The Electrodeposition of Metallic Molybdenum Thin-Film Coatings, from Aqueous Electrolytes Containing Molybdate Ions

by

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Abstract

Electrodeposition of metallic molybdenum from aqueous electrolyte has in most cases previously yielded poor results due to the extremely high rate of the secondary hydrogen evolution reaction occurring at the cathode. This results in low current efficiencies and thin brittle films. The use of a highly concentrated aqueous-acetate based electrolyte containing molybdate ions has been used to deposit thick (~50 µm) adhered, mirror like metallic molybdenum coatings. Plating variables were investigated to determine the optimum deposition conditions; it was seen that current density was the most influential factor for the successful deposition of the refractory metal. The coating surface was analysed using SEM and EDX. XRD analysis confirmed the deposits were amorphous in nature with broad peaks in the (110) orientation.

The deposition mechanisms were studied through electrochemical techniques such as PDP and CV. It was concluded that metallic molybdenum is deposited in a two-step reduction process, with the formation of an intermediate coating of molybdenum oxide, requiring hydrogen gas to fully reduce. Corrosion studies have shown the coatings stability in a chlorinated environment however active uniform corrosion in alkaline conditions resulted in film failure. Exposure to strong acidic conditions result in oxidation and delamination of the coating.

Up-scaling of the process was seen to be successful and large deposits of well adhered and uniform metallic molybdenum were formed under high applied currents.
Preface

I am responsible for designing the experimental process described in this thesis, conducting all electrochemical tests, surface characterization, and analysis of results. Professor Edouard Asselin supervised the progress of the research, providing support throughout.
Table of Contents

Abstract................................................................................................................................................. ii
Preface................................................................................................................................................... iii
Table of Contents .................................................................................................................................... iv
List of Figures ......................................................................................................................................... vii
List of Symbols ....................................................................................................................................... ix
List of Abbreviations ............................................................................................................................... x
Acknowledgements ................................................................................................................................. xi

Chapter 1 : Introduction ......................................................................................................................... 1

Chapter 2 : Literature Review ................................................................................................................ 4
  2.1 Properties of Molybdenum.................................................................................................................. 4
  2.2 Coatings ........................................................................................................................................... 6
  2.3 Thermal Spraying ............................................................................................................................. 8
  2.4 Chemical Vapour Deposition, CVD, and Physical Vapour Deposition, PVD ......................... 9
  2.5 Theory of Electrodeposition ........................................................................................................... 11
  2.6 Electrodeposition via Molten Salt and Ionic liquid Baths.............................................................. 14
  2.7 Co-Electrodeposition of Mo-Ni Alloys from Aqueous Based Solutions....................................... 15
  2.8 Cathode Electrochemistry .............................................................................................................. 19
  2.9 Electrodeposition via Acetate Based Baths................................................................................... 23
  2.10 Deposition of Metallic Molybdenum from an Aqueous Acetate Electrolyte ............................ 27
  2.11 The Effects of Thiourea on Cathode Reactions........................................................................... 28
6.1 Potentiodynamic Polarization .................................................................................. 81
6.2 Cyclic Voltammetry .................................................................................................. 87
6.3 Potentiodynamic Polarization of coating in 3.5 wt% NaCl solution ......................... 88
6.4 Potentiodynamic Polarization in Alkaline Environment ........................................ 90
6.5 Potentiodynamic Polarization in Highly Acidic Environment .............................. 92

Chapter 7: Up-Scaling of the Deposition Process ....................................................... 93

Chapter 8 : Conclusion ................................................................................................. 99
  8.1 Summary of Results ............................................................................................... 99
  8.2 Significance ............................................................................................................ 101
  8.3 Strengths and Limitations ..................................................................................... 101
  8.4 Future Work and Applications of Research ....................................................... 102

References ..................................................................................................................... 104
List of Figures

Figure 4.1: Schematic of resin mounted copper electrode..................................................... 38

Figure 4.2: A schematic flow diagram of experimental procedure........................................ 43

Figure 4.3: Schematic of single cell experimental setup, using a stirred water jacketed cell; Cu cathode and Pt counter electrode 45 mm apart; saturated calomel reference electrode........... 47

Figure 5.1: Effect of electrolyte pH on coating phase and uniformity. Decreasing pH at constant 35 °C and 0.4 Acm⁻², decreasing pH from left to right, A. pH 7.5; B. pH 7.2; C. pH 6.8; D. pH 6.5 and E. pH 6.2. ................................................................. 53

Figure 5.2: Schematic of sample coating results if current density is too low, resulting in metallic Mo coating of outer regions, with a central band of Mo oxide/hydroxide, and an uncoated center. ............................................................................................ 60

Figure 5.3: Effect of applied current density on deposit on a Cu cathode. A, 0.2 A cm⁻²; B, 0.3 A cm⁻²; C, 0.4 A cm⁻² and D, 0.5 A cm⁻². ......................................................................................................................... 61

Figure 5.4: Optical microscopy images of coatings prepared over different deposition times. Images taken at x50 magnification, with a blue filter applied................................................................. 65

Figure 5.5: Scanning Electron Microscopy images of molybdenum film growth after increasing deposition periods; 1 hour, 4 hours and 10 hours................................................................. 66

Figure 5.6: Scanning Electron Microscopy image of a coating produced over a period of 10 hours. Smooth particulate growth can be seen in A, around vent like surface holes. Cross-sectional imaging shows internal cracking and the vent system, B......................................................... 68

Figure 5.7: Scanning Electron Microscopy image of film particulate after a 10 hour coating period. High level of residual stress resulting in complete fracture of particle. ...................... 69

Figure 5.8: Schematic of film growth over time with comparison to cross-sectional scanning electron microscopy images of coatings; 1. 1 hour; 2. 4 hours; 3. 10 hours............... 71

Figure 5.9: Scanning Electron Microscopy images of molybdenum films created on different surface roughness copper substrates, under the same deposition conditions........... 75

Figure 5.10: X-ray diffraction spectroscopy pattern of Mo coatings on copper. (A) Copper S ubstrate. (B) 10 hour Mo deposition, (C) 4 hour Mo deposition and (D) 2 hour Mo deposition. 77
Figure 5.11: Scanning electron microscopy images of coatings deposited with electrolytes containing 0.01 g/l thiourea. Deposition was performed via potentiodynamic polarization from +0.250 vs. OCP to – 4V vs SCE at a scan rate of 0.166 mVs⁻¹ .......................................................... 79

Figure 6.1: Cathodic potentiodynamic polarization scans of electrolyte with (blue) and without (red), molybdate ions present. Scans ran +0.250 vs OCP to -4.00 V vs SCE ........................................ 81

Figure 6.2: Cyclic Voltammetry curve of deposition reduction reactions in molybdate containing electrolyte. Scan rate of 50 mVs⁻¹ .......................................................... 87

Figure 6.3: Potentiodynamic polarization of molybdenum coating deposited on copper, compared to the performance of pure copper and pure molybdenum. Performed in a 3.5% NaCl solution, at 25 °C. Scanned from -0.250 V SCE to +0.400 V vs SCE with respect to OCP........ 88

Figure 6.4: Potentiodynamic polarization of pure copper and pure molybdenum. Performed in a 1% NaOH solution, at 25 °C. Scanned from -0.250 V SCE to +0.400 V vs SCE with respect to OCP.......................................................... 90

Figure 6.5: Potential- pH equilibrium diagram for the system molybdenum-water, at 25 °C. Pourbaix [1966]. ........................................................................................................ 91

Figure 7.1: HDPE sample holder with an uncoated copper cathode, and two molybdenum coatings deposited over a 5 minute period............................................................. 96
List of Symbols

$B$ – Average crystal size

$\delta$ – Film thickness

$\eta$ – Overpotential

$E$ – Cell Potential

$E^0$ – Standard chemical potential

$E_{eq}$ – Equilibrium potential

$F$ – Faraday’s constant

$i$ – Current density

$I$ – Applied current

$\lambda$ – X-ray wavelength

$m$ – Moles of metal

$M_w$ – Atomic weight of metal

$N_a$ – Avagadro’s Number

$R$ – Resistance of System

$Q$ – Charge

$W$ – Mass of deposited metal
List of Abbreviations

BCC – Body Centered Cubic
CV – Cyclic Voltammetry
CVD – Chemical Vapour Deposition
FCC – Face Centered Cubic
FWHM - Full Width, Half Maximum
HAR - Hydrogen Absorption Reactions,
HDPE – High Density Poly Ethylene
HER – Hydrogen Evolution Reaction
OER – Oxygen Evolution Reaction
OCP – Open Circuit Potential
OM – Optical Microscopy
ORR – Oxygen Reduction Reaction
PVD – Physical Vapour Deposition
PDP – Potentiodynamic Polarization
SEM – Scanning Electron Microscope
Wt% - Weight %
XRD – X-ray Diffraction
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Chapter 1 : Introduction

Molybdenum is used in a wide range of industries due to its impressive material properties. Molybdenum’s high level of physical and chemical stability comes from its core BCC crystal structure that provides its structure immense resistance to thermal degradation. The benefit of molybdenum’s high level of hardness, wear and corrosion resistance are harnessed through alloying with other metals; engineering and stainless steels, and super alloys, accounts for around 86% of the metal’s consumption, CRU [2011].

Molybdenum has a large number of oxidation states with two stable oxides of MoO₂ and MoO₃. These have been investigated for their electrocatalytic properties for application in photoelectrics, such as photovoltaic cells and photocatalytic coatings, as well as gas sensors and the next generation of batteries [Yang [2008]; Histia [1992]; Lee [1993]; Dukstiene [2013]; Jubault [2011]].

Molybdenum is increasingly being investigated for its interesting physical and electrochemical properties, commonly exploited through the use of coatings and thin films. Due to its high melting temperature and electrochemical stability these have previously been difficult to manufacture. Thermal spraying is a simplistic method to deposit thick coatings of molybdenum, but low spray control results in poor control over morphology and uniformity. Chemical and physical vapour deposition, CVD and PVD, has been used to grow metallic thin films, but with high operating costs and reagents these techniques have not gained traction in industry.
Electrodeposition has a number of benefits over the previously mentioned techniques. Coatings can be grown with a high level of control and precision through tuning of the deposition conditions. A wide range of conductive substrates can be used and deposition does not require line of sight unlike thermal spraying. Molybdenum has been successfully deposited with the use of molten salt baths. Although due to the operating temperatures of 800 - 1200 °C and requirement for inert bath atmospheres due to air sensitive reagents, molten salt baths are extremely high cost and impractical.

Historically refractory metals have proven to be difficult to electrodeposit using aqueous electrolytes. High overpotential and the resultant elevated rate of parallel competing hydrogen evolution reaction occurring simultaneously on the cathode results in thin, brittle and non-uniform deposits, formed at poor current efficiencies. However metallic molybdenum has been observed to be successfully deposited through highly concentrated acetate based aqueous electrolytes; allowing the formation of metallic molybdenum coatings at near room temperature and neutral pH, without the need for high cost bath conditions or reagents.

The main objective of this study was to investigate the electrodeposition of metallic molybdenum coatings from an aqueous bath. The bath condition variables were studied in an attempt to optimise the coating process and film properties. Particular emphasis was placed on the reduction reactions occurring in the solution, driving film growth.

Chapter 2 is a literature review that discusses the unique properties of molybdenum and its coatings. A review of molybdenum deposition and co-deposition with other metals was
carried out to gain an understanding of the metal’s reduction in aqueous solutions, and the
difficulties that it faces. The produced coating’s unique properties were also presented. Research
objectives will be presented in Chapter 3. Chapter 4 details the experimental approach and
procedure used in the investigation.

Chapter 5 contains the main discussion of the deposition process, with the goal to
optimise the coating created. The results are discussed at each stage, with the proposed effects of
each condition change. Chapter 6 presents a more in-depth investigation of reduction reactions
occurring during the deposition of the metallic film. Through the use of potentiodynamic
polarization and supporting techniques, a mechanism for film growth is offered. Also included in
this chapter are the corrosion testing results of the film, in a number of different damaging
environments. The results of up-scaling the deposition process are presented in Chapter 7.
Finally, conclusions and future recommendations are presented in Chapters 8 and 9, respectively.
Chapter 2 : Literature Review

2.1 Properties of Molybdenum

Molybdenum is a material that has many desirable properties. It is a group 6 transition metal, commonly referred to as a refractory metal. A BCC crystal structure that remains unchanged in orientation from heating to melting, which occurs at a temperature of 2610 °C Tietz [1965]. This structural stability gives molybdenum high heat resistant properties, such as resistance to creep, thermal shock, and thermal degradation, as well as an elevated level of hardness and wear resistance.

The attractive properties of molybdenum are commonly harnessed through alloying with other elements; 86 % of the world’s molybdenum supply is used in the production of stainless and engineering steels, which contain 1 – 4 % molybdenum. As molybdenum is a larger sized atomic element, its addition to the smaller atom lattice present in steel has the effect of solid solution hardening. Molybdenum is also known as a ferrite former, inducing a shift in the steel lattice to BCC, rather than the FCC lattice present in austenitic steel. This lattice shift has a strong effect on the mechanical properties of the alloy, also making it magnetic and greatly increasing the alloy’s resistance to stress corrosion cracking. [Yun [2012]; Bond [1969]]

Molybdenum is added to stainless steel primarily to increase its corrosion resistance, particularly pitting resistance, Galvele [1978]. It is the chromium atoms present in the steel lattice that provide fundamental corrosion resistance however studies have shown that it is the
addition of molybdenum that greatly increases this basic resistance due to its ability to create a more uniform grain structure and distribution of chromium in the lattice, reducing the number of pitting sites present that reduce the effectiveness of the protective passive film. Molybdenum content in steel has been shown to greatly increase the metal’s resistance to hydrogen embrittlement and sulphide stress cracking, Mesquita [2012]

Hydrogen diffusion is a major issue in the petroleum industry particularly due to the elevated operating temperatures. The diffused hydrogen can react with the steel’s carbon forming methane, resulting in the decarbonisation of the alloy, which in turn increases the internal stress due to gas build up, resulting in increased stress corrosion cracking. The addition of 0.5 - 1 % Mo results in the increased formation of carbide complexes at grain boundaries, resulting in the decrease of grain boundary energies, which is seen to reduce the effect of internal stress build up Davenport [1971].

With a density of 10188 kg m⁻³, molybdenum is around 200 kg m⁻³ heavier than steel however its mechanical properties far exceed that of steel and most other metals. Due to its higher density, and far higher processing cost and scarcity it is not a feasible bulk metal to use in common manufacturing situations however its surface properties makes it a desirable material, making it an ideal coating.
2.2 Coatings

There are a plethora of materials available to manufacture coatings from, whether they are polymer, ceramic or metal based, their purpose is usually always to provide decorative or functional substrate coverage. The most common use of functional coatings is to protect an underlying substrate from attacks from the harmful external environment that it is used in, whether it be wear, erosion, oxidation or corrosion. Many metals are not thermodynamically stable in an open environment and so if left unhindered, return to their natural lower Gibbs free energy states as oxides and various other corrosion products, known as electrochemical degradation. This natural degradation of materials has an incredible financial cost; repair, maintenance and replacement of materials and parts is estimated to cost a staggering $2.2 trillion USD, 3 % of the worlds GDP, annually, Hays [2010]. Corrosion leads to major health and environmental risks, from structural support and public bridge failures to pipeline spills. Degradation can come in many forms, the greatest being caused by chemical and mechanical corrosion.

Protective coatings allow the utilization of material for their strengths, regardless of the environment they will be used in, forming a composite product with the benefits of both material properties. This results in the lifetime of the bulk material being extended, reducing the cost of the replacement. It also allows thin layers of expensive materials to be exposed on a cheaper bulk substrate, for example the use of platinum in catalysts.
Steel is the most commonly used metal, however to make it corrosion resistant it requires the addition on expensive alloying elements which cannot always be feasible on large scales, such as bridges and pipelines. Instead base steel can be used in an open environment once given a protective coating, exploiting its high strength properties and low cost, while staying relatively chemically unreactive. The choice of coating material is selected on a number of factors, the largest being if it fulfills the purpose of being protective in operating conditions, and if so, is it feasible for the size and scale of the project. Coatings stability over time also needs to be considered, how long will the layer keep its integrity and remain protective. Coating-substrate adhesion is an important factor for the effective lifetime of a coating.

