ELECTRODEPOSITION OF TANTALUM AND NIOBIUM USING IONIC LIQUID

by

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ABSTRACT

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Using Ionic Liquid

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Ionic liquids are molten salts with melting points below 100 °C and they consist entirely of cations and anions. The development of ionic liquids, especially air and water stable types, has attracted extensive attention since they have outstanding physical properties. Part I of the study focused on the pre-electrolysis process performed to remove impurities from the ionic liquid, 1-butyl-1-methyl-pyrrolidinium bis(tri-fluoromethylsulfonyl)imide, ([BMP]Tf₂N). Part II investigated the electroreduction of TaF₅ and NbF₅ from room temperature ionic liquid at 100 °C at a wide range of potentials and different time durations for the purpose of determining the optimal conditions for the electrodeposition of tantalum. The study was carried out using potentiostatic polarization for the pre-electrolysis treatments and electrodeposition and cyclic voltammetry to study the behaviour of the liquid at various stages. Potentiostatic depositions were complemented by scanning electron microscopy (SEM)/energy-dispersive x-ray analysis (EDX), x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) for characterization of the electrodeposits.
To my mom Maria, my brother G.B. and my sister Santina,

for their unconditional love, support and understanding

throughout all my studies
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NOTATION AND ABBREVIATIONS

\[ \text{[PF}_6\text{]} : \text{hexafluorophosphate} \]

\( \text{AlCl}_3 \): aluminium chloride

\( \text{Au} \): gold

\( \text{BCC} \): body-centered cubic

\[ \text{[BF}_4\text{]} : \text{tetrafluoroborate} \]

\[ \text{[BMP]}\text{[TF}_2\text{]}\text{N} \text{ or [Py}_{1,4}\text{]} \text{ TFSA: 1-butyl-1-methyl-pyrrolidinium bis(tri-fluoromethylsulfonyl)imide} \]

\[ \text{[BPCI]} : \text{1-butylpyrroldinium chloride} \]

bis(triflyl)imide \[ \text{[NTf}_2\text{]} : \text{bis(triflyl)imide} \]

\[ \text{[Cl]}^{-} : \text{chloride,} \]

\[ \text{[C}_n\text{MIm}]\text{Cl} : 1\text{-alkyl-3-methylimidazolium chloride} \]

\( \text{EDX} \): energy-dispersive x-ray analysis

\( \text{FCC} \): face-centered cubic

\( \text{I} \): current

\( \text{K}_2\text{TaF}_7\): potassium fluorotantalate

\( \text{LiF} \): lithium fluoride

\( \text{M} \): molar

\( \text{mS} \): millisiemens

\( \text{mV} \): milli volts

\( \text{Nb} \): niobium
NbF₅: niobium fluoride

[NTf₂]⁻: bis(triflyl)imide

ppm: parts per million

[PF₆]⁻: hexafluorophosphate

Pt: platinum

RTILs: room temperature ionic liquids

SbF₆: hexafluoroantimonate

SEM: scanning electron microscopy

Ta: tantalum

Ta₂O₅: tantalum oxide

TaF₅: tantalum fluoride

Tₘ: melting point

V: volts (potential)

XPS: x-ray photoelectron spectroscopy

XRD: x-ray diffraction

μA: microampere

μm: micrometer
1.0 INTRODUCTION

Over the last few decades, room temperature ionic liquids have been widely studied in various scientific fields due to their interesting properties, such as negligible vapour pressures, high chemical and thermal stability, acceptable intrinsic ionic conductivity and wide potential window $^{1,2}$. Moreover, there have been many reviews on the electrochemical use of ionic liquids examining the current state of ionic liquid-based electrochemistry. The widespread types of ionic liquids can be divided into three groups: a) systems based on $\text{AlCl}_3$ and organic salts such as 1-butylpyrridinium chloride, 1-alkyl-3-methylimidazolium chloride and derivatives; b) systems based on organic cations as in the first group as well as anions $\text{BF}_4$, $\text{PF}_6$ and $\text{SbF}_6$ and (c) systems based on the aforementioned organic cations with anions of the type $\text{CF}_3\text{SO}_3$ and similar. $^3$ Liquids made from the latter group are air and water stable. In comparison to aqueous solutions, ionic liquids have several advantages: depending on the system they are stable up to temperatures of 350$^\circ$C with low vapour pressures, many organic and inorganic compounds can easily be dissolved in them, they have sufficiently high specific ionic conductivities between $0.001$ ($\Omega\text{cm})^{-1}$ and $0.01$ ($\Omega\text{cm})^{-1}$ and they can have wide electrochemical windows of more than 6 V. As a matter of fact, the electrodeposition of reactive metals such as aluminum (Al), magnesium (Mg) and tantalum (Ta) from aqueous solutions is impossible causing hydrogen evolution to occur at the cathode, due to the narrow potential window in aqueous solutions. The advantage of wide electrochemical windows is of significant interest for material electrodeposition in ionic liquids as will be seen throughout the present study.

The electrodeposition process involves a reduction of metal ion from solution with a corresponding anodic reaction. These reactions occur through the flow of an electric current in solution and the separation of a metal on one of the electrodes. Both of these fundamental processes depend on the existence of charged particles known as ions, in the solution. Ionic liquids are solely composed of anions and cations, are highly conductive and along with other physical and chemical properties, are ideal solvents for the electrodeposition of refractory metals such as tantalum and niobium. The present study will focus on the four main aspects of the deposition process which involve: the metal-solution interface as the locus of the deposition process, kinetics and mechanisms of electrodeposition, the nucleation and growth process and finally the structure of deposits.
The aim of this current research is two-fold. Part I of the experimental investigation focuses on purifying the ionic liquid of interest. A pre-electrolysis procedure is implemented to extract water and other impurities from the ionic liquid. Part II investigates the electrodeposition process using the purified form of the ionic liquid. It provides an understanding on the effect of the pre-electrolysis treatment on the ionic liquid and on electroplating tantalum and niobium on nickel. As well, in Part II, experiments are carried out in determining the optimal electrochemical conditions for electroplating tantalum and niobium on nickel in order to obtain a continuous, adherent layer. Although studies have been done on electroplating tantalum using ultra-pure grade ionic liquid, no attempts have been made to purify a low grade ionic liquid using pre-electrolysis and then use the purified liquid to electrodeposit tantalum and niobium, which this work has set out to do. Furthermore, the second part of the experiments, examines the thin film deposit structure using several analytical techniques such as scanning electron microscopy, energy-dispersive x-ray spectroscopy, x-ray photoelectron spectroscopy and x-ray diffraction.

The main objective of this research was to synthesize a coating, which would protect the underlying metal from corroding when exposed to atmospheric or other aggressive conditions. More specifically, the two objectives of this present study, which are of relevance to the nuclear industry, are the following: (1) to design parts with improved corrosion resistance and enhance its compatibility in corrosive environments as well as (2) to improve service life of materials used in nuclear applications. Tantalum is investigated as a suitable protective coating for applications such as heat exchangers, valve linings, condensers and other components exposed to extremely corrosive fluids due to the presence of a tenacious oxide film that forms on the metal, spontaneously in air. This thin surface film exhibits a high stability in most mineral acids, even in concentrated, hot ones, except in hydrofluoric acid or hot concentrated sulfuric acid. Niobium is also investigated as it would be a more suitable coating material for use in atomic reactors due to its low thermal neutron cross-section compared to other refractory metals.

Moreover, it is of interest for the nuclear industry to study electrodeposition on nickel substrate. Nickel, which is used in parts of the nuclear systems, has inherent corrosion resistance in aqueous environments. Nickel oxides have poor solubility in most aqueous environments and form tenacious and impermeable oxide layers that passivate the metal substrate. Consequently, the solubility of nickel oxides becomes significant at low pH, high redox and high temperatures such as in nuclear environments. Therefore, this work was set out to layer nickel with an adherent and
continuous film of tantalum and niobium which have the required irradiation damage resistance, high temperature strength, high temperature liquid metal corrosion resistance besides transparency to neutrons. As this study will prove, ionic liquids have unique properties that give access to the electrodeposition of these materials.

This thesis is organized as follows. Chapter 2 is a literature review and is divided into six main subsections- the first a review of ionic liquids, the second a review of tantalum and niobium refractory properties, the third a review of the electrodeposition of these metals in high temperature molten salts, the fourth a review of electrodeposition of these metals in ionic liquids, the fifth a discussion on the effect of LiF to the electrodeposition of tantalum and niobium and lastly, a discussion on the purity of ionic liquids. The experimental methods used are described in Chapter 3. Chapter 4 presents the experimental results and discussion. Finally, Chapter 5 contains a summary of the experimental results. Chapter 6 gives suggestions for future work.
2.0 LITERATURE REVIEW

2.1 Introduction

Almost the entire electroplating sector is generally based on aqueous solution electrochemistry although certain applications use organic solvents, plasma or chemical vapour deposition techniques amongst other various processes. Aqueous media has been the most widely used process mainly because of the knowledge and experience accumulated throughout history of electrodeposition. The key advantages of using aqueous solutions are cost, non-flammability, high solubility of electrolytes, high conductivities resulting in low ohmic losses, high solubility of metal salts and high rates of mass transfer. However, despite these advantages, there are several limitations in using aqueous solutions such as limited potential windows, gas evolution processes that can result in hydrogen embrittlement, passivation of substrates, electrodes and deposits, and the necessity for hazardous complex agents such as cyanide, causing environmental contamination. Out of all the above limitations, the one of most concern in this thesis is the use of aqueous electrolytes restricting the electrochemical deposition of metals to those metals which have a higher standard reduction potential than hydrogen. Consequently, the primary reason for using non-aqueous electrolytes became the ability to deposit refractory metals such as titanium, aluminum and tantalum which exhibit excellent corrosion resistance. The following literature review will begin by briefly discussing various electrodeposition techniques used over the years leading up to the discovery of non-aqueous electrodeposition, followed by a focused discussion on the use of ionic liquids in electrochemical applications and important research findings involving this relatively new electrodeposition medium.

One of the main limitations in using aqueous solutions is their narrow electrochemical window. Therefore, two ways in which the problem was initially overcame, were by using organic solvents or a eutectic mixture of two inorganic salts with a relatively low melting point. Eutectic-based ionic liquids involved just the simple mixing of two components with moderate heating. This technique is of low cost and permits large-scale applications such as metal deposition. The eutectic mixtures were used extensively for applications of molten salts to reduce the operating temperature and so the significant area of ionic liquids developed from the search to find aluminum-based salt
mixtures. Choline chloride based eutectics are the closest to commercialization in the metal finishing industry and as a result highlight the benefits and difficulties associated with process scale-up. However, there were still limitations in using the above solvents and mixtures. In using organic solvents, the deposition from these electrolytes showed some negative effects such as easy decomposition during the electrochemical deposition leading to products being found as impurities in the deposits. In addition, their extreme high vapour pressure, their flammability and their explosiveness make these solvents dangerous. Moreover, in using eutectic mixtures, the preparation of nanostructures from these electrolytes is not possible since the high temperature of this process causes crystallite growth and therefore the product eventually is of microcrystalline structure.

Alternatively, high temperature molten salts have been used extensively for the electrowinning of metals such as lithium, sodium, titanium and aluminum at temperatures of up to 1000 °C. They have wide potential windows, high conductivities and high solubility for metal salts. In fact, they have most of the advantages of aqueous solutions and overcome most of the limitations of aqueous solutions, but their one major limitation is that the operational conditions are difficult to achieve and limit the range of substrates that can be used for deposition. However, since they have the ability to deposit refractory metals, high temperature molten salts have been used in developing a process for the electrodeposition of tantalum. As a result, these salts were found to be efficient baths for the electrodeposition of tantalum. Senderoff and Mellors reported the first results on the electrodeposition of tantalum using the ternary eutectic mixture LiF-NaF-KF as a solvent and K$_2$TaF$_7$ as a source of tantalum at temperatures between 650 °C and 850 °C. The results will be discussed a little later, but it is important to mention that these baths proved to have many technical and economic problems such as loss in current efficiency of the electrolysis process due to the dissolution of metal after its deposition and the expected corrosion problems at high temperatures.

Therefore, the alternative to high temperature molten salts was an ionic substance that melts at a low temperature. A significant amount of work was carried out in the middle of the twentieth century with the aim of developing lower temperature molten salts. One of the key aims was a lower temperature melt for aluminum deposition, which led to the formation of Li$^+$/K$^+$/AlCl$_3$ eutectics with freezing points close to 100 °C. These freezing points arise due to the large chloroaluminate anions that form in the eutectic mixtures and have low lattice energies. The use of quaternary ammonium salts, particularly pyridinium and imidazolium salts, had pushed the freezing point down to ambient
conditions. As a result, the term ‘ionic liquid’ was created to distinguish these lower temperature ionic fluids from the high temperature molten salts, which are composed predominantly of inorganic ions. For electrodeposition from room temperature ionic liquids (RTILs), metal chlorides are often used as the feeding compounds, due to their availability, low cost and also simple electrode reactions upon electrolysis. Furthermore, haloaluminate RTILs are favoured for their good solubility for many metal chloride salts but one drawback is that they cannot be exposed to the atmosphere since moisture would react with the aluminum halide species and produce aluminum oxide halide complexes and protons impurities.

