b)**. Different sized Cu particles can be seen in the morphology of the Cu film obtained from a Cu electrolyte containing EDTA. The change in the morphologies of the Cu deposits is due to the slow electroplating kinetics resulting from the presence of EDTA.⁷²

The addition of NaI, **Figure 3.19 (c)**, has a marked effect on the morphology of the Cu deposition, where Cu crystals have clearly been obtained; also, a bright Cu film was produced. This is because, as explained previously, the triiodide ion, I_3^- , is produced in the Cu solution as a later consequence of adding NaI.

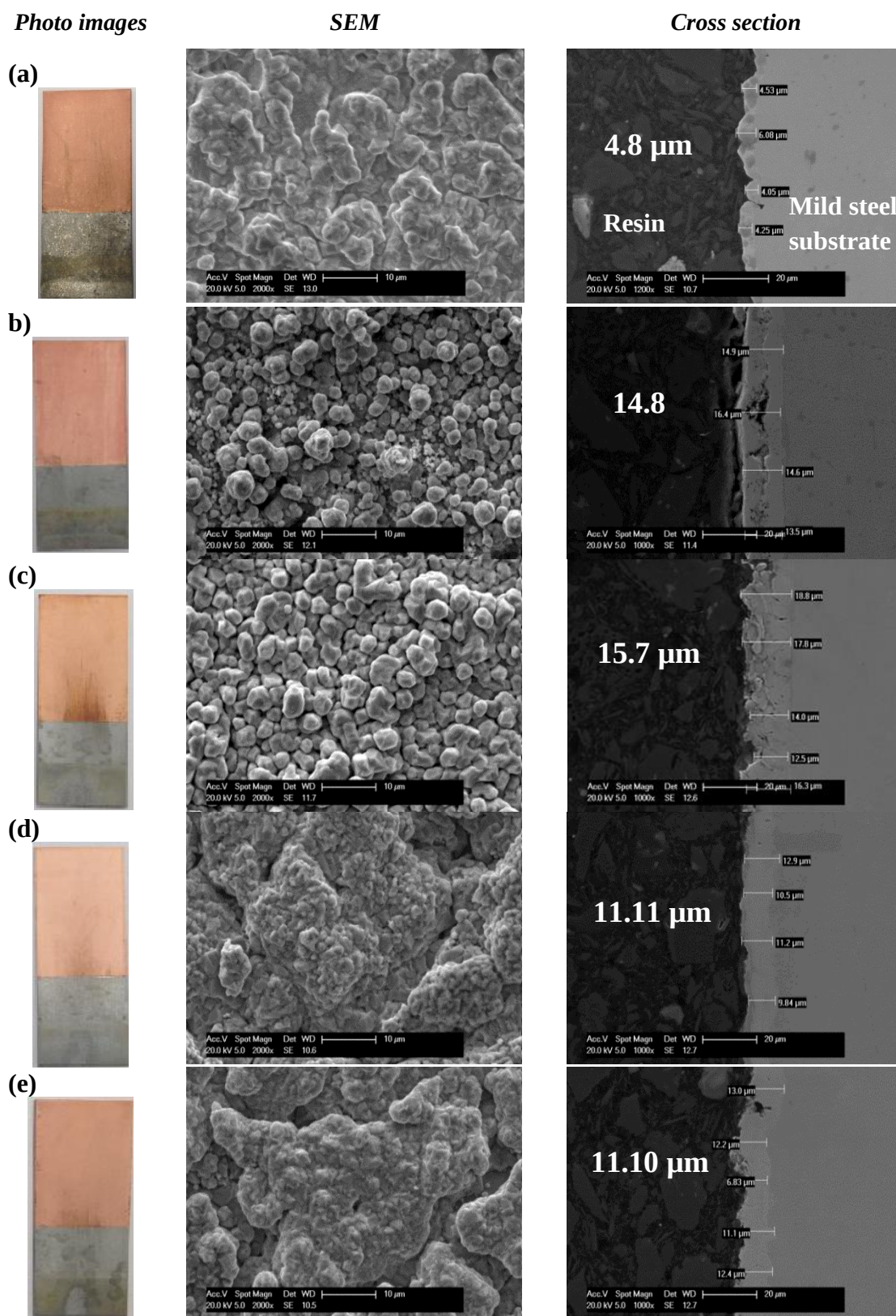


Figure 3.19 SEM images with cross-sections showing samples electrodeposited from 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 systems in the absence and presence of additives: (a) without additives; (b) 0.03 M EDTA; (c) 0.1 M NaI; (d) 0.2 M BH; and (e) 0.2 M DMH. (all experiments were achieved at 80°C for 1 h on a mild steel electrode (width 2cm) at an applied current density of 2.5 mA cm^{-2} (sample width 2 cm)).

Some researchers have suggested that the triiodide ion or iodine can be adsorbed onto the electrode surface and prevent the formation of a passivation layer⁷⁴ on the cathode substrate, leading to an increase in the rate of deposition and causing changes in the morphology. Moreover, the triiodide ion monolayer can help protect these surfaces from oxidation and contamination under ambient conditions.⁷⁴ These iodine/triiodide ion adlayers, in addition to such surface passivation effects, may also act as surfactants, enhancing conformal Cu growth,^{74, 88} though this would require that the iodine adatoms adsorbed at the electrode surface are not subsequently buried as the Cu is deposited, but instead remain at the electrode surface. This effect has been seen for Cu underpotential deposition on various electrodes.^{74, 89} Adding NaI to the Cu bath caused an increase in conductivity (**Figure 3.5**) and also formed iodine in solution that accelerated and stimulated the oxidation and reduction processes, leading to an increase in the thickness of the Cu film (to 15.8 μm).

A bright Cu film was also obtained when BA and DMH were added to the system, as shown in **Figures 3.19 (d) and (e)**, respectively. It can be seen that the morphology of the Cu deposit was changed when DMH was added to the Cu bath. DMH is a relatively strong hydrogen bond donor and will effectively coordinate to the chloride anions in solution, leading to a reduction in chloride adsorption on the electrode surface and a consequent enhances the growth of Cu; furthermore, DMH may adsorb on the surface of substrate, retarding Cu deposition on the active site. In addition to this, DMH could also be incorporated with the Cu deposition, leading to a completely different deposit morphology, as well as an increase in the thickness of the coating. The thickness of the Cu film obtained from the Cu electrolyte without additives was 4.50 μm , while the thickness was increased to 14.85 μm when Cu electrodeposition was achieved from an electrolyte including DMH; the thickness of Cu deposited increased to 11.11 μm when BA was added to the plating bath, as can be seen in **Figure 3.19**.

BA and DMH did not complex with Cu, as evidenced by the UV-Vis data in **Figure 3.3**. Therefore, these same additives are free to adsorb on the electrode surface and, as a consequence, deposition of Cu cannot take place on the sites occupied by additive molecules. Adsorption of these molecules on the active sites leads to an increased rate of Cu deposition, or the additives could otherwise co-deposit with Cu, consequently increasing the thickness of the Cu film.

It is well known in the electroplating of metals from aqueous solution that BA is considered a suitable buffer to prevent any alkalisation processes in the vicinity of the electrode due to hydrogen evolution.⁹⁰ Furthermore, numerous publications suggest that boric acid acts as a surfactant, that can be adsorbed on the electrode surface and inhibit the deposition of metals.^{39, 90, 91}

Recently our group reported that additives such as boric acid and 5,5-dimethylhydantoin have the ability to produce a bright Ni coating from Ethaline 200.⁴⁸ However, the mechanism of the metal growth in the presence of additives still needs further study. It was found that BH was able to prevent the formation of a surface passivation layer during the electrodeposition of Ni from aqueous solution.⁹⁰ However, the mechanism of BH in the electrodeposition of metals in DESs is still under investigation.

3.3.4.3 AFM study

Atomic force microscopy (AFM) is a surface probe technique; it can be performed to study the structure of conducting and insulating surfaces in both liquid and air environments. It is an important technique that is used to study the nucleation and topography of metal deposits. In addition to using the Scanning Electron Microscopy (SEM) technique, AFM has been used to examine the morphology of Cu electrodeposited from Ethaline 200 in the absence and presence of additives. Based on UV-Vis data, cyclic voltammetry, chronoamperometry and gravimetric analysis data, the morphology of the Cu deposit can be changed because of the differences in the initial nucleation and growth mechanisms of Cu in the absence and presence of the different additives.

Figure 3.20 illustrates an AFM image of a Cu deposit from Ethaline 200 in the absence and presence of various types of organic/inorganic additives at 80°C on a mild steel substrate and at a current density of 2.5 mA cm⁻² for 1 h. **Figure 3.20 (a)** obviously demonstrates the formation of small Cu nucleation sites the growth of these nuclei has been followed, which led to the change in the size and shape of Cu crystallites. As seen previously in the discussion of the chronoamperometry data, the nucleation mechanism of Cu in Ethaline 200 without additives corresponded well to the instantaneous mechanism, **Figure 3.12**.

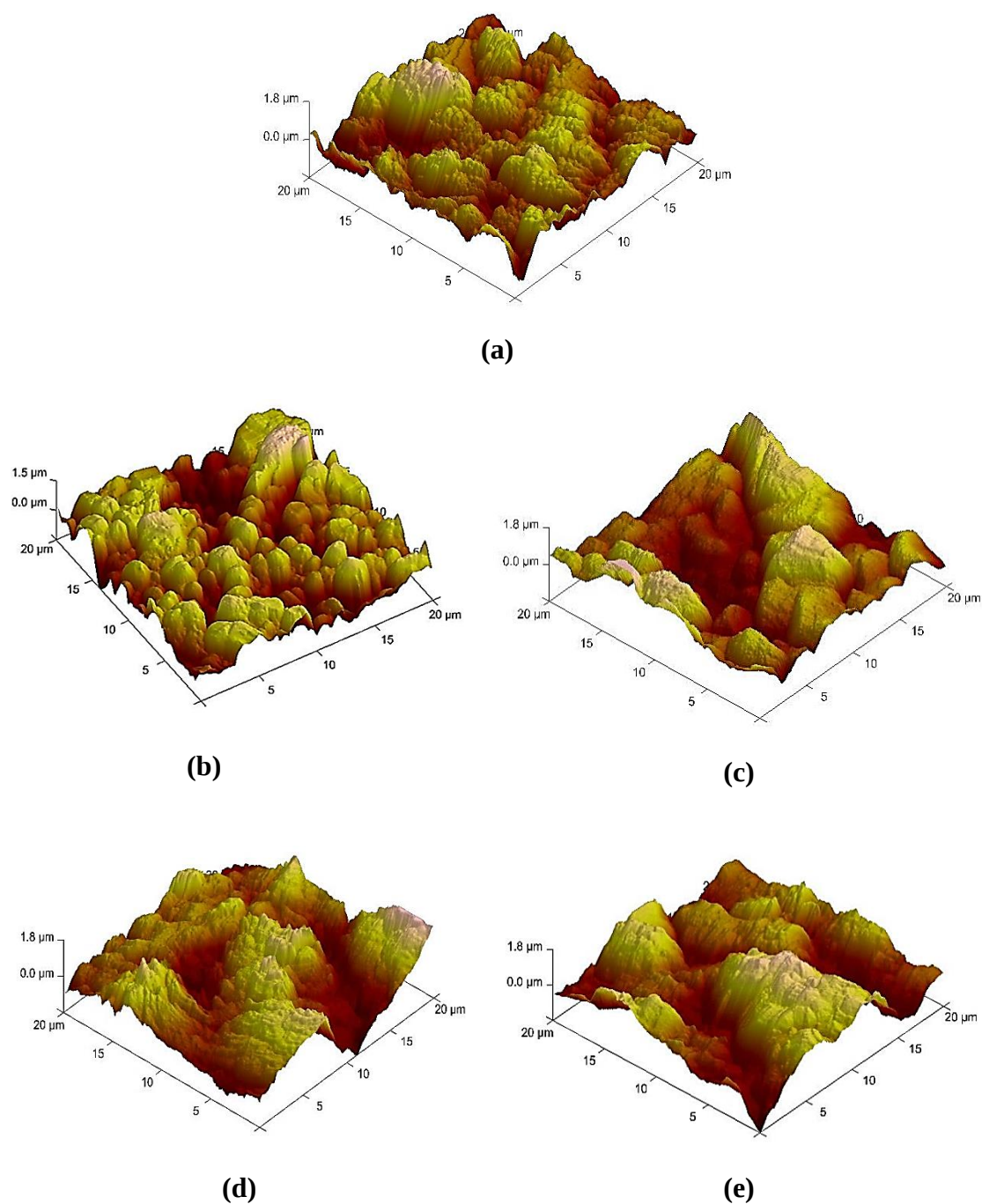


Figure 3.20 AFM images showing samples after bulk electrodeposition from Ethaline 200 systems, 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (all depositions achieved at 80°C for 1 h on a mild steel substrate with an applied current density of 2.5 mA.cm^{-2}) (a) without additives; (b) 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, (c) 0.1 M NaI ; (d) 0.2 M BH ; and (e) 0.2 M DMH .

Addition of $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$ to the Cu plating bath causes a significant change in the shape and crystal sizes in the Cu deposit, **Figure 3.20 (b)**, compared to the structure of the Cu film obtained from the system without additives. In metal electroplating, additives normally work as complexing agents, or they can adsorb on the electrode surface and inhibit the electrodeposition of the metal. As mentioned previously, the EDTA chelates with Cu, which changes the electroplating kinetics, the rate of deposition and the morphology of the Cu deposit. Electrodeposition of Cu is inhibited when the EDTA forms a complex with the Cu ion, which is clear from the cyclic voltammetry, **Figure 3.10 (a)**.

The use of NaI in the electrodeposition of Cu from Ethaline 200, **Figure 3.19 (c)**, changes the shapes and sizes of the Cu crystallites. The difference in crystallite size is indicative of a progressive nucleation mechanism, identical to our chronoamperometry data, **Figure 3.12 (c)**, which suggests that the nucleation of Cu deposition tended towards that of a progressive mechanism when using NaI. There are no significant changes in the topography of the Cu deposition growth when BA and DMH were added to the Cu solution. The nucleation mechanisms of Cu deposition using these additives corresponded to an instantaneous nucleation mechanism.

3.3.4.4 X-Ray diffraction analysis (XRD)

It is very important to study the microstructure of electrodeposited Cu because Cu depositing mechanisms are important to electronics applications. The texture of copper films can affect electromigration. There are a number of parameters such as temperature, current density, electrolyte, pH of the electrolyte, and additives, etc., which can influence the textures of the electrodeposited metal films. Consequently, the X-ray diffraction (XRD) technique is considered necessary to examine the texture of metal deposits.

Figure 3.21 illustrates X-ray diffraction spectra for Cu films obtained from 0.2 M $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ in Ethaline 200 in the absence and presence of various types of organic/inorganic additives at 80°C on a mild steel substrate and a current density of 2.5 mA cm^{-2} for 1 h. The diffractograms for Cu film that have been obtained from the solution in the presence and the absence of additives are shown in **Figure 3.21**.

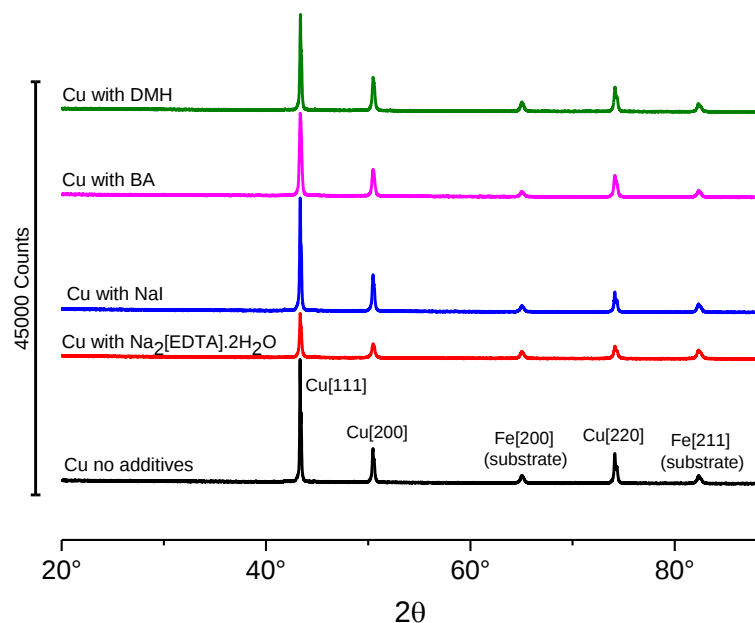


Figure 3.21 XRD patterns for Cu deposits from 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1:2 ChCl:EG-based liquid with the following organic / inorganic additives: 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$, 0.1M NaI, 0.2 M BA and 0.2 M DMH. All experiments were performed for 1h at 80°C and at a current density of $2.5 \text{ mA} \cdot \text{cm}^{-2}$.

The XRD pattern of the sample deposited matches well with the standard JCPDS card of Cu,^{92, 93} and the crystallographic texture of the deposits changes with the different types of additives. The calculated texture coefficients of the Cu deposits obtained with each of the additives are listed in **Table 3.1**.

Table 3.1 Texture coefficients of the Cu deposits prepared from 1:2 ChCl:EG-based liquid containing 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the absence and presence of 0.1M NaI, 0.2 M BA, 0.2 M DMH and 0.03 M $\text{Na}_2[\text{EDTA}] \cdot 2\text{H}_2\text{O}$. All experiments were performed for 1h at 80°C and at a current density of $2.5 \text{ mA} \cdot \text{cm}^{-2}$.

Component	Relative intensity [111]	Relative intensity [200]	Relative intensity [220]
Pure Cu	0.634	0.195	0.170
Cu + EDTA	0.738	0.196	0.064
Cu + NaI	0.641	0.224	0.133
Cu + BA	0.602	0.219	0.178
Cu + DMH	0.600	0.229	0.170

All diffraction peaks are sharp and characteristic of pure crystalline copper. In the absence of additives, a strong (111) diffraction peak is observed, as are the (200) and (220) diffraction peaks, albeit with relatively low intensities. The intensity of the (111) peak decreased to 0.196 when the deposition was achieved in presence of EDTA, while the relative intensity of the (200) peak increased to 0.738, as shown in **Table 3.1**. It can be said that using EDTA in the electrodeposition of Cu causes a change in the orientation of the Cu crystallites, as EDTA is considered a strong ligand, it can therefore form a strong complex with the Cu ions, which in turn may cause a change in the growth rate of different crystal faces. When NaI was added to the system, the intensity of the (220) peak decreased to 0.133.

As can be seen from the X-ray diffraction spectra and data presented in **Figure 3.21** and **Table 3.1**, the addition of BA to the plating bath inhibits crystal growth in the direction of the (111) planes. This change in crystal plane could be attributed to the adsorption of BA on this plane during the crystal growth process.⁹⁴ The same thing was obtained when DMH was added, where the intensity of the (111) plane was reduced.

3.4 Summary

In aqueous electrodeposition baths, organic or inorganic additives are often used as levellers and brighteners. However, little work has been undertaken as to the effect of additives on Cu electrodeposition from deep eutectic solvents.

In this chapter, the first study into the effect of additives on Cu electrodeposition from Ethaline 200 has been investigated. The additives studied, $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$, NaI, BA and DMH, were shown to have varying effects on Cu deposition properties. $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$, as a strong multidentate ligand, has significant effects on the Cu species, where this was investigated using UV-Vis spectroscopy. No significant change was found in the physical properties (viscosity and conductivity) of the Cu electrolyte in the absence and presence of $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$. It was shown that $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$ influenced the Cu deposition, where the electrochemical properties and morphology of the Cu deposit were changed when this additive was used. Cyclic voltammetry demonstrated an inhibition in the reduction of Cu peaks as a result of using $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$ as an additive. Surface analysis techniques (SEM, AFM and XRD) showed a change in the morphology and texture of the Cu film with $\text{Na}_2[\text{EDTA}]\cdot 2\text{H}_2\text{O}$.

NaI has been demonstrated to be an effective brightener for Cu deposition; the triiodide ion can be produced when NaI is added to the Cu electrolyte. Physical properties, cyclic voltammetry, chronoamperometry, rate of deposition and morphology were all modified due to the formation of iodine in the Cu electrolyte. The triiodide ion prevented the formation of a passivation layer of Cu oxide on the electrode, leading to a significant improvement, and increased thickness, in the Cu coating. No significant change could be detected in the electrochemical properties of the Cu electrolyte when DMH and BA were added. However, increases in the rate of Cu deposition were obtained with these additives in the plating bath, and the morphologies of the Cu deposit were also found to have been changed when DMH and BA were added.

It is clear that the addition of these additives to DESs represents a significant and extensive area of study; organic or inorganic additives that lead to brightener and leveller systems will very likely be unique to each ionic liquid/ metal system of interest. The next chapter will describe the effects of additives on Zn electrodeposition from deep eutectic solvents.

3.5 References

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Chapter 4: Effect of Additives on the Electrodeposition of Zinc from Deep Eutectic Solvents

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4.1 Introduction

In **Chapter 3**, the effects of additives on the electrodeposition of Cu from the deep eutectic solvent 1:2 ChCl:ethylene glycol were investigated. Clear differences were observed in the cyclic voltammetry and gravimetric data that were obtained for Cu electrodeposition from Ethaline 200 in the presence of additives. Additionally, the bulk Cu deposit morphology was significantly changed as the additives were used in the electrodeposition process.

The electrodeposition of metal from ionic liquids (ILs) is an area that has received intense study;^{1, 2} however, relatively few studies have investigated the role of additives.^{1, 3} Zinc coatings are widely used in the field of corrosion-resistant coatings and energy storage.⁴⁻⁶ Traditional zinc electrodeposition is usually performed in cyanide baths, acidic sulphate baths and acid chloride zinc baths.^{4, 7, 8} The clear problem with these electrolytes, however, is that they are all both corrosive and highly toxic; furthermore, they all have a significant negative impact on the environment. Consequently, there is considerable interest in alternative electrolytes for zinc deposition.

Recently, Liu *et al.* have studied zinc electrodeposition from ionic liquids.⁹ Chlorozincate ionic liquids were used for the deposition of Zn.¹⁰ The electrochemical potential windows of ILs are unusually wide compared to those of aqueous electrolytes, therefore, ILs can be used in the electrodeposition of Zn. Moreover, ILs can be used in the electrodeposition of metals such as Al that cannot be otherwise deposited from aqueous electrolytes.

Around ten years ago, deep eutectic solvents (DESs) were suggested as alternatives to classical room temperature ionic liquids,¹¹⁻¹⁴ as deep eutectic solvents, compared to ionic liquids, have excellent properties such as low cost, minimal toxicity, high metal solubility and are less sensitive to water.^{12, 13, 15-18} DESs are used in various electrochemical applications such as metal electrodeposition.¹⁹ Significant hydrogen evolution can result from the electrodeposition of metals from aqueous solutions. Hydrogen evolution, which is produced on the cathodic electrode surface, results in lowered current efficiency. In addition, hydrogen evolution can cause cracks in the electrode coating. Given that hydrogen evolution and low current efficiency are clearly

issues in the industrial plating of zinc, DESs could offer an attractive alternative for Zn plating that would allow these problems to be circumvented.²⁰

In this research, the effect of organic additives on Zn electrodeposition from deep eutectic solvents was investigated at 80°C. Different types of organic additives have been used in the electroplating of Zn from aqueous systems. It is extremely important to use these additives in the electrodeposition solvent due to their effect on the growth, morphology and structure of the resulting deposits.²¹ They are normally added to the plating bath to improve the physical and mechanical characteristics of the electrodeposit, such as grain size, brightness, internal stress, hardness and resistance to corrosion.²¹⁻²³ However, whilst additives might promote such desirable properties, the actual role they play in the electrodeposition process is not clearly understood, so rapid development in the field is inevitably hampered by the empirical nature of the associated research.²¹ Researchers have suggested that additives can be adsorbed on the active side of the substrate and raise the activation polarization of single ions, or otherwise that some additives act as inhibitors, or the additives could be acting as complexing agents.²¹

Additives are normally high molecular weight polymeric organic compounds, such as polyethoxylated compounds, which are normally used to produce bright Zn deposits from acidic electrolytes.²¹ Alternatively, additives can be species that form colloidal suspensions, which are more effective than small ions or single molecules. Organic additives that have been used in Zn electroplating from aqueous solution include benzoic acid (BA), polyethylene glycols (PEGs), *p*-benzoquinone (BQ) and boric acid (H₃BO₃).^{21, 22} The influence of additives on Zn electrodeposition from ionic liquids has also been studied. Iwagishi studied the effects of ethylene glycol, 1,3-propanediol, 1,2-butanediol and 1,3-butanediol on the electrodeposition of Zn from the Lewis base of liquid 1-ethyl-3-methylimidazoliumbromide:ZnCl₂,^{24, 25} demonstrating that the addition of each of these species enhanced the current efficiency of the process, obtaining a smooth Zn deposit in each case. Bright metal deposits were achieved from ILs when phenanthroline, acetonitrile, ethylenediaminetetraacetic acid (EDTA) and sodium acetylacetonate were added to the plating bath.²⁶ Endres *et al.*²⁷ showed that a brighter surface finish was produced for Pd and Al-Mn alloys from the AlCl₃-1-butyl-3-methylimidazolium-chloride IL when nicotinic acid was used as an additive.

Five years ago, Xingwu Guo *et al.*²⁸ studied the effects of nicotinic acid on the electrodeposition of Ni from deep eutectic solvents. They found that nicotinic acid was able to produce a uniform smooth and bright Ni coating. As mentioned in **Chapter 3**, our ionic liquid group has recently, studied the effects of nicotinic acid, methyl nicotinate boric acid and 5,5-dimethylhydantoin on the electrodeposition of Ni from Ethaline 200 as a DES.²⁹ It was interesting to note that bright mirror Ni coatings were produced as a result of using these additives. Therefore, it was suggested that the effects of these additives on the electrodeposition of different metals from DESs should be studied.

Few studies have examined the effects of additives on the electrodeposition of metals from deep eutectic solvents. This work reports the effects of three different additives (referred to as levellers and brighteners) on the electrodeposition of zinc on copper from a deep eutectic solvent (Ethaline 200). The additives tested included nicotinic acid (NA), boric acid (BA) and *p*-benzoquinone (BQ). The physical and mechanical properties of the zinc electrodeposit were found to be improved compared to the corresponding system without additives, and for the first time a bright zinc coating has been achieved on a copper substrate. Physical properties (viscosity and conductivity) of the Zn electrolyte, with and without additives, were measured. The electrochemical properties of the plating liquid have been studied using cyclic voltammetry, chronocoulometry, chronoamperometry and EQCM; redox peak currents decrease when additives were included in the zinc solution. Total charge was also reduced in experiments where additives were present. The nucleation and growth behaviour was examined by chronoamperometry, with the zinc deposition being in good agreement with an instantaneous growth mechanism without additives that changed to one of a progressive growth mechanism when additives were included in the coating bath. The current efficiency of zinc deposition in Ethaline 200 without additives was ~ 95%, which was reduced when additives were included. The resultant surface morphologies, thickness, topography, roughness and crystal structure of the Zn coating were revealed by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD), demonstrating that those additives serve as highly effective brighteners that can produce highly uniform and smooth zinc deposits.

4.2 Aims and objectives of the work

As in Chapter 3 the aim of this research is to investigate the effect of additives on the brightness and morphology of Zn deposited from the same DES. In this chapter the classical aqueous brightener, boric acid (BA) is compared with additives which have worked for other metals in DES; nicotinic acid (NA), and benzoquinone (BQ). The purpose of this investigation will focus on the production of Zn brightness with a highly uniform layer in the presence of organic and inorganic additives. In addition, this work aims to improve the properties of the Zn coating, such as roughness, thickness and brightness, through the use of these additives, where this will be examined using SEM and AFM.

4.3 Results and discussion

4.3.1 Physical properties

4.3.1.1 Viscosity

As has been previously mentioned, the novelty of this work is one of studying the effect of additives on the electrodeposition of Zn from an Ethaline 200 DES. Therefore, it is necessary to study the influence of additives on the physical properties (viscosity and conductivity) of a Zn electrolyte. **Figure 4.1** shows the effects of adding 0.05 M NA, 0.15 M BA and 0.03 M BQ on the viscosity of Ethaline 200 containing 0.4 M ZnCl_2 as a function of temperature. It is clear from **Figure 4.1** that the viscosity of Ethaline 200 containing 0.4 M ZnCl_2 increased with increasing temperature. Normally, DESs have relatively high viscosities (> 100 cP) at room temperature.¹¹ The high viscosity of DESs corresponds to the presence of an extensive intermolecular hydrogen bonding network, which leads to a decreased movement of free species within the DES. Moreover, the large ionic radius and very small void volume of most DESs results in decreased viscosities, whilst electrostatic or van der Waals interactions can contribute to the high viscosities of DESs.¹¹ Increasing the temperature results in an increase in the void volume of the liquid and may reduce the effects of van der Waals interactions, which can lead to a decrease in viscosity.

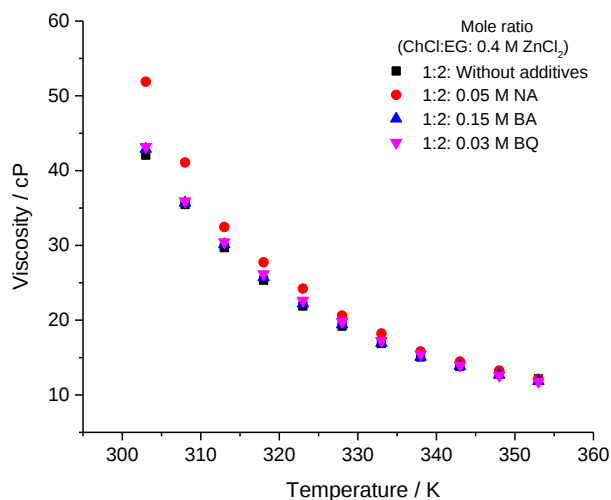


Figure 4.1 The viscosity of 0.4 M ZnCl_2 in Ethaline 200 as a function of temperature and different additives.

In **Figure 4.1** no obvious change can be seen in the viscosity of the Zn electrolyte when the additives were each individually added to the Zn plating bath, except for a slight increase when 0.05 M NA was added. As has already been mentioned, the ability of ions to move in such a medium is dependent on there being a nearby void of equal or greater size. The ability of the ion to move within a given medium is thus a function of ionic radius and the relative density of suitably sized holes.^{30, 31} Here, it may well be that the molecular size of NA is slightly greater than those of BA and BQ and this may, therefore, be the reason for the increased viscosity of the electrolyte when NA was added to the Zn bath. The same effect was observed for these additives in the Cu electrolyte (**Chapter 3**), where an increase in the viscosity of the Cu electrolyte was achieved in each case as a result of including these additives within the plating bath.

4.3.1.2 Conductivity

As the viscosity of the Zn solution was increased with the additives, the conductivity of the liquid was accordingly decreased, as is clear from **Figure 4.2**. The increase in the viscosity of Zn in Ethaline in the presence of NA caused a decrease in the conductivity of the electrolyte, as is clear in **Figure 4.2**. Additionally, a slight decrease in the conductivity of the Zn bath, **Figure 4.2**, was achieved as a result of individually adding BA and BQ to the Zn solution. Our group (ionic liquid group in Leicester) have recently published the effects of nicotinic acid and boric acid on the electrodeposition of Ni from

Ethaline 200.²⁹ We also found that these additives increased the viscosity and decreased the conductivity of the Ni electrolyte.

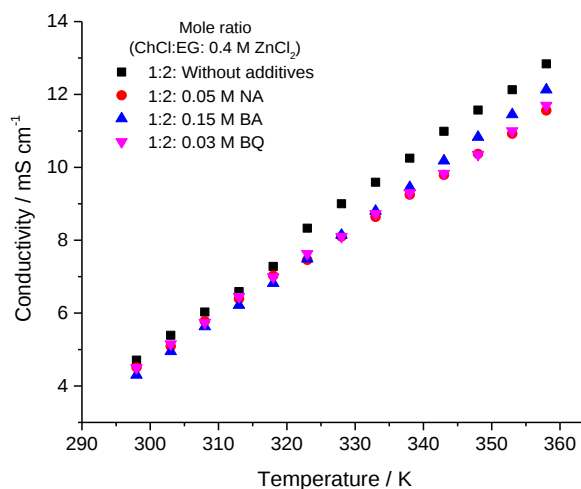


Figure 4.2 The conductivity of 0.4 M ZnCl_2 in Ethaline 200 as a function of temperature and different additives.

4.3.2 Voltammetry

It is interesting to study the cyclic voltammetry of different concentrations of ZnCl_2 in Ethaline 200 at elevated temperature. **Figure 4.3** shows cyclic voltammograms of various concentrations of ZnCl_2 in Ethaline 200 at 80°C, where the voltammetry was carried out in the potential range 0.0 V to 1.5 V and a scan rate 30 mV s^{-1} , using a Pt disc (1 mm diameter) electrode; a Pt flag was used as the counter-electrode, and Ag/AgCl as the reference electrode.

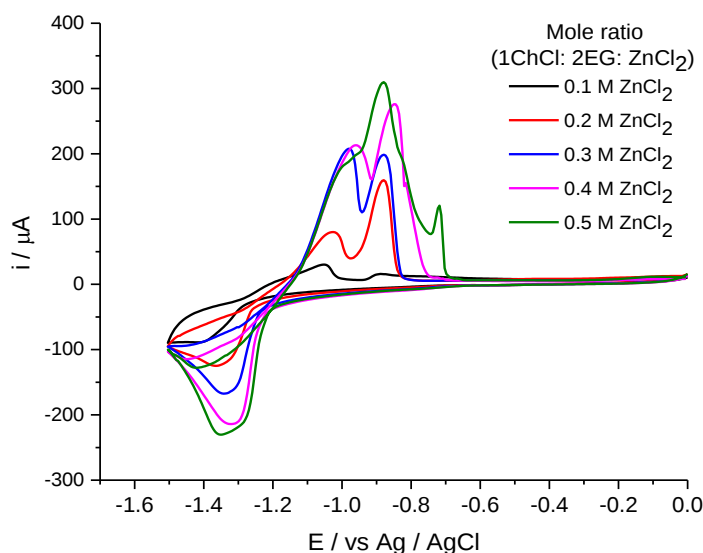


Figure 4.3 Cyclic voltammograms recorded for ZnCl_2 in Ethaline 200 at 80°C as a function of increasing concentration of ZnCl_2 at a scan rate of 30 mV s^{-1} , using a Pt disc (1 mm diameter) electrode, a Pt flag was used as the counter electrode, and Ag/AgCl as the reference electrode.

It is clear from **Figure 4.3** that the reduction in the current peak increased with increasing concentration of ZnCl_2 . It is entirely unsurprising to observe an increase in the Zn deposition as a function of increased concentration of ZnCl_2 in the electrolyte; a positive shift was also seen in the Zn reduction potential when the concentration of ZnCl_2 was increased. In the electrolyte containing 0.1 M ZnCl_2 , the Zn started to deposit at about -1.28 V. However, the potential was shifted in the positive direction to -1.20 V when the concentration of ZnCl_2 was increased to 0.5 M. It has been established that the Zn species in Ethaline 200 is $[\text{ZnCl}_4]^{2-}$.^{1, 32} Increasing the concentration of ZnCl_2 in the Ethaline 200 means increasing the concentration of $[\text{ZnCl}_4]^{2-}$, which leads to an increase in the deposition peak. Ethaline 200 has a large concentration of Cl^- anions which, under cathodic potentials, may be preferentially incorporated into the double layer, effectively preventing $[\text{ZnCl}_4]^{2-}$ from approaching the electrode surface on the basis of electrostatics. Thus, a low concentration of ZnCl_2 in the electrolyte means a low concentration of $[\text{ZnCl}_4]^{2-}$ and a high concentration of Cl^- anions at the electrode surface. This leads to an increase in the amount of energy that is required to deposit Zn. When the concentration of $[\text{ZnCl}_4]^{2-}$ increases in the solution, the number of free Cl^- anions will be effectively lowered at the electrode surface, and less energy will be needed for the deposition process, resulting in the positive shift in the Zn deposition potential seen in **Figure 4.3**. In addition, a nucleation loop is observed in the cyclic

voltammograms of electrolytes that contain high concentrations of ZnCl_2 (for example, 0.3 M, 0.4 M and 0.5 M), whereas the same cannot be seen in the cyclic voltammograms of solutions with low concentrations of ZnCl_2 (for example, 0.1 and 0.2 M). This indicates that the nucleation rate for Zn deposition was slow for cyclic voltammetry conducted with an electrolyte that has a low concentration of $[\text{ZnCl}_4]^{2-}$ and that this rate increases as a result of increasing the concentration of ZnCl_2 .

Two stripping peaks are obtained from the cyclic voltammetry of ZnCl_2 in Ethaline 200, which were observed at -1.10 V and -0.95 V, and have been suggested to be due to the formation of two separate Zn phases (nanoscale and micro scale).^{1, 16, 20} Furthermore, an increase in the stripping of Zn current peaks was observed as a result of increasing the concentration of $[\text{ZnCl}_4]^{2-}$; this may simply be due to an increased amount of Zn being deposited.

4.3.2.1 Effect of temperature on the voltammetric behaviour of Zn (II)

Cyclic voltammetry of ZnCl_2 in Ethaline 200 has been studied at room temperature and at elevated temperature (80°C). **Figure 4.4** shows a comparison of the cyclic voltammetry of Ethaline 200 containing 0.4 M ZnCl_2 at room temperature and at 80°C; both experiments were recorded at a scan rate of 30 mV s^{-1} . The cyclic voltammograms of ZnCl_2 recorded at 80°C differed significantly from those recorded at room temperature, showing a remarkable increase in Zn deposition and dissolution of the current peak of Zn when performed at 80°C. This was anticipated for various reasons: firstly, as temperature was increased, the viscosity of the Zn electrolyte decreased, allowing an increase in the rate of mass transport toward the electrodes. This was due to the consequent increase in the free void volume in the solution, as explained in the previous chapter. Secondly, as discussed earlier in this section, the Zn electrolyte contains a high number of Cl^- anions which, through adsorption into the electrode surface, may thus impede the approach of $[\text{ZnCl}_4]^{2-}$ towards the electrode surface. As the temperature of the electrolyte was increased, the number of adsorbed Cl^- anions on the electrode surface was reduced, allowing an increase in the concentration of $[\text{ZnCl}_4]^{2-}$ at the electrode surface. This would in turn act to promote Zn reduction.¹ From the cyclic voltammetry of ZnCl_2 (**Figure 4.4**) it could be suggested that the electrodeposition of Zn from Ethaline 200 at elevated temperature is considerably better

that at room temperature due to the increased rate of the Zn deposition, and thus the efficiency of deposition will be increased at higher temperature.

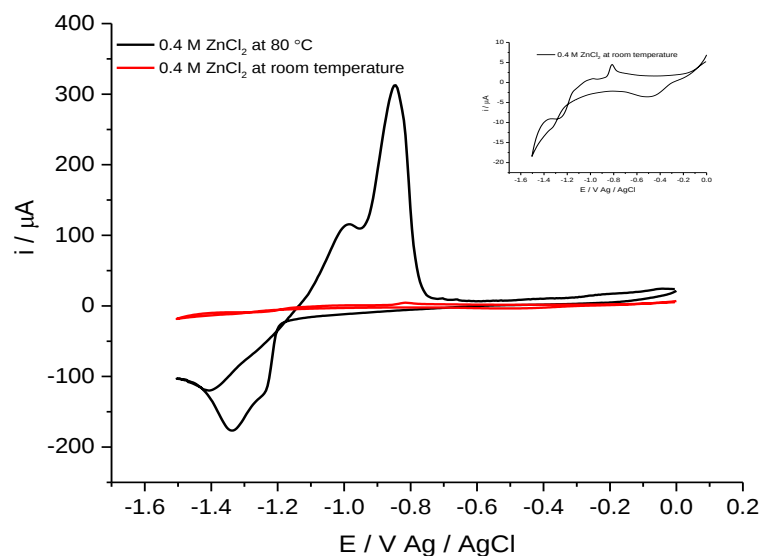


Figure 4.4 Cyclic voltammograms of 0.4 M ZnCl_2 in Ethaline 200 at 80°C (black line) and at room temperature (red line), recorded at a scan rate of 30 mV s^{-1} , using a Pt disc (1 mm diameter) electrode, a Pt flag as the counter-electrode and Ag/AgCl as the reference electrode.

4.3.2.2 Effect of additives on the voltammetric behaviour of Zn (II)

As can be concluded from **Figure 4.4**, the electrodeposition of Zn from Ethaline 200 at 80°C is considerably better than at room temperature due to the increased efficiency and rate of deposition of Zn. Therefore, it is recommended to perform the electrodeposition of Zn from Ethaline 200 at 80°C. **Figure 4.5** shows the cyclic voltammetry of 0.4 M ZnCl_2 in Ethaline 200 at 80°C in the absence and presence of different concentrations of the following additives: **(a)** nicotinic acid (NA), **(b)** boric acid (BA), and **(c)** *p*-benzoquinone (BQ). The cyclic voltammograms were recorded at a scan rate of 30 mVs^{-1} using a 1.0 mm Pt disc electrode, a Pt flag counter-electrode and an Ag/AgCl reference electrode. The concentrations used were influenced by the work by Juma which in turn were limited by solute solubility.³³

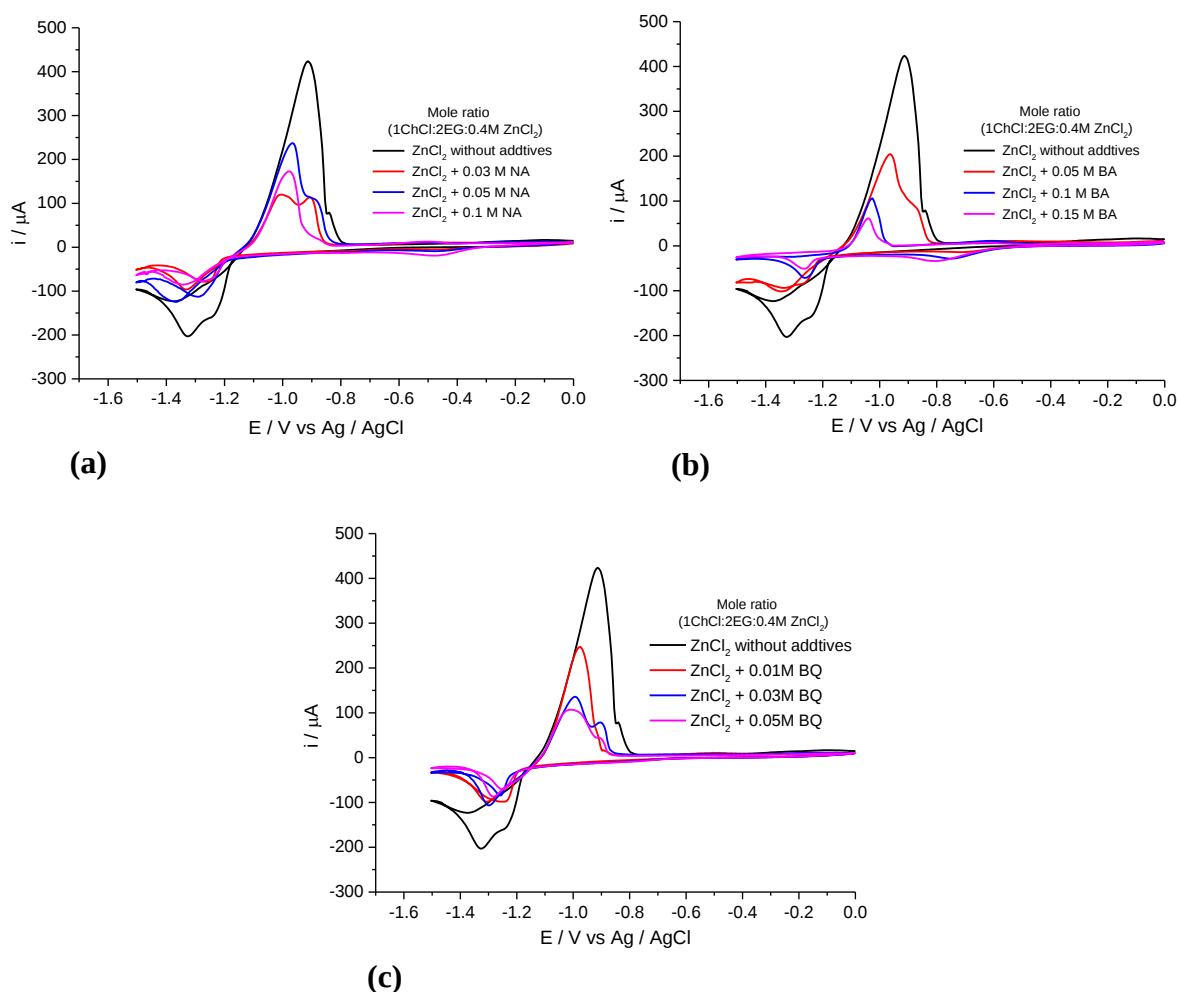


Figure 4.5 Cyclic voltammograms for 0.4 M ZnCl_2 obtained from Ethaline 200, using a Pt disc electrode (1 mm diameter) at 80°C and at a scan rate of 30 mV s^{-1} with the following organic additives: **(a)** nicotinic acid, **(b)** boric acid, and **(c)** p-benzoquinone.

