Copper Electrodeposition in the Presence of Guar or Activated Polyacrylamide

Thesis submitted by
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ABSTRACT

In the copper electrodeposition industry, it is essential to dose very small concentrations of additives including chloride ions to control the physical and chemical properties of the copper deposit. It is also widely recognized in the industry that the adsorption of these additives at electrode surfaces significantly influences the current-potential relationships. This thesis presents the development of a new organic additive for copper electrowinning and electrorefining. This thesis also presents the comparison between the new organic additive 'activated polyacrylamide' and Guartec (Guar), the industry-standard organic additive for electrowinning under industrial conditions.

The first half of the thesis presents the results of bulk electrolysis experiments using either a rotating cylinder electrode (RCE) or parallel plate electrodes. The RCE was selected since it yields an uniform current distribution. In these experiments, the effectiveness of both organic additives in the presence of chloride ions was determined by directly measuring the surface roughness of the copper deposit. The second half presents Cyclic Voltammetry and Electrochemical Impedance Spectroscopy data using a rotating cylinder electrode to measure and quantify the behaviour of Guar and APAM at the electrolyte/electrode interface also in the presence of chloride ions.

It has been found from the literature review that polyacrylamide hydrolysis in weakly acidic solutions produces block copolymers. The diffusion layer thickness was determined from experimental limiting current density data. In this thesis/work, a

15million Dalton molecular weight polyacrylamide was dissolved in full-strength electrolyte (Cu, 36g/L; H_2SO_4, 160 g/L and chloride ions, 25mg/L) and in solutions with systematically halved concentrations, and in water and alkaline solutions at 50^{o}C for two hours under stirring. The effect of the preparation media of polyacrylamide was tested by measuring the surface roughness of the copper deposits obtained after 6-hours electrowinning at 50^{o}C using a rotating cylinder electrode. The statistically significant lowest surface roughness (6.59μm ± 0.49) was obtained when polyacrylamide was prepared in 16-fold diluted electrolyte (10g/L sulfuric acid and 2.25g/L cupric ions and 1.56mg/L chloride ions). The chemical structure of the polyacrylamide was examined after the preparation in 16-fold electrolyte using NMR. The NMR indicated that less than 10% of the non-ionic polyacrylamide was hydrolysed and it appears to consist of a block copolymer of polyacrylamide and polyacrylic acid. The new organic additive was named activated polyacrylamide (APAM)[1].

A comprehensive study on the effect of Guarfloc66 (Guar), the 40-year-old industry-standard organic additive, on copper electrowinning was lacking prior to this thesis. Guar was used as a basis against which to compare the effectiveness of APAM.

This study provides an industrial-relevant baseline against which the new additive was compared. Therefore, the fundamental processes occurring at the stainless steel/copper metal-electrolyte interface in the presence and absence of Guar and APAM were investigated. Fractional factorial experimental designs for copper electrowinning (EW) were conducted in which the effect of current density, temperature, diffusion layer thickness, Guar and APAM on surface roughness was studied. The evolution of dendrite formation was evaluated using Peaks-per-Centimeter and surface roughness. These above tests were verified by experimental design tests up to 12-hours EW time. The overall results indicated that a more uniform surface and lower roughness was obtained using APAM than Guar.

Cyclic voltammetry (CV) was used to understand the polarization behaviour of Guar and APAM at the interface of the copper electrolyte/copper cathode. Cyclic

[1] A property rights application (PCT/AU2005/001262) for this material has been filed with Intellectual Property, Australia.

voltammetry tests on the ageing of 2mg/L Guar in the electrolyte at 45°C indicated that Guar *depolarized* the electrode. At 300A/m^2 current density about 14mV maximum depolarization was obtained at 2-3 hours residence time whether the working electrode was stainless steel or freshly pre-plated copper metal. In contrast, CV tests showed that the presence of 2mg/L APAM *polarized* the electrode at 45°C and 65°C. At 300A/m^2 current density and 45°C the presence of APAM resulted in a significant polarization of the electrode on pre-plated copper over a 5-hour period, i.e., 13 mV at 5-hours residence time. This polarization value at 65°C was achieved after 1-hour residence time and the electrode remains significantly polarized over a 7-hour period.