2.2 Ionic Liquids

Ionic liquids are molten salts with melting points below 100 °C and they consist solely of cations and anions. The charge on these ions is delocalized or shielded by side groups, which is one reason why the melting points of ionic liquids are remarkably low. There are a wide range of different ionic liquids, binary and ternary mixtures with versatile properties. In contrast to conventional molecular solvents, ionic liquids are usually non-volatile, non-flammable, less toxic, good solvents for both organics and inorganics and can be used over a wide range of temperatures. Most ionic liquids have at or near room temperature vapour pressures of $10^{-11} - 10^{-10}$ mbar allowing experiments to be done at temperatures up to 400 °C. The very small vapour pressure of ionic liquids also allows their use in vacuum experiments even at elevated temperatures. The most important advantage of ionic liquids which is of significant relevance to this study, is their large electrochemical windows (>$5$V) which gives access to elements that cannot be electrodeposited from aqueous or organic solutions such as for example, Al, Mg, Ti and Ta, at moderate temperatures. A series of transition and main group-metal containing ionic liquids have been formulated and electrodeposition of these metals have been achieved. It is important to review the principle factors that make ionic liquids differ from aqueous solutions. Some of these principle factors are conductivity, viscosity and potential window. All of these factors will affect the rate at which metal ions diffuse to the electrode surface and the thermodynamics and kinetics of the metal reduction process. These in turn control the nucleation and growth mechanisms and affect the material morphology and it is the fundamental mechanism of material growth that needs to be understood. It must be stressed however, that while the deposition of a wide range of metals has been demonstrated from a number of ionic liquids, the
practical aspects of controlling deposit morphology have not been significantly addressed in literature
due to the complex nature of the process parameters that still need to be understood. Furthermore,
there are still a lack of reliable models to describe mass transport and material growth in ionic
liquids\textsuperscript{1}.

Ionic liquids are composed of an organic cation, typically imidazolium-, pyridinium-, ammonium-, or phosphonium-based and organic or inorganic anions. There is a diverse choice of
cation and anion pairs in the synthesis of ionic liquids. Modifications of linear alkyl-substituents, for
example with branched, chiral, fluorinated or an active-functionality, can yield further useful
materials. The degree and type of substitution determines the salts low melting point, largely by
reducing cation-anion Coulombic interactions and disrupting ion-ion packing. This results in low
melting salts with reduced lattice energy and a marked tendency to form glasses on cooling, rather
than crystalline solids. Common anions that yield useful ionic liquids include hexafluorophosphate
$[\text{PF}_6]^-$, tetrafluoroborate $[\text{BF}_4]^-$, bis(triflyl)imide, $[\text{NTf}_2]^-$ and chloride, $[\text{Cl}]^-$. Although high
symmetry, pseudo-spherical, non-coordinated anions are commonly regarded as optimal for
formation of ionic liquids, the existence of low melting ionic liquids containing anions such as
methyisulfate, dicynamide, and bis(trifyl)imide, show that shape and ion-interaction factors are more
complex than predicted. Generally, the cation controls the physical properties of the salt such as its
structure and morphology and the anion affects the stability and chemical reactivity\textsuperscript{21}. Moreover,
the anion affects coordination geometry around the metal ion which effects reduction potential,
reduction current and nucleation. Both the anion and cation affect the conductivity and viscosity.
The anions, in particular, have been substituted by increasingly stable alternatives. Anions such as
hexafluorophosphate and tetrafluoroborate, which are known to be susceptible to hydrolysis and can
potentially cause the evolution of toxic hydrogen fluoride, have been replaced by more hydrophobic
anions such as bis-trifluormethylsulfonyl)imide and trifluorotris(pentafluoroethyl)phosphate\textsuperscript{22}. As a
result, anions can control the solvent’s reactivity with water, coordinating ability, and hydrophobicity.
The $[\text{PF}_6]^-$ and $[\text{NTf}_2]^-$ anions produce hydrophobic solvents due to their lack of hydrogen-bond
accepting ability, though not all ionic liquids containing these anions are hydrophobic as the control
over hydrophobicity and other physical properties is largely governed by cation-anion pair
interactions. Properties of ionic liquids, such as dissolving ability from metal salts, polarity, viscosity
and density can be tuned by an appropriate choice of the anion and the cation. Overall, ionic liquids
are inevitably advanced, technological solvents that can be designed to fit a particular application.
One of the fundamental properties of an ionic liquid is ion conductivity. Ionic liquids have reasonably good ionic conductivities, between $10^{-3}$ and $10^{-2} \ \Omega^{-1} \ \text{cm}^{-1}$, compared with those of organic solvents/electrolyte systems $^3, 18$. These conductivities make ionic liquids interesting solvents for low-temperature electrodeposition studies. At elevated temperatures of e.g. 200°C, a conductivity of $0.1 \ \Omega^{-1} \ \text{cm}^{-1}$ can be achieved for some systems $^{18}$. However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolytes. Aqueous electrolytes typically have conductivities in the region of 100-500 mS cm$^{-1}$ because they are mostly high strength aqueous acids. The reason for significantly lower conductivities at room temperatures is the large constituent ions of ionic liquids which reduce the ion mobility which, in turn, leads to lower conductivities$^{18}$. However, another way to increase the conductivity could be to add a small organic cation such as lithium (Li$^+$) that could have an increased mobility compared to the large organic cation. This could have an effect upon the viscosity and the freezing point of the liquid as the small cation will be strongly associated with the anions, but the presence of a small amount should be negligible. El Abedin et al $^{19}$ studied the effect of LiF on the nucleation of tantalum in the ionic liquid used in this present study, which will be further discussed later. The conductivity of ionic liquids is inversely linked to their viscosity$^1$. One of the main differences between ionic liquids and aqueous solutions is the comparatively high viscosity of the former $^{20}$. Viscosities are typically in the range 10-500 cP (0.01-0.5 Pa s) $^{18}$ and this has a direct effect upon the diffusion coefficients not only of the metal species to the electrode but also the counter ions and complexants away from the diffusion layer. The viscosity of room temperature ionic liquids is several orders of magnitude higher than high temperatures molten salts due partially to the difference in size of the ions, but also due to the increased void volume. At elevated temperatures, however, the viscosity decreases by more than one order of magnitude. Hence, increasing the temperature increases conductivity and lowers viscosity. Generally, ionic liquids are also denser than water with values ranging from 1 to 1.6 g/cm$^{-3}$ and their densities decrease with increase in the length of the alkyl chain in the cation $^{18}$. The density of ionic liquids is also affected by the identity of anions, as different anions have different densities.

Another fundamental property of ionic liquids is that they have a wide liquid range and thermal stability $^3, 18, 21$. Thus these liquids can be used at wider temperature ranges and still have great thermal control of electrochemical processes, unlike when using conventional molecular solvent/electrolyte systems. Moreover, due to their extremely low vapour pressures, ionic liquids can be thermally stable up to temperatures of 400 °C $^{18}$. Studies have shown though, that high
temperatures are only tolerated by most liquids for a short time and that long time exposure to high temperatures leads to decomposition \(^\text{18}\). The decomposition temperature of ionic liquids depends on the component ion structure, similarly to other thermal properties \(^\text{1}\). The ionic liquid used in the present thesis, 1-butyl-1-methyl-pyrrolidinium bis(tri-fluoromethylsulfonyl)imide, is known to be thermally stable up to 350 °C after which the liquid starts to decompose. Decomposition temperature is affected by water content and impurities. Witkamp and coworkers investigated the reductive decomposition of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide \(^\text{1}\). The degradation product of [BMP][NTf\(_2\)] was analyzed via gas chromatography, mass spectroscopy as well as nuclear magnetic resonance spectroscopy. In general, the cations were reduced more easily than the anions on the cathodic limit. After electron transfer from the electrode to the cation the obtained radical can undergo several possible decomposition and rearrangement pathways. Upon formation of the analogue radical of 1-butyl-1-methyl-pyrrolidinium, it can decompose into methylpyrrolidine and a butyl radical, whereupon the energy of the products amounts to \(-61\ \text{kJ mol}^{-1}\) in vacuum \(^\text{1}\).

Ionic liquids are differentiated from typical inorganic salts by their low melting point (T\(_m\)). Typical inorganic salts have a high T\(_m\) around 1000 °C reflecting high lattice energies, i.e., the high T\(_m\) is attributable to a strong electrostatic attractive force between the ions \(^\text{1}\). Since the ionic liquids are organic compounds, van der Waals interaction, hydrogen bonding, and π-π interaction are additionally present among the component ions and affect the T\(_m\) of ionic liquids. Accordingly, the structural design of component ions to weaken the electrostatic interaction as well as other interactions is directly effective in lowering the T\(_m\) of the salts \(^\text{1}\). When ions have equivalent charges, the electrostatic interaction decreases with increasing ion radius since the surface charge density decreases with increasing ion radius and the separation between the ions also increases. As a result, the electrostatic interaction of larger ions is then weaker and accordingly the salts show lower T\(_m\). In general, organic salts have lower T\(_m\) than inorganic salts because of their larger ion size. Symmetry is another factor to affect T\(_m\). The salts with symmetric ions generally show higher T\(_m\) than those with asymmetric ones \(^\text{1}\).

The electrochemical window of ionic liquids is an important property and plays a key role in using ionic liquids in the electrodeposition of metals \(^\text{18},\text{21}\). The electrochemical window is the electrochemical potential range over which the electrolyte is stable and neither reduced nor oxidized at an electrode, which in turn determines the electrochemical stability of solvents. The potential
window is influenced not only by the chemical structure of the materials used but also by the electrode materials, sweep rate of the potential, temperature, atmosphere, solvent and impurity. In addition, the use of various reference electrodes for the determination of cathodic and anodic limits of ionic liquids makes the situation even more complicated. Although pseudo-metal electrodes such as Ag wire and Pt wire are often used as reference electrodes, these are not stable enough due to the generation of unstable membrane potentials and chemical reactions on the metal surface. The potential windows are usually evaluated by cyclic voltammetry or linear sweep voltammetry. In the cyclic voltammetry method, it must be noted that the electrochemically oxidized (or reduced) products of the first sweep must affect the voltammograms of the reverse sweeps. The anodic and cathodic limits are defined as the voltage where the current density reaches a certain value. Generally, cathodic and anodic limits of pure ionic liquids are attributed to the oxidative decomposition of the anion and the reductive decomposition of the cation, respectively. Impurities, especially water and halide anions, must be removed carefully, otherwise these drastically narrow the potential window. The electrodeposition of elements and compounds in water is limited by its low electrochemical window of only about 1.2 V. The following two reactions: $2H_2O \rightarrow O_2 + 4e+ 4H^+$ and $2H^+ + 2e \rightarrow H_2$, limit the potential window in water hence materials with a redox potential outside of the window, such as refractory metals, will be thermodynamically unstable. On the other hand, ionic liquids have significantly larger electrochemical windows and can go up to 6 V. As a result, the wide electrochemical windows of ionic liquids have given access to the electrodeposition of metals and semiconductors at room temperature, which were formerly obtained only from high temperature molten salts. However, ionic liquids can have a significant impact on the potential limits and the corresponding electrochemical window. Fluorine anions can easily oxidize which results to a reduction in the anodic potential limit. In addition, residual water in ionic liquids can be reduced and oxidized within the electrochemical window of many ionic liquids. Consequently, contamination of an ionic liquid with significant amounts of water can decrease the overall effective electrochemical window. Furthermore, water can react with anions in the ionic liquid to produce products that are electroactive in the electrochemical potential window. This has been found with chloroaluminate ionic liquids where water will react to produce electroactive proton-containing species (e.g., HCl). In addition, water appears to react with some of the anions commonly used in the non-haloaluminate ionic liquids. For instance, the [PF$_6$] anion is known to react with water to form hydrofluoric acid.
Due to their multitude of useful properties and abilities, ionic liquids have become alternatives for many industrial applications such as synthesis and extraction processes, electrochemistry, electrodeposition, photochemistry, liquid crystals, CO$_2$ capture, desulfurization of fuel, enzymatic synthesis, lubrication, rocket propulsion and thermal storage devices, to name just a few. One of the main reasons in using ionic liquids is because electroplating a range of metals, ie: Al, Ti, Ta and Nb is impossible in aqueous solutions due to hydrolysis \(^1\). Moreover, the ability to deposit these metals in ionic liquids will bring forth opportunities in various industries because of these metals’ heat corrosion resistance, abrasion resistance and high or low density. Furthermore, due to the absence of water, problems associated with hydrogen ions in conventional protic solvents, such as hydrogen embrittlement, are eliminated in ionic liquids because they are normally aprotic. As a result, quality coatings with better mechanical properties can be obtained. Therefore, ionic liquids, especially air and water stable types, are considered as promising solvents for a wide variety of applications including electrodeposition, batteries, catalysis, separations and organic synthesis. In addition, metal ion electrodeposition potentials are much closer together in ionic liquids compared with water, enabling easier preparation of alloys and the possibility of a much wider range of possible electroplated alloys, which are difficult or impossible in water.

From the environmental perspective ionic liquids are environmentally cleaner than other media. When used in electroplating processes, strongly aqueous electrolytes create quantities of metal-laden, corrosive effluent solution, whereas in ionic liquid electrolytes the metals will precipitate and be readily separated and recycled. Most of the ionic liquids are non-toxic and non-flammable. In addition, their very low vapour pressures allows them to be used in open galvanic baths at variable temperatures without releasing harmful vapours, which, in turn, reduces the amount of volatile organic compounds released into the atmosphere \(^{13}\). Finally, although the cost of ionic liquids will be greater than aqueous electrolytes, high conductivity and better efficiency will provide significant energy savings compared with water. Furthermore, ionic liquids have been considered to be possible environmentally friendly, recyclable media for synthetic organic chemistry, separation sciences and other chemical sciences and engineering. Ionic liquids contain organic cations and anions which melt at or close to room temperature. Their low vapor pressures allow chemical processes to be carried out with essentially zero emission of toxic organic solvents into the environment. Their high ionic conductivity, high ion concentration and good electrochemical stability make them beneficial for electrical energy storage devices, such as electrolytic capacitors,
batteries and fuel cells, as well as supporting media for catalysts. They have also been found to be efficient in standard separating processes, which eliminate the need of noxious organic solvents. Therefore, such systems are becoming increasingly technologically important. However, due to considerable lack of appreciation and basic research, the use of ionic liquids in chemical industry and other disciplines has not yet become widespread.