Figure 4.5 (a) shows the cyclic voltammetry of 0.4 M ZnCl_2 in Ethaline 200 in the absence and presence of different concentrations of NA. In the absence of NA, the onset of Zn reduction (vs. Ag vs. Ag/AgCl) in Ethaline 200 at $E = -1.18 \text{ V}$ and the oxidation of Zn occur via a two-stage process, with two oxidation peaks at $E = -0.95 \text{ V}$ and at -0.85 V . As described in **Figure 4.3**, these two stripping peaks corresponded to the presence of two energetically distinct phases of Zn. The deposition and stripping processes of Zn have been altered as a result of using NA, as shown in **Figure 4.5 (a)**. A clear decrease in the reduction peak currents can be seen with an increasing amount of NA in the electrolyte. In addition, a negative shift of around 30 mV in the Zn reduction potential occurred as NA was introduced to the Zn electrolyte. The negative shift in the overpotential for the reduction of Zn can be attributed to the adsorption of

NA on the electrode surface,^{28, 34} thus requiring additional energy to discharge the Zn ions.

The adsorption of NA on different substrates has been confirmed by Auger and SERS spectroscopy.^{28, 35, 36} NA can be adsorbed on the electrode surface through the lone pair of electrons on either its nitrogen or oxygen atom, or both.^{36, 37} NA molecules can be absorbed on the surface in different ways, namely perpendicular or parallel to the electrode surface, as shown in **Figure 4.6**.

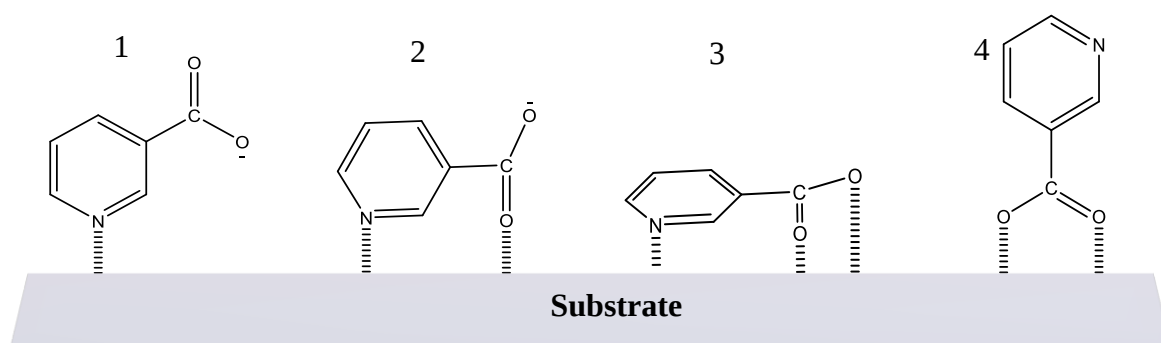


Figure 4.6 The orientation and probability of molecular adsorption of nicotinic acid.

It can be seen from **Figure 4.5 (a)** that the deposition and stripping peaks of Zn decreased when 0.03 M NA was added to the Zn electrolyte. However, when the amount of NA that was added was sufficient to increase its concentration to 0.05 M, the deposition and stripping current peaks of Zn were enhanced. This could be related to the adsorption position of NA. The parallel adsorption position of NA on the electrode surface (as shown in **Figure 4.6**) can block a large area of the surface, and this may be more prevalent when a low concentration of NA is present in the bath. Perpendicular NA adsorption could occur when one increases the concentration of NA, where this orientation only blocks a small area of the surface and thus allows for a relatively increased amount of Zn deposition. Therefore, the increase in the reduction and oxidation current peaks of Zn that were achieved when 0.05 M NA was added could correspond to the orientation in which NA was adsorbed on the electrode surface.

The same effect has been obtained for the cyclic voltammetry of Zn when different concentrations of BA and BQ were introduced into the Zn electrolyte. An obvious decrease in the deposition of Zn occurred with an increasing concentration of BA, and a negative shift in the Zn reduction potential was also produced as a result of adding of BA to the Zn electrolyte. In aqueous electrodeposition, boric acid is often used to

prevent an increase in pH at the cathodic electrode. However, it has been reported in the literature that BA can be adsorbed onto the electrode surface.^{38, 39} The behaviour of BA in DES is currently undetermined. However, a bright and smooth Zn deposit was achieved when BA was added to Ethaline 200 containing a 0.4 M ZnCl₂ solution. Therefore, the BA in the Zn bath could be absorbed onto the cathode surface and inhibit Zn deposition.

4.3.2.3 Voltammetric behaviour of additives in Ethaline 200

The electrochemical behaviour of NA, BA and BQ in Ethaline 200 at 80°C was studied using the cyclic voltammetry method. **Figure 4.7** shows the cyclic voltammetry of Ethaline 200 in the absence and presence of NA, M BA and BQ at 80°C on a Pt disk electrode (vs. an Ag/AgCl reference). The cyclic voltammograms were recorded in the negative direction from 0.0 V to -1.5 V, and then reversed to the starting potential; this window was same window that was used to study the effect of these same additives on the voltammetry of Zn in Ethaline 200.

Figure 4.7 (a) demonstrates the cyclic voltammetry of Ethaline 200 in the absence and presence of different concentrations of NA at 80°C, where in the cyclic voltammetry of Ethaline 200 a reduction peak was obtained at about -0.9 V. This peak corresponded to hydrogen evolution, but is shifted positively by 20 mV at a concentration of 0.05 M NA in the electrolyte. The shift and the increase in the reduction peak corresponded to an increase in hydrogen evolution. In **Figure 4.7 (a)**, a small reduction peak can be seen at about -0.5 V, which is associated with the reduction of NA. From **Figure 4.5 (a)** and **Figure 4.7 (a)**, the onset potential of 0.4 M Zn without NA is more negative in comparison to the onset potential of NA in Ethaline 200 by -0.5 V. This means that NA has been reduced, and blocks the active points of the surface before Zn deposition. As a consequence of these differences in the potential, the cathodic reaction is more likely to be inhibited. It has been reported that voltammograms of NA dissolved in a pH 5.0 phosphate buffer saline on a polycrystalline gold electrode appear in the positive potential.⁴⁰ However, the cathodic peak is twice as high as the anodic peak current.

As we have been using BA as a brightener in the electrodeposition of Zn from Ethaline 200, it is necessary to study the electrochemical behaviour of BA itself in Ethaline 200. **Figure 4.7 (b)** shows the cyclic voltammograms of different concentrations of BA in Ethaline 200 at 80°C. There is a clear new cathodic peak that has started to appear at

about -0.5 V as BA was introduced into the electrolyte, whose intensity increases with an increasing concentration of BA. Boric acid could be dissociated in Ethaline 200 to form the $[\text{H}_2\text{BO}_3]^-$ anion and H^+ . Therefore, the peak that started to appear at -0.5 V could specifically correspond to the adsorption of BA on the Pt electrode surface that then reduces with the consequent evolution of hydrogen, or this peak could otherwise be attributed to the adsorption of dihydrogen borate on the electrode surface via a one-electron transfer reaction. EI-Shafei and Aramata reported that BA can be adsorbed on a Pt (111) surface in acidic aqueous solutions.^{41, 42} They found that the specific adsorption of BA takes place at more positive potentials. This is could be due to the effect of the natural electrolyte and electrode substrate. Thus, from the voltammetry of BA in Ethaline 200, as shown in **Figure 4.7 (b)**, it can be suggested that BA is adsorbed on the electrode surface and inhibits Zn deposition.

Figure 4.7 (c) shows the cyclic voltammograms recorded for different concentrations of BQ in Ethaline 200 at 80°C. Significant changes have occurred in the cyclic voltammograms of Ethaline 200 through the use of BQ. The onset of cathodic reduction for Ethaline 200 was at -0.9 V. However, using BQ, the onset of cathodic reduction was shown to occur at about -0.1 V where this corresponds to the reduction of BQ. As has been shown previously, Zn can be deposited in Ethaline at -1.18 V. Thus, it can be said that BQ adsorbs on the electrode surface and blocks the active sides before deposition of Zn.

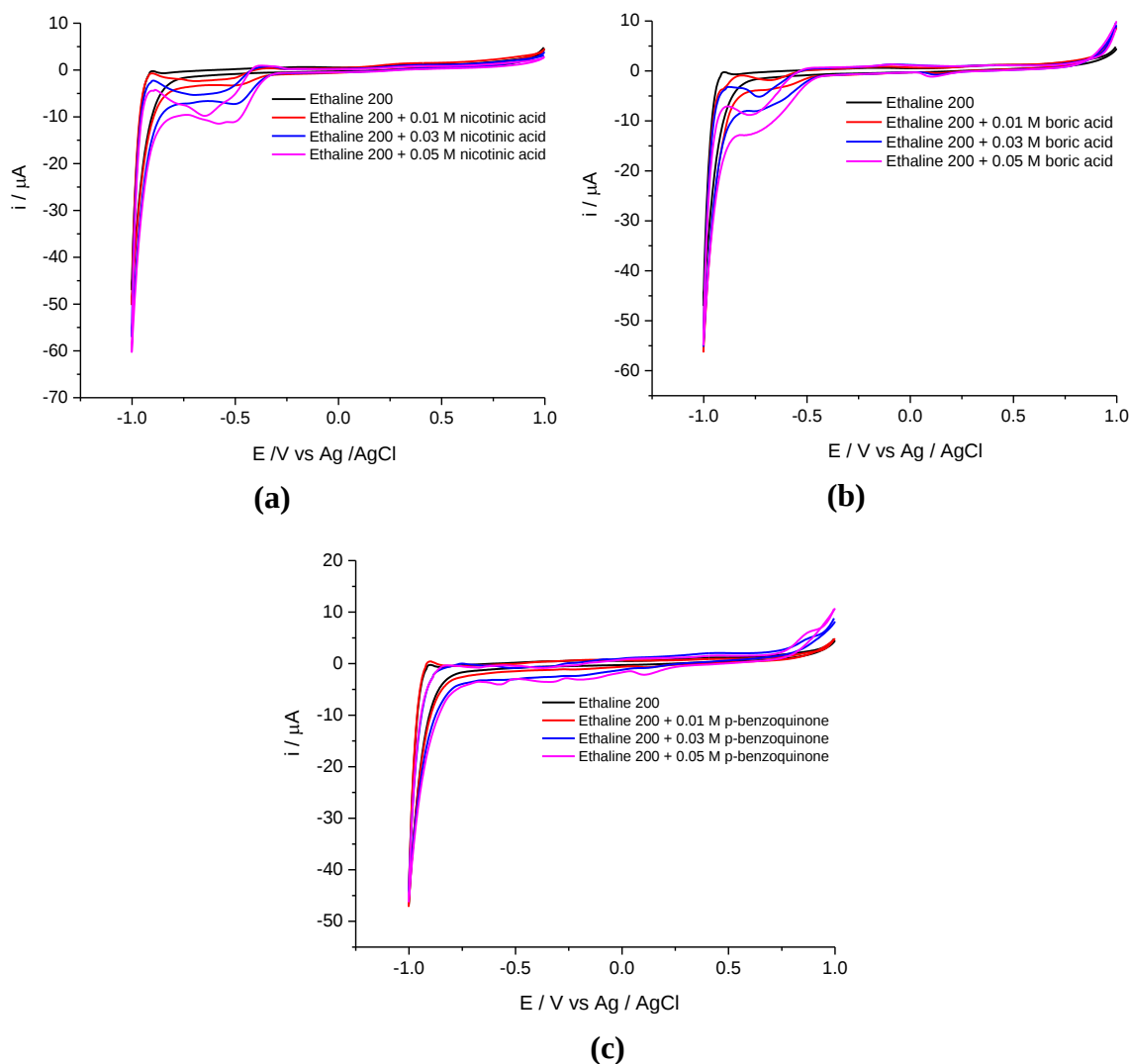


Figure 4.7 Cyclic voltammogram at 80 °C of Ethaline 200 with varying amounts of (a) NA, (b) BH and (c) BQ. Measured using a 1 mm Pt disc working electrode, Pt flag counter electrode and reference against Ag / AgCl at 10 mV s^{-1} .

4.3.3 Chronocoulometry

Chronocoulometry (CC), which measures charge as a function of time, is considered to be a classic electrochemical method used in electroanalytical chemistry.⁴³ The plots one obtains from this method can be interpreted in terms of the concentration gradients in the solution adjacent to the electrode surface. Abbott *et al.*¹⁹ examined the chronocoulometry of 0.01 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in Ethaline 200 using a Pt disc electrode, and found that metal growth was diffusion controlled.

In the current study, Zn chronocoulometry experiments were performed on a Pt disc electrode from Ethaline 200 containing 0.4 M ZnCl_2 at 80°C in the absence and

presence of 0.05 M nicotinic acid, 0.15 M boric acid and 0.03 M *p*-benzoquinone, as shown in **Figure 4.8**, where all experiments were performed for potential steps from 0.0 V (held for 10 s) to -1.3 V for 30 min. **Figure 4.8** shows the plots of charge vs. $t^{1/2}$ are not linear suggesting that the processes are not controlled by diffusion.

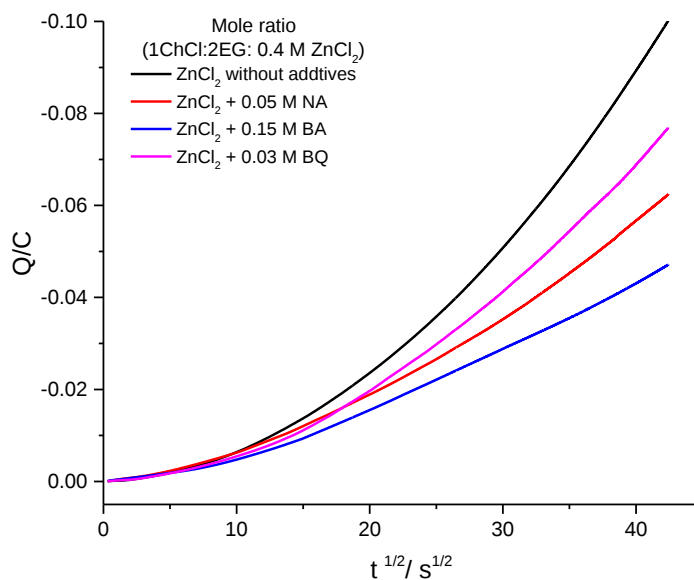


Figure 4.8 Chronocoulometry of 0.4 M $[ZnCl_2]$ in Ethline 200 in the absence and presence of 0.05 M NA, 0.2 M BA and 0.03 M BQ. All experiments were achieved at a potential of -1.3 V for 1800 s on Pt (1.0 mm diam) and at 80°C.

It is clear from **Figure 4.8** that the charge (Q) for Zn deposition in the presence of additives decreased. This indicates that electrodeposition of Zn from an additive-free system is faster than in a system containing additives; the same conclusion was drawn from the results of our cyclic voltammetry. According to Faraday's Law ($Q = nFN$), the charge measured is directly proportional to the number of species deposited in moles (N). This means that current efficiency of Zn deposition from Ethline 200 in the presence of additives will be less than the efficiency of Zn deposition from an additive-free electrolyte. The current efficiencies of Zn electrodeposition from Ethline 200 in the absence and presence of these additives were investigated using a quartz crystal microbalance (QCM), which will be discussed later.

4.3.4 Chronoamperometry

In order to further probe the possible change in the mechanism of Zn reduction, the nucleation mechanism needs to be investigated. Therefore, the chronoamperometry method was used to study the nucleation mechanism of Zn deposition. The chronoamperometric study was performed using a potential between -0.50 V to -1.25 V with a polished Pt disk vs. Ag/AgCl.

To identify the nucleation mechanisms of metal electrodeposition, a number of methods have been devised, the most widely used being the model developed by Scharifker and Hills,⁴⁴ which allows chronoamperometric data to be assigned to one of two limiting nucleation mechanisms, instantaneous or progressive. In an instantaneous nucleation process, the model assumes the rate of nucleation is high and that coverage of all active sites by nuclei is essentially instantaneous. This process is described by **Equation (4.1)**:

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.9542}{\frac{t}{t_m}} \left\{1 - \exp\left[-1.2654 \left(\frac{t}{t_m}\right)\right]\right\}^2 \quad \text{Equation 4.1 (Instantaneous)}$$

In the progressive nucleation mechanism, the rapid growth of a large number of active sites is achieved throughout the reduction, a process which is described by **Equation 4.2**:

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.2254}{\frac{t}{t_m}} \left\{1 - \exp\left[-2.3367 \left(\frac{t}{t_m}\right)\right]\right\}^2 \quad \text{Equation 4.2 (Progressive)}$$

In both processes, i_m is the maximum current density and t_m is the time taken to achieve i_m .

Figure 4.9 shows the i - t curves associated with the theoretical models for three-dimensional instantaneous and progressive nucleation of Zn deposited from Ethaline 200 at 80°C in the absence and the presence of additives: **(a)** without additives, **(b)** 0.05 M NA, **(c)** 0.15 M BA and **(d)** 0.03 M BQ. When the overpotential is applied, the current initially rises quite sharply due to double layer charging, followed by a relaxation in current. A subsequent rise to the current maximum, indicative of a nucleation process, is then observed. This current increase is proposed by Scharifker and Hills to be caused by the formation and growth of nuclei. As the individual nuclei growth zones begin to overlap, the current falls to a level indicative of a diffusion-limited process.

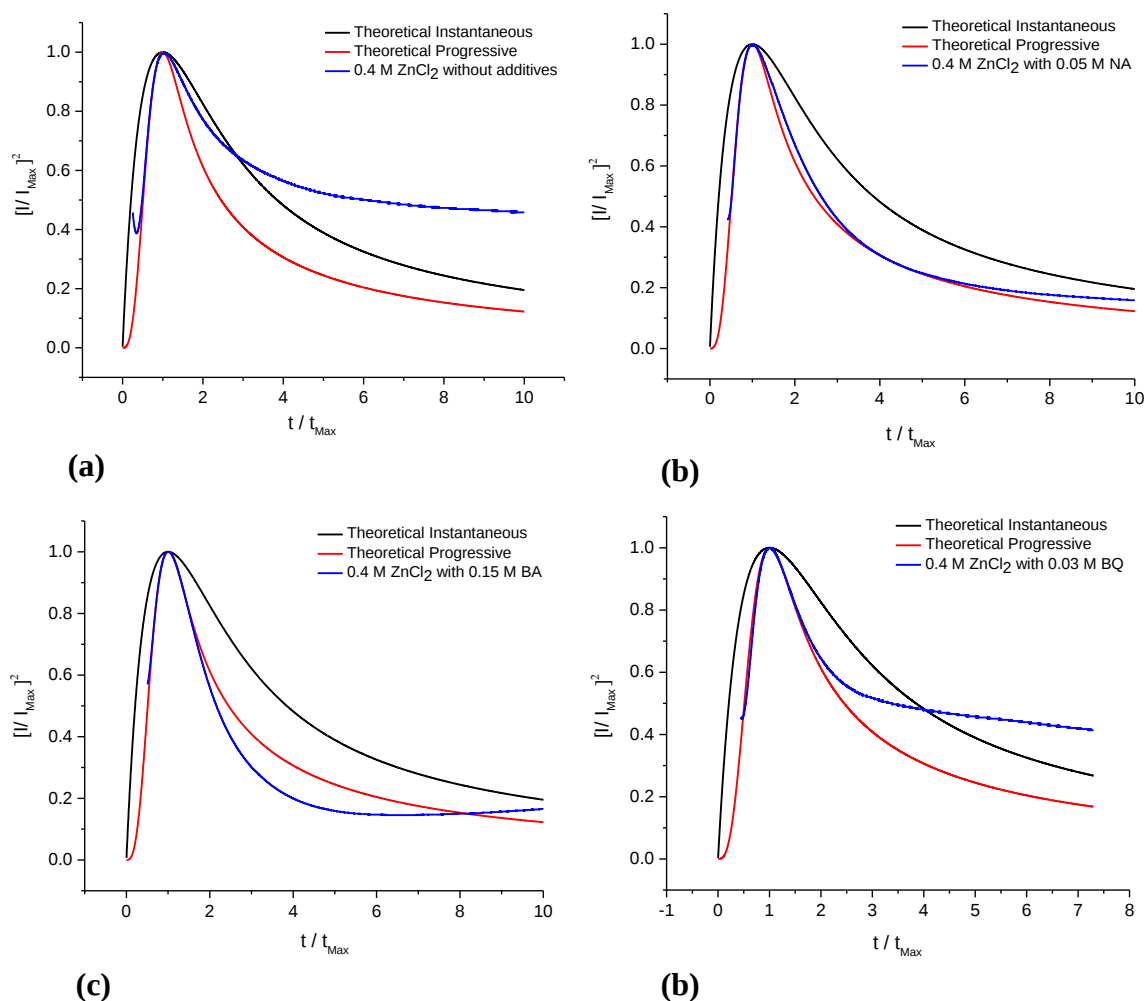


Figure 4.9 The experimental i - t data for electrodeposition of 0.4 M ZnCl_2 from Ethaline 200 on a Pt disc (1 mm diameter) at 80°C vs. an Ag/AgCl reference electrode in the absence and presence of additives: (a) without additives; (b) 0.05 M NA; (c) 0.15 M BA; and (d) 0.03 M BQ. The applied potential was -1.25 V for all experiments.

The nucleation mechanism for Zn deposition on a Pt electrode from Ethaline 200 without additives using the Scharifker-Hills model is shown in **Figure 4.9 (a)**, where the nucleation mechanism fit well with that of a progressive growth mechanism. However, the mechanism becomes one of instantaneous growth after the current maximum, $(i/i_{\text{m}})^2$. The nucleation mechanism of Zn in the presence of NA and BA in Ethaline 200 is shown in **Figures 4.9 (b)** and (c), respectively, where the mechanism fit well with one describing progressive growth. The nucleation mechanism of Zn deposition in the presence of BQ also suggested a progressive growth mechanism, which becomes one of instantaneous growth after a long period of time, as is clear in **Figure 4.9 (d)**. This suggests that with increasing induction time, the electrode surface is subject to a considerable blocking effect by additives. A transition between the two

nucleation mechanisms has been reported for nucleation and growth processes controlled by mass transfer.^{21, 45-47}

4.3.5 Gravimetric analysis

In addition to the cyclic voltammetry, chronocoulometry and chronoamperometry, the Electrochemical Quartz Crystal Microbalance (EQCM) technique has been used to study the effect of NA, BA and BQ on current efficiency and rate of Zn deposition from Ethaline 200. As discussed previously in **Chapter 3**, the QCM technique uses a resonant quartz crystal, where this crystal is used as a mass probe for the electrolytic deposition of the metal. The consequent change in resonant frequency of the quartz crystal corresponds to the mass of metal deposited. The data regarding the effect of the addition of 0.05 M NA, 0.15 M BA and 0.03 M BQ on the growth rate of Zn from Ethaline 200 at 80°C is shown in **Figure 4.10**. Nicotinic acid and *p*-benzoquinone both act to increase the rate of Zn deposition from Ethaline 200, as can be seen in **Figure 4.10 (a)**. These additives may adsorb on the electrode surface and decrease the rate of ethylene glycol decomposition increasing the rate deposition.^{48, 49} As was discussed in the voltammetry section (**Figures 4.5 and 4.7**), the additives can be preferentially adsorbed on the active points of the electrode surface. Adsorption of the additives on such active sites could result in an increase in the current density and thus lead to an increased rate of Zn deposition. Otherwise, the additives could be incorporated with the Zn deposition, which could also lead to an increase in Zn deposition rate.^{48, 49} No significant change can be observed in the rate of Zn deposition when boric acid was used as an additive.

A mass-charge plot is shown in **Figure 4.10 (b)**. It can be seen from **Figure 4.10 (b)** that using NA and BA caused a decrease in the rate of Zn mass deposition. Here, this decrease in rate could be related to a side-effect reaction (hydrogen evolution).

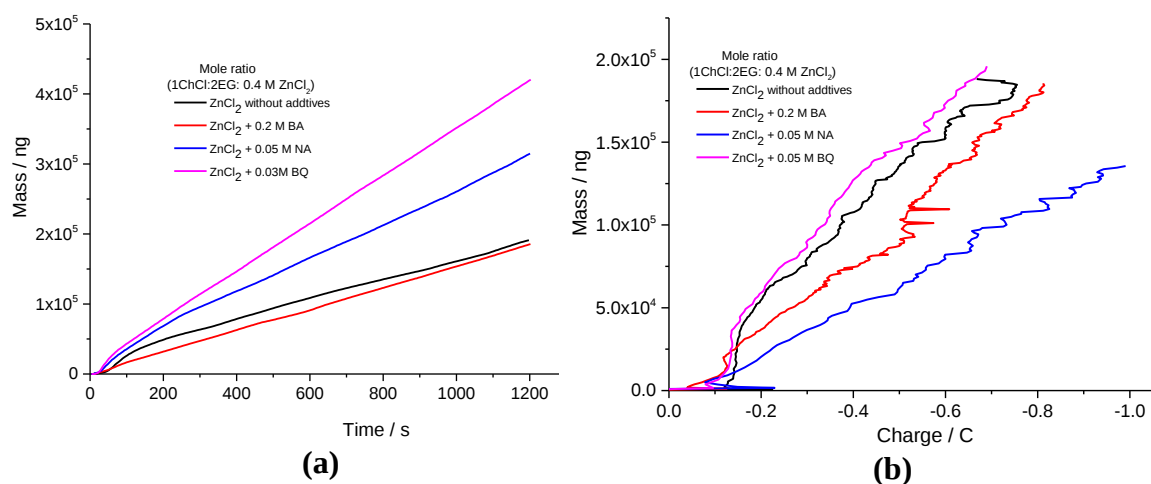


Figure 4.10 Gravimetric EQCM traces for Zn metal deposition on a Pt-coated quartz crystal (10 MHz) surface in **(a)** mass vs. time, and **(b)** mass vs. charge. All experiments were performed in Ethaline 200 at a concentration of 0.4 M ZnCl₂ at 80 °C in the presence and absence of additives. The applied potential was -1.3 V vs. Ag/AgCl for 500 s.

Figure 4.10 (b) shows the mass/charge transient for electrodeposition of Zn from Ethaline 200 in the presence and absence of additives. From **Figure 4.10 (b)**, the current efficiencies of Zn depositions from Ethaline 200 in the presence and absence of 0.05 M NA, 0.15 M BA and 0.03 M BQ at 80°C were measured. Metallic Zn was deposited on a Pt-coated resonant quartz crystal under a constant potential of -1.3 V from Ethaline 200-based liquids containing 0.4 M ZnCl₂ at 80°C in the absence of additives.

Current efficiencies of Zn deposition in the absence and presence of 0.05 M NA, 0.2 M BA and 0.03 M BQ were measured. The current efficiencies of Zn deposition were each decreased in presence of these additives. **Table 4.3** shows the current efficiencies of Zn electrodeposition from Ethaline 200 at 80°C in the absence and presence of 0.05 M NA, 0.15 M BA and 0.03 M BQ as additives.

Table 4.1: Current efficiencies of Zn deposition from Ethaline 200 at a concentration of 0.4 M ZnCl_2 in the absence and presence of 0.05 M NA, 0.15 BA and 0.03 BQ. All experiments were performed on a Pt-coated EQCM crystal at 80°C and at an applied potential of -1.3 V.

ChCl:EG: ZnCl_2	Cathode Current efficiency %	-r
1:2: 0.4 M Zn	90.8 ± 3	0.99989
1:2: 0.4 M Zn: 0.05 M NA	52.1 ± 2	0.99984
1:2: 0.4 M Zn: 0.15 M BH	70.6 ± 5	0.99991
1:2: 0.4 M Zn: 0.03 M BQ	82.7 ± 3	0.99993

It is clear from **Table 4.1** that the current efficiency of Zn deposition was decreased to 52.1% when NA was added to the plating bath. As discussed in the voltammetry section in **Figure 4.5**, the shift and decrease in the Zn deposition peak occurred when NA was added to the Zn electrolyte. The suggestion is that NA was adsorbed on the electrode surface and inhibited Zn deposition, which in turn could lead to reduced current efficiency of Zn deposition; adding NA to the plating bath could also have led to an increase in hydrogen evolution and thus a reduction in the efficiency of Zn deposition. The current efficiencies of Zn deposition from Ethaline 200 in the presence of boric acid and *p*-benzoquinone were $\sim 70\%$ and $\sim 83\%$, respectively. Here, also, there is a clear decrease in the efficiencies of Zn deposition as a result of using BA and BQ as additives, the underlying reason being due to hydrogen evolution.

4.3.6 Deposit morphology

4.3.6.1 Effect of temperature on morphology of Zn deposit in Ethaline 200

In this work, electrodeposition of Zn from Ethaline 200 was achieved at 80°C. It was found that electrodeposition of metal from Ethaline 200 at elevated temperatures such as 70, 80 and 90°C were considerably better than at low temperature (for example room temperature). A comparison between the morphologies of Zn film deposited from Ethaline 200 at room temperature and at 80°C is shown in **Figure 4.12**. Both electrodepositions were achieved from Ethaline 200 containing 0.4 M ZnCl_2 on a Cu substrate for 2 h at a current density of 3.3 mA cm⁻². A bright Zn film was obtained as the electrodeposit at 80°C. However, a dark grey Zn film was obtained when the

coating occurred at room temperature. As has already been shown (in the voltammetry section, and in particular in **Figure 4.4**), there was a strong change in the cyclic voltammograms of Zn when the process was performed at high temperature. Higher temperatures could reduce the specific adsorption of Cl^- ion on the electrode surfaces, and this in turn could enhance the rate of Zn deposition. Additionally, the higher temperatures could be enhancing mass transport effects through the consequent decrease in the viscosity of the Zn electrolyte. An expected morphology has been obtained for the Zn deposit produced when the electroplating was performed at 80°C . **Figure 4.12 (b)** shows the Zn deposit to have the form of a hexagonal plate, which is typical for pure Zn electrodeposits produced from aqueous solution.^{21, 50} No obvious Zn particles can be seen in the morphology of the Zn film, **Figure 4.12 (a)**, when the electroplating of Zn was achieved at room temperature. This corresponded to specific adsorption of Cl^- anions on the electrode surface impeding the growth of Zn particles. Thus, from cyclic voltammetry and morphological data, the electrodeposition of Zn from Ethaline 200 at high temperature is recommended for the production of a bright, uniform Zn deposition. Therefore, in this work, the electrodeposition of Zn from Ethaline 200 in the absence and presence of additives has been performed at 80°C .

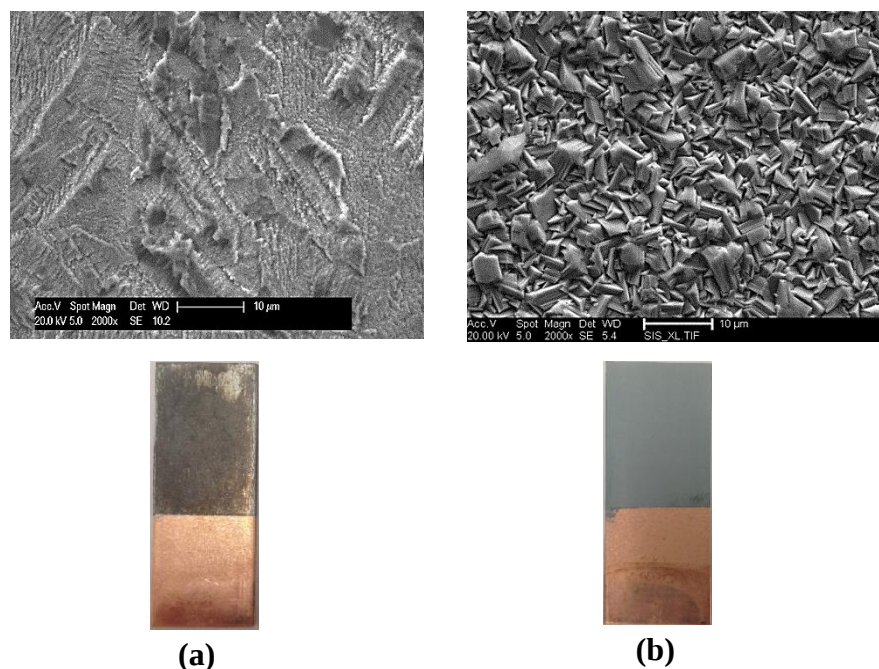


Figure 4.12 SEM images for samples electrodeposited from 0.4 M ZnCl_2 in Ethaline 200 systems **(a)** at room temperature and **(b)** at 80°C (both samples were achieved on a Cu electrode and at an applied current density of 3.3 mA cm^{-2} for 2 h (sample width 2 cm).

4.3.6.2 Effect of additives on morphology of Zn deposit in Ethaline 200

Photographs, morphologies and cross-sections of Zn deposits that have been obtained from Ethaline 200 with a concentration of 0.4 M ZnCl_2 in the presence and absence of NA, BA and BQ are shown in **Figure 4.13**. All Zn electrodepositions were achieved on Cu substrates at 80°C for 2 h at a current density of 3.3 mA cm⁻². **Figure 4.13 (a)** shows the morphology of the Zn deposit that was obtained from an additive-free electrolyte, where it can be seen that different-sized Zn particles were obtained with a much more random morphology. Clear changes in the morphologies of the Zn deposit occurred when NA, BA and BQ were added individually to the Zn electrolyte.

In previous work, the effects of nicotinic acid on the electrodeposition of Ni (II) from DES were investigated. It was found that nicotinic acid inhibited Ni deposition; at the same time, it acted as a brightener, and produced highly uniform and smooth Ni deposits.¹⁸ In this study, when NA was used in the Zn electrodeposition, a significant change was observed in the morphology of the Zn film. A bright Zn coating was deposited from Ethaline 200 with a concentration of 0.4 M ZnCl_2 and 0.05 M NA. According to the voltammograms of NA in Ethaline 200, as shown in **Figure 4.7**, it can be suggested that NA adsorbs on the cathodic electrode and inhibits the deposition of Zn. An improvement in the smoothness and refinement in the grain size of the Zn deposit, as can be seen in **Figure 4.13 (b)**, has been obtained as a result of using NA as an additive. Thus, NA can act as a very effective brightener in Zn deposition.

The cross-sectional morphology of the Zn coating deposited from the additive-free electrolyte is shown in **Figure 4.13 (a)**. It was found that the Zn coating exhibits good adhesion with the Cu substrate, and the thickness of the coating was uniform with an average value of ~11.1 µm, as based on four thicknesses measured at random positions. A theoretical thickness for Zn film can be calculated based on Faraday's electrolysis law, and was found as 11.67 µm for a deposition current density of 3.3 mA cm⁻². Consequently, the current efficiency was about ~95%, which is close to the efficiency measured from QCM data. The cross-sectional morphology of the Zn coating deposited from the electrolyte containing 0.05 M NA is shown in **Figure 4.13 (b)**, where small holes were observed in the cross-sectional morphology of the Zn film. The presence of these holes could correspond to hydrogen evolution occurring on the cathode surface during the electrodeposition process. The thickness of the Zn coating obtained from a system containing NA was increased compared to the above, being found as 15.4 µm,

where the recorded increase in film thickness could be attributed to the presence of the small holes in the Zn film.

Figure 4.13 (c) shows photographs, morphologies and cross sections of the Zn deposits obtained from a system containing boric acid. Boric acid is one of the most common compounds to be added to Ni electroplating baths. Researchers have suggested that when boric acid is added to the electroplating bath it acts as a buffering agent to stop or reduce the alkalisation process at the cathodic electrode, which normally occurs due to hydrogen evolution.^{42, 51, 52} However, several reports in the literature have confirmed that BA acts as a surfactant,⁵² and also that BA interferes with the metal nucleation processes.⁵²⁻⁵⁴ Supicová *et al.*⁵² found that the presence of high concentrations of boric acid in aqueous baths inhibited nickel deposition itself but improved the morphology, brightness, and adhesion of the deposited Ni.

In this project, BA was used as a brightener during the electrodeposition of Zn from Ethaline 200. A significant change in the Zn film morphology, where a clear refinement in the grain size of the Zn was obtained, along with a bright Zn film resulting from the use of boric acid, is shown in **Figure 4.13 (c)**. Here, BA most likely adsorbs on the electrode surface as a neutral molecule and strongly inhibits the deposition of Zn.

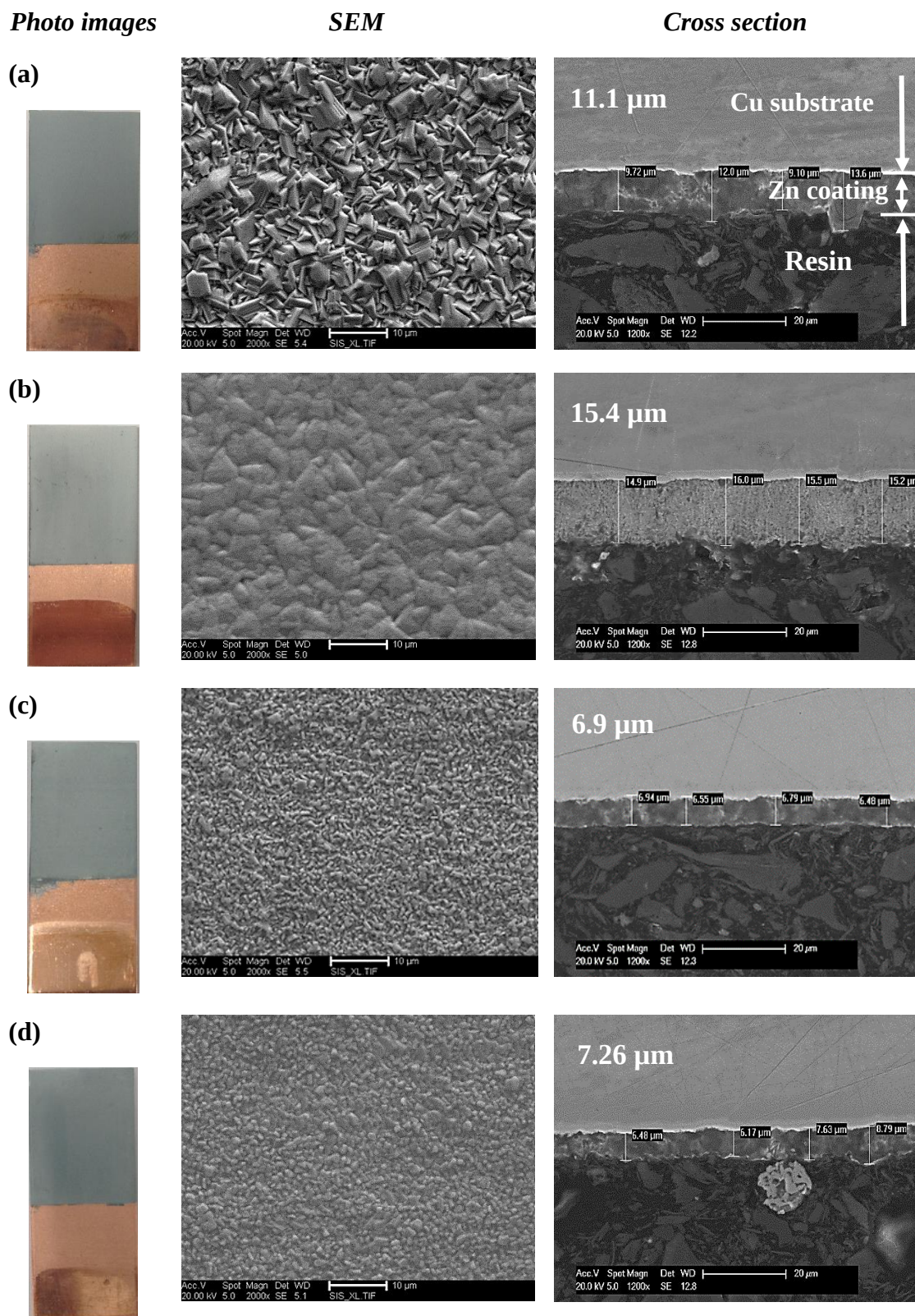


Figure 4.13 Optical photographs and SEM images with cross-sectional samples after bulk electrodeposition from Ethaline 200 systems containing 0.4 M ZnCl_2 using following additives: (a) without additives; b) 0.2 M BA; c) 0.05 M NA; and d) 0.03 M BQ. (All experiments were performed at 80°C for 2 h on a Cu electrode with an applied current density of 3.3 mA cm^{-2} (sample width 2 cm)).

The thickness of the Zn deposit was 6.9 μm when the deposition was performed using 0.15 M BA, a significant decrease compared to the thickness of Zn film obtained from the additive-free system. The decrease in the thickness of Zn film in the presence of BA could be due to the adsorption of BA onto the electrode surface, inhibiting the growth of Zn nuclei and enhancing nucleation rate.

Figure 4.13 (d) shows optical photographs, the morphology and cross sections of the Zn deposit obtained from a system containing 0.03 M BQ. A bright and smooth Zn film was obtained as a result of adding BQ to the Zn electrolyte, and clear refinement in the crystal size of the Zn deposit can be observed in **Figure 4.13 (d)**. However, a decrease in the thickness of the Zn film occurred when BQ was used. Here, BQ was thought to be adsorbed on the electrode surface thus inhibiting Zn deposition.

4.3.7 AFM study

Scanning Electron Microscopy (SEM) was used to study the morphologies and cross-sectional morphologies of the Zn deposits obtained from Ethaline 200 with and without additives. It also is necessary to study the nucleation, topography and roughness of Zn deposits. Therefore, Atomic Force Microscopy (AFM) was used to study these properties for the Zn deposit surfaces. **Figure 4.14** demonstrates an AFM image of a Zn deposit from Ethaline 200 in the absence and presence of various types of organic additives (NA, BA and BQ) at 80°C on a Cu substrate at a current density of 3.3 mA cm^{-2} for 2 h. AFM results are in good agreement with SEM results. **Figure 4.14 (a)** shows the topography of the Zn deposit from Ethaline 200 containing 0.4 M ZnCl_2 without additives. The micrographs reveal that the Zn deposits consist of randomly-sized Zn grains. A small Zn grain size is formed from the deposition achieved from a system containing additives, especially when using boric acid and *p*-benzoquinone, as can be seen in **Figures 4.14 (c) and (d)**.

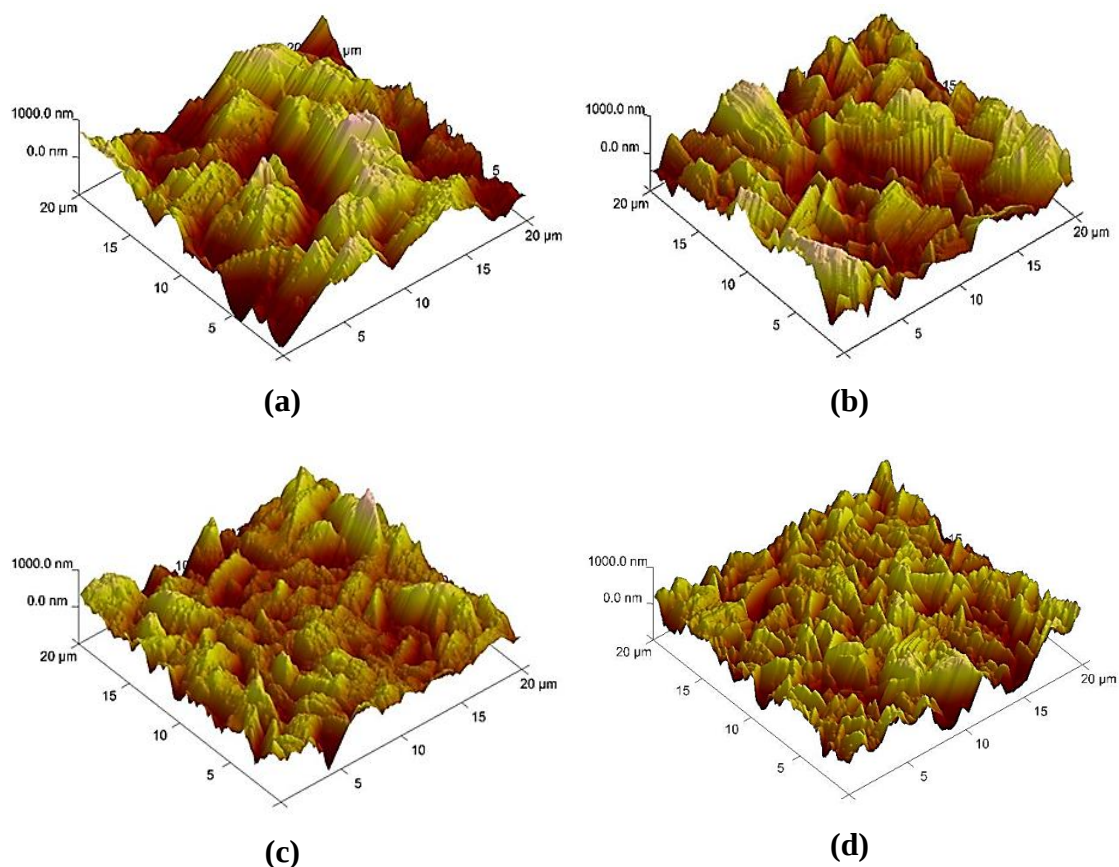


Figure 4.14 SEM images of samples after bulk electrodeposition from Ethaline 200 systems containing 0.4 M ZnCl_2 using the following additives: **(a)** without additives; **(b)** 0.15 M BA; **(c)** 0.05 M NA; and **(d)** 0.03 M BQ. (All depositions were performed at 80°C for 2 h on a Cu electrode at an applied current density of 3.3 mA cm^{-2}).

Through the use of AFM, the roughness of the Zn films has been measured. Smoother Zn films were produced when the electrodeposition was performed in the presence of additives. **Table 4.2** reports the roughness of Zn deposits produced from electrolytes with and without additives. The roughness of the Zn deposit obtained from a system without additives was about 334 nm. However, the thickness of the Zn deposit decreased by 184 nm when the electroplating process was performed in an electrolyte containing NA, along with a decrease in its roughness. A remarkable decrease in the roughness of the Zn film deposit occurred as a result of using BQ as the additive, where the roughness was reduced to 157 nm. Here, the additives may work as levellers; as explained in the previous chapter, some additives may be absorbed onto, and thus block, the high points of the electrode surface. The metal will thus be deposited on the electrode's recesses, leading to the production of a smoother coating than can otherwise be achieved from a system without additives.