Electrochemical Impedance Spectroscopy (EIS) tests were also conducted to characterize the electrode processes in the presence and absence of Guar and APAM. The electrochemical kinetics of the process was evaluated in terms of the charge-transfer resistance (or polarization resistance) and the double-layer capacitance. The electrochemical system of copper deposition in the presence and absence of Guar and APAM is described theoretically in terms of an equivalent circuit. The EIS experimental data was fitted to the equivalent circuit using complex nonlinear least-squares (CNLS) technique with LEVM and ZSimpWin™ software packages. The electrode process in the presence of Guar or APAM was quantitatively characterized using the high frequency loop only since it represents the kinetic control of the process. The low frequency loop that represents the mass-transfer control was used qualitatively only.

EIS tests indicate that Guar *decreased* the charge-transfer resistance values obtained from equivalent circuit modelling from about 0.83ohm.cm^2 in its absence to 0.74ohm.cm^2 at 2mg/L, -490mV versus the Hg/Hg_2SO_4 saturated in K_2SO_4, (MSE) for about 5-hours therefore *increasing* the electrochemical kinetics. The maximum reduction was determined to be 0.086ohm.cm^2 at 2-3hours residence time of Guar in the electrolyte. Therefore, electrowinning using the RCE, CV and EIS indicated that the role of Guar during the deposition process is to act as a *depolarizer*.

The presence of APAM in the electrolyte, in contrast, indicated that the charge-transfer resistance *increased* from about 0.79-ohm.cm^2 to 1-ohm.cm^2 for over 7-hours at 45°C and -490mV vs. MSE. The maximum increase in the charge-transfer resistance

value was 0.23-ohm.cm^2 at 3-5hours residence time. These set of tests with APAM were also repeated at -470mV vs. MSE and 45^{o}C, the results also indicated that APAM *increased* the charge-transfer resistance under these conditions. At this potential, a maximum increase of 0.42-ohm.cm^2 was determined at 3-5hours. When these tests were also repeated at electrorefining temperature (65^{o}C) and -445mV vs. MSE, the presence of APAM in the electrolyte also *increased* the charge-transfer resistance from about 0.39 up to 0.69-ohm.cm^2 for over 5-hours. The maximum increase of 0.34-ohm.cm^2 was at 2-hours for 65^{o}C. Electrowinning tests using the RCE, CV and EIS overall results with APAM were found to be consistent. In summary, APAM was found to *decrease* the electrochemical kinetics and that the role of APAM is as a levelling agent during the deposition process.

Guar and APAM decreased the double-layer capacitance but the equivalent circuit simulation data indicated that while the maximum reduction for Guar was 0.46 x 10^{-5} μF/cm^2, the maximum reduction for APAM was 1.2 x 10^{-5} μF/cm^2 at 45^{o}C and 6.8 x 10^{-5} μF/cm^2 at 65^{o}C. The overall EIS results may indicate that APAM is adsorbed more specifically than Guar.

It was also shown that the effect of temperature on the ageing sequence of APAM is consistent with reaction kinetics, i.e., it is faster at 65^{o}C than at 45^{o}C as would be expected. Results were presented for the rotating disc electrode (RDE) also. The EIS data at 65^{o}C and 45^{o}C are consistent with the CV data whether the RCE or RDE was used. However, the EIS data with the RDE was not amenable to being modelled using the most commonly referred equivalent circuit for electrochemical systems.

Bench-scale *continuou*s electrowinning tests using parallel plate electrodes where APAM and Guar were also dosed continuously and independently also indicated that APAM produces smoother deposits than Guar. The cross sections of the copper deposits were examined using scanning electron microscopy (SEM) and showed that Guar produced *porous* deposits and APAM produced *slightly columnar* deposits.