Coatings can also provide functional properties other than corrosion resistance. They can control the surface conductivity, making a substrate a conductor or non-conductor, layered and doped to form transistors, the foundation of our digital world. They can increase wear resistance and form solid self-lubricating coatings, for harsh environments not suitable for oils, such as MoS$_2$, Sliney [1982]. Coating surface activity and chemistry can be manipulated to facilitate and catalyse reactions through the choice of surface materials and morphology, forming the basis of commercial and industrial catalysts. Molybdenum oxide catalysts are used in the desulfurization of hydrocarbons, the coatings react with the sulfur compounds, forming molybdenum sulfide compounds, removing the harmful impurities from the petroleum products, Riaz [1994].

Surface engineering has evolved further to created self-cleaning glass and paint, with the incorporation of photocatalytic TiO$_2$ particles and form hydrophobic, water and dirt shedding surfaces, reducing the cost of cleaning, Hashimoto [2005]. Coating engineering is a broad field
but serves a similar purpose, to increase product efficiency, whether that is through energy savings, increasing part service life or reducing waste emissions.

2.3 Thermal Spraying

There are many techniques for the preparation of coatings. They greatly depend on the coatings requirements, material and the substrate it will cover. Molybdenum films can be prepared through a number of methods, however the most common technique is via thermal spraying. Molybdenum in the form of wire, powder or rods, is melted by a powerful heat source. This molten metal is then accelerated towards and then deposited on the desired substrate in a spray and splatter method. The heat source can be supplied in a number of methods, but is usually either electrical or chemical. A higher quality coating is observed when substrates are preheated. However with a low temperatures set at 115 °C and high as much as 465 °C, this technique is very limited to the location it can be carried out in and what substrate can be sprayed. [Jiang [1999]; Sampath [2003]; Vaidya [2005]]. Sampath [2003] saw that at high temperature substrates, the internal stress of the deposited film changed from tensile to compressive, which in a similar manner to shot peening, increased the fracture resistance of the sprayed coating. A decrease in coating porosity is also observed when spraying onto high temperature substrates.

The benefit of thermal spraying is that thick coatings can be built up with relative ease, especially when plasma assisted. Spraying metallic molybdenum due to the high temperatures required to melt the refractory metal can produce oxides that form within the coating. These
oxides can be beneficial for increasing film hardness and reducing wear. However if a pure metallic molybdenum film is required, it can cause complications. Plasma spraying can be used to deposit high thickness coatings up to 100 μm, in a relatively short period of time, with minimal surface preparation required [ASM Thermal Spray Society- Molybdenum Plasma Coatings].

There are some obvious limitations to thermal spraying. Due to the high operating temperatures, the substrate material is limited to higher T\textsubscript{m} materials. Spraying of steel substrates exhibit strong film adherence after limited surface cleaning, however other substrate materials can require the pre-treatment of a bond coating of Ni-Al. Precise control of thermal spraying can be difficult on smaller sized surfaces, making coating morphology hard to regulate. To reduce porosity and oxide inclusions, it is advisable to spray in a vacuum or inert environment, making this a higher cost technique.

2.4 Chemical Vapour Deposition, CVD, and Physical Vapour Deposition, PVD.

Chemical Vapour Deposition, CVD and Physical Vapour Deposition, PVD, are also promising techniques capable of depositing molybdenum and molybdenum alloy coatings. These techniques enable the deposition of most materials, independent of their melting temperatures and reactivity. CVD requires high operating temperatures and pressures which can limit the substrate material and size. Fukutomi [1975] reduced molybdenum pentachloride vapour with hydrogen at 750 °C and 45.5 MPa, depositing 20 - 40 μm films on vanadium samples. Due to the hydrogen rich reducing environment that the films were grown in, they required a post-process
annealing at 500 °C to remove absorbed hydrogen, however Fukutomi [1975] observed a decrease in coating ductility after this heat treatment.

A benefit of CVD and PVD is their ability to coat complex shapes, rather than line-of-sight deposition seen with the use of thermal spraying. This has allowed the coating of intricate shapes and hollow substrates, Gesheva [1993]. Using high pressure PVD, molybdenum films can be deposited into a porous substrates; Weigert [2005] attempted to coat a porous carbon foam substrate with a thin molybdenum film for application as an electrocatalyst. Using PVD’s ability to evenly coat inside a pore structure, nano films of molybdenum were deposited inside the carbon foam features. The coated foam was annealed at 500 °C to react the molybdenum with the carbon substrate to form a high surface area carbide coating, for use as a catalyst.

Harnessing molybdenum’s high refractory nature and its thermal stability, Gurev [1976] and Carver [1978], produced highly reflective thin films via CVD for use in photo-thermal solar convertors, high temperature solar mirrors. Molybdenum is an ideal candidate for infra-red mirrors due to its resistance to thermal shock; most noble metals were seen to degrade and loose reflectiveness under the 500+ °C operating temperatures, greatly reducing their IR reflecting efficiency. CVD deposition operating at atmospheric pressure and 400 °C resulted in the formation of mirror finish films coatings in 1 hour; high temperature post-deposition annealing is required.
CVD and PVD allow semi-continuous deposition on complex surfaces, however these methods are limited by high operating temperatures, expensive reagents, impurity sensitive atmospheres and high tooling costs.

2.5 Theory of Electrodeposition

Electrodeposition is the electrochemical reduction of ions in solution, to produce metal, alloys, ceramic or polymer coatings upon a conductive surface by an electric current [ASTM Int. B374-96 [2003]]. Positively charged metal ions in an electrolyte are driven to a negatively charged cathode under an applied current. Once the positive ion reaches the cathode, it is reduced after a surface interaction, gaining electrons from the cathode, resulting in a deposited metal. An inert or sacrificial anode is used to complete the circuit.

Electrodeposition is a more sensitive coating technique compared to thermal spraying or CVD as there are many more controlling variables effecting the successful deposition of the film and the electrochemical reactions occurring in the cell. It is a technique that has the ability to coat complex shapes. Coating morphology can be precisely tailored to the specific role of the film. It can also be a relatively low cost technique, operating under atmospheric conditions. The scalability of this process is typically current limited, theoretically allowing electrodeposition to operate on vast scales, allowing such processes as the electrowinning of zinc and nickel, to be viable methods of ore extraction.
A metal’s capacity to be electrodeposited is dependent on its thermodynamic activity when in solution. When a metal electrode is placed in a metal ion containing electrolyte, an equilibrium is formed:

\[ M \leftrightarrow M^{n+} + n e^- \]  

(2.1)

Equation 2.1 describes the tendency of metal to dissolve into solution creating ions, or the reverse to occur resulting in ions deposited as metal. When the net rate of these reactions is 0, this is known as thermodynamic equilibrium.

The equilibrium potential is described by the Nernst equation:

\[ E_{eq} = E^0 + \frac{RT}{nF} \ln[M^{n+}] \]  

(2.2)

In order to deposit the positive metal ions on to the electrode, the potential must be shifted into the cathodic direction. This shift require the application of a negative potential to drive the reduction, this potential value is known as the overpotential, \( \eta \):

\[ \eta = E - E_{eq} \]  

(2.3)

The overpotential represents the energy required to force the metal ion to migrate through the electrolyte, and reduce on the cathode, it can also be known as the polarization voltage. The overpotential required for the reduction of metal ions at a cathode, is a unique value for that
certain metal, and is also dependent on a number of other variables, such as electrolyte pH, temperature and stirring velocity. The lower a metal’s overpotential, the easier it is to reduce from the bath. An electrolyte is an ionic conductor formed of metal salts dissolved in a solvent or heated until molten allowing free ion movement. Water is a common electrolyte solvent as it is low cost, has a high solubility limit and it is readily available. Due to water’s narrow potential window, large applied overpotentials can result in the decomposition or electrolysis of the solvent simultaneously with metal deposition.

Molybdenum is known as a high overpotential metal that naturally exists in a stable oxidation state of Mo (VI). Reducing Mo (VI) leads to a number of oxidation states, ranging from −2 to +6, with highly stable oxides of MoO₂, MoO₃. When dissolved in water the anion molybdate, MoO₄²⁻, is formed Deltombe [1956], and it’s full metal reduction in water is given by, [Latimer (1952)]:

\[
\text{MoO}_4^{2-} + 4\text{H}_2\text{O} + 6e^- \rightarrow \text{Mo} + 8\text{OH}^- \quad E^0 = -0.913\text{V}
\]

The complete reduction of Mo(VI) to Mo has a very high standard potential \(E^0 = -0.913\) V. What makes electrodeposition of metallic Mo from aqueous solutions so difficult is the secondary cathodic reaction of hydrogen evolution. Mo has a low hydrogen overpotential, \(E_{eq} = -0.430\) V, at pH 6.8, which is a far more thermodynamically favourable reaction than the metal ion reduction. This equates to a high rate of parasitic hydrogen evolution reaction, HER, occurring simultaneously, consuming most of the applied current. The use of aqueous based electrolytes for the electrodeposition of refractory metals, such as metallic molybdenum, due to
the need of a high reducing overpotential, has previously yielded poor results, with low current efficiencies and brittle coatings.

2.6 Electrodeposition via Molten Salt and Ionic liquid Baths

Non-aqueous molten salt and ionic liquid baths have shown potential as electrolytes for the electrodeposition of refractory metals, Simka [2009]. The advantages of ionic liquids and molten salts are their wide potential windows, high solubility, high conductivity and the removal of HER issues, Abbot [2006].

Molten alkali halide salts baths of KCl–K₃MoCl₆ at temperatures of 800 °C and LiCl–KCl–K₃MoCl₆ at 400 °C, have been used to deposit dense thick metallic coatings, [Kipouros (1988)]. Koyama [2007] acknowledged the beneficial effects of the addition of KF to their bath of KF–Na₂B₄O₇–K₂MoO₄ fused salts at operating temperatures of 998 – 1173 K.

Nakajima [2006] successfully electrodeposited metallic molybdenum from a ZnCl₂-NaCl-KCl-MoCl₃ systems at 250 °C, a relatively low temperature for a molten salt bath. They did observe that film growth was limited to 0.5 µm, and showed poor adherence. It was noted that the addition of KF to the bath increased adherence, density and film thickness, resulting in a 3 µm coating. Ene [2006] used a similar alkali halide bath of NaCl-KCl-NaF at a higher temperature of 1100 °C, to deposit dense coatings of 10 µm and non-dense powder deposits of 50 µm.
There are a number of obvious disadvantages to the use of molten salts and ionic liquids. High operating temperatures greater than 1000 °C, the requirement of inert atmospheres due to water sensitivity and costly equipment reduce the possibility of large-scale commercialization. The reagents required are also costly and require a high level of processing.

2.7 Co-Electrodeposition of Mo-Ni Alloys from Aqueous Based Solutions

Molybdenum can be successfully deposited with a number of other metals, such as nickel, cobalt and iron, in aqueous solution to form co-deposited alloy coating. Ernst and Holt [1955] described an aqueous solution formed from sodium molybdate, nickel metal sulphate, sodium citrate and ammonium hydroxide, adjusted to pH 10.5. Deposits of 20 wt% Mo were created, with a current efficiency ranging from 75 - 85 %. Studies were performed on the solution before deposition, to classify the quality of the deposition. Through the use of these studies it was determined that sodium citrate prepared through neutralized citric acid was the best performing complexing agent. Ernest and Holt [1958] saw that with increasing temperature, 30, 55, 70 °C, cathode current efficiency and Mo wt % increased. Bright deposits were formed that exhibited good adherence to flat, clean substrates.

Building on their earlier work, Ernst and Holt [1958] performed further studies on the effects of cathode potentials during deposition to gain a better understanding of the mechanisms occurring during co-deposition. The potential studies were used to observe the reduction of molybdate ions in aqueous citrate solutions. Six electrons are required for the reduction of a molybdate ion, but it was seen to occur in a two-step mechanism. Ernst and Holt [1958]
predicted that the initial reduction mechanism is a molybdate ion reacting with water to form a Mo-hydroxide with a metal-hydrogen bond. The molybdenum hydroxide is then further reduced by an activated complex of Ni, created by hydrogen generated from the HER due to the large supplied over-voltage; this reduction reaction forms the final Mo-Ni deposits.

Chassaing [1989] investigated the deposition kinetics of Ni and Mo in a citrate-ammonia solution using polarization and A.C. impedance techniques. Analyzing the effects of three potential ranges, Low, Intermediate and High, they saw that at low polarization the main reaction occurring in the cell was HER, resulting from the reduction of citrates in the electrolyte. This lead to the deposition of a porous film of MoO₂, further catalyzing the HER.

At an intermediate polarization, HER was seen to quickly decrease as the reaction progressed, with Ni and Mo deposited at an equal rate. At a high polarization they observed that Mo deposition was under diffusion control, limiting the Mo content of the film. From the analysis of the polarization range, they concluded that the intermediate polarization produced the best quality Ni-Mo film with the lowest HER rates.

Nee [1988] used a similar electrolyte bath to Ernst and Holt to perform pulsed electrodeposition tests with intent to reduce internal stresses issues in Ni-Mo deposits that leads to their brittle nature. A nickel sulfate hexahydrate, sodium molybdenate bihydrate, sodium citrate bath were prepared with the addition of sodium bicarbonate to adjust to pH 10.5. With a constant bath temperature of 60 °C, different pulsing frequencies and peak current densities were applied to determine their effects on the deposit’s internal stress. They observed that through the
use of a pulsing current, coatings could be created with a higher Mo content, at the same average
current density, achieving a maximum of 25 % wt Mo. Nee [1988] saw that the internal stresses
caused by hydrogen content were reduced by current pulsing, as it allowed relaxation of
crystallite coalescence after each pulse. It was also seen that the high-frequency deposition
coatings displayed the greatest increases in yield and tensile strengths. The coating mechanical
properties were increased by a final annealing at 300 °C.

A more advanced form of pulse deposition method is pulse reverse potential. Chassaing
[1995] used this technique to create Ni-Mo alloy coatings using a similar bath solution to Nee
[1988]. Pulse reverse potential generates a combination of cathodic and anodic potential pulses
at different frequencies. This technique was used to deposit a film on a mild steel substrate. It
was predicted that the reverse pulse could act as a levelling mechanism through the reduction of
hydrogen content in the deposited coating. Chassaing [1995] saw that coatings created using a
reverse pulse method had a nodular morphology, where surface roughness did not increase with
thickness, a common observation in normal D.C. electrodeposition.

The use of rotating cylinder electrode, RCE, substrates for deposition has been shown to
produce high Mo content Ni-Mo co-deposits; Mo wt% previously not possible to produce.
Podlaha [1993] produced co-deposits with 48 wt % Mo, the highest to date of publication from
an aqueous ammonia citrate bath. The rotating cylinder allowed full control of the
hydrodynamics present. Using this setup, Podlaha [1993] was able to show the dependence of
film composition on convection, and so ion transport. The bubbles generated during rotation
were predicted to enhance the transport phenomena occurring during the deposition process.
With a current density of 150 mA cm\(^2\), deposits of 9.3 \(\mu\)m in thickness at an efficiency of 46% were produced, achieving a 48-49 wt % of Mo.

Podlaha [1996] continued their work with the creation of a mathematical model to describe the kinetic and mass-controlled regions of the co-deposition of Ni and Mo on a RCE. The kinetic region was described using a Tafel slope while the mass transfer of ions through the diffusion layer was predicted using a Nernst boundary layer method. Podlaha [1996] was able to describe molybdenum’s dependence on nickel. Mo can only be deposited from an absorbed intermediate releasing ionized Ni species. Ni can be deposited independently. Therefore Mo deposition is dependent on the kinetic parameters of the Ni deposition, as well as limited by the parasitic HER. Ni presence acts as a catalytic intermediate for Mo deposition. They saw through their calculations that there was no theoretical maximum limit of Mo wt% possible to deposit. They also saw that rotation speed of the cylindrical substrate was a governing factor on Mo content, with a high rotation speed beneficial for Mo deposition.

Marlot [2002] used a pulse plating technique to produce Ni-Mo films using a rotating copper disk substrate. They observed that for pulse periods greater than 10 seconds the films showed the same composition as a standard non-pulsed D.C. deposited film. With pulse periods less than 10 seconds, the Mo content was greatly increased. They deduced that this was due to the Mo deposition being dependent on mass transport of Mo ions in the electrolyte, and the rotation speed of the disk substrate.