The early history of ionic liquids began in 1914 when the first report of a room temperature molten salt was reported by Walden. He reported the physical properties of ethylammonium nitrate, which has a melting point of 12 °C, formed by the reaction of ethylamine with concentrated nitric acid. The major interest in ionic liquids was first connected with their potential for the development of new electrolytes to be used in the electrical batteries and electroplating of aluminum. One such kind of room-temperature molten salt system was reported in the late 1940s by Hurley and Wier. They stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. In the 1970s and 1980s, Osteryoung and Hussey et al. carried out extensive research on organic chloride-aluminum chloride ambient temperature ionic liquids and the first major review of room temperature ionic liquids was written by Hussey. It was the discovery of 1-ethyl-3-methylimidazolium [EMIm]-based chloroaluminate ionic liquids in 1982 that drove further research in the area of room temperature ionic liquids. The above salt is one of the most widely studied room-temperature melt systems, which is liquid at room temperature for compositions between 33 and 67 mol % AlCl₃. Consequently, these salts based on AlCl₃ and organic salts such as 1-butylpyrrdinium chloride [BPCI], 1-alkyl-3-methylimidazolium chloride [C₆MIm]Cl, and derivatives became the first generation of ionic liquids. However, a considerable drawback of aluminum chloride-based ionic liquids is their moisture sensitivity, thus need to be protected from moisture. As a result, the hygroscopic nature of AlCl₃ based ionic liquids had delayed the progress in their use in many applications since they had to be prepared and handled under inert gas atmosphere. Thus, the synthesis of air and water stable ionic liquids, which are considered as the second generation of ionic liquids, attracted further attention in the use of ionic liquids in various fields. The second generation are based on organic cations as in the first generation and anions such as BF₄, PF₆ and SbF₆. In 1992, Wilkes and Zaworotko reported the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium cation with either tetrafluoroborate or hexafluorophosphate as anions. Following this discovery, it was found that exposure to moisture for a long time can cause decomposition of the anions liberating hydrofluoric acid. Therefore, ionic
liquids based on more hydrophobic and stable anions such as, e.g; bis(trifluoromethylsulfonyl)amide 
\[(\text{CF}_3\text{SO}_2)_2\text{N}^-\] and many others, had been developed, becoming the third generation of ionic liquids 
28. Unlike the chloroaluminate ionic liquids, these ionic liquids could be prepared and safely stored outside of an inert atmosphere. Generally, these ionic liquids are water insensitive however it was found that long-term exposure to moisture can cause changes in their physical and chemical properties 14, 18. In all the generations of liquids that have been studied over the years, most of the basic studies on metal and alloy deposition have been performed in AlCl₃-based ionic liquids 3. However, systems made from organic salts and different metal salts had also been reported in the literature and the new air-stable liquids are now being intensively investigated. A more detailed discussion of past work using these three generations of liquids will follow as well as important findings.

Ionic liquids of the first generation are comparatively easy to synthesize from AlCl₃ and organic halides. Aluminum can quite easily be electrodeposited in these liquids as well as many noble elements such as silver, copper, palladium and others. AlCl₃-based ionic liquids were the first to be used for the electrodeposition of metals however, the major disadvantage of these liquids is their extreme sensitivity to moisture which requires handling under a controlled inert gas atmosphere 29, 30. A sample of work performed using first generation ionic liquids is based on a 2006 published study by El Abedin et al 31, where cyclic voltammograms were performed from the upper phase of the biphasic mixture of AlCl₃/1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonylimide on gold substrates at different temperatures, 25, 50, 75 and 100 °C as shown in Figure 1.
Figure 1: Cyclic voltammograms recorded on Au substrate in the ionic liquid 1-butyl-1-methyl pyrrolidinium-bis(trifluoromethylsulfonyl)imide containing AlCl$_3$ at different temperatures. (Scan rate 10 mV s$^{-1}$) $^{31}$.

The cyclic voltammograms recorded at 50 and 75 °C exhibit a nucleation loop similar to the one recorded at room temperature. At 50°C, there is a broad reduction process from -0.6 to -0.9 V. Then the current rises steeply at -0.9 V and less steeply at -1.1 V. These processes are correlated to the aluminum deposition and reduction of the organic cation begins at about -2.0 V vs. Al/Al$^{III}$. There is a slight oxidation peak located at 0.1 V. At 75 °C, there is only one reduction shoulder at -0.5 V, followed by a steep increase and aluminum deposition beginning at -0.7 V, and then by a nucleation loop, before the deposit starts to be oxidized incompletely at 0 V. At 100 °C, there is no evidence for a nucleation loop and there is only one steep rising deposition current beginning at -0.2 V $^{32}$. The incomplete oxidation of the deposit begins at 0 V vs Al/Al$^{III}$. The visibly observable deposition of aluminum is highly irreversible in this ionic liquid. The oxidation of aluminum is likely to be hindered for kinetic reasons. In the authors’ experience, aluminum is passivated in ultrapure and well dried liquids with the Tf$_2$N anion. The aluminum electrodeposits obtained at different temperatures were investigated by means of a high resolution scanning electron microscope. Visually, the deposits appeared to be thick, shiny, and well-adhering to the gold substrate $^{32}$. Generally, the
electrodeposited layers contain very fine crystallites in the nanometer regime. The electrodeposits obtained at 25, 50 and 75 °C were found to be stressed, as observed by visual inspection. Occasionally, the aluminum film made at room temperature peeled off due to internal or residual stresses that almost always appear in the electrodeposition of metals. The stresses can originate from intrinsic film stress and from interfacial stress between the deposit and the substrate. Possible stress mechanisms that cause these stresses are (i) deviations from perfect crystallinity within the films such as grain boundaries, dislocations, impurities, film/substrate interfacial strain due to lattice mismatch between film and substrate upon epitaxial growth or due to different thermal expansion. Moreover, in thin film deposition, the differences in thermal expansion coefficients between the film and the substrate, is a major cause of mechanical stress. This is caused when the thin film is deposited onto a substrate at elevated temperatures at which point after deposition, the substrate cools down to room temperature. Interestingly, the quality of the deposit obtained at 100 °C improved enormously in this study and also the crystallites became finer. Moreover, there is no residual stress in the electrodeposited aluminum film.

On the other hand, ionic liquids of the third generation are strongly hydrophobic resulting from fluorine rich anions. The bis(trifluoromethylsulfonyl)imide and the trifluoromethanesulfonate anions combined with pyrrolidinium, imidazolium or trimethyl-n-hexyl ammonium cations are examples for such ionic liquids. From these liquids, metals like In, Se, Si, Ge and also Ta have been deposited. These liquids have attractive electrochemical windows (up to +/- 3V vs. NHE) and extremely low vapour pressures. Then, several liquids consisting of 1-ethyl-3-methylimidazolium, 1,2-dimethyl-3-propylimidazolium or 1-butyl-1-methyl-pyrroldinium cations with various anions, such as tetrafluoroborate [BF₄⁻] and tri-fluoromethanesulfonate (CF₃SO₃⁻), were found and received much attention because of low reactivity against moisture. Usually, these ionic liquids can be well dried to water contents below 1ppm under vacuum at temperatures between 100 and 150 °C. It was in using the air and water stable ionic liquid 1-butyl-1-methylpyrroldinium bis(trifluoromethylsulfonyl)imide, that the first results on the additive free electrodeposition of nanocrystalline aluminum in the ionic liquid [BMP]Tf₂N, saturated with AlCl₃; with an average crystallite size of 34 nm, were reported. Furthermore, it has been known that room temperature ionic liquids composed of bis(trifluoromethylsulfonyl)imide anion are not only stable against moisture but also immiscible in water. Although the solubility of water in TFSI -based room temperature ionic liquids is not negligible, it is easy to eliminate water from the TFSI- based room temperature ionic liquids
compared with other ionic liquids miscible with water. Therefore, TFSI-based ionic liquids are expected to be the alternative media for various practical electrochemical processes such as the electrodeposition of refractory metals.

### 2.3 Tantalum and Niobium

Tantalum and niobium are members of a group of materials known as refractory metals because their melting points are greater than that of platinum at 1750 °C. They are known for their high melting point, high temperature strength, irradiation damage resistance and excellent corrosion resistance which make them ideal metals for use in the chemical and nuclear industry. In addition, these materials exhibit remarkable resistance to the harshest of chemical environments due to presence of a tenacious oxide film that forms spontaneously in air. This thin surface film, exhibits a high stability in most mineral acids, except in hydrofluoric acid or hot concentrated sulfuric acid. This study investigates these two materials as coatings electrodeposited using ionic liquids. Coatings provide a way of extending the limits of use of materials at the upper end of their performance capabilities, by allowing the mechanical properties of the substrate materials to be maintained while protecting them against wear or corrosion. A review of tantalum and niobium will follow including a description of each of their properties and a discussion on their applications in the nuclear industry.

Tantalum has properties that make it useful for many applications, from electronics, to mechanical and nuclear power systems. Its high melting point, ductility, toughness and excellent corrosion resistance make it an ideal coating material for components exposed to high temperature, wear and severe chemical environments. In the nuclear power industry, tantalum is applied in condensers, columns, heat exchangers, helical coils, valve linings and a variety of other components exposed to extremely corrosive fluids. Tantalum thin films exhibit two crystalline phases, body-centered cubic (alpha phase, the bulk structure of tantalum) and a meta-stable tetragonal beta-phase. The structure of deposited thin films is usually the metastable beta-phase or a mixture of the two phases. Even though the exact mechanisms leading to the formation of alpha-Ta or beta-Ta are not clearly identified, the empirical finding is that oxide substrates or materials that readily form surface oxides at room temperature and vacuum system impurities support the nucleation of the beta-phase.
Bulk tantalum has a BCC crystallographic structure with the lattice constant of 3.306 Å\textsuperscript{39}. The alpha-phase of tantalum is tough and ductile, with a Knoop hardness of 300-400, and has a relatively low electrical resistivity (13.5 µΩ cm)\textsuperscript{39}. The tetragonal structure of tantalum, also known as beta phase is found in the meta-stable phase which is hard, has a Knoop hardness > 900, brittle and has an order of magnitude higher electrical resistivity than the bcc phase\textsuperscript{39}. The beta phase of tantalum is very brittle and so this meta-stable phase is undesired in coatings subjected to mechanical and thermal stresses. Therefore, having a significant presence of beta-phase combined with alpha-phase material in the film may alter and have an adverse effect on film integrity, adhesion and other properties. It has been found that when depositing high quality tantalum films and particularly thicker coatings using molten salts\textsuperscript{40}, the beta-phase dominates the deposits on most substrates under most processing conditions\textsuperscript{40, 41}. The metastable beta-phase converts to the alpha-phase upon heating to 750 °C\textsuperscript{39}, but annealing of the deposited film to this temperature would adversely affect the properties of a heat treated substrate. For this reason, deposition of tantalum on substrates at high temperatures is not suitable. Therefore, it is preferred to electroplate refractory metals, such as tantalum using ionic liquids, a process that can be carried out at significantly lower temperatures compared to other plating processes\textsuperscript{39}.

In addition to a high melting point, niobium offers lower density and low thermal neutron cross-section compared to other refractory metals, which makes niobium useful in atomic reactors. In addition to its small capture cross-section for fast neutrons, niobium is highly recommended in nuclear reactors because of its good high temperature creep strength, its resistance to corrosion by liquid sodium-potassium alloys, and its outstanding compatibility with nuclear fuels. However, because of the poor oxidation resistance of high temperatures of niobium-base alloys, they must be coated before use in nuclear environments. Therefore, a niobium 1% zirconium alloy is used as a construction material in nuclear engineering, where its low neutron absorption coefficients, along with its good resistance to liquid sodium or lithium are utilized. The corrosion resistance of niobium is similar to, but not quite as good as that of tantalum, being less resistant to very strong acids. Furthermore, niobium has a melting point of 2465 °C\textsuperscript{42} and it is resistant to humid corrosion in a highly acidic environment subsequent to the formation of a particularly stable passivating surface layer of niobium oxide. Similarly to tantalum, niobium is attacked by fluorides and embrittled by hydrogen.
Although tantalum and niobium are very resistant to both acidic and basic environments, they are subject to complexation by fluoride ions in aqueous and ionic liquid environments. The variety of fluoride compounds that exist are related to the properties of fluorine and above all to fluorine’s high electronegativity. Low dissociation energy of the fluorine molecule, F₂, relatively high energies of bond formation found in most fluoride compounds, as well as fluorine’s strong oxidizing ability lead, in some cases, to spontaneous fluorination. Fluorination of both metals and oxides of niobium and tantalum can take place even at low temperatures. Precipitation of fluorine compounds from solutions of hydrofluoric acid, HF, is performed by the addition of certain soluble compounds to solutions containing niobium or tantalum. Furthermore, in the absence of water molecules in the system, similar compositions of fluoride complexes of tantalum and niobium are expected. The most universal method for the synthesis of tantalum and niobium fluoride compounds is based on direct interaction between their pentafluorides, TaF₅ or NbF₅ and fluorides of other metals. TaF₅ and NbF₅ are prepared from their respective oxides by fluorination with fluorine, F₂, or with anhydrous hydrogen fluoride, HF. Rakov et al reported the interaction between niobium metal and anhydrous hydrogen fluoride as being the most effective way of preparing NbF₅.

One of the restrictions to using metals such as tantalum and niobium as coatings, despite being versatile materials with superior properties, is that electrodeposition of these refractory metals is not possible using aqueous media, due to their quite negative deposition potential. The reason for this is because tantalum and niobium belong to a group of metals easily passivated in aqueous electrolyte solutions. From the Pourbaix diagrams for tantalum and niobium in water systems shown in Figure 2 it can be seen that the electrochemical window for the reduction of Ta and Nb is below –0.8 V. The Pourbaix diagrams also display the electrochemical window of water, a range of 1.2 V. Therefore, since aqueous solutions have such a narrow electrochemical window range of 1.2 V, tantalum and niobium deposition is not possible.
As a result, efforts have been made to develop an electroplating process for the electrodeposition of tantalum and niobium. There is a considerable amount of literature on deposition of tantalum and niobium films using high temperature molten salts, but as will be shown, those molten salts do not offer the exceptional advantages that are obtained through using ionic liquids. Prior to reviewing some published work on the deposition of tantalum and niobium using ionic liquids, it is first essential to review some work performed on these metals using high temperature molten salts in order to compare the two processes.