Table 4.2 Roughness of Zn deposits obtained from Ethaline 200 containing 0.4 M ZnCl_2 in presence and absence of 0.05 M NA, 0.15 M BA and 0.03 M BQ. (All depositions were achieved at 80°C for 2 h on a Cu electrode at an applied current density of 3.3 mA cm^{-2}).

Metal salt	Additives	Roughness, R_a /nm
ZnCl_2	Non	334 ± 7
ZnCl_2	nicotinic acid	184 ± 3
ZnCl_2	boric acid	169 ± 5
ZnCl_2	benzoquinone	157 ± 3

The AFM results illustrated in **Figure 4.15** show a clear change in the surface roughness of Zn film that occurs when NA, BA and BQ were individually added to the Zn solution as brighteners. It is clear from **Figure 4.15** that the Zn deposit obtained from the additive-free solution was rougher than those produced from systems containing additives. The decrease in the roughness of the Zn film corresponds to the refinement in the Zn grain size when the additives were individually added to the Zn electrolyte.

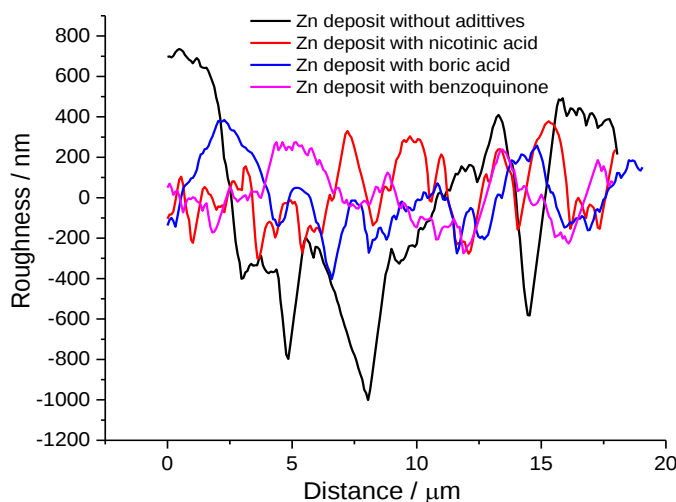


Figure 4.15 Roughness of Zn deposits obtained from Ethaline 200 containing 0.4 M ZnCl_2 in both the presence and absence of 0.05 M NA, 0.15 M BA and 0.03 M BQ. (All depositions were achieved at 80°C for 2 h on a Cu electrode at an applied current density of 3.3 mA cm^{-2}).

4.3.8 X-Ray diffraction analysis (XRD)

Here, the XRD technique was used to study the crystal orientations of Zn film produced from Ethaline 200 in the presence and absence of additives. **Figure 4.16** shows XRD patterns for the Zn film obtained from Ethaline 200 at a concentration of 0.4 M ZnCl_2 in the absence and presence of 0.05 M nicotinic acid, 0.15 M boric acid and 0.03 M *p*-benzoquinone, where all Zn film were achieved on Cu substrate at 80°C, for 2 h at a current density of 3.3 mA cm^{-2} . XRD patterns of the Zn film obtained from an additive-free system illustrate peaks at $2\Theta = 36.16^\circ$, 38.9° , 42.04° , 54.32° , 70.09° , 82.16° and 86.56° which are related to the (002), (100), (101), (102), (103), (112) and (201) planes of hexagonal zinc, respectively.^{55, 56} The diffraction peaks observed at $2\Theta = 43.2^\circ$, 50.4° and 74.14° corresponded to the Cu substrate. It can be seen that the growth of Zn in the additive-free electrolyte preferentially takes place along the (002), (102) and (103) planes.⁵⁶ However, Zn growth from an electrolyte containing nicotinic acid and boric acid is strongly directed along the (100), (110), (112) and (201) planes where as shown in **Figure 4.16** and **Table 4.3**. No significant difference was noted in the crystal orientation of Zn film obtained from the system containing *p*-benzoquinone compared to that produced from the Zn electrolyte without any additive.

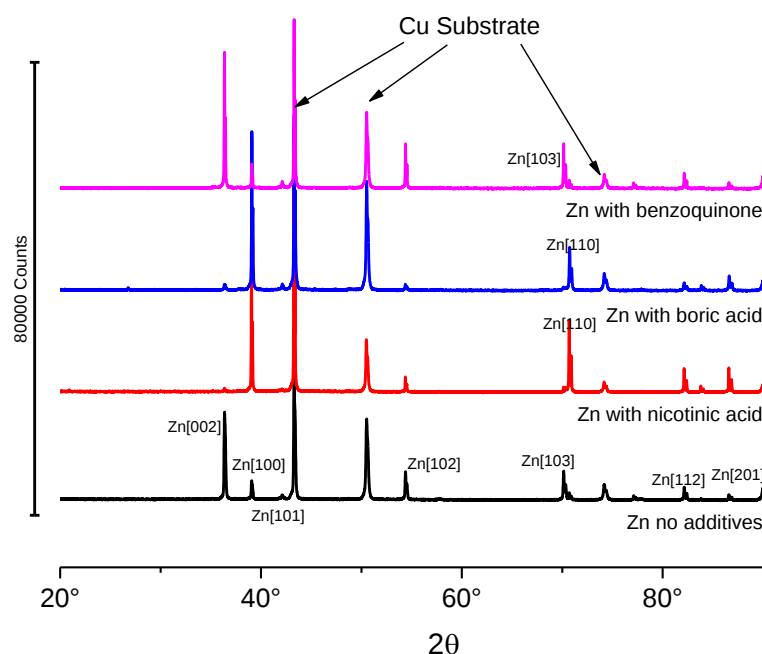


Figure 4.16 XRD patterns for Zn deposits from 0.4 M ZnCl_2 in Ethaline 200 with the following organic additives: 0.05M nicotinic acid, 0.15 M boric acid and 0.03 M *p*-benzoquinone. All experiments were performed for 2 h at 80°C and at a current density of 3.3 mA cm^{-2} .

Table 4.3 Texture coefficients of the Zn deposits prepared from 1:2 ChCl:EG-based liquid containing 0.4 M ZnCl_2 in the absence and presence of 0.05M nicotinic acid, 0.15 M boric acid and 0.03 M *p*-benzoquinone. All experiments were performed for 2h at 80°C and at a current density of 3.3 mA.cm⁻²

Component	Relative intensity [002]	Relative intensity [100]	Relative intensity [102]	Relative intensity [103]	Relative intensity [112]	Relative intensity [201]
Pure Zn	0.402	0.118	0.154	0.162	0.098	0.064
Zn + NA	0.135	0.269	0.145	0.135	0.155	0.155
Zn + BA	0.152	0.250	0.148	0.147	0.148	0.153
Zn + BQ	0.324	0.150	0.168	0.165	0.101	0.090

4.3.9 Bright zinc deposit

Brightness is related to the smoothness surface and its ability to reflect visible light without significant scattering, where roughness should be less than 400 nm. Brightening can be defined as a deposit having crystals of a smaller size than the wavelength of visible light, which on average could be nominally taken to be smaller than 400 nm. Small crystals are essential for brightness, but this in itself is not a satisfactory condition. A number of studies have found that brightness also depends on the orientation of crystallites that are deposited on the surface in the same plane.⁴⁸

Shiny Zn deposits have been obtained when the deposition has been achieved from Ethaline 200 with 0.6 M ZnCl_2 and 0.15 M NA. **Figure 4.17** shows the morphology of a Zn film obtained from Ethaline 200 with 0.6 M ZnCl_2 in both the absence and presence of 0.15 M NA, where both experiments were performed at 80°C for 2 h at a current density of 6.15 mA cm⁻². As mentioned earlier in this chapter, NA can be adsorbed on the electrode surface and impede nucleation of large Zn crystals. It is clear from **Figure 4.17** that a Zn film obtained from a system without additives shows the unorganised deposition of Zn particles in random forms. However, shiny and highly smooth Zn film is produced when electroplating is achieved from Ethaline 200 containing 0.6 M ZnCl_2 and 0.15 M of NA.

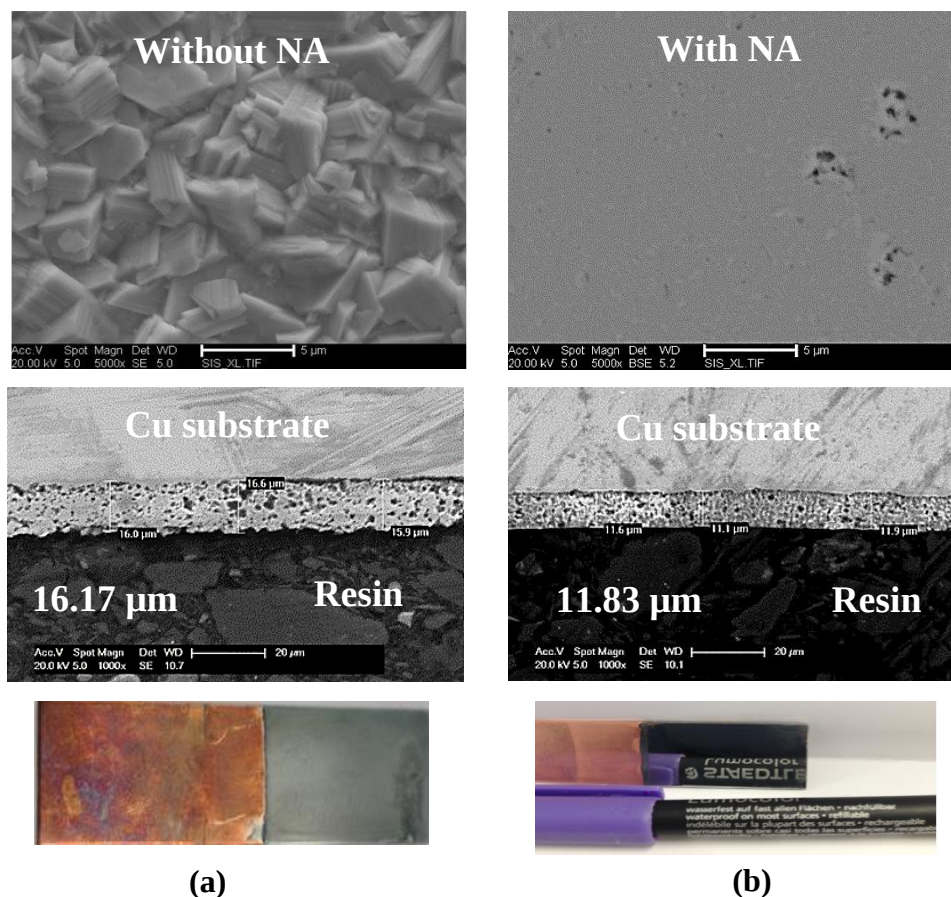


Figure 4.17 Morphologies of Zn films obtained from Ethaline 200 in the absence and presence of NA, **(a)** without NA and **(b)** with NA. (the deposition was achieved from Ethaline 200 with 0.6 M ZnCl_2 , with and without 0.15 M NA, at a current density of 5 mA cm^{-2} for 2 h on a Cu substrate at 80°C (sample width 2 cm).

Earlier in this chapter, a Zn electrodeposit was produced from an electrolyte containing 0.4 M ZnCl_2 with 0.05 M NA at a current density of 3.3 mA cm^{-2} . However, when the conditions of the coating changed (0.6 M ZnCl_2 , 0.15 M NA and 5 mA.cm^{-2}), a shiny Zn deposit was obtained after cleaning the Zn film surface (via mechanical polishing). It can be seen that the thickness of the Zn film was decreased when the process was performed in the presence of NA. This may due to a high concentration of NA, allowing its adsorption on the electrode surface and increasing the associated hydrogen evolution, which in turn could lead to a decrease in the thickness and current efficiency of Zn deposition.

Cyclic voltammograms of 0.6 M ZnCl_2 in Ethaline 200 in the absence and presence of 0.15 M NA are shown in **Figure 4.18**. The voltammetry was carried out in the potential range 0.0 V -1.5 V at a scan rate of 30 mVs^{-1} using a Pt disc (1 mm diameter) electrode; a Pt flag was used as the counter-electrode, and Ag/AgCl as the reference electrode. In

the absence of NA, the onset of Zn reduction (vs. Ag/AgCl) in Ethaline 200 was at $E = -1.18$ V. However, this potential was shifted negatively by 15 mV when 0.15 M of NA was added to the Zn solution. Additionally, a significant decrease in the deposition/dissolution of Zn occurred when NA was added to the Zn electrolyte. NA has been used in the electrodeposition of Ni from DES from which a bright and smooth Ni film was achieved, where it was suggested that NA adsorbed on electrode surface inhibited Ni deposition.²⁸ Here, with Zn deposition, it can be similarly suggested that NA adsorbs on electrode surface and inhibits Zn deposition.

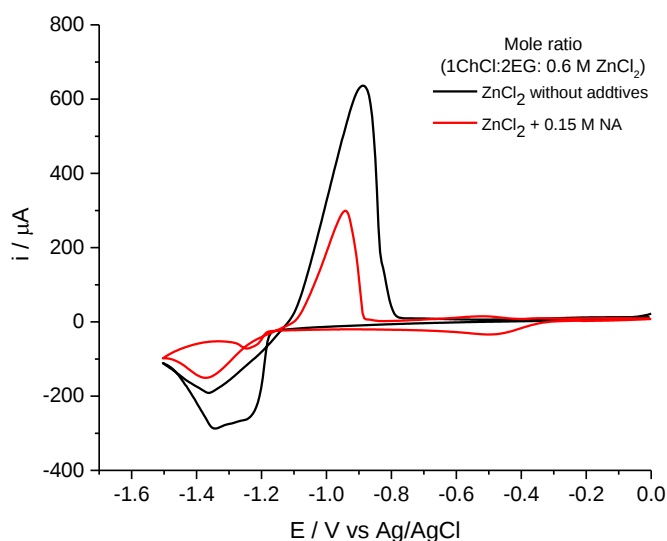


Figure 4.18 Cyclic voltammograms of 0.6 M ZnCl_2 in Ethaline 200 in the absence and presence of 0.15 M nicotinic acid using a Pt disc (1 mm diameter) electrode, a Pt flag counter electrode and Ag/AgCl as the reference electrode at 30 mVs^{-1} and 80°C .

Cyclic voltammograms of NA in Ethaline 200 were investigated, as shown previously in **Figure 4.7 (a)**, and NA was deposited at a potential lower than that at of the Zn deposition potential. This means that NA adsorbs on the surface electrode and impedes Zn deposition. In **Figure 4.18**, in the presence of NA, a small peak can be observed at -0.47 V which corresponds to the hydrogen evolution that occurs as a result of its reduction. This confirms that NA adsorbs on the electrode surface and inhibits Zn deposition.

The roughness and topography of the Zn films obtained from Ethaline 200 in the absence and presence of NA were studied using AFM. **Figure 4.19** illustrates the AFM image of a Zn deposit obtained from the electrodeposition of 0.6 M ZnCl_2 in Ethaline 200 in the absence and presence of 0.15 M nicotinic acid at 80°C . The roughness of the

Zn film obtained from a solution containing NA was about 10 nm; however, the roughness of the Zn film that was achieved from an additive-free solution was about 174 nm.

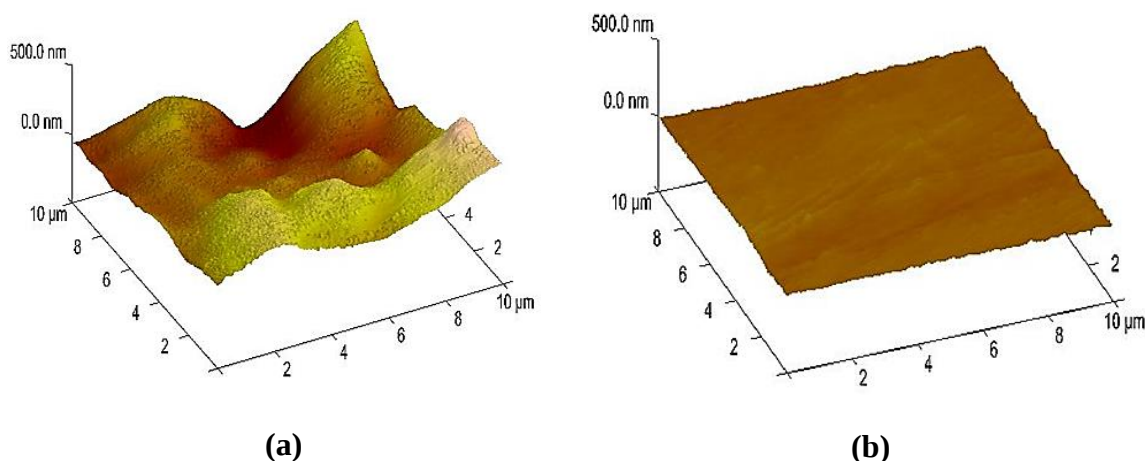


Figure 4.19 AFM images of the Zn electrodeposit from Ethaline 200 containing 0.6 M ZnCl_2 in the presence and absence of NA. (a) The Zn electrodeposit from a system without NA, and (b) the Zn electrodeposit from a system containing 0.15 M NA. The electrodeposition was achieved on Cu substrates at 80°C and at a current density 5 mA cm^{-2} for 2 h.

XRD patterns of Zn film obtained from Zn solutions in the absence and presence of nicotinic acid are shown in **Figure 4.20**. In the case of the solution without NA, the Zn deposit shows the (002), (100), (101), (102), (103), (112) and (201) orientations and it has been shown that the growth of Zn preferentially takes place along the (002), (101), (102) and (103) planes; however, Zn growth from an electrolyte containing nicotinic acid preferentially take place along the (100) and (110) planes.

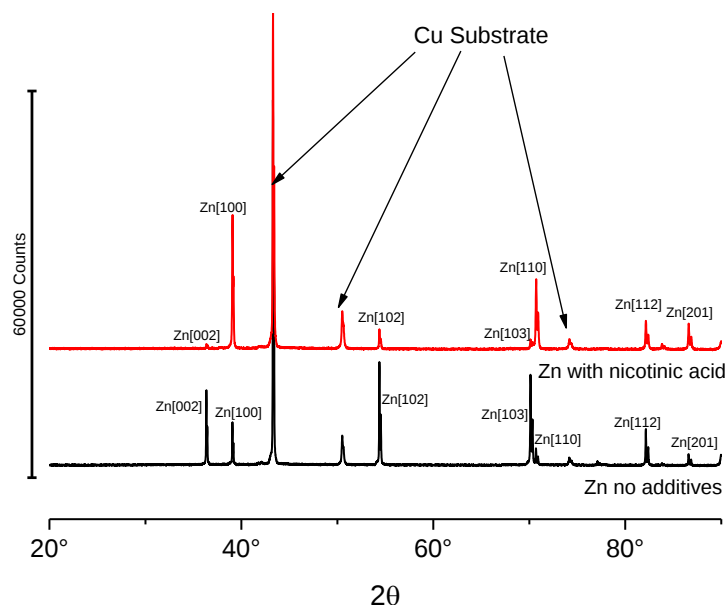


Figure 4.20 XRD patterns for Zn deposits from 0.6 M ZnCl_2 in Ethaline 200 in the absence and presence of 0.15 M nicotinic acid, 0.15 M boric acid and 0.03 M *p*-benzoquinone. All experiments were performed for 2 h at 80°C and at a current density of 6.5 mA cm^{-2} .

4.4 Summary

Organic additives are often added to aqueous electrodeposition baths as levellers and brighteners. However, few studies have considered the effects of additives on the electrodeposition of metals from deep eutectic solvents.

In this thesis, a full investigation into the effects of additive addition to the Zn electrodeposition process from Ethaline 200 has been presented. The additives studied, nicotinic acid, boric acid and *p*-benzoquinone, have been shown to have varying effects on the mechanism of Zn deposition. The physical and mechanical properties of the Zn electrodeposit have been improved compared to the corresponding system without additives, and for first time a mirror zinc coating has been achieved on a copper substrate when nicotinic acid was used as the additive. It was found that boric acid and *p*-benzoquinone work as brighteners for Zn deposition. It was observed that those additives caused a slight decrease in the conductivity of the Zn electrolyte.

Electrochemical experiments, including cyclic voltammetry, chronocoulometry and chronoamperometry, have established a clear difference in Zn electrodeposition processes when the additives were used and in the control experiments where no additive was used. Cyclic voltammetry has shown that these additives can be adsorbed

on the electrode surface during the experiment and then inhibit Zn deposition. The morphologies of the Zn deposits using additives were improved compared to the corresponding systems without additives, showing considerable decreases in the roughness of the Zn films obtained when electrodeposition was achieved from a system containing an additive. Rates of Zn deposition were increased as a result of adding either NA or BQ to the Zn bath. However, decreases in the current efficiency of Zn deposition occurred when using these additives, especially with NA. In the XRD data shown, the (002), (101) and (102) planes were noted in the crystal orientation of the Zn film obtained from the system without additives. However, Zn growth from an electrolyte containing nicotinic acid and boric acid is strongly directed along the (100), (101) and (110) planes.

In **Chapter 5**, the effects of additives on the electrodeposition of Zn-Ni alloys from Ethaline 200 as a deep eutectic solvent under various physical conditions will be examined.

4.5 References

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Chapter 5: Electrodeposition of Zinc-Nickel alloys from Deep Eutectic Solvents

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5.1 Introduction

In recent years, electrodeposition of alloys has been used in the automotive and aerospace industries; this technique is of particular use in these industries as the physical and mechanical properties of metals can be improved by alloying. Cadmium and cadmium alloys are generally used for preventing the corrosion of steel plates or other metal pieces. However, because of cadmium's toxicity, it is desirable to replace it with non-toxic metals.¹⁻³ Electrodeposition of Zn-Ni alloys can be seen as a 'green' alternative to cadmium and hexavalent chromium as corrosion-resistant coatings on automotive, aerospace, and fastener components.⁴ Zn and its alloys have been widely used for imparting corrosion resistance to active metal substrates from aggressive, corrosive environments.⁴ Recently, Zn-Ni alloys have attracted considerable interest because they possess higher corrosion resistance, have higher thermal stability, higher hardness and better mechanical properties than pure zinc and other Zn alloys.^{5, 6} They have been used in a wide range of applications such as aerospace, automobile, and electronics and other industries.^{7, 8} It has been reported that Zn-Ni alloys that contain 8-14 wt.% Ni and have a single γ -phase structure that has five times the corrosion resistance of a pure Zn coating;^{5, 7, 9-13} others studies have concluded that Zn-Ni alloys with a Ni content in the range 5-20 wt.% are more resistant to corrosion than pure Zn in salt electrolytes.^{4, 14}

In the electrodeposition of Zn-Ni alloys, parameters such as current density, temperature and composition of the bath affect the microstructure and mechanical properties of the alloy thus deposited. This is due to their effect on the Ni content of the deposits, which consequently leads to differences in the properties of the associated Zn-Ni alloy.^{11, 15} Additives can also significantly affect the properties of Zn-Ni alloys; Albalat *et al.* proved that additives in the plating bath can be optimised for homogeneity of surface, which leads to an increased corrosion resistance even for alloy deposits that contain a low percentage of Ni atoms.^{7, 16} Additives can reduce the grain size of Zn-Ni deposits, leading to other improvements in the properties of the alloy. Li *et al.*¹⁷ studied the effect of laboratory-made additives on the electrodeposition of Zn-Ni alloy from an alkaline bath, where their results showed the deposition of a monocrystalline alloy with high corrosion resistance. Muresan *et al.*¹⁸ studied the effect of saccharin on surface roughness and crystallite size of the Zn-Ni alloy from alkaline glycinate bath deposits, finding that crystallite size and roughness of deposits decreased with an increasing

concentration of saccharin. Rao *et al.*¹⁹ studied the synergistic effect of gelatin and glycerol on corrosion stability and the electrocrystallisation process of Zn-Ni alloys. One can summarise that additives play a very important role in improving, and indeed tuning, the physical properties of Zn-Ni alloy deposits.

Zn-Ni films were produced from aqueous bath formulations.^{4, 20, 21} They were obtained from sulphate baths on addition of *p*-toluene sulphonic acid and boric acid. Sulphate-sulphamate combinations have also been used to produce Zn-Ni layers. Bright deposits have been achieved from chloride baths with SrSO₄. Furthermore, acetate baths, on addition of boric acid, produced Zn-Ni films with less than 15% Ni content.²⁰ However, electroplating from aqueous solutions is undesirable due to the evolution of hydrogen at the cathode electrode, which can affect current efficiency and thus the properties of Zn-Ni deposits. Furthermore, most aqueous plating systems are toxic and uneconomical. Ionic liquids (ILs) have been used as alternatives for the electrodeposition of Zn and its alloys. ILs have desirable properties such as potential windows, wide temperature ranges can be employed, good conductivity for electrolysis, and they are free from hydrogen evolution owing to the absence of water.^{4, 22-24} Chloroaluminate ILs have been used for the electrodeposition of Zn-Ni.^{4, 25-27} However, these liquids are hygroscopic, reducing the potential scope for their practical application.^{4, 28-30} More recently, generation of air and water-stable ionic liquids has been achieved; these types of liquid see use in various different fields. However, they have some disadvantages, such as low solubility to metal halides, because these liquids are naturally weak Lewis bases;^{4, 31, 32} the exception here is dicyanamide (DCA⁻) anion-based liquids, which can be used for dissolving various metals halides. However, anion-based liquids have their own disadvantages, for instance high cost, toxicity, and difficulty of preparation.

An anomalous co-deposition of Zn-Ni deposits can be obtained from aqueous plating baths, though producing alloys with a high percentage of Ni from such baths can be difficult. Considerable effort has been made to increase the amount of Ni in the deposition and to optimise the anomalous co-deposition.^{4, 33-35} The production of this anomalous co-deposition could be due to the hydrogen evolution at the cathode surface, as this can lead to a localised increase in pH near the cathode electrode; this favours the formation of zinc hydroxide, and therefore inhibits Ni discharge.^{4, 36} Phenomena associated with hydrogen evolution in ILs is considerably reduced compared to aqueous solutions, and different Zn-Ni films can be obtained as a consequence. High Ni content

and non-anomalous co-deposition have been achieved from zinc chloride-1-ethyl-3-methylimidazolium chloride.^{4, 27, 37} However, there are a few reports in the literature on the electrodeposition of Zn-Ni from air- and water-stable ILs.

Eutectic-based ionic liquids (called deep eutectic solvents, or DESs) were recently produced, and have been used in various fields. Deep eutectic solvents were one of the classes of ionic liquids that solved a number of problems associated with electrodeposition of metals from aqueous and non-aqueous solutions. DESs have significant advantages in terms of their physiochemical properties,³⁸⁻⁴¹ such as a wide potential window, non-flammability, high solubility for metal salts, low cost and non-toxicity. The electroplating of several metals and their alloys, such as Ni, Sn, Cu, Zn, Co and Ag, has been achieved from DESs. Recently, Ni-Zn, Ni-Mo and Ni-Sn alloys have been deposited from a 1:2 ChCl:urea-based liquid.^{4, 42}

To date, a number of investigations have focused on the properties of Zn-Ni alloys derived from aqueous and non-aqueous solutions using different complexing agents. However, to the best of our knowledge, no work has been conducted on the effect of additives on the electrodeposition of Zn-Ni from a deep eutectic solvent. This work reports the study of electrodeposition of Zn-Ni alloy on copper from a DES consisting a 1:2 stoichiometric mix of choline chloride and ethylene glycol (Ethaline 200) using boric acid and sodium bromide as additives. The electrodepositions have been achieved through varying a number of parameters, namely those of current density, temperature, additives and different metal ratios in the plating bath. The physical and mechanical properties of the Zn-Ni alloys so produced are considerably improved compared to those achieved from systems without additives, and for the first time a bright Zn-Ni alloy coating has been achieved on a copper substrate. The different Ni species present in the Ethaline 200 at various temperatures have been studied using UV-Vis spectroscopy. The electrochemical properties of the plating liquid have been studied using cyclic voltammetry. The chronoamperometry method has been used to study the nucleation/ growth processes of Zn-Ni deposition, and its resultant surface characteristics, such as morphology, alloy composition and roughness were revealed by SEM/EDXS and AFM. The XRD technique was used to examine the crystal structure of Zn-Ni alloy. The hardness and corrosion resistance of the bright the Zn-Ni alloy were also studied.

5.2 Aims and objectives of the work

Electrodeposition of Zn-Ni alloys has been suggested as an alternative to cadmium and hexavalent chromium to produce corrosion-resistant coatings on automotive, aerospace, and fastener components. Zn-Ni alloys electrodeposition has previously been studied within the group but the deposits were dull and showed poor adhesion. The aims of this work is to deposit Zn-Ni alloy from Ethaline 200 in a bright, dense, thick and adherent coating. The additives chosen for this chapter are boric acid and sodium bromide which work well for the individual metals and the aim is to see how they affect the deposition of the alloy in terms of the deposit morphology, corrosion resistance and hardness.

5.3 Results and discussion

5.3.1 Speciation

Electrodeposition of Zn-Ni alloys from Ethaline 200 has been achieved over a range of temperatures to examine the effects of temperature on the composition and morphology of the Zn-Ni film. It is clear that increasing the temperature causes a decrease in the viscosity and an increase in conductivity of the electrolyte; temperature, however, can also change the chemical species formed by some of the metal ions present. Metal ion speciation can be indicated by the colour of the solution, and many metal salts can be identified through displaying significant thermochromism, as has been reported for both conventional ionic liquids and DES solutions.⁴³⁻⁴⁶ In the present work, electroplating of Zn-Ni alloys is achieved from Ethaline 200 containing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 0.5 M and 0.1 M concentrations, and has been investigated over a range of temperatures (50, 60, 70, 80 and 90 °C). Therefore, it is necessary to study the thermochromic behaviour of a ZnCl_2 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 200. **Figure 5.1** shows UV-Vis spectra of 0.03 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.15 M ZnCl_2 in Ethaline 200 measured over a range of temperatures. It can be seen that the UV-Vis spectroscopy of Ni^{2+} ions in Ethaline is temperature dependent; at low temperatures, spectra show two distinct features at 425 nm (band I) and at 655-715 nm (band II).

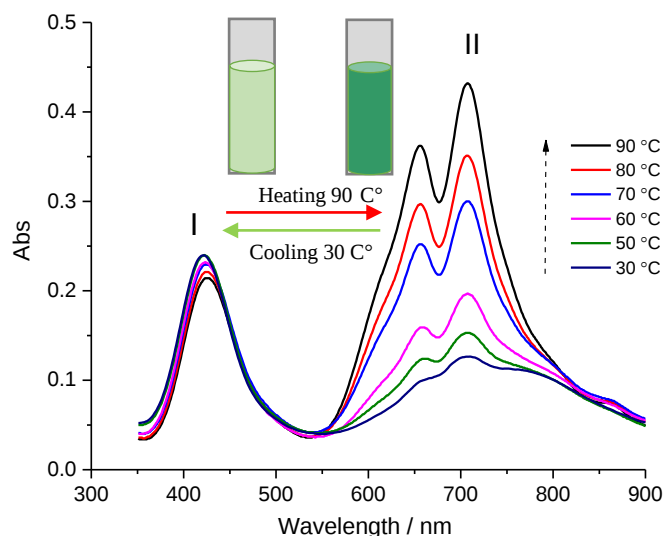
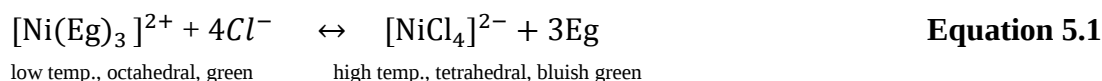


Figure 5.1 UV-Vis spectra of Ethaline 200 containing 0.03 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.15M ZnCl_2 measured over a range of temperatures.

The low wavelength electronic transition, assigned to the ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition of octahedral Ni^{2+} ^{45, 46} is commonly observed due to formation of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. In Ethaline, however, the Ni^{2+} species can be attributed to formation of $[\text{Ni}(\text{Eg})_3]^{2+}$, which is the analogous ethylene glycol (Eg) complex. The position of this band is only weakly dependent on temperature; its intensity decreases very slightly with increasing temperature. However, as indicated above, it has recently been reported that in Ethaline the Ni^{2+} species can be attributed to the ethylene glycol (Eg) complex $[\text{Ni}(\text{Eg})_3]^{2+}$.⁴⁷ This band does not show a strong temperature dependence, although the intensity does decrease with increasing temperature.

Band II is strongly affected by the increasing temperature of the electrolyte, with new bands starting to appear to lower wavelength at around 600 nm with increasing temperature. The intensity of this band is enhanced with increasing temperature, with the band itself being attributed to the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition of the tetrahedral $[\text{NiCl}_4]^{2-}$ species,⁴⁵ where the latter is responsible for the solution changing colour from pale green (at low temperature) to bluish green (at high temperature).^{45, 46} The associated thermochromic process is shown in **Equation 5.1**.



This change of Ni^{2+} species at high temperature has a significant effect on its role in the electroplating of Zn-Ni alloy from Ethaline 200, as will be discussed later.

Zn^{2+} species are not detected by UV-Vis spectroscopy, which may be due to the fact that no transition occurred in its d^{10} configuration. However, it has recently been reported that Zn species in Ethaline 200 can react with chloride ions (Cl^-) to form $[\text{ZnCl}_4]^{2-}$.^{47, 48}

The UV-Vis spectra of 0.03 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.15 M ZnCl_2 in Ethaline 200 were measured separately at 80°C, as shown in **Figure 5.2**.

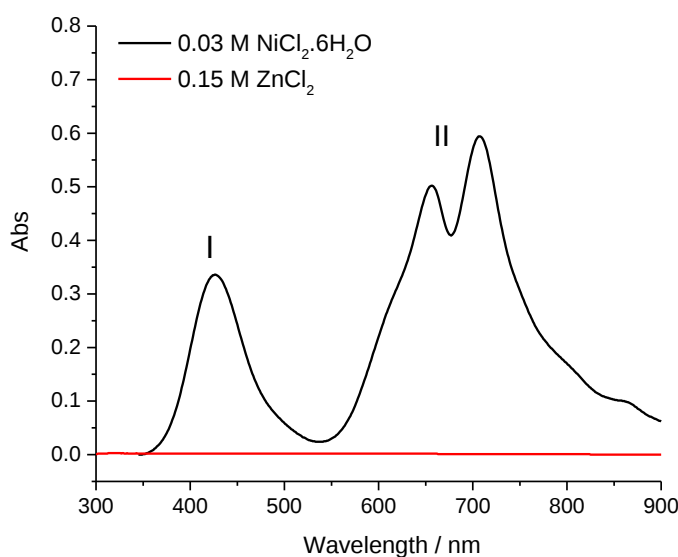


Figure 5.2 UV-Vis spectra of 0.03 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.15 M ZnCl_2 in Ethaline 200 as measured separately at 80°C.

In **Figure 5.2**, the UV-Vis spectrum of Ni^{2+} ions in Ethaline is shown in the same graph as the UV-Vis spectrum of the mixture of Zn and Ni ions at 80°C (**Figure 5.1**). In **Figure 5.2**, the spectrum of Ni shows two distinct peaks at 425 nm (band I) and at 655-705 nm (band II). Band I corresponds to the $[\text{Ni}(\text{Eg})_3]^{2+}$, which has been recently reported.⁴⁷ The absorptions in band II show a strong temperature dependence. There is a shift to lower wavelength with increasing temperature and there are additional bands appearing at lower wavelength around 600 nm. This is consistent with the previous observations and the increasing intensity of the lower wavelength bands with increasing temperature is attributed to the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition of the tetrahedral $[\text{NiCl}_4]^{2-}$ species.^{45, 49} In **Figure 5.2**, no absorption bands can be seen in the UV-Vis spectrum of Zn^{2+} ions, as no transition occurs in the d^{10} configuration. Therefore, the UV-Vis

spectra shown in **Figure 5.1** correspond to the absorption bands of Ni^{2+} ions in Ethaline 200.

5.3.2 Cyclic voltammetry

5.3.2.1 Cyclic voltammetry of Zn and Ni in Ethaline 200

Cyclic voltammetry has been used to investigate the electrochemical behaviour of Zn and Ni in Ethaline 200. **Figure 5.3** shows separate cyclic voltammograms for 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 200, performed at 30 mV s^{-1} and at 80°C using three electrodes. A Pt microelectrode of 1 mm diameter was assembled as the working electrode, an Ag/AgCl was used as the reference electrode, and a Pt flag was used as the counter electrode. These voltammograms were initially scanned cathodically from 0.5 V, and then reversed to the initial point. From the Zn voltammograms in **Figure 5.3**, it can be seen that Zn species started to reduce at -1.2 V; however, Ni species started to reduce at -0.7 V. A comparison between the voltammograms of Zn and Ni shows that Zn species need more energy to be deposited compared to the energy needed to reduce the Ni species. This means that Ni metal is deposited first on the cathode electrode from a solution containing Zn and Ni ions when a certain potential is applied. Zn metal started to oxidize at -1.15 V, while dissolution of Ni started at -0.2 V, as is clear in **Figure 5.3**.

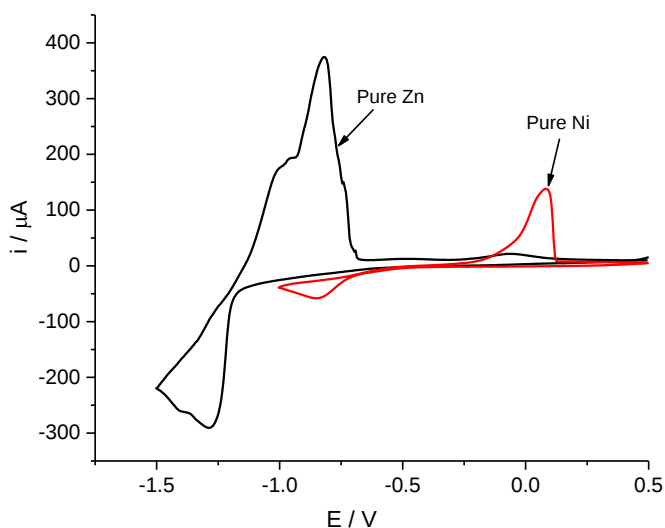


Figure 5.3 Cyclic voltammograms of 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 200 at 80°C and at a scan rate of 30 mV s^{-1} , using a Pt disc (1 mm diameter) as the working electrode, a Pt flag counter electrode and Ag/AgCl as the reference electrode.

5.3.2.2 Effect of boric acid on voltammetry of Zn (II) and Ni (II)

In this work, boric acid (BA) is one of the additives that has been used in the electrodeposition of Zn-Ni from Ethaline 200. Therefore, it is necessary to study the effect of BA on the electrochemical behaviour of Zn and Ni in Ethaline 200 separately. **Figures 5.4 (a) and (b)** show the effects of BA on cyclic voltammograms of Zn and Ni from Ethaline 200, respectively. The voltammograms were measured at 30 mV s^{-1} , 80°C and using a Pt disc (1 mm diameter) working electrode, a Pt flag counter electrode and Ag/AgCl as the reference electrode. It can be seen from **Figure 5.4 (a)** that deposition of Zn was inhibited with increasing concentrations of BA. This corresponds to the adsorption of BA onto the electrode surface, thus impeding the reduction of Zn^{50, 51}. Two stripping peaks have been produced in the cyclic voltammograms of Zn without using BA. The first stripping peak was seen at -1.1 V , while the second was observed at -0.95 V . Similar results have been obtained for a number of ionic liquid systems, and it has been suggested that two different morphologies of Zn deposit were formed (nanometer sized and micrometer sized). Therefore, the first stripping peak corresponds to the dissolution of the nanostructure which appears at -1.1 V , and the second to the dissolution of the microstructure appearing at -0.95 V .^{48, 52-54}

As BA was added to the Zn electrolyte, the dissolution peak at -1.1 V can be observed in the anodic process of Zn, as shown in **Figure 5.4 (a)**. This implied that only a single phase of Zn was formed as a result of adding BA to the plating bath.

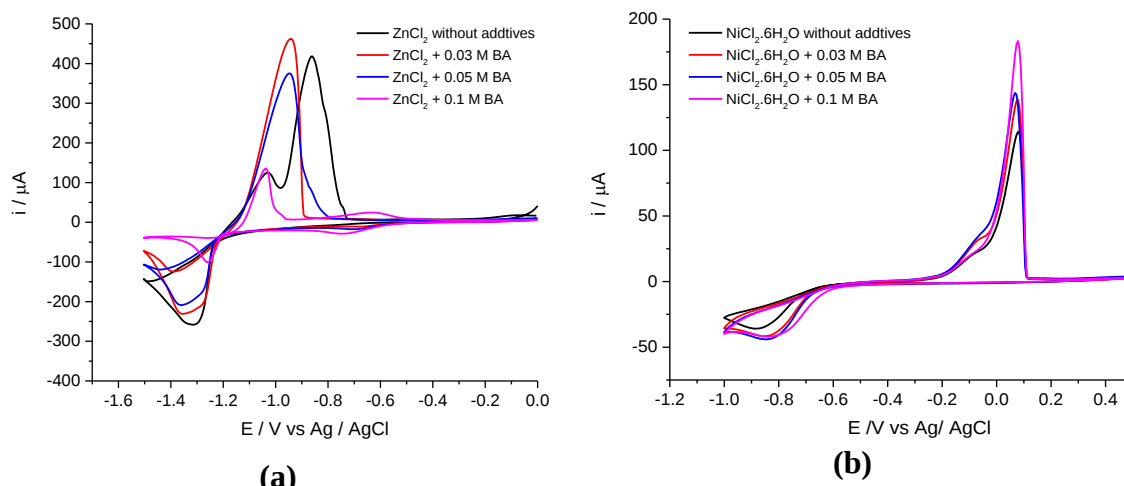


Figure 5.4 Cyclic voltammograms of Zn and Ni obtained from (a) 0.5 M ZnCl₂ in Ethaline 200 in the absence and presence of BA and (b) 0.1 M NiCl₂·6H₂O in Ethaline 200 in the absence and presence of BA. The voltammograms were measured at a scan rate of 30 mV s⁻¹, a temperature of 80°C and using a Pt disc (1 mm diameter) working electrode, a Pt flag counter electrode and Ag/AgCl as the reference electrode.

Figure 5.4 (b) shows cyclic voltammograms of Ni in Ethaline 200 containing 0.1 M NiCl₂·6H₂O in the absence and presence of a series of concentrations of BA, with the voltammograms being recorded at a scan rate of 30 mV s⁻¹ and at 80 °C. It can be seen from **Figure 5.4 (b)** that the current peak for Ni deposition increased in the presence of BA. Moreover, it can be seen that there is an increase in the stripping current peak of Ni using BA as an additive. Therefore, it could be suggested that BA increases the rate of Ni deposition. BA can be adsorbed onto the electrode surface and inhibit Ni deposition.^{3, 55} On the other hand, this adsorption can inhibit the growth of Ni nuclei, and increase the nucleation rate.⁵⁵ BA can prevent the formation of a passivation layer, thus leading to an enhanced rate of Ni deposition.⁵⁶

The effect of sodium bromide on the voltammetry of Zn and Ni in Ethaline 200 was also studied, and it was found that there was no obvious change that can be seen in the voltammograms of Zn and Ni, as shown in **Figure 5.5**.

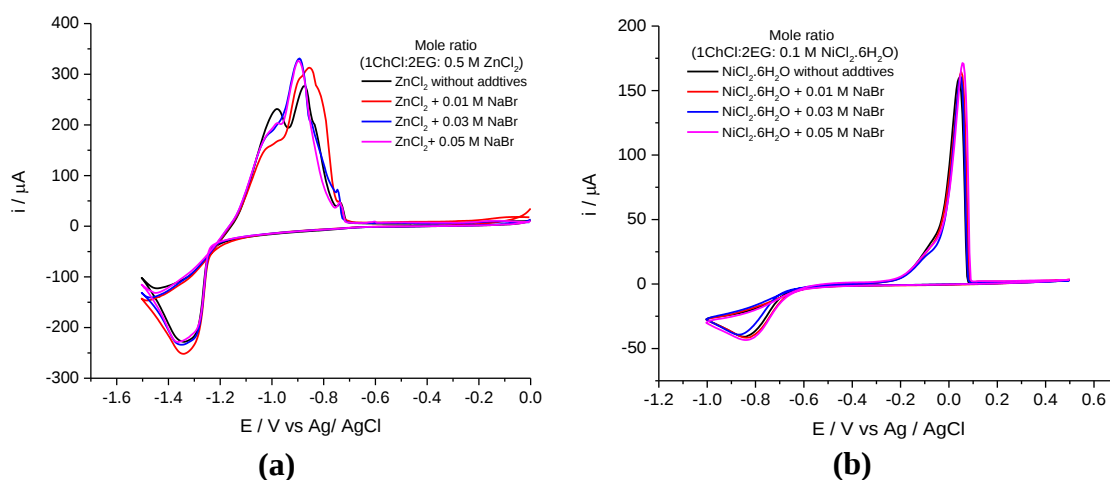


Figure 5.5 Cyclic voltammograms of Zn and Ni obtained from (a) 0.5 M ZnCl₂ in Ethaline 200 in the absence and presence of NaBr, and (b) 0.1 M NiCl₂.6H₂O in Ethaline 200 in the absence and presence of NaBr. The voltammograms were recorded at a scan rate of 30 mV s⁻¹, at 80°C and using a Pt disc (1 mm diameter) working electrode, a Pt flag counter electrode and Ag/AgCl as the reference electrode.

