Electrodeposition of polyaniline coatings for corrosion prevention

Wang, Ting

2007

Wang, T. (2007). Electrodeposition of polyaniline coatings for corrosion prevention.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/5128>

<https://doi.org/10.32657/10356/5128>

Nanyang Technological University

Downloaded on 26 Apr 2023 19:24:08 SGT

NANYANG TECHNOLOGICAL UNIVERSITY

SCHOOL OF MATERIALS SCIENCE & ENGINEERING

DIVISION OF MATERIALS SCIENCE

ELECTRODEPOSITION OF POLYANILINE COATINGS FOR CORROSION PREVENTION

A thesis submitted to Nanyang Technological University in fulfillment of
the requirement for the degree of Doctor of Philosophy

by

Wang Ting

Supervisor: Associate Professor Chen Zhong

June 2007

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	VI
LIST OF SYMBOLS AND ABBREVIATIONS	VII
LIST OF FIGURES	IX
LIST OF TABLES	XVIII
ABSTRACT	XIX

CHAPTER 1

Introduction	1
---------------------	----------

CHAPTER 2

Literature Review: Metal Corrosion and Control by Intrinsically

Conducting Polyaniline	5
2.1 The Electrochemical Principles of Metal Corrosion.....	5
2.1.1 The Thermodynamics of Electrochemical Corrosion	7
2.1.2 The Kinetics of Electrochemical Corrosion.....	9
2.2 Corrosion of Major Engineering Metals	15
2.2.1 Corrosion Behaviour of Stainless Steel	15
2.2.2 Corrosion Behaviour of Carbon Steel.....	18
2.2.3 Corrosion Behaviour of Aluminium and Its Alloys	20
2.3 Corrosion Prevention Technologies and Protective Coatings.....	23
2.4 Intrinsically Conducting Polymers (ICPs)	28
2.4.1 Key Features of ICPs	28
2.4.2 Structure and Properties of PANI.....	30

2.4.3 Synthesis of PANI Coatings.....	34
2.5 Electrodeposition and Corrosion Protection by PANI Coatings	37
2.5.1 Difficulties of PANI Electrodeposition	37
2.5.2 PANI Coatings for Corrosion Prevention	42
2.6 Electrochemical Methods for Electrodeposition of PANI Films	48
2.6.1 Potentiostatic Electrodeposition.....	48
2.6.2 Cyclic Voltammetric Electrodeposition	50
2.7 Electrochemical Methods for Evaluating of Protective Coatings.....	54
2.7.1 Conventional Electrochemical Methods	54
2.7.2 A Novel Technique for Studying Coating Performance — Wire Beam Electrode (WBE).....	55

CHAPTER 3

Experimental	62
3.1 Materials	62
3.2 Electrode Preparation.....	63
3.3 Electrodeposition of PANI on One-Piece Electrodes and WBEs	65
3.3.1 Electrodeposition of PANI on One-Piece Electrodes.....	65
3.3.2 Electrodeposition of PANI on WBEs.....	68
3.4 Corrosion Testing Using Potentiodynamic Polarisation and Open-Circuit Potential	70
3.5 Corrosion Testing Using the Wire Beam Electrode	71
3.6 Microscopic and Surface Analysis.....	76
3.7 Salt Spray (Fog) Testing	77
3.8 Experimental Procedures	78

CHAPTER 4

Results and Discussion I: Electrodeposition of Polyaniline (PANI) on Stainless Steel 304 (SS304) 80

4.1 Electrodeposition of PANI on SS304 Using Cyclic Voltammetry in Various Electrolytes	80
4.2 Electrodeposition of PANI Using Potentiostatic (PS) Method.....	87
4.3 Characterisations of Electrodeposited PANI on SS304.....	89
4.4 Corrosion Evaluation of Electrodeposited PANI Film	92
4.4.1 Potentiodynamic Polarisation Measurement.....	92
4.4.2 Open-Circuit Potential Measurement	93
4.5 Studying PANI Electrodeposition and Anti-Corrosion on SS304 Using the WBE.	96
4.5.1 Anodic Polarisation Current Mapping over the SS304 WBE.....	96
4.5.2 Galvanic Current Mapping over SS304 WBE	98
4.5.3 Anti-Corrosion Performance and Mechanism of PANI on SS304	101
4.5.4 Anti-Corrosion Behaviour of Incomplete PANI Film on the SS304 WBE..	105