2.4 Tantalum and Niobium Deposition in High Temperature Molten Salts

High temperature molten salts were found to be efficient baths for the electrodeposition of refractory metals. Senderoff and Mellors reported the first results on the electrodeposition of coherent coatings of niobium (Nb), tantalum (Ta), zirconium (Zr) and molybdenum (Mo) on steel from molten fluorides. High temperature molten salts of alkali metal halides as a solvent and K$_2$TaF$_7$ as a source of tantalum have been considered the most efficient baths for tantalum
electrodeposition. For tantalum deposition, the ternary eutectic mixture LiF-NaF-KF has been used as a solvent and K$_2$TaF$_7$ as a source of tantalum at temperatures between 650 and 850 °C. Using the same eutectic mixture and K$_2$TaF$_7$ as a source of tantalum, Dutra et al, reported that compact tantalum deposits, free of dendrites, can be obtained using pulse currents. Furthermore, Chamelot et al, have shown the optimum conditions for tantalum electroplating in the electrolyte LiF-NaF-K$_2$TaF$_7$ at a temperature of 800 °C. Lantelme et al have stated that tantalum can be electrodeposited from NaCl-KCl-K$_2$TaF$_7$ melts at 720°C and that the quality of deposit improves on addition of NaF to the melt. Furthermore, in a study by Grinevitch et al in 2006, where the electrodeposition of tantalum products in CsCl melt was investigated, multi-phase deposits were crystallized and the number of phase inherent in one deposit were more than six suggesting electrocrystallization non-equilibrium conditions for the most instances. Also, the conditions for the electrodeposition of only pure, almost oxygen-free tantalum from oxygen containing melts were only found at 750 °C. In this case, the cubic tantalum modification appeared to be formed by direct electrochemical crystallization and a metallothermic reduction of tantalum oxide or other tantalum compounds with potassium or caesium as reducing agents. Results from this paper show that the electroreduction of TaOF$_6$ complexes can only occur by reactions at temperatures 650 and 750 °C. Furthermore, the decomposition of TaO was found to be more rapid at 850 °C than for 750 °C.

As published results have shown, tantalum deposition using melts can only be achieved at extremely high temperatures. However, besides high temperature requirements for the reduction of tantalum, these baths have many technical and economic problems, such as the loss in the current efficiency of the electrolysis process due to the dissolution of metal after its deposition and the expected corrosion problems at high temperatures. Only one attempt to electrodeposit tantalum at 100 °C in a mixture of TaCl$_5$, LiF and 1-ethyl-3-methyl imidazolium chloride has been reported. In 2001, Masatsugu and Morihisa claimed that they could make Ta films of thickness up to 100 μm in the former bath with a composition of 30 mol% TaCl$_5$, 10 mol % LiF and 60 mol % Cl, but other authors have stated that they were unsuccessful in electroplating tantalum using the same bath composition. Overall, a few studies have been performed on electroplating tantalum using high temperature molten salts at very high temperatures. However, due to the inconveniences of using high temperatures in various applications, air- and water stable ionic liquids have inevitably attracted the interest of chemists and engineers over the last couple of decades because of their attractive
properties, such as low melting points, good thermal and chemical stabilities, high ionic conductivities, low vapour pressures and large electrochemical windows.

Furthermore, niobium electrodeposition in fluoride melts has been extensively investigated. It has been shown that the nucleation process of niobium in molten LiF-NaF is instantaneous, three-dimensional and closely controlled by linear diffusion \(^{42}\). Under these conditions a columnar structure of coarse grains forms. To improve the coating, pulsed electrolysis should be explored to improve the process since pulsed electrodeposition of various metals in aqueous media have given good results in terms of high electrodeposition rates and smoothness of the coatings \(^{47}\). Recently, Gillesburg et al published work on niobium electrodeposition by using pulsed electrolysis in molten chlorides \(^{48}\). This work observed a strong influence of the pulse parameters on the crystallographic properties of the coating.

The electrochemical reduction process involved in the electrodeposition of niobium has been studied. The first coherent and adhesive deposits were obtained in the sixties by Senderoff and Mellors \(^{42}\). The electrolyte consisted of a LiF/NaF/KF eutectic mixture as solvent and K\(_2\)NbF\(_7\) as solute heated to approximately 800 °C. A three-stage mechanism was proposed leading to the deposit of the niobium, as follows:

\[
\begin{align*}
\text{Nb(V) + e}^- &= \text{Nb(IV)} \\
\text{Nb(IV) + 3e}^- &= \text{Nb (I)} \\
\text{Nb(I) + e}^- &= \text{Nb(0)}
\end{align*}
\]

However, a two-stage mechanism was later proposed by Qiao and Taxil, then approved by Christensen et al \(^{42}\):

\[
\begin{align*}
\text{Nb(V) + e}^- &= \text{Nb(IV)} \\
\text{Nb(IV) + 4e}^- &= \text{Nb(0)}
\end{align*}
\]

In studies of niobium electrocrystallization in molten fluorides, it was found that the niobium forms initially in hemispherical shape, interpreted as Volmer-Weber growth. It was also observed that niobium forms instantaneously on application of the potential pulse and their growth is three-dimensional and limited by the diffusion of the electrolyte \(^{42}\). In addition, alkali chloride melts have
been used to produce niobium coatings. Attempts to deposit niobium at low temperatures, ie: 200 °C, from chloroaluminate melts failed due to the formation of insoluble subvalent niobium species. Higher temperatures were then studied using the eutectic mixture LiCl-KCl as solvent to plate high quality niobium layers. At temperatures between 550 and 650 °C, the deposits were dendritic and non-adherent, whereas pure niobium layers were obtained at 750 °C.

Although the electrodeposition of refractory metals is possible using molten salt baths, as proven by past research results, there are several disadvantages in using these baths. Electrodeposition of refractory metals in molten salts is, in general, diffusion controlled, which leads to the formation of dendrite structures, with consequent lower current efficiency and co-deposition of alkali metals from the solvent. In addition, electrodeposition using these baths is only possible by using high temperatures, which can pose problems in large-scale applications. However, it was not until the discovery of ionic liquids and their superior advantages that the advancement in research on the electrodeposition of refractory metals using ionic liquids began. Accordingly, the following presents some past work on the deposition of tantalum using ionic liquids.

### 2.5 Tantalum Deposition in Ionic Liquids

The first results of tantalum deposition in the air and water stable ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide involved 0.5 M TaF₅ on Au(111) at room temperature. As shown in Figure 3, two reduction processes are recorded in the forward scan.
The first peak at -0.75 V might be correlated to the electrolytic reduction of Ta (V) to Ta (111). The second process starts at a potential of -1.5 V and is accompanied by the formation of a black deposit on the electrode surface. The authors attribute this peak to the reduction of Ta (111) to tantalum metal simultaneously with the formation of insoluble tantalum compounds. Along the anodic scan, the peak was assumed to be due to the dissolution of the electrodeposit which is not completely reversible. The resulting deposit on the substrate only loosely adhered to the surface and was easily removed by washing with acetone.

A whole range of research work has and continues to be performed on the electrodeposition of tantalum using ionic liquids. In a study performed by El Abedin, it was shown that compact thin layers of tantalum can be electrodeposited on platinum at moderate temperatures. As shown in Figure 4, at 25 °C, the cyclic voltammogram exhibited only one cathodic process in the forward scan at -2.0 V (v. Pt). The reduction peak was said to be attributed to the electrodeposition of tantalum and to other insoluble tantalum compounds at the electrode surface, as the formation of a black deposit on the electrode surface was clearly seen. In the reverse scan, the cathodic current continued to flow and crossed the forward scan at negative currents. This current loop is typical for
nucleation processes. The anodic scan crossed the voltage axis at a potential of about $-1.3$ V producing a cathodic over-potential of about $-0.3$ V for the deposition process. The anodic peak observed on the anodic scan at $-0.25$ V is attributed to the incomplete stripping of the electrodeposit. The potential was then set to $-2.3$ V for 1 hour in order to form a thick layer of the electrodeposit on the electrode surface. The deposit was described as black in colour and also as in the case of gold, appeared to be loosely adhering to the surface since it was easily removed by washing with acetone.

![Cyclic voltammograms of ionic liquid [Py$_{1,4}$] TFSA containing 0.5 M TaF$_5$ recorded on Pt at different temperatures (Scan rate 10 mV s$^{-1}$)](image)

Figure 4: Cyclic voltammograms of ionic liquid [Py$_{1,4}$] TFSA containing 0.5 M TaF$_5$ recorded on Pt at different temperatures (Scan rate 10 mV s$^{-1}$).

Moreover, in the experiments performed at 100 °C and higher, the cyclic voltammograms show two reduction peaks on the cathodic branch and two oxidation peaks on the anodic branch of the cyclic voltammograms. In this work, it was assumed that the first cathodic peak was correlated to the electrolytic reduction of Ta (V) to Ta (111), since TaF$_3$ is known to be a stable compound. The second reduction peak was attributed to the reduction of Ta (111) to Ta (0), as a black deposit was clearly seen. Additionally, along the anodic scan, the first peak was said to be attributed to the oxidation of Ta to Ta (111) and the second peak was correlated to oxidation Ta (111) to Ta (V).
was observed that the peak potentials of the cathodic peaks shift slightly to less negative values and the potential of the oxidation peaks move slightly to the positive direction with increasing temperature. In addition, the peak currents of the reduction and oxidation peaks remarkably increase with rising temperature. Finally, both conductivity and viscosity of the ionic liquid improved as the temperature increases. In the experiments performed at 200 °C, the potential was held at –1.3 V (v. Pt) for 1 hour on platinum substrate in the employed ionic liquid and the electrodeposit was found to be dense and thick as seen in Figure 5.

![SEM micrograph of electrodeposit formed potentiostatically on Pt in [Py$_{1,4}$] TFSA containing 0.5 M TaF$_5$ at potential of -1.3 V for 1 hour at 200 °C and b) EDX profile of area shown in SEM micrograph.](image)

**Figure 5:** a) SEM micrograph of electrodeposit formed potentiostatically on Pt in [Py$_{1,4}$] TFSA containing 0.5 M TaF$_5$ at potential of -1.3 V for 1 hour at 200 °C and b) EDX profile of area shown in SEM micrograph.  

In addition, the accompanied EDX profile revealed the presence of a relatively high concentration of fluorine indicating the formation of insoluble tantalum subfluorides. However, when LiF was then
added to the ionic liquid, it was found that the quality and the adherence of the electrodeposit were considerably improved \(^{19}\). During the electrodeposition of tantalum, a non-stoichiometric layer of tantalum subhalide on top of tantalum was also formed which could be removed after washing with isopropanol and then boiled in water. After cleaning, only crystalline and elemental tantalum was detected at the electrode surface. One possible explanation that arose from this work was that Li\(^+\) destabilised the Ta-F bonds thus facilitating tantalum deposition lowering the probability of formation of tantalum subvalent deposits \(^{5,19}\). Another possible explanation was that the structure of the double layer was altered by Li\(^+\), thus facilitating TaF\(_5\) reduction \(^7\). As a result, a layer deposited when the potential was held at \(-1.8\) V in the ionic liquid containing 0.25 M TaF\(_5\) and 0.25 M LiF on platinum electrode at 200 °C for 1 hour, showed to be a smooth, coherent and dense layer, which was revealed to be elemental tantalum based on the EDX profile shown in Figure 5. However, to determine whether or not the electrodeposit contained crystalline tantalum, x-ray diffraction patterns (XRD) were acquired. The XRD patterns of the initial deposits showed only the characteristic patterns of the platinum substrate and no evidence for crystalline tantalum. This meant that the electrodeposits were either amorphous or so small in their crystal size that within the resolution of the device, no XRD peaks could be obtained. In order to improve the crystallinity of the electrodeposits, the samples were annealed at 800 °C under vacuum for 5 hours \(^{19}\). The sample was then analyzed through XRD in which patterns clearly showed the characteristic signals of crystalline tantalum and Ta\(_2\)O\(_5\). The presence of Ta\(_2\)O\(_5\) was attributed to the trace of oxygen when annealed. The absence of fluoride in the deposit after thermal annealing was said to be due to the high vapour pressure in the low valent Ta-F compounds. The results presented in this work showed that first a thin crystalline tantalum layer was deposited (about 200-300 nm) and then a non-stoichiometric tantalum subfluoride layer was deposited on top, with some trapped ionic liquid growing with thicknesses of several micrometers \(^{19}\).

In other work by El Abedin in 2008 \(^7\), it was shown that a thin layer of tantalum can also be electrodeposited on stainless steel. The coating of stainless steel by thin, self-passivating layers of tantalum would improve its corrosion resistance and thus enhance its biocompatibility. A layer of tantalum film was deposited galvanostatically on stainless steel in the ionic liquid used in this study, containing 0.25 M TaF\(_5\) and 0.25 M LiF at a current density of \(-8\) mA cm\(^{-2}\) for 30 minutes at 200 °C. The thickness of the tantalum layer was shown to be roughly 1.2 µm, compact and it contained crystallites in the micrometer regime \(^7\).
2.6 Effect of Addition of LiF to the Electrodeposition of Tantalum

In the same study by Abedin et al in 2005, the effect of addition of LiF was investigated when added to the above mentioned ionic liquid containing TaF$_5^{50}$. From literature data in high temperature molten salts, it was found that the addition of fluorides of alkali metals, such as LiF or NaF, to the fused salts facilitates the electrodeposition of tantalum. Upon addition of LiF to the ionic liquid, the study found that the mechanical quality and adherence of the electrodeposited Ta in [BMP]Tf$_2$N containing TaF$_5$ can be improved by addition of LiF to the electrolyte $^{14, 50}$. Figure 6 shows the cyclic voltammogram of [BMP]Tf$_2$N containing 0.25 M TaF$_5$ and 0.25 M LiF on Pt electrode at 200 °C.