It is therefore concluded that the results of electrowinning, CV and EIS tests correlate: Guar *depolarizes* the electrode enhancing *depolarization* of the electrode by chloride ions and therefore increasing the growth rate with simultaneous formation of

voids and porosity. APAM *polarizes* the electrode or decreases the rate of the deposition process and therefore assists the nucleation rate and produces purer copper deposits. Voids and porosity are probably reduced by the continuous formation of crystallites and their coalescence as indicated by x-ray diffraction data. The overall results indicate that APAM is more specifically *adsorbed* than Guar at the electrolyte/copper-metal interface and APAM acts as a levelling agent.

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TABLE OF CONTENTS

STATEMENT OF ACCESS ..... **II**

STATEMENT OF SOURCES ..... **III**

DECLARATION ..... **III**

ABSTRACT ..... **IV**

TABLE OF CONTENTS ..... **X**

LIST OF TABLES ..... **XIV**

LIST OF FIGURES ..... **XVI**

CHAPTER 1 ..... **1**

INTRODUCTION **1**

1.1 Problem Statement 4
1.2 Thesis Objectives 5

CHAPTER 2 ..... **7**

LITERATURE REVIEW **7**

2.1 Electrodeposition Process Fundamentals 7
2.2 Transport Processes in Electrolytic Solutions 8
2.2.1 Mass Transfer 8
2.3 Rotating Cylinder Electrodes 10
2.4 Electrochemical Kinetics Fundamentals 14
2.5 Effect of Additives on Copper Electrocrystallization 17
2.5.1 Introduction 17
2.5.2 Effect of Chloride Ions on Nucleation and Growth 19
2.5.3 Effect of Organic Additives on Nucleation and Growth 20
2.5.4 Copper Electrowinning in the Presence of Organic Additives 22
2.5.5 Physicochemical Properties of Guar 23
2.6 Polyacrylamide Hydrolysis and Adsorption 24
2.6.1 Introduction 24
2.6.2 Polyacrylamide Hydrolysis Mechanisms 26
2.6.2.1 Polyacrylamide Hydrolysis in Neutral and Alkaline Solutions 27
2.6.2.2 Polyacrylamide Hydrolysis in Acid Solutions 28
2.6.3 Polyacrylamide Adsorption Mechanisms 31
2.6.3.1 Polyacrylamide Adsorption onto Metals and Metal Alloy 32
2.6.3.3 Cleavage of Polyacrylamide 34
2.6.3.4 Adsorption Mechanism of Polyacrylamide 34

2.7 Summary 36
2.8 References 38

CHAPTER 3 44

EFFECT OF PREPARATION MEDIA OF POLYACRYLAMIDE ON SURFACE ROUGHNESS 44

3.1 Introduction 44
3.2 Experimental 46
3.2.1 Design and Construction of Rotating Cylinder Electrode for Copper Electrowinning 46
3.2.3 Determination of Limiting Current Density and Diffusion Layer Thickness 50
3.2.4 Effect of Fluid Flow on Surface Roughness of Electrowon Copper 57
3.2.5 Experimental Results 57
3.3 Effect of Polyacrylamide Preparation Media on Surface Roughness of Electrowon Copper 59
3.3.1 Introduction 59
3.3.2 Experimental Conditions 59
3.4 Experimental Results on the Effect of Polyacrylamide Preparation Media on Surface Roughness of Electrowon Copper 60
3.4.1 NMR Analysis of Activated Polyacrylamide 64
3.5 Effect of Activated Polyacrylamide Ageing on Surface Roughness 65
3.6 Comparison of Polyacrylic Acid and Activated Polyacrylamide 67
3.6.1 Introduction 67
3.6.2 Comparison of Polyacrylic Acid and Activated Polyacrylamide in 4 Hour Electrowinning Test 68
3.6.3. Comparison of Polyacrylic Acid and Activated Polyacrylamide in 12-Hours Continuous Electrowinning 69
3.7 Discussion and Conclusions 70
3.8 References 73