CHAPTER 5

Results and Discussion II: Electrodeposition of Polyaniline (PANI) on Low Carbon Steel 110

5.1 The Electrodeposition of PANI on Mild Steel Using Cyclic Voltammetry in Various Conditions	110
5.1.1 Passivation of a Mild Steel Electrode in Oxalic Acid Based Electrolyte	112
5.1.2 Initiation of PANI Electrodeposition on a Mild Steel Electrode	113
5.1.3 The Electrodeposition of PANI on Mild Steel at Different Potentials	116
5.2 Electrodeposition of PANI Using the Potentiostatic Method	119
5.3 Characterisations of the Electrodeposited PANI on Mild Steel	120
5.4 Corrosion Evaluation of the Electrodeposited PANI Film.....	123

5.4.1 Potentiodynamic Polarisation Measurements	123
5.4.2 Salt Spray (Fog) Tests.....	125
5.4.3 Open-Circuit Potential (OCP) Measurements	127
5.5 Studying PANI Electrodeposition and Anti-Corrosion on Mild Steel Using the WBE	131
5.5.1 Anodic Polarisation Current Measurements over Mild Steel WBE	131
5.5.2 Galvanic Current Map Measurements over a Mild Steel WBE.....	133
5.5.3 Anti-Corrosion Performance and the Mechanism of PANI Film on Mild Steel	137
5.5.4 Anti-Corrosion Behaviour of Incomplete PANI Film on a Mild Steel WBE	140

CHAPTER 6

Results and Discussion III: Electrodeposition of Polyaniline (PANI) on Aluminium Alloy 142

6.1 Electrodeposition of PANI on AA1100 Using Cyclic Voltammetry in Various Conditions	142
6.2 Studying the Electrodeposition of PANI on AA1100 Using the WBE	148
6.3 Electrodeposition and Characterisations of PANI on AA1100	157
6.4 Corrosion Evaluation Testing of the Electrodeposited PANI Film	162
6.4.1 Corrosion Testing of Electrodeposited PANI on a One-Piece AA1100 Electrode	162
6.4.2 Anti-Corrosion Performance and Mechanism of the Electrodeposited PANI Film on an AA1100 WBE	163

CHAPTER 7

Conclusions & Future Work 173

7.1 Conclusions..... 173

7.2 Future Work..... 176

LIST OF PUBLICATIONS 179

REFERENCE 180

ACKNOWLEDGEMENTS

The author would particularly like to express sincere gratitude to her former supervisor, Associate Professor Tan Yong Jun, for his continuous guidance and support throughout this project. The tremendous help in imparting his knowledge, experience and experimental skills has been greatly appreciated. The author would especially like to commend his drive and enthusiasm for the research work.

The author is also grateful to Associate Professor Chen Zhong for his kindly help during the oral examination.

Thanks also go to Ms Nang Nang Aung, Mr. Liu Tie, Mr. Robin Leong, Mr. Johnny Tan Chor Meng, Ms. Ng Siu Din and other friends and staff at the School of Materials Science and Engineering for their constant support in imparting technical skills and thesis submission.

Finally, the author would like to thank her family for being so supportive during the course of this project.

LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Meaning
A	ampere
A_n	Concentration of aniline monomer
β	equals to $2.3RT/\alpha nF$
C_{red}	Concentration of reduced species
C_{red}	Concentration of oxidised species
<i>Chromium (VI)</i>	Cr^{6+} cations
E	Electrical potential
E_0	the potential of charge-transfer reaction in equilibrium
E_{corr}	the corrosion potential or open circuit potential in contact with an electrolyte
E_k	Corrosion potential of wire k in a WBE
E_{pp}	Protection potential
E_{pit}	Pitting potential
E_{sys}	Overall system potential of a WBE
I_{corr}	Corrosion current density
I_{max}	Maximum anodic current density obtained from WBE measurement
I_{tot}	Total anodic current density obtained from WBE measurement
I_{gk}	Galvanic corrosion current of wire k in a WBE
M	Metal substrate
mA	Milliampere
mV	Millivolt
M_w	Weight average molecular weight
V	Volt
<i>AA1100</i>	Aluminium alloy 1100
<i>APC</i>	Anodic polarisation current density
<i>CV</i>	Cyclic voltammogram; cyclic voltammetric
<i>DOP</i>	dopant anion
<i>ED</i>	Electrochemical deposition
<i>EIS</i>	Electrochemical impedance spectroscopy
<i>ENA</i>	Electrochemical noise analysis
<i>FTIR</i>	Fourier transformed infrared spectroscopy
<i>FESEM</i>	Filed emission scanning electronic microscopy
<i>GC</i>	Galvanic current density
<i>ICP</i>	Intrinsically conducting polymer
<i>LE</i>	Leucoemeraldine state
<i>LPR</i>	linear polarisation resistance
<i>M</i>	Metal substrate
<i>OCP</i>	Open-circuit potential or corrosion potential
<i>PA</i>	Pernigraniline
<i>PANI</i>	polyaniline
<i>PANI-ES</i>	Polyaniline in emeraldine salt
<i>PANI-EB</i>	Polyaniline in emeraldine base
<i>PANI-EM</i>	Polyaniline in emeraldine state

<i>PANI-LE</i>	Polyaniline in leucoemeraldine state
<i>PPY</i>	polypyrrole
<i>PT</i>	polythiophene
<i>PS</i>	Potentiostatic/ potentiostat
<i>PP</i>	Potentiodynamic polarisation
<i>PU</i>	polyurethane
<i>SCE</i>	Saturated calomel electrode
<i>SEM</i>	Scanning electronic microscopy
<i>SHE</i>	Standard hydrogen electrode
<i>SS304</i>	Stainless steel 304
<i>V</i>	Volt
<i>WBE</i>	Wire beam electrode

LIST OF FIGURES

Figure 2.1 A typical dual electrode galvanic corrosion cell.....	6
Figure 2.2 Typical Pourbaix diagrams for iron at 25°C (approximate unit activity assumed for dissolved species) [Source: Verink 2000]	8
Figure 2.3 Schematically illustrated equilibrium potentials, corrosion potentials and effect of galvanic coupling of iron to copper.....	12
Figure 2.4 Typical anodic dissolution behaviour of an active-passive metal [Source: Jones 1996]	14
Figure 2.5 Schematic illustration of the spontaneous passivation of an active-passive metal by galvanic coupling with a noble metal	15
Figure 2.6 Autocatalytic process occurring in a corrosion pit [Source: Evens 1951]	18
Figure 2.7 The effect of aggressive chloride ions in the anodic dissolution behaviour of stainless steel [Source: Jones 2005].....	19
Figure 2.8 Schematic illustration of the corrosion reaction in a drop of seawater on carbon steel [Source: Donovan 1986]	20
Figure 2.9 Typical Pourbaix diagrams for aluminium at 25°C (approximate unit activity assumed for dissolved species) [Source: Shreir 1994]	21
Figure 2.10 The electrochemical mechanism of pit growth on aluminium, showing its autocatalytic self – stimulating nature [Source: Wranglen 1972].....	22
Figure 2.11 Schematic illustration of the effect of anodic dissolution current on the anodic protection of an active-passive metal.....	24
Figure 2.12 Schematic illustrations of the electrochemical cells of anodic and cathodic electrodeposition	27
Figure 2.13 Typical conducting polymer structures (in un-doped form) [Source: Tallman <i>et al.</i> 2000]	29