5.3.2.3 Effect of NaBr and boric acid on voltammetry of Zn (II) and Ni (II)

As mentioned earlier, boric acid and sodium bromide will be used together as additives in the electrodeposition of Zn-Ni from Ethaline 200. Boric acid is added to the plating bath to refine the grain size of the Zn-Ni coating, through it inhibits the reduction of Zn and Ni ions, while sodium bromide is used to increase the conductivity of the plating and to improve the adhesion of the coating. Therefore, it is necessary to study the effects of these additives on the redox of Zn and Ni from the plating electrolyte. **Figure 5.6** shows cyclic voltammograms of Ethaline 200 containing 0.5 M ZnCl₂ and 0.1 M NiCl₂.6H₂O at 80°C in the absence and presence of 0.2 M boric acid and 0.05 M NaBr. Two deposition peaks can be seen in the cyclic voltammograms of Zn-Ni that were recorded for an additive-free electrolyte. The first deposition peak, which is at -0.75 V, corresponds to the deposition of Ni, while the deposition peak that appeared at -1.25 V was related to the deposition of Zn. The reduction peak that can be observed at -1.5 V is related to the reduction of the electrolyte (Ethaline 200) and the subsequent evolution of hydrogen gas. The anode branch also shows two peaks at -1.1 V and -0.2 V, which are related to the dissolution of Zn and Ni, respectively, from the electrode surface.

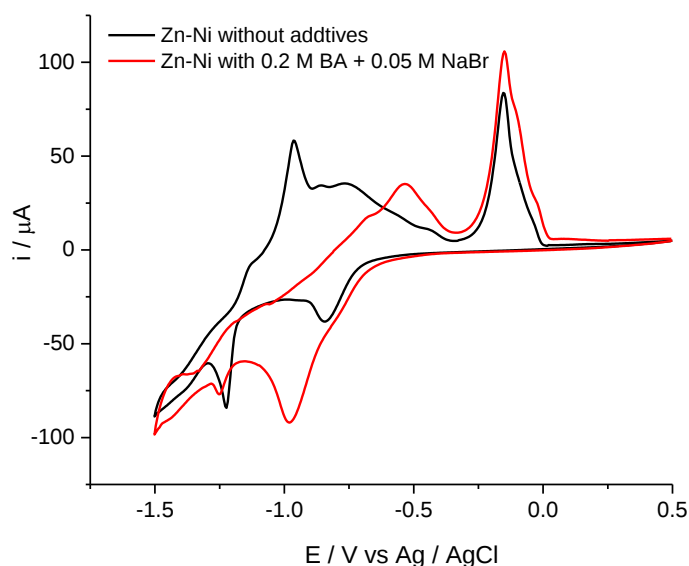


Figure 5.6. Voltammograms of Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 80 °C in the presence and absence of 0.2 M boric acid and 0.05 M sodium bromide. The experiments were performed using a Pt electrode (1.0 mm diameter) at a sweep rate of 30 mV s^{-1} vs. an Ag/AgCl reference electrode.

In **Figure 5.6**, cyclic voltammograms of Zn-Ni performed in an additive-free electrolyte showed two separate reductions peaks for Ni and Zn at potentials identical to those found previously for Ni and Zn in **Figure 5.3**. Therefore, it cannot be suggested that a Zn-Ni alloy has actually formed. However, the presence of BA and NaBr in the bath changed the behaviour of the cyclic voltammograms significantly, as shown in **Figure 5.6**. Mainly, one broad deposition peak at -1.0 V can be observed in the cyclic voltammograms of Zn-Ni as a result of using BA and NaBr as additives. Barron studied the Zn-Ni alloy in the same DES and found that the voltammetry and alloy composition were significantly changed by the initial concentrations of metals in solution. The voltammogram with NaBr and BA look similar to those observed with a high Zn:Ni ratio suggesting that the additives slow down the deposition of Ni with respect to Zinc. This is in agreement with the data in the previous chapter.^{57 50, 55, 58} The presence of a high concentration of BA in the Ni electrolyte bath can shift the reduction potential of Ni negatively.⁵⁵ Thus, this can facilitate the deposition of Zn and Ni at roughly the same potential, which leads to the production of a Zn-Ni alloy. The adsorption of BA onto the electrode surface can inhibit the growth of Ni nuclei and increase nucleation rates.⁵⁵ Therefore, the increase in height of the peak reduction of Zn-Ni could be due to an increasing nucleation rate of Ni and hydrogen evolution.

In **Figure 5.6**, the cyclic voltammograms of Zn-Ni obtained from a system containing additives show a new dissolution peak at about -0.6 V, which is related to the dissolution of Zn from Zn-Ni alloy film. As mentioned earlier in this chapter, in **Figure 5.3**, Zn oxidises at -1.2 V, thus the positive shift in the Zn oxidation potential shown in **Figure 5.6** in the presence of BA and NaBr could indicate the existence of an interaction between the zinc and nickel.^{1, 4} The dissolution of the porous Ni matrix left after dissolution of Zn from the Zn-Ni alloy film was seen at -0.2 V. An increase in the height of the dissolution peak of Ni in the bath containing BA and NaBr can be seen, indicating that the amount of Ni deposited was greater than that deposited from the additive-free electrolyte.

5.3.2.4 Effect of scan rate on voltammetry of Zn (II) and Ni (II)

Figure 5.7 shows cyclic voltammograms of Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M BA and 0.05 M NaBr at 80°C using different scan rates; all experiments were achieved using a Pt electrode, Pt flag electrode and Ag/AgCl as the reference electrode. It is clear from **Figure 5.7** that the reduction peaks of Zn-Ni, which occurred at about -1 V, shifted cathodically with increasing scan rate; also, we can see that the intensities of these peaks are enhanced as scan rate is increased. In the reverse scans, double oxidation peaks have appeared, with the more cathodic stripping peaks belonging to the oxidation of Zn from Zn-Ni alloy crystals, which took place at -0.51 V. This peak cannot correspond to the oxidation of pure Zn due to the fact that Zn is oxidized in Ethaline 200 at about -1.15 V, as shown previously in **Figure 5.3**. The second stripping peak, which appeared at about -0.20 V, corresponds to the dissolution of the pure Ni remaining after the dissolution of Zn from the Zn-Ni alloy film.

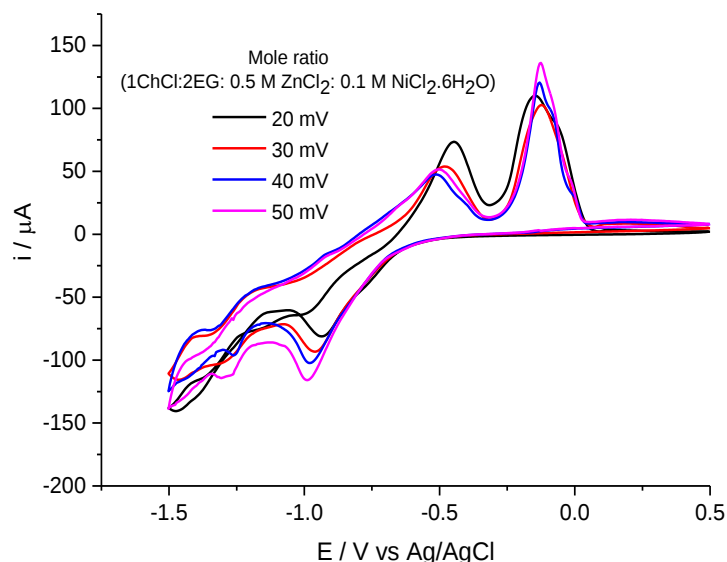


Figure 5.7 Cyclic voltammograms obtained for electrodeposition of Zn-Ni from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M boric acid and 0.05 M sodium bromide at 80°C on a Pt disc (1 mm dia.) vs. an Ag/AgCl reference electrode for various different scan rates.

5.3.2.5 Effect of temperature on voltammetry of Zn (II) and Ni (II)

Temperature plays a significant role in the electrodeposition of metals, where it can affect the physical properties of the coating. Temperature is one of parameters that has been chosen to study the effect of on the electrodeposition of Zn-Ni from Ethaline 200. Cyclic voltammograms of Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M BA and 0.05 M sodium bromide over a range of temperatures (50, 60, 70, 80 and 90°C) are shown in **Figure 5.8**. The voltammograms were recorded at a scan rate of 50 mVs^{-1} using a Pt disc (1 mm dia.) vs. an Ag/AgCl reference electrode. The electrochemical behaviour of Zn and Ni changes significantly with increasing temperature of the plating solution.

At 50 °C, the deposition of Zn-Ni alloy takes place at -1.05 V. Zn-Ni deposition peaks have been shifted anodically with the increasing temperature of the bath; furthermore, the current intensities of these peaks have also increased with increasing temperature. The reasons behind the increased intensity of and positively shifted Zn-Ni reduction peaks with increasing temperature can be related to the decreasing viscosity of the solution and its consequent increase in conductivity. Decreasing the viscosity can affect the thermodynamic process, which means that mass transport increases as function of

increasing temperature and decreasing viscosity of the solution. Thus, when mass transport increases, deposition of both Zn and Ni will increase.

With the increasing temperature of the Zn-Ni solution, species of Ni^{2+} in Ethaline 200 will be changed. The Ni^{2+} species that forms in Ethaline 200 is $[\text{Ni}(\text{Eg})_3]^{2+}$, as reported recently by Abbott *et al.*⁴⁷ With increasing temperature, a new Ni^{2+} species starts to form, namely $[\text{NiCl}_4]^{2-}$ ⁴⁶; this is supported through studying the spectra of Zn-Ni in Ethaline 200, as discussed previously in **Figure 5.1**. $[\text{NiCl}_4]^{2-}$ species could be much more easily deposited on the electrode surface compared to the $[\text{Ni}(\text{Eg})_3]^{2+}$ complex, where the latter needs more energy (a higher voltage) to deposit. Consequently, with the increasing temperature, the reduction potential of Ni is shifted anodically. Moreover, it can be said that the rate of Ni deposition is enhanced when $[\text{NiCl}_4]^{2-}$ is formed in the solution.

These results show that in Ethaline 200, the production of Zn-Ni alloy is more likely at higher temperature. As mentioned in **chapters 3 and 4**, a high concentration of Cl^- ions present in the plating electrolyte means they can be preferentially adsorbed on the electrode surface, inhibiting the deposition of metals. High temperatures can decrease the activity of free chloride ions at the surface of the electrode.⁴⁸ This allows more Zn and Ni species to reduce, and thus increases the rate of Zn and Ni deposition.

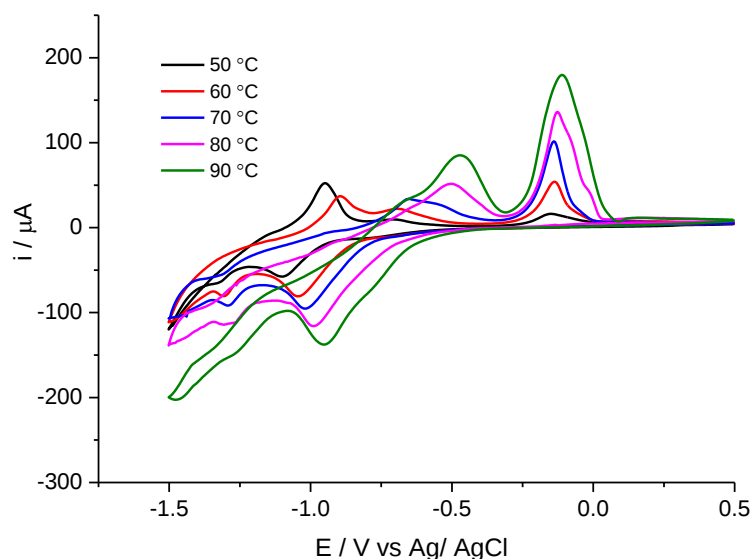


Figure 5.8 Cyclic voltammograms obtained for electrodeposition of Zn-Ni from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M boric acid and 0.05 M sodium bromide at a scan rate 50 mVs^{-1} on a Pt disc (1 mm dia.) vs. an Ag/AgCl reference electrode at different temperatures.

In **Figure 5.8**, it can be seen that Ni^{2+} started to deposit at -0.95 V at 50 °C. However, with increasing temperature, Ni^{2+} began to reduce with a low negative potential. At 90°C, the deposition of Ni^{2+} has starts -0.55 V, where it is shifted by -40 mV compared to the initiation of reduction at 50 °C. Therefore, the first film that was deposited on electrode surface was just a nickel film, because normally Zn^{2+} ions starts to reduce in Ethaline 200 at about -1.2 V, as shown in **Figure 5.3**. Since the voltammetry scans continuously towards a more negative potential (to -1.5 V), so Ni species can deposit with Zn species to form a film of Zn-Ni alloy.

In **Figure 5.8**, as the scans are reversed, two stripping peaks are produced; the stripping peaks observed at the more cathodic potential could be related to the dissolution of Zn from the Zn-Ni film, while the stripping peaks observed at more anodic potentials corresponded to those of pure Ni.^{1, 4} At 50 °C, dissolution of Zn from Zn-Ni film is achieved at -0.95 V. However, the potential of Zn dissolution is shifted anodically with increasing temperature. This positive shift in the Zn dissolution could relate to the increasing number of Ni atoms in the Zn-Ni alloy with increasing temperature. A large number of Ni atoms can be linked strongly to the Zn atoms, inhibiting dissolution of Zn and requiring higher energies to dissolve it. This also implies that Zn-Ni alloys produced from an electrolyte at high temperature have a higher resistance to corrosion than those produced at lower temperatures. **Figure 5.8** shows the dissolution of pure Ni at -0.15 V, where the intensities of the Ni dissolution peaks increase with increasing the temperature, confirming that the amount of Ni that has been deposited at high temperature is greater than that at low temperature.

It can be concluded from **Figure 5.8** that electrodeposition of Ni^{2+} ions is enhanced as the temperature of the solution is increased. In addition, it might be suggested that the deposition of Zn-Ni alloy film is more likely using high temperature systems.

5.3.2.6 Effect of Zn:Ni ratio on voltammetry of Zn (II) and Ni (II)

The last parameter that was studied in the electrodeposition of Zn-Ni was that of changing the concentration of ZnCl_2 in the plating bath. **Figure 5.9** shows cyclic voltammograms of Ethaline 200 containing different concentrations of ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 80°C, and a scan rate of 50 mV s⁻¹; the cyclic voltammograms were measured in the presence 0.2 M BA and 0.05 M NaBr as additives. Here, the cyclic

voltammetry method was used to study the effect of increasing the concentration of ZnCl_2 on the electrochemical behaviour of deposition of Zn-Ni alloy from Ethaline 200 at 80°C .

As has been shown in **Figures 5.7** and **5.8**, scan rate and temperature both affect the oxidation-reduction characteristics of Zn-Ni from Ethaline 200. **Figure 5.9** shows that increasing the concentration of ZnCl_2 in the Zn-Ni electrolyte also affects the cyclic voltammograms of Zn-Ni. When the concentration of ZnCl_2 is increased in the electrolyte, the amount of Ni deposition decreases, whilst that of Zn increases. It is hardly a surprise to observe an increase in the rate of Zn deposition with increasing concentrations of Zn species in solution. The increasing rate of Zn deposition leads to an increase in the amount of Zn in the Zn-Ni alloy film. The increases in the intensity of the oxidation peaks that appear at -0.5 V indicating an increasing amount Zn in the Zn-Ni alloys; this has been investigated in terms of the Zn-Ni coatings that have been achieved from electrolytes containing different concentrations of ZnCl_2 using EDX, as will be discussed later in this chapter.

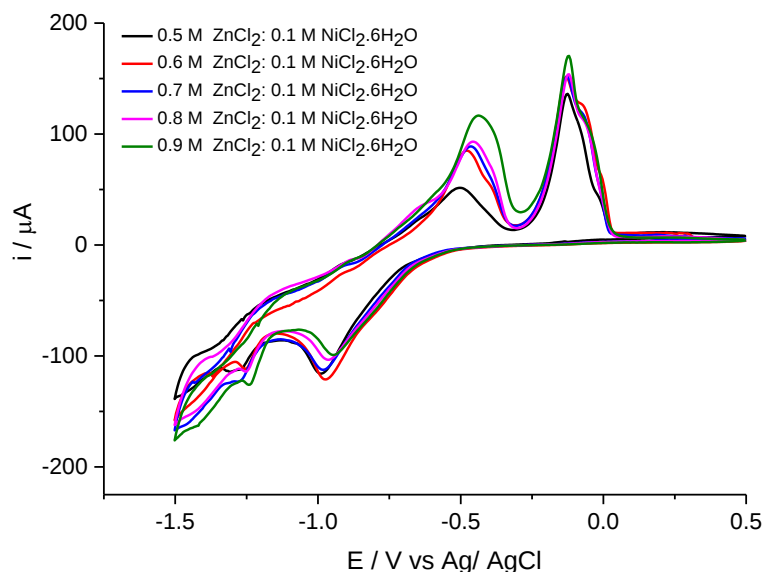


Figure 5.9 Cyclic voltammograms obtained for electrodeposition of Zn-Ni from Ethaline 200 containing 0.5 M ZnCl_2 , $0.1\text{ M NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M BA and 0.05 M sodium bromide at 80°C and a scan rate 50 mVs^{-1} on a Pt disc (1 mm dia.) vs. an Ag/AgCl reference electrode for different concentrations of ZnCl_2 .

5.3.3 Chronoamperometry

The chronoamperometry technique has been used to study the nucleation/ growth process of Zn-Ni deposition. The nucleation rate and competition between growth and nucleation can be affected by the formation of particular phase structures of the alloy. Some forms of three-dimensional nucleation process are used, generally speaking, for electrodeposition of metals/ alloys on a foreign substrate. The three-dimensional nucleation/ growth can be characterised as either instantaneous or progressive. Formation of an alloy phase tends to towards instantaneous nucleation, i.e., solid solution, while a phase that has a small amount of one species inserted in the matrix of another, principal, species tends to show progressive nucleation.⁵⁹

Nucleation mechanisms for Zn-Ni deposition have been investigated using the chronoamperometry method; in particular, they have been used here to investigate deposition from Ethaline 200 containing 0.5 M ZnCl_2 M and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M BA and 0.05 M sodium bromide on a polished Pt disk vs. an Ag/AgCl reference electrode. Here, the nucleation of the Zn-Ni deposit from Ethaline 200 has been investigated by varying conditions such as potential, temperature and concentration of Zn, as the nucleation mechanisms for the electrodeposition of Zn-Ni alloy can be significantly affected by these factors. **Figure 5.10 (a)** shows current-time data for the electrodeposition of Zn-Ni from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 80°C by stepping the potential from the value where the deposition of Ni^{2+} occurs. The potential values selected to study the nucleation mechanism of the Zn-Ni deposition were -0.75 V, 0.85 V, 0.95 V, 1.05 V, 1.15 V, and 1.25 V; the potentials were selected where the reduction current of the Zn-Ni was monitored, as shown previously in **Figure 5.7**. The mechanism of nucleation tends towards being progressive with an increasing potential, as can be seen in **Figure 5.10 (a)**.

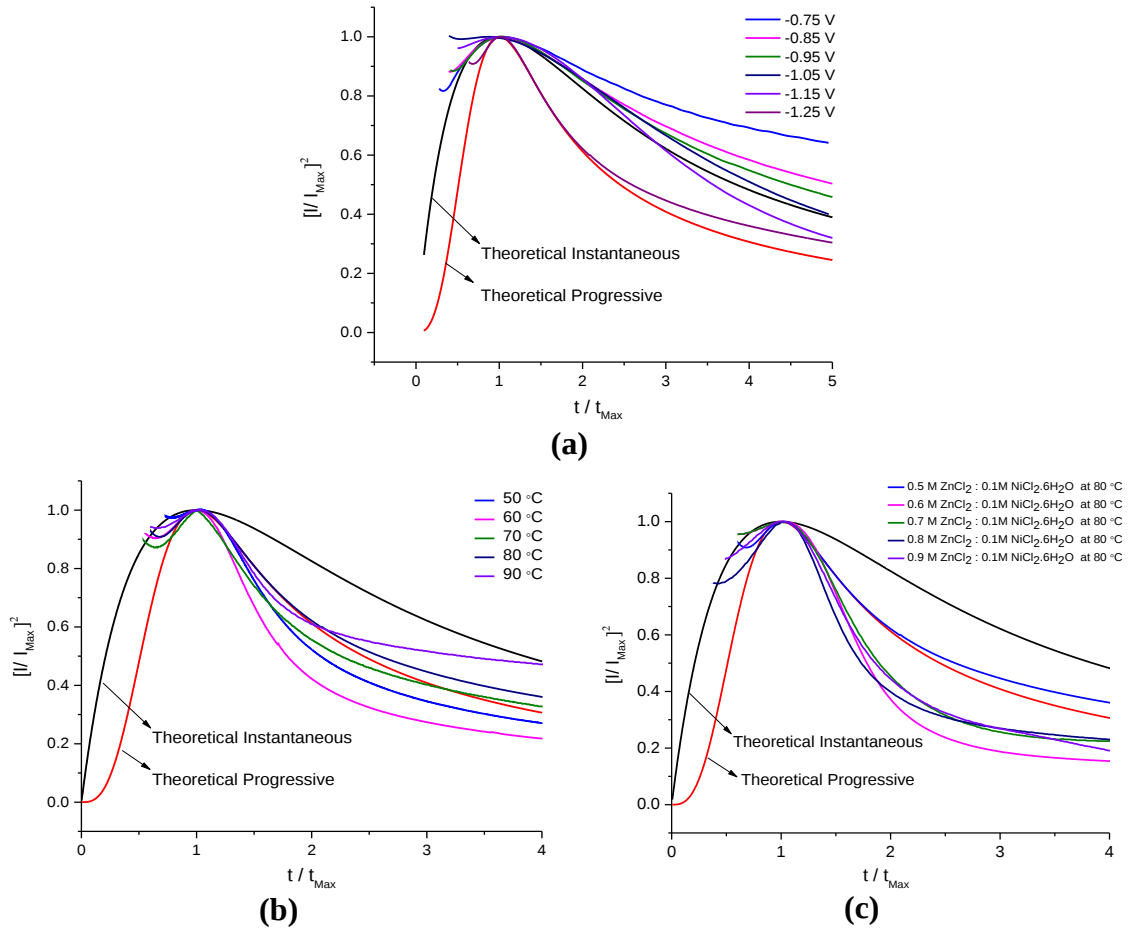


Figure 5.10 The experimental i - t data for electrodeposition of Zn-Ni from Ethaline 200 containing 0.5 M ZnCl_2 M, 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M boric acid and 0.05 M sodium bromide on a Pt disc (1 mm dia.) vs. an Ag/AgCl reference electrode for (a) different potentials, (b) different temperatures and (c) different concentrations of ZnCl_2 . In (b) and (c), the applied potential was -1.25V, with the electrolyte bath held at 80 °C.

The nucleation processes have been studied using different theoretical models. In this study, the model proposed by Scharifker and Hills has been used to identify the nucleation mechanism for the electrodeposition of Zn-Ni alloy from Ethaline 200. The Scharifker and Hills^{60, 61} models for instantaneous and progressive nucleation can be illustrated through **Equation 5.2** and **Equation 5.3**, respectively.

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.9542}{\frac{t}{t_m}} \left\{1 - \exp\left[-1.2654 \left(\frac{t}{t_m}\right)\right]\right\}^2 \quad \text{Equation 5.2 (Instantaneous)}$$

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.2254}{\frac{t}{t_m}} \left\{1 - \exp\left[-2.3367 \left(\frac{t}{t_m}\right)\right]\right\}^2 \quad \text{Equation 5.3 (Progressive)}$$

Here, i is current (A), t is time (s), i_m is the maximum current and t_m is the time at which the maximum current occurs.

The results implied instantaneous three-dimensional nucleation, as identified by **Equation 5.2**, because when the applied potential was more positive (> -0.75 V), only Ni was reduced; however, when the applied potential was decreased to -1.25 V, Zn began to be co-deposited with Ni, causing the nucleation mechanism to change to that of progressive nucleation.

Figure 5.10 (b) shows the experimental current-time data for the electrodeposition of Zn-Ni from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M BA and 0.05 M sodium bromide at different temperatures and an applied potential of -1.25 V. It is clear from **Figure 5.10 (b)** that the nucleation mechanism of Zn-Ni deposition fits well with that of progressive nucleation. Slight changes can be observed with changes in temperature. The nucleation mechanism of Zn-Ni deposition at 90°C fitted well to that of progressive growth, as is clear from **Figure 5.10 (b)**; however, over a long period of time, the mechanism began to tend towards that of instantaneous nucleation. This is likely due to the fact that at high temperature, the viscosity of the liquid decreases and thus mass transport increases. A transition between two nucleation mechanisms has been reported for nucleation and growth processes controlled by mass transfer.^{60, 62, 63}

In **Figure 5.10 (c)**, no significant change can be seen in the nucleation mechanism for Zn-Ni deposition within an increasing amount of Zn in the plating bath, where all mechanisms fitted well to those of progressive growth.

5.3.4 Electrodeposition and characterisation of Zn-Ni alloy

Figure 5.11 shows SEM images of Zn, Ni, Zn-Ni deposits: **(a)** shows the morphology of the Zn deposit obtained from Ethaline 200 containing 0.5 M ZnCl_2 ; **(b)** shows the morphology of the Ni deposit achieved from Ethaline 200 containing 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; **(c)** shows the morphology of the Zn-Ni deposit obtained from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ without additives; and **(d)** shows the morphology of the Zn-Ni deposit obtained from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M BA and 0.05 M sodium bromide. All the above coatings were achieved on a Cu substrate electrode at 80°C for 1 h at a current density of 8 mA cm^{-2} .

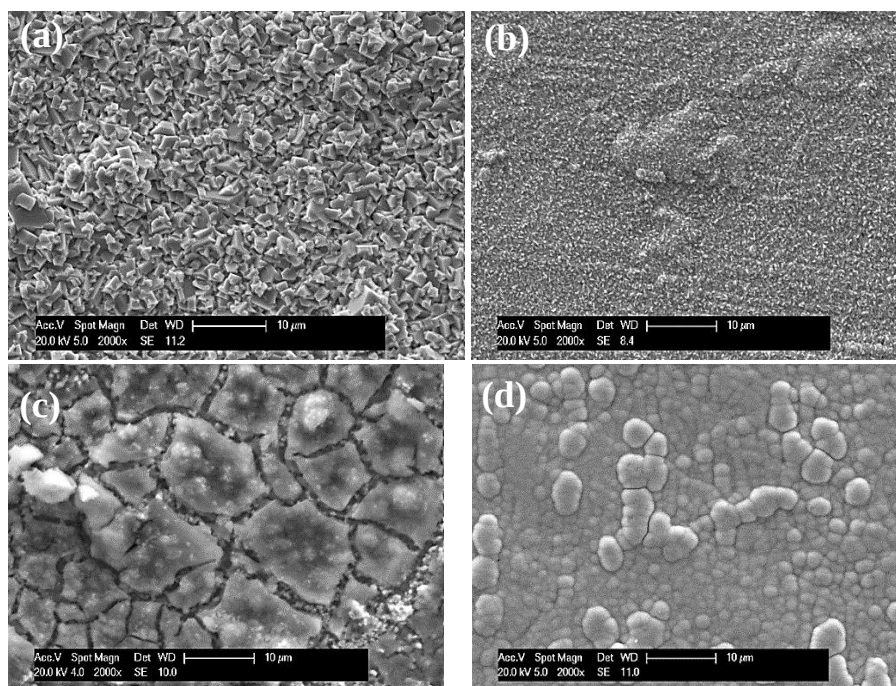


Figure 5.11 Representative SEM of (a) Zn electrodeposited from 0.5 M ZnCl_2 , (b) Ni electrodeposited from 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, (c) Zn-Ni electrodeposition from 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ without additives, and (d) Zn-Ni electrodeposition from 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M boric acid and 0.05 M sodium bromide. All experiments were achieved in Ethaline 200 on a Cu electrode at 80 °C, at a current density of 8 mA cm^{-2} for 1 h.

A pure Zn coating with hexagonal crystallites was obtained from Ethaline 200, as shown in **Figure 5.11 (a)**, and is typical of pure zinc electrodeposition,^{62, 64, 65} while **Figure 5.11 (b)** shows a pure Ni coating with smooth and fine crystallite deposits, suggesting nanocrystalline growth. The morphology of the Zn-Ni co-deposition achieved from a system containing no additives is shown in **Figure 5.11 (c)**, where a cracked, non-homogenous, deposit has been produced. A significant change occurred in the morphology of the Zn-Ni deposit when the deposition was achieved from a system containing BA and sodium bromide as additives; a uniform, homogenous and bright Zn-Ni deposit was obtained in this latter instance. Here, BA works as a brightener through refining the crystallite size in the Zn-Ni deposit, while sodium bromide helps to increase the conductivity and cohesion of the coating. From voltammograms of Zn-Ni achieved from a system without additives (**Figure 5.6**) and the morphology of the Zn-Ni coating (**Figure 5.11 (c)**), it cannot be conformed that a Zn-Ni alloy coating has been produced. The morphology of the Zn-Ni coating produced from the system

without additives seems to be more random in terms of deposits of Zn and Ni than any kind of co-deposition. XRD may be considered the best technique to determine whether this is an alloy or otherwise as it can be used to examine the crystal structure of the Zn-Ni deposit. **Figure 5.12** shows the XRD patterns for pure Zn, pure Ni, Zn-Ni deposits without additives and Zn-Ni deposits using BA and NaBr as additives. All depositions were achieved from Ethaline 200 on a Cu electrode at 80°C for 1 h using identical current densities.

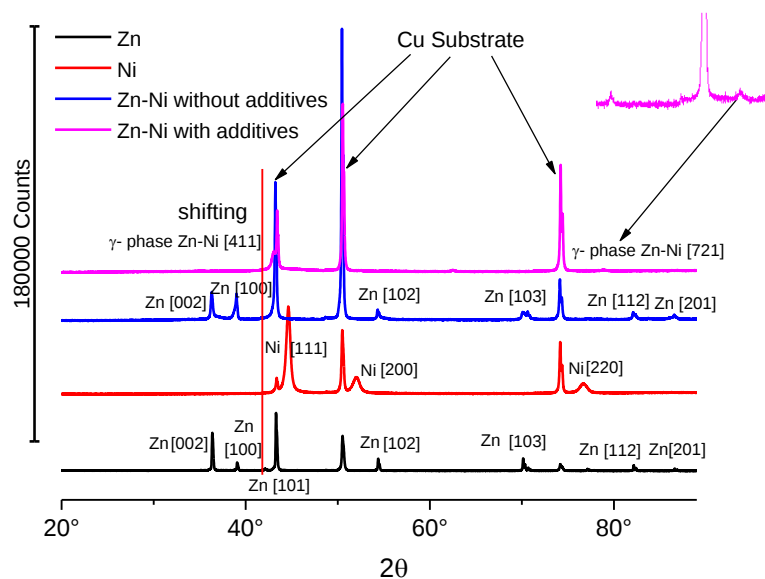


Figure 5.12 XRD patterns of the Zn electrodeposited from 0.5 M ZnCl_2 , Ni electrodeposited from 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Zn-Ni electrodeposition from 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ without additives, and Zn-Ni electrodeposition from 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M boric acid and 0.05 M sodium bromide. All experiments were achieved in Ethaline 200 on a Cu electrode at 80 °C, at a current density of 8 mA cm^{-2} for 1 h.

The (002), (100), (102), (103), (112) and (201) planes were observed in the pure Zn deposit, as shown in **Figure 5.12**, while the (111), (200) and (220) planes were observed in the pure Ni deposit at 2θ values of 44.57° , 51.81° and 76.41° , respectively.^{66, 67} XRD patterns for Zn-Ni deposits without additives showed only Zn planes, which were (002), (100), (102), (103), (112) and (201).⁶⁶ No Ni phases were observed, and also no specific shifting was observed in the XRD patterns of the Zn-Ni deposit derived from the electrolyte without additives. In **Figure 5.12**, there are some signs of other phases which could be Zn-Ni alloys, but these are extremely small compared with the pure metal phases.^{68 68}

The composition of the deposits (**Figure 5.11**) was subsequently determined using EDAX, as shown in **Table 5.1**. A significant change occurred in the composition of the Zn-Ni deposits when the deposition was achieved from a system containing additives, as shown in **Table 5.1**.

Table 5.1 Composition of Zn-Ni deposits obtained from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the absence and presence of 0.2 M BA and 0.05 M NaBr. The deposition was achieved on a Cu substrate at 80 °C, at a current density of 8 mA cm^{-2} over a period of 1 h.

Zn-Ni coating	Zn% Wt.	Ni% Wt.
No additives	90.8	9.2
With additives	27.6	72.3

A remarkable decrease in the amount of Zn in the Zn-Ni deposit occurred when the deposition was achieved from electrolyte containing BA and SB. The Ni content in the Zn-Ni film increased to 71.53% as a result of adding BA and SB to the electrolyte bath. The composition of the Zn-Ni deposits obtained from the Ethaline 200 in the absence and presence of BA and SB were compatible with the voltammetry data shown in **Figures 5.4 (a) and (b)** and **Figure 5.6**, where the amount of Ni deposition increased when BA was used, as shown in **Figure 5.4 (b)**, and the Zn deposition peak decreased when using BA, as shown in **Figure 5.4 (a)**. As has already been explained from the voltammetry data, BA is able to increase the rate of Ni nucleation through its adsorption on the electrode surface, which subsequently inhibits the growth of Ni nuclei. Moreover, it has been reported in the literature that BA can prevent formation of a passivation layer.⁵⁶ Thus, the Ni content of the Zn-Ni deposited from Ethaline 200 containing BA is increased.

5.3.4.1 Electrodeposition of Zn-Ni alloy under stirring

In the previous section, it was determined that the Zn-Ni alloy cannot be produced from Ethaline 200 at 80°C in the absence of BA and NaBr, as shown from the morphology and XRD data of the Zn-Ni deposition (**Figure 5.11** and **Figure 5.12**). The reasons for obtaining a non-homogeneous and black Zn-Ni coating from a solution that does not contain additives are unknown, but may be due to strong competition between the

deposition of Zn and Ni ions causing considerable hydrogen evolution on the cathode surface, thus only allowing for a random Zn and Ni coating to be achieved.

In fact, we have tried to deposit Zn-Ni alloy from Ethaline 200 under stirring in order to reduce the competition between Zn and Ni ions and also to push the Zn and Ni ions regularly over the cathode electrode (decreasing the diffusion layer).

A very interesting Zn-Ni coating was produced when the deposition occurred in an electrolyte that did not contain BA and NaBr but was achieved under stirring, where a bright and uniform Zn-Ni alloy was produced. **Figure 5.13** shows SEM images of Zn-Ni deposits **(a)** without stirring and **(b)** under stirring. The depositions were achieved in Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ on a Cu electrode at 80°C , using a current density of 8 mA cm^{-2} for 1 h.

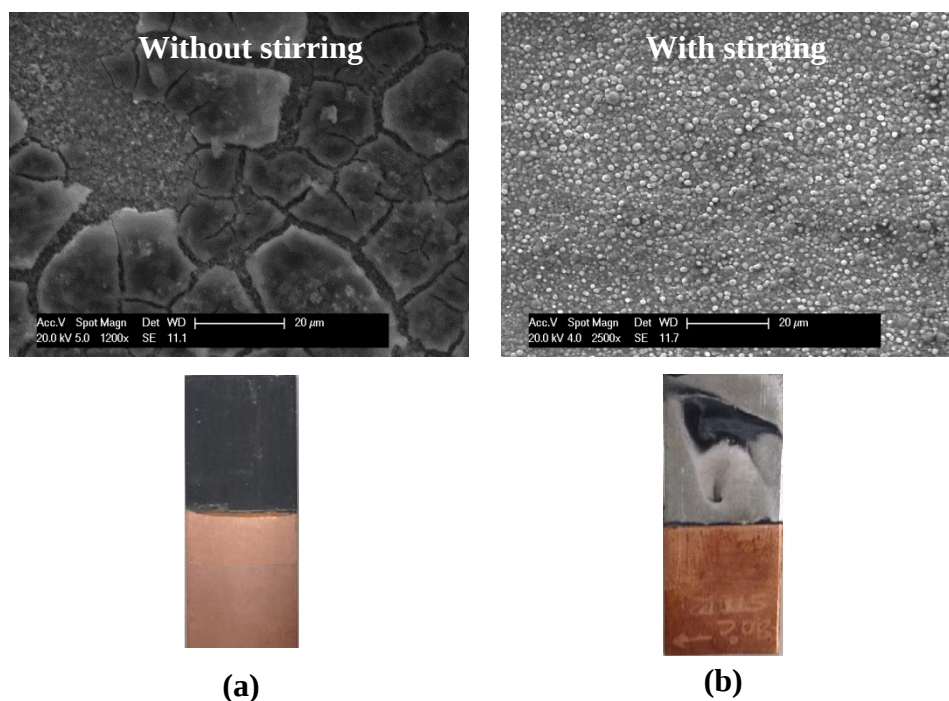


Figure 5.13 SEM and photographic images of Zn-Ni deposits in Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ on a Cu electrode at 80°C , using a current density of 8 mA cm^{-2} over 1 h. **(a)** Without stirring and **(b)** under stirring (sample width 2 cm).

Figure 5.13 (a) shows a black Zn-Ni coating with clear cracks that can be observed in the morphology of the deposit. In this case a co-deposit of Zn and Ni might well have been achieved. However, a huge change in the morphology of the Zn-Ni coating occurred as a result of performing the electrodeposition under stirring, where the coating was brighter although not uniform and had a finer grain size than the coating

without stirring. It can be said that the stirring has changed the nucleation mechanism of the Zn-Ni deposit. For the coating achieved under stirring, the rate of nucleation is faster than the growth rate and thus a fine grain size can be seen for the coating. It is very important to examine the crystal structures of the Zn-Ni coatings obtained from Ethaline 200 with and without stirring. Consequently, the crystal structures of the coatings were examined by XRD. **Figure 5.14** demonstrates the X-ray diffraction spectra found for Zn-Ni films obtained from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ on a Cu electrode at 80°C , using a current density of 8 mA cm^{-2} over 1 h. The coating was performed once with, and once without, stirring.

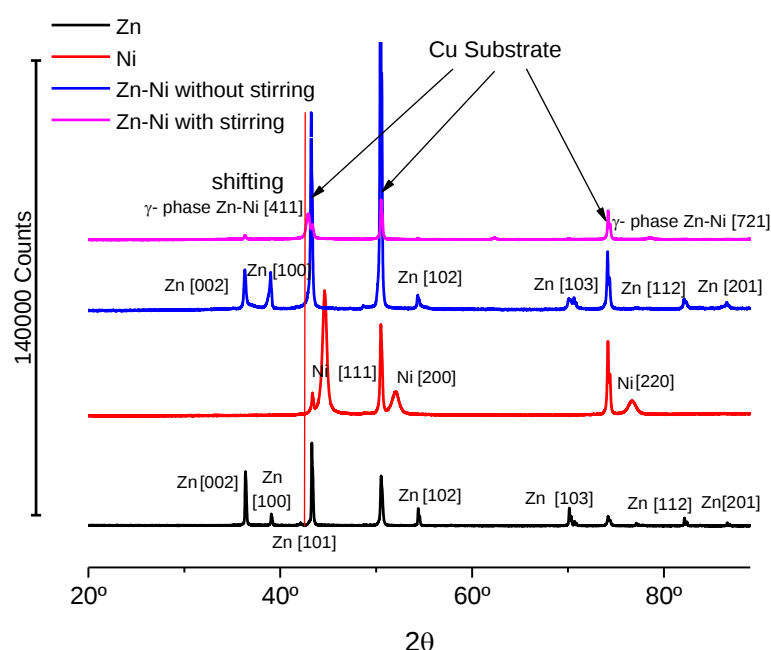


Figure 5.14 XRD patterns of the Zn electrodeposited from 0.5 M ZnCl_2 , Ni electrodeposited from 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and Zn-Ni electrodeposited from 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with and without stirring. All depositions were achieved in Ethaline 200 on a Cu electrode at 80°C and at a current density of 8 mA cm^{-2} for 1 h.

XRD patterns of the Zn-Ni deposited from Ethaline 200 without stirring (**Figure 5.14**) showed that there was no change in the diffraction spectra of coatings where all diffraction peaks were related to the Zn planes, where the peaks were (002), (100), (102), (103), (112) and (201) which, as mentioned are related to the Zn coating.⁶⁹ Also, no shifts were observed in the diffraction peak of the Zn-Ni deposited without stirring. However, a clear shift can be seen in the diffraction peak of Zn (101) in the Zn-Ni deposited from the electrolyte under stirring. In **Figure 5.14**, the diffraction peak for Zn

(101) in the pure Zn coating can be observed at 2θ values of 42° ,⁶⁶ while in the Zn-Ni coating the diffraction peak of Zn (101) was shifted to 42.9° . This indicates that a new face has been formed in the deposition achieved under stirring. Furthermore, a diffraction peak was obtained at 78.8° in the Zn-Ni coating, this peak being related to the formation of the γ -phase ($\text{Ni}_5\text{Zn}_{21}$). Therefore, it can be suggested from XRD data that a Zn-Ni alloy coating can be produced on a Cu substrate from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ under stirring at 80°C and at 8 mA cm^{-2} .

The compositions of the Zn-Ni coatings produced from the electrolyte with and without stirring were studied by EDAX, as shown in **Table 5.2**. No considerable change can be detected in the composition of the Zn-Ni deposits achieved from a system using stirring, or otherwise.

Table 5.2 Composition of Zn-Ni deposits obtained from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with and without stirring. The deposition was achieved on a Cu substrate at 80°C and a current density of 8 mA cm^{-2} over a period of 1 h.

Zn-Ni coating	Zn% Wt.	Ni% Wt.
Without stirring	90.6	9.4
With stirring	86.2	13.8

5.3.4.2 Effect of current density on Zn-Ni deposition

From the previous section, it was concluded that a Zn-Ni alloy deposit had indeed been produced on a Cu substrate from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence 0.2 M BA and 0.05 M SB at 80°C and a current density 8 mA cm^{-2} over 1 h.

Current density is one of the parameters that is considered to influence morphology, thickness, and composition of Zn-Ni alloy deposits. Electrodeposition of Zn-Ni alloy deposits was consequently attempted at different current densities (4, 6, 8, 10, and 12 mA cm^{-2}), where all the depositions were achieved on a Cu substrate from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M BA and 0.05 M SB at 80°C for 1 h. It was found that the surface morphology and composition of the Zn-Ni alloy deposits were mainly dependent on the current density of the deposition. **Figure 5.15** shows an abridged summary of the composition of electrodeposited Ni-Zn, as determined using

EDXS, as a function of current density. All deposits obtained consist of Ni, Zn, and Cu, with an insignificant amount of O due to surface oxidation.

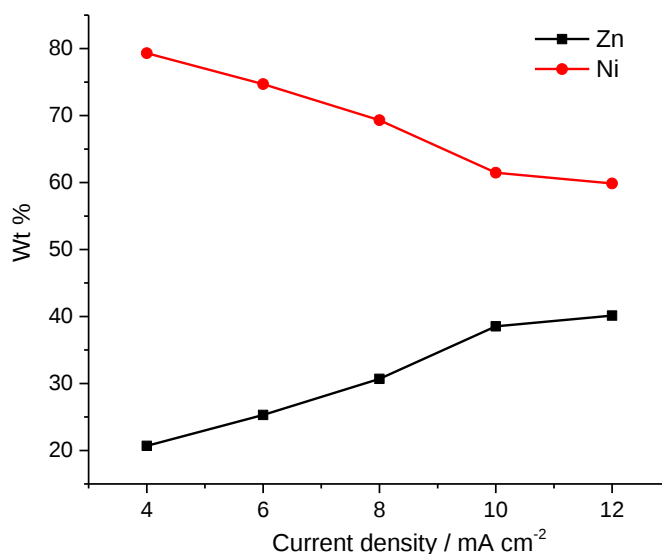


Figure 5.15 Compositions of the electrodeposited Zn-Ni alloys, as investigated by EDXS as a function current density. Electrodeposition was achieved in each case from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M boric acid and 0.05 M sodium bromide at 80°C on a Cu substrate for 1h.

The Zn content in the Zn-Ni deposits increased with increasing current density, whilst the rate of Ni deposition consequently decreased. In the Zn-Ni deposits shown in **Figure 5.15**, it can be observed that the amount of Ni in each deposit is greater than that of Zn, even though the concentration of the Ni species in the bath is lower than the concentration of Zn species. This could be due to side reactions between zinc and ethylene glycol.⁴

Figure 5.16 shows SEM images, cross-sectional morphologies and AFM topographies of the Ni-Zn alloy films obtained from an Ethaline 200-based liquid containing 0.5 M ZnCl_2 and 0.1 M NiCl_2 , at different current densities of **(a)** 4 mA cm⁻² **(b)** 6 mA cm⁻² **(c)** 8 mA cm⁻² **(d)** 10 mA cm⁻² and **(e)** 12 mA cm⁻², where all coatings were achieved with the electrolyte at 80°C for 1 h on a Cu substrate, from an electrolyte containing 0.2 M boric acid and 0.05 M sodium bromide as additives.

As is clear from **Figure 5.16** that the surface morphology of the Zn-Ni deposits has been altered with the changing current density. There could also be a decrease in current efficiency resulting in thinner films. As shown in **Figure 5.15**, the percentage of

both Zn and Ni in the Zn-Ni deposits varies as a function current density. Thus, it can be confirmed that the composition has a direct effect on surface morphology.

A hemispherical morphology was obtained for the Zn-Ni deposit when a current density of 4 mA cm^{-2} was applied. However, cracks can be seen in the deposition surface, as is clear in **Figure 5.16 (a)**. Furthermore, **Figure 5.16 (a)** shows a clear cross section across the Zn-Ni film, where the thickness of the deposition was $5.7 \text{ }\mu\text{m}$ as a result of the 4 mA cm^{-2} current density. Here, since the composition is mostly nickel (about 80%), the cross-sectional morphology can consequently be viewed as being homogenous in appearance. Atomic force microscopy was used to measure the roughness and topography of the Zn-Ni alloy coating.