CHAPTER 4 76

EXPERIMENTAL DESIGNS FOR COPPER ELECTROWINNING 76

4.1. Introduction 76
4.2 Experimental Conditions 77
4.2.1 Copper Electrowinning and the Effect of its Main Operating Variables 79
4.3 Experimental Results 80
4.3.1 2^{5-2} Experimental Design Results at 45^{o}C - 55^{o}C 80
4.3.2 2^{5-2} Experimental Design Results at 45^{o}C - 65^{o}C 85
4.3.3 Scanning Electron Microscopy of Electrowon Copper Deposits 87
4.3.4 Summary from Fractional Factorial Experimental Design 92
4.3.5 2^{2} Experimental Design – APAM *to* Guar Ratio at 50^{o}C and 6-Hours EW Time 93
4.3.6 2^{2} Experimental Design APAM or Guar at 50^{o}C and 4.6 Hours EW Time 98

4.3.7 2^2 Experimental Design – APAM or Guar at 50°C and 6 Hours EW Time 102
4.3.8 APAM or Guar at 50°C for 12 Hours EW Time 108
4.4. Discussion and Conclusions 111
4.5 References 113

CHAPTER 5 115

KINETICS OF COPPER DEPOSITION IN THE PRESENCE OF GUAR AND ACTIVATED POLYACRYLAMIDE USING CYCLIC VOLTAMMETRY AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY 115

5.1 Introduction 115
5.1.1 Equivalent Circuit for Electrochemical Systems – Copper Deposition 118
5.1.2 Measurement Modelling of Electrochemical Impedance Spectroscopy Data 122
5.2 Experimental 125
5.3 Cyclic Voltammetry in the Presence of Guar at 45°C 129
5.4 Cyclic Voltammetry in the Presence of Activated Polyacrylamide at 45°C 132
5.5 Cyclic Voltammetry in the Presence of Activated Polyacrylamide at 65°C 134
5.6 Electrochemical Impedance Spectroscopy Results in the Absence of Additives 138
5.7 Electrochemical Impedance Spectroscopy Results in the Presence of Activated Polyacrylamide at -470mv vs. MSE and 45°C 141
5.8 Electrochemical Impedance Spectroscopy Results in the Presence of Guar at -490mV vs. MSE and 45°C 147
5.9 Electrochemical Impedance Spectroscopy Results in the Presence of Activated Polyacrylamide at -490mV vs. MSE and 45°C 150
5.10 Electrochemical Impedance Spectroscopy Results in the Presence of Activated Polyacrylamide at -445mV vs. MSE at 65°C156
5.11 Discussion and Conclusions 159
5.12 References 162

CHAPTER 6 169

BENCH SCALE COPPER ELECTROWINNING TESTS 169

6.1 Introduction 169
6.2 Experimental 170
6.3 Experimental Results 173
6.4 Scanning Electron Microscopy of Copper Cathode Cross-Sections179
6.5 Determination of Crystallite Size 180
6.6 Conclusions 183
6.7 References 184

CHAPTER 7 186

SUMMARY AND CONCLUSIONS 186

7.1 Introduction 186
7.2 Hydrolysis and Adsorption of Polyacrylamide 187
7.3 Rotating Cylinder Electrodes 189
7.4 Effect of Polyacrylamide Preparation Media on Surface Roughness 190
7.5 Comparison of Activated Polyacrylamide with Guar 192
7.5.1 Effect of Guar and APAM on Surface Roughness of Copper Deposits 193
7.5.2 Physical Appearance, Scanning Electron Microscopy and General Area Detection Diffraction Solutions (GADDS) Results 195
7.5.3 Cyclic Voltammetry and Electrochemical Impedance Spectroscopy Results 196
7.6 References 201