Figure 2.14 General structure of PANI; Y=1 (leucoemeraldine), 0.5 (emeraldine) and 0 (pernigraniline) [Source: MacDiarmid 2001]	31
Figure 2.15 Three basic oxidation states including the base and salt forms of PANI [Source: Tallman <i>et al.</i> 2002].....	32
Figure 2.16 The reversible protonation and electron transfers of PANI in emeraldine and leucoemeraldine state. [Source: Tallman <i>et al.</i> 2002]	32
Figure 2.17 A self-doped (or sulphonated) PANI redox scheme showing cation (C+) incorporation upon reduction [Source: Tallman <i>et al.</i> 2002].....	34
Figure 2.18 Pourbaix diagram of PANI and iron in water. (a) and (b) represent the reduction potential for oxygen and hydrogen ions, respectively [Source: Dominis <i>et al.</i> 2003] [Source: Ramanarayanan 2003].....	43
Figure 2.19 Schematically illustrated principle of potentiostat (can also serve as principle of cyclic voltammetry) [Source: Ramanarayanan 2003]	49
Figure 2.20 (a) Triangular E (t) signal of a cyclic voltammetric scan. (b) Cyclic voltammetric current vs. potential for an ideal, reversible one-electron redox couple [Source: Bocarsly 2002]	51
Figure 2.21 Schematic cyclic voltammograms for EC reactions ($K_s = 10 \text{ s}^{-1}$) at scan rates of (a) 10 V/s (b) 1 V/s. current in amperes and potential in voltage [Source: Bocarsly 2002].....	52
Figure 2.22 Cyclic voltammograms of PANI on a glassy carbon electrode, including the potentials at which structural and colour changes occur, doped by 1 M HCl (pH=0), scan rate 50 mV/s [Source: Wallace <i>et al.</i> 2003]	53
Figure 2.23 A Classic Tafel Analysis [Source: Ramanarayanan 2003].....	55
Figure 2.24 Experimental setup showing measurements of (a) galvanic corrosion currents and (b) corrosion potential of individual wires of the WBE.....	58
Figure 2.25 Typical results of WBE measurements; (a) corrosion profile (b) potential (V) (c) galvanic current (mA/cm^2) and (d) corrosion rate (mm/year) maps [Source: Tan <i>et al.</i> 2001b]	59
Figure 2.26 Electroplating current (mA/cm^2) distribution maps measured in Watts' nickel bath after 30 minutes (a) the thickness profile of nickel deposit at -40 mV for ~ 5 hours,(b) -120 mV,(c) -80 mV and (d) -40 mV cathodic polarisation [Source: Tan and Lim 2004].....	61

Figure 3.1 (a) Side view, (b) top view of the one-piece electrode and (c) photograph of the one-piece electrode	64
Figure 3.2 Schematic of the design of WBE.....	65
Figure 3.3 Photographs of the (a) SS304 (b) mild steel and (c) AA1100 WBE surfaces	65
Figure 3.4 Schematic diagram of experimental setup for the electrode position, including cyclic voltammetry and potentiostatic methods on SS304, G10530 and AA1100 electrodes	66
Figure 3.5 Photograph of experimental setup for PANI electrodeposition on WBE.....	68
Figure 3.6 Schematic diagram of experimental setup for PANI electrodeposition on WBE	70
Figure 3.7 Schematic diagram of the experimental setup for potentiodynamic polarisation experiments on electrodes including PANI coated SS304, MS G10530 and AA1100	71
Figure 3.8 Photograph of experimental setup for corrosion testing in 0.5M NaCl solution (pH ~ 5.8) of PANI coated WBE	72
Figure 3.9 Schematic illustrations of the measurement of potential and galvanic current of each wire of a WBE specimen	73
Figure 3.10 Schematic diagram illustrating the experimental setup for the corrosion evaluation of PANI deposited WBE in 0.5 M NaCl solution	74
Figure 3.11 Salt spray test machine	77
Figure 3.12 (a) Photograph illustrating the positions of thickness measurement, (b) and (c) data obtained from the thickness measurement by the surface profiler.....	78
Figure 3.13 Routes presenting the experimental procedures on one-piece electrodes and WBEs involving different materials (SS304, MS G10530, AA1100)	79
Figure 4.1 Comparison of cyclic voltammograms on one-piece SS304 electrode in 0.75 M H ₂ SO ₄ with and without 0.1 M aniline monomer	81
Figure 4.2 Cyclic voltammogram of the 2 nd to 9.5 th cycles during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H ₂ SO ₄ solution with 0.1 M aniline	82