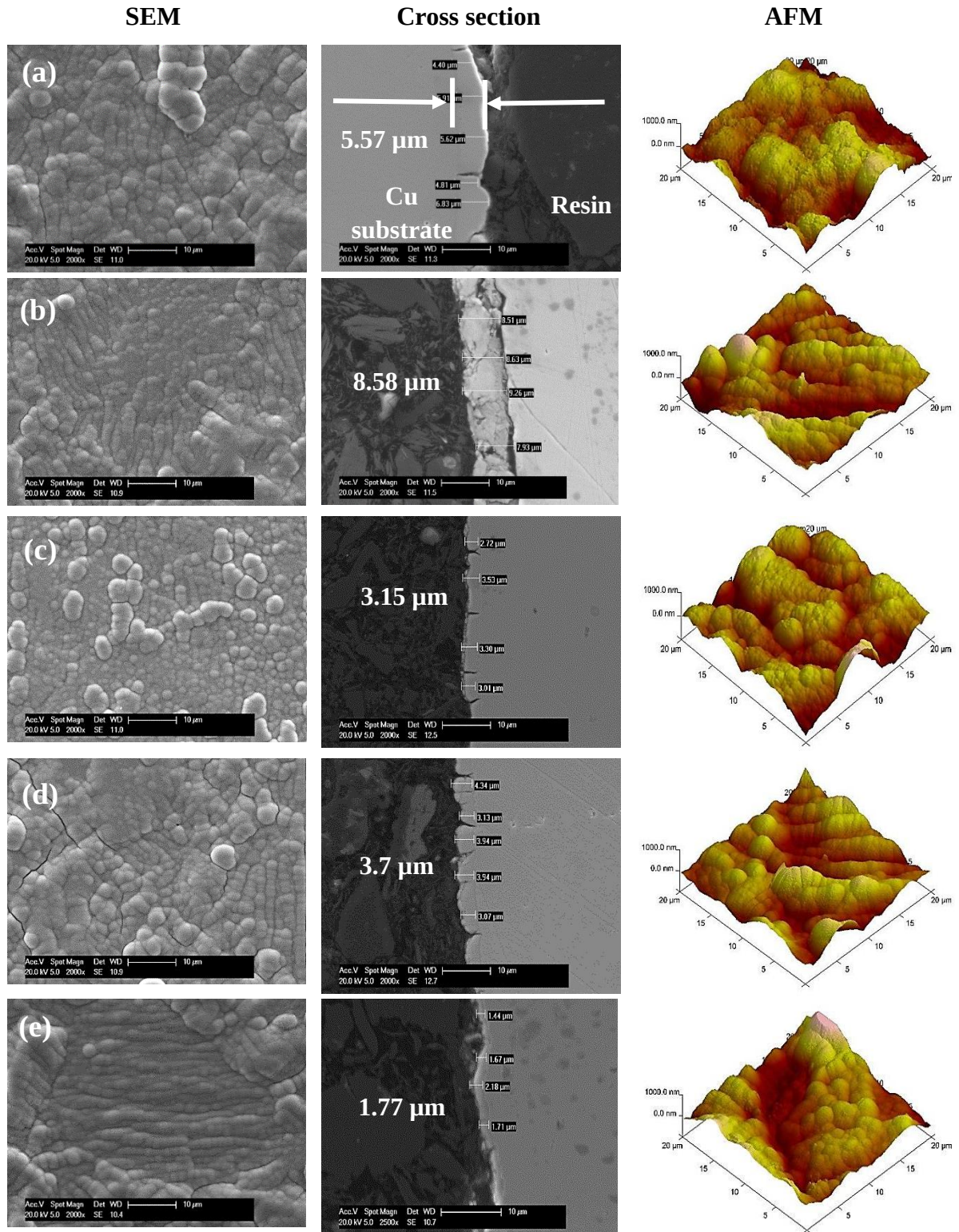


Figure 5.16 SEM images, cross-sectional morphologies and AFM topographies of the Ni–Zn deposits from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M BA and 0.05 M SB at (a) 4 mA cm^{-2} , (b) 6 mA cm^{-2} (c) 8 mA cm^{-2} (d) 10 mA cm^{-2} and (e) 12 mA cm^{-2} (all depositions achieved at 80°C for 1 h on a Cu substrate).

The current density used for the Zn-Ni deposition was increased to 6 mA cm^{-2} , and the filament morphology obtained for this deposit can be seen in **Figure 5.16 (b)**; the thickness of the coating was increased to $8.58 \text{ }\mu\text{m}$, as reported in **Table 5.3**. It is not surprising to see an increase in thickness of the Zn-Ni deposit with increasing current; as has been discussed regarding **Figure 5.15**, current density can be influenced by the amount of Zn and Ni in the Zn-Ni coating. Here, the change in the percentage of Zn and Ni in the coating resulted in a change in the morphology of the deposit surface. **Figure 5.16 (c)** shows the surface morphology and cross-section of the Zn-Ni deposit obtained from Ethaline 200 at a current density 8 mA cm^{-2} . Here, no significant change can be observed in the morphology Zn-Ni deposit in comparison to the morphologies of the Zn-Ni deposits achieved at 4 and 6 mA cm^{-2} . The morphology appears to have spherical nodules, and cracks can be seen in cross-sectional images. The reasons for these cracks occurring could be due to secondary reactions which occur on the cathode, such as hydrogen evolution (bubbles were observed on the cathode) through the electrodeposition process). Another reason for the appearance of the cracks could be due to the stress relaxation within the plating after cooling from $80 \text{ }^{\circ}\text{C}$. The Ni content is decreased to $\sim 69.1\%$ and the thickness of the coating is only $3.14 \text{ }\mu\text{m}$. In this case, the decrease in thickness with increasing current density could corresponded to the increase in hydrogen evolution and the decrease in the amount of Zn and Ni deposited. The surface morphology and cross-section of the Ni-Zn alloy coating obtained from the electrolyte containing 0.5 M ZnCl_2 and $0.1 \text{ M NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 10 mA cm^{-2} is shown in **Figure 5.16 (d)**. Here, the morphology of the Zn-Ni coating has changed, taking the form of 'strings' and spherical nodules; cracks can also be observed in the coating. The surface morphology and cross section of the Ni-Zn deposit obtained at 12 mA cm^{-2} is shown in **Figure 5.16 (e)**. Zn content increases to 40.13% with the increasing current density, while Ni content decreases to 59.8% . The roughness of the Zn-Ni alloys that were produced at different current densities were measured using AFM, and the data thus derived is reported in **Table 5.3**. No significant change in the roughness of Zn-Ni alloys coating was observed.

Generally, from **Figure 5.16** it can be seen that the morphology of the Zn-Ni coating changes with increasing current density due to the associated variations in the amounts of Zn and Ni in the coating. The thickness of the film decreased with increasing current density, which may be due to increased hydrogen evolution at the cathode. The

topographies of the Zn-Ni deposit determined by AFM were typically identical to the SEM morphologies.

Table 5.3 Composition, thickness and roughness of Zn-Ni deposits obtained from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M BA and 0.05 M NaBr. All depositions were achieved on a Cu substrate at 80°C using different current densities over 1 h.

Composition of Zn-Ni coating	Current density/ mA cm^{-2}	Thickness/ μm	Roughness/ nm
20.69% Zn, 79.31 Ni%	4	5.51	248
25.3% Zn, 74.7 Ni%	6	8.58	223
30.69% Zn, 69.31 Ni%	8	3.14	324
38.54% Zn, 61.46 Ni%	10	3.7	274
40.13% Zn, 59.87 Ni%	12	1.77	268

5.3.4.3 Effect of temperature on Zn-Ni deposition

The second factor whose effect on the electrodeposition of Zn-Ni from Ethaline 200 was studied was temperature. Temperature plays a significant role in the electrodeposition of metals from deep eutectic solvents; it can influence viscosity and the conductivity of the plating electrolyte, and thus affect the morphology and composition of deposits. It has been shown previously in **chapters 3** and **4** that temperature strongly affects the morphology and rate of deposition of Cu and Zn from Ethaline 200. Recently, it has been found that the electrodeposition of Ni from Ethaline 200 is highly influenced by temperature.⁴⁶ It was shown in **Figure 5.1** that temperature changed the Ni species present in Ethaline 200, and also produced a remarkable change in the voltammetry of Zn-Ni deposition, as shown in **Figure 5.8**.

Figure 5.17 shows the compositions of Zn-Ni alloy deposits obtained from Ethaline 200 at different temperatures (50, 60, 70, 80 and 90 °C). Here, the deposition was achieved on a Cu substrate from a solution containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M BA and 0.05 M SB as additives, at a current density of 8 mA cm^{-2} for 1 h. It can be seen in **Figure 5.17** that the Ni content significantly increased within the Zn-Ni deposits as the temperature of the plating bath was increased. This is due to the fact that at high temperature, the number of Ni species

in the electrolyte has been modified. The Ni species present in Ethaline 200 at room temperature is $[\text{Ni}(\text{Eg})_3]^{2+}$,⁴⁷ but when the temperature is increased, a new form of Ni^{2+} species, $[\text{Ni}(\text{Cl})_4]^{2-}$, starts to form. This was also conformed in **Figure 5.1** through studying the spectroscopy of Ni species in Ethaline 200 at different temperatures. The $[\text{Ni}(\text{Cl})_4]^{2-}$ complex is more easily deposited than $[\text{Ni}(\text{Eg})_3]^{2+}$, and thus the absence of the latter can result in an increase in the rate of Ni deposition. The amount of Ni in the Zn-Ni alloy deposit was 48.99% when the electrodeposition was achieved at 50 °C; however, the Ni percentage was increased to the 77.32% when the coating process was achieved at 90°C. These results are corroborated by the voltammetry data in **Figure 5.8**. Therefore, it can be suggested that an increase in the temperature of the electrolyte results in an increase in the percentage of Ni in the Zn-Ni deposit.

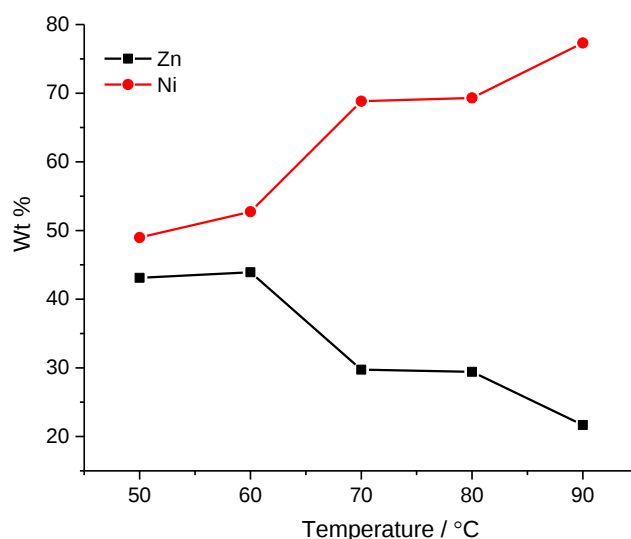


Figure 5.17 Composition of electrodeposited Zn-Ni alloys as a function of temperature. Deposition was achieved from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M boric acid and 0.05 M sodium bromide at a current density 8 mA cm^{-2} on a Cu substrate for 1 h.

Figure 5.18. shows SEM images, cross-sectional morphologies and AFM topographies of the Ni-Zn alloy films obtained from an Ethaline 200-based liquid containing 0.5 M ZnCl_2 and 0.1 M NiCl_2 in the presence of 0.2 M BA and 0.05 M SB as additives. The deposition was achieved on a Cu substrate, for 1 h, at a current density of 8 mA cm^{-2} and temperatures of (a) 50°C, (b) 60°C (c) 70°C (d) 80°C and (e) 90°C. The surface morphologies of Zn-Ni deposits have been changed as the temperature of the coating process was varied, as in clear in **Figure 5.18**. A black Zn-Ni deposit was obtained when the deposition occurred at 50 °C. The morphology of the Zn-Ni deposit produced

at 50 °C shows a small grain size, as can be seen in **Figure 5.18 (a)**. However, this does not look particularly homogenous. Moreover, a thin layer of Zn-Ni film was formed at 50 °C. **Figure 5.18 (b)** shows significant change has occurred to the morphology of Zn-Ni deposits when electrodeposition was achieved at 60 °C. The morphologies of the Zn-Ni deposits have clearly been modified as a result of performing the deposition at higher temperature.

Changes in the cross-sectional morphologies of the Zn-Ni alloy can be seen in **Figure 5.18** as a result of changing the temperature of the plating bath. From the cross-sectional morphologies shown in **Figure 5.18 (a)** and **(b)**, a porous or non-compact Zn-Ni coating was produced when the deposition occurred at 50 °C and 60 °C; however, these morphologies were modified when deposition was achieved at 70°C, 80°C and 90°C.

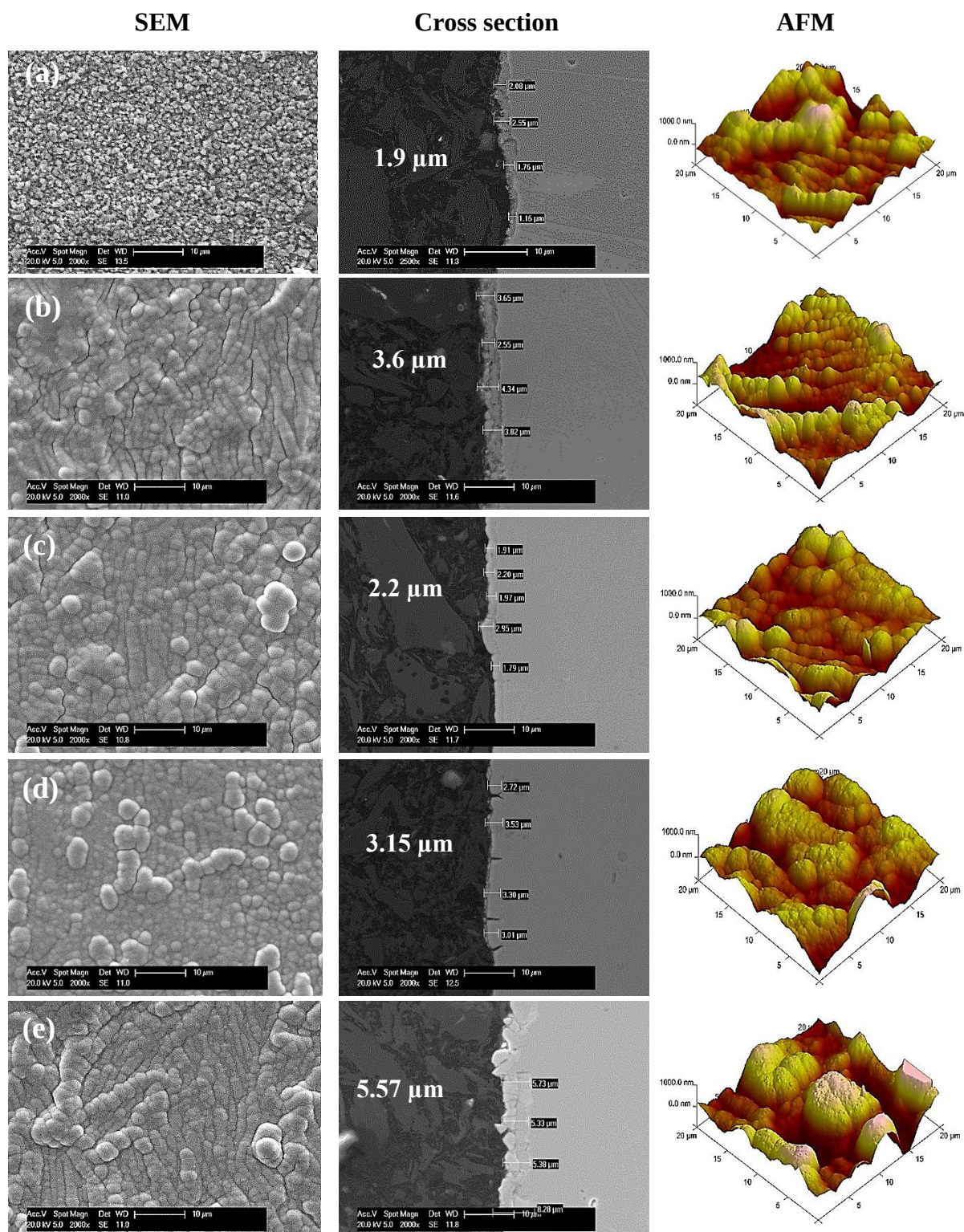


Figure 5.18. SEM images, cross-sectional morphologies and AFM topographies of the Ni-Zn deposits from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at (a) 50 °C, (b) 60 °C, (c) 70 °C, (d) 80 °C and (e) 90 °C (all experiments achieved at 8 mA cm^{-2} for 1 h on a Cu substrate using 0.2 M boric acid and 0.05 M sodium bromide as additives).

As discussed earlier, the content of Ni increases in the Zn-Ni alloy with increasing temperature of the bath. This is due to the changing Ni species in Ethaline 200. That data reported in **Table 5.4** shows an increase in the thickness of Zn-Ni coating with increasing temperature of the plating bath. The thickness of the Zn-Ni coating obtained at 90 °C was greatest at about 5.6 μm which is greater than those produced when the bath was held at lower temperatures. This corresponds to a decrease in the viscosity of the plating electrolyte and the associated increase in conductivity. **Table 5.4** shows an increase in the roughness of the coating with increasing temperature.

Table 5.4 Composition, thickness and roughness of Zn-Ni deposits obtained from Ethaline 200 containing 0.5 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M BA and 0.05 M NaBr. All depositions were achieved on a Cu substrate using a current density of 8 mA cm^{-2} , at different temperatures for 1 h.

Composition of Zn-Ni coating	Temperature / °C	Thickness/ μm	Roughness/ nm
51.01% Zn, 48.99 Ni%	50	1.9	212
47.26% Zn, 52.74 Ni%	60	3.6	245
31.17% Zn, 68.83 Ni%	70	2.2	207
30.69% Zn, 69.31 Ni%	80	3.15	324
22.68% Zn, 77.32 Ni%	90	5.57	532

5.3.4.4 Effect of Zn:Ni ratio on Zn-Ni deposition

The last parameter that was studied in the electrodeposition of the Zn-Ni alloy was changes to the concentration of ZnCl_2 in the plating bath. This effect was investigated in terms of current density and temperature on electrodeposition from Ethaline 200 containing 0.5 M ZnCl_2 , 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and in the presence of 0.2 M BA and 0.05 M sodium bromide as additives on a Cu substrate. All depositions were carried out for 1 h.

It is interesting to study the effect of concentration of Zn species on the characteristics of Zn-Ni deposits from Ethaline 200. **Figure 5.19** shows the composition of Zn-Ni deposits as studied by EDXS as a function of increasing concentrations of ZnCl_2 in the plating electrolyte. Zn-Ni deposits were obtained from Ethaline 200 containing 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and a series of concentrations of ZnCl_2 (0.5, 0.6, 0.7, 0.8 and 0.9 M), where

all depositions were achieved on a Cu substrate at 80°C, for 1 h at a current density of 8 mA cm⁻², whilst using 0.2 M boric acid and 0.05 M sodium bromide as additives.

From **Figure 5.19**, it can be seen that the amount of Zn in the Zn-Ni alloy film was enhanced as a result of increasing the concentration of ZnCl₂ in the bath, which corresponds to an increase in the concentration of the [ZnCl₄]⁴⁻ anion in the electrolyte in comparison to [Ni(Cl)₄]²⁻. This means that the concentration of [ZnCl₄]⁴⁻ near the electrode is higher than the concentration of [Ni(Cl)₄]²⁻ species.

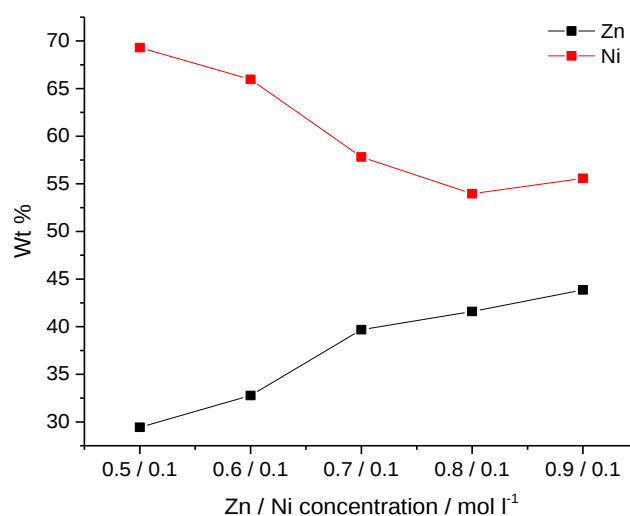


Figure 5.19 Composition of electrodeposited Zn-Ni alloys from Ethaline 200 containing a range of ZnCl₂ concentrations (0.5, 0.6, 0.7, 0.8 and 0.9 M) and 0.1 M NiCl₂·6H₂O. The depositions were achieved from an electrolyte containing 0.2 M BA and 0.05 M sodium bromide at 80°C on a Cu substrate for 1 h at a current density of 8 mA cm⁻².

Figure 5.20 shows SEM images, cross-sectional morphologies and AFM topographies of the Zn-Ni alloy films obtained from an Ethaline 200-based liquid containing a range of ZnCl₂ concentrations (0.5, 0.6, 0.7, 0.8 and 0.9 M), 0.1 M NiCl₂·6H₂O, 0.2 M BA and 0.05 M sodium bromide. All depositions were achieved at 80°C on a Cu substrate for 1 h at a current density of 8 mA cm⁻². **Figure 5.20 (a)** shows a Zn-Ni deposit with a hemispherical morphology, as obtained from a plating bath containing a 0.5 M of ZnCl₂ and 0.1 M NiCl₂·6H₂O. However, the morphologies of Zn-Ni deposits change to be similar to the ropes monolith to each other when the concentration of Zn species in the bath changes, as shown in **Figures 5.20 (b), (c), (d) and (e)**. The change in the morphologies of the Zn-Ni alloy may correspond to the increasing amount of Zn in the deposit.

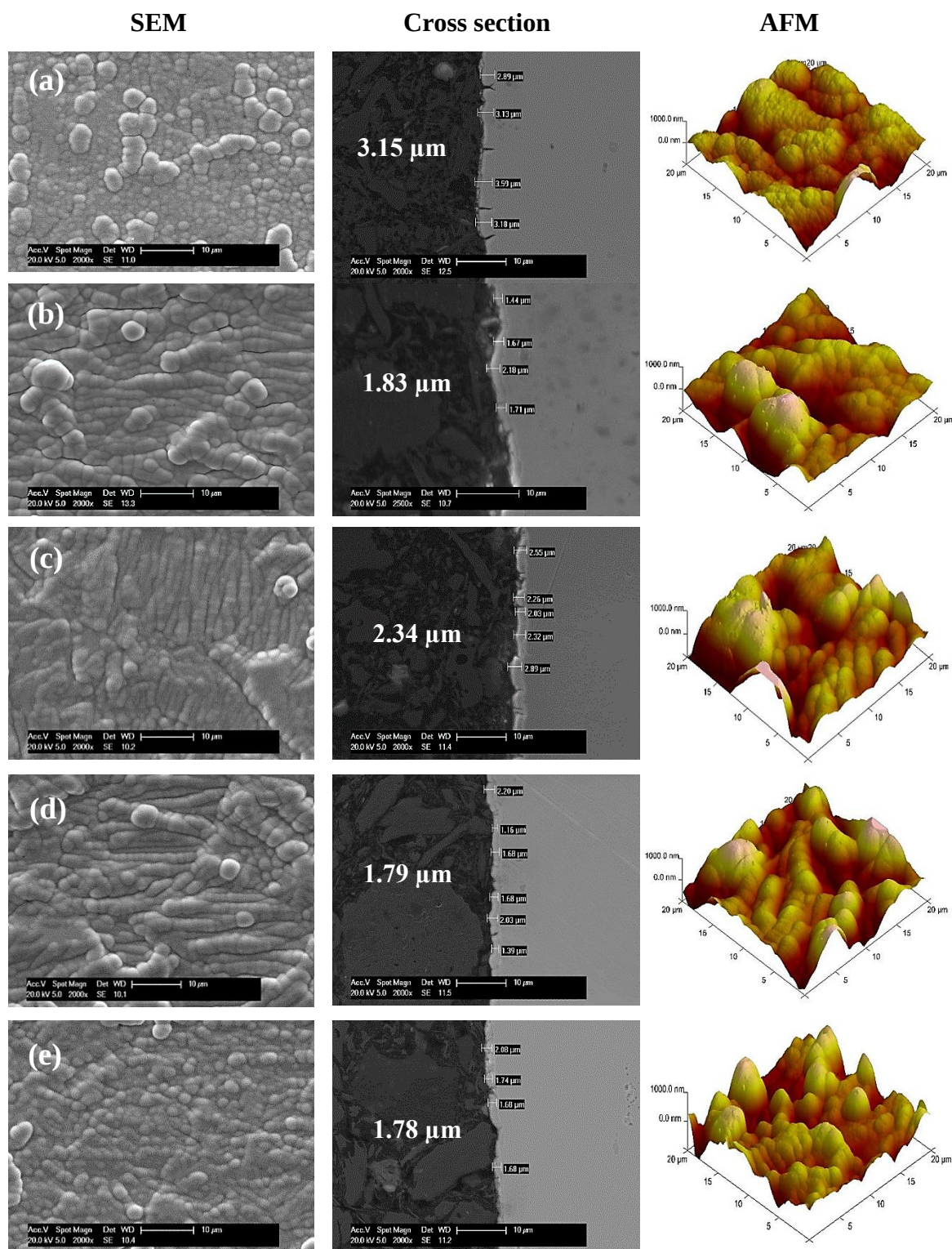


Figure 5.20. SEM images, cross-sectional morphologies and AFM topographies of the Ni-Zn deposits from Ethaline 200 containing 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and a range of ZnCl_2 concentrations at (a) 0.5 M, (b) 0.6 M, (c) 0.7 M, (d) 0.8 M and (e) 0.9 M. The depositions were achieved from an electrolyte containing 0.2 M BA and 0.05 M sodium bromide at 80°C on a Cu substrate for 1 h at a current density of 8 mA cm^{-2} .

It is interesting to note that the thickness of the Zn-Ni deposits decreased with increasing concentration of Zn ions in the plating bath, as shown in **Table 5.5**. This decrease in thickness might correspond to the increasing viscosities of the plating electrolytes with the increasing concentration of ZnCl_2 . The increase in the viscosity of the solution means a decrease in mass transport, resulting in a reduction in the rate of deposition, and thus a thin layer of Zn-Ni being obtained.

This behaviour was also observed for the roughness of the Zn-Ni coating (shown in **Table 5.5**) with increasing concentration of ZnCl_2 in the plating bath, where the roughness of the coating is increasing and decreasing. The change in the roughness could be due to the change in the grain size of the coating. This, of course, corresponds to the different amount of Zn and Ni in the coating.

Table 5.5 Composition, thickness and roughness of Zn-Ni deposits obtained from Ethaline 200 containing a range of ZnCl_2 concentrations and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M BA and 0.05 M NaBr. All depositions were achieved on a Cu substrate at a current density of 8 mA cm^{-2} for 1 h.

Composition of Zn-Ni coating	Concentration of ZnCl_2 / M	Thickness/ μm	Roughness/ nm
30.69% Zn, 69.31 Ni%	0.5	3.15	324
34.03% Zn, 65.97 Ni%	0.6	1.83	338
42.18% Zn, 57.82 Ni%	0.7	2.34	404
46.06% Zn, 53.94 Ni%	0.8	1.79	350
44.42% Zn, 55.58 Ni%	0.9	1.78	292

5.3.5 Deposition of bright Zn-Ni alloy from Ethaline 200

It has been reported in the literature that Zn-Ni alloy deposits that include 10-15% Ni are more resistance to corrosion. In this project, considerable effort has been made to obtain Zn-Ni alloy deposits containing 10-15% Ni from Ethaline 200. Bright Zn-Ni alloy deposits can be obtained from Ethaline 200 with a composition of about 14% Ni. This type of alloy was obtained when specific conditions were applied to the electrodeposition; the deposition was achieved on a Cu substrate from Ethaline 200 containing 0.8 M ZnCl_2 and 0.05 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.2 M BA and 0.1 M sodium bromide as additives with the bath held at 80°C and using a current density of 5 mA cm^{-2} for 1 h. As mentioned earlier in this chapter, when BA is used as a brightener, it can refine the grain size of both Zn and Ni deposits. Sodium bromide was added to the plating bath to improve the adhesion and cohesion of the coating.

It is necessary to study the cyclic voltammetry of any plating electrolyte that is considered capable of producing a bright Zn-Ni alloy coating. **Figure 5.21** shows the cyclic voltammograms recorded for 0.8 M ZnCl_2 and 0.05 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 200 in the presence and absence of 0.2 M boric acid and 0.1 M sodium bromide. The voltammograms were recorded at 80°C and at a scan rate 50 mV s^{-1} , using a 1.0 mm Pt disc electrode, a Pt flag counter-electrode and an Ag/AgCl reference electrode. The cyclic voltammetry was performed from 0.5 V in the negative direction to -1.5 V, and then reversed to the starting point.

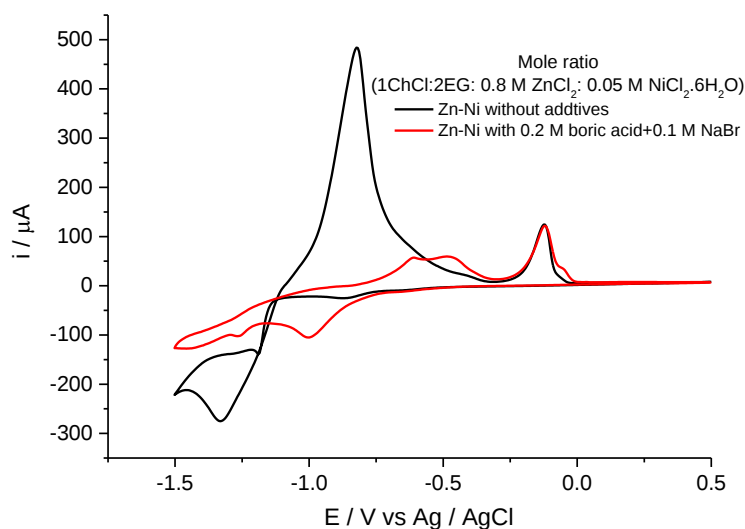


Figure 5.21. Voltammograms of Ethaline 200 containing 0.8 M ZnCl_2 and 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 8°C in the presence and absence of 0.2 M BA and 0.1 M sodium bromide. The experiments were performed using a Pt electrode (1.0 mm diameter) at a sweep rate of 50 mV s^{-1} vs a Ag/AgCl reference electrode.

In **Figure 5.21**, the voltammetry of the Zn-Ni electrolyte in the absence of BA and sodium bromide show two main deposition peaks. The small reduction peak observed at -0.8 V corresponds to the deposition of Ni, while the reduction peak that appeared at -1.3 V corresponds to the deposition of Zn. Two stripping peaks have also been observed in the anode branch of the cyclic voltammograms of Zn-Ni without additives; the stripping peak at -0.82 V is associated with dissolution of Zn metal from the electrode surface into solution, whilst the dissolution of Ni metal can be observed at -0.12 V. A significant change can be achieved in the voltammograms of Zn-Ni when BA and sodium bromide were added to the solution. In particular, the appearance of a deposition peak at 1.01 V was observed when these additives were added to the Zn-Ni electrolyte. BA can be adsorbed on the electrode surface and inhibit deposition of Ni. This can result in shifts in the deposition being shifted to a more negative potential, subsequently allowing the Ni and Zn ions to reduce at nearly the same potential. A clear positive shift occurs for the Zn oxidation peak as a result of using these additives. The shift and decrease in intensity in the Zn deposition peak indicated that a Zn-Ni alloy deposit had been formed.

The surface characteristics of the bright Zn-Ni deposit have been investigated by SEM/EDXS, AFM and XRD. **Figure 5.22** shows the photography, morphology, cross-sectional morphology, composition, and AFM imaging of the bright Zn-Ni deposit achieved from Ethaline 200. A bright deposit with a fine grain size was achieved on a Cu substrate, as shown in **Figure 5.22 (a)**; the deposit contained about 85% Zn and 15% Ni, as shown in **Figure 5.22 (b)**, where this was investigated using the EDXS technique. The thickness of the Zn-Ni deposit was $\sim 6.6 \mu\text{m}$. Moreover, the roughness of the bright Zn-Ni deposit was measured using AFM as 114 nm.

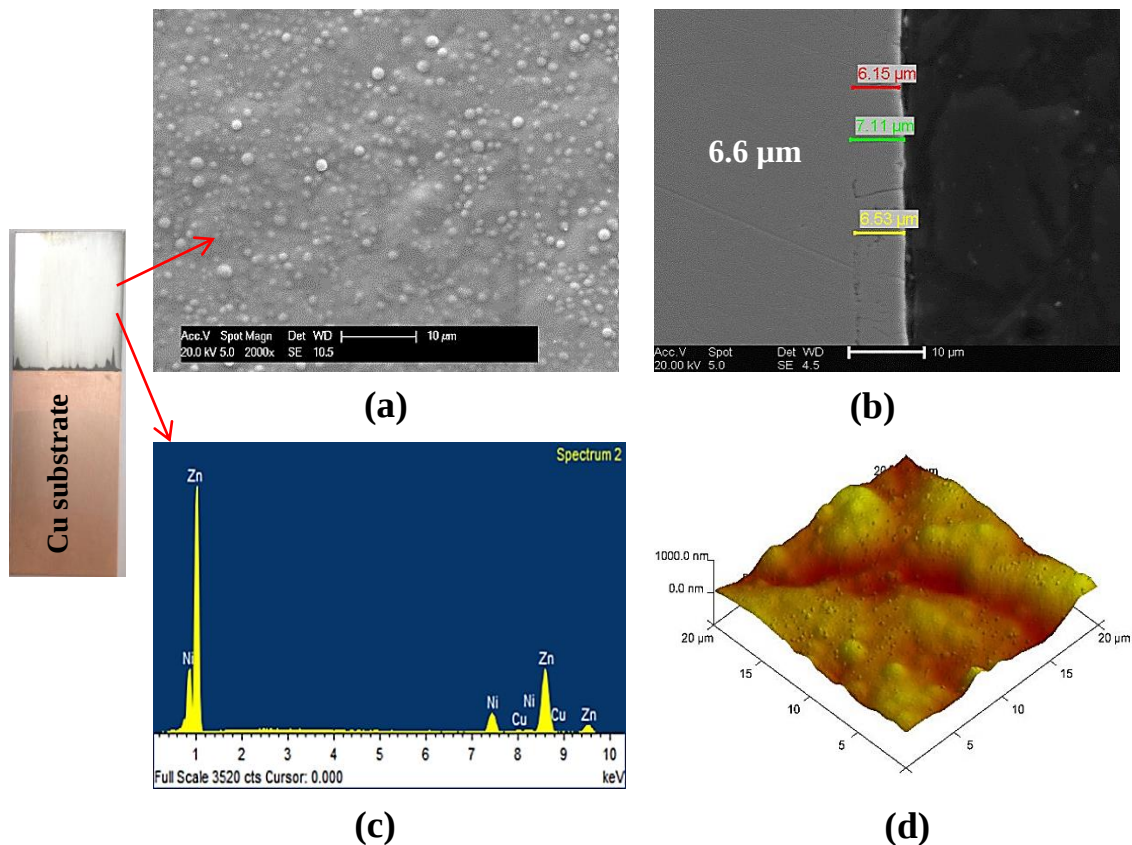


Figure 5.22 (a) Photography, (b) morphology, (c) cross-sectional morphology, composition, and (d) AFM imaging of the bright Zn-Ni alloy deposit obtained from 0.8 M ZnCl_2 to 0.05 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 200 at 80°C on copper at a current density of 5 mA cm⁻² for 1 h using 0.2 M BA and 0.1M NaBr as additives (sample width 2 cm).

The current efficiency of the bright Zn-Ni alloy coating (85% Zn, 15% Ni) was about 82%, where the calculated efficiency depended on the thickness of the coating as per the following:

85% Zn 15% Ni

$$65.39 \text{ g.mole}^{-1} \times 0.85 + 58.69 \text{ g. mole}^{-1} \times 0.15 = 64.38 \text{ g.mole}^{-1}$$

$F = C/\text{mole}$

So, mole = time(s) x Current (A) / F

$$= 3600 \text{ s} \times 0.05 \text{ A} / 96485 \text{ C.mole}^{-1}$$

$$= 1.865 \times 10^{-3} \text{ mole} / 2 \text{ (n = 2 for Ni}^{2+} \text{ and Zn}^{2+})$$

$$= 9.32 \times 10^{-4} \text{ mole}$$

Wt theory = no. of mole x M.wt of Zn-Ni alloy

$$\text{Wt}_{\text{theory}} = 9.32 \times 10^{-4} \text{ mole} \times 64.38 \text{ g mol}^{-1}$$

$$= 0.059 \text{ g theoretical weight.}$$

$$\text{Density of Zn} = 7.14 \text{ g.cm}^{-3}$$

$$\text{Density of Ni} = 8.90 \text{ g.cm}^{-3}$$

$$\text{Density of Zn-Ni alloy (85\% Zn, 15\% Ni)}$$

$$= \text{density of Zn} \times 0.85 + \text{density of Ni} \times 0.15$$

$$= 7.405 \text{ g.cm}^{-3}$$

$$\text{Volume (v)} = \text{Area (cm}^2\text{)} \times \text{thickness of coating cm}$$

$$= 10 \text{ cm}^2 \times 0.00066 \text{ cm}$$

$$= 0.0066 \text{ cm}^3$$

$$\text{Density} = \text{wt. (gm)} / \text{v (cm}^3\text{)}$$

$$\text{Wt}_{\text{experimental}} = 7.405 \text{ g.cm}^{-3} \times 0.0066$$

$$= \mathbf{0.048 \text{ g experimental weight}}$$

$$\text{Current efficiency\%} = (\text{wt}_{\text{experimental}} / \text{wt}_{\text{theory}}) \times 100$$

$$= (0.048 \text{ gm} / 0.059 \text{ gm}) \times 100$$

$$= \mathbf{81.35\%}$$

Otherwise, the current efficiency of the Zn-Ni alloy can be measured using the classic method of weighing of cathode substrate before and after coating, as per the following:

$$\text{Weight of cathode substrate after coating} - \text{weight of cathode substrate before coating}$$

$$= 9.27121 \text{ g} - 9.22121 \text{ g}$$

$$= 0.05 \text{ g experimental weight of Zn-Ni alloy coating}$$

$$\text{Current efficiency\%} = (\text{wt}_{\text{experimental}} / \text{wt}_{\text{theory}}) \times 100$$

$$= 0.05 \text{ gm} / 0.059 \times 100$$

$$= \mathbf{84.74\%}$$

It is necessary to examine the crystal structure of the Zn-Ni deposit. Therefore, XRD was used to investigate its phase structure. **Figure 5.23** shows XRD patterns for pure Zn, pure Ni and the bright Zn-Ni deposits (85% Zn and 15% Ni) deposited from Ethaline 200 on a Cu electrode at 80 °C. In **Figure 5.23**, the pure Zn deposit shows five planes, which are (002), (100), (102), (103) and (112), while the pure Ni deposit shows the (111), (200) and (220) planes at 2θ values of 44.57° , 51.81° and 76.41° , respectively. The bright Zn-Ni deposit shows the two diffraction peaks for the γ -phase

($\text{Ni}_5\text{Zn}_{21}$) which are the (411) and (721) plane orientations at 2θ values of 43° and 78.8° , respectively.

The γ -phase, which has a Zn:Ni ratio of 4:1, exhibits a body-centred cubic structure.⁶⁸ The type of phase depends on the percentage of Ni in the deposition. In our study, the bright Zn-Ni alloy deposit contained more than 10 wt.% Ni, with only the γ -phase being predominantly observed. The peak that appeared at $2\theta = 62.2^\circ$ corresponds to a variation in the growth of the grains.⁷⁰

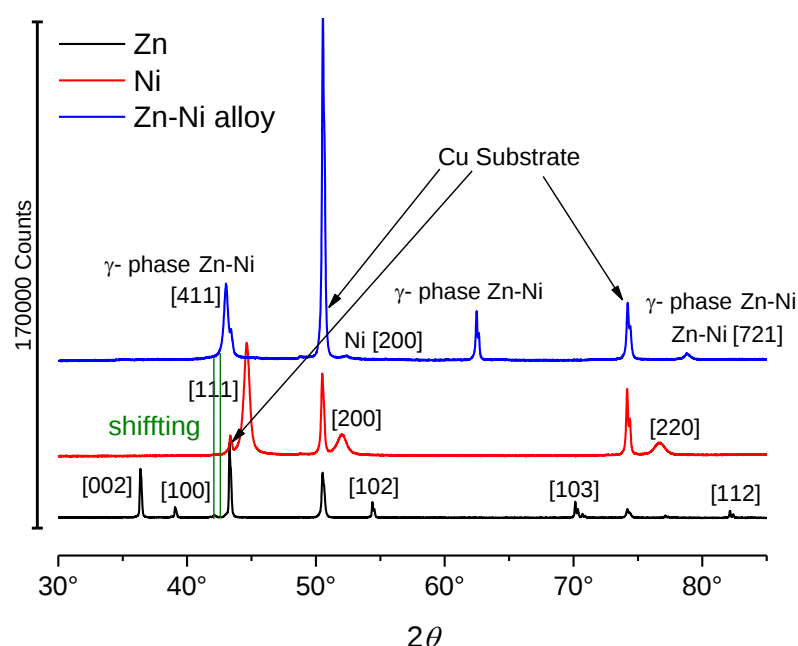


Figure 5.23 XRD patterns of the Zn, Ni and bright Zn-Ni deposits (85% Zn and 15% Ni) obtained from Ethaline 200 on a Cu electrode at 80°C .

5.3.6 Corrosion behaviour of Zn-Ni deposits

5.3.6.1 Tafel plot measurements

Various techniques, such as Tafel curves, electrochemical impedance spectroscopy (EIS) and the measurement of open circuit potentials (OCPs)^{5, 71} have been employed in the literature to study deposits resistance to corrosion. Generally speaking, this corrosion resistance has been found to improve due to the formation of corrosion products that act as barriers against diffusion (and hence corrosion). The common corrosion products for Zn and Zn alloys are zinc oxide (ZnO), zinc hydroxide (Zn(OH)_2), smithsonite (ZnCO_3) and simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$).^{5, 11, 72, 73}

In this work, the corrosion resistance of the bright Zn-Ni alloy deposit was investigated using Tafel curves and the electrochemical impedance spectroscopy (EIS) methods, where the corrosion study was achieved in 0.1 M NaNO₃ solution at 25 °C, and the applied potential was between -0.25 V to +0.25 V at a scan rate of 10 mV s⁻¹.

Figure 5.24 shows the potentiodynamic polarization curves for pure Zn, pure Ni and the bright Zn-Ni alloy deposits (85% Zn and 15% Ni) that were obtained from Ethaline 200 at the corrosion current densities (j_{corr}) and corrosion potentials (E_{corr}) summarised in **Table 5.6**. The information obtained from the cathodic and anodic Tafel slopes, such as the corrosion mechanism for the pure Zn and Zn-Ni alloy deposit in 0.1 M NaNO₃ solution, suggest that the Zn dissolution is balanced by the reduction of oxygen at the cathode, leading to the formation of Zn(OH)₂ (**Equations 5.4 and 5.5**), which can then lose a water to form ZnO (**Equation 5.6**). In an NaNO₃ electrolyte, Na⁺ diffuses towards the cathode, while NO₃⁻ diffuses towards the anodic side, which contains dissolved zinc.



The comparison of the Tafel plots of pure Zn, pure Ni and the Zn-Ni alloy (85% Zn, 15% Ni) in 0.1 M NaNO₃ solution at 25 °C is shown in **Figure 5.24**. It can be seen that the cathodic and anodic branches are shifted to lower current densities in the case of the Zn-Ni alloy compared to pure Zn. The corrosion current density, i_{corr} , for the pure Zn deposit was 4.64×10^{-6} A cm⁻² at a corrosion potential, E_{corr} , of -0.620 V. The corrosion rate of the pure Zn layer was about 0.107 mm / year. The pure Ni coating has a higher resistance to corrosion in 0.1 M NaNO₃ solution than pure Zn, where the corrosion current density, i_{corr} , of pure Ni was found as 2.05×10^{-6} A cm⁻², while the corrosion rate was 0.047 mm / year. The corrosion rate of bright Zn-Ni alloy film (85% Zn and 15% Ni) was found to be 0.06 mm / year, which is approximately half that of the corrosion rate of pure Zn, as reported in **Table 5.6**. It was assumed that the presence of Ni as an alloying element decreases the density of active sites on the alloy surface and, consequently, this can lead to a decrease in the corrosion rate of the coating.