![Cyclic voltammogram](image)

**Figure 6: Cyclic voltammogram of ([BMP]Tf$_2$N) containing 0.25 M TaF$_5$ and 0.25 M LiF on NiTi alloy at 200 °C $^{50}$.**

Three cathodic peaks are seen in the forward scan in which authors suggested that the electrochemical reduction of Ta (V) occurs in three steps. The first reduction peak was observed at a potential of about -1.3 V, the second peak was located at a potential of about -1.5 V and finally the
onset of tantalum deposition occurred at a potential of about -1.8 V accompanied by the formation of a black layer on the electrode surface. Without LiF, only two reduction peaks were observed. This observation indicated that the reduction of Ta (V) to tantalum metal occurs via Ta (IV) and Ta (III) upon the addition of LiF. The SEM micrograph of the resulting 500 nm thick deposit on a NiTi electrode electrodeposited potentiostatically at -1.8 V for 1 hour at 200 °C, shows a smooth, coherent and dense layer as shown in Figure 7a). The electrodeposit was analyzed as metallic tantalum, as revealed from the corresponding XRD patterns in Figure 7b), which show the characteristic peaks of crystalline tantalum.

Figure 7: a) SEM micrograph of the electrodeposit formed potentiostatically on NiTi alloy in ([BMP]Tf2N) containing 0.25 M TaF5 and 0.25 M LiF at a potential of -2.0 V for 1 hour at 200 °C. b) EDAX profile of the area shown in the SEM micrograph.
However, for micrometer thick layers varying amounts of fluoride were found in the deposit. Although the role of LiF was not completely clear, the authors suggested that maybe its effect is due to the ionic polarizability of \( \text{Li}^+ \), resulting in a weakening of the Ta-F bonds, leading to a facilitation of tantalum deposition \(^{50}\). Despite this prediction, further work is in progress to shed more light on the influence of addition of lithium salts.

### 2.7 Purity of Ionic Liquids

The use of ionic liquids in electrochemistry is not complete without discussing the importance of purity in ionic liquids. Room temperature ionic liquids are known to be hygroscopic and can absorb significant amounts of water from the atmosphere \(^{33}\). This is because water and oxygen molecules are easily dissolved into the liquid from air. Consequently, water and halide impurities are prominent impurities that are widely found in commercial liquids, including ultra-pure grade quality liquids \(^{49}\). These impurities can cause changes in the physical and chemical properties of the liquid \(^{33, 51}\). Furthermore, the impurities interfere with the dissolved metal salts and/or the deposits and may lead to misinterpreted results \(^{49}\). Residual water in ionic liquids and/or halides affect the rate and/or selectivity of reactions carried out in ionic liquids and their physical properties \(^{33, 51}\). There exist literature reports on the influence of moisture on the electrochemical behaviour of room temperature ionic liquids \(^{53, 54}\). Properties of room temperature ionic liquids, including their solubility, polarity, viscosity and conductivity are not only changed by but are also dependent on the amount of absorbed water \(^{33}\). As a result, absorbed water may alter rates of chemical reactions and efficiencies of various processes in room temperature ionic liquids \(^{33}\). Therefore, since water and oxygen are electrochemically active, the removal of these molecules is essential before any voltammetric measurements. However, since ionic liquids have no significant vapour pressure, their purification using conventional methods is extremely difficult. Thus, it is critical to remove as many impurities as possible from the starting materials and to use synthetic procedures that produce as few side products as possible, or allow their easy separation from the final product \(^{1}\).

The effect of water on the electrochemical window of ionic liquids has been studied in ionic liquids containing the imidazolium cation and fluoroanions \(^{51, 52}\). A dramatic narrowing in the potential window available for voltammetric studies in the ionic liquid was detected. For example,
both the $E_{\text{Cl}}$ and $E_{\text{Al}}$ were reported to have shifted toward positive and negative potentials, respectively, with the addition of more than 3 wt% of water and this has been shown to cause a decrease in the wide electrochemical window of over 2.0 V \textsuperscript{26}. However, there is a study of the effects of a very small amount of water (100 ppm) on the voltammogram of a room temperature ionic liquid containing N-butylpyrridinium and chloroaluminate anion \textsuperscript{53}. For a platinum working electrode, a reduction current of HCl, which is generated from the reaction between water and the chloroaluminate anion, was observed at a potential much more positive than that of the cathodic limiting potential of this system \textsuperscript{53}.

The purity of ionic liquids can be determined using a variety of spectroscopic techniques. UV-Vis spectroscopy is the simplest method to determine optical purity in the ionic liquids \textsuperscript{55, 56}. However, the simplest electrochemistry of ionic liquids provides a very quick indicator of the general purity. Figure 8 shows the cyclic voltammograms for dry 1-butyl-1-methylpyrroldinum bis(trifluoromethanesulfonyl)amide.

![Figure 8: Cyclic voltammogram of dry 1-butyl-1-methylpyrroldinum bis(trifluoromethanesulfonyl)amide (blue is commercial, red is prepared in laboratory), platinum working electrode, platinum counter electrode and a silver reference electrode scanned at 50 mV/s \textsuperscript{55}.](image)
The authors in this particular paper employed a platinum working electrode, platinum counter electrode and a silver wire as the reference electrode. All that they were interested in was the electrochemical window and the current therein.

Quantifying the levels of impurities is always problematic. Without a clear understanding of the nature of the impurity it is impossible to accurately determine the level of impurities in any given sample. In summary, many have shown that traces of water can have a dramatic effect on the electrochemical characteristics observed voltammetrically in ionic liquid media.
3.0 EXPERIMENTAL METHODS

3.1 Introduction

This section describes the materials and the experimental set-up used in the current work. The pre-electrolysis treatment performed to remove contained impurities in the ionic liquid is also described. Electrochemical measurement techniques such as cyclic voltammetry, potentiostatic polarization and microstructural characterization techniques such as scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) are also presented.

3.2 Materials and Chemicals

The electrodeposition of tantalum was studied in the water and air stable ionic liquid 1-butyl-1-methyl-pyrrolidinium bis(tri-fluoromethylsulfonyl)imide ([BMP]Tf$_2$N) purchased from Merck KGaA (EMD). The ionic liquid was a low purity grade containing >98% assay, <1,000 ppm halides and <1% water. Prior to use, the ionic liquid underwent a vacuum drying procedure to remove as much water as possible 57. The liquid was transferred to a Schlenk tube and pumped under vacuum (with stirring) for 17 hours, in an oil bath set at 100 °C and directly transferred and stored in a nitrogen filled glove box (Nexus II) with water and oxygen below 1 ppm. TaF$_5$ (99.99%) and LiF (98.5%) were purchased from Alfa Aesar and dried under vacuum for 1 hour at 100 °C, to remove any water contained in the water sensitive compounds. Nickel substrates were used as working electrodes for electrochemical measurements. Platinum (Pt) wires were purchased from Alfa Aesar, 99.999% in which 0.33 cm$^2$ of wire was immersed in solution and applied as the quasi-reference (RE) and 0.44 cm$^2$ of wire was immersed in solution and applied as the counter (CE) electrode. For the present study, Pt quasi reference electrodes were used as past research with this type of ionic liquid has shown Pt to be stable 16,50. Therefore, it is critical to keep in mind from herein that all results are based on a quasi-reference electrode and not a true reference electrode.
3.3 Electrochemical Set-Up

All electrochemical measurements including electrodeposition experiments were conducted at 100 °C in the nitrogen-filled glove box as seen in Figure 9. Reproducible voltammetric results were very difficult to obtain outside the glove box. The electrochemical cell for the pre-electrolysis process consisted of two pyrex cylindrical beakers creating a two-compartment cell. The two beakers were connected by a plastic U-shaped tube bridge that allowed ions to flow through. The upside-down U-shaped tube bridge consisted of commercialized, multi-use sponge pieces soaked in ionic liquid that were inserted tightly through the tube to form a sponge-filled tube. The tube was saturated with the soaked sponge so that there were no air gaps, in order to provide a consistent current through the bridge. From herein, this bridge will also be known as the ionic liquid bridge. There was no evidence that the pyrex flask was etched by the fluoride of TaF$_5$.

![Figure 9: a) Nitrogen-filled glove-box in which all experiments were performed. b) The two-compartment cell consisting of two beakers separated by an ionic liquid bridge which passes the current through from the reference electrode to the counter electrode; separating any residual impurities from the counter electrode mixing with the solution being purified.](image-url)
The electrochemical cell consisted of a counter electrode with an area of 0.44 cm$^2$ immersed in solution, a quasi-reference electrode with an area of 0.33 cm$^2$ immersed in solution, and a working electrode of 3.0 cm$^2$ surface area which were all used during the pre-electrolysis treatment. Cross-sectional nickel wires of 1 mm, 2 mm and 6.35 mm with areas 0.00785 cm$^2$, 0.0314 cm$^2$ and 0.316 cm$^2$ respectively, were used as working electrodes during the electrodeposition experiments. The nickel wires were embedded in epoxy prior to the electrochemical experiments. Once mounted, the samples were ground successively using grinding papers with grits of 400, 600, 800 and 1200, washed with water, rinsed with distilled water and dried prior to use. A close-up of the electrochemical set-up can be seen in Figure 10.

3.4 Electrochemistry

3.4.1 Cyclic and Potentiostatic Voltammetry

All electrochemical measurements were carried out using a PARSTAT 2263 potentiostat/galvanostat (Princeton Applied Research) controlled by PowerCV, PowerStep and
PowerCorr software. All voltammetry scans were performed at a scan rate of 5 mV/s at 100 °C. The ionic solution was magnetically stirred immediately prior to each scan to avoid ion concentration gradients in the electrolyte. Stirring during the scan was avoided since it caused interference with the electrodes in the solution as only a small amount of ionic liquid was used at a time.

3.4.2 Pre-electrolysis Process

Cyclic voltammetry was performed on the vacuum dried ionic liquid to study its electrochemical behaviour. Potentiostatic voltammetry was performed to electrochemically reduce residual water active in solution by using a copper treatment. The copper treatment consisted of inserting a 3.0 cm² piece of copper foil as the working electrode and holding the potential at -0.8 V for approximately 30 hours at 100 °C. The copper was then removed from solution, rinsed in water, grinded down to a fresh new copper surface using 1200 grit paper, rinsed with distilled water and dried before use. The copper was then re-immersed into solution. A cyclic scan was then performed to compare the electrochemical behaviour before and after the potential hold in the liquid. Figure 11 illustrates the set-up of the pre-electrolysis process.

![Figure 11: Schematic of the pre-electrolysis process consisting of a two-compartment cell connected by an ionic liquid bridge.](image-url)
3.4.3 Electrodeposition Process

Upon purification of the ionic liquid, indicated by extremely low currents shown on the cyclic voltammetry scans in the pre-electrolysis process, the ionic liquid bridge was removed. The two-compartment cell became a single electrochemical cell. However, instead of using the copper working electrode that was used in the pre-electrolysis process to remove impurities, a nickel working electrode was used for electrodeposition. Furthermore, 0.25 M vacuum dried LiF was added to the ionic liquid and stirred until dissolved at 100 °C. Then 0.25 M TaF₅ was added into the solution and stirred until mostly dissolved. It was observed that TaF₅ does not fully dissolve in the liquid as partial residue of the electrolyte was seen at the bottom of the liquid after magnetically stirring for long durations. A cyclic scan was then performed to -2.5 V to study the behavior of the liquid containing the LiF and TaF₅. The solution was then left in the glove box overnight to settle and allow any further dissolution of the powders to occur.

Potentiostatic scans were performed at various potentials for 1 hour intervals to test deposition conditions. All electrodeposition experiments were performed at 100 °C. Between each potentiostatic scan, the sample was removed from solution, taken outside the glove box and cleaned. The sample was washed in water, rinsed in distilled water and dried. The sample was then analyzed through an optical microscope to detect any deposits. If there were no deposits on the sample, the sample surface was mechanically ground from 800 to 1200 grit to ensure a clean surface prior to repeating the electrodeposition process. After 1200 grit, the sample was rinsed in distilled water, dried and inserted back into solution. Potentiostatic scans were repeated at different potentials until deposition was observed.

3.5 Surface and Structure Analysis

Prior to electrodeposition, the nickel mounted samples were observed optically to ensure the required, slightly rough surface finish for the electrodeposition process. Upon completion of the electrodeposition process, various analytical techniques such as scanning electron microscopy, energy-dispersive x-ray analysis, x-ray photoelectron spectroscopy and x-ray diffraction were used to study the deposited layer on the substrate.
3.5.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to investigate the surface morphology of the deposited film and energy dispersive X-ray analysis (EDX) was used to determine the film composition (Hitachi S-570, accelerating voltage: 20 keV). The working distance for the EDX measurements was 15 mm between the objective lens and the specimen.

3.5.2 X-ray Photoelectron Spectroscopy

Surfaces of the coated samples were characterized using a Thermo Fisher Scientific ThetaProbe with a monochromated Al K-alpha X-ray source. The ion sputter profiling was performed with a 1 keV Ar\(^+\) ion beam. Survey spectra were acquired by scanning through the energy range of the instrument at low energy resolution (ie: high pass energy) and low point density. Regional spectra (C1s, O1s, F1s, Ta4f) were acquired at high energy resolution (lower pass energy) for the purposes of chemical analysis and quantification. Point density which is the number of data points per unit energy, was reduced so as to fully explore the shape of each signal in the survey spectrum. The data acquired from the instrument was processed using Avantage software provided by the instrument manufacturer. Surface elemental compositions were calculated from subtracting the background peak areas. Sensitivity factors used to calculate the relative atomic percentages were provided by the manufacturer.