Figure 4.3 Cyclic voltammogram of 9.5 cycles during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H ₂ SO ₄ solution with 0.1 M aniline	84
Figure 4.4 (a) Potentiodynamic polarisation of SS304 and (b) voltammogram of 9.5 cycles during the electrodeposition of PANI on one-piece SS304 electrode in 0.3 M oxalic acid with 0.1 M aniline	85
Figure 4.5 Cyclic voltammogram of 9.5 cycles during the electrodeposition of PANI on one-piece SS304 electrode in 1.0 M tosylic acid with 0.17 M aniline	86
Figure 4.6 Chronoampergram during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H ₂ SO ₄ with 0.1 M aniline	88
Figure 4.7 Chronoampergram during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H ₂ SO ₄ with 0.1 M aniline at various potentials.....	89
Figure 4.8 Micrographs of electrodeposited PANI film on one-piece SS304 using (a) cyclic voltammetry and (b) potentiostatic methods in 0.75 M H ₂ SO ₄ with 0.1 M aniline	90
Figure 4.9 FTIR spectrum of the electrodeposited PANI at a fixed potential of 0.75 V on SS304 in 0.75 M H ₂ SO ₄ solution with 0.1 M aniline	91
Figure 4.10 Comparison of potentiodynamic polarisation of PANI coated SS304 and bare SS304 electrodes in an aerated 0.5 M NaCl solution (pH $\approx$ 5.8).....	93
Figure 4.11 Photographs of (a) a complete PANI coated and (b) an incomplete PANI coated SS304 electrode before OCP testing	94
Figure 4.12 OCPs vs. time for one-piece SS304 electrodes completely and incompletely coated with PANI and one-piece bare SS304 electrode in aerated 0.5 M NaCl solution	94
Figure 4.13 Photographs of the corroded SS304 electrodes with (a) a complete PANI coverage and (b) an incomplete PANI coverage after being exposed in 0.5 M NaCl solution for one week.....	96
Figure 4. 14 Chronoampergram during the electrodeposition of PANI at 0.75 V on SS304 WBE in 0.75 M H ₂ SO ₄ with 0.1 M aniline.....	97
Figure 4.15 (a) Photograph of a PANI coated SS304 WBE; (b)-(d) corresponding APC maps (mA/cm ²) measured at 20, 30 and 40 minutes, respectively	98
Figure 4.16 (a) Photograph of corroded SS304 WBE after one week's OCP testing in 0.5 M NaCl solution; (b)-(d) GC (mA/cm ²) maps measured at 0.5, 72 and 100 hours, respectively; major cathodic area was labelled by dotted cycles.....	99

Figure 4.17 Comparison between the SS304 WBE APC maps measured at (a) 30 minutes and (b) 40 minutes of PANI electrodeposition with GC maps measured at (c) 72 hours and (d) 120 hours.....	101
Figure 4.18 Comparison of the (a) $i_{\max}$ and (b) i_{tot} of PANI coated SS304 WBE with bare SS304 WBE in an aerated 0.5 M NaCl solution.....	103
Figure 4.19 Schematic illustration of the anti-corrosion mechanism of PANI on stainless steel in near neutral chloride containing solution	105
Figure 4.20 OCP vs. time for incompletely PANI coated SS304 WBE in 0.5 M NaCl solution.....	106
Figure 4.21 (a) Photograph of the corroded SS304 WBE after one week's OCP testing; (b)-(d) GC maps (mA/cm^2) over the three steps at 0.2, 7.1 and 11.5 hours of OCP change. The location of the exposed metal area (at wire no.95) was indicated by a dotted cycle.....	107
Figure 5.1 Cyclic voltammogram of a one-piece mild steel electrode in 0.8 M H_2SO_4 acid with 0.1 M aniline	111
Figure 5.2 Passivation of one-piece mild steel electrode using potentiodynamic polarisation in 0.3 M oxalic acid ($\text{pH} \approx 0.8$).....	113
Figure 5.3 Four cycles of potentiodynamic polarisation for the one-piece mild steel electrode in 0.3 M oxalic acid with 0.1 M aniline	114
Figure 5.4 Potentiodynamic polarisation of the passivated mild steel in 0.3 M oxalic acid with 0.1 M aniline	116
Figure 5.5 Cyclic voltammograms of electrodeposition of PANI on mild steel electrodes at potentials of (a) 0.05 ~ 0.8 V and (b) 0.3 ~ 0.85 V in 0.3 M oxalic acid with 0.1 M aniline	117
Figure 5.6 Chronoampergram during the electrodeposition of PANI on one-piece mild steel electrodes in 0.3 M oxalic acid with 0.1 M aniline at various potentials	120
Figure 5.7 Micrographs of (a) the top view and (b) a cross-section of the electrodeposited PANI film obtained at a fixed potential of 0.85 V on one-piece mild steel electrodes in 0.3 M oxalic acid with 0.1 M aniline	121
Figure 5.8 FTIR spectrum of the electrodeposited PANI at a fixed potential of 0.85 V on a mild steel electrode in 0.3 M oxalic acid with 0.1 M aniline	122