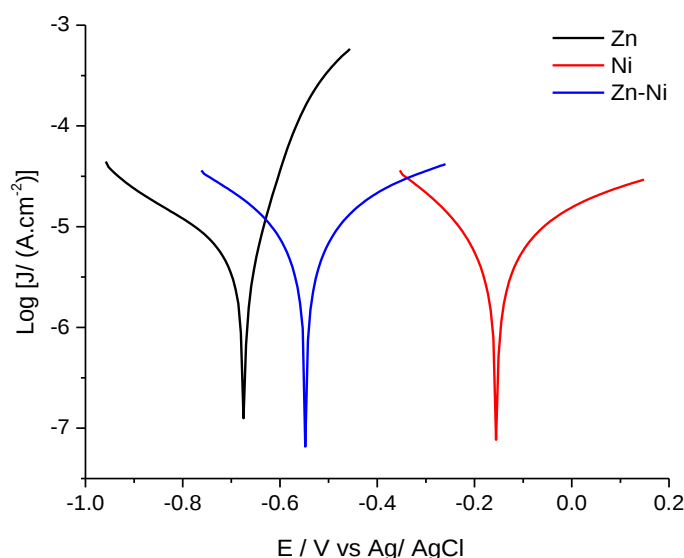


Figure 5.24 Potentiodynamic polarisation curves of the Zn, Ni and bright Zn-Ni (85% Zn and 15% Ni) deposits obtained from Ethaline 200. All depositions were achieved on a Cu substrate at 80°C for 1h at a current density of 5 mA cm⁻².

Table 5.6 Corrosion characteristics, obtained by polarization in 0.1 M NaNO₃ solution, of the pure Zn, pure Ni and bright Zn-Ni deposits obtained from Ethaline 200. All depositions were achieved on Cu substrate at 80°C using a current density of 5 mA cm⁻² for 1 h.

Metal or alloy coating	E_{corr} vs. Ag/AgCl/ V	i_{corr} /A cm ⁻²	Corrosion rate mm/year
Pure Zn	-0.672	4.64×10^{-6}	1.07×10^{-1}
Pure Ni	-0.303	2.05×10^{-6}	4.77×10^{-2}
Zn-Ni alloy (85% Zn-15% Ni)	-0.547	2.80×10^{-6}	6.05×10^{-2}

5.3.6.2 Electrochemical impedance spectroscopy (EIS)

To further investigate the corrosion resistance of Zn-Ni alloy, impedance measurements were studied. The impedance of Zn, Ni and the Zn-Ni alloy were investigated in 0.1 M NaNO₃ at room temperature. **Figure 5.25 (a)** shows a Nyquist plot of Zn, Ni and bright Zn-Ni (85% Zn and 15% Ni) deposits at a potential selected from -0.25 V to +0.25 V with respect to the OCP. An analysis of the impedance in the examined potential range was made.

As seen in **Figure 5.25 (a)**, Nyquist responses of Zn, Ni and Zn-Ni samples are in a depressed semicircle (unfinished) shape. In the Nyquist plots, the polarization resistance

is roughly proportional to the size of the semicircle.^{8, 74, 75} The resistance to corrosion of the Zn-Ni coatings can be explained via a simple Randles circuit;⁷⁶ the equivalent circuit in this case is presented in **Figure 5.25 (b)**, where R_s is the solution resistance, R_p is the polarization resistance (also known as charge transfer resistance) and CPE is the constant phase element. The diameter of this semicircle reflects the corrosion resistance of the associated sample. In **Figure 5.25 (a)**, the diameter of the semicircle for the pure Zn deposit obtained from Ethaline 200 is larger than that of the pure Ni deposit. Consequently, the Zn metal has lower corrosion resistance than the Ni film. The diameter of the semicircle of the bright Zn-Ni alloy deposit was smaller than that of pure Zn film, as shown in **Figure 5.25 (a)**. This indicated that the bright Zn-Ni alloy film was more resistant to corrosion than pure Zn film.

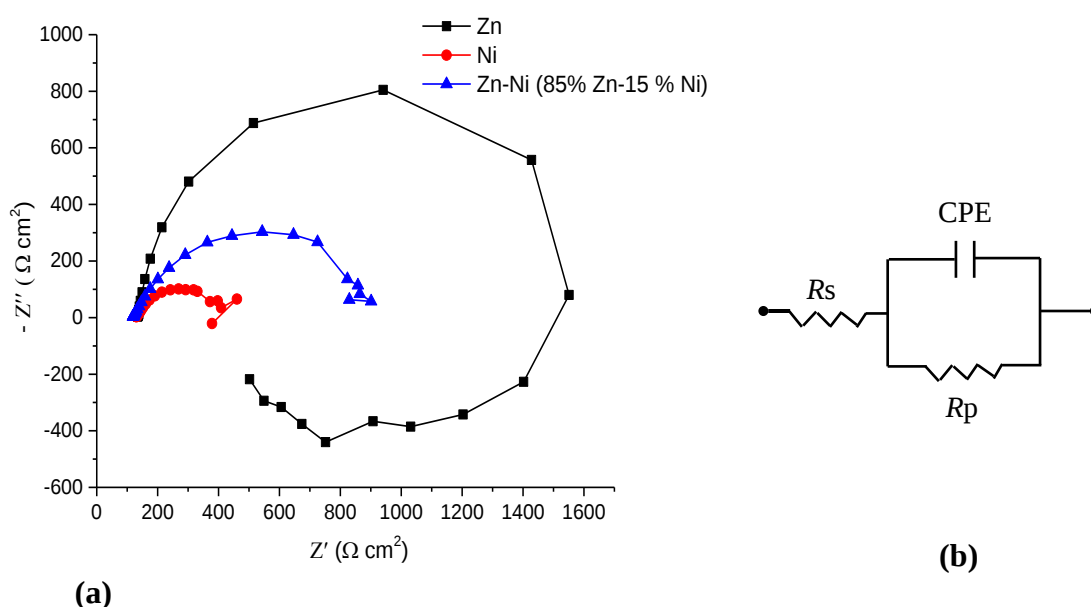


Figure 5.25 (a) Nyquist plot of Zn, Ni and bright Zn-Ni (85% Zn and 15% Ni) deposits obtained from Ethaline 200. All depositions were achieved on a Cu substrate at 80°C for 1 h at a current density of 5 mA cm⁻², **(b)** Randles circuit.

Table 5.7 Impedance parameters obtained for the corrosion of pure Zn, pure Ni and bright Zn-Ni deposits in 0.1 M NaNO₃ solution at OCP, and at room temperature. The deposition was obtained from Ethaline 200 on a Cu substrate at 80 °C, using a scan rate of 5 mA cm⁻² for 1 h.

Metal or alloy coating	$R_s / (\Omega \cdot \text{cm}^{-2})$	$R_p / (\Omega \text{ cm}^{-2})$	CPE/F
Pure Zn	164.4	1436	5.3×10^{-6}
Pure Ni	136.4	267.4	2.35×10^{-4}
Zn-Ni alloy (85% Zn-15% Ni)	134.7	751.6	1.07×10^{-4}

The fitted data from the equivalent circuit is shown in **Table 5.7**. Here, solution resistance is determined by the conductance of the NaNO_3 solution; from the results, solution resistance does not differ significantly between coatings. Generally speaking, impedance values measured in the low-frequency region of EIS spectra reflect corrosion resistance when the impedance in this region is independent of frequency. In this instance, such impedance values correspond to the R_p values of the Zn-Ni deposits.

Table 5.7 shows a high R_p value for pure Zn film, which means low resistance to corrosion, while by contrast the R_p value of pure Ni was very low. **Table 5.7** also shows the R_p value of the bright Zn-Ni alloy film, which was about two times smaller than the R_p value of pure Zn. According to **Figure 5.25** and **Table 5.7**, the corrosion resistance of the bright Zn-Ni alloy was improved compared to the pure Zn deposit. Finally, it can be concluded that the impedance measurements are consistent with the potentiodynamic polarization study (Tafel plot measurements), as shown in **Figure 5.24** and **Table 5.6**.

5.3.7 Hardness of bright Zn-Ni alloy deposit

The hardness of the Zn-Ni alloy deposit obtained from Ethaline 200 was one of the more interesting characteristics that was investigated. The data presented in **Figure 5.26** shows the Vickers hardness of the pure Zn, pure Ni and Zn-Ni alloy films obtained from Ethaline 200. Each hardness measurement was determined from an average of five indentations made over a representative area of the coating. The hardness of the bright Zn-Ni alloy film (85% Zn and 15% Ni) was about 260 HV, which is significantly higher than the hardness of the pure Zn deposit at 116.4 HV. This is because Ni is harder than Zn, and thus the presence of Ni in the deposit increases the hardness of the coating. The hardness of pure the Ni film was ~482 HV, as shown in **Figure 5.26**. The hardness of the Zn-Ni alloy deposit is mainly dependent on the Ni content, and thus increases with increasing Ni content in the deposits.^{11, 15} It was recently reported in the literature that the hardness of a mirror Zn-Ni alloy coating containing 13 wt.% Ni was about 424 HV₁₀₀.¹¹ However, Soroor reported that hardness of the Zn-Ni alloy coating was in the range of 250 HV₂₅ when the amount of Ni in the coating was ~10 wt.%.¹³ As has already been mentioned, the amount of Ni strongly effects the hardness of the Zn-Ni alloy coating; also, the grain size of the Zn-Ni deposit plays a significant role in this

hardness. With a decreasing grain size in the Zn-Ni deposit, the hardness of the coating increases due to the increase in grain boundaries.

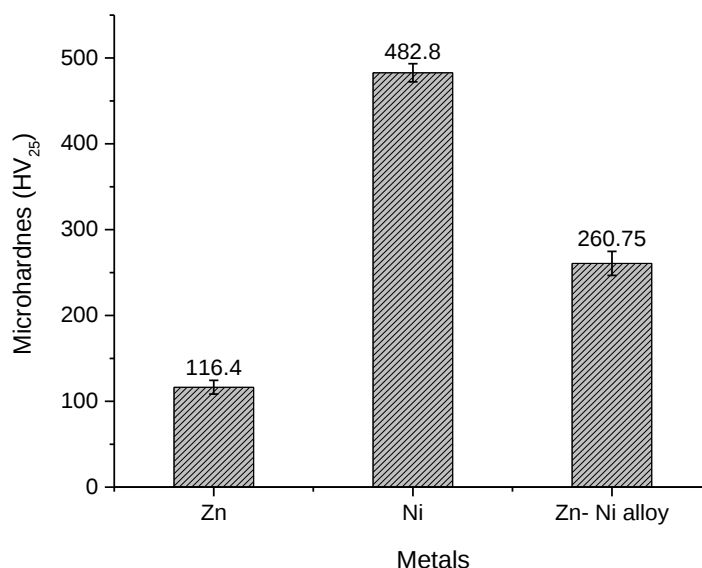


Figure 5.26 Vickers hardness of the pure Zn, pure Ni and Zn-Ni alloy (85 wt.% and 15 wt.% Ni) film deposited on a Cu substrate from Ethaline 200 at 80 °C. In each case, the pure metal and alloy coating thickness was measured as being approximately 70 μm . The applied load was 25 gf.

5.4 Summary

This work shows that a Zn-Ni alloy deposit can be obtained from Ethaline 200 in the presence of boric acid and sodium bromide as additives. It has been found that the electrodeposition of Zn-Ni alloys from Ethaline 200 in the absence of these additives will be unsuccessful. The effect of current density, temperature and concentration of Zn species on the Zn-Ni electrodeposition has been investigated, and it was found that the content of Zn in the Zn-Ni alloy deposits increased with increasing current density and concentration of Zn species in the bath. However, the amount of Zn decreased in the Zn-Ni alloy deposits with increasing temperature of the electrolyte due to formation of $[\text{NiCl}_4]^{2-}$ species in the solution. The morphologies of the Zn-Ni deposit were improved when the deposition was achieved from an electrolyte containing boric acid and sodium bromide as additives. Moreover, it was found that current density, temperature and Zn:Ni ratio effects the composition and morphologies of Zn-Ni deposits. The thickness of the Zn-Ni coatings increased with increasing temperature of the plating bath due to the associated decrease in viscosity and increase in conductivity of the Zn-Ni electrolyte.

Moreover, high temperature reduces the specific adsorption of Cl^- ions and modified the Ni species. However, the thickness of the Zn-Ni alloys decreased with increasing concentration of the Zn species in the solution due to the increasing viscosity of the electrolyte. Voltammetry of Zn, Ni and Zn-Ni was performed in Ethaline 200 in the absence and presence of boric acid and sodium bromide as additives. Boric acid is adsorbed on the electrode surface and inhibits the deposition of Zn, while the rate of Ni deposition is increased as boric acid is introduced into the bath, which could be because boric acid reduces the passivation layer. Nucleation mechanisms of Zn-Ni alloy deposits were studied by chronoamperometry, with all mechanisms fitting those of a progressive growth mechanism.

A bright, nanocrystalline Zn-Ni alloy deposit (85% Zn and 15% Ni) was produced from Ethaline 200 containing a high concentration of ZnCl_2 . SEM showed a small grain size in the Zn-Ni alloy coating, with AFM showing that the roughness of this type of Zn-Ni alloy was 114 nm. The current efficiency of the bright Zn-Ni alloy was found as being around 82%. The XRD data was shown that the bright Zn-Ni deposit shows the two diffraction peaks associated with the γ -phase ($\text{Ni}_5\text{Zn}_{21}$), which are the (411) and (721) plane orientations. Corrosion behaviour of bright Zn-Ni deposits was studied in sodium nitrate using Tafel curves and electrochemical impedance spectroscopy (EIS), where it has been observed that bright Zn-Ni has a corrosion resistance that is almost twice that of a pure Zn coating. Increases in hardness of the bright Zn-Ni alloy deposit (85% Zn and 15% Ni) were thus obtained.

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Chapter 6: Electrodeposition of Aluminium from Ionic Liquids

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6.1 Introduction

Aluminium coatings have, quite understandably, attracted a great deal of interest in the literature, mostly due to aluminium's well-known resistance to corrosion, non-toxicity and low density.¹ The conventional methods used for aluminium coating were thermal spraying, hot dipping, sputter deposition, vapour deposition and electrodeposition.¹⁻⁷ Among these methods, the electrodeposition method has the most favourable characteristics, such as high reaction efficiency, low energy consumption, ease of control over the Al structure and the generally mild experimental conditions required.^{2, 8} However, Al is considered as one of a number of active metals that cannot be electrodeposited from aqueous solution because of the extensive evolution of hydrogen at the electrode before an Al deposit can even be produced. In the past century, electroplating of Al has instead been achieved in organic solvents.^{9, 10} However, these solvents suffer from numerous disadvantages such as low conductivity, narrow potential windows, low metal solubility, high volatility and flammability, with each one of these disadvantages representing a further limit on the use of such methods.

In contrast, the liquid salts, or so-called ionic liquids, used in electrodeposition of metals have shown multiple advantages, such as high chemical stability and better electrochemical properties.^{1, 2} In the case at hand, Al was first deposited from an ionic liquid formed from a mixture of *N*-ethylpyridinium chloride and AlCl_3 by Hurley and Wier in 1951.¹¹ Since that time, numerous research efforts have concentrated on the electrodeposition of Al and Al alloys in ionic liquids,¹²⁻¹⁷ from which it can be broadly concluded that the properties of Al deposits can be improved when the deposition is achieved from ionic liquids, showing high conductivities and having broad electrochemical windows. Amongst such systems, chloroaluminate ionic liquids, prepared by mixing organic chloride salts with AlCl_3 , are the most commonly studied. Lewis acidity can be controlled by adjusting the molar percentage of AlCl_3 , and Al can be deposited when the molar percentage of AlCl_3 is higher than 50%. The Al species found in these liquids is the $[\text{Al}_2\text{Cl}_7]^-$ anion, which are responsible for the deposition itself. The associated counter ions are in these ionic liquids are commonly alkyl pyridine, alkyl imidazole, and quaternary ammonium cations;¹⁸⁻²⁰ usually, alkyl imidazole cations are used out of preference, due to the high conductivity, lower viscosity and improved stability of the associated ionic liquid, within which 1-ethyl-3-methylimidazolium ($[\text{Emim}]^+$) and 1-butyl-3-methylimidazolium ($[\text{Bmim}]^+$) in

particular are the most commonly used.^{15, 19, 21, 22} However, application of these ionic liquids in Al deposition is limited due to the high cost of quaternary ammonium halide salts, and because they are hygroscopic in nature. Given these properties, it is clear that the development of ionic liquids from readily available, hydrophobic, ‘neutral’ ligands is of particular interest as regards the practical electroplating of Al. Recently, Abbott *et al.*²³ prepared eutectic Al solvents by mixing AlCl_3 with acetamide or urea, with the complex thus produced being liquid at ambient temperature. However, these types of liquids have low conductivities and high viscosities compared to the imidazolium chloroaluminate systems. It was found that characteristics of these eutectic solvents are similar to those of most common ionic liquids.²³ The advantages of these systems are that they can be produced more cheaply than Al-chloroaluminate liquid due to acetamide and urea being inexpensive compared to the quaternary ammonium halides such as 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium. In addition, Al-acetamide and Al-urea eutectic solvents are relatively insensitive to water.²³

Liu *et al.*²⁴ studied the preparation of several amide- AlCl_3 -based ionic liquids. They used different structured amides as donor molecules, which were acetamide, *N*-methylacetamide and *N,N*-dimethylacetamide. It was found that these different amides each altered the percentage of ionic species in the liquid due to differences in the amide coordination site with the AlCl_3 .

Al liquids are used in various fields such as catalysis, extraction and electrodeposition. Usually, electrodeposition of Al from achieves from ionic liquids. However, the properties of Al deposited from ionic liquids still need to be improved. Therefore, to get Al deposits with good surface properties, it is necessary to add additives to the deposition electrolyte. In aqueous solution, additives are used to improve the physical and mechanical properties of metal depositions such as brightness, roughness and resistance to corrosion.

There are numerous types of additives used in the electrodeposition of metals from aqueous solution, but few that can be used with ionic liquid systems. Recently, the use of certain additives with ionic liquids has been reported. Endres *et al.*²⁵ studied the effect of nicotinic acid on the electrodeposition of Al from an $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ system, where a nanoscale Al deposit was produced with an average particle size of around 14 nm. Subsequently, Abbott *et al.*²² studied the effect of toluene and LiCl on Al deposit morphologies from $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ ionic liquid. It was found that an Al ‘mirror’

coating was obtained when toluene was added to the plating bath, whilst addition of LiCl caused the production of a dark grey Al deposit. The effect of phenanthroline on Al electrodeposition from [Bmim]Cl/AlCl₃ was investigated by Caporali *et al.*,²⁶ who obtained bright Al deposits that showed high resistance to corrosion. Liu *et al.*²⁷ studied the effects of different kinds of additives on the electrodeposition of Al deposits using cyclic voltammetry. The effects of methyl nicotinate, nicotinic acid and 3-methylpyridine on Al electrodeposition from [Bmim]Cl/AlCl₃ system have been recently investigated by Zhang *et al.*,²⁸ who showed that a uniform, mirror Al deposit was achieved when MN and nicotinic acid were used as additives. Therefore, to date, a number of investigations have focused on the effects of additives on the properties of Al coating from conventional ionic liquids; however, no work has been undertaken as to the effects of additives on the electrodeposition of Al from deep eutectic solvents.

This study is divided into three parts: the first will study the effect of methyl nicotinate (MN) on properties of Al deposited from 1-ethyl-3-methylimidazolium chloride/AlCl₃ and 1-butyl-3-methylimidazolium/AlCl₃ ionic liquids. A mirror Al coating has been achieved on a copper substrate from these classic ionic liquids as a result of using MN as an additive. The current efficiencies of the electrodepositions of Al from these classical ILs were calculated in presence and absence of MN. The resultant surface morphologies and roughness of the associated Al coatings were revealed by SEM/EDXS and AFM, demonstrating that MN serves as a highly effective brightener, producing highly uniform and smooth Al deposits. The second part of this chapter will show, for the first time, the electrodeposition of Al from different amide-AlCl₃ eutectic solvents, where these solvents were (1.5:1) AlCl₃:acetamide, (1.5:1) AlCl₃:*N*-methylacetamide and (1.5:1) AlCl₃:*N,N*-dimethylacetamide eutectic liquids. The conductivities of these solutions were measured, as were the current efficiencies of the Al electrodepositions from these liquids.

The third part will study the effect of MN on electrodeposition of Al from novel Al eutectic solvents which are (1.5:1) AlCl₃:acetamide, (1.5:1) AlCl₃:*N*-methylacetamide and (1.5:1) AlCl₃:*N,N*-dimethylacetamide-based liquids. Electrochemical properties of the plating liquid have been studied using cyclic voltammetry. The morphologies of Al films produced from ionic liquids in presence and absence of MN were investigated by SEM. Moreover, the roughness of Al coatings has been measured using AFM. XRD was used to examine the crystal structure of Al films produced from amide/AlCl₃

mixtures in the absence and presence of methyl nicotinate. The corrosion behaviour of Al coatings obtained from these mixtures with and without MN were studied using the potentiodynamic polarisation method (Tafel plot).

6.2 Aims and objectives of the work

Aluminium electrodeposition is seen as an important replacement for cadmium. Electroplating of Al is difficult but has been extensively studied using ionic liquids such as 1-ethyl-3-methylimidazolium chloride. While some additives have been studied (methyl nicotinate, MN) with this liquid, the deposits obtained are not particularly thick or dense. The purpose of this work is to study Al deposition from an alternative DES composed of (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide. The aim of this section of work is to study effect of MN on electrodeposition of Al from these novel liquids and see if an improved deposit morphology and density can be achieved.

6.3 Results and discussion

6.3.1 Voltammetry

Cyclic voltammetry has been employed in this work to study the electrodeposition behaviour of Al. **Figure 6.1 (a)** illustrates the cyclic voltammograms (CVs) of Lewis acidic 1:2 [Emim]Cl:AlCl₃ ionic liquid recorded on a polished Pt disk as the working electrode, and using a Pt flag counter electrode and Ag wire as a reference electrode. These voltammograms were initially scanned from +0.4 V to -1.2 V and then reversed to the initial point at different scan rates and a constant temperature of 30°C.

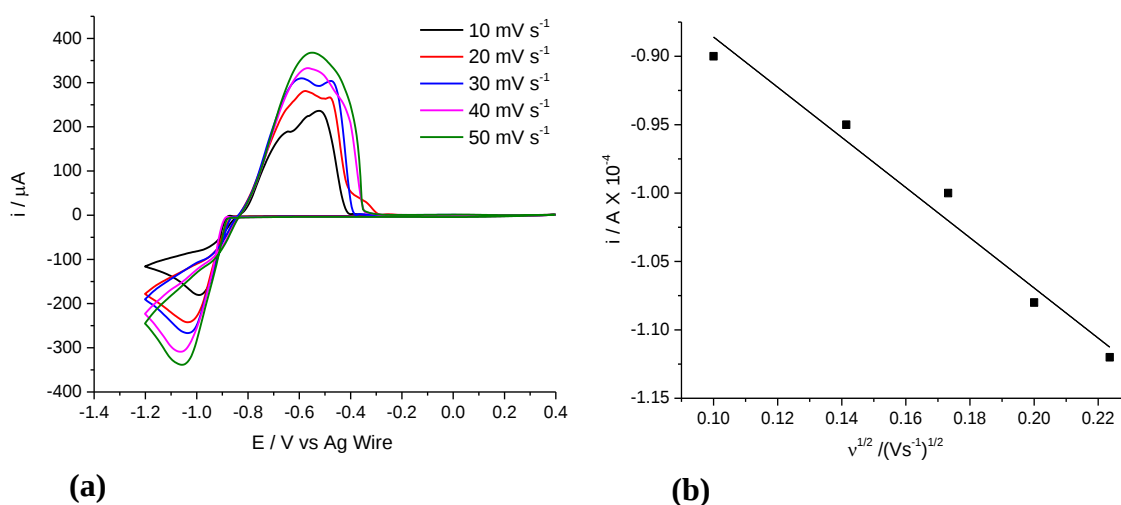
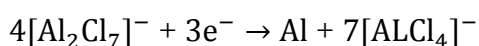
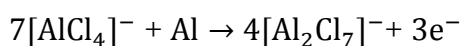


Figure 6.1 (a) Cyclic voltammograms of 1:2 [Emim]Cl:AlCl₃ ionic liquid recorded on a Pt as working electrode, Pt flag counter electrode and Ag silver wire as a reference electrode at different scan rates and at room temperature, **(b)** reduction current peaks for a 1:2 [Emim]Cl:AlCl₃ ionic liquid as a function of the square root of the scan rate.

It can be observed that a couple of peaks are obtained between +0.4 V and -1.2 V at all scan rates. The reduction peaks at -1.05 V on the negative scan are attributed to the bulk electrodeposition of Al, while the oxidation peaks around -0.5 V on the reverse scan are related to the dissolution process of deposited Al. In most of chloroaluminate ILs, the common species in these liquids are [Al₂Cl₇]⁻. Therefore, reduction and oxidation process of Al in the 1:2 [Emim]Cl:AlCl₃ ionic liquid can be explained by **Equation 6.1** and **Equation 6.2**.



Equation 6.1



Equation 6.2

It can be seen from **Figure 6.1 (a)** that the reduction of Al starts to take place at around -0.9 V, which is much more positive than the standard potential of Al/Al³⁺ couple in aqueous solutions (-2.47 V, vs. Ag⁺/Ag). This difference could be attributed to the different coordination pattern of Al³⁺ in 1:2 [Emim]Cl:AlCl₃ and aqueous solutions.² From **Figure 6.1 (a)**, it can be seen that the Al deposition potential shifted negatively when the scan rate was increased. This indicates that diffusion rates of Al species toward the electrode are slow. Good linearity was achieved in plots of i_{pc} against the square root of scan rate ($v^{1/2}$), as shown in **Figure 6.1 (b)**. However, the straight line obtained by plotting i_{pc} vs. $v^{1/2}$ does not pass through the origin of this graph as might be expected for a simple linear diffusion-controlled process. Therefore, it can be suggested that the electrodeposition of aluminium from 1:2 [Emim]Cl:AlCl₃ IL is mainly influenced by mass diffusion and kinetic limitations, such as electron transfer or surface chemical reaction steps.¹⁶

Cyclic voltammograms of Al from 1:2 [Emim]Cl:AlCl₃ in **Figure 6.1 (a)** show two Al dissolution peaks, which are particularly apparent at low scan rates, for example at 10, 20 and 30 mV s⁻¹. These two dissolution peaks suggest either alloy formation with the Pt electrode, or that different Al morphologies were formed.^{22, 29} Whereas, when high scan rates are applied such as 40, 50 mV s⁻¹, only one oxidation peak for Al can be seen. At high scan rates, it could be that the nucleation rate of Al deposition is faster than the growth rate, and thus that there is not enough time to form different size Al grains or to form alloy with the Pt electrode.

Additionally, cyclic voltammograms of 1:2 [Emim]Cl:AlCl₃ ionic liquid at various temperatures have been investigated. The experimental results for 1:2 [Emim]Cl:AlCl₃ are presented in **Figure 6.2**, where all experiments have been run at a scan rate 20 mV s⁻¹, using a Pt working electrode vs. an Ag reference wire. The Al deposition peak shifts to less negative values with increasing temperature of the electrolyte. Furthermore, increases in the oxidation and reduction current peaks of Al were observed with increasing the temperature, due to an increase in reaction rate associated with an increasing mobility of the electroactive species with temperature. It is not surprising in any way that this increase was observed, as the conductivity and viscosity of ionic liquids are, generally speaking, strongly dependent on temperature,³⁰ the increase in temperature decreases the viscosity of the ionic liquid, with a consequent increase in conductivity and increased deposition of Al.

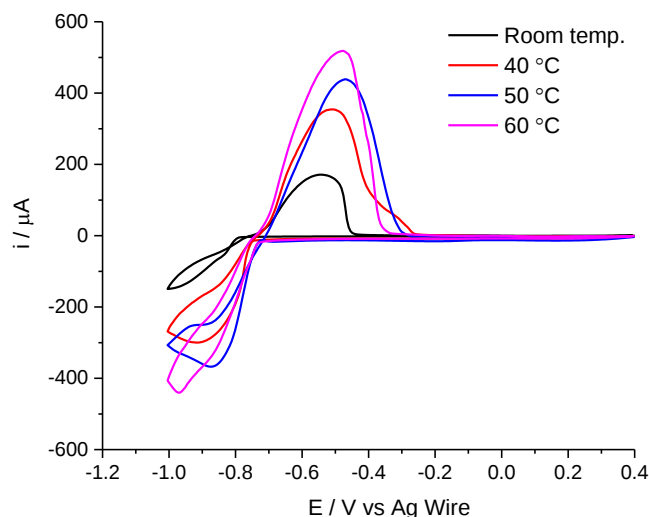


Figure 6.2 Cyclic voltammograms of 1:2 [Emim]Cl:AlCl₃ ionic liquid recorded at various temperatures on a polished Pt as a working electrode, Pt flag counter electrode and Ag silver wire as reference and at fixed scan rates of 20 mV s⁻¹.

6.3.1.1 Effect of MN on CVs of Al in [Emim]Cl/AlCl₃ IL

Electrodeposition of Al from a 1:2 [Emim]Cl:AlCl₃ IL was achieved on a Cu substrate using a pure Al plate as the anode. The deposition was achieved in absence and presence of 10 mM methyl nicotinate. Therefore, it is interesting to study cyclic voltammograms of Al from 1:2 [Emim]Cl/AlCl₃ IL using a Cu working electrode, an Al flag as a counter electrode and an Al wire as the reference electrode. **Figure 6.3** shows cyclic voltammograms of Al from 1:2 [Emim]Cl/AlCl₃ IL in the absence and presence of 10 mM methyl nicotinate.

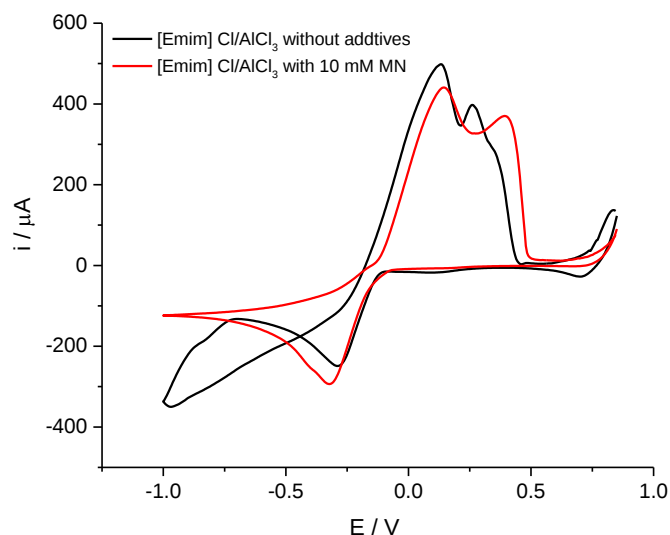


Figure 6.3 Cyclic voltammograms of a 1:2 [Emim]Cl:AlCl₃ ionic liquid in the absence and presence of 10 mM MN (MN), the experiment was recorded on a polished Cu working electrode, using an Al flag counter electrode and Al wire reference electrode at a scan rate of 20 mV s⁻¹ and a temperature of 30°C.

The cyclic voltammograms run from +0.85 V to -1.0 V using a Cu working electrode, an Al flag counter electrode and Al wire reference electrode, at a scan rate of 20 mV s⁻¹ and at 30°C. From **Figure 6.3**, there is clear change in the deposition of Al peaks in the absence and presence of methyl nicotinate. A nucleation loop is observed in the reduction of Al from [Emim]Cl/AlCl₃ IL without methyl nicotinate. This indicates that the nucleation/ growth rate for Al deposition is high compared to the nucleation rate for Al deposition from the system that included methyl nicotinate. Furthermore, it can be seen that there is a negative shift of about 45 mV in the Al deposition potential when MN was added to the [Emim]Cl/AlCl₃. This could correspond to the adsorption of MN on the electrode surface, and the consequently inhibited deposition of Al. The MN contains a pyridine ring and an ester group, as shown in **Figure 6.4**.

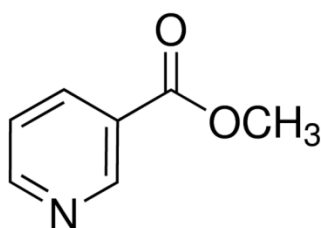


Figure 6.4 Structural of methyl nicotinate

The ester group is electron-withdrawing, while methyl group is considered to be slightly electron-donating. It was reported that the nitrogen in the conjugated ring has a much stronger polarization ability than that of carboxyl.^{1, 31} Consequently, the active centre of MN should be the nitrogen atom of the pyridine ring. **Figure 6.5** shows why MN has a stronger adsorption ability in the cathode. **Figure 6.5 (a)** shows the anions, cations and the additive molecules that exist freely in solution before the potential is applied or while potential is applied; the cathodic charge is compensated for by the first layer of cations, followed by a series of layers of counter ions, as shown in **Figure 6.5 (b)**.¹⁴ The electron density around the nitrogen atom decreases when electron-withdrawing groups are connected to the pyridine ring, leading to the adsorption of the MN on the cathode.

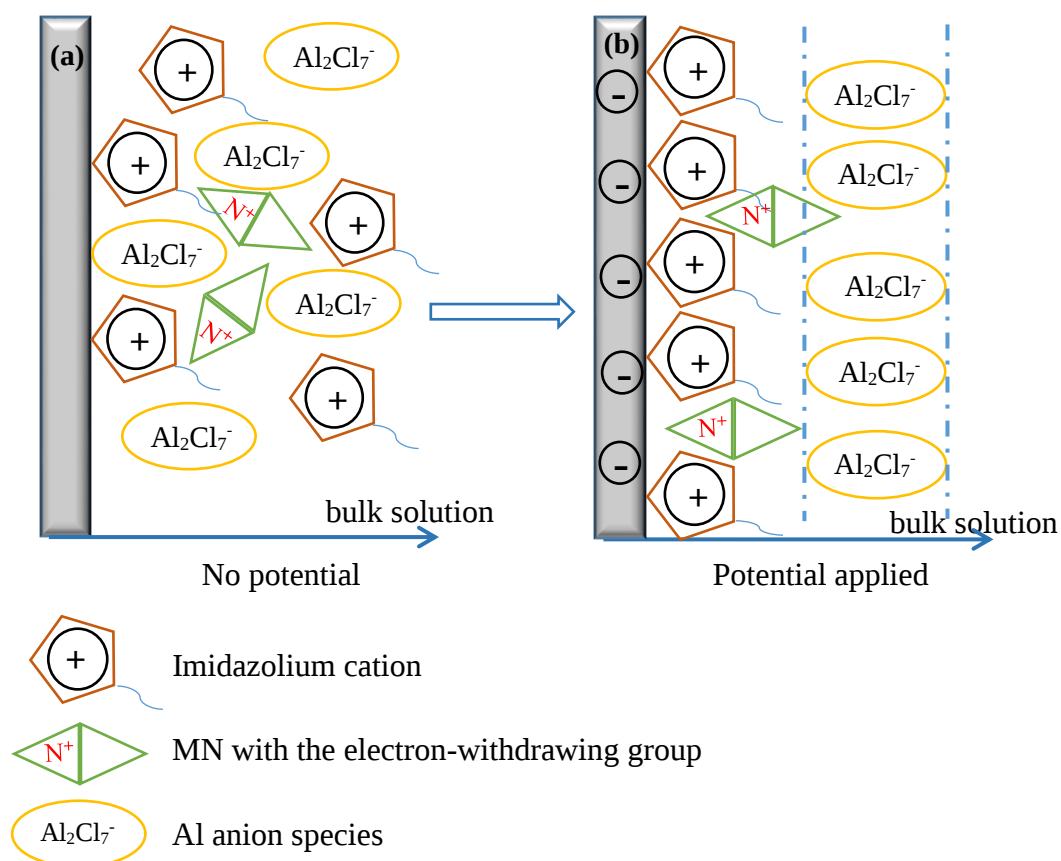


Figure 6.5 Schematic diagrams of the presence of the MN in the $[\text{Bmim}]\text{Cl} / \text{AlCl}_3$ ionic liquid when potential is not applied (a) or applied (b)

In **Figure 6.3**, two stripping peaks can be observed in the cyclic voltammograms of Al in both states in the presence and the absence of MN; similar results have been obtained for a number of ionic liquid systems. The two peaks have been suggested to either be alloy formation with the Cu electrode, or different morphologies of Al forming during the deposition process.^{20, 22, 29} The dissolution peak which is appeared at about +0.4 V could be related to the oxidation of Cu, as we have used a Cu working electrode. Adding MN to the [Emim]Cl/AlCl₃ resulted for the first time in the production of a bright Al coating, as will be explained later in this chapter.

6.3.1.2 Effect of MN on CVs of Al in [Bmim]Cl/AlCl₃ IL

The effect of MN on the electrodeposition of Al from 1:2 [Bmim]Cl:AlCl₃ IL was also investigated. **Figure 6.6** shows cyclic voltammograms of Al from 1:2 [Bmim]Cl:AlCl₃ IL in the absence and presence of 10 mM methyl nicotinate. The voltammograms were performed using a Cu working electrode, Al flag counter electrode and an Al wire as the reference electrode at a fixed scan rate of 20 mV s⁻¹ and temperature of 30°C. It can be seen from **Figure 6.6** that the reduction potential of Al was cathodically shifted when MN was added to the electrolyte. This was due to adsorption of MN on the electrode surface, impeding the deposition of Al.^{28, 32} Moreover, it can be seen that there was a decrease in the intensity of the reduction / oxidation current peaks, indicating that the amount of Al being reduced had decreased due to blocking of the electrode surface by the MN. A small reduction peak can also be seen in **Figure 6.6** at +0.15 V in the voltammograms of Al achieved in the system containing MN. This peak corresponds to the underpotential deposition (UPD) of Al on Cu.^{28, 33}

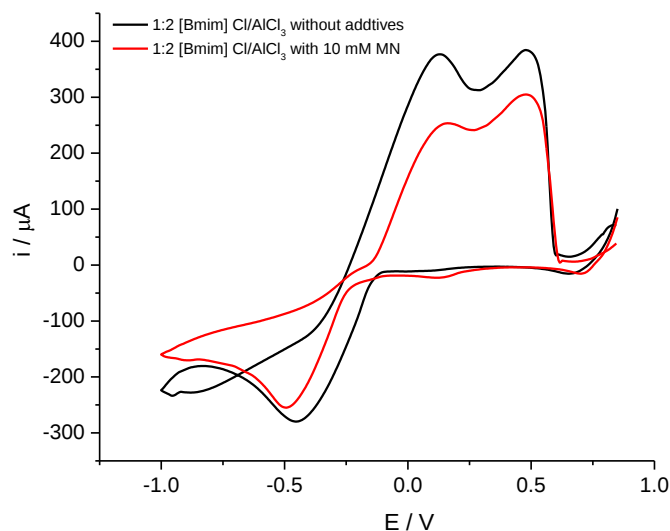


Figure 6.6 Cyclic voltammograms of 1:2 [Bmim]Cl:AlCl₃ ionic liquid in the absence and presence of 10 mM methyl nicotinate. The experiment was performed at a scan rate of 20 mV s⁻¹ on a polished Cu working electrode, using an Al flag counter electrode and an Al wire reference electrode at 30°C.

A nucleation loop appeared in the reduction peak of Al from [Bmim]Cl/AlCl₃ IL without MN in **Figure 6.6**, which disappeared in voltammograms measured in [Bmim]Cl/AlCl₃ IL with the presence 10 mM of methyl nicotinate, as happened for the [Emim]Cl/AlCl₃ IL shown in **Figure 6.3**. Zhang *et al.*¹ reported that MN can be adsorbed on the Cu electrode surface and inhibit deposition of Al. Therefore, adsorption of MN onto electrode surface impedes the growth of Al nuclei and thus decreases the reduction and oxidation current peaks of Al, as can be seen in **Figure 6.6**. Two oxidation peaks can be observed in the cyclic voltammograms of Al from [Bmim]Cl/AlCl₃ IL in the presence and absence of MN. These two peaks were attributed to either alloy formation with the Cu electrode or different morphologies of Al forming throughout the deposition process.

6.3.1.3 Cyclic voltammetry of Al in acetamide/AlCl₃-based liquid

In this work, we are interested in the electrodeposition of Al from liquid less sensitive to air and inexpensive than ionic liquids discussed earlier (Emim and Bmim systems). [Emim]Cl/AlCl₃ and [Bmim]Cl/AlCl₃ ILs suffering from some disadvantages, such as being expensive and sensitive to the moisture content of the air. Recently, Abbott *et al.*²³ have made Al eutectic solvents by mixing AlCl₃ with acetamide or urea in 1:1 molar ratios. These remain in the liquid phase over a wide range of temperatures and are insensitive to water; moreover, they have the properties of ionic liquids. The

associated ionic species found in these solvents are $[\text{AlCl}_2.n\text{Amide}]^+.\text{AlCl}_4^-$. **Figure 6.7** shows cyclic voltammograms of Al from 1.5:1 AlCl_3 :acetamide-based liquid, which were recorded at 30°C using a polished 1.0 mm Pt disc vs. Ag wire as a function of sweep rate. The cyclic voltammograms were run from +1.5 V to -1.5 V, and two distinct processes were observed. These processes corresponded to the reduction and oxidation of Al. The cyclic voltammograms of platinum in acetamide/ AlCl_3 -based liquid that are shown in this section revealed peak shapes characteristic of aluminium electrodeposition reported for other ionic liquids systems.³⁴⁻³⁶ Underpotential deposition UPD of Al was observed at +0.35 V, while bulk deposition of Al started at -0.78 V. Oxidation of pure Al, as reduced on the Pt electrode, occurred at about -0.025 V.

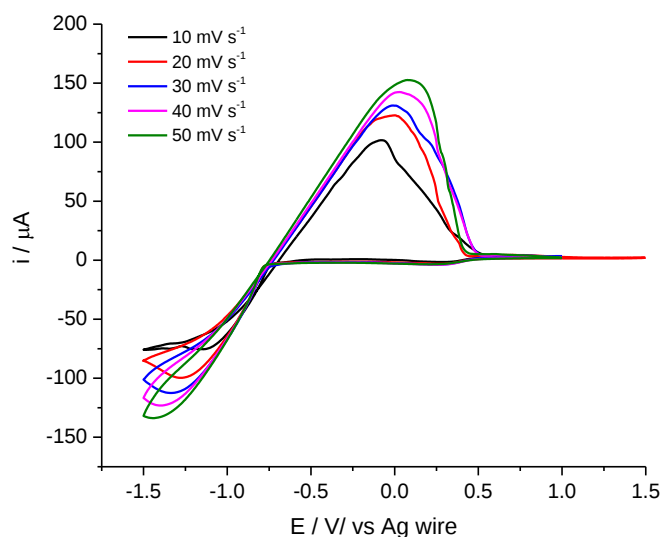


Figure 6.7 Cyclic voltammograms of Al from 1.5:1 AlCl_3 :acetamide-based liquid recorded on a polished 1.0 mm Pt disc vs. Ag wire at 30°C as a function of scan rate.

The data obtained from **Figure 6.7** were analysed as a function of scan rate (v), or square root of scan rate ($v^{1/2}$), as characterised by the cathodic peak current (I_{pc}), the anodic peak current (I_{pa}), the cathodic peak potential (E_{pc}) and the anodic peak potential (E_{pa}), as shown in **Figure 6.8**.

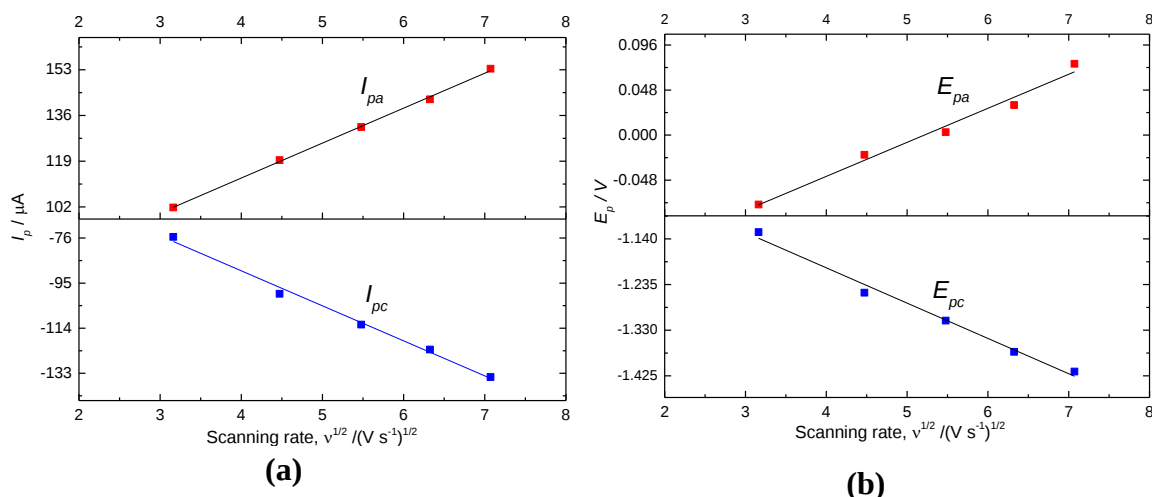


Figure 6.8 Relationships between electrochemical parameters deduced from the cyclic voltammograms depicted in **Figure 6.7**, at different scan rates; **(a)** differences of cathodic (I_{pc}) and anodic (I_{pa}) peak currents as per the square root of scan rate, (v), and **(b)** differences of cathodic (E_{pc}) and anodic (E_{pa}) peak potentials as per the square root of scan rate, (v).

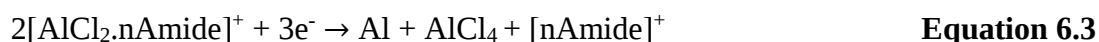
Table 6.1 Data derived from cyclic voltammetry of Al in a 1:1 acetamide/ $AlCl_3$ -based liquid obtained using a Pt electrode vs. Ag wire at 30°C using various scan rates.