3.5.3 X-Ray Diffraction

The 0.316 cm\(^2\) samples were placed onto a low background Silicon sample holder and run on an automated Siemens/Bruker AXS D5000 diffractometer. The system is equipped with a high power line focus Cu K-\(\alpha\) source operating at 50 kV/35 mA. The diffraction patterns were collected on a 0/20 Bragg-Brentano reflection geometry with fixed slits. A step scan mode was used for data acquisition with step size of 0.02° 20 and counting time of 2.5 seconds per step. The preliminary qualitative phase analysis was performed by Bruker AXS data processing software Eva\textsuperscript{TM} v. 8.0.
The 0.0314 cm$^2$ samples were run on Bruker AXS D8 Discovery Microdiffraction System with Cu K-$\alpha$ point-focus x-ray source operating at 40 kV/40 mA. The experimental data was collected on two frames at 600 seconds exposure of each one that cover the range of 20° - 58° 2θ. The 2D diffraction images were then integrated with step size of 0.005° 2θ and converted to standard I vs. 2θ diffraction patterns. The phase identification was done by Diffrac Plus™ data processing software Eva™ v. 8.0.
4.0 EXPERIMENTAL RESULTS and DISCUSSION

4.1 Introduction

Purity of ionic liquid and electrochemical conditions are key factors in controlling the electrodeposition of tantalum and niobium in ionic liquids. Accordingly, this chapter unfolds in three sections; the first discusses the pre-electrolysis treatment implemented in order to remove the water impurities from the liquid, while the second reviews the electrochemical conditions investigated for electrodeposition and the last section involves microstructure analysis of the electrodeposition results. This thesis has attempted to show that tantalum and niobium layers can be electrodeposited on nickel using an ionic liquid that underwent a pre-electrolysis treatment.

4.2 Purity of the Ionic Liquid

Controlling the composition of the plating bath is one of the most important factors contributing to the quality of the electrodeposited layer. At the outset, the bath must be prepared to the specific composition but most importantly purified before use. Impurities in ionic liquids can strongly alter the deposition process in initial stages leading to the misinterpretation of the surface processes. Consequently, the first part of the experiments in this study involved purifying the as-received low-purity ionic liquid, 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide. To determine the purity level of the as-received ionic liquid, cyclic voltammetry was performed. As-received ionic liquid refers to the ionic liquid in the same conditions as from the manufacturer. For a comparative analysis, Figure 12 illustrates how the curve of the as-received ionic liquid behaved compared to the behaviour of a theoretical pure ionic liquid cyclic curve.
As seen from Figure 12, theoretically pure ionic liquid should have no current running through it, resulting in a linear curve as it is free of impurities. However, it is seen that the ionic liquid purchased for this present study, has an end current density of approximately 200 µA·cm$^{-2}$, indicating that the ionic liquid is not pure, containing some impurities. The types of impurities that could exist in the ionic liquid studied are halides and water as the ionic liquid purchased contained < 1,000 ppm halides and < 1 % water. A significant increase in current density can be seen through the ionic liquid, which is probably due to water reduction or impurities. The exact impurities in the ionic liquid are unknown. Chemical testing of the ionic liquid purchased was beyond the scope of this work therefore the impurities in the liquid have not been chemically identified.

Since one of the known impurities was water, the as-received ionic liquid was vacuum dried to remove as much water as possible from the ionic liquid. The experimental process used in
removing the water can be referred to in the experimental section for details. The corresponding curve after vacuum drying the ionic liquid is shown in Figure 13.

![Figure 13: Cyclic voltammetry of vacuum dried ionic liquid. (Scan rate 5 mV/s vs. Pt).](image)

After 17 hours of vacuum drying at 100 °C, it is evident that there is some current flowing through the ionic liquid, however not as high as the current seen in the as-received ionic liquid. Vacuum drying decreased the end cathodic current density from 200 µA·cm⁻² to 100 µA·cm⁻². This suggests that the water was not entirely removed and the difficulty of extracting the water molecules from the liquid. As a result, a pre-electrolysis process was implemented in order to remove the impurities. A two-compartment cell was created to keep the H⁺ and OH⁻ ions separated and whatever else might be produced at the counter electrode, in order to ensure the water extracted from the liquid remained separated from the ionic liquid undergoing pre-electrolysis.
4.3 Pre-electrolysis Process

The objective of the pre-electrolysis process was to remove the impurities out of the ionic liquid, using copper foil as the working electrode and running a current through the ionic liquid at a constant voltage. The current flows through the ionic liquid bridge, which maintains the separation of the reduction reaction of water from the oxidation reaction of water. By using the bridge to keep the two reactions separate, any impurities formed by oxidation at the anode remained separated from the ionic liquid being purified. At the cathode, it is likely that water is reduced to hydrogen gas and maybe other organic impurities are reduced as well.

The pre-electrolysis involves holding the potential while decreasing the overall current through the liquid by using copper foil as the working electrode. All pre-electrolysis experiments were performed at 100 °C. A higher temperature was chosen rather than using room temperature, so that there was less concern about viscosity and conductivity of the liquid. After repetitive potentiostatic holds at -0.7 V (vs. Pt) for 3 hours, in a single quantity of ionic liquid (15 mL), the current was observed to stabilize with time. The current stabilizing was attributed to the removal of impurities from the ionic liquid. In Figure 14, cathodic end current densities from various cyclic voltammograms obtained in between potential holds were plotted versus different cycles, to illustrate the general decrease in current density as a result of the pre-electrolysis process used. In addition, Figure 15 shows the beginning and end results of the pre-electrolysis process described above, depicting how much the overall current stabilized. Furthermore, as the potential was held at -0.7 V (vs. Pt) for 3 hours between each cyclic scan, the end current densities on the cyclic scans stabilized, clearly indicating the removal of impurities from the ionic liquid although a flow of current remained in the liquid.
Figure 14: Decreasing trend of end current densities extracted from the cathodic cyclic scans between potentiostatic hold cycles. Current decreasing during pre-electrolysis indicates impurities are being extracted from the liquid.

Figure 15: Cyclic voltammetry before pre-electrolysis (dashed-line curve) and after pre-electrolysis (solid-line curve). Potential held at -0.7 V. (Scan rate 5 mV/s vs. Pt).
The lowest current density achieved by holding the voltage only as far negative as -0.7 V (vs. Pt), was 50 µA·cm\(^{-2}\). All tantalum electrodeposition experiments were performed using the ionic liquid which underwent the above pre-electrolysis process.

The remaining flow of current is a result of only holding the potential at only -0.7 V (vs. Pt). This potential was the lowest that could have been applied in the above process, due to the resistance encountered through the bridge which contained only ionic liquid. If a more negative potential was applied, the electrochemical potentiostat equipment would have showed an overload fault because of the high resistance through the bridge. Based on the above pre-electrolysis process applied, the remaining flow of current can be explained by using the impurity model illustrated in Figure 16.

![Figure 16: Impurity model depicting the pre-electrolysis effect on the behavior of the ionic liquid cyclic voltammograms.](image)

The impurity model illustrated in Figure 16 aims to show that holding the potential at -0.7 V (vs. Pt) or at less negative values, is not enough to remove all impurities from the ionic liquid. As is seen from the model, holding the potential at -0.7 V (vs. Pt) only removes the impurities that are located at less negative potentials (to the right of the reference line) and will not help in removing the impurities
found at more negative potentials (to the left of the reference line). Thus, a more negative potential must be held for all the impurities to be removed.

In order to stabilize the current even more than what was achievable in the above pre-electrolysis experiments, three different modifications were made to the pre-electrolysis process. The first modification involved an alteration to the ionic liquid bridge. Instead of having the bridge consist of a sponge saturated with only vacuum dried ionic liquid, the sponge was also saturated with LiF to improve the conductivity of the ions flowing through the bridge. The increase in conductivity through the bridge lowered the resistance through the bridge, thus allowing a more negative potential to be applied without causing an overload fault to the system. The second modification was the duration that the potential was held for. Previously, the potential holds were for 3 hours and the sample was then removed, cleaned and immersed back into solution for another 3 hour potential hold. This process was repeated numerous times until the lowest amount of current was obtained.

![Graph](image.jpg)

**Figure 17:** Decreasing trend of end current densities extracted from the cathodic cyclic scans between potentiostatic hold cycles. Current decreasing during pre-electrolysis indicates impurities are being extracted from the liquid. In this pre-electrolysis process, the ionic liquid bridge contained LiF and the potential hold was extended from 3 hours at a time to one continuous hold for 52 hours.
However, in this set of experiments, the potential was held for a total of 52 hours continuously. Lastly, the LiF added within the bridge enabled a more negative potential to be held, thus the potential was held at -0.8 V. Consequently, using a more negative potential for a longer holding period, caused the overall end current to stabilize even further, as shown in Figure 17. Furthermore, Figure 18 shows the beginning and end results of the modified pre-electrolysis process, with the inset figure showing the end result on an enlarged scale.

![Cyclic voltammograms](image)

**Figure 18:** Cyclic voltammograms before pre-electrolysis (dashed-line curve) and after pre-electrolysis (solid-line curve). In this pre-electrolysis process, the ionic liquid bridge contained LiF and the potential hold was extended from 3 hours at a time to one continuous hold for 52 hours. Inset: The same cyclic voltammetry obtained after pre-electrolysis as shown in this figure displayed on a larger scale.

As shown in Figure 18 inset, a current density as low as 5 μA·cm⁻² was obtained. Overall, it was observed that the pre-electrolysis process involving a two-compartment cell connected by a bridge containing ionic liquid with LiF and a copper cathode proved to be an effective process in extracting most impurities from the as-purchased, vacuum dried ionic liquid.
4.4 Addition of TaF₅ and LiF in Purified (Dry) Ionic Liquid

Upon purification of the as-purchased ionic liquid, 0.25 M TaF₅ and 0.25 M LiF were added to the liquid. LiF was added to the ionic liquid as it is known to increase the conductivity of the ionic liquid ⁵⁰. All electrochemical experiments were performed at 100 °C so that there was less concern about viscosity and conductivity of the liquid. Figure 19 shows the behaviour of the liquid when LiF was added to the ionic liquid, prior to the addition of TaF₅.

![Cyclic voltammetry scan of ionic liquid containing 0.25 M LiF at 100°C. (Scan rate 5 mV/s vs. Pt).](image)

**Figure 19:** Cyclic voltammetry scan of ionic liquid containing 0.25 M LiF at 100°C. (Scan rate 5 mV/s vs. Pt).

Furthermore, it can be seen from Figure 20 that the reduction current increases upon addition of 0.25 M TaF₅ to the ionic liquid containing 0.25 M LiF.
Figure 20: Cyclic voltammogram of ionic liquid containing 0.25 M TaF$_5$ and 0.25 M LiF recorded on Ni substrate at 100 °C. (Scan rate 5 mV/s vs. Pt).

The electrode potential was scanned from the open circuit potential in the negative direction at a scan rate of 5 mV/s. At 100 °C, the cyclic voltammogram shows several cathodic peaks. In research performed by El Abedin et al.$^{50}$, it was suggested that the three cathodic processes obtained from their cyclic voltammetry were due to the three step electrochemical reduction of Ta (V), with the onset of tantalum deposition occurring at a potential of about -1.8 V. Based on their study and the voltammetry data presented in Figure 20, it could be suggested that step-by-step reduction of the Ta (V) ions occurs. In this case and with reference to Figure 20, there exists a limitation in current which begins at roughly -2.1 V which could be attributed to the build up of intermediate species and not enough ions to sustain the reduction process. Alternatively, it could be suggested that some ions are used partially to form complexes of TaF$_x$ which may then be speculated that TaF$_5$ species could also be produced by such partial reduction aside from metallic tantalum. Whether fluorine-containing ionic liquids such as the type used in this study are specific for the reduction of fluorine complexes of refractory metals, is not for certain. To the best of the author’s knowledge, tantalum electrodeposition has only been performed in the same fluorine-containing ionic liquid as used in this
study. It could be suggested that tantalum salts are more soluble in fluorine containing ionic liquids and that fluorine facilitates the reduction of metallic tantalum. Furthermore, for the recovery of tantalum and niobium, the extraction method which has gained the most success in practice and which is used exclusively, consists in the extraction of an aqueous tantalum- and niobium- containing solution containing hydrofluoric acid and possibly sulphuric acid in high concentration. It is most likely that a high concentration of fluorine in ionic liquid is necessary for the separation effect. Therefore, it would be of interest to experiment with the electrodeposition of tantalum in other ionic liquids to examine the effect of fluorine on the reduction of tantalum.

Furthermore, it can be noticed while scanning the potential in the positive direction, the anodic scan crosses over the cathodic scan resulting in a current loop. In a study by El Abedin et al \(^{31}\), it was suggested that such current loop is typical of continuous nucleation processes. Furthermore, in order to understand how the current was behaving at the potentials where the cathodic peaks can be seen, potentiostatic polarization experiments were performed.

![Figure 21: Potentiostatic curve depicting the flow of current density through the ionic liquid at -2.4 V.](image-url)
Potentiostatic experiments were carried out at -2.5 V, -2.4 V, -2.3 V and -2.2 V, for 1 hour to observe the trend in current density. Figure 21 depicts the typical trend in current density obtained after 1 hour hold at -2.4 V (vs. Pt). After numerous potential holds ranging from -1.9 V (vs. Pt) to -2.5 V (vs. Pt), held between 30-60 minutes, some deposits were seen but they were not very adherent and uniform. The conditions at which an almost adherent layer was obtained although not completely uniform was at -2.2V (Vs. Pt) after a 40 minute hold. Since there were many variables involved such as different potentials and time, the strategic approach taken to obtain the best layer was as follows.

It is known that the longer the deposition process, the higher the probability of the depositing layer to flake or peel off the substrate. Based on this fact, since the layer deposited at -2.4 V (vs. Pt) was the most adherent layer of all conditions tested initially, an experiment was performed in which the potential at -2.2 V (vs. Pt) was held until the total charge was close to the amount of charge obtained during the -2.4 V (vs. Pt) potentiostatic experiment after 1 hour. This was performed to see if the layer at -2.2 V (vs. Pt) with similar charge would be more uniform and more adherent. As a result, the potentiostatic curves obtained at -2.4 V (vs. Pt) for 1 hour and the curve obtained at -2.2 V (vs. Pt) for approximately 40 minutes with a charge close to the one obtained at -2.4 V (vs. Pt) after 1 hour, are plotted in Figure 22.
Figure 22: Potentiostatic voltammetry obtained at -2.4 V (vs. Pt) for 1hr (lowest current density) and -2.2 V (vs. Pt) for ~40 minutes (highest current density).