Figure 5.9 Potentiodynamic polarisation of (a) bare mild steel, (b) passivated mild steel in 0.3 M oxalic acid, and (c) PANI electrodeposited mild steel in 0.5 M NaCl solution	124
Figure 5.10 Photographs of (a) bare mild steel and (b) PANI primer on mild steel after salt spray for 12 hours; (c) Acrylic coating and (d) PANI primer/Acrylic on mild steel after salt spray for 108 hours; (e) anti-rust oil and (f) PANI primer /anti-rust oil on mild steel after salt spray for 12 hours	127
Figure 5.11 Photographs of (a) a complete PANI and (b) an incomplete PANI coated one-piece mild steel electrode in 0.3 M oxalic acid with 0.1 M aniline, before OCP testing.....	
Figure 5.12 OCP <i>vs.</i> time for a PANI coated one-piece mild steel electrode and a bare mild steel electrode without PANI in aerated 0.5 M NaCl solution	128
Figure 5.12 OCP <i>vs.</i> time for a PANI coated one-piece mild steel electrode and a bare mild steel electrode without PANI in aerated 0.5 M NaCl solution	130
Figure 5.13 Photographs of (a) a complete PANI and (b) an incomplete PANI coated mild steel one-piece electrodes after exposed in aerated 0.5 M NaCl solution for about 24 hours and 12 hours, respectively.....	130
Figure 5.14 Chronoampergram during the electrodeposition of PANI at 0.85 V on a mild steel WBE in 0.3 M oxalic acid with 0.1 M aniline.....	132
Figure 5.15 (a) Photograph of a mild steel WBE with PANI deposits; (b)-(d) APC maps (mA/cm ²) measured at the times of 30, 40 and 50 minutes, respectively.....	133
Figure 5.16 (a) Photograph of corroded mild steel WBE after 30 hours' OCP testing in 0.5 M NaCl solution; (b)-(d) GC maps(mA/cm ²) measured at 0.5, 2, and 30 hours, respectively	135
Figure 5.17 Comparison between (a) the APC map measured at 50 minutes of PANI electrodeposition on mild steel WBE and (b) the GC map measured at 0.5 hour during OCP testing in 0.5 M NaCl solution	136
Figure 5.18 OCP <i>vs.</i> time for the PANI coated mild steel in 0.5 M NaCl solution	137
Figure 5.19 Comparison of the (a) $i_{\max}$ and (b) i_{tot} between PANI coated mild steel WBE and a bare mild steel WBE.....	139
Figure 5.20 Schematic illustration of the anti-corrosion mechanism of PANI on mild steel in near neutral chloride containing solution	140

Figure 5.21 (a) Photograph of corroded mild steel WBE with a pinhole after 30 hours' OCP testing in 0.5 M NaCl solution; (b)-(d) GC maps of PANI coated mild steel WBE measured at 0.5 hour, 3.5 hours, and 30 hours, respectively141