To gain an understanding of the limiting mechanisms controlling Mo wt % in the Ni-Mo
alloy deposition, from an aqueous citrate solution, Sun [2012] performed galvanostatic deposition with the intent to produce a film with the maximum Mo content possible. They saw that in order to achieve 62 - 82% wt % Mo films, a high cathodic current density greater than 200 mA cm$^{-2}$ was needed. As Ni is required to catalyze the Mo deposition reaction, Sun [2012] postulated that it would be beneficial to block Ni deposition, while maintaining it in solution for the required intermediate reaction, necessary for Mo deposition. Their work produced the highest Mo % films to date of publication.

Using an electrolyte solely containing Mo ions, and a Ni substrate, Shunsuke [2007] created a Ni-Mo film through the use of alternating pulsed electrolysis. On the anodic pulses Ni ions were dissolved into the solution from the substrate, providing the Ni ion source for the deposited Ni-Mo alloy. They observed that with increasing solution pH, the at% of Mo increased, reaching a maximum of 41.8 at% Mo at pH 5. A pH greater than 5 did not show a change in Mo content. They concluded that it would be possible to deposit metallic Mo from a Mo ion containing bath onto a Ni substrate via alternating pulsed electrolysis, as the Ni ion concentration can be controlled through the pulse characteristics.

2.8 Cathode Electrochemistry

Ernst and Holt [1958] proposed a two step process for the reduction of the molybdate ion in an aqueous citrate bath:
\[
\text{MoO}_4^{2-} + 4\text{H}_2\text{O} + n\text{e}^- \rightarrow \text{Mo(OH)}_{(6-n)} + (2+n)\text{OH}^- \quad (2.8.1)
\]

\[
\text{Mo(OH)}_{(6-n)} + (6-n)\text{H}^+ + \text{M} \rightarrow \text{M} \cdot \text{Mo} + (6-n)\text{H}_2\text{O} \quad (2.8.2)
\]

Where \( n \) is 1, 2 or 3, and \( \text{M} \) is the co-deposited metal. Ernst and Holt hypothesized that if the deposition process is a multi-step electron process, equation (2.8.1), then formation of an initial molybdenum oxide or hydroxide layer is likely. If this is the reaction occurring, then further deposition is now not plating on the original base cathode material, but now onto the molybdenum oxide or hydroxide film, therefore changing the reaction kinetics.

For a full reduction of molybdenum, Ernst and Holt saw that an increased overpotential would be required, equation (2.8.2). The simultaneous cathodic reaction of hydrogen evolution limits the deposition reaction due to faster kinetics, resulting in poor deposition current efficiency and high levels of hydrogen evolved. Ernst and Holt further believed that there is a strong dependence on hydrogen in the deposition of Mo. It was their belief that the role of hydrogen was to act as a reducing agent for the molybdenum oxide or hydroxide film. This role of hydrogen was observed in the co-deposition of Mo with Fe, Co and Ni. They concluded that through their study of the molybdate ion reduction, that it was their belief that \( n \) in equations (2.8.1) and (2.8.2) appeared to be a valence of 3+. Ernst and Holt acknowledged the role of the complexing metal in the co-deposition process, and its ability to reduce the overpotential of reaction (2).

Gomez [2003] during their investigation of Co-Mo film deposition, observed a 2-part reduction mechanism similar to the one defined by Ernst and Holt [1958]; with an initial oxide deposition
phase followed a further reduction to a metallic phase. A model was proposed to describe the reduction process; it stated that the initial stages of deposition are controlled by charge transfer, then moves into a mass-transport controlled system, as observed by Podlah [1996]. A delay time was observed in the initial stages of deposition, where no metal film was deposited. Oxide growth of MoO$_2$ and MoO$_3$ was seen in this period; it was concluded that these oxides were the result of the reduction of MoO$_{2.4}^-$ on the substrate surface, this was described as Step 1. Step 2 was only seen to occur when catalyzed by Co(II), resulting in the reduction of the Mo oxide to form co-deposits of metallic Mo and Co.

It was deduced that Step 1 was a charge-transfer-controlled due to the delayed formation of oxides on the substrate surface. After an initial oxide layer is deposited, the secondary reduction Stage 2, producing metallic Mo is accelerated, allowing growth in the depletion zone.

Cyclic voltammetry is a powerful tool that can be used study the mechanisms involved in the deposition process, where the position of the peaks can be correlated to reduction reactions. Sanches [2004] used a cyclic voltammetry technique to investigate the co-deposition of Ni-Mo in a citrate solution containing different molar ratios of Ni and Mo.

They acknowledged the reduction potential of Mo to be more negative than Ni, at around -0.80 V, and so has a preference for reduction. Two obvious cathodic peaks were visible during their scans, $c_1$ and $c_2$, at around -0.80 V and -1.50 V, respectively.

Sanches [2004] attributed the -0.80 V peak to the deposition of Mo hydroxide, while the second peak, at -1.5 V, is the result of the reduction of deposited Mo oxides or hydroxides to metallic Mo, simultaneously with HER. The findings from the cyclic voltammetry complements
earlier literature, previously discussed. It was also visible from the CV scan that the higher the ratio of Mo in the plating bath, the greater the current needed due to the increased rate of hydrogen evolution.

Electrodeposition of pure metallic molybdenum from aqueous solutions has repeatedly been shown to be unsuccessful in nearly all cases. This is due to the high overpotential of molybdenum or the low overpotential of hydrogen on Mo, Hovey [1963], therefore requiring extremely high applied potentials, that in turn cause the more favourable production of hydrogen from the aqueous solution. When co-deposited with a Fe-group metal, such as Fe, Co or Ni, a Mo containing alloy coating can be formed, as the overpotential is reduced, due to the catalyzing effect of the metal, allowing the secondary reduction reaction of the Mo oxide or hydroxide. It is harder to achieve high Mo content deposits, as the competing HER, catalyzed by the deposited Mo, greatly reduces the current efficiency of the deposition process, while producing a non-uniform film containing cracks and poor adhesion. So far, we have considered electrodeposition in an aqueous citrate complexing bath.

Citrate is a common additive to an aqueous electrolyte used for electrodeposition. A citrate-based electrolyte enables control over the homogeneity of deposits with changing bath composition as deposition progresses; it is also vital in controlling a constant pH during the electrodeposition process, Gómes [2001].

The citrate driven system was observed by Gómez [2001] in the co-deposition of Co-Mo alloys to see how the presence of Mo influenced the magnetic properties of Co-Ni alloys. It was observed that Mo containing alloy coatings were deposited crack free and homogeneous in composition and morphology using a citrate bath. They acknowledged the presence of the citrate
electrolyte as a pH-stabilizing buffer. Gómes [2001] saw that as the concentration of Mo was increased, the solution yielded a more porous, less dense film. At too high a content of Mo, the film became heavily cracked.

2.9 Electrodeposition via Acetate Based Baths

Electrodeposition of pure metallic molybdenum and molybdenum co-deposits using an acetate bath has not been a common topic for research due to inconsistent and poor results over the years. However the deposition of nickel binary alloys using acetate baths has been shown to produce successful coatings on a wide number of substrates. Adb El Rehim [1995] observed the successful formation of Zn-Ni binary alloys on steel substrates with the use of an acetate based bath. With a controlled pH of 4.4 - 4.6 Adb El Rehim suggested that the deposition of each metal was independent through two successive one-electron transfer steps. Contrary to their predictions, the formation of an anomalous co-deposit rich in Zn were always obtained. They observed at low current densities, < 0.7 A cm⁻², the coating consisted of porous layer of nodular, randomly orientated grains, however with an increase in in applied current density, the formation of uniform coatings with smaller, smoother and more compact grains were seen. They saw that with the increase of bath temperature, they were able to further reduce the grain size. When the bath reached temperatures greater than 60 °C, cracks propagated on the coating surface and the quality of the coating was reduced. They deduced that the cracks were caused by the accelerated hydrogen evolution becoming more prolific at the increased temperature. The generated hydrogen was thought to be adsorbed by the coating, suppressing grain growth and promoting nucleation creating finer grains. This adsorption of generated hydrogen had the negative effect of
creating gas filled voids that with continued growth promoted stress in the coating leading to pressure cracks. Abd El Rehim [1995] noted the stability of the acetate solution and its ability to greatly reduce hydrogen evolution, but at higher temperature and current densities blamed the hydrogen generation for the poorer coating morphology and cracking.

Beltowaska-Lehman [2002] investigated the deposition of Zn-Ni binary alloys using an acetate based bath similar to Abd El Rehim [1995]. Beltowaska-Lehman [2002] observed the anomalous behaviour of zinc as the favoured deposit, this effect was greatly increased in baths with a pH greater than 3.3. With the decrease in Ni content, they noticed a decrease in the corrosive protection of the coating showing nickel’s corrosion resistant properties. The deposition bath used was an acetate-sulphate electrolyte; the pH stabilizing buffer action of acetate complexes was observed in the pH 2 - 5.2 ranges. A change in grain morphology with increasing nickel wt % was also observed with a shift from platelet hexagonal morphology (<8%) to polyhedral grains (12 - 16 wt %).

Golodnitsky [2000] studied the effects of different anion additives to a sulphamate electrolyte bath during the co-depositions of Ni-Co. A series of electrodeposition experiments were carried out using a standard three-electrode system. Acetate complexes in the form of sodium acetate were added to the sulphamate bath; they deduced that the acetate complexes did not participate directly in the cathodic reaction, but acted as a pH buffer, preventing an increase of the sulphamate electrolyte pH, a common response to hydrogen evolution. Like Abd El Rehim [1995], they observed the formation of an anomalous co-deposition, with Co deposits favoured; they believed this was due to the stronger reduction of high-spin Co(II) complexes over nickel,
leading to a higher deposition rate of Co. A greater stability of electrolyte pH directly surrounding the cathode with the addition of 500 mM sodium acetate was observed.

Building on their previous work, Golodnitsky [2002] deposited Ni-Co alloys from a sulfamate electrolyte, with the addition of acetate and citrate-anion complexes. Again they acknowledged the pH stabilizing effect of the buffering sodium acetate and observed the citrate complexes to be vital in the alloy deposition, reducing the incorporation of hydroxides into the coating, which they blamed for the cause of cracking in higher pH deposition baths due to internal strains.

An advantage of using an acetate bath, is its stability over a long period of time. With the intention of creating high surface area Ni-Cu-Fe co-deposit for the use as hydrogen generating electrodes, Giz [2003] needed a deposition bath that was capable of being stable over several weeks. Giz [2003] observed that the baths of lower pH, less than 3.2, showed high stability. Experiments carried out over a 15-day period showed the bath produced an acceptable level of deposits, without loss of electrochemical activity, after this time period.

Bath operating conditions have a significant impact on a coating’s composition and hardness. To better understand the effect temperature and additives have on the electrodeposition of Ni-Co alloys from acetate electrolytes, Marikkannu [2007] created a number of Mo-Co alloys from acetate electrolytes with different additives, at temperatures ranging from ambient 30 °C to 60 °C. Again Marikkannu [2007] recognized the buffering ability of the acetate bath. They visually characterized their deposits from a scale of semi-bright, bright or mirror bright. They
observed that with an increase in temperature the coatings changed from mirror bright and became duller in appearance. At temperatures greater than 60 °C the coating became dull, powdery or black. They concluded that the best results were achieved at ambient temperatures; they based this on the assumption that the grains grew too fast at elevated temperatures, and so nucleation was hindered as well as grain refinement, creating an uneven, low quality coating. They also saw that a bath of pH 5 produced the highest quality deposits, this value is slightly higher than previous stated values. An increase in coating hardness and corrosion resistance was noticed with the addition of saccharin and also formaldehyde, due to their deposit grain enhancement during the deposition process.

Marikkannu [2007] saccharin additives findings were supported by the later work of Yang [2010], who also observed an increase in deposit density and hardness. A number of additive effects were observed on nickel coatings deposited from high temperature sulphamate and Watt’s solutions. A decrease in particle size, due to increased nucleation and growth inhibition, and therefore an increase in coating hardness was noticed with the use of a saccharin additive, supporting Marikkannu [2007].

Co-deposited ternary alloys of Ni-Mo-Co can be created using an acetate based electrolyte bath. Singh [1978] deposited coatings under a variety of conditions but found that a bath at ambient temperature and pH 4.5 - 5.5 created the most uniform, adherent deposits. These conditions are confirmed throughout literature, seemingly the ideal when depositing using an acetate bath.
2.10 Deposition of Metallic Molybdenum from an Aqueous Acetate Electrolyte

Acetate baths have been successfully used to deposit coatings of pure metallic molybdenum in a small number of cases. The first recorded study was performed by Ksycki [1949]. Metallic Mo coatings were electrodeposited from an aqueous acetate containing solution over a pH range of 5.5 - 6.8, on a variety of substrates: copper, nickel and iron. Ksycki [1949] acknowledged the high rate of hydrogen evolution present during the deposition process. Bright metallic deposits were achieved using a highly concentrated bath of acetate ions. They observed a degree of surface pitting and imperfections along the edge of the cathode; this was attributed to accelerated hydrogen generation where current density was greatest. Ksycki [1949] hypothesized that Mo metal deposits may be formed due to a reduction of oxides in situ by hydrogen, which is now a commonly thought mechanism for Mo(VI) reduction.

It wasn't until 60 years later that a similar technique was used to successfully produce pure metallic molybdenum. Morley [2012] deposited metallic Mo coatings up to 20 µm from a high concentration acetate bath containing molybdate ions. Morley [2012] observed electrodeposition in baths at pH 6.6; no deposits were formed at less a pH less than 5.5, complimenting Ksycki [1949]. High levels of hydrogen evolution were seen during deposition, due to the catalytic properties of the Mo coating; as high as 99 % of the applied current is consumed by the parasitic hydrogen production. Morley [2012] observed that with a reduction in acetate concentration, there is also a decrease in coating-substrate adherence.

Acetate, as a deposition electrolyte has been shown to yield successful uniform Ni, Ni
alloys, Mo alloys and pure metallic Mo coatings. The optimum conditions for its use appear to be at ambient temperature, favouring a slightly acidic bath, varying from 3.2 - 6.8. The greatest issue associated with an aqueous bath is the secondary parasitic HER yielding a high amount of generated hydrogen, resulting in a loss of deposition efficiency and increased embrittlement of the coating. The addition of saccharin reduces grain size and the negative effects of hydrogen.

2.11 The Effects of Thiourea on Cathode Reactions

Brightening and leveling agents are commonly added to plating baths to aid in the growth of a more uniform film, acting to reduce surface roughness during deposition. One such additive is thiourea, an organosulphur compound, SC(NH$_2$)$_2$, that possesses a unique molecular orientation. It exhibits a high levels of polarizability, allowing the molecule to act as a surface absorbed surfactant. This dipole makes it an interesting additive to the plating solutions. The molecules are thought to be attracted to areas of higher charge therefore raised areas and protrusions with higher current densities, on the cathode surface. Due to the dipole of the molecule, once the positive head is adsorbed to the raised region, the negative tail will repel positive metal ions. This has the overall effect of reducing deposition at the raised regions, having the effect of leveling the film’s growth.

Thiourea has been acknowledged as a brightener, allowing the effective leveling and smoothing of a plated surface, with the benefit of allowing the application of an increased current density range, Ke [1959]. Plating experiments were carried out on metal spheres, one set in a controlled acid copper bath, the other in a bright acid copper bath, with an addition of 0.01g L$^{-1}$
of thiourea. The plated sphere coatings were analyzed and compared using x-ray diffraction patterns. The results showed the thiourea additive to have formed a bright coating of uniform coverage and structure. Ke [1959] observed the additive strongly modified the crystal structure of the deposit, acting as an inhibitor to crystal growth, and an enhancer to crystal nucleation, resulting in a finer grain deposit. An amount of thiourea absorption was observed, but was not seen to be biased towards a specific crystal orientation, and so was uniform throughout the coating, with a tendency to produce a more polycrystalline deposit.