As seen from Figure 22, there is an increase in current density going from -2.4 V (vs. Pt) to -2.2 V (vs. Pt). Although an increase in current density would be expected going from -2.2 V to -2.4 V, the reverse is seen when referring to the cyclic curve obtained in Figure 20. As can be seen from Figure 20, the current density is higher at -2.2 V than at -2.4 V which explains why a higher current density is seen for the potentiostatic hold at -2.2 V than at -2.4 V in Figure 22. Accordingly, the microstructures corresponding to the conditions in Figure 22 are shown and explained in the Microscopy and Analysis of Electrodeposits section.

4.5 Addition of NbF$_5$ and LiF in Purified (Dry) Ionic Liquid

The same procedures in the above tantalum experiments involving the addition of 0.25 M TaF$_5$ and 0.25 M LiF were followed to study the electrochemical behaviour of the addition of 0.25 M
NbF$_5$ and 0.25 M LiF to the ionic liquid. Since niobium has very similar properties as tantalum it was expected that niobium would behave similarly to tantalum in the ionic liquids.

![Cyclic voltammograms of ionic liquid containing 0.25 M NbF$_5$ and 0.25 M LiF recorded on Ni substrate at 100 °C. (Scan rate 5 mV/s vs. Pt).](image)

Figure 23: Cyclic voltammograms of ionic liquid containing 0.25 M NbF$_5$ and 0.25 M LiF recorded on Ni substrate at 100 °C. (Scan rate 5 mV/s vs. Pt).

Figure 23 shows the cyclic voltammetry scans of ionic liquid, upon the addition of 0.25 M NbF$_5$ to the ionic liquid containing 0.25 M LiF at 100 °C. The electrode potential was scanned from the open circuit potential in the negative direction at a scan rate of 5 mV/s. At 100 °C, it was observed that the reduction reactions occurred at relatively the same potentials as the tantalum reduction reactions, which was expected. However, the reduction current began to increase at a little less negative potential in the niobium experiments compared to the tantalum experiments. As in the tantalum experiments, it can again be noticed while scanning the potential in the positive direction that the anodic scan crosses over the cathodic scan resulting in a current loop, which was studied by El Abedin et al.\textsuperscript{31} to be typical for continuous nucleation. Furthermore, potentiostatic experiments were performed at various potentials in order to study current behaviour.
Since -2.2 V was the potential at which an almost uniform, thin layer of tantalum was obtained, the first potentiostatic experiment with NbF$_5$ began at -2.2 V for 1 hour. Figure 24 depicts the current density obtained after a 1 hour hold at -2.2 V (vs. Pt).

Figure 24: Potentiostatic curve depicting the flow of current through the ionic liquid containing 0.25 M NbF$_5$ and 0.25 M LiF, at -2.2 V.

In comparison to the current flow at -2.2 V in the tantalum experiments, the current flow is lower in the ionic liquid containing NbF$_5$, with a charge of -3.0 C/cm$^2$. This resulting lower current at -2.2 V explains why niobium was not deposited at this potential but did in the tantalum experiments at the same potential.

The next approach taken to obtain a deposit was to perform a potentiostatic hold at a less negative potential. A potential hold was performed at -1.9 V for 30 minutes as shown in Figure 25.
Figure 25: Potentiostatic curve depicting the flow of current through the ionic liquid containing 0.25 M NbF$_5$ and 0.25 M LiF, at -1.9 V.

The duration of hold was decreased since it is known that there is a higher probability of getting an adherent layer at a shorter potential hold time. Figure 25 shows the potentiostatic scan for a hold at -1.9 V for 30 minutes. It is under this potentiostatic condition that a thin film was observed as will be seen in the following section.

4.6 Microscopy and Analysis of Electrodeposits

Prior to examining the microstructures obtained, it is important to briefly discuss a few factors that have substantial influence on electrodeposits, their structure and their properties. One of the factors is the nature of the substrate upon which the plating occurs. In this present study involving tantalum and niobium deposition on nickel, the coating metal and substrate metal have
different crystal structures. Nickel has a face centered cubic (FCC) crystal structure, whereas tantalum has a body centered cubic crystal structure. The difference in crystal structures may have a large impact on the adhesiveness of the layer. In addition, prior cleaning or the cleanliness state of the substrate, also greatly influences the structure and adhesion of the deposit. All nickel samples were thoroughly cleaned prior to performing electrodeposition. Furthermore, electrochemical parameters and not substrate properties are the main deciding factors in the texture of deposits, specifically if the layer is 1µm or more. However, in deposits of lesser thickness, such as those in the present study as will be seen, the substrate plays an important role in texture of deposits. Moreover, texture of the deposit is also influenced by deposition current density, which is a function of bath parameters. Another factor that influences the electrodeposits is the inclusions or impurities that electroplated films almost always contain. In this study, impurities may have been hydroxides of the depositing metals caused from any residual water trapped in the liquid and/or from the actual impurities in the ionic liquid. Lastly, another parameter that must be considered in electrodeposition of materials is internal stresses. Electrodeposits are often laid down in a state of stress. Such a stress is named internal or residual because all or part of it remains in the deposit as will be seen in the following microstructures. Internal stresses can cause distortions, cracking of the deposit, loss of adhesion to the substrate and increased corrosion.

All the above factors that influence electrodeposition will be addressed through the analysis of the microstructures obtained at different potentials at the same temperature. The potentials at which microstructures of the deposited layers were studied are marked on the cyclic voltammetry shown in Figure 26. The layers were initially analyzed by scanning electron microscopy and energy-dispersive x-ray analysis to determine the elemental composition of the layers.
Figure 26: Cyclic voltammetry depicting the potentials at which the microstructures of the electrodepositions were studied in ([BMP]Tf$_2$N) containing 0.25 M TaF$_5$ and 0.25 M LiF. (Scan rate 5 mV/s vs. Pt).

4.6.1 Influence of Different Potentials on Tantalum Deposition

The deposits obtained potentiostatically at -2.5 V (vs. Pt) after 1 hour on nickel substrate in the employed ionic liquid containing 0.25 M TaF$_5$ and 0.25 M LiF appeared loosely adherent. As seen in Figure 27, the substrate was largely exposed with some island deposits scattered across the surface.
Figure 27: Microstructure of deposited layer at -2.5 V (vs. Pt) after 1 hour, on nickel substrate.

Since the deposits obtained at -2.5 V (vs. Pt) were not adherent, a less negative potential was applied. The deposits obtained potentiostatically at -2.4 V (vs. Pt) after 1 hour on nickel in the same solution appeared to be more adherent. Figure 28 a)-d) shows some micrographs of the resulting deposits at -2.4 V (vs. Pt). It is evident from Figure 28a) that the deposit is more adherent than the deposit obtained at -2.5 V (vs. Pt) at the same temperature. It is also seen through Figure 28c) that the deposited layer contains some stress cracks, which is not surprising as it is known that during the electrodeposition of metals, internal or residual stresses almost always appear. The stress can originate from intrinsic film stress and from interfacial stress between the deposit and the substrate, which may be attributed to some factors, such as coalescence of the crystallites, inclusion of foreign species, incorporation of evolved gases or generation of structural defects.
Figure 28a)-d): Microstructure of deposited layer at -2.4 V (vs. Pt) after 1 hour, on nickel substrate.
The accompanied EDX spectrum in Figure 29 reveals the elemental composition of the deposited layer obtained at -2.4 V (vs. Pt) after 1 hour. The deposits obtained contained elemental tantalum as well as oxygen, fluorine and sulphur. The presence of O, F and S is attributed to the remaining ionic liquid that was trapped between the layer and the electrode surface. However, it is important to note that although O and F are shown in the EDX spectrums by opening the window, EDX cannot fully detect the lightest elements, typically below Na. Therefore, although the open window option was used, O and F cannot be accurately quantified using this technique.

Figure 29: EDX spectrum taken from the deposit in the center of sample in Figure 28a.
Figure 30: EDX spectrum taken from the edge of sample where the substrate is exposed in Figure 28a.

Figure 30 shows the EDX spectrum obtained from the substrate. A comparison of the intensity peaks in each of the above two EDX spectra, indicates that a layer containing elemental tantalum was deposited onto the substrate and that the layer is clearly distinguishable from the substrate.

Potentiostatically deposited layers at -2.3 V (vs. Pt) after 1 hour were more adherent than at -2.4 V (vs. Pt) but were still not covering the substrate uniformly. However, although the layer did not uniformly cover the surface, the layer looked very dense. Scanning electron micrographs of the structures obtained at -2.3 V (vs. Pt) after 1 hour are shown in Figure 31.
Figure 31: Microstructures of deposited layer at -2.3 V (vs. Pt) after 1 hour, on nickel substrate.

The corresponding EDX spectra in Figure 32 and Figure 33 show the elemental compositions obtained from the layer deposited and from the nickel substrate, respectively. Again, the strong tantalum peaks in Figure 32 clearly indicate that a layer containing elemental tantalum was deposited. This layer is quite distinguishable from the substrate area shown in Figure 31. The corresponding EDX spectrum taken of the exposed substrate area is shown in Figure 33.
Figure 32: EDX spectrum taken from the deposited layer shown in Figure 31.

Figure 33: EDX spectrum taken from the exposed area on the substrate shown in Figure 31.
Evidently, the deposited layer obtained at -2.3 V also contains internal or residual stress-induced cracking as shown in Figure 34.

![Image of microstructure](image)

**Figure 34**: Microstructure of the deposited layer at -2.3 V (vs. Pt) after 1 hour, containing internal or residual stresses.

Since the deposits obtained at -2.3 V (vs. Pt) were not very uniform, a lower (absolute) voltage was used. The deposits obtained potentiostatically at -2.2 V (v. Pt) for approximately 40 minutes, with an overall charge equivalent to the charge obtained at -2.4 V (vs. Pt) after 1 hour, appeared to be more adherent. Visually, the deposit was black and appeared to be thick. Figure 35a)-d) shows SEM micrographs of the tantalum electrodeposit prepared potentiostatically at -2.2 V (vs. Pt) for 40 minutes. It is evident from Figure 35a) that the deposit is more adherent than the deposit obtained at -2.5 V (vs. Pt) at the same temperature. Moreover, EDX analysis reveals the formation of a layer containing some form of tantalum. It is also seen from Figure 35c) that the deposited layer contains internal or residual stresses.
Figure 35a-d): The deposited layer at -2.2 V (vs. Pt) after 40 minutes at 100 °C.
Based on the above tantalum results, it was observed that at the more negative potentials, the deposit is very porous, whereas at less negative potentials, a more uniform layer is formed. One may attribute this to the rate of deposition. If the deposition is too fast, F– may be trapped in the deposit leading to the formation of non-stoichiometric metal halide compounds. In summary, it was seen that at less negative potential and at the same temperature, the quality of the deposits remarkably improved.

4.6.2 Influence of Different Potentials on Niobium Deposition

The potentials used for tantalum deposition were also studied for niobium deposition. As niobium has similar properties to tantalum, the experiment conditions found for tantalum deposition were applied to the niobium deposition experiments. A potential of -2.2 V was held in purified ionic liquid containing 0.25 M NbF₅ and 0.25 M LiF for 1 hour, at 100 °C. Figure 24 depicts the potentiostatic voltammetry scan for the deposit obtained in Figure 36. The current density remained consistently in the range between -0.005 A·cm⁻² and -0.010 A·cm⁻². The corresponding EDX spectrum in Figure 37 depicts a strong intensity niobium peak with very low intensity nickel peaks.

![Figure 36: Microstructure of the deposited layer at -2.2 V (vs. Pt) after 1 hour.](image)
Further potentiostatic tests were performed at -1.9 V for 1 hour, giving the corresponding microstructures shown in Figure 38. The microstructures reveal a layer deposited on the surface although it is not very uniform. It can be clearly seen from these microstructures that there are areas in which the substrate is exposed.
Figure 38: Microstructures of the deposited layer at -1.9 V after 1 hour, at 100 °C.
To prevent the possibility of the very thin layer of deposit flaking off, EDX analysis was performed at 5 keV, a low enough voltage at which EDX was still able to be performed using a 2 nA probe current. However, as shown in the EDX spectrum there is no evidence of niobium detected. There are two suggestions for the absence of niobium detection since it can be clearly seen from Figure 38 that a form of layer was deposited.

**Figure 39:** Microstructure and the corresponding EDX spectrum of the layer deposited at -1.9 V for 1 hour in ionic liquid containing 0.25 M LiF and 0.25 M NbF₅.
The first suggestion could be that since the layer deposited in ionic liquid containing NbF$_5$ was very thin, it was not able to be detected in relation to the x-ray depth in EDX analysis. The second possibility could be that since the EDX spectrum was obtained from a spot analysis, it does not provide a good representation of whether or not niobium exists anywhere on the substrate.

### 4.6.3 Cross-Section Analysis of Tantalum Deposit

Cross-sections of the deposited layer were analyzed using scanning electron microscopy. The potentiostatic curve obtained at -2.2 V (vs. Pt) after 40 minutes is shown in Figure 40. The area under the curve is used in equation (1), in order to calculate the thickness of the deposited layer.

\[
\text{Figure 40: The area under the current density versus time plot is used in eqn. (1) to calculate the thickness of the deposit.}
\]

\[
t_{\text{layer}} = \frac{Z(Q)}{(\rho_{\text{Ta}})} \quad \cdots \quad (1)
\]

where, \(t_{\text{layer}}\) = thickness of deposited layer,
\(Z_{\text{Ta}}\) = electrochemical equivalent of Ta (3.75 x10$^{-4}$ g C$^{-1}$)
\(Q\) = total charge (-39.85 mC)
\(\rho_{\text{Ta}}\) = density of tantalum (16.65 g cm$^{-3}$)
Using equation (1), the thickness was calculated to be approximately 1µm thick on a sample size of 0.00785 cm². Moreover, an SEM micrograph in Figure 41 depicts the cross-sectional layer thickness measurements obtained. Upon deposition of the thin film, the film layer was embedded in epoxy in order to perform a cross-sectional examination of the layer. Consequently, as the epoxy on the deposited layer settled and dried, the thin layer peeled off the substrate, forming a gap in between the layer and the substrate as is seen in the cross-sectional micrograph in Figure 41. The layer peeling off could suggest that the forces of adhesion were stronger between the atoms of the layer and the epoxy than between the layer and the substrate. The overall average of the thickness measurements from this micrograph was calculated to be 1µm, which is in approximate agreement with the calculated thickness from the potentiostatic curve in Figure 40.