Figure 6.1 Cyclic voltammogram of 9.5 cycles during the electrodeposition of PANI on an AA1100 electrode at a potential of -0.2 ~ 1.25 V in 1 M H₂SO₄ solution with 0.1 M aniline.....144

Figure 6.2 (a) Anodic polarisation for a half cycle of an AA1100 electrode in 0.3 M oxalic acid and (b) voltammogram of 9.5 cycles during electrodeposition of PANI on one-piece AA1100 electrode in 0.25 M oxalic acid with 0.1 M aniline.....145

Figure 6.3 Cyclic voltammogram of 9.5 cycles electrodeposition of PANI on the AA1100 electrode in 1 M tosylic acid with 0.16 M aniline146

Figure 6.4 Chronoampergram during the electrodeposition of PANI on the AA1100 one-piece electrodes at a fixed potential of 1.25 V in 0.75 M H₂SO₄ containing 0.1 M aniline, 0.3 M oxalic acid with 0.1 M aniline, and 1 M tosylic acid with 0.16 M aniline.....147

Figure 6.5 Photographs of one-piece AA1100 electrode surfaces with PANI deposits from (a) 1 M H₂SO₄ with 0.16 M aniline, (b) 0.25 M oxalic acid with 0.1 M aniline, and (c) 1 M tosylic acid with 0.16 M aniline147

Figure 6.6 (a) Photograph of an AA1100 WBE with PANI deposits after 60 minutes of potentiostatic electrodeposition (1.25 V vs. SCE); (b)-(d) corresponding APC maps (mA/cm²) of PANI electrodeposition in 1 M tosylic acid with 0.16 M aniline after 30, 40 and 50 minutes, respectively.....149

Figure 6.7 Cathodic pre-treatment of the AA1100 WBE at a fixed potential of -0.9 V for 5 minutes in 1 M tosylic acid with 0.16 M aniline151

Figure 6.8 (a) Photograph of an AA1100 WBE with PANI deposits after 30 minutes of electrodeposition; (b)-(d) APC maps (mA/cm²) after 20, 25 and 30 minutes of PANI electrodeposition at 1.25 V in 1 M tosylic acid with 0.16 M aniline.....152

Figure 6.9 Comparison of the GC maps of the AA1100 electrode (a) before, (b) after the cathodic pre-treatment in 1 M tosylic acid with 0.16 M aniline, and (c) the corresponding APC map after electrodeposition for 20 minutes at a fixed potential 1.25 V in the same electrolyte.....154

Figure 6.10 Cathodic pre-treatment of the AA1100 WBE at -0.9 V for 8 minutes in 1 M tosylic acid with 0.16 M aniline.....155

Figure 6.11 (a) Photograph of an AA1100 WBE with PANI deposits after 30 minutes of

electrodeposition; (b)-(d) APC maps (mA/cm^2) after 20, 25 and 30 minutes of PANI electrodeposition at a fixed potential of 1.25 V in 1 M tosylic acid with 0.16 M aniline156

Figure 6.12 Cyclic voltammogram of 15 cycles of the electrodeposition of PANI on a one-piece AA1100 electrode in 1 M tosylic acid with 0.16 M aniline158

Figure 6.13 Photograph of the electrodeposited PANI film using cyclic voltammetry on the AA1100 one-piece electrode in 1 M tosylic acid with 0.16 M aniline after cathodic pre-treatment for 5 minutes.....158

Figure 6.14 (a) The cathodic pre-treatment for 5 minutes in 1 M tosylic acid with 0.16 M aniline and (b) chronoampergram during electrodeposition at a fixed potential of 1.25 V in 1 M tosylic acid with 0.16 M aniline159

Figure 6.15 Photograph of the PANI film on the AA1100 one-piece electrode deposited in 1 M tosylic acid with 0.16 M aniline after cathodic pre-treatment for 5 minutes160

Figure 6.16 FTIR spectrum of the electrodeposited PANI at 1.25 V on one-piece AA1100 electrode in 1 M tosylic acid with 0.16 M aniline after cathodic pre-treatment for 5 minutes.....161

Figure 6