Rogers [1960] observed a similar leveling effect with the addition of thiourea to a Watts plating solution, while measuring the incorporation of sulfur into electrodeposited nickel. Plating on a roughened surface, they saw that for thiourea to act as a leveler, it altered the surface current densities, reducing the peaks or raised surface morphology, and so increasing deposition rates in trough regions. Higher sulfur incorporation was therefore seen in the raised regions, where the lower current density controlled thiourea peaks were more prominent. Their findings complimented that of Beacon [1959], who used a radioactive addition agent to locate and analyze the effects of leveling agents. Their results showed that more nickel is plated in the recesses than on the top of the peaks, where the radioactive isotope was concentrated, giving preferential deposition, in a leveling process.

As well as acting as a brightening and leveling agent, thiourea has also been studied for its influence on hydrogen evolution during electrodeposition. Bukowska [1993] studied the effects of thiourea on hydrogen evolution in solutions of varying pH. In neutral media, thiourea was seen to catalyze hydrogen evolution, however under acidic conditions, it was seen to inhibit
the generation of hydrogen. This inhibiting action lacked clear explanation in literature, therefore Bukowska [1993] used linear sweep voltammetry and surface enhanced Raman spectroscopy, SERS, to gain a better understanding of the surface reactions occurring. It was observed that the surface orientation of the thiourea molecule to the electrode surface governed whether it is catalytic or inhibiting. When the thiourea molecule is in a parallel orientation to the electrode, hydrogen evolution is seen to be faster. When it is positioned perpendicular to the surface, it is seen to inhibit hydrogen evolution. This is due to the NH$_2$ groups in the thiourea molecule interacting with the anions in acidic media. In neutral solutions, the anions are not adsorbed by the NH$_2$ which are hydrogen bonded to water molecules instead, allowing discharge of H$^+$. Angelo [1995] performed hydrogen evolution reactions on Ni-Zn (25% of Ni before leaching) coated electrodes. They monitored the hydrogen absorption in the surface layers and the effects thiourea and cyanide additives had on absorption rates. The Ni-Zn coating was characterized with very low Tafel slopes of 67 mV dec$^{-1}$. Anelo [1995] determined that this was due to hydrogen absorption in the surface layers of the deposited coating. Analysis of tests in solutions containing thiourea and cyanide showed that the poisons inhibited hydrogen absorption, and so returned the Tafel slopes to the normal range. As a surface activity poison, thiourea was seen to increase the electrode activity at lower overpotentials. Cyanide was seen to cause the opposite, producing a decrease in activity due to absorption on to the electrode surface acting as a poison towards HER. It was determined that thiourea and cyanide caused different surface affecting mechanisms, but both acted to restore the Tafel slope to normal regions.
Using AC impedance spectroscopy, interfacial electrochemical reactions such as hydrogen absorption reactions, HAR, can be analyzed and the effects of catalyst poisons can be quantified. Han [1997] used such a technique, with cyclic voltammetry to analyze the change in electrochemical activity of hydrogen absorption on Palladium foil electrodes in under-potential deposition conditions. Han [1997] observed that the hydrogen absorption mechanism changed depending on the concentration of thiourea. Below $10^{-8}$ M thiourea, HAR is controlled by hydrogen diffusion; but at concentrations greater than $10^{-7}$ M, HAR is controlled by interfacial reactions. Han and Yang, observed the concentration dependence and proposed that thiourea acts as a hydrogen absorption inhibitor. They also saw that the addition of thiourea inhibited the formation of beta-phase Pd hydride.

During the electrodeposition of zinc, Song [2004] saw that the addition of thiourea to the deposition bath, had an effect on the HER and HAR. They saw that thiourea acted as an inhibitor of the HER but promoted the HAR. Using an Electrochemical Quartz Crystal Microbalance, EQCM, the mass change on a quartz crystal working electrode was monitored during Zn deposition. The effect of thiourea in the deposition solution was compared to gelatin and PEG. It was seen that gelatin was the strongest HER suppressor. The effect of thiourea on the current density was negligible, but a decrease in hydrogen evolution in comparison to an additive free solution, was observed, indicating HAR occurring in the OPD region, agreeing with previous literature.

Paseka [1999] studied the influence thiourea had on the HER and HAR on electrolytically prepared amorphous Ni-P layers. The hydrogen displacing nature of thiourea was
observed through the analysis of potential decay method on steady state polarization curve of the HER. It was seen that at higher current densities, the inhibiting nature of thiourea was much greater. A decrease in hydrogen absorption by as much as 3 times was seen with the addition of thiourea in the range of positive potentials, this in turn lead to an increase in the over-voltage of the HER.

2.12 Corrosion studies: Mo and Mo-Alloys

It has long been known that the addition of molybdenum as an alloying element to steel has beneficial effects to its corrosion resistance, thermal stability and hardness. To better understand the role of Mo in increasing the corrosion resistance of ferritic stainless steel, Hashimoto [1979] performed an x-ray photo-electron spectroscopic, XPS, study of the alloyed steel in the presence of HCl. The steel used was a 30Cr ferritic stainless steel, which is known to form a hydrated chromium oxy-hydroxide protective passive film. They saw that the addition of Mo did not change the thickness of the passive film, but decreased the number of steel crystal defects. The decrease in defects reduced the active sites for corrosion initiation. They saw that alloying with Mo allows the formation of a homogeneous, single-phase alloy through the formation of molybdenum oxy-hydroxide (molybdates) which reduce the prominence of active sites, creating a more uniform passive film coverage.

Non-steel alloys such as Ni-Mo superalloys were recognized as potential nuclear immobilization container materials for the Canadian Nuclear Fuel Waste Management Program, CNFWMP, due to their stability in corrosive environments, Nuttall [1981]. The alloy’s resistance
to radioactive isotopes over time was a strong argument for the material selection, with a high thermal stability and resistance to corrosion and radiation degradation. Postlethwaite [1988] performed immersion tests to mimic the corrosive chlorine rich environment the Ni-Mo alloy would be exposed to. Cyclic potentiodynamic polarization was used to study the effect of localized corrosion at increasing temperatures. The two alloys used, C-276 and 625, with a Mo content of 15.69 and 8.52 wt%, respectively, were observed to have an increase in localized corrosion with temperature gain; C-276, with the higher Mo wt% alloy showing a greater corrosion resistance. The immersion tests showed the presence of crevice corrosion, but no pitting. No corrosion was visible at temperatures below 100 °C. At temperatures greater than 100 °C, corrosion is accelerated. It was predicted that this was due to the higher concentration of Cl\(^-\), caused by the boiling off of steam, creating a more corrosive environment, as well as the increase in corrosion kinetics. It was concluded that the Ni-Mo alloys, especially the higher Mo wt% exhibited good corrosion resistance in the chlorine rich solutions. It was deemed that further work was required to understand the effects of the gamma radiation emitted by the radioactive contents, on the protective properties of the super alloy.

Williams [1994] observed that Mo acts to stabilize corrosion micro-pits in stainless steel. It was concluded that the alloying Mo atoms reduce the current density at the pit mouth, reducing the likelihood of pit expansion, complementing the results observed by Postlethwaite [1988].

The protective properties of Mo and its alloys can be harnessed through the use of coatings and thin films. Metallic molybdenum coatings have been investigated for their corrosion resistance at high temperature applications. Barker [1975] examined the corrosion effect of static
and liquid sodium at 400 - 600 °C on immersed molybdenum sheets over periods of up to 24 days. The results were compared with tungsten, 316 stainless steel and titanium carbide samples under the same conditions. Corrosion of Mo was not found to be oxygen dependent as no ternary oxide corrosion products were seen. However the formation of carbides, Mo$_2$C, was observed through XRD analysis; this was seen to be a function of temperature. This was very different to the effects inflicted on the tungsten sample under the same conditions. It was seen that the corrosion of tungsten was dependent on dissolved oxygen in molten Na. The independence to oxygen concentration, showed Mo had a very strong corrosion resistance compared to the other metals which all showed strong dependence and poor results. Weight loss experiments were performed on the Mo sample; no measurable change was noted, supporting the lack of corrosion seen in the previous test. Barker [1975] concluded that the greatest factor that would affect the integrity of a protective Mo film was the presence of carbides, which would be most harmful if formed in a wedging mechanism, leading to film delamination and failure.

Through the use of anodic dissolution, Johnson [1970] was able to study the dissolution oxidation states of molybdenum to better understand the mechanisms of the metal’s corrosion. Using acidic electrolytes, H$_2$SO$_4$ (pH=0.4) and H$_2$SO$_4$-K$_2$SO$_4$, and alkali electrolytes K$_2$CO$_3$-K$_2$SO$_4$ (pH = 9.5) and K$_2$CO$_3$ (pH=11.5) at a controlled 25 °C, electrolyses tests were carried out on Mo anodes. A weight-loss method was used to monitor the dissolution of the Mo sample in the different electrolytes. When no current was applied, no dissolution was observed. A rapid uniform formation of Mo$_2$O$_5$ was seen, forming a corrosion resistant passive film. It was proposed that it is only when the Mo$_2$O$_5$ is further oxidized to form MoO$_3$, that is then hydrolyzed, leading to dissolution. This mechanism was later confirmed by Goebel [1973] and
Lee [1971] performed corrosion studies on RF sputtered Mo thin films, in a range of different environments, consisting of, air, fluorochemical liquid coolant and deionized water, from 70 - 100 °C. It was seen that the Mo films remain unchanged in dry conditions, but as previously seen by Hornung [1972], wet and humid environments cause a degree of corrosion, that is accelerated by increases in temperature and humidity. It was observed that Mo forms a non-protective, porous corrosion product that is dissolved at 85 °C in deionized water. Lee [1971] stated that the corrosion mechanism of Mo is dependent on the presence of water and oxygen, contradictory to the later work of Barker [1975] who claimed the process was oxygen independent.

A more thorough recent study of the wet corrosion of Mo thin films was carried out by De Rosa [2004]. Corrosion studies were performed on PV deposited Mo films in chloride and sulphate solutions at a range of pH at a fixed temperature of 25.8 °C. A passive oxide film formation was observed, however it was not seen to provide protection to the under film which was still corroded. It was seen that pH was a greater factor influencing corrosion speed rather than the corrosive chloride or sulphide ions present. Alkali conditions resulted in a faster corrosion rate. At pH 7, in the sulphate solution, after 3 days an oxide layer formed, after 13 days the surface changed to a brown/blue color. The chloride solution, at pH 7, took 34 days before full discoloration occurred, indicating the films stronger resistance to the chloride ions, compared to the more harmful sulphide species.
De Rosa [2004] performed the same tests at an elevated temperature, 80 °C. De Rosa [2004] concluded that the results followed the same pattern as the 25.8 °C tests, but the rate of corrosion was seen to be significantly accelerated due to the increased temperature, as predicted.

We see that molybdenum exhibits poor corrosion resistance under alkali conditions, as it does not form a passive film but actively corrodes. Mo has shown strong resistance to chlorine rich environments, and mild acids. The addition of Mo to stainless steel results in a grain refinement mechanism, producing a more homogeneous crystal structure, providing a better resistance to pitting. The corrosion resistive properties of molybdenum are greatly reduced at elevated temperatures, however alloying with nickel allows the creation of stable super-alloys.
Chapter 3 : Objectives

Considering the previous discussion, the following objectives have been considered:

1. Determine the variables affecting the deposition of a uniform, oxide free, metallic molybdenum coating.
2. Through systematic condition testing, determine the plating variables that repeatedly produce adhered mirror finish metallic coatings.
3. Study the deposition mechanism in aqueous electrolytes.
4. Use mechanistic study results to increase deposit thickness to 25 μm.
5. Characterize the coating to determine microstructural characteristics.
6. Analyse the coating’s corrosion resistance in different environments.
7. Investigate the scalability of the deposition process.
Chapter 4: Experimental

4.1 Materials and Preparation Procedures

Working electrodes were prepared from Alfa Aesar copper sheet, 1.5 mm thick, 99.9 % purity, machined to produce 2 different electrode substrate sizes (34.4 x 13 mm and 10 x 10 mm). The copper surface was mechanically ground to 1200 grade SiC emery paper, cleaned with acetone, then rinsed with deionized water. When further polishing was required, 6 µm and 1 µm Leco diamond suspension was used.

The larger copper cathodes (34.4x 13 mm) were mounted in a PTFE holder for deposition, to expose a known working surface area (32 x11 mm) to the deposition bath. Smaller electrodes (10 x 10 mm) were prepared by attaching conductive wire, jacketed in pyrex tubing, using silver epoxy then cold mounting in epoxy resin using a Cold Cure System by Three Resins, Inc. Figure 4.1.

![Figure 4.1: Schematic of resin mounted copper electrode.](image)
The cylindrical platinum mesh counter electrode was degreased before each experiment, using acetone and rinsed with deionized water.

The standard aqueous electrolyte contained a fixed ratio (1.9:1, Morley [2012]) of potassium acetate, >99.0% ACS, VWR, CH₃CO₂K, to ammonium acetate, for molecular biology >98% (stored at 2 °C), C₂H₃O₂NH₄. Molybdate ions in solution were provided by ammonium heptamolybdate, Sigma Aldrich, USP, (NH₄)₆Mo₇O₂₄ 4H₂O. All solutions were prepared with deionized water. The pH of the solution was adjusted by the addition of glacial acetic acid, Fisher Scientific, at 35 °C. The final solution had an acetate concentration of 10 M, if full dissociation of acetate compounds is assumed. Due to pH adjustment with acetic acid, the acetate concentration and final solution volume deviated by as much as 20%.

4.2 Experimental Plan

Morphology is commonly thought of as the most significant property of an electrodeposited thin film; determining many of the coating’s physical and chemical properties. High porosity produces a larger surface area, providing a more reactive surface for catalysts; whereas a dense and uniform film can act as a greater protective coating for the base material. Film morphology can be tailored through control of the deposition variables.

Electrolyte conditions influence the deposition kinetics. Applied current density and deposition time are the main parameters affecting the deposition process. Each variable was altered systematically, to determine the optimum conditions, with the objective of depositing a
dense, uniform metallic molybdenum coating, with focus on maximizing film thickness. It was assumed that inter-variable interactions were negligible, and therefore factorial design was not applicable. This was deduced due to the short window of effective conditions available for the deposition of metallic molybdenum using the chosen electrolyte.

Visual characterization of film morphology and deposit colour is a quick and fairly accurate method of assessing deposit quality. Metallic molybdenum is a bright silvery-white metal; it has many oxide and hydroxide complexes, appearing a variety of duller colours, from straw-brown to purple, Deltombe [1956]. With this understanding, deposits in the early experimental stages, were quickly characterized after deposition without the need for slower phase determining analysis.

Smother and more uniform films reflect more light, appearing brighter and mirror-like. Altering deposition conditions to produce mirror-like coatings, again allows rough visual assessment of the film’s morphology.

**Standard conditions**

Unless stated otherwise, the standard electrolyte used during deposition is described in solution preparation; deposition time was set to 1 hour, under galvanostatic conditions with a constant current density of 0.4 A cm\(^{-2}\), similar to the conditions described by Morley [2012].

**Objective:** Determine optimum deposition conditions to achieve desired phase and morphology.
4.2.1 Temperature

Temperature change has a strong effect on the deposition. Temperature affects the reaction kinetics taking place in the electrolyte, changing the deposited films properties. To gain a better understanding of the dependence on temperature, a temperature range was set and increased incrementally by 5 °C, using a heated water jacketed cell, from 25 °C to an upper limit (65 °C), where deposition is no longer possible, or deposit quality decreases. Deposits were visually analyzed, to determine the temperature at which the most uniform metallic coating were achieved. This bath temperature was then fixed for all further deposition, with the intent of optimizing the deposition process.

4.2.2 Electrolyte pH

To investigate the effect of electrolyte pH on the deposition process and the produced film, a pH range was set from pH 6.5 to 7.5 and fresh samples and solutions were made at each increment of 0.1. Addition of glacial acetic acid was used to adjust solution pH. Any change in electrolyte properties was noted. Coatings were continuously assessed to observe any change in appearance. Again the pH condition producing the coating with properties most matching the objectives was selected and fixed for further testing.
4.2.3 Current Density

Galvanostatic deposition was chosen over potentiostatic, as a constant current allows known current density and controlled kinetics of deposition. Constant applied voltage could allow a fluctuation in current density with changing electrolyte conditions and electrode surface conditions.