Scan rate ($mV s^{-1}$)	$\Delta E_p(mV)$	$I_{pc}(\mu A)$	$I_{pa}(\mu A)$	I_{pa}/I_{pc}	$I_{pc}/v^{1/2} (\mu A s^{1/2} V^{-1/2})$	$I_{pa}/v^{1/2} (\mu A s^{1/2} V^{-1/2})$
10	1.05	75.49	101.83	1.34	23.67	32.19
20	1.23	99.51	119.40	1.2	22.25	26.71
30	1.30	112.53	131.09	1.17	20.56	24.07
40	1.34	123.0	142.0	1.15	19.46	22.46
50	1.35	134.61	153.40	1.13	19.03	21.69

From the data presented in **Figure 6.7**, **Figure 6.8** and **Table 6.1**, the following can be concluded:

- Increases in the cathodic peak current, I_{pc} , and the anodic peak current, I_{pa} , with increasing square root of scan rate ($v^{1/2}$), **Figure 6.8 (a)**.
- The ratio I_{pa}/I_{pc} is greater than unity, and decreases towards unity as v increases.
- E_{pc} becomes more cathodic with increasing scan rate (v), **Figure 6.8 (b)**.
- ΔE_p ($| E_{pc} - E_{pa} |$) increases with increasing scan rate, v , **Figure 6.8 (b)**.

From these four points, and according to Brown and Large,³⁷ it can be said that oxidation and reduction of Al from 1.5:1 AlCl₃:acetamide-based liquid at 30°C are in agreement with the criteria defining a quasi-reversible charge transfer mechanism. In general, the redox process in electrochemical reactions at an electrode surface can be characterised by two processes; a charge transfer process ($O + ne^- = R$), and mass transfer (diffusion) of electroactive species. When the rate of charge transfer process is fast, mass transfer alone determines the flux of electroactive species at the electrode surface; if there is no coupled chemical reaction involved in the total electrochemical reaction, then the reaction is known as a *reversible* charge transfer reaction. However, if the charge transfer process is slow compare to mass transfer, then the process is *irreversible*. On the other hand, when the reaction is one where the current is controlled partly by charge transfer kinetics and partly by diffusion of electroactive species, this corresponds to a *quasi-reversible reaction*. In this study, the cathodic charge transfer reaction of Al from 1.5:1 AlCl₃:acetamide-based liquid may be typically represented by the following equation:



Here, the actual process may be more or less complex than is actually represented. A quasi-reversible reaction will proceed at a rate comparable to that of the associated diffusion process.

In a quasi-reversible process, the current function, $I_p/v^{1/2}$, should be almost independent of scan rate;^{36, 37} however, this is not satisfied with our data as presented in **Table 6.1**. The cathodic current peak shows a linear relationship with the square root of the scan rate, as clear in **Figure 6.8 (a)**, indicating that the deposition rate is determined by the diffusion process.^{16, 36, 38-41} It can be seen from **Figure 6.8 (a)** that the representative line does not intercept with the origin, as might expected for a simple diffusion controlled process; this could be due to the contributions of a side reaction to the main deposition reaction.^{16, 36, 38, 41} Such a side reaction could be related to the reduction of some electroactive impurities in the ingredients of the Al liquid. The same can be seen in **Figure 6.8 (a)**, where it is similarly observed that the plot of I_{pa} vs. $v^{1/2}$ does not pass through the origin, meaning that the oxidation kinetics are also effected by some other chemical reaction; in this case, this is mostly likely to be the chemical corrosion of Al film deposited by the ionic liquid, or otherwise its impurities.⁴²

Cyclic voltammograms of Al from acetamide/ AlCl_3 -based liquid using different types of reference electrodes have also been investigated, as shown in **Figure 6.9**. The reference electrodes used were Ag and Al wire. The voltammograms were recorded at 30°C and a scan rate 20 mV s^{-1} , using a 1.0 mm Pt disc as the working electrode, and a Pt flag as the counter electrode. A remarkable change occurs in the cyclic voltammograms of Al as a result of using different reference electrodes, as can be clearly seen in **Figure 6.9**. Oxidation and reduction Al peaks have shifted to more positive potentials when Al wire was used as a reference electrode. No underpotential deposition for Al can be seen when Al wire was used, whereas underpotential deposition for Al was achieved at $+0.35\text{ V}$ when cyclic voltammograms were recorded using Ag wire, an effect which is quite obvious from **Figure 6.9**.

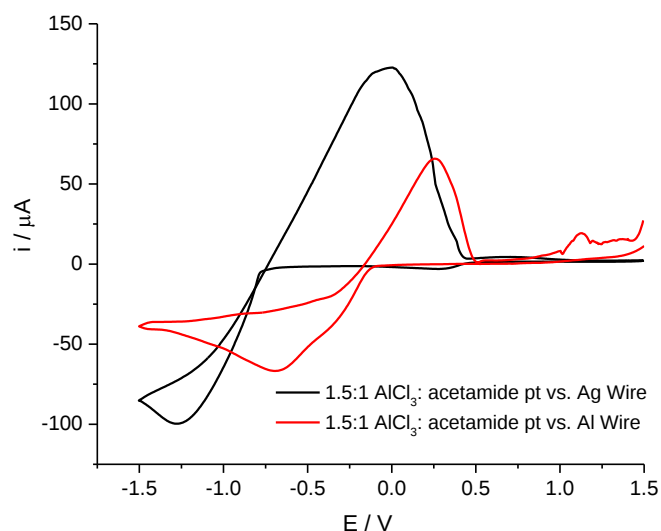


Figure 6.9 Cyclic voltammograms of Al from acetamide/ AlCl_3 -based liquid using different types of reference electrodes, Ag and Al wire. Pt was used as the working and counter electrode. The voltammograms were recorded at scan rates of 20 mV s^{-1} and at 30°C .

6.3.1.4 Cyclic voltammetry of Al in amide/ AlCl_3 eutectic solvents

As has been mentioned previously, it is important to deposit Al from liquids that are essentially insensitive to air moisture levels and are inexpensive. The new Al deep eutectic solvents that have been prepared in this work are (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide. Therefore, it should be interesting to study the electrochemical behaviour of Al in these types of liquids. **Figure 6.10** shows the cyclic voltammetry of Al in AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids. The voltammograms

were achieved on a 1.0 mm Pt disc working electrode, Pt counter electrode and Ag wire reference electrode. No significant change can be seen in the cyclic voltammograms of Al between these liquids except for voltammetry of Al from the AlCl_3 :*N*-methylacetamide-based liquid. Al in the AlCl_3 :acetamide and AlCl_3 :*N,N*-dimethylacetamide liquids has begun to reduce at -0.79 V, while Al species in the AlCl_3 :*N*-methylacetamide-based liquid start to deposit at -0.66 V, which is less, by about -15 mV, than the deposition potential of Al in AlCl_3 :acetamide-based liquids. Additionally, it can be seen that the oxidation/ reduction current peaks of Al in AlCl_3 :*N*-methylacetamide were higher than those that obtained from AlCl_3 :acetamide and AlCl_3 :*N,N*-dimethylacetamide liquids. This can be related to the difference in the species or coordination of Al to the amide molecules, which can effect the viscosities and conductivities of the Al liquids. The conductivities of these liquids were measured and were found as 0.94 mS cm^{-1} for the AlCl_3 :acetamide-based liquid, and 1.416 mS cm^{-1} and 1.249 mS cm^{-1} for the AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide liquids, respectively.

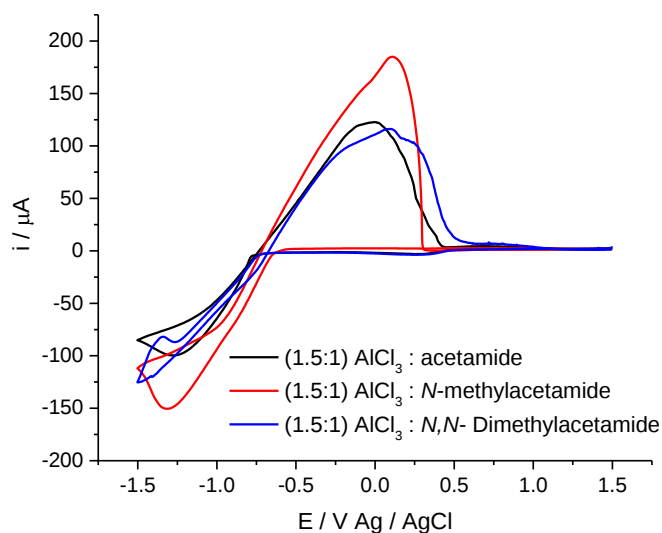


Figure 6.10 Cyclic voltammograms of Al in (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide liquids. The experiments were performed at a fixed scan rate of 20 mV s^{-1} on a polished Pt working electrode, using a Pt flag counter electrode and Ag wire as reference electrode at 30°C .

A nucleation loop can be seen in the reduction of Al from *N,N*-dimethylacetamide liquids. However, this loop cannot be seen in the reduction peak of Al from AlCl_3 :acetamide and AlCl_3 :*N*-methylacetamide-based liquids. This could correspond to natural Al species in liquids, where the major Al species present are

$[\text{AlCl}_2.\text{nAmide}]^+.\text{AlCl}_4^-$. However, coordination of Al to the amide in each case is different, according to the type of amide in use. In the acetamide/ AlCl_3 -based liquid, the complex formation between Al and acetamide occurs through co-ordination of the oxygen atoms on the acetamide.²³ However, the complexation of Al to *N*-methylacetamide and *N,N*-dimethylacetamide occurs through both the oxygen *and* nitrogen atoms, because of the inductive effect of the methyl group on the nitrogen atoms,²⁴ as shown in the structures of the amides in **Figure 6.11**.

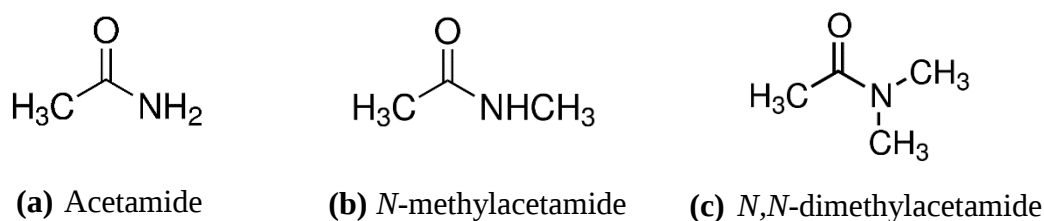


Figure 6.11 (a) Structures of acetamide, (b) *N*-methylacetamide and (c) *N,N*-dimethylacetamide.

Compared with the monodentate coordination of acetamide, bidentate coordination in the methylated species was favourable to the asymmetric splitting of AlCl_3 with the amides. The steric and inductive effects of the methyl group resulted in ionic species percentages in these IL analogues being ranked in the following order: *N*-methylacetamide > *N,N*-dimethylacetamide > acetamide. The difference in the coordination of Al according to amide used could be influenced by the viscosity and conductivity of these liquids, which could then further affect the electrochemical behaviour of Al.

6.3.1.5 Effect of MN on CVs of Al in amide- AlCl_3 eutectic solvents

The main point of this work was to study the effects of additives on electrodeposition of Al from different types of ionic liquids. The effects of MN on the electrochemical behaviour of Al in 1:2 $[\text{Emim}]\text{Cl}:\text{AlCl}_3$ and 1:2 $[\text{Bmim}]\text{Cl}:\text{AlCl}_3$ ILs have been investigated, as shown in **Figure 6.3 (a)** and **Figure 6.6**, respectively. MN has been shown to significantly affect the electrodeposition of Al from $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ and $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ ILs, where mirror Al coatings were produced as MN was added to the plating electrolyte, as will be explained later in this chapter. Therefore, it is very

interesting to study effect of MN on the electrochemical behaviour of Al from amide/ AlCl_3 eutectic solvents.

Figure 6.12 shows cyclic voltammograms of Al in (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic liquids in the absence and the presence of a 10 mM MN. All experiments were recorded at scan rates of 20 mV s^{-1} on a Pt working electrode, a Pt flag counter electrode and an Ag wire as a reference electrode at 30°C .

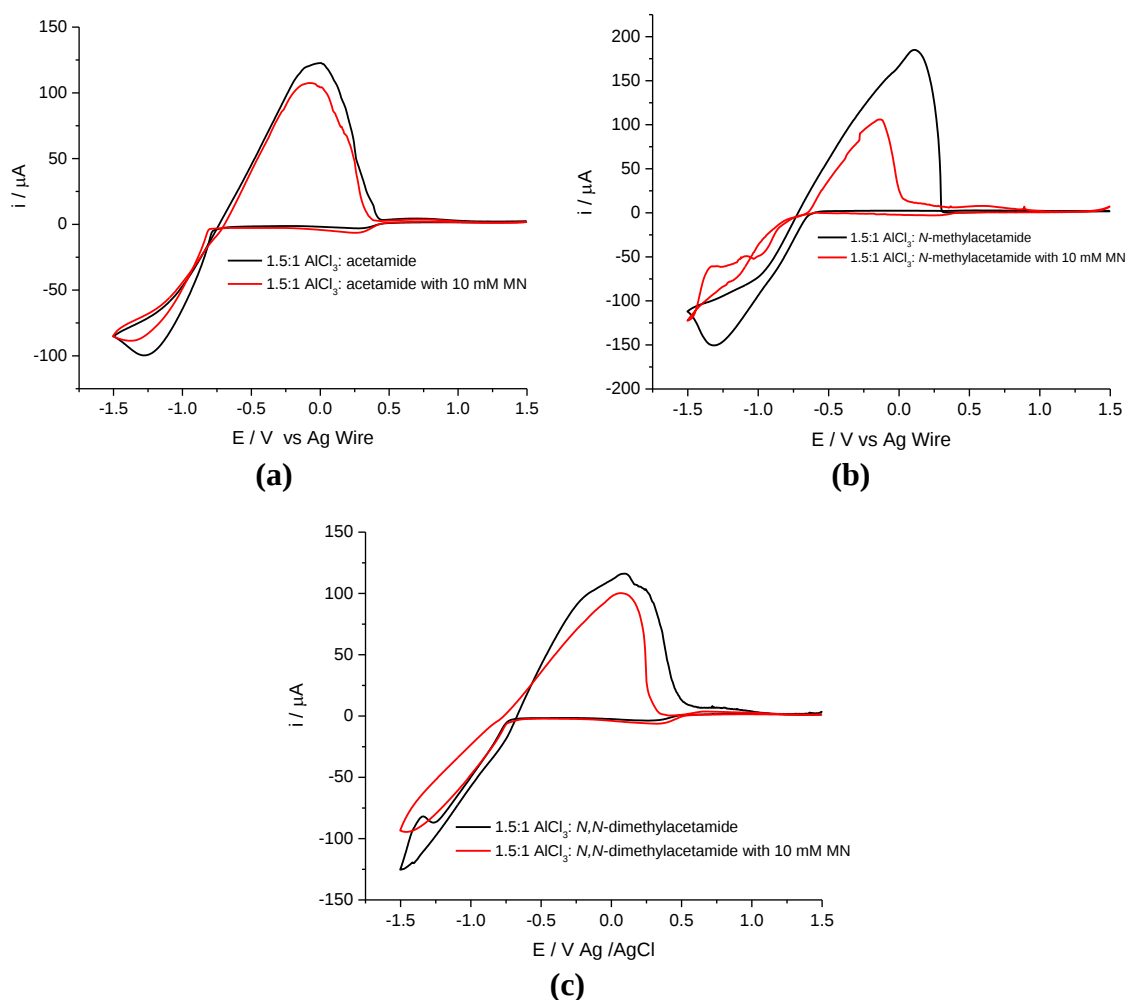


Figure 6.12 (a), (b) and (c) show cyclic voltammograms of Al in (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic liquids, respectively. The voltammograms were recorded in the presence and absence of a 10 mM MN on at fixed scan rates of 20 mV s^{-1} on a Pt working electrode, a Pt flag counter electrode and an Ag wire as reference electrode at 30°C .

Figure 6.12 (a) shows cyclic voltammograms of Al from AlCl_3 :acetamide in the absence and the presence of a 10 mM concentration of MN. The voltammograms show two cathodic peaks and one anodic peak, with the small reduction peak that can be seen at positive potentials at +0.35 V corresponds to the underpotential deposition process, while the deposition peak at -1.25 V related to bulk deposition of Al. **Figure 6.12 (a)** shows a slight negative shift in the deposition potential of Al as a result of adding MN to the AlCl_3 :acetamide-based liquid, and a slight decrease in the deposition and stripping peaks of Al were also observed. There is a clear negative shift in the reduction potential of Al in the (1.5:1) AlCl_3 :*N*-methylacetamide-based liquid when MN was used. Furthermore, a clear nucleation loop has appeared in the reduction peak of Al as a result of adding MN to the (1.5:1) AlCl_3 : *N*-methylacetamide liquid, as shown in **Figure 6.12 (b)**. Moreover, decreases in the deposition and dissolution Al peaks occurred when using MN as an additive, as well as the deposition potential of Al shifting cathodically as a result of introducing of MN to the (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic liquid, as shown in **Figure 6.12 (c)**. Generally speaking, the changes in the cyclic voltammograms of Al in these types of eutectic mixtures could be related to the adsorption of MN on the electrode surface and inhibition of Al deposition.

6.3.2 Chronocoulometry

Figure 6.13 shows the results of chronocoulometry experiments for a Pt disc electrode in a (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic solvents. The results are for a potential step from 0.0 V (held for 10 s) to -1.25 V over 10 minutes. **Figure 6.13** shows the plots of charge vs. $t^{1/2}$ are not linear, suggesting that the processes are not diffusion controlled. It is clear from **Figure 6.13** that the charge, Q , for Al deposition from (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic solvents less than the charge, Q , for Al deposition from (1.5:1) AlCl_3 :acetamide. This could indicate that electrodeposition of Al from the AlCl_3 :acetamide system is faster than in AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide-based liquids. According to Faraday's Law ($Q = nFN$), the charge measured is directly proportional to the number of species deposited in moles (N). This means that current efficiency of Al deposition from AlCl_3 :acetamide liquid is higher than the current efficiency of Al deposition from the other types of liquids.

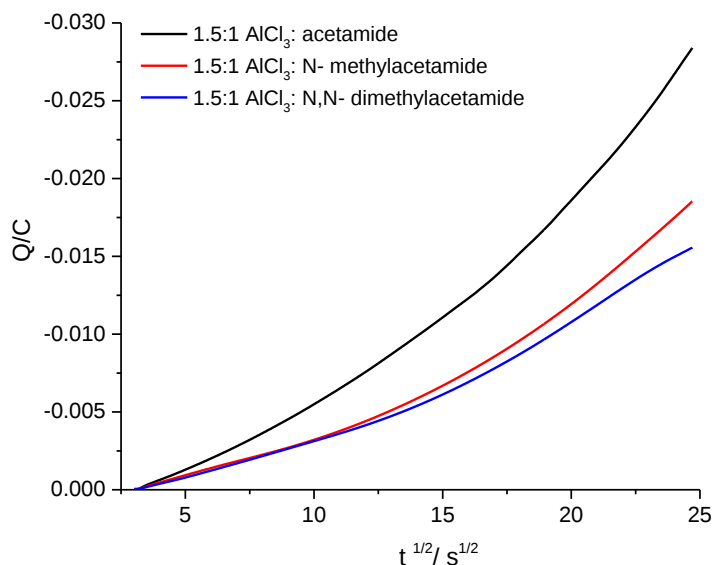


Figure 6.13 Chronocoulometry of Al in (1.5:1) $AlCl_3$:acetamide, (1.5:1) $AlCl_3$:N-methylacetamide and (1.5:1) $AlCl_3$:N,N-dimethylacetamide liquids. The experiments were recorded for a potential step from 0.0 V (held for 10 s) to -1.25 V over 10 min on a polished Pt working electrode, a Pt flag counter electrode and an Ag wire as the reference electrode at 30°C.

6.3.3 Deposition morphology

6.3.3.1 Effect of MN on morphology of Al coated in [Emim]Cl/ $AlCl_3$

In the beginning of our study, we investigated the effect of MN as an additive on the surface properties of the Al deposited from a conventional type of ionic liquid, which is 1:2 [Emim]Cl: $AlCl_3$. **Figure 6.14** shows SEM, AFM and optical images of Al coatings obtained from [Emim]Cl/ $AlCl_3$ IL in the absence and presence of 10 mM MN. The deposition was achieved on a Cu substrate at 30°C and at current density of 6 mA cm⁻² for 1 h.

It was found that MN has a significant impact on the surface morphology of Al deposits. Mirror finish coatings were obtained, as shown in **Figure 6.14 (b)**, when 10 mM MN was added to the [Emim]Cl/ $AlCl_3$ IL. However, the crystal/grain size of Al deposit increased when the deposition was achieved from a system without MN, as is clear in **Figure 6.14 (a)**. Therefore, it can be suggested that MN can result in a considerably refined grain size in the Al films, producing mirror-bright Al coatings.

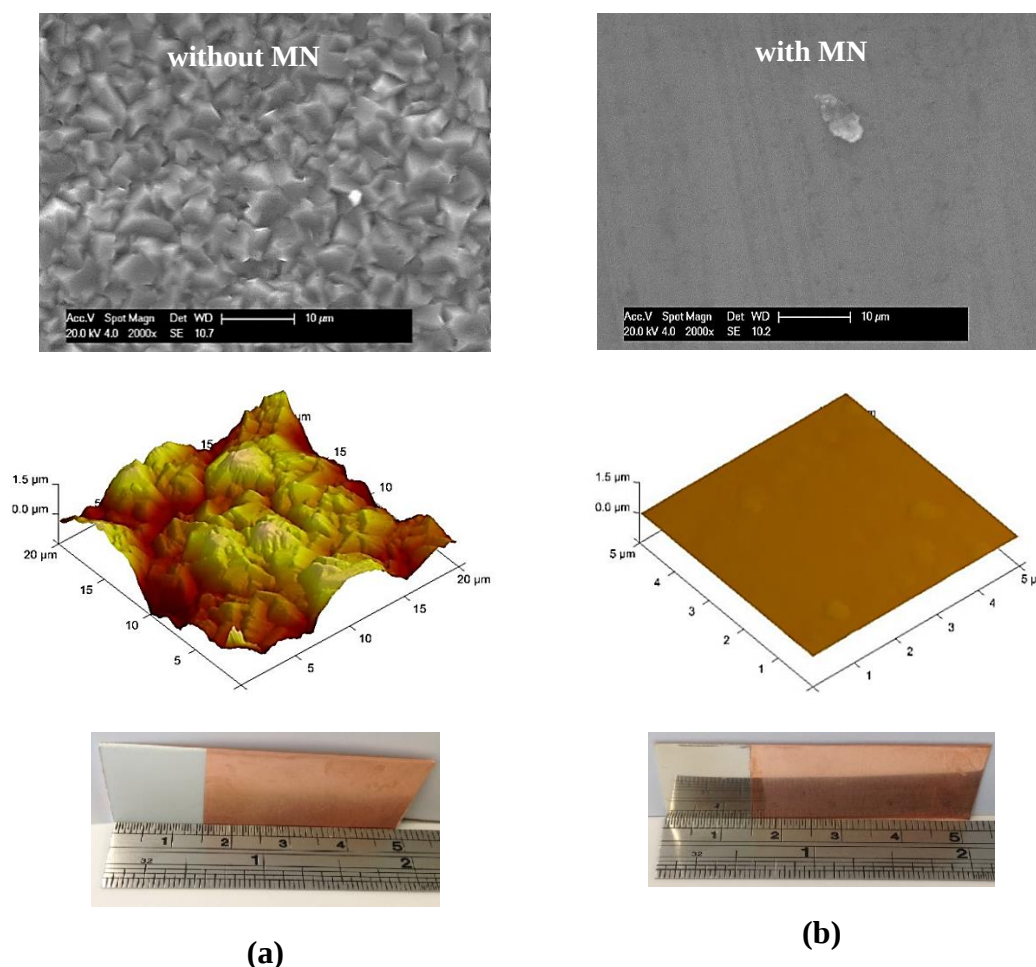


Figure 6.14 (a) and (b) show SEM, AFM and optical images of Al coatings obtained from an $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ IL in the absence and presence 10 mM of MN, respectively. The deposition achieved on the Cu substrate at a current density of 6 mA cm^{-2} for 1 h and at 30°C (sample width 2 cm).

In **Figures 6.14 (a) and (b)**, the topographies and roughness of the Al deposits were determined by AFM. The topographies of the Al coatings were typically identical to the SEM morphologies. The roughness of the Al film produced from the system without MN was 618 nm. However, this roughness decreased to 11.4 nm when MN was added to the electrolyte. The current efficiency of the electrodeposition of Al from $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ IL in the absence of MN was $\sim 97\%$, where these values were calculated as follows:

$$F = C/\text{mole}$$

$$\begin{aligned}\text{So, mole} &= \text{time(s)} \times \text{Current (A)} / F \\ &= 3600 \text{ s} \times 0.02 \text{ A} / 96485 \text{ C.mol}^{-1} \\ &= 0.74 \times 10^{-3} \text{ mole} / 3 \quad (n= 3 \text{ for Al}^{3+}) \\ &= 0.24 \times 10^{-3} \text{ mole}\end{aligned}$$

$$\text{Wt theory} = \text{no. of mole} \times \text{A.wt of Al}$$

$$\begin{aligned}\text{Wt theory} &= 0.24 \times 10^{-3} \text{ mole} \times 27 \text{ g.mole}^{-1} \\ &= 0.0067 \text{ g theoretical weight.}\end{aligned}$$

$$\begin{aligned}\text{Weight of cathode substrate after coating} - \text{weight of cathode substrate before coating} \\ &= 9.08185 \text{ g} - 9.07535 \text{ g} \\ &= 0.0065 \text{ g experimental weight of Zn-Ni alloy coating}\end{aligned}$$

$$\begin{aligned}\text{Current efficiency\%} &= \text{wt experimental} / \text{wt theory} \times 100 \\ &= 0.0065 \text{ gm} / 0.006 \times 100 \\ &= \mathbf{96.8\%}\end{aligned}$$

The current efficiency of the Al electrodeposition formed from [Emim]Cl/AlCl₃ IL in the presence of 10 mM MN was calculated by the same method, and its efficiency was found to be ~90%.

MN serves as a very effective brightener, producing highly uniform and smooth Al deposits. As has been discussed regarding the cyclic voltammetry data shown in **Figure 6.3**, MN can be adsorbed onto the electrode surface, thus inhibiting the growth of Al nuclei and increasing the nucleation rate.

6.3.3.2 Effect of MN on morphology of Al coated in [Bmim]Cl/AlCl₃

The effect of MN on the surface morphology on Al deposits from 1:2 [Bmim]Cl:AlCl₃ IL was also investigated. **Figure 6.15** shows SEM, AFM and optical images of Al coatings obtained from [Bmim]Cl/AlCl₃ IL in the absence and presence of 10 mM MN. Here, the conditions for Al deposition were the same as those used for deposition of Al from 1:2 [Emim]Cl:AlCl₃ IL.

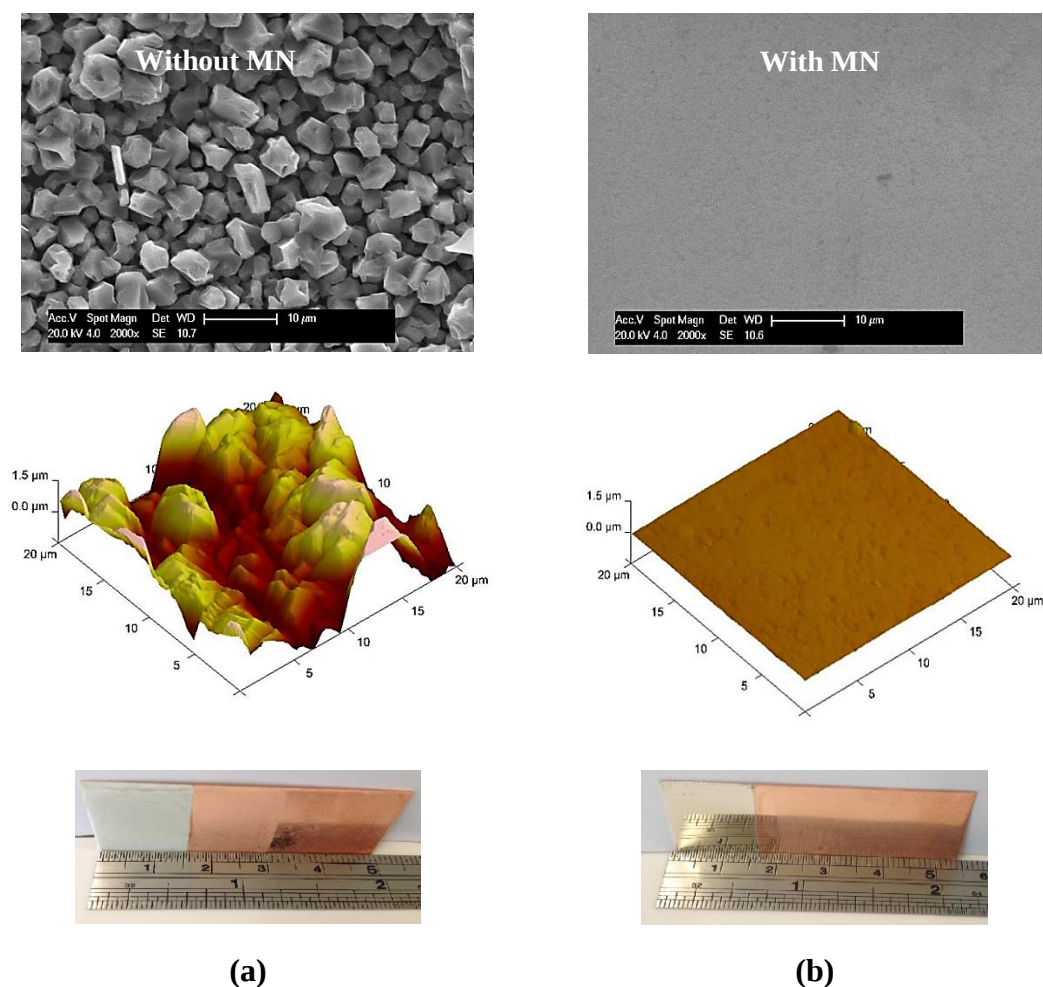


Figure 6.15 (a) and (b) show SEM, AFM and optical images of Al coatings obtained from 1:2 [Bmim]Cl:AlCl₃ IL in the absence and presence of 10 mM MN, respectively. The deposition was achieved on the Cu substrate at a current density of 6 mA cm⁻² for 1 h and at 30°C (sample width 2 cm).

A clear crystalline Al coating can be seen in the SEM morphology of Al deposited from [Bmim]Cl/AlCl₃ IL without MN, as shown in **Figure 6.15 (a)**. The Al coating was white-grey with a roughness of. However, an Al mirror coating was obtained when 10 mM of MN was added to the [Bmim]Cl/AlCl₃ IL, as is clear in **Figure 6.15 (b)**. The mean roughness (Ra) of the Al coatings produced from [Bmim]Cl/AlCl₃ IL in the absence and presence of MN were also calculated using AFM. The roughness of Al deposited from [Bmim]Cl/AlCl₃ IL in the absence of MN was 647 nm, while the roughness of Al film decreased to 43.6 nm as a result of introducing the MN into the plating bath. Clearly, the roughnesses observed are in agreement with the AFM images

shown in **Figure 6.15 (a)** and **(b)**. This indicates that MN acts as an effective levelling agent.⁴³

In aqueous solution, additives are thought to behave in one of two ways: either they form a complex with metal ions, meaning they cannot be easily reduced, or they adsorb onto the electrode surface and block metal nucleation.⁴⁴ Recently, Liu *et al.*^{1, 28} have investigated the effect of MN on the electrodeposition of Al from 1:2 [Bmim]Cl:AlCl₃ IL, reporting that MN adsorbed on the electrode surface and inhibited deposition of Al. The current efficiencies of the Al coatings produced from the [Bmim]Cl/AlCl₃ IL in the absence and presence of MN were calculated by the classic method of finding the difference in weight of the cathode substrate before and after coating, and the comparing this with the theoretical weight. The current efficiency of depositing Al from [Bmim]Cl/AlCl₃ IL in the absence of MN was close to 100%, while this value decreased to ~92% as a result of adding 10 mM MN to the plating bath.

6.3.3.3 Electrodeposition of Al from acetamide/AlCl₃-based liquid

It is very important to study electrodeposition of Al from easily prepared liquids that are cheap and less sensitive to the moisture content of air. Deep eutectic solvents, as recently discovered by Abbott *et al.*^{45, 46} have caused a great sensation in the field of electroplating.^{14, 32, 47, 48} In 2011, Abbott *et al.*²³ prepared a new type of Al liquid which is a mixture of acetamide and AlCl₃ in a 1:1 molar ratio. In this work, electrodeposition of Al from a 1.5:1 AlCl₃:acetamide eutectic solvent was investigated.

Figure 6.16 shows optical images, the morphology and EDX analysis of an Al coating produced from a 1.5:1 AlCl₃:acetamide -based liquid achieved on mild steel at a current density of 3.5 mA cm⁻² at 30°C for 1 h. **Figure 6.16 (a)** shows that the mild steel substrate is covered by a grey deposit after the electrodeposition. Moreover, SEM image, **Figure 6.16 (b)**, shows the random distribution of grains of the Al coating. EDX analysis was used to identify the composition of the electrodeposited film which, as shown in **Figure 6.16 (c)**, is composed of pure Al. The current efficiency of the electrodeposition of Al from these types of liquids on the mild steel was 54.9%, where this value was calculated by measuring the change in weight of the cathode substrate before and after coating and compared to its theoretical value.

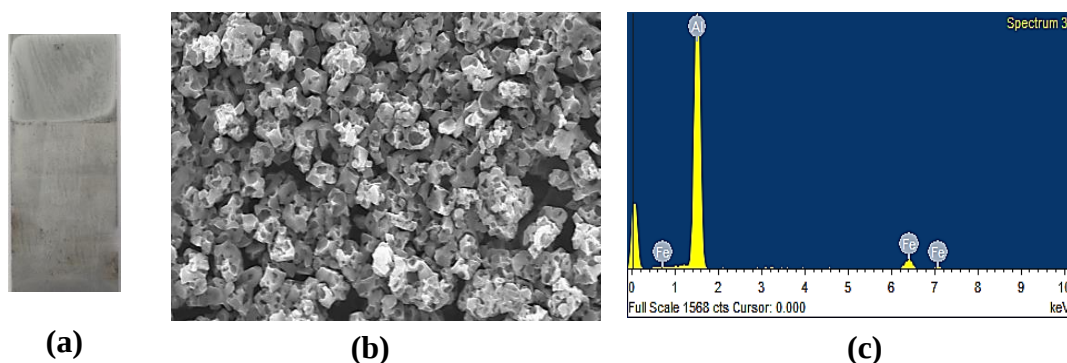


Figure 6.16 (a) optical image, (b) scanning electron micrograph and (c) EDX analysis of electrodeposited Al on mild steel substrates at current densities of 3.5 mA cm^{-2} and 30°C for 1 h (sample width 2 cm).

6.3.3.4 Electrodeposition of Al coatings from amide/ AlCl_3 -based liquids

As mentioned earlier in the chapter, the electrodeposition of Al from conventional ionic liquids is currently limited due to the high cost of quaternary ammonium halide salts and their hygroscopic nature. Therefore, in this project, three types of Al containing DES were prepared and used in the electrodeposition of Al. In this work, electrodeposition of Al was achieved for first time from these types of deep eutectic solvent. **Figure 6.17** shows the morphologies of the Al coatings obtained from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids. The deposition was achieved on a Cu substrate at 30°C and at a current density of 3.5 mA cm^{-2} for 1 h with stirring. A porous Al coating with a small grain size was obtained from a 1.5:1 AlCl_3 :acetamide -based liquid, as shown in **Figure 6.17 (a)**. A significant change in the morphology of the Al film is achieved when the deposition occurs in 1.5:1 AlCl_3 :*N*-methylacetamide-based liquid, where a homogenous and uniform Al coating can be seen in **Figure 6.17 (b)**; a uniform Al coating is also obtained from deposition achieved in 1.5:1 AlCl_3 :*N,N*-dimethylacetamide-based IL, as shown on **Figure 6.17 (c)**. It can be seen from **Figures 6.17 (b) and (c)** that the grain size of the Al deposit obtained from AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide systems are bigger than those achieved for Al film produced from the AlCl_3 :acetamide-based liquid. This means that rate of Al growth in the AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based ILs is greater than the rate of Al growth in the AlCl_3 :acetamide system. The difference in the size of crystals/ grains corresponds to the kind, or coordination, of Al with the amide. Liu *et al.*²⁴ reported that

a bidentate coordination through both the O and N atoms was dominant in the *N*-methylacetamide- AlCl_3 and *N,N*-dimethylacetamide- AlCl_3 -based IL analogues because of the inductive effect of the methyl group(s), while the acetamide- AlCl_3 -based IL analogue presented mainly in the form of a monodentate coordination via the O atom only.

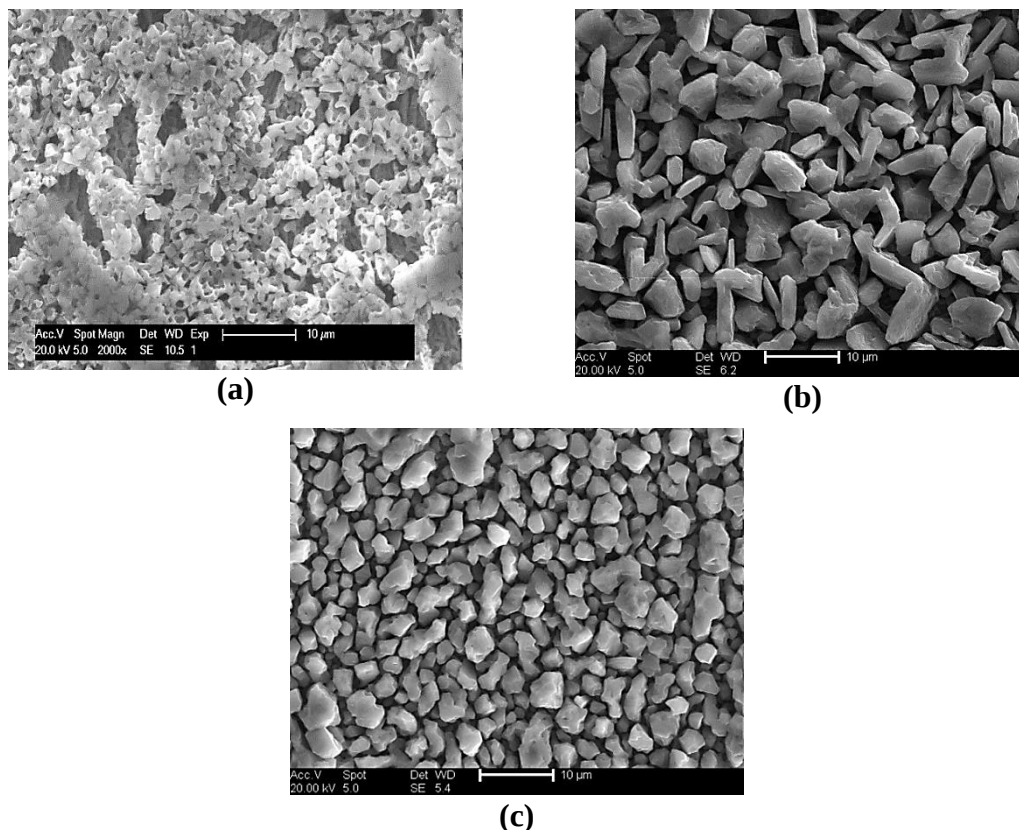


Figure 6.17 (a), (b) and (c) show SEM images of Al coatings obtained from (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide-based liquid. The deposition was achieved on Cu substrates at a current density of 3.5 mA cm^{-2} for 1 h at 30°C .

The current efficiencies of the electrodepositions of Al from amide/ AlCl_3 -based liquids were calculated. It was found that the current efficiency of the electrodeposition from the AlCl_3 :*N*-methylacetamide liquid was about 82%, which is higher than the current efficiency of Al deposited from acetamide- AlCl_3 and *N,N*-dimethylacetamide- AlCl_3 -based liquids, whereas the efficiencies of these liquids were $\sim 62\%$ and $\sim 77\%$, respectively. As mentioned previously, the conductivity of the AlCl_3 :*N*-methylacetamide liquid was 1.416 mS cm^{-1} , while the conductivity of the acetamide- AlCl_3 and *N,N*-dimethylacetamide- AlCl_3 -based liquids were 0.93 mS cm^{-1} and 1.249 mS cm^{-1} , respectively. Since the conductivity of the AlCl_3 :*N*-methylacetamide liquid

was greater than the conductivity of acetamide- AlCl_3 and N,N -dimethylacetamide- AlCl_3 -based liquids, this is probably the reason for the high current efficiency of the Al electrodeposition from the AlCl_3 : N -methylacetamide liquid compared to those observed with the acetamide- AlCl_3 and N,N -dimethylacetamide- AlCl_3 -based liquids

6.3.3.5 Effect of MN on Al deposit from AlCl_3 :acetamide-based liquid

No work has been conducted on the effects of additives on the electrodeposition of Al from DESs. Earlier in this chapter, the effect of MN on the electrodeposition of Al from classic ionic liquids, such as $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ and $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$, was studied. Using MN in electroplating of Al from these ionic liquids led to the production of an Al mirror coating, as was shown in **Figure 6.14 (b)** and **Figure 6.15 (b)**. Therefore, it is suggested that this kind of additive might be tried in the electrodeposition of Al from acetamide: AlCl_3 eutectic solvent.

Figure 6.18 shows SEM and AFM images of the Al coating obtained from a 1.5:1 AlCl_3 :acetamide-based IL in the absence and presence of a 10 mM concentration of MN. The deposition was achieved on a Cu substrate at 30°C and a current density 3.5 mA cm^{-2} for 1 h. A significant modification in the morphology of Al coating occurred compared to that obtained from the AlCl_3 :acetamide-based IL containing MN, as is clear from **Figure 6.18 (b)**. A non-porous and a homogenous Al film was obtained as a result of adding MN to the plating bath. The crystal size of the Al coatings produced from systems containing MN was larger than those produced from systems without MN, where can be clearly seen in **Figures 6.18 (a)** and **(b)**. When MN was added to the AlCl_3 :acetamide-based IL, no change in the colour of solution was observed. Therefore, it can be suggested that MN adsorbs on the electrode surface and inhibits nucleation and an increased rate of growth. The roughness of the Al film produced from a AlCl_3 :acetamide-based IL in the absence of MN was 510 nm, while the roughness has been increasing and become 573 nm when the deposition of Al achieves from system coating 10 mM MN. The increase in the roughness of the Al film could be related to the increasing rate of Al growth from the AlCl_3 :acetamide-based IL in the presence of MN.

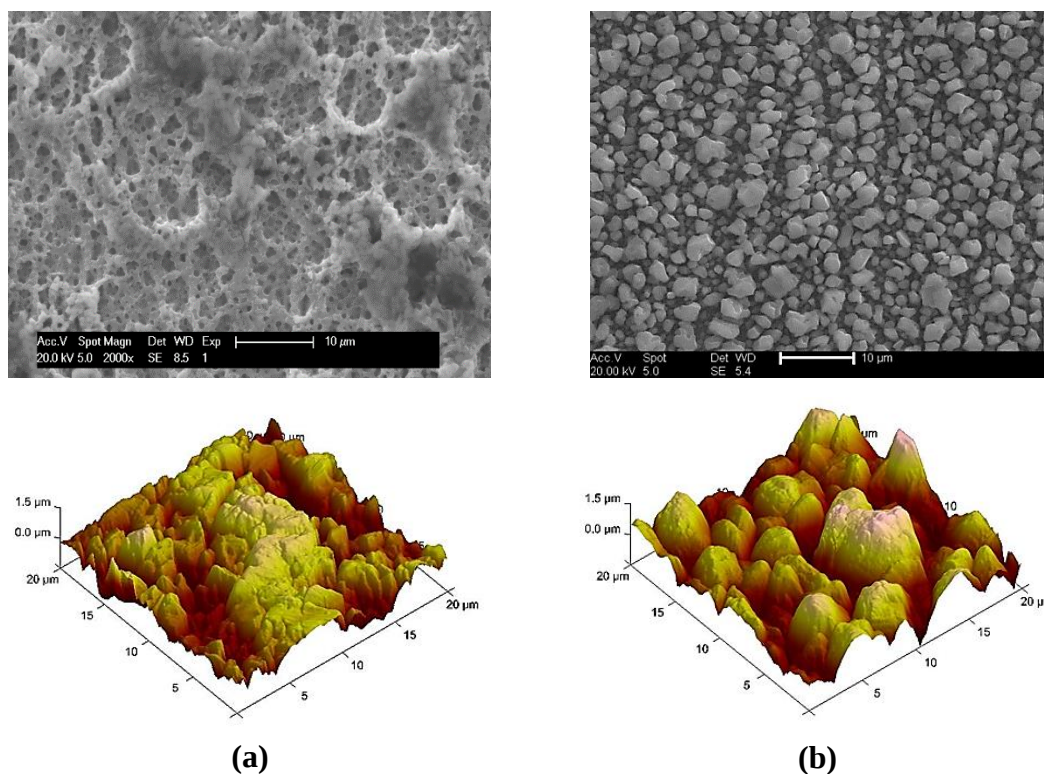


Figure 6.18 (a) and (b) show SEM, and AFM of Al coatings obtained from 1.5:1 AlCl_3 :acetamide-based IL in the absence and presence of a concentration of 10 mM MN, respectively. The deposition was achieved on a Cu substrate at a current density of 3.5 mA cm^{-2} for 1 h at 30°C .