LIST OF TABLES

Table 1-1: Industry-Standard Additives Used in Copper Electrodeposition 5
Table 2-2: Effect of Hydrolysis Media on the Population of Various Structures Starting from Non-hydrolysed Polyacrylamide[54] 29
Table 2-3: Hydrolysis Level and Triad Mole Fractions[56, 58] 30
Table 3-4: Electrolyte Composition and Other Variables 51
Table 3-5: Effect of RPM and Temperature on Diffusion Layer Thickness 56
Table 3-6: Electrolyte Composition and Other Variables 57
Table 3-7: Effect of Diffusion Layer Thickness on Surface Roughness 58
Table 3-8: Effect of Polyacrylamide Preparation Media on Surface Roughness 61
Table 3-9: Effect of APAM Degradation in 16-fold DE and Full-Strength Electrolyte. 66
Table 3-10: Surface Roughness Using Polyacrylic Acid and Activated Polyacrylamide 69
Table 3-11: Comparison of PAA and APAM in 12 Hours Continuous EW 70
Table 4-12: Electrolyte Composition and Additives Preparation Media..... 78
Table 4-13: Two 2^{5-2} Fractional Factorial Experimental Designs 80
Table 4-14: 2^{5-2} Fractional Factorial Experimental Results–Temperature Levels 45°C-55°C..... 81
Table 4-15: 2^{5-2} Fractional Factorial Experimental Results–Temperature Levels 45°C-65°C..... 85
Table 4-16: Electrowinning Conditions for APAM-to-Guar Ratio 93
Table 4-17: 2^2 Experimental Design and Results for APAM-to-Guar Ratio 94
Table 4-18: Electrowinning Conditions for APAM or Guar 98
Table 4-19: 2^2 Guar-or-APAM Experimental Design and Results..... 99
Table 4-20: 2^2 Experimental Design APAM-or-Guar at 10 RPM - 50°C - 6 Hours EW 102
Table 4-21: Effectiveness of Guar and APAM to Control Dendrite Growth 109
Table 5-22: Experimental Conditions for CV and EIS Experiments..... 128
Table 5-23: De-polarization Behaviour of Guar at 45°C 131
Table 5-24: Kinetic Parameters for Copper Deposition in the Presence of Guar at 45°C 132
Table 5-25: Polarization in the Presence of APAM at 45°C..... 133

Table 5-26: Polarization in the Presence of APAM at 65^{o}C 136
Table 5-27: Results for APAM at 45^{o}C and -470mV CD versus MSE 144
Table 5-28: Simulation Results for Guar at 45^{o}C and -490 mV DC versus MSE 148
Table 5-29: Results for APAM at -490mV CD versus MSE and 45^{o}C 151
Table 5-30: Results for APAM at 65^{o}C and -445mV CD versus MSE 157
Table 5-31: Maximum Change in Charge-Transfer Resistance and Double-Layer Capacitance Relative to the Presence and Absence of Guar and APAM .. 161
Table 6-32: Experimental Conditions 172
Table 6-33: GADDS Diffractometer Parameters 181
Table 6-34: Kruskal-Wallis Test Results for APAM Crystallite Size 182
Table 6-35: Kruskal-Wallis Test Results for APAM and Guar Crystallite Size 183
Table 7-36: Industry-Standard Additives Used in Copper Electrodeposition 187
Table 7-37: Two 2^{5-2} Fractional Factorial Experimental Designs 193
Table 7-38: Charge-Transfer Resistance and Double-Layer Capacitance Differences due to the Presence of Guar and APAM 199

LIST OF FIGURES

Figure 1-1: Mount Gordon Operations Flowsheet[4, 5] 3
Figure 2-2: Schematic representation of the structure of the double-layer in electrolyte solution during electrochemical reactions where anions are specifically adsorbed. 18
Figure 2-3: Schematic Representation of Different Growth Modes in Metal Deposition on Foreign Substrates. 21
Figure 2-4: The chemical structure of Guar[44] 24
Figure 2-5: Nonionic polyacrylamide 26
Figure 2-6: Anionic or Hydrolysed polyacrylamide 26
Figure 2-7: Polyacrylimide Molecule 28
Figure 2-8: Hydrogen Bonding of Non-ionic Polyacrylamide 31
Figure 2-9: Blocky polyacrylamide may exhibit covalent bonding with divalent ions Calcium and Iron [64] 32
Figure 2-10: Postulated Structure of Adsorbed Partially Hydrolysed Polyacrylamide Layer at the Copper-Electrolyte Interface 35
Figure 3-11: Rotating Cylinder Electrode – Top Section 47
Figure 3-12: Rotating Cylinder Electrode – Bottom Section 48
Figure 3-13: M1 Mahr Perthometer Measuring the Surface Roughness of Electrowon Copper 50
Figure 3-14: Current-Potential Curve – First Cycle Starting on pre-plated copper at 1mV/sec with the RCE at 0rpm (Free Convection) and 45^{o}C and 65^{o}C in the Absence of Additives to determine the Limiting Current Density (1037 and 1432 A/m^2). 52
Figure 3-15: Current-Potential Curve – Initial Cycle Starting on Bare Stainless Steel at 1mV/sec with the RCE at 10rpm and 45 and 65^{o}C in the Absence of Additives to determine the Limiting Current Density (1118 and 1497 A/m^2). 52
Figure 3-16: Current-Potential Curve – First Cycle Starting on Bare Stainless Steel at 1mV/sec with the RCE at 25rpm and 65^{o}C in the Absence of Additives to determine the Limiting Current Density (1155 and 1666 A/m^2). 53
Figure 3-17: Schematic Presentation of the Concentration Profile of Cupric Ions at the Electrode/ electrolyte Interface and the Diffusion Layer Thickness. 54