Current density had the greatest impact on the deposition process, controlling the morphology of the film as well as its phase. Deposits with increasing applied currents were formed to see the influence current and the corresponding potential have on the films. Starting from 0.1 A cm\(^2\), current density was increased incrementally and applied for 1 hour, on fresh copper substrates. A value of 0.1 A cm\(^2\) was selected as it was predicted no deposition product would be formed at that corresponding potential. Appearance of deposits formed was recorded, along with any change in the electrolyte bath. Current density was increased until the coating was no longer possible.
Figure 4.2: A schematic flow diagram of experimental procedure.
4.3 Solution Preparation

50g of potassium acetate (510 mmol) was added to 50ml of stirred DI water in a 35 °C jacketed cell. Once fully dissolved, 40g of ammonium acetate (520 mmol) was added, this was followed by 500mg of ammonium molybdate (0.8 mmol). It was observed after the addition of molybdate ions, that the solution was fully saturated, with a small amount of precipitate formed. Upon heating the solution to 50 °C, the precipitate dissolved. At lower temperatures, the solution appeared more viscous, and milky in colour.

The solution had a natural pH of 8.6; glacial acetic acid was used to reduce pH; a pH probe was used to monitor solution pH; probe was calibrated using standard buffers at pH 4, 7 and 10 solutions on a regular basis, and washed before each test. The addition of acetic acid was also seen to increase the viscosity of the electrolyte, and induce a colour change from colourless to milky. It should also be noted that the fully saturated solution was vigorously stirred, during preparation and deposition process. If not stirred, solids were seen to form on solution surface and cell edges. Final solution volume was around 150 ml. Solution was magnetically stirred for up to 10 minutes to allow temperature to stabilize and ensure homogeneity before deposition. Fresh solutions were prepared before each deposition.

It was observed that solutions that had been left to cool and precipitate for up to 4 days, were able to be reheated and used to produce a uniform coating, similar in appearance to those deposited from fresh solution.
4.4 Electrochemical Methods

All electrochemical tests were performed using an EG&G Princeton Applied Research (PAR) Potentiostat/Galvanostat 273A, except cyclic voltammetry testing, which was carried out using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA. A saturated calomel electrode (SCE), (Hg₂Cl₂/Hg, [KCl]=4 M), where E(V, SCE) = E(V, SHE) - 0.241 V, mounted in a Luggin probe with a Vycor frit was used as a reference electrode for all electrochemical experiments.

4.4.1 Galvanostatic Experiments

Deposition was carried out under galvanostatic conditions. A constant direct current was applied across the electrodes in solution, inducing cathodic deposition to occur. Applied current was increased on known area substrates, to vary effective current densities, \( i \), from 0.05 - 0.5 A cm\(^{-2}\), for a chosen amount of time.

4.4.2 Open Circuit Potential (OCP) Measurements

The Open Circuit Potential (OCP) was monitored through time. In most solutions a stable value was obtained within 1 hour of immersion, but for some solutions it was necessary to wait longer before a steady state potential was reached.
4.4.3 Potentiodynamic Polarization Experiments

Potentiodynamic Polarization (PDP) tests were employed to investigate a number of electrochemical properties of the deposited films. To study the deposition mechanisms occurring in the bath, PDP ran from +0.250 V OCP to -4.00 V vs SCE. To study the corrosion behavior of the coatings in different environments, PDP ran from −0.250 V OCP to +0.400 V vs SCE. A scan rate of 0.166 mVs⁻¹ was implemented for all tests.

4.4.4 Cyclic Voltammetry Experiments

Cyclic Voltammetry was performed on samples to study the reduction reactions occurring during deposition at a rate of 50 mV s⁻¹ across a potential range from +0.5 to -1.5 V vs SCE. Scans were performed in sets of 10 full cycles, in stirred and unstirred solutions.
4.5 Cell Apparatus

**Figure 4.3:** Schematic of single cell experimental setup, using a stirred water jacketed cell; Cu cathode and Pt counter electrode 45 mm apart; saturated calomel reference electrode.
Chapter 5 : Results and Discussions

5.1 Bath Temperature

Deposition experiments were carried out using freshly prepared standard solutions under increasing bath temperatures to investigate the change in the electrolytes properties and the effect of temperature on the reaction kinetics. As stated previously, all deposits were carried out under galvanostatic conditions, at a current density of 0.4 A cm\(^{-2}\) over a period of 1 hour. Deposits were formed on copper substrates polished up to a grade of 1 \(\mu\)m diamond suspension. It was decided to mirror polish the substrate before deposition as it would aid in determining the quality of the deposited coating, as surface features would be accentuated and easier to see, compared to a rough substrate.

5.1.1 Bath Temperature: 25 – 30°C

It was observed that solutions prepared at 25 and 30 °C were characterized as a white-milky colour, with a pearl like sheen. These solutions were fully saturated, and required constant stirring, with a colourless crystalline salt constantly forming on the surface of the electrolyte, edges of the cell and building up around the electrodes; the electrolyte was thick in consistency and hard to keep molten. Solid white salt crystals nucleated and grew on any body or surface where solution velocities were low.
The deposits were a dull metallic colour. The 25 °C coating had reasonable uniformity and showed good adherence to the substrate; however in the center of the coating, and at the edges, the deposits were discoloured, appearing as a darker brown and blue material, indicating the formation of Mo oxides. It is postulated that during deposition, solid salt crystals built up on the cathode, blocking fresh electrolyte from reaching the surface. This unwanted salt coating allowed the deposition of Mo oxide or hydroxide, but inhibited the full reduction to metallic molybdenum.

At the higher bath temperature of 30 °C, the coating exhibited increased uniformity with a full coating of metallic grey, but was dull in lustre. The higher temperature of the bath increased the solubility limit of the solution, reducing the formation of the damaging colourless solid salt.

5.1.2 Bath Temperature: 32 – 35 – 37 °C

Mirror finish metallic molybdenum films were achieved exhibiting strong adherence to the copper cathode. At higher temperatures the electrolyte has turned from an opaque milky-white colour to a more translucent free flowing solution. The 35 °C bath consistently produced the most visibly perfect samples. The rate of the HER on the cathode and OER on the anode were seen to increase as expected due to the increased reaction kinetics driven by the temperature increase. At 37 °C the coating was noticeably thinner, with the copper substrate visible, through the thin metallic film. The thinnest region of the film was the top center. This
thinning of the coating was likely caused by the increased rate HER, creating a hydrogen bubble shield, preventing the diffusion of species from the electrolyte to the cathode.

5.1.3 Bath Temperature: 40 – 50 °C

The rate of HER and OER dramatically increased at these elevated temperatures, having a detrimental effect on the deposition process. The gas shielding effect of the generated hydrogen greatly reduced fresh electrolyte from reaching the cathode, limiting the Mo ion diffusion to the electrode, resulting in a non-uniform thin film. The area where material was deposited was visibly oxidized, appearing as darker regions of brown and black. This could be due to the effective area of the substrate exposed to the electrolyte, being largely reduced due to hydrogen shielding, resulting in a localized increase in current density, producing a burning effect in the deposited coating. Another cause of the highly oxidized film could be due to localized pH changes.

5.1.4 Bath Temperature: 55 – 60 °C

At temperatures greater than 55 °C, it is no longer possible to deposit a solid adhered film. Any coating deposited appears oxidized, with poor adhesion to the cathode substrate, resulting in deposit delamination. This is thought to be due to the highly aggressive rate of HER on the cathode.
5.1.5 Optimum temperature

Visual analysis of the temperature series resulted in the conclusion that a bath temperature of 35 °C consistently produced the most uniform, bright deposits. The bath appeared fully saturated at the elevated temperature, with a reduced viscosity compared to the room temperature electrolyte, which required aggressive agitation to prevent solid salt deposits nucleating on cell walls and electrodes. This bath temperature increased the reaction kinetics in the cell, increasing the metal deposition rate, while keeping the parasitic HER at an acceptable rate, creating a uniform coating.

5.2. Electrolyte pH

Electrolyte pH appeared to have a strong influence on the successful deposition of metallic molybdenum. Deposits were produced using an applied current density of 0.4 A cm$^{-2}$ for 1 hour from a series of 35 °C baths of decreasing pH, of 0.2 increments, adjusted with glacial acetic acid. The solution has an initial pH of 8.6.

The solution was seen to increase by a pH of 0.1 over an hour long deposition period, showing the stability of the electrolyte pH during deposition. The buffering capabilities of acetate ions have been discussed previously, but their buffering ability is effective in the 3.6 - 5.6 pH range. [Dawson; Elliot; Jones1986]. It is believed that the buffering mechanism in the solution is controlled by the ammonia/ammonium acid-base shift, supplied by the ammonium acetate. During the preparation of the solution, the addition of acetic acid produces a release of
ammonia from the solution, this is confirmed with the use of filter paper saturated in Nessler’s reagent, a common ammonia test, resulting in a positive colour change from colorless to orange.

Equations (5.2.1) and (5.2.2) describe the buffering nature of the ammonia/ammonium acid-base shift:

\[
\begin{align*}
\text{NH}_4^+ (aq) + \text{OH}^- (aq) & \rightarrow \text{NH}_3 (aq) + \text{H}_2\text{O} \quad (5.2.1) \\
\text{NH}_3 (aq) + \text{H}^+ (aq) & \rightarrow \text{NH}_4^+ (aq) \quad (5.2.2)
\end{align*}
\]

Equations (5.2.1) and (5.2.2) describe the buffering nature of the ammonia/ammonium action. To resist the increase in pH as protons are used up by the HER, the ammonium ion, releases a proton, forming ammonia. At the anode protons generated by the OER react with ammonia, thus forming ammonium and resisting a pH change.

5.2.1 Alkali Conditions: pH 7.6 – 7.4 – 7.2

A higher pH electrolyte required less acetic acid added to adjust it from its initial conditions, therefore the electrolyte is of lower volume and more viscous, in comparison to a deposition bath of neutral pH or lower. This results in a solution that is of higher saturation, and therefore precipitates and salts nucleate more easily. It was seen that at a pH higher than 7.4, a white basic molybdenum salt precipitated out of solution, reducing the concentration of molybdenum ions in the electrolyte.
Adhered mirror deposits were achieved, of higher quality than the coatings produced in lower pH baths. However due to the reduced proton concentration, the growth rate was slower than films deposited at near neutral pH, often resulting in a thin film, where the underlying copper substrate was still visible below.

5.2.2 Acidic Conditions: pH 6.5 – 6.2 – 6.0

Poor quality films were deposited when using acidic baths of a pH lower than 6.5. Due to the higher concentration of protons in the electrolyte, the rate of HER at the cathode is dramatically increased. This increases the degree of hydrogen shielding occurring on the substrate, blocking the diffusion of Mo ions to its surface and the subsequent reduction reaction from occurring. This results in a non-uniform, patchy brown-gray-black film.

Figure 5.1: Effect of electrolyte pH on coating phase and uniformity. Decreasing pH at constant 35 °C and 0.4 Acm⁻², decreasing pH from left to right, A. pH 7.5; B. pH 7.2; C. pH 6.8; D. pH 6.5 and E. pH 6.2.
Where deposition is allowed to occur, typically around the edges of the cathode, film delamination and strong oxidation is observed. This is postulated to be caused by a high Pilling-Bedworth ratio; the change of metallic molybdenum to molybdenum oxide due to the acidic electrolyte, lead to a significant shift in the coating elementary cell volume, leading to induced film internal stress, resulting in delamination, and failure. [Pilling, Bedworth [1923]; Davis [1997]].

Conductive surface salt layers form at the electrolyte-air boundary, having a damaging effect on the deposition process, when using a solution of less than pH 6.5. The salt cap could prevent the release of hydrogen and oxygen gases produced at the electrodes, into the atmosphere. This created a solution saturated with gas bubble. Some gas is hypothesized to re-dissolve into the bath, helping to keep a balanced pH, but the majority of the waste reduction products remain as trapped gas. This reduces the rate of hydrogen release from the cathode, increasing the level of hydrogen shielding.

It is also postulated that the solid salt cap reduces the deposition efficiency of the cell, by providing an alternate conductive route through the cell for the applied current. This bypassing of the electrolyte reduces the diffusion of Mo ions to the cathode, resulting in a drop in efficiency.

The most detrimental effect at low pH is seen to be the strong rate of hydrogen shielding and high Pilling-Bedworth ratio, resulting in a delamination of the oxidized film.
5.2.3 Near Neutral Conditions: pH 6.8 – 7.0

Coatings produced in an electrolyte bath of pH 6.8 - 7, were consistently seen to be a lustrous metallic white metal, exhibiting even and uniform coverage. The pH of the solution was seen to increase from 6.8 to 6.9 over the hour long deposition period, showing the stability of the electrolytes pH during deposition.

After pH adjustment, the bath volume is ~150 ml, and milk-clear in colour. Small amounts of salts formed on the electrolyte surface, but dissolve quickly after nucleation. Fine white precipitates were seen at the bottom of the bath, but dissolve over the course of the deposition process, indicating that the solution is at constant saturation. Electrolyte solutions of pH 6.8 were used to deposit metallic molybdenum repeatedly on a number of substrate sizes, over increasing time periods.

It was during this experimental stage that the original electrode setup of a 3.5 cm$^2$ cathode mounted in a PTFE holder was changed to a 1 cm$^2$ cathode mounted in epoxy resin, previously described in Figure 4.1. The smaller cathode size allowed full submersion in the electrolyte bath, compared to the half submerged, larger cathode. This new setup had a number of improvements over the original, most notably allowing an accurate control over the applied current and the corresponding current density, as well as removing the issue of a solid salt cap coming into contact with the copper substrate.
5.3 Current Density

Applied direct current is the driving force for the reduction mechanisms occurring in the plating process, as Faraday’s First and Second Law of electrolysis state that the amount of material deposited on an electrode is proportional to the amount of electricity supplied. When considering charge, $Q$, measured in coulombs, $C$, we introduce a rate or time dependence, where $1C = 1 \text{ A s}^{-1}$. From this basic understanding of charge transfer, Faraday developed a simplified explanation and equation to describe the deposition process, and its dependence on current.

For the reduction of Mo(VI) $\rightarrow$ Mo, the valence change is 6. However when considering that in an aqueous electrolyte, we see that the reduction of Mo(VI) is a two step process with an Mo(II) or Mo(III) hydroxide-oxide intermediate formed, then the electrochemical equivalents change for the different reactions occurring. But what remains constant is that for an overall valence change $6^+ \rightarrow 0$, 6 moles of electrons are needed.