6.3.3.6 Effect of MN on Al deposit from AlCl_3 :*N*-methylacetamide

AlCl_3 :*N*-methylacetamide is one of the more interesting DESs that can be used in the electrodeposition of Al. Here also, MN was introduced to study its influence on the surface properties of the Al coating. **Figure 6.19** shows SEM and AFM images of the Al coatings obtained from a 1.5:1 AlCl_3 :*N*-methylacetamide-based IL in the absence and presence of 10 mM of MN. The deposition was achieved on a Cu substrate at 30°C and at a current density of 3.5 mA cm^{-2} for 1 h. Contrary to the acetamide liquid, where the grain sizes in the Al coating increased when using MN. However, with the *N*-methylacetamide liquid, a clear refinement in the grain size of the Al coating was found to occur as a result of adding MN to the AlCl_3 :*N*-methylacetamide-based IL, as is clear in **Figure 6.19** (b). The roughness of the Al film obtained from AlCl_3 :*N*-methylacetamide-based IL in the presence and absence of 10 mM MN were measured by using AFM. The roughness of the Al film obtained from the system without MN was 672 nm, which decreased to 552 nm when the Al was deposited from a bath containing MN.

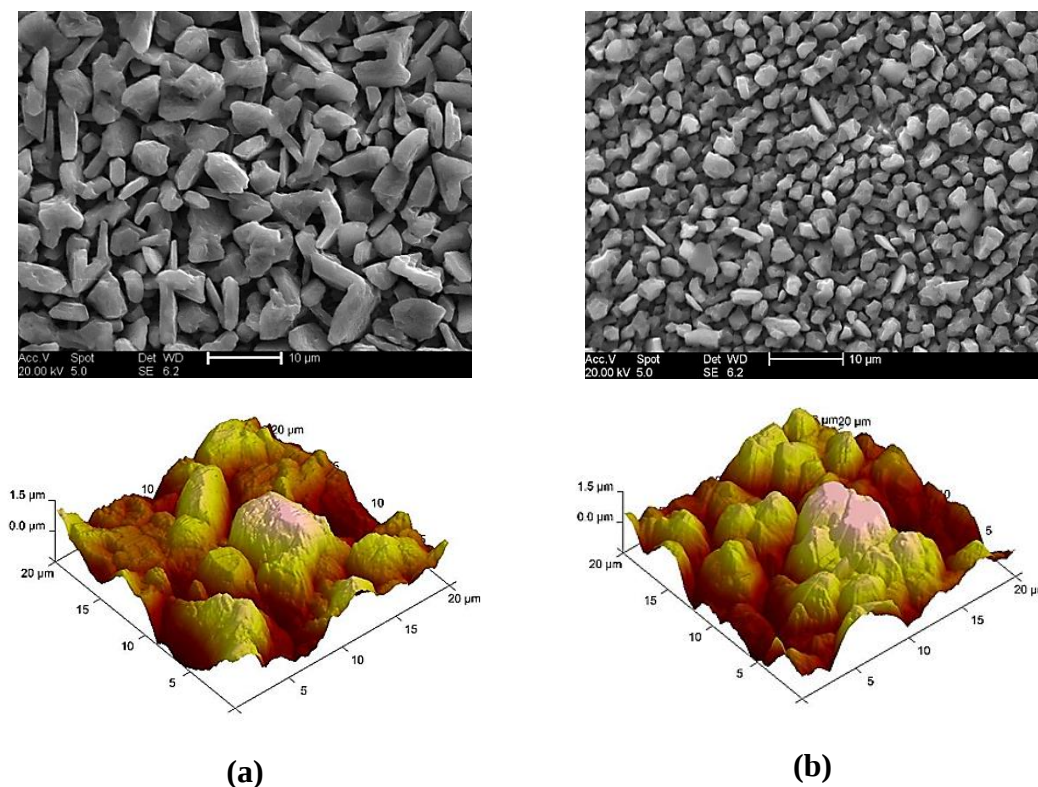


Figure 6. 19 (a) and (b) show SEM, and AFM of the Al coatings obtained from an AlCl_3 :*N*-methylacetamide-based IL in the absence and presence of 10 mM MN, respectively. The deposition was achieved on a Cu substrate at a current density of 3.5 mA cm^{-2} for 1 h at 30°C .

6.3.3.7 Effect of MN on Al deposit from AlCl_3 :*N,N*-dimethylacetamide

The effect of MN on the electrodeposition of Al from a 1.5:1 AlCl_3 :*N,N*-dimethylacetamide-based IL has also been studied. **Figure 6.20** shows SEM and AFM images of the Al coating obtained from 1.5:1 AlCl_3 :*N,N*-dimethylacetamide-based IL in the absence and presence of 10 mM MN. Generally, the deposition was achieved on a Cu substrate at 30°C and at a current density of 3.5 mA cm^{-2} for 1 h. No significant change in morphology of the Al coating produced from the system containing MN compared to that achieved from 1.5:1 AlCl_3 :*N,N*-dimethylacetamide without MN was observed. A small refinement of grain size in the Al coating and grains that contacted each other was observed when deposition was achieved in the presence of MN.

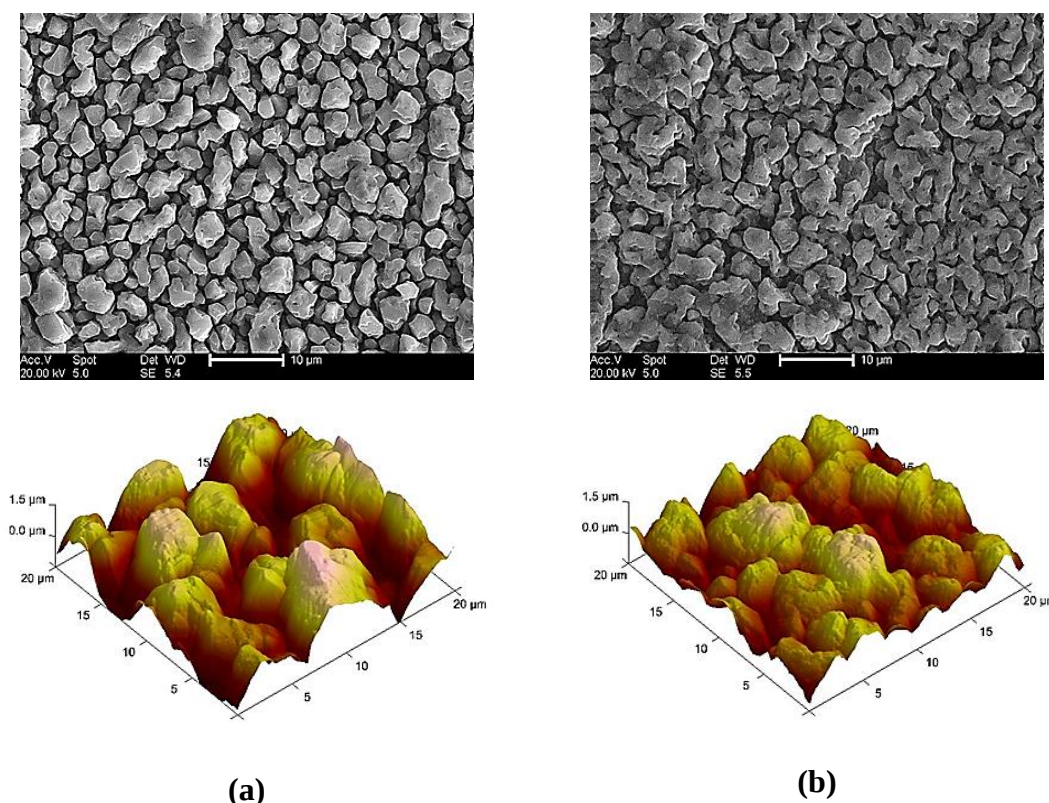


Figure 6.20 (a) and (b) show SEM and AFM of Al coatings obtained from AlCl_3 :*N,N*-Dimethylacetamide-based IL in the absence and presence of 10 mM MN, respectively. The deposition was achieved on a Cu substrate at a current density of 3.5 mA cm^{-2} for 1 h at 30°C .

6.3.4 XRD analysis

6.3.4.1 Crystal structures of Al deposit from amide- AlCl_3

The relationship between the crystal structures and surface morphologies of Al deposits was further explored via XRD. In this study, XRD was used to examine the crystal structures of Al deposits. **Figure 6.21** shows the XRD patterns of the Al coatings produced from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids. The deposition for each was achieved on a Cu substrate at 30°C and at a current density of 3.5 mA cm^{-2} for 1 h under stirring. As expected, the XRD pattern of the Al coatings deposited from amide/ AlCl_3 ionic liquids matches well with the standard JCPDS card for Al.^{1, 2} The XRD spectra obtained for all the three type of samples show that the coatings to be constituted by pure fcc phase Al in each case.

The intensities of the planes are weak because the deposit is thin. The Al deposits obtained from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-

dimethylacetamide-based liquids show (111), (200), (220) and (211) diffraction peaks. The (220) and (211) cannot be seen clearly in the Al coating achieved from the AlCl_3 :acetamide liquid. This could be due to thickness of Al deposit being very thin in this case compared to those obtained from AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids.

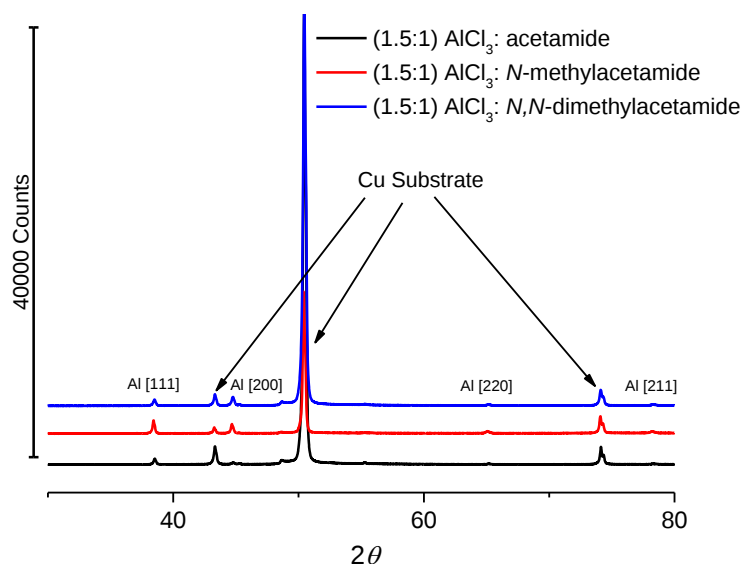


Figure 6.21 The XRD patterns of the Al coatings produced from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids. The deposition was achieved on a Cu substrate at 30°C and at a current density of 3.5 mA cm^{-2} for 1 h under stirring.

6.3.4.2 Effect of MN on orientation of Al deposits in amide- AlCl_3

Figures 6.22 (a), (b) and (d) show the XRD patterns of Al deposited from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids, respectively. The depositions were achieved in the absence and presence of 10 mM MN on a Cu substrate at 30°C and at a current density 3.5 mA cm^{-2} for 1 h. Each diffraction peak in **Figure 6.22** can be assigned to the Al coating or to the Cu substrate.

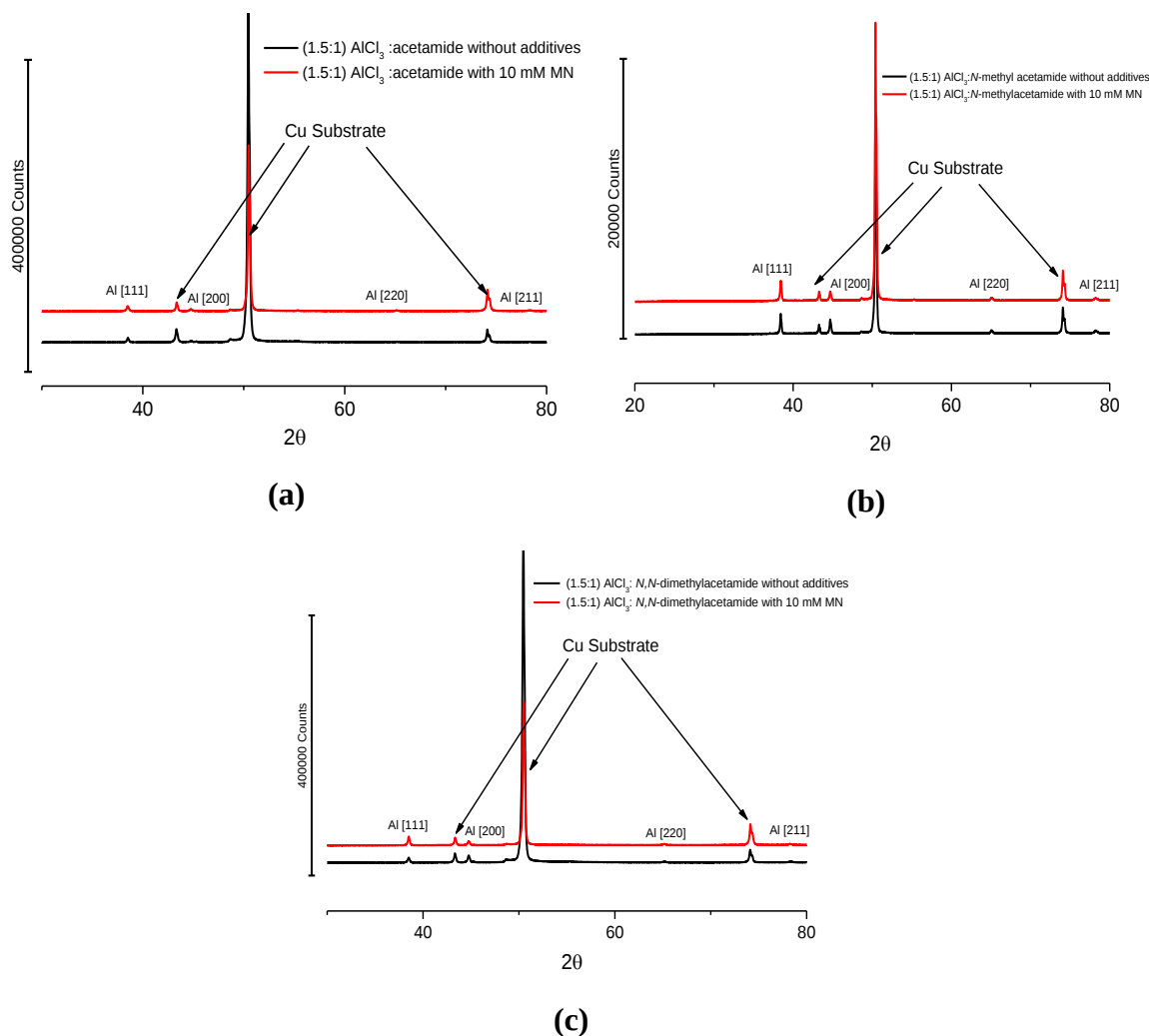


Figure 6.22 (a), (b) and (d) are the XRD patterns of the Al deposited from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids, respectively. The deposition was achieved in absence and presence of 10 mM MN on a Cu substrate at 30°C and at a current density of 3.5 mA cm^{-2} for 1 h.

The XRD patterns produced for the Al coatings obtained from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids in the absence and presence of 10 mM MN matches the standard JCPDS card of Al.^{1, 2} **Table 6.2** shows the relative intensities of the crystal planes for Al coatings obtained from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids deposited on Cu substrate. It can be seen that there were tiny changes in the relative intensities of the crystals plan for Al that deposited from AlCl_3 :acetamide in the presence and absence of MN, as shown in **Table 6.2**. The intensity of the (111) peak increased, whilst the intensity of the (200) peak decreased in the Al coating produced from the AlCl_3 :*N*-methylacetamide liquid containing MN compared to the system

without MN, as well as the increasing and decreasing intensities of (111) and (200) peaks, respectively, which occurred when an Al coating was achieved from AlCl_3 :*N,N*-dimethylacetamide-based liquids containing MN. Therefore, it can be said that MN encourages the formation of a (111) plane in the Al grains produced from AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids containing MN, or otherwise suggests that MN is able to change the orientation of the Al crystals. **Table 6.2** shows negligible changes in the intensities of the (220) and (212) planes in the Al film obtained from amide/ AlCl_3 systems containing MN.

Table 6.2 Texture coefficients of the Al deposits prepared from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids. All depositions were performed on a Cu substrate for 1h at 30°C and at a current density of 3.5 mA cm⁻²

Component	Relative intensity [111]	Relative intensity [200]	Relative intensity [220]	Relative intensity [212]
AlCl_3 :acetamide	0.342	0.242	0.207	0.207
AlCl_3 :acetamide + MN	0.351	0.246	0.190	0.195
AlCl_3 : <i>N</i> -methylacetamide	0.385	0.304	0.159	0.154
AlCl_3 : <i>N</i> -methylacetamide + MN	0.413	0.252	0.163	0.156
AlCl_3 : <i>N,N</i> -dimethylacetamide	0.284	0.351	0.174	0.177
AlCl_3 : <i>N,N</i> -dimethylacetamide + MN	0.381	0.254	0.176	0.175

6.3.5 Corrosion behaviour of Al coating

The corrosion behaviour of Al films deposited from different DESs were obtained by potentiodynamic polarisation in 0.1 M NaNO_3 solution at 25 °C, where the applied potential was between -0.20 V and +0.20 V at a scan rate of 10 mVs⁻¹. **Figure 6.23** and **Table 6.3** illustrate the corrosion resistance of Al deposited from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids on a Cu substrate at 30°C and at a current density of 3.5 mA cm⁻² for 1 h. **Figure 6.23** show the potentiodynamic polarisation curves for Al films obtained from three different DESs, where the polarisation curves of Al films obtained from AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids are shifted towards more negative potentials. This could be related to the natural protection layer that forms on the Al films. The natural Al coating surface could be affected on the protection layers.

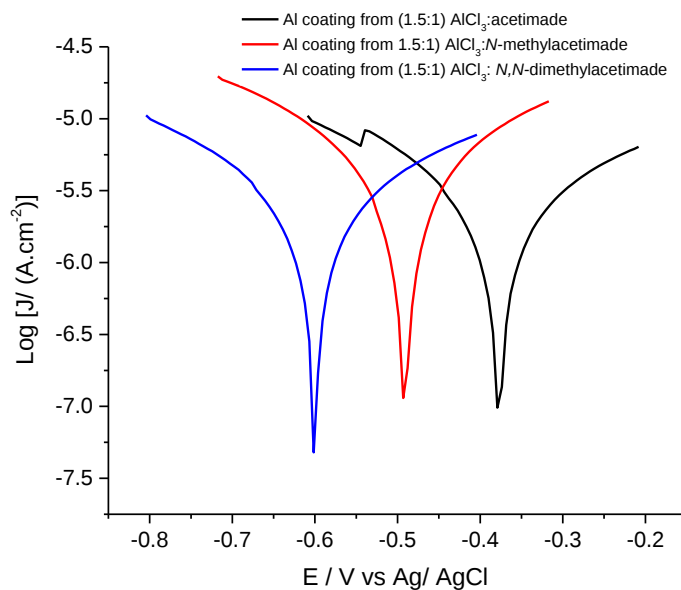
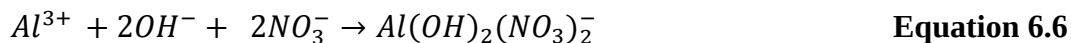


Figure 6.23 Potentiodynamic polarisation curves of Al deposits obtained from AlCl_3 :acetamide, AlCl_3 :N-methylacetamide and AlCl_3 :N,N-dimethylacetamide-based liquids. All dispositions were achieved on a Cu substrate at 30°C for 1 h at a current density of 3.5 mA cm^{-2} .

Table 6.3 Corrosion characteristics, obtained by polarization in 0.1 M NaNO_3 solution, of Al deposits obtained from AlCl_3 :acetamide, AlCl_3 :N-methylacetamide and AlCl_3 :N,N-dimethylacetamide-based liquids. All depositions were achieved on a Cu substrate at 30°C using a current density of 3.5 mA cm^{-2} for 1 h.

Materials	E_{corr} vs. Ag/AgCl/ V	$i_{\text{corr}} / \text{A cm}^{-2}$	Corrosion rate / mm year
Al deposited from AlCl_3 : acetamide	-0.377	1.89×10^{-6}	4.38×10^{-2}
Al deposited from AlCl_3 : N-methylacetamide	-0.492	3.24×10^{-6}	7.53×10^{-2}
Al deposited from AlCl_3 : N,N-dimethylacetamide	-0.601	1.84×10^{-6}	4.28×10^{-2}

The corrosion mechanism of the Al film in 0.1 M NaNO_3 solution can be suggested to be the dissolution of Al, which leads to the formation of $\text{Al}(\text{OH})_3$ or $\text{Al}(\text{OH})_3(\text{NO}_3)_3^-$, as shown in **Equations 6.4 and 6.5**, where these species could be transformed to the Al_2O_3 layer.^{49, 50} In an NaNO_3 electrolyte, Na^+ diffuses towards the cathode, while NO_3^- diffuses towards the anode, which contains dissolved Al.



The results of **Figure 6.23** and **Table 6.3** illustrate that the Al deposited from $AlCl_3$:acetamide and $AlCl_3$:*N,N*-dimethylacetamide-based liquids have higher corrosion resistance than Al deposited from and $AlCl_3$:*N*-methylacetamide. From **Table 6.3**, it can be seen that the corrosion rate of Al deposited from $AlCl_3$:acetamide and $AlCl_3$:*N,N*-dimethylacetamide-based liquids are 4.38×10^{-2} and 4.28×10^{-2} mm/year, respectively, while the corrosion rate of Al deposited from $AlCl_3$:*N*-methylacetamide-based liquid was 7.53×10^{-2} mm/year, which is roughly twice the corrosion rate of the pure Al coating produced from $AlCl_3$:acetamide and $AlCl_3$:*N,N*-dimethylacetamide-based liquids.

6.3.5.1 Effect of methyl nicotinate on corrosion of Al coating

It is interesting to study the effect of MN on the corrosion behaviour of Al deposited from amide/ $AlCl_3$ -based liquids. **Figure 6.24** and **Table 6.4** demonstrate the corrosion resistance of Al deposited from $AlCl_3$:acetamide, $AlCl_3$:*N*-methylacetamide and $AlCl_3$:*N,N*-dimethylacetamide-based liquids in the presence and absence of MN as an additive. The potentiodynamic polarisation study was achieved in 0.1 M $NaNO_3$ solution at 25 °C, with an applied potential between -0.20 V and +0.20 V at a scan rate of 10 mV s^{-1} . It can be seen from **Figure 6.24 (a)** and the data reported in **Table 6.4** that MN caused a decrease in the corrosion resistance of Al deposited from $AlCl_3$:acetamide and $AlCl_3$:*N*-methylacetamide-based liquids. This could be due to the surface roughness of the Al coating produced from the system containing MN was greater than that produced from the system without MN, where the roughness of the Al coating, as shown previously in this chapter, was found using AFM. An increased roughness of the surface coating means an increased surface area, and thus an increased rate of corrosion.

A remarkable improvement in the corrosion resistance of the Al layer was obtained from $AlCl_3$:*N,N*-dimethylacetamide-based liquid containing MN compared to that

without is shown in **Table 6.4**. The corrosion current density i_{corr} and the corrosion rate for the Al deposit obtained from the *N,N*-dimethylacetamide-based liquid containing MN were $5.40 \times 10^{-7} \text{ A cm}^{-2}$ and $1.25 \times 10^{-2} \text{ A cm}^{-2}$, respectively. These values are lower than the corrosion parameter values of the Al layer obtained from *N,N*-dimethylacetamide-based liquid without MN. Here, also, the reason can be related to the area of the electrode. As the grain size of the Al coating produced from the *N,N*-dimethylacetamide-based liquid with MN decreased compared to that produced without MN, this caused the surface area of the Al coating and roughness of the surface of the former to be similarly decreased. Materials with less rough surfaces have fewer active sites and, consequently, this can lead to a decrease in the corrosion rate of the coating. Moreover, the coating with a small grain size is considered more resistance to corrosion due to the small grain size causing an increase in the number of grain boundaries.⁵¹ A small grain size in Al coating will result in an increase in the number of active atoms on the surface; this behaviour will accelerate the formation of a protective corrosion product layer.

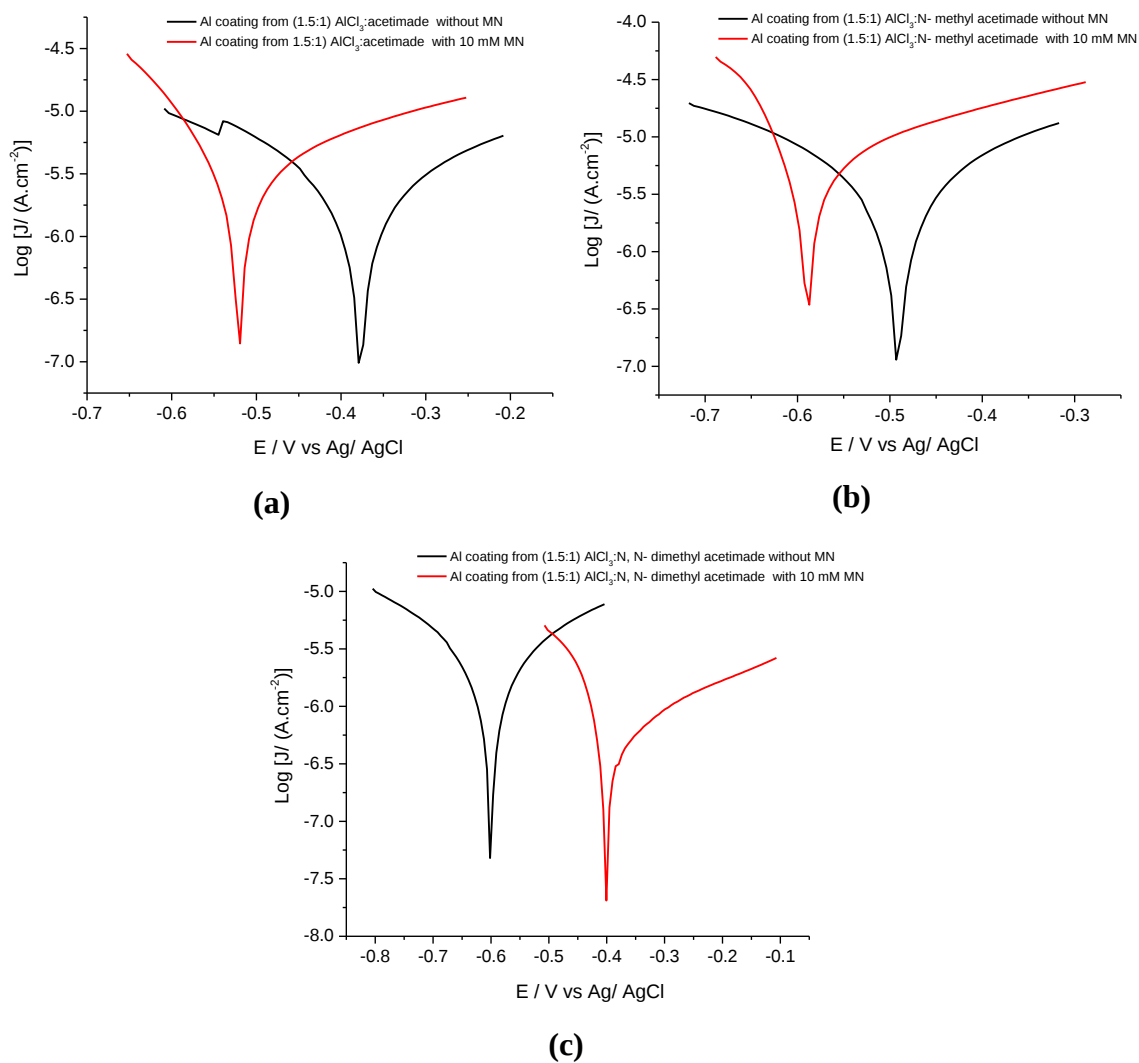


Figure 6.24 Potentiodynamic polarisation curves of the Al deposits obtained from (a) AlCl_3 :acetamide-based liquid with and without 10 mM MN, (b) AlCl_3 :N-methylacetamide-based liquid with and without 10 mM MN and (c) AlCl_3 :N,N-dimethylacetamide-based liquid with and without 10 mM MN. All dispositions were achieved on a Cu substrate at 30°C for 1 h at a current density of 3.5 mA cm^{-2} .

Table 6.4 Corrosion characteristics, obtained by polarization in 0.1 M NaNO₃ solution, of Al deposits obtained from AlCl₃:acetamide, AlCl₃:N-methylacetamide and AlCl₃ N,N-dimethylacetamide-based liquids in the absence and presence of 10 mM MN. All depositions were achieved on a Cu substrate at 30°C using a current density of 3.5 mA cm⁻² for 1 h.

Materials	E _{corr} vs. Ag/AgCl/ V	i _{corr} /A cm ⁻²	Corrosion rate / mm year
Al deposited from AlCl ₃ : acetamide	-0.377	1.89 x 10 ⁻⁶	4.38 x 10 ⁻²
Al deposited from AlCl ₃ : acetamide with 10 mM MN	-0.521	2.30 x 10 ⁻⁶	5.35 x 10 ⁻²
Al deposited from AlCl ₃ : N- methylacetamide	-0.492	3.24 x 10 ⁻⁶	7.53 x 10 ⁻²
Al deposited from AlCl ₃ : N- methylacetamide with 10 mM MN	-0.589	5.44 x 10 ⁻⁶	1.26 x 10 ⁻¹
Al deposited from AlCl ₃ : N,N- dimethylacetamide	-0.601	1.84 x 10 ⁻⁶	4.28 x 10 ⁻²
Al deposited from AlCl ₃ : N,N- dimethylacetamide with 10 mM MN	-0.401	5.40 x 10 ⁻⁷	1.25 x 10 ⁻²

6.4 Summary

This chapter was divided into three parts. The first considered the effects of MN on the morphologies, roughness and crystal textures of Al coatings electrodeposited on a Cu substrate from 1:2 [Bmim]Cl:AlCl₃ and 1:2 [Emim]Cl:AlCl₃ ionic liquids at 30°C. Al mirror coatings were achieved from [Bmim]Cl/AlCl₃ and [Emim]Cl/AlCl₃ as a result of using MN as an additive. The results of the cyclic voltammograms of Al from these types of ionic liquids in the presence and absence of MN prove that methyl nicotinate, with its electron-withdrawing group, has an increased adsorption ability on the Cu substrate, so the Al deposition can be tailored to produce Al mirror deposits. The current efficiency of Al electrodeposited from the [Emim]Cl/AlCl₃ ionic liquid was ~97%; however, the efficiency decreased to ~90% as a result of adding MN to the plating bath. The current efficiency of Al electrodeposited from the [Bmim]Cl/AlCl₃ liquid was close to 100%, while the efficiency reduced to ~92% when the deposition was achieved from an electrolyte containing MN.

The second part of this chapter has shown, for the first time, the electrodeposition of Al from different amide-AlCl₃ eutectic solvents, where these solvents were (1.5:1) AlCl₃:acetamide, (1.5:1) AlCl₃:*N*-methylacetamide and (1.5:1) AlCl₃:*N,N*-dimethylacetamide eutectic liquids. The conductivities of these solutions were measured, and it was found that AlCl₃:*N*-methylacetamide liquid has a higher conductivity than the AlCl₃:acetamide and AlCl₃:*N,N*-dimethylacetamide eutectic liquids, which could be due to the difference in coordination of Al ions with amide molecules. Thick and adherent pure aluminium films have been deposited on copper and mild steel substrates from these types of solvents. Al films obtained from the (1.5:1) AlCl₃:acetamide-based liquid were produced with a small grain size, while the Al films produced from (1.5:1) AlCl₃:*N*-methylacetamide and (1.5:1) AlCl₃:*N,N*-dimethylacetamide eutectic liquids were uniform, with Al grain sizes that were larger than those obtained from the acetamide system. The current efficiency of electrodeposition of Al from AlCl₃:*N*-methylacetamide was ~82%, which is higher than the current efficiencies of Al deposited from AlCl₃:acetamide and AlCl₃:*N,N*-dimethylacetamide eutectic liquids, which could be due to the high conductivity of the AlCl₃:*N*-methylacetamide liquid compared to the others.

The last part of this work investigated the influence of MN on the electrodeposition of Al from (1.5:1) AlCl₃:acetamide, (1.5:1) AlCl₃:*N*-methylacetamide and (1.5:1)

AlCl_3 :*N,N*-dimethylacetamide eutectic liquids. The SEM results show changes in the morphology of the Al coatings produced from electrolytes containing MN. The XRD patterns of Al deposited from AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide-based liquids in the absence and presence of MN were investigated. It was found that there was a very small change in the relative intensities of the crystals plane for Al that deposited from AlCl_3 :acetamide in presence and absence of MN. However, the intensity of the (111) peak increased whilst that of the (200) peak decreased in the Al coating produced from AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide eutectic liquids containing MN compared to the analogous systems without MN.

It was found that the Al coating that achieved from AlCl_3 :acetamide eutectic liquid has a high resistance to corrosion compared to the Al films produced from AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide eutectic liquids. Corrosion of the Al coatings that were produced from (1.5:1) AlCl_3 :acetamide, and (1.5:1) AlCl_3 :*N*-methylacetamide containing MN was increased, which corresponded to the increasing roughness and grain size of Al coating produced from these liquids. However, the corrosion resistance of the Al coating produced from the AlCl_3 :*N,N*-dimethylacetamide eutectic liquid in the presence of MN was increased due to the decreasing roughness of the Al coating as a result of adding MN to the Al plating bath.

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Chapter 7: Conclusion and Future Directions

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7.1 Conclusion

The aim of this thesis was to study the influence of additives on the electrodeposition of Cu, Zn and Zn-Ni alloy from 1:2 ChCl:ethylene glycol (Ethaline 200). In addition, this work included the effects of additives on the electrodeposition of Al from traditional and novel Al ionic liquids. It was found that the additives used strongly affected the deposition of the metals mentioned above. The results showed for the first time that bright Zn, Zn-Ni and Al coatings could be produced from ionic liquids with the use of additives.

7.1.1 Effect of additives on Cu electrodeposition from deep eutectic solvents

The electrodeposition of Cu from deep eutectic solvents has been achieved. However, no work to study the effect of additives on electrodeposition of Cu from DESs has been undertaken. The influences of ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), sodium iodide (NaI), boric acid (BA) and 5,5-dimethylhydantoin (DMH) on the electrodeposition of Cu from Ethaline 200 were investigated. It has been shown that these additives have varying effects on Cu deposition properties. The UV-Vis spectroscopy results show that EDTA and NaI changed the Cu species in the plating bath, which in turn led to significant changes in the electrochemical properties and morphologies of the Cu coatings. Physical properties, cyclic voltammetry, chronoamperometry, rate of deposition and morphologies of Cu deposits were achieved from Ethaline 200 in both the absence and presence of additives. Addition of NaI to the Cu electrolyte caused an increase in the conductivity of the electrolyte. The triiodide ion I_3^- can be produced when NaI is added to the Cu electrolyte, with the I_3^- in solution on occasion forming a monolayer on the electrode surface that prevented the formation of a passivation layer of Cu oxide on the electrode itself. Cyclic voltammograms of Cu showed an increase in the oxidation and deposition current peaks when NaI was added to the Cu electrolyte. Chronoamperometry data showed that the nucleation mechanism of the Cu deposition changed to the progressive mechanism of growth as a result of adding NaI to the Cu plating bath. Addition of NaI to the Cu bath led to the formation of iodine and an increase in the conductivity of the electrolyte that resulted in a bright and thick Cu coating. Therefore, NaI has been demonstrated to be an effective brightener for Cu deposition.

No significant change could be detected in the species and the electrochemical properties of the Cu electrolyte when DMH and BA were added. However, a bright deposit and increases in the rate of Cu deposition were obtained by adding these additives to the plating bath. Therefore, it was suggested that DMH and BA were adsorbed on the electrode surface and inhibited Cu deposition.

7.1.2 Effects of additives on Zn electrodeposition from deep eutectic solvents

The effects of additives on the electrodeposition of Zn from aqueous solution have been recorded. However, the few studies in the literature that have themselves studied the influence of additives on the electrodeposition of Zn from DESs and Zn deposited from DES are relatively incomplete, and can be considerably expanded upon.

One of the intentions of this work was to study the effects of additives on the electrodeposition of Zn from Ethaline 200 as a DES. The additives used were nicotinic acid (NA), boric acid (BA) and *p*-benzoquinone (BQ). The physical and mechanical properties of the zinc electrodeposit were considerably improved compared to the corresponding system without additives and, when nicotinic acid was used as the additive, a bright zinc coating has been achieved on a copper substrate for the first time. The additives did not produce any significant changes in the viscosity or conductivity of the Zn solution. Electrochemical experiments, including cyclic voltammetry, chronocoulometry and chronoamperometry, established a clear difference between Zn electrodeposition processes where these additives were used and the control experiments where no additive was used. Cyclic voltammetry shows that the Zn oxidation and reduction current peaks were decreased when the additives were introduced into the plating bath due to adsorption of the additives onto the electrode surface, inhibiting the deposition of Zn. It was found that there was a considerable increase in the Zn redox current peaks when the cyclic voltammograms were recorded at high temperature (80°C) due to the associated decrease in viscosity and increase in conductivity of the solution and also due to reducing the specific adsorption of the Cl⁻ ion on the electrode surface at high temperature. The nucleation mechanism for Zn deposition on a Pt electrode from Ethaline 200 without additives fitted well with the supposition of an instantaneous growth mechanism. However, the nucleation mechanism of Zn in the presence of NA and BA fit well with that of progressive growth. The nucleation mechanism of Zn deposition in the presence of BQ also

suggested a progressive growth mechanism, which becomes one of instantaneous growth after a long period of time.

The additives were shown to significantly alter the morphology of the Zn deposit. The physical and mechanical properties of the zinc electrodeposit have been improved compared to the corresponding system without additives, and for first time a mirror zinc coating has been achieved on a copper substrate when nicotinic acid was used as the additive. Rates of Zn deposition were increased as a result of adding either NA or BQ to the Zn bath. However, decreases in the current efficiency of Zn deposition occurred when using these additives. The XRD data showed the crystal orientation within the Zn film obtained from a system containing nicotinic acid and boric acid was changed compared to that produced from a system without additives.

7.1.3 Electrodeposition of Zn-Ni from deep eutectic solvents

The effects of the addition of boric acid and sodium bromide on the electrodeposition of Zn-Ni alloy was studied in Ethaline 200 as a DES. The results of this addition showed that the reduction of Ni^{2+} and Zn^{2+} to metallic Ni and Zn, respectively, on a Pt electrode are separated by 350 mV. The reduction potential of Ni^{2+} was shifted towards a negative potential by adding boric acid to the electrolyte. In the presence of boric acid, the reduction of both metals occurred at almost the same potential. Boric acid adsorbed on the electrode surface inhibits the deposition of Zn, while the rate of Ni deposition is increased as boric acid was introduced to the bath as the latter reduces the passivation layer. The surface morphology was significantly improved after adding boric acid and sodium bromide to the plating bath; the surface morphology of the deposit obtained from each was found to be compact, with small spherical crystals.

The effect of current density, temperature and concentration of Zn species on Zn-Ni electrodeposition was investigated, and it was found that the Zn content of the Zn-Ni alloy deposits were increased with increasing current density and concentration of Zn species in the bath. However, the amount of Zn decreased in the Zn-Ni alloy deposits with increasing temperature of the electrolyte, which showed that at high temperature, the types of Ni species were modified, where $[\text{NiCl}_4]^{2-}$ was formed. The thickness of the Zn-Ni coatings was increased with increasing temperature of the plating bath due to the associated decrease in viscosity and increase in conductivity of the Zn-Ni electrolyte.

Moreover, higher temperatures reduced the specific adsorption of Cl^- ions and modified the Ni species present. However, the thickness of the Zn-Ni alloys decreased with an increasing concentration of Zn species in the solution due to the increased viscosity of the electrolyte.

A bright, nanocrystalline Zn-Ni alloy deposit (85% Zn and 15% Ni) was produced from Ethaline 200 containing a high concentration of ZnCl_2 . XRD data recorded for the bright Zn-Ni deposit showed the two diffraction peaks characteristic to the γ -phase ($\text{Ni}_5\text{Zn}_{21}$), which are the (411) and (721) plane orientations. The behaviour towards corrosion of the bright Zn-Ni deposits was studied in sodium nitrate using Tafel curves and electrochemical impedance spectroscopy (EIS), where it was observed that the bright Zn-Ni has a corrosion resistance of almost twice that of a pure Zn coating. The results showed a considerable increase in hardness of the bright Zn-Ni alloy compared to the pure Zn coating.

7.1.4 Electrodeposition of Al ionic liquids

In this body of work, the electrodeposition of Al was divided into three parts. The first considered the effects of methyl nicotinate on the morphologies, roughness and crystal textures of Al coatings electrodeposited on Cu substrates from classical ionic liquids ($[\text{Bmim}]\text{Cl}/\text{AlCl}_3$, $[\text{Emim}]\text{Cl}/\text{AlCl}_3$) at 30°C . Al mirror coatings were achieved from both liquids as a result of using methyl nicotinate as an additive. From the cyclic voltammograms of Al deposits from $[\text{Emim}]\text{Cl}/\text{AlCl}_3$, it can be suggested that the electrodeposition of aluminium was mainly influenced by mass diffusion and kinetic limitations, such as electron transfer or surface chemical reaction steps. Moreover, it has been observed that the reduction potential of Al deposition is shifted towards a positive potential with an increasing temperature of the electrolyte due to the associated decrease in viscosity and increase in conductivity. The results of the cyclic voltammograms of Al from these types of ionic liquids in both the presence and absence of methyl nicotinate showed that methyl nicotinate, with its electron-withdrawing group, has a stronger adsorption ability on the Cu substrate, and consequently the deposition of Al can be tailored to produce Al mirror deposits.

The second part of this work has shown, for the first time, that the electrodeposition of Al from different amide- AlCl_3 eutectic solvents, where these solvents were (1.5:1)

AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic liquids. Thick and adherent pure aluminium films have been deposited on copper and mild steel substrates from these types of solvents.

The final part of this work investigated the influence of methyl nicotinate on the electrodeposition of Al from (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic liquids. It was found that the Al coating achieved from the AlCl_3 :acetamide eutectic liquid had a high resistance to corrosion when compared to the Al films produced from the AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide eutectic liquids. There was a clear negative shift in the reduction potential of Al in the (1.5:1) AlCl_3 :acetamide, (1.5:1) AlCl_3 :*N*-methylacetamide and (1.5:1) AlCl_3 :*N,N*-dimethylacetamide eutectic liquids when methyl nicotinate was used. The changes in the cyclic voltammograms of Al in these types of eutectic mixtures could be related to the adsorption of methyl nicotinate on the electrode surface and subsequent inhibition of Al deposition. The SEM results showed considerable changes in the morphologies of the Al coatings produced from the eutectic mixtures that contained methyl nicotinate. The XRD data showed no significant change occurred in the intensities of the crystal planes for the Al coatings obtained from AlCl_3 :acetamide in either the presence or the absence of methyl nicotinate. The intensity of the (111) peak increased and the intensity of the (200) peak decreased in the Al coating produced from the AlCl_3 :*N*-methylacetamide liquid containing methyl nicotinate compared to the system without. Increases and decreases in the intensities of the (111) and (200) peaks, respectively, have been observed to occur when an Al coating is achieved from AlCl_3 :*N,N*-dimethylacetamide-based liquids containing methyl nicotinate. The corrosion resistance of the Al coatings produced from (1.5:1) AlCl_3 :acetamide and (1.5:1) AlCl_3 :*N*-methylacetamide containing methyl nicotinate were increased; this corresponded to the increasing roughness and grain size of the Al coatings derived from these liquids. However, the corrosion resistance of the Al coating produced from the AlCl_3 :*N,N*-dimethylacetamide eutectic liquid in the presence of methyl nicotinate was increased, which was attributed to the decreased roughness of the Al coating as a result of adding methyl nicotinate to the Al plating bath.

7.2 Further work

This thesis has illustrated the effects of additives on the electrodeposition of Zn, Cu, Al and Zn-Ni in deep eutectic solvents. The main advantages of using deep eutectic solvents in the electrodeposition of metals, compared to aqueous solutions and traditional ionic liquids, are their wide potential windows, high metal solubility, non-toxicity, high current efficiency, ease of production and low cost. It was found that the additives used during the course of the work reported in this thesis improved the physical and mechanical proprieties of the metals' depositions. The electrodeposition of different types of metal has been achieved from deep eutectic solvents. However, very little work has been undertaken as to the effects of additives on the electrodeposition of metals and their alloys, and considerably more work is required to characterise the effects of different types of additives in this regard. The following are areas that should be studied:

1. The effects of the additives used in this project, namely boric acid, nicotinic acid, methyl nicotinate, 5,5-dimethylhydantoin, *p*-benzoquinone, sodium iodide and sodium bromide, on the electrodeposition of different types of metal such as Co, Cr, Sn, Pb, Mn, Bi and Ag from Ethaline 200 as a DES. Moreover, the effects of other types of additives, such as polyethyleneglycol, sorbitol, coumarin, vanillin and nicotinamide on the electrodeposition of Cu and Zn from Ethaline 200 can also be studied.
2. The effects of the additives mentioned in point (1) on the electrodeposition of Zn-Ni, Zn-Sn, Zn-Co, Zn-Cu, and Cu-Al alloys from Ethaline 200.
3. The effects of the additives mentioned in point (1) on the electrodeposition of metals and metal alloys from reline (1:2 molar mixture of choline chloride and urea) as a deep eutectic solvent.
4. The influence of different concentrations of sodium bromide, nicotinamide, nicotinic acid, 3-methylpyridine and 1,10-phenolphthalein on the electrodeposition of Al from AlCl_3 :urea, AlCl_3 :acetamide, AlCl_3 :*N*-methylacetamide and AlCl_3 :*N,N*-dimethylacetamide eutectic liquids at different temperatures and different current densities.