Figure 3-18: Variation in Kinematic Viscosity with Temperature 55
Figure 3-19: Dependence of Diffusion Coefficient of Cupric Ions as a Function of Temperature 55
Figure 3-20: Effect of RPM on Calculated and Experimental Diffusion Layer Thickness at 45°C and 65°C 56
Figure 3-21: Error bar plot of the effect of preparation media on surface roughness of the copper deposits. 62
Figure 3-22: ^{13}C NMR signal intensity of activated polyacrylamide prepared in 10g/L sulfuric acid and deuterium oxide (D_2O) solutions at 50°C for 2 hours. 65
Figure 3-23: Degradation of Polyacrylamide in 16-fold Diluted Electrolyte and Full-Strength Electrolyte 67
Figure 4-24: Rotating Cylinder Electrode Equipment 79
Figure 4-25: Effect of Diffusion Layer Thickness and Current Density on Surface Roughness 82
Figure 4-26: Effect of Current Density and Guar on Surface Roughness 83
Figure 4- 27: Studentized Residuals Plot 83
Figure 4-28: Residuals vs. Predicted Plot 84
Figure 4-29: Outlier T Diagnostic Plot 84
Figure 4-30: Significant Effect of APAM Concentration on Surface Roughness 87
Figure 4-31: Run 1- Cross section of copper cathode obtained at 45°C, 28mA/cm2, 0.5mg/L Guar, 1mg/L APAM and 110μm δ. Surface Roughness, Ra = 5.95±0.47 microns. 88
Figure 4-32: Run2 - Cross section of copper cathode obtained at 65°C, 28mA/cm2, 0.5mg/L Guar, 0.5mg/L APAM and 87μm δ. Surface Roughness, Ra = 6.36±0.64 microns. 88
Figure 4-33: Run 3 - Cross section of copper cathode obtained at 45°C, 32mA/cm2, 0.5mg/L Guar, 0.5mg/L APAM and 110μm δ. Surface Roughness, Ra = 7.08±1.38 microns. 89
Figure 4-34: Run 4 – Cross section of copper cathode obtained at 65°C, 32mA/cm2, 0.5mg/L Guar, 1mg/L APAM and 87μm δ. Surface Roughness, Ra = 5.56±0.67 microns. 89
Figure 4-35: Run 5- Cross section of copper cathode obtained at 45°C, 28mA/cm2, 1mg/L Guar, 1mg/L APAM and 87μm δ. Surface Roughness, Ra = 5.83±0.72 microns. 90