The total cathodic charge required for the deposition of metallic molybdenum, $Q$ (C), is the product of the number of moles of deposited metal, $m$, (mol), the number of electrons required for reduction, $n$, Avagadro’s number, $N_a$, and the electrical charge of an electron, $Q_e$. From this Faraday developed an equation to describe the charge, $Q$, required to reduce $m$ moles of metal:

$$Q = m \ n \ N_a \ Q_e \quad (5.1)$$
Where Faraday’s constant, $F = N_a Q_e$. The number of moles of metal, $m$, reduced by charge $Q$ is represented by:

$$m = \frac{Q}{n F} \quad (5.2)$$

The benefit of using the galvanostatic, or fixed current, technique rather than potentiostatic, fixed potential, is that we can apply a fixed rate of deposition, allowing an accurate control of film growth. Therefore Faraday’s law can develop and a variable of time can be added. The total charge used during a coating deposition can be calculated as the current applied, $I$, multiplied by the deposition period, $t$ (s).

$$Q = \int I \, dt \quad (5.3)$$

Combining equations (5.2) and (5.3) the weight of deposited metal, $W$ (g), can be calculated by multiplying by the metals atomic weight, $M$.

$$W = \frac{M}{n F} \int I \, dt \quad (5.4)$$

Using (5.4) we can calculate the theoretical thickness, $\delta$ (cm), of deposited metal at a fixed applied current, over a set deposition time. This can easily be calculated when the surface area, $A$ (cm$^2$) and density, $\rho$ (g cm$^{-1}$) of the coating is known.
\[ \delta = \frac{W}{\rho A} = \frac{M}{nF\rho A} \int I \, dt \] (5.5)

Faraday’s Law of electrolysis gives a simplified theoretical estimate of coating thickness in ideal conditions. However in reality, the coating process has many external parameters that make this calculation value unachievable. In ideal conditions, if the parasitic HER is ignored, and the reduction is considered as a single reduction process, then theoretically a 234 µm film can be deposited in 1 hour, if a current density of 0.4 A cm\(^{-2}\) is applied to a 1 cm\(^2\) cathode, where the density of Mo, \(\rho = 10.2\) g cm\(^{-3}\):

\[
0.4\, \text{A} \times 3600\, \text{s} = 1.44 \times 10^3\, \text{C}
\]

\[
1.44 \times 10^3\, \text{C} \times \frac{1}{96485} = 1.492 \times 10^{-2}\, \text{moles e}^-
\]

\[
1.492 \times 10^{-2}\, \times \frac{1\, \text{moles Mo}}{6\, \text{moles e}^-} = 2.487 \times 10^{-3}\, \text{moles of Mo}
\]

\[
2.487 \times 10^{-3}\, \text{mole Mo} \times \frac{95.95\, \text{gMo}}{1\, \text{mole Mo}} = 0.239\, \text{Mo}
\]

\[
\delta = \frac{0.239}{10.2 \times 1} = 234\, \mu\text{m}
\]

This value calculated is the theoretical maximum thickness achievable under those set conditions, if the only cathodic reaction occurring was Mo reduction. Realistically the actual thickness value is as much as 100 times less. In the aqueous electrolyte system, as previously discussed, the most thermodynamically favourable and overwhelming reaction taking place in the bath is the hydrogen evolution reaction occurring alongside Mo reduction on the cathode.
This results in an extremely low current efficiency. We see coatings deposited over 1 hour to vary from 2-5 µm, resulting in a calculated deposition current efficiency of 0.85 – 2.1 %. However accurate efficiencies are difficult to calculate for coatings due to their imperfections and porosity reducing density and therefore creating efficiency values higher than we actually see. Current efficiency by weight change, consistently produced irregular results due to the extremely low mass of metal deposited, falling close to the weigh scales minimum capacity. However it is seen that more than 99 % of the applied current is used for HER.

When investigating the effect of current density on a deposit’s properties, the influence of the electrode’s potentials must also be considered. To activate the deposition process, the system must be shifted from its equilibrium. This is the role of the applied potential, driving the chemical reactions, supplying the energy. The potential difference across the electrodes, over the equilibrium is known as the overpotential. Therefore theoretically if an overpotential is applied to the system greater than the reduction reaction activation energy, then ions will be discharged at the cathode, and metal atoms or particles will be deposited.

To investigate the effect of current density on coating phase and uniformity, deposits were made under the same bath conditions, with increased current density, over a 1 hour period, on copper cathodes. We can see that by increasing $I$ (A) on a known area, and so the current density, $i$, (A cm$^{-2}$) we increase the overpotential between the electrodes. By raising the potential further we increase the rate of the reaction occurring, and so the deposition speed. Throughout this experimental stage, the greatest challenge we faced was an edge effect, caused by the
irregular current flow through the cathode, resulting in ‘burning’ and often no coating in the central region of the cathode.

In Figure 5.2, we can see a schematic of the resultant coating, if the applied current density was below that of the critical coverage current. We repeatedly saw that metallic molybdenum deposition was favoured on the outer regions of the substrate. If the applied current was too low, the central region would either be un-coated copper, or would have a blue-brown hue, indicating the deposition of an oxide/hydroxide film.

This edge effect results in outer areas, edges and corners of electrodes producing current disturbances, resulting in higher current flow, or a poor distribution of current, leaving localized current densities. From our understanding of Ohm’s law, we know that if the local current density is too low, equating to a surface potential below the necessary reduction potential, then deposition does not occur.

Figure 5.2: Schematic of sample coating results if current density is too low, resulting in metallic Mo coating of outer regions, with a central band of Mo oxide/hydroxide, and an uncoated center.
However if the outer edges have a higher current density due to an edge effect, then the full reduction to form a metallic molybdenum coating is achievable. We saw a decreasing current density gradient towards the central region. The inner band formed an intermediate reduction zone, where it was supplied a potential great enough for the primary reaction of Mo(VI) to Mo hydroxide/oxide, however not high enough to drive the secondary reduction of the hydroxide/oxide to metallic metal, this is indicated in Figure 5.2 and Figure 5.3 by the blued region.

Therefore to produce a full, even coverage of metal, the central region must have a surface potential greater than the secondary reaction’s reduction potential. This results in a far higher overall applied potential and current density than theoretically necessary.

Figure 5.3: Effect of applied current density on deposit on a Cu cathode. A, 0.2 A cm\(^{-2}\); B, 0.3 A cm\(^{-2}\); C, 0.4 A cm\(^{-2}\) and D, 0.5 A cm\(^{-2}\).
This high applied current has two detrimental effects, the first being the increase in the rate of HER and the second being the range of regional growth rates, and so localized morphology changes; both factors have damaging effects on the film’s uniformity and integrity. These issues will be further discussed in Section 5.4 Film Growth and Morphology Change with Time.

From Figure 5.3 we can see a visible change in the coating’s phase with applied current density. With a current density of 0.2 and 0.3 A cm\(^{-2}\) we can see the outcome of applying an insufficient current. We observed a thinned inner region of blue deposit indicative of MoO\(_2\), a product of Step 1, equation 2.8.1. This indicates that the applied current was too low. We repeatedly saw that a current density of 0.4 A cm\(^{-2}\) produces a uniform mirror like metallic molybdenum coating. From the coating produced using a current density of 0.5 A cm\(^{-2}\), we saw an increase in surface roughness and morphology, particularly in the outer region. This rougher growth is accompanied with a change of deposit colour and phase, possibly due to an elevated surface temperature causing a burning effect and deposit oxidization.

Localized temperature changes can have a significant affect on the deposition process. When applying a high current density, such as 0.4 or 0.5 A cm\(^{-2}\), the high-energy input can cause a temperature gradient in the electrode-electrolyte boundary and than lead to an overall increase the bath operating temperature, altering the reaction kinetics.
5.4 Film growth and Morphology Change with Time

All previous experimental testing was run under standard conditions, which included a deposition time of 1 hour. This was to allow the accurate comparison of film phase and morphology to assess the coating qualities and determine the optimum operating conditions. To gain an understanding of the effect that time had on the deposition process, a series of deposits were produced with increasing periods of applied current. The main focus of this study was to investigate how deposit morphology changed over time, with a focus on grain growth.

A significant problem concerning an electrodeposited film is the build up of residual stress in the coating. This stress is commonly thought to result from hydrogen incorporation in the deposited metal structure. Hydrogen evolution as described previously is considered essential for the electrodeposition of metallic molybdenum, as it acts as an intermediate reducing agent. However it was observed that it had a parasitic and damaging result on film growth at higher rates. A certain degree of the evolved hydrogen is co-deposited with the metallic molybdenum, affecting the morphology and properties of the film, including the structure and crystallinity of the deposits. Gas bubbles become trapped in the film and at grain boundaries, as well as gas fixed in the crystal lattice, Nikolić [2010]. This incorporation of gases causes internal tensile stresses. If the build up of the residual stresses becomes too great, cracking and delamination occurs, resulting in film failure.

At the beginning of the plating process, film and grain growth rate can be thought of as constant. Deposition can occur immediately after ion diffusion is controlled, resulting in a
constant rate of $\text{MoO}_4^{2-}$ and $\text{H}^+$ diffusion to the cathode, with a resultant flow of $\text{OH}^-$ ions to the anode. Therefore within the first nanoseconds of applied current, a theoretically perfect Cu substrate is uniformly covered with a film of metallic molybdenum. After an even coverage of molybdenum is deposited, the reaction thermodynamics and kinetics change as Cu is no longer the substrate material; now a nano-layer of molybdenum and molybdenum oxide/hydroxide is the new reaction surface. At 100 mA cm$^{-2}$ copper has a hydrogen evolution overpotential of 0.801 V [International Critical Tables, 6, 339 [1929]], which is higher than molybdenum, 0.56 V at 100 mA cm$^{-2}$, Petcherskaia [1950], and so molybdenum acts as a HER catalyst. As the current density is kept constant, throughout the deposition process, once the nano-film of molybdenum is deposited, the kinetics of the HER will increase, increasing the level of absorbed hydrogen gas, and so the residual stresses as the film grows. A secondary negative effect for the increased rate of HER, is that the overall current efficiency of molybdenum deposition is reduced, as a higher percentage of the applied current is used to evolve hydrogen at the cathode, reducing the growth rate of the film.

From this understanding, we can see that increasing deposition time increases the level of residual stresses in the film. In the early stages of film growth, the coating is formed from dense, compact layers of nano-sized particles. We observed smooth bright uniform coatings, 2-3 $\mu$m thick, deposited after 1 hour, but early signs of fine cracks appear across the film surface, due to internal stresses. We see that the cracks form in a regular repeating pattern, forming 10-20 $\mu$m sized diameter patches, adhered to the substrate.
Figure 5.4: Optical microscopy images of coatings prepared over different deposition times. Images taken at x50 magnification, with a blue filter applied.

From analysis of the optical microscopy images in Figure 5.4, we can see distinctive changes in surface morphology over time. After 1 hour of deposition, we can see that the film exhibits a high degree of pitting. But further analysis, at a higher magnification, revealed that the pits were only surface defects that recessed into the coating, less than 1 µm, therefore no copper substrate is exposed. However these pits in a corrosive environment, would decrease the film’s protective properties, acting as an active site as well as acting as a stress concentration zone. After 4 hours of deposition, we see the repeating cracks form a wrinkled scale that is evenly spread across the entire coating, indicating that the internal stress is distributed across the film, revealing of the residual stress issues previously examined.
Figure 5.5: Scanning Electron Microscopy images of molybdenum film growth after increasing deposition periods; 1 hour, 4 hours and 10 hours.
Scanning electron microscopy, SEM, images were taken using a Hitachii S3000 N, in a secondary electron detector, under a range of accelerating voltages and working distances, to optimise image clarity. Samples were pre-coated with a 5 nm layer of gold, using an Edwards S150A Sputter coater, to increase surface conductivity and reduce charging.

Another prominent surface feature that was observed in the early stages of the deposit’s morphology was the formation of enlarged metal sphere protrusions, growing on the regular coating, clearly seen in the SEM image of the 4 hour film exhibited in Figure 5.5. Particulate growth appears to be favoured over the underlying film. This is hypothesized to be the result of an increased current density effect occurring on higher surface areas and raised regions of the cathode, which increases the deposition rate at the domain. It was observed that it was common for the particulates to be sited above a surface pit or hole in the film. It was not until the round deposits are removed or detached from the coating surface that the hole beneath were visible. The surface pits are as common and as evenly distributed across the film surface as the particulates. It is postulated that the pits are actually regions of increased HER activity, becoming hydrogen vents from beneath the film surface. As hydrogen is required for the secondary reduction reaction, it could be that the regions of increased hydrogen gas density and flow, would have a higher rate of molybdenum reduction and deposition. The increase in reducing agent could lead to the formation of larger deposits such as the metallic spheres.

As deposition time was increased, we saw these surface features grow. As discussed, raised regions and protrusions were favoured, affecting the growth rate of the film. Film growth
Figure 5.6: Scanning Electron Microscopy image of a coating produced over a period of 10 hours. Smooth particulate growth can be seen in A, around vent like surface holes. Cross-sectional imaging shows internal cracking and the vent system, B.
was not uniform, the coating did not continuously increase in thickness; instead over time morphology was increased, with surface defects becoming more extreme and film density reduced.

We can see from Figure 5.5 after 10 hours, growth is centered around the vents. This could be caused by concentrate gas streams, produced at the cathode, shielding specific areas, while promoting growth at the surface vents. This extended growth time promotes the formation of ‘flower shaped’ smooth protrusion conglomerations up to 100 µm in diameter formed from fused compact particles. From Figure 5.6, we can see from the cross sectional image, the poor uniformity and structural integrity of the coating. The film is 50 µm at its thickest however some regions are less than 10 µm thick. There is a high level of internal cracking in the deposit particulates, which is proposed to be due to the high level of absorbed hydrogen.

![Figure 5.7: Scanning Electron Microscopy image of film particulate after a 10 hour coating period. High level of residual stress resulting in complete fracture of particle.](image)
From Figure 5.7 we can see the final result of the high level of residual stress in the deposit. We can see an individual particle, exhibiting complete fracture, initiated from the central crater. It appears to be shattered leaving splinters, showing the brittleness of the deposit.

The resultant affect of increasing deposition time was an increase in film morphology and surface area. We saw with film deposition time an increase in coating thickness, with a maximum uniform, dense deposit of up to 25 μm, however less uniform coatings, such as Figure 5.6, reaching a thickness of 50 μm. We observed initial cracks that propagate the coating in the early stages of deposition, grow with deposition time, and possibly form the initial foundations for the protruding grains, Figure 5.8.

We saw that the optical appearance of the coating changed with time. Deposits made in under 4 hours, were a bright mirror like metallic silver, smooth and uniform. However as the morphology increases, the coatings lost their sheen, and mirror like reflectiveness. This is caused by a decrease in the amount of light rays having a total reflection, due to the surface roughening. The outer regions of the deposit also had increased roughening, compared to the central film. This is caused by the increased current density due to the edge effect, leading to higher deposition rates, resulting in a rougher, higher surface area film.
Figure 5.8: Schematic of film growth over time with comparison to cross-sectional scanning electron microscopy images of coatings; 1. 1 hour; 2. 4 hours; 3. 10 hours.
5.5 Effect of Substrate on Film Growth

Cathode chemistry and surface morphology had strong effects on the overlaying coatings deposited on its surface. The requirements of a cathode are to have a low hydrogen overpotential, to be a good conductor, exhibit good electrocatalytic properties, corrosion resistance to the immersed bath solution, minimum gas bubble retention and be mechanically rigid.

Copper was used as the primary substrate material as it fulfilled all of the requirements needed. Morley [2012] acknowledged the independence of cathode material on the ability to deposit molybdenum films, achieving coatings on nickel, steel, iron, tantalum and rhodium.

Molybdenum coatings were successfully deposited on a number of carbon steel substrates, however it was observed to be a more difficult substrate to coat. A greater current density was required to deposit a uniform metallic molybdenum coating on steel, due to the requirement of a larger overpotential. A decrease in current efficiency was observed, with the HER becoming more prominent. Even coverage was not achieved until a current density of 0.55-0.6 A cm\(^{-2}\) was applied to the steel cathode, with the sample exhibiting strong edge effect tendencies. Originally 0.4 A cm\(^{-2}\) was applied to the 1 cm\(^{2}\) steel substrates, however this resulted in a composite coating, similar to Figure 5.3.1, with an uncoated central region. Applied current was increased systematically, until the thinned region and surrounding blue oxide film had been replaced by metallic molybdenum. This requirement for a higher reducing current, resulted in an increase in hydrogen evolution, as well as higher induced substrate temperatures, leading to a degree of surface burning.
Substrate surface roughness was seen to have an influencing effect on coating morphology. A highly polished substrate, using 1 µm Leco diamond suspension, results in the growth of a highly reflective mirror-finish thin film. Polishing removes surface features that can distort the electric field, resulting in a more even deposition. The films showed strong adherence up to 2 µm, around 1 hour of deposition. It was after periods greater than 1 hour, that the hydrogen induced internal stresses caused film cracking. When the substrate was polished the substrate-film surface area was reduced, reducing the contact area. This had two detrimental effects; firstly the number of physical bonds adhering the film to the substrate was reduced with decreasing area, and so when cracking occurs, this results in delamination. The second effect is that surface roughness provides barriers to crack propagation. Without the higher number of physical bonds, adhesion was reduced and cracks were able to spread deep through the film unhindered. This reduced the protective nature of the film, as it could cause delamination of the coating. The smoother coating surface could however increase the corrosion resistance of the coating, as there is a reduction of localized sites for pitting.