![Cross-section of deposited layer at -2.2 V after 40 minutes, showing thickness measurements.](image)

Furthermore, the EDX spectrum in Figure 42 shows high intensity peaks of tantalum with lower intensity peaks of nickel. As mentioned previously, O and F cannot be accurately quantified using EDX however it can be seen that this layer contains some form of tantalum.
Figure 42: EDX spectrum obtained from the cross-sectional layer shown in Figure 41.

Although all the above EDX spectra depict strong peaks of elemental tantalum, the results from using scanning electron microscopy technique are alone inconclusive for this study since it only provides elemental information. Also, when relating elemental composition of a layer provided by the EDX technique, it is important to consider the thickness of the deposits to the analysis depth of EDX. The layers deposited in ionic liquid containing TaF₅ and in ionic liquid containing NbF₅, were calculated to be roughly 1 µm and 0.3 µm thick, respectively. On average, the EDX analysis depth is roughly between 1-2 µm, which means that the layers deposited are thinner than the depth of analysis and which is another reason why EDX analysis is inconclusive. Therefore, x-ray photoelectron spectroscopy (XPS) analysis was performed on the above deposits to obtain more information about the deposited layer.
4.7 XPS Analysis of Tantalum Deposition

The chemical composition and binding states of the deposited films were studied using the XPS depth profiling analysis technique. Figure 43 depicts the area of the sample that was analyzed, indicated by the black dot in the center. The bigger circles around it are scale bars for XPS optical viewing such that the x-ray point is then adjusted to target the center black dot. As can be seen from Figure 43, the deposited layer was not uniform and the thickness of the layer was unknown. Since tantalum is well known to form a spontaneous oxide layer, the sample was sputtered through to reach to the deposited coating underneath the oxide layer. XPS measurements were made during sputter removal of the oxide layer through to the tantalum layer.

Figure 43: The area of the sample analyzed by XPS depicted by the black dot in the center. The bigger circles around it are used for XPS optical viewing in order to adjust the x-ray to target the black dot.

Prior to sputtering, the survey spectrum shown in Figure 44 was obtained in order to determine what was deposited at the surface. Evidently, strong peaks of fluorine (19.7 atomic %), oxygen (22.3 atomic %) and chlorine (56.6 atomic %) were found. The carbon and oxygen peaks are attributed to the thin tantalum oxide film that is formed on the outermost surface of the tantalum coating as a result of natural passivation of tantalum in the atmosphere, as expected. The fluorine peak can be attributed to several sources such as from the ionic liquid itself, from LiF and/or from TaF₅. In addition, for the sake of analyzing the elemental characteristics of the coating obtained which is shown above as not being fully adherent, the surface of the sample was only rinsed in de-ionized water to remove any residual ionic liquid as much as possible, in order to prevent the
loosely adherent layer from peeling off the substrate. The cleaning process involved rinsing with de-ionized water, wetting in methanol and re-rinsing with de-ionized water. As a result of not applying a more aggressive cleaning procedure, which would have involved ultrasonic cleaning, it is reasonable to attribute the fluorine peak to the residual ionic liquid trapped in between the coating and the substrate that was not removed. Consequently, if ionic liquid is trapped in between the layer and the substrate, other elements contained in the ionic liquid such as lithium should be seen but since lithium has a very low XPS sensitivity factor, another technique such as secondary ion mass spectrometry (SIMS) is required as it would be more effective in detecting its presence. Furthermore, the Ta4f peak (1.5 atomic %) is significantly weak compared to the oxygen peak, which is a direct result of the oxide layer that spontaneously forms on tantalum.

Figure 44: XPS survey spectrum of nickel sample coated with tantalum before sputtering.

Figure 45 shows the XPS survey spectrum after 120 seconds argon sputtering. After 120 seconds sputtering, the carbon peak (22.3 atomic. %) and oxygen peak (12.6 atomic. %) significantly
decreased in intensity. It could be suggested that the significant decrease in the oxygen peak intensity is due to the transition from the oxide layer to the underlying metal 59. Overall, the fluorine peak (55.9 atomic. %) is seen to remain significantly high in intensity compared to the other peaks shown, although the intensity of fluorine tends to decrease between sputtering times. The overall high intensity of fluorine is most likely due to the ionic liquid trapped underneath the tantalum coating, between the coating and the substrate since the layer is not completely adherent. It was also observed that the peaks belonging to various tantalum species, Ta4s, Ta4p3/2, Ta4d, Ta5s and Ta4f become more distinctive after 120 seconds sputtering as shown in Figure 45. Although weak in intensity, the peaks are more evident compared to the previous spectrum obtained before sputtering, indicating the sputtering is approaching a form of tantalum layer underneath the oxide layer.

![Survey](image)

Figure 45: XPS survey spectrum of nickel sample coated with tantalum after 120 seconds sputtering.
Figure 46 shows the survey spectrum after the sample was sputtered for 300 seconds. Although the fluorine peak (53 at.%) decreased from 120 seconds sputtering, it remains high, while the carbon peak (19.6 at.%), oxygen peak (13.1 at.%) decreased in intensity as well. This indicates that there still exists fluorine trapped in between the substrate and the coating. Furthermore, there is an increase in Ta4s, Ta4p3/2, Ta4d, Ta5s and Ta4f peaks.

Figure 46: XPS survey spectrum of nickel sample coated with tantalum after 300 seconds sputtering.

In order to determine if a pure metallic tantalum layer exists further down under the layer, a high resolution spectrum of tantalum was taken as shown in Figure 47 with increased sputtering, indicating the in-depth chemical structure of the coating. Before sputtering, the Ta4f peaks were centered at 27.8 eV and 25.6 eV, respectively, which correspond to the binding energies for (+5) oxidation states. Although the binding energies are not the same, the peak at 25.6 eV is close to the
26.3 eV line position, which may suggest a tantalum chemical state of Ta$_2$O$_5$. After sputter removal of the Ta$_2$O$_5$, the Ta4f doublet changed its typical form and was found gradually broadened and shifted in energy. The shift of the Ta4f doublet toward a higher binding energy after 1 minute of sputtering is presumably due to increased charging under ion bombardment. After 3 minutes, some of the Ta4f peak was still in the Ta$_2$O$_5$ chemical state, yet the peak shifted to further lower binding energies. This shifting to lower binding energies continued with further sputtering, indicating the gradual absence of oxides and an increase in tantalum metal. Accordingly, after 40 minutes of sputtering, the Ta4f photoelectron spectrum was shown to be consistent with contributions of metallic tantalum. The XPS spectrums observed are a weighted sum of all the contributions obtained from the analysis volume.

Figure 47: XPS depth profile showing the shift in binding energies of the high resolution Ta4f photoelectron peaks with sputtering time to determine if there is an underlying layer of metallic tantalum.
Moreover, the 4f7/2 peak appeared at a binding energy of 22 eV and the 4f7/2 peak appeared at 24 eV, which is consistent with the standard metallic tantalum spectrum shown in Figure 48. As a result, contributions of metallic tantalum are seen after 40 minutes of sputtering. Furthermore, based upon approximations from the experimental conditions used in the experiments, calculations suggest an estimated erosion rate of ~ 0.15 nm s⁻¹. Evidently, the material’s density, composition and structure all play a role in modifying this value. All that can be stated based on this information is that the estimated erosion rate becomes more accurate when moving from the oxide layer to pure tantalum. In addition, since the sample was not sputtered entirely through to the nickel substrate, it was difficult to estimate, based on the XPS depth profiling results given in Figure 47 and the estimated erosion rate, the actual thickness of the tantalum layer on the sample analyzed. However, given the estimated erosion rate, one could only estimate that the layer consistent with contributions of metallic tantalum was at least 0.315 µm thick, since relatively pure tantalum was reached between 300 seconds and 2400 seconds of sputtering. Overall, it is evident that with increasing sputtering time, composition of the coating evolves from Ta₂O₅ to contributions of metallic tantalum.
4.8 XRD Analysis of Tantalum Deposition

In addition to the XPS results showing the presence of metallic tantalum peaks from the deposited layer, x-ray diffraction patterns were acquired from the sample analyzed by XPS, to determine if the layer obtained at -2.2 V after 40 minutes was crystalline. As a result, the XRD pattern in Figure 49 depicts the characteristic signals for crystalline tantalum, although the peaks are of very low intensity compared to the peaks from the nickel substrate. The nickel peaks are also labelled as shown however the peak located at approximately 78° 2θ is unknown as there was no information in the database that would be able to identify it. The dividing double lines depicted in the figure signify that in between 30-42° and 56-73° 2θ, the graph was magnified in order to distinguish the labelled tantalum peaks.

With respect to the amount of tantalum that is expected to be transmitted through the material, the following Beer-Lambert equation can be used to relate the attenuation coefficient of tantalum when using a Cu K-alpha source, to the transmitted intensity through the layer:

\[ I_T = I_0 e^{-\alpha \chi} \]  \hspace{1cm} (2)

where,
- \( I_T = \) transmitted intensity through a layer of material
- \( \chi = \) material thickness
- \( I_0 = \) incident intensity
- \( \alpha = \) attenuation coefficient (the extent to which the intensity of the energy beam is reduced as it passes through a specific material)

Using the attenuation coefficient of tantalum, 68 cm\(^{-1}\), obtained from the NIST database and approximating the depth of the deposited layer to be 1 µm, \( I_T/I_0 \) is calculated to be roughly 17%. Although significant, it is much lower than 50%, which suggests that the attenuation coefficient of tantalum may partially be the reason why the peaks are of very low intensity, suggesting that the electrodeposits obtained at -2.2 V (vs. Pt) after 40 minutes are crystalline.
Figure 49: XRD pattern of the deposited layer on a Ni sample collected on the D8 GADDS microdiffraction system with beam placement positioned at center of sample as shown by inset.

Moreover, since these peaks were of very low intensity and to improve the crystallinity of the electrodeposits, the sample was annealed at 800 °C under vacuum for 5 hours, and then reinvestigated by XRD. It has been shown in literature that annealing tends to improve the crystallinity of the electrodeposits.°
Figure 50: XRD pattern of deposited layer on Ni sample collected on D5000 diffraction system after annealing at 800 °C for 5 hours. The XRD pattern consists of strong Ni peaks, weak Ta peaks and unidentified peaks which may be attributed to oxides.

Figure 50 shows the labelled α-Ta and β-Ta peaks and shows other forms of oxides, which have not been identified. It is predicted that the shift in peaks could be due to the surface of the sample not being flat enough to be aligned to the diffraction surface. In addition, the corresponding tantalum peaks were not as high in intensity as would be expected after the stated annealing conditions, but it is not surprising since a low vacuum (of approximately 1 torr) was used. A high vacuum furnace was not available during the time of these experiments. Accordingly, one or a combination of the following two suggestions can be made. Either the tantalum peaks are of low intensity indicating that the tantalum layer was extremely thin relative to the bulk substrate material or the annealing was performed at such low vacuum causing oxides to form on the layer deposited. Although the unlabelled peaks in Figure 50 were not analyzed, they may be a result of oxides formed.
5.0 SUMMARY and CONCLUSIONS

Based on the objectives introduced at the beginning of this thesis, several conclusions can be drawn from this study. The pre-electrolysis process implemented in this study was shown to be effective in removing impurities from the as-received ionic liquid. Accordingly, current density was shown to gradually stabilize in time through the pre-electrolysis experiments by using a large surface area copper cathode and by creating a two compartment cell to separate the impurities between the as-received and the purified ionic liquid.

In addition, the purified ionic liquid was used to deposit a 1 µm thin film of tantalum on nickel in the ionic liquid, 1-butyl-1-methyl-pyrrolidinium bis(tri-fluoromethylsulfonyl)imide ([BMP]Tf₂N) at -2.2 V after 40 minutes, at 100 °C. Preliminary niobium deposition experiments showed that a thin layer of niobium deposit could be achieved at around a potential between -2.2 V and -1.9 V under 1 hour, however further electrochemical experiments are required to improve the electrochemical parameters in order for a uniform, adherent layer of niobium to be obtained.

Accordingly, the x-ray photoelectron spectroscopy surveys and high resolution spectra taken from a small area on the tantalum deposited layer show a thin oxide film of Ta₂O₅ on the outermost layer and a layer underneath which is suggested to be consistent with contributions of metallic tantalum. High amounts of fluorine were also detected from the surveys which may be attributed to trapped fluorine in between the layer and the substrate. In addition, x-ray diffraction patterns of the electrodeposit obtained potentiostatically at -2.2 V in ([BMP]Tf₂N) containing 0.25 M TaF₅ and 0.25 M LiF at 100°C, show low intensity characteristic peaks of crystalline tantalum. Annealing treatments at 800 °C under an extremely low vacuum for 5 hours to improve the crystallinity of the electrodeposits were not found to provide higher intensity peaks, which was largely attributed to the insufficient vacuum applied.
6.0 FUTURE WORK

The present work has shown that it is possible to deposit a layer of tantalum and niobium from an ionic liquid which underwent a specialized pre-electrolysis process. However, further work is recommended in improving the adherence and uniformity of the tantalum and niobium layers on the nickel substrate as well as determining the ideal electrochemical parameters for depositing niobium on nickel. Upon deposition of a fully adherent layer of metallic tantalum, annealing treatments under high vacuum should be performed to study the effect on intensity of the tantalum peaks. Furthermore, hardness and adhesion tests on the tantalum and niobium deposited samples are required to investigate their properties. In addition, immersion and corrosion tests should be performed on the tantalum and niobium deposited samples to test their properties. It would also be of interest to build a new reference electrode that would prove to be completely stable in the ionic liquid used in this study.
Figure A: XRD pattern of annealed sample taken from the D8 GADDS diffractometer with the respective d-values of each peak.
Table A: List of d-values for the unlabelled peaks in Figure A.

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REFERENCES