Figure 4-36: Run 6 – Cross section of copper cathode obtained at 65°C, 28mA/cm2, 1mg/L Guar, 0.5mg/L APAM and 110μm δ. Surface Roughness, Ra = 6.86±2.28 microns. 90
Figure 4-37: Run 7 – Cross section of copper cathode obtained at 45°C, 32mA/cm2, 1mg/L Guar, 0.5mg/L APAM and 87μm δ. Surface Roughness, Ra, = 5.99±0.66 microns. 91
Figure 4-38: Run 8 – Cross section of copper cathode obtained at 65°C, 32mA/cm2, 1mg/L Guar, 1mg/L APAM and 110μm δ. Surface Roughness, Ra, = 5.66±069 microns. 91
Figure 4-39: Error Box Plot of the Effect of APAM-to-Guar Ratio on Surface Roughness. Run 1 – Guar 0.25mg/L and APAM 0.125mg/L, Run 2 – Guar 0.25mg/L and APAM 0.375mg/L, Run 3 – Guar 1mg/L and APAM 0.5mg/L and Run 4 – Guar 1mg/L and APAM 1.5mg/L 94
Figure 4-40: Significant Effect of APAM/Guar Ratio and Guar on Surface Roughness 95
Figure 4-41: Error Box Plot of the Effect of APAM-to-Guar Ratio on PPC. Run 1 – Guar 0.25mg/L and APAM 0.125mg/L, Run 2 – Guar 0.25mg/L and APAM 0.375mg/L, Run 3 – Guar 1mg/L and APAM 0.5mg/L and Run 4 – Guar 1mg/L and APAM 1.5mg/L. 96
Figure 4-42: Studentized Residuals Plot 97
Figure 4-43: Residuals vs. Predicted Plot 97
Figure 4-44: Outlier T Diagnostic Plot 98
Figure 4-45: Error Bar Plot of Surface Roughness, Ra, μm after 4.64-Hours EW Time. Run 1 - Center Point, 0.5mg/L APAM and 0.5mg/L Guar; Run 2 – Nil additives; Run 3 – 1mg/L APAM; Run 4 – 1mg/L Guar and Run 5 – 1mg/L both APAM and Guar. 99
Figure 4-46: Error Bar Plot of PPC after 4.64-Hours EW Time. Run 1 - Center Point, 0.5mg/L APAM and 0.5mg/L Guar; Run 2 – Nil additives; Run 3 – 1mg/L APAM; Run 4 – 1mg/L Guar and Run 5 – 1mg/L both APAM and Guar. 100
Figure 4-47: Effect of Guar or APAM on PPC after 6-Hours. EW Time 103
Figure 4-48: The Significant Effect of Guar and APAM on PPC after 6-Hours EW Time 104
Figure 4-49: Run 1 - No Additives 106
Figure 4-50: Run 2 – Guar Only 106

Figure 4-51: Run 2R – Guar Only 107
Figure 4-52: Run 3 – APAM Only 107
Figure 4-53: Run 4 – APAM and Guar..... 108
Figure 4-54: SEM Micrograph of the Copper Cathode obtained using APAM after 12 Hours EW time (75X Mag)..... 110
Figure 4-55: Photograph Comparing Guar and APAM after 12 Hours EW Time. 110
Figure 5-56: Parameters Definition in LEVM Equivalent Circuit B[28] 120
Figure 5-57: Complex-Plane Plot for an Electrochemical System 121
Figure 5-58: Rotating Cylinder Electrode Configuration used for CV and EIS..... 125
Figure 5-59: Fluid Flow Produced by the RCE at 25rpm and 25°C in Water 127
Figure 5-60: Effect of Guar Residence Time on Depolarization at 45°C. 129
Figure 5-61: Effect of Time on the De-polarization Behaviour of Guar at 45°C at 300A/m^2 Current Density. 131
Figure 5-62: Effect APAM Residence Time on Polarization at 45°C. 133
Figure 5-63: Effect of APAM Ageing on Polarization on Pre-plated Copper at 45°C. 134
Figure 5-64: Effect of APAM Residence Time on Polarization at 65°C and 10rpm... 135
Figure 5-65: Polarization of APAM on Pre-plated Copper at 65°C 136
Figure 5-66: Effect of Temperature on APAM Polarization at 300 A/m^2 and 45°C and 65°C..... 137
Figure 5-67: Complex-Plane Plot of Experimental and Simulated EIS data at -470 (30mA/cm^2 - red) and -490mV (34.2mA/cm^2 - blue) vs. MSE and 45°C in the Absence of Organic Additives. 138
Figure 5-68: Complex-Plane Plots of Experimental EIS in the Presence and Absence of APAM at -470mV vs. MSE and 45°C 142
Figure 5-69: Complex-Plane Plot of Experimental and Simulated Impedance Spectra in the Presence and Absence of APAM at -470mV versus MSE and 45°C. Overpotential: 93mV vs. SHE. 143
Figure 5-70: Effect of Time on Simulated Charge-Transfer Resistance (P4) in the Presence of APAM at -470mV DC versus MSE at 45°C. 145
Figure 5-71: Effect of Time on the Simulated Double-Layer Capacitance (P5) in the Presence of APAM at -470mV DC vs. MSE and 45°C 145
Figure 5-72: Complex-Plane Plot of Experimental and Simulated Impedance Spectra at 45°C in the Presence and Absence of Guar. Overpotential: 113mV vs. SHE 147