Mechanical locking has been shown as a mechanism of adhesion. Inter-fingering of deposited metal into surface features of the substrate has been shown to mechanically lock the coating layer to the substrate Kinloch [1988]. It was observed that surface preparation by grinding to 1200 grit with wet and dry paper, increased the adhesion of the films. This could be demonstrated by simple scotch tape pull-off tests which resulted in small amounts of detached metal particulate, but no large film deposits removed, therefore no substrate was exposed.
However this high roughness substrate resulted in a high morphology film, as the protrusions of the rough substrate distorted the current field, increasing the deposition rate in the localized area, increasing morphology. This had the effect of reducing the reflectiveness of the coating, and also could result in reducing the coating’s corrosion resistance, as it provided a higher concentration of pitting and stress initiation sites. Due to the increased morphology, and slight reduction in coating density, cracks are unable to spread through the film. This could increase the wear resistance of the coating, although an increase in the surface friction coefficient due to roughness could be possible. However we may see that the smaller protrusions once detached from the surface due to wear could increase the surface lubrication through a tribological mechanism.

It was found that polishing with a 6 µm sized diamond suspension produced a high mirror like film. We observed surface cracking, however the cracks were superficial surface defects, which did not penetrate far into the coating, Figure 5.9.
Figure 5.9: Scanning Electron Microscopy images of molybdenum films created on different surface roughness copper substrates, under the same deposition conditions.
5.6 Film composition and Phase Analysis

Throughout the film optimization process, the coatings were characterized to analyze their physical appearance as well as their composition and phase, Figure 4.2: Experimental procedure flow diagram. Metallic molybdenum and it’s wide-range of hydroxides and oxides have many varied and distinctive colors; therefore visual inspection could be a useful tool to characterize the phase of the coatings. In the early experimental stages, film colour examination was a rapid technique to suggest whether the deposition condition changes have a positive or negative outcome. Optical and scanning electron microscopy techniques were necessary to understand how the film morphology and thickness changed with the condition variables. However to accurately and confidently determine the composition and phase of the coating, chemical analysis was required.

Energy Dispersive X-ray Spectroscopy, EDX, was used in correlation to the SEM imaging. An EDX Advanced Analysis Techniques system was used, mounted in a Hitachi S3000N SEM and operated in situ with a HLK backscatter diffraction analysis system. To improve the conductivity of the samples and to reduce surface charging, the samples were coated with a nano layer of carbon, using an Edwards 360 Evaporator.

EDX could provide an elemental compositional map, which could be useful to quickly provide a semi-quantitative analysis of the coatings and determine the presence of impurity elements. However EDX cannot be used to determine a coatings phase, i.e. whether it is metallic
or an oxide, or provide information on film crystallinity. For this analysis, X-ray Diffraction Spectroscopy, XRD, was used.

A Rigaku MultiFlex XRD was used to analyze coating samples bonded to copper substrates. Using a reference spectrum, a wide initial 2θ scanning range was selected. Initial full spectrum scans yielded poor film analysis, producing strong diffraction patterns of the copper substrate. From cross-sectional SEM imaging, we knew that the scanned samples range from 2 μm - 50 μm in thickness, well within the Rigaku diffractometer operating capabilities. To not produce an XRD pattern indicates the lack of strong crystallinity in the metallic film. Slower scan rates of 0.05 degrees per minute were used to perform more thorough analysis of the coatings, building up a more accurate pattern, Figure 5.10.

![X-ray diffraction spectroscopy pattern of Mo coatings on copper](image)

**Figure 5.10:** X-ray diffraction spectroscopy pattern of Mo coatings on copper. (A) Copper Substrate. (B) 10 hour Mo deposition, (C) 4 hour Mo deposition and (D) 2 hour Mo deposition.
A broad peak was identified at 40.5° in all samples. This peak corresponds to the Mo(110) orientation. The X-ray diffraction forms a broad peak indicating the amorphous structure of the deposit. We predict that the low intensity of the Mo peak is the result of the far greater diffraction pattern of the copper substrate, overwhelming the normalised intensity. We can see that as deposition time is increased, the (110) peak intensity is increased, and the peak broadness is decreased. This change in peak proportions denotes the increase of film thickness as a higher intensity reading is produced; this was confirmed through cross sectional SEM analysis. A reduction in peak broadness also indicates an increase in deposit particulate or grain size in the coating, this was also observed through top-down SEM analysis.

Implementing the Scherrer equation, an estimate for crystal size can be calculated:

\[ B(2\theta) = \frac{0.94\lambda}{L\cos\theta} \]

A Sherrer constant of 0.94 for full width, half maximum, FWHM, of spherical crystals with cubic symmetry was used, Langford [1978]. Crystal size was generally estimated to range from 0.9 nm – 3 nm, showing a highly fine nano-crystalline structure, expected for the use of high current densities when depositing a high overpotential metal. The lack of a sharp Bragg peak is the result of x-rays scattered in many directions leading to a broadened \((2\theta)\) signal, this is caused by amorphous materials. However micro-strain in a crystal structure can also result in peak broadening as well as shift. The deposited Mo coatings are known to contain a high level of
residual stresses, which makes determining crystal grain size difficult, using the XRD patterns achieved, however it is our belief that the coatings are amorphous in nature.

5.7 Effect of Thiourea on Film Deposition

The beneficial levelling and brightening effects of thiourea, as discussed in Chapter 3, were investigated for the reduction in surface roughness. A 0.01g/L solution of thiourea was prepared and the standard electrolyte was prepared, however, the thiourea solution replaced the normal source of the DI water. Deposition was performed via potentiodynamic polarization from +0.250 vs. OCP to – 4V vs SCE at a scan rate of 0.166 mV s⁻¹.

![Figure 5.11](image_url)

**Figure 5.11:** Scanning electron microscopy images of coatings deposited with electrolytes containing 0.01g/l thiourea. Deposition was performed via potentiodynamic polarization from +0.250 vs. OCP to – 4V vs SCE at a scan rate of 0.166 mVs⁻¹.
From Figure 5.11, we can see a very different film morphology of the deposit. The first obvious difference is the coating density. From the top left image, we can see that the film is made from small sub micron sized particulate, tightly packed and well adhered. The surface morphology seems smoother and more uniform, with less cracks and pits present. From the cross sectional image, we can see that a dense 20 µm coating was deposited. It appears that the leveling properties of the thiourea, reduced the surface morphology, decreasing the height and frequency of the protrusions. It is also clear that nucleation was favored over grain growth, as seen by the dense layers for nano sized metal spheres making up the coating.

However, we saw that coating thickness varied significantly across the sample. Figure 5.7, image C, was a cross-sectional image taken near the edge of the sample, where due to the significant edge effect, local current density is very high, resulting in a higher rate of coating growth. The central region of the sample had a much thinner film, of around 1-2 µm deposited. This region was also mainly blue brown in colour, indicating its oxide nature.

We saw that thiourea did act as a brightening and leveling additive in the outer regions of the cathode, however poor uniformity and oxide issues in the central region, made a full metallic molybdenum coating hard to achieve.

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Chapter 6: Electrochemical Testing

6.1 Potentiodynamic Polarization

Potentiodynamic polarization tests were performed to study the reduction reactions occurring in the electrolyte bath during deposition. Polarization scans were carried out in standard electrolytes containing molybdate ions, as well as solutions without the presence of molybdate. Scans were run +0.250 vs OCP to -4.00 V vs SCE, Figure 6.1.

Figure 6.1: Cathodic potentiodynamic polarization scans of electrolyte with (blue) and without (red), molybdate ions present. Scans ran +0.250 vs OCP to -4.00 V vs SCE.
From Figure 6.1 we can see that both cathodic profiles exhibit diffusion controlled behavior due to characteristic limiting current density, resulting in 3 distinct cathodic regions. We predict that the first reduction profile, Region I, occurring on both plots is the reduction of oxygen on the cathode, this is supported by the naturally aerated conditions of the electrolyte. The oxygen diffusion towards the electro-active surface gives the cathodic region of the PDP plot the distinctive cathodic diffusion limiting curve towards a potential of -0.75 V vs SHE. The ORR seen in Region I, in non-acidic conditions:

\[ O_2 + H_2O + 4e^- \rightarrow 4OH^- \quad E_{eq} = 0.351 \text{ v SHE at pH 6.8} \quad (6.1) \]

The increased cathodic current density reached by the blue curve, \( a_1 \), points towards the involvement of molybdenum ions in the overall cathodic process. This could be superimposed onto the existing oxygen reduction current, or be directly affecting its rate. Molybdenum dioxide’s high ORR activity has the effect of catalyzing the reaction compared to the less active copper surface under the same conditions. It is postulated that this one order of magnitude increase in current density is the current being used for ORR on MoO\(_2\). The current density inflection in the potential region - 0.750V vs SHE, is the first step in the 2 part reduction of Mo(VI) to form MoO\(_2\). Step 1:

\[ \text{MoO}_4^{2-} + 2H_2O + 2e^- \rightarrow \text{MoO}_2 + 4OH^- \quad E^0 = -0.78 \text{ V vs SHE} \quad (6.2) \]
You [1986] observed a similar inflection in the reduction of Mo(VI) in an aqueous environment at -0.8 V. We can confirm the deposition of MoO$_2$ is occurring due to the visibly blue film coating the cathode in this potential range.

At a potential of around - 0.850 V vs SHE we see a rapid current increase from 10 µA cm$^{-2}$ to 10 mA cm$^{-2}$, forming a distinct cathodic plateau. This is described as Region II. It is proposed to be the result of direct water reduction in the bath. It follows a Tafel slope of 0.1 V dec$^{-1}$, indicating a change from diffusion control to charge transfer control. Using the Nernst equation we can calculate that under our operating conditions, the HER occurs at a potential, $E_{eq} = -0.43$ V vs SHE.

The ORR seen in Region I in non-acidic conditions results in the production of OH$^-$ at the electrode that leads to a strong increase in localized pH at the surface of the cathode. This higher concentration of OH$^-$ at the cathode surface could be seen to cause the suppression of HER to a lower potential, due to reduced active sites on the cathode filled by adsorbed hydroxides and limited surrounding water molecules.

A similar cathodic plateau was observed by Tran [2006] on their investigation of the cathodic reactions on steel in aqueous solutions, at a comparable pH. They reported a Tafel slope of 0.12 V dec$^{-1}$, in a similar charge transfer controlled region, in a comparable potential range of -0.8 V. We confirmed a similar current consuming plateau in the polarization of DI water, adjusted to pH 6.8 with sodium hydroxide.
We are confident that Region II is the result of direct water reduction:

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{E}_{\text{eq}} = -0.43 \text{ V vs SHE at pH 6.8} \quad (6.3) \]

However the influence of the high concentrations of acetate and potassium ions on this reaction is not fully understood. The highly conductive salt solution would facilitate a high rate of charge transfer, and therefore an accelerating rate of HER, resulting in accelerated current consumed.

It is not until a current density of 0.1 A cm\(^{-2}\) is reached that we see the final region III, corresponding to a potential of around -1.00 to -1.50 V. Limiting current density appears in both curves, following the same trend, indicating hydrogen evolution reactions on the cathode are limited below current density of 0.1 A cm\(^{-2}\).

The solution remains highly saturated during deposition and so there is no observed change in bath conditions over time. Due to the stable nature of acetate ions it is unlikely that they are reduced in the bath. The high concentration of potassium ions could limit the activity of water present in the electrolyte.

Comparing the behaviors of the Mo coating vs Mo free profiles, it is not evident that MoO\(_2\) reduction affects the cathodic profile to form metallic Mo. In the -1.00 to -1.50 V region, on the blue curve at \(b_i\), we can see a very slight change in the cathodic plot. This does not appear to be a reduction feature, as there is no overall change in the consumed current. At higher
potentials than this both curves become identical. Reduction to Mo is obscured by the overwhelming, current consuming rate of HER. Current after -1.50 V vs SCE, is under pure mass transport control.

From the understanding that Ernst and Holt [1958] and Ksycki [1949] outlined, and the previous investigations, we can assume that there is a secondary reduction reaction occurring on the cathode, resulting in the formation of metallic molybdenum at a current density greater than 0.2 A cm^-2. We see from the Step 1 reaction, (6.2), that MoO₂ is deposited. We clearly see this through the creation of highly uniform oxide films.

We are not able to observe the reduction profile of molybdenum oxide to metallic molybdenum, due to the vastly overwhelming HER occurring depleting more than 99% of the supplied current. However the formation of molybdenum is visible, with a surface film colour change from blue to bright metallic.

Through our previous literature review, it is understood that hydrogen is the reducing agent for the reduction of MoO₂:

\[
\text{MoO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Mo} + 2\text{H}_2\text{O} \quad E^o = -0.98 \text{ V vs SHE} \quad (6.4)
\]

We propose that reduction occurs by adsorbed hydrogen atoms on the cathode surface, on the MoO₂ coating. We know that there is a high concentration of adsorbed hydrogen, due to the intense rate of HER:
If we consider the reduction driven by surface absorbed hydrogen, then we would produce metallic molybdenum through the combination of reactions (6.4) and (6.5), we get (6.6), Step 2:

\[
\text{MoO}_2 + 4H_{ad} \rightarrow \text{Mo} + 2\text{H}_2\text{O} \quad E^0 = -0.913 \text{ V vs SHE} \quad (6.6)
\]

This mechanism allows the formation of MoO\(_2\) deposits that actively increase the rate of HER occurring on the cathode due to their catalytic nature. This generated hydrogen is then used as a reducing agent, resulting in the formation of metallic deposits.
6.2 Cyclic Voltammetry

Cyclic Voltammetry scans complement the previous results from the potentiodynamic polarization tests. Scans were performed from 0.5 to -1.5V vs SHE, in the cathodic direction. From Figure 6.2 we can see a very similar reduction peak occurring at around -0.75 V vs SHE, \( a_{ii} \), corresponding to the reduction of Mo(VI) to MoO\(_2\). After a potential of -1.00 V a rapid reduction in current density is observed, with the curve becoming featureless, without the secondary reduction peak, \( b_{ii} \), predicted to be the highly vigorous generation of hydrogen, fully limited by mass transport control. Deposited molybdenum was observed at lower potentials.

\[ \text{Figure 6.2: Cyclic Voltammetry curve of deposition reduction reactions in molybdate containing electrolyte. Scan rate of 50 mVs}^{-1}. \]
6.3 Potentiodynamic Polarization of coating in 3.5 wt% NaCl solution.

Potentiodynamic polarization tests were carried out, in the anodic regions, in a number of corrosive environments, to investigate the protective nature of the molybdenum coatings. The coatings performance was compared to that of pure copper and pure molybdenum. 1 cm$^2$ test samples were immersed in a standard 3.5 wt% solution of NaCl, prepared at 25 °C. A platinum mesh counter electrode was used to complete the circuit, with a SCE to measure surface activity. The solution was not stirred or aerated.

![Potentiodynamic Polarization of Mo on Cu - 3.5% NaCl](image)

**Figure 6.3**: Potentiodynamic polarization of molybdenum coating deposited on copper, compared to the performance of pure copper and pure molybdenum. Performed in a 3.5% NaCl solution, at 25 °C. Scanned from -0.250 V SCE to +0.400 V vs SCE with respect to OCP.
Pure molybdenum is less prone to corrosion in comparison to pure copper, which can be observed from the PDP curve in Figure 6.3 by the pure Mo curve’s lower current densities. Initially the corrosion tendency of the molybdenum coating on copper is better than the pure copper in the NaCl solution, as the current density for the former is much lower than the latter. There is 2 orders of magnitude difference between the curves current densities. Copper is seen to corrode much faster than molybdenum, showing the refractory metals stability in NaCl.

A secondary oxidation peak at a potential of \( E = -0.50 \) V vs SHE, is observed in both the coated copper and the copper samples. This peak is present in the coating curve due to a breakdown of the protective coating, exposing the less corrosion resistant copper substrate. The pure molybdenum PDP curve shows that the metal is uniformly corroded. Therefore we would expect that the thin coating of ~ 2-3 µm to lose its protective integrity with time. The active region is 1 to 2 orders of magnitude lower for the pure molybdenum, than the molybdenum coating. This difference in current density could be attributed to a number of factors such as high surface area of the deposited coating compared to the polished pure molybdenum sample. This may also be due to micro cracks and pits exposing regions of underlying copper. This is believed to result in the short-lived current density acceleration at around -0.1 V vs SCE right before the small peaks. The decrease in current density following these peaks at higher potentials alludes to the passivating behavior of the underlying copper substrate. Analysis of the PDP tests clearly shed light on the protective qualities of the coating in a chlorinated environment.
6.4 Potentiodynamic Polarization in Alkaline Environment

Potentiodynamic polarization tests were also performed in an alkaline solution of 1 wt % NaOH, using a similar experimental set up to the chlorinated corrosion study. Pure molybdenum is unstable in basic conditions, and shows little resistance to corrosion, Figure 6.4, which can be observed through the considerably high current densities. Molybdenum was so unstable that the thin coating dissolved before current was applied, showing its poor corrosion resistance in an alkaline environment.

Figure 6.4: Potentiodynamic polarization of pure copper and pure molybdenum. Performed in a 1% NaOH solution, at 25 °C. Scanned from -0.250 V SCE to +0.400 V vs SCE with respect to OCP.
As seen in the comparison of pure copper and pure molybdenum, molybdenum corrodes vigorously and uniformly, before a complex layer is formed, suppressing further corrosion. We can see that a thin molybdenum coating would rapidly corrode, quickly exposing the copper substrate. A PDP plot could not be obtained due to the rapid dissolution of the coating once immersed in solution.

From Figure 6.5, we can see that in alkaline media, a passive layer does not form, and Mo actively dissolves to form MoO$_3^-$, in the ionic region of the Pourbaix diagram. This supports our observation of the thin molybdenum coating degrading in the alkaline solution of pH 12.4.

**Figure 6.5**: Potential- pH equilibrium diagram for the system molybdenum-water, at 25 °C. Pourbaix [1966].
6.5 Potentiodynamic Polarization in Highly Acidic Environment

To investigate the possible use of the deposited molybdenum coating as a potential anode material for use in electro-winning processes, such as zinc processing, potentiodynamic polarization testing was carried out using a high morphology, 50 µm thick molybdenum coated anode in concentrated 10 % sulphuric acid, a typical electrolyte used in the electro-winning of zinc.

Due to molybdenum’s high corrosion resistance in mild acids as previously discussed in Chapter 3, and the metal’s low overpotential, it is an ideal candidate for catalyzing the oxygen evolution reaction, OER, enhancing the OERs efficiency. This increase improves the anodes lifespan as well as increasing the energy efficiency of the electro-winning process.

To assess the coatings performance as an oxygen evolving catalyst, and so its resistance to anodic corrosion by oxygen evolution, PDP tests were carried out in a 10% sulphuric acid solution, using a similar experimental setup to the previous corrosion studies.

We observed a rapid oxidation and delamination of the coated anode once the film was immersed in the high acidic environment. We postulate that due to the coating’s high surface area and so increased reactivity, resulted in a rapid surface oxidation by the aggressive environment. This oxidation caused a lattice structure shift due to molybdenum high Pilling-Bedworth ratio. This change in orientation resulted in a build up of internal stresses that once a critical limit was reached, lead to delamination of the film, from the substrates surface.
Chapter 7: Up-Scaling of the Deposition Process

During the previous experimental stages, the electrodeposition process of metallic molybdenum coatings has been explored on relatively small scale; predominantly, coatings were prepared on 10 x 10 mm copper and steel cathodes. This allowed the investigation of the deposition process and the reactions involved, at relatively low current densities, permitting the use of a potentiostat. It also had the added benefit of using a small deposition bath, a 600ml jacketed cell, reducing the cost and final waste of a high concentration electrolyte.

To investigate the effect of up-scaling the coating process, a number of increasingly sized copper cathodes were used to study the feasibility of deposition on larger substrate sizes. From our previous findings we saw that the deposition mechanism is current dependent, therefore it was hypothesized that if the applied current is sufficient to produce a localized current density of 0.4 A cm$^{-2}$, the optimal coating parameter, then successful deposition of metallic molybdenum will occur. To enable the supply of a current density of 0.4 A cm$^{-2}$, on cathodes greater than 3 cm$^2$, a larger current source would be required, as the Princeton Potentiostat used from previous galvanostatic experiments was limited to supplying a current of 1.2 A. To achieve the higher currents necessary a 25 A DC Xantrex XKW 40 - 25 power supply was used. Carbon fibre felt, mounted on a graphite rod was employed as an anode, giving a greater electrode surface area to electrolyte interface. Cathodes were formed from 0.15 mm thick copper sheet cut to the desired electrode area. Initial attempts to mask the back surface of the cathode sheet were unsuccessful. It was found that insulating tape was easily delaminated from the cathode surface by hydrogen gas generated behind the backing, from leaked electrolyte. Tolber MicroStop lacquer was a
successful non-conductive surface barrier, but it was observed that at higher currents, due to the increased temperature of the electrode, the lacquer was softened, and delaminated. Another issue concerning the MicroStop was its difficulty to remove. To enable the coating of both sides of the electrode, one side must be painted, the other plated, then this process reversed. We saw that it was difficult to remove lacquer from the metal coating due to its high surface morphology; soaking and cleaning with acetate resulted in a damaged film. We found the solution to surface shielding was to manufacture a chemically stable HDPE sample holder, allowing quick and easy shielding of the back of the cathode, Figure 7.1. A rubber gasket on either side of the copper sheet acted as an insulating mask and seal from the electrolyte. Nylon bolts were used to seal the holder, and apply pressure to the gasket. The benefit of the holder was that it allowed firm placement in the bath, the desired distance from the anode, as we saw that the thin lacquered copper sheet was deformed by the necessary, aggressive stirring of the solution.

Initial deposition attempts in the standard 300 ml of electrolyte in the 600 ml water jacketed cell, were successful up to a cathode area of 8.89 cm$^2$ (3.5 x 0.39 in$^2$), requiring a theoretical 3.6 A of applied current. However we observed two detrimental changes in the electrolyte over the deposition at that applied current and greater. After 10 minutes of coating, an increase in bath temperature was seen. The original water bath had the capability of heating the cell to a fixed 35 °C, however during deposition at a high-applied current, due to the resistance in the solution and cathode surface, an increase of 10 °C was seen in 5 minutes. This had the negative counter effect of increasing the HER rate, causing gas shielding of the central zone of the electrode. This increased HER also created an unwanted surface froth. The secondary observation was a solution colour change from translucent white to a pale brown-green. This
colour change could represent a reduction of Mo ions in solution from Mo(VI) to a soluble Mo(III) Deltombre [1956]. This reduction of ions in solution could lead to a decrease in effective Mo reduction at the cathode surface, limiting film growth. To accurately reproduce the plating process at a larger scale the whole system required expansion, including bath size and electrolyte volume, and a cooling system to suppress the temperature change.

Coating of 33.9 cm$^2$ (3.5 x 1.5 in) copper shims required an electrolyte volume increase to 1 L. The increase in bath size required a more powerful method of agitation to keep the solution fully molten, therefore the magnetic stirrer was swapped for a rotating Teflon stirring rod adjusted to 500 rpm. We found this to be an improved method of agitation, as the propeller head could be positioned directly between the anode and cathode faces, allowing a greater velocity of electrolyte movement over their surfaces, reducing the amount of surface gas, and so shielding.

For each fresh electrolyte, new carbon fibre felt anodes were manufactured, with matching electrode sizes. The felt rectangles were pierced and mounted onto a 1 cm diameter graphite rod to allow them to be firmly suspended in the electrolyte without stirring induced sway. The anodes were washed to remove loose surface carbon fibres that could detach in the bath, increasing solution viscosity and nucleation sites. Before deposition, the anode was left in the solution to become saturated in the electrolyte, allowing a better conductive connection.

Once in the holder, the exposed surface area of the cathode is 17.75 cm$^2$ (1 x 2.75 in), when a current density of 0.4 A cm$^{-2}$ was applied for a period of 5 minutes, a metallic
molybdenum coating was produced. However the coating was noticeably thinner in the central region of the cathode. The film also had poor adherence. Although the poor adherence of film could be caused by improper surface cleaning, the cleaning process remained constant throughout the experimental stages, and had not previously been shown to reduce the coatings adherence.

To counteract the adherence and uniformity issues, the applied current was systematically increased until film coverage was even and strongly bonded. It was seen that 10.6 A, and so a current density of 0.6 A cm\(^{-2}\) was required. The increase in current density compared to the smaller current densities required to plate the 1 cm\(^2\) scale samples, is thought to be necessary due to the increased resistance in the system, especially the larger copper cathode.

**Figure 7.1**: HDPE sample holder with an uncoated copper cathode, and two molybdenum coatings deposited over a 5 minute period.
It was seen that successful plating could only be carried out for a maximum of 5 minutes. After 5 minutes, the cathode increases in temperature, even with the cooling water jacket system chilling the electrolyte; we saw that the resultant HER rate increases, and a solution colour change. To prolong the life of the electrolyte and allow thicker coatings to form, the deposition current would be switched off for a 2 minute cooling break, allowing the cathode temperature to stabilize to normal conditions. The cathode was not removed from the bath solution, and so not exposed to air. The deposition process was then initiated again, after sufficient cooling. It was seen the cooling intermission period did not have any harmful effects on the metallic film, and continuous plating was possible after. This technique yielded a higher quality film to that of constant applied current, Figure 7.1.

Metallic molybdenum coatings were also deposited on similar sized steel shims. As seen previously, the deposition current required to form a uniform, even molybdenum coating on a steel cathode is higher than that needed on copper, due to the lower hydrogen overpotential of steel. An applied current of 12 A was necessary to produce an adhered film with no central thinning, 1.4 A greater than the current required for copper coating; giving a current density, \(i\), of 0.68 A cm\(^{-2}\). Steels instability in the electrolyte was also observed, in the form of iron corrosion products formed on the electrodes surface, in areas exposed to the acetate solution. This resulted in the need to wash the steel cathodes immediately after the deposition period. It was also important to establish a tight seal between the cathode and gasket in the holder, to prevent leakage of corrosive electrolyte.
A number of Mo-Ni coatings were also co-deposited on to the larger sized copper cathodes. A standard 1L molybdate acetate bath was prepared, with the addition of a 0.1 M solution of nickel sulfate. Using the deposition apparatus used to prepare the large copper and steel coatings, 48 ml of 0.1 M nickel sulfate were added to the electrolyte bath, supplying 1.26 g of nickel sulfate to the solution. This value was calculated for coating area, using the findings of Ni-Mo co-deposition, by Ksycki [1949]. The applied current was kept at 10.6 A, the same used to deposit metallic molybdenum on copper.

The main observation during the co-deposition was the increased effect on uniformity the addition of nickel on the coatings. The coatings appeared a lighter grey in colour, compared to the brighter metallic molybdenum films, but more even in coverage and thickness. This is thought to be caused by the catalytic effect of nickel on the molybdenum deposition reaction. As discussed in Cathode Chemistry, Ernst and Holt [1958], saw the effect of nickel reducing the hydrogen overpotential of the co-deposition process, and acting as an intermediate for the secondary reduction of molybdenum hydroxide to metal, increasing deposition rate at a lower potential.
Chapter 8: Conclusion

8.1 Summary of Results

We demonstrated bright mirror finish metallic molybdenum coatings, up to 50 µm thick were deposited from an aqueous electrolyte bath, containing high concentrations of acetate complexing ions. From our investigation into the deposition process, we can confidently state that the deposition mechanism occurs over a 2 step reduction process, with the formation of an intermediate oxide or hydroxide film, complimenting the findings of Ernst and Holt [1955]. From the deposition condition studies, we found that coatings of the highest uniformity and adherence were obtained from super saturated acetate baths, up to 10 M, at a pH of 6.8 and 35 °C.

A strong edge effect was observed on coatings deposited with a current density less than 0.35 A cm\(^{-2}\), resulting in the incomplete reduction of an intermediate blue-brown coating. Burning of coating occurs at current densities greater than 0.5 A cm\(^{-2}\). It was seen that 0.4 A cm\(^{-2}\) repeatedly produce the highest quality coating on copper. A slightly higher applied current was required to coat steel.

Surface morphology was seen to drastically increase with time, driven by favored local deposition on protrusions, reducing the density and stability of the film. Thiourea acted as a leveling agent in some cases, resulting in regions of increased coating density. The crystal
structure of the coating was seen to be amorphous in nature, as confirmed by XRD analysis, producing low intensity, broad peaks favoring the Mo (110) orientation.

The significant HER occurring simultaneously on the cathode resulted in low deposition current efficiencies of less than 1 %. This parallel reaction was credited for the cracked nature of the films, and reduced density and limited growth. PDP and CV techniques were used to investigate the reduction reactions occurring in the bath during deposition, however due to the elevated levels of HER, the reduction of metallic molybdenum was obscured at low potentials. An increase in current density was observed which was attributed to the deposition of MoO$_2$, catalyzing the rate of OER. A reduction mechanism was suggested, with adsorbed hydrogen on the oxide surface, reducing it to form metallic metal and expelling water.

Up-scaling of the deposition process was investigated with well adhered, uniform metallic coatings achieved up to 32 cm$^2$; this required an increased deposition current with substrate area, maintaining current density. Heat dissipation is a significant issue that required the use of a cooling bath.

The coatings exhibited good corrosion resistance in chlorinated solutions, protecting the underlying copper substrate. Molybdenum offered little protection in alkaline conditions where rapid coating dissolution was observed. Exposure to strong acids resulted in rapid oxidation and delamination from the substrate, caused by internal stresses, induced by a lattice shift.
8.2 Significance

Electrodeposition of metallic molybdenum from aqueous electrolytes has historically been dismissed as unfeasible. With less than 3 published papers investigating molybdenum deposition in the last half century, it is an area of research with many opportunities and possible advances. Molybdenum has many interesting and desirable properties that could potentially be harnessed though coating engineering. Aqueous electrolytes make this a more economic and viable solution to the current costly, and complex systems currently deployed.

The investigation we outlined has given us a greater knowledge and understanding of the deposition process and mechanisms involved. With a practical method of film deposition described, in a stable and simple system. We saw that the process could be used to form uniform, mirror finish coatings on a larger scale.

8.3 Strengths and Limitations

We saw metallic molybdenum can consistently be deposited indicating the repeatability of the process, with a number of substrate materials possible to deposit on. Short deposition times were seen to produce dense, uniform crack free coatings. However they were sub 3 µm thick.

Deposition current density is heavily limited by the parallel HER, however it is proposed that it is this mechanism that produces the reducing agent we need for the full reduction to metal.
Growth rate is restricted by the low deposition current efficiencies that are reduced further once MoO$_2$ is formed on the copper surface, due to its more catalytic nature.

However the real limit to successful continuous growth of thick coating is hydrogen inclusion. A dense thin film was observed to be deposited over 1 hour. It is at longer deposition periods that we see residual stress limits reached, and we observe the propagation of cracks, and the subsequent reduction in film integrity resulting in roughened coating, described in Chapter 5.4.

Acetate’s reaction in the bath during the deposition process is not fully understood. It is commonly described as a bath stabilizer and a buffer in literature, however no detailed studies have been performed on its specific role as a complexing ion. Without this knowledge, only assumptions can be made.

### 8.4 Future Work and Applications of Research

With the limitations considered, we can see that the aim of the future work would be to reduce the inclusion of hydrogen and the roughness of the film during growth. Attempts to limit hydrogen evolution could have the effect of limiting the growth of the film, due to the requirement of the reducing nature of hydrogen, at the cathode. However, if reducing the incorporated hydrogen were possible, we would reduce the internal stresses and prevent film cracking, which as we saw in Chapter 5.4 were the cause for the un-uniform thickness growth.
A method for the reduction of hydrogen incorporation is depositing the coating using pulse and reverse pulse deposition. This technique allows for a set frequency off time, the benefit being that the deposit has time for surface adsorption and desorption reactions to occur, and grain recrystallization, both actions reduce film internal stresses. Pulse deposition also allows for the ability to use much higher instantaneous current densities resulting in an increase in the nucleation rate, as there is enough energy in the system to form new grains. This produces a denser, smoother, harder coating. Increasing pulse off time can also result in the growth of larger grains. (Devaraj [1990]; El-Sherik [1996]; Landolt [2003]).

Another method to allow a more controlled film growth is the use of brightening and leveling agents. The mechanism for brightening and leveling was discussed in Chapter 2, with the discussion of thiourea. It is proposed that further investigation of thiourea on deposition control is needed. The use of citrates, saccharine and bone glue has also been observed to reduce film roughness during deposition in a similar current density controlling method. They could be shown to allow the growth of a denser film, with the ability to heal propagating cracks, through preferential deposition, and stabilize continuous growth.

Further coating characterization is required to confidently determine crystallinity. We suggest TEM analysis to give a precise characterization of the film.
References


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