Figure 5-73: Effect of Time on Charge-Transfer Resistance in the Presence of Guar at 45°C..... 149
Figure 5-74: Effect of Time on the Double-Layer Capacitance in the Presence of Guar 150
Figure 5-75: Complex-Plane Plot of Experimental and CNLS Simulated Impedance Spectra in the Presence and Absence of APAM at -490mV versus MSE and 45°C. Overpotential: 113 vs. SHE. 152
Figure 5-76: Effect of Time on the Simulated Charge-Transfer Resistance in the Presence of APAM at -490mV DC versus MSE and 45°C. 152
Figure 5-77: Simulated Double-Layer Capacitance versus Time in the Presence of APAM at -490mV DC versus MSE and 45°C. 153
Figure 5-78: Comparison of Complex-Plane Plot of Experimental and Simulated Impedance Spectra in the Presence of both APAM and Guar at -490mV DC and at 45°C. 154
Figure 5-79: Complex-Plane Plot using RDE at -490mV vs. MSE, 25rpm and 45°C (50^3Hz-0.2Hz). 155
Figure 5-80: Complex-Plane Plot of Experimental and CNLS Simulated Impedance Spectra in the Presence and Absence of APAM at -445mV versus MSE and 65°C. Overpotential: 90mV vs. SHE. 156
Figure 5-81: Effect of Time on the Simulated Charge-Transfer Resistance (P4) in the Presence of 2mg/L APAM at 65°C and -445mV DC vs. MSE 157
Figure 5-82: Effect of Time of the Simulated Double-Layer Capacitance (P5) in the Presence of 2mg/L APAM at 65°C and -445mV DC vs. MSE. 158
Figure 5-83: Complex-Plane Plot using RDE at -445mV vs. MSE, 25 rpm and 65°C (50^3 Hz-0.2Hz). 159
Figure 6-84: EW cell design – parallel plate electrodes 170
Figure 6-85: Bench Scale Process 171
Figure 6-86: Photograph of Bench Scale Equipment 171
Figure 6-87: Copper Deposit Obtained with Guar at 340A/m^2 and 44 hours - 35minutes 175
Figure 6-88: Copper Deposit Obtained with Guar at 340A/m^2 and 44 hours - 35minutes 176
Figure 6-89: Copper Deposit Obtained with APAM at 340A/m^2 and 44hours-35minutes 177

Figure 6-90: Copper Deposit Obtained with APAM at 340A/m^2 and 44hours-35minutes 178
Figure 6-91: SEM micrograph of the copper deposit obtained using 0.68mg/L APAM (200 g/tonne Copper Cathode) at 340 A/m^2 current density. Note the slightly fibrous or columnar structure. 179
Figure 6-92: SEM micrograph of the copper deposit obtained using 0.68mg/L Guar (200 g/tonne Copper Cathode) at 340 A/m^2 current density. *Note a porous copper cathode.* 180
Figure 6-93: Median of Crystallite Size 182
Figure 7-94: Hydrogen Bonding of Non-ionic Polyacrylamide 188
Figure 7-95: Blocky polyacrylamide may exhibit covalent bonding with divalent ions such as calcium and iron [64] 189
Figure 7-96: Effect of Time on the De-polarization Behaviour of Guar at 45^{o}C at 300A/m^2 Current Density. 197
Figure 7-97: Effect of Temperature on APAM Polarization at 300 A/m^2 and 45^{o}C and 65^{o}C 197
Figure 7-98: Parameters Definition in Equivalent Circuit B[33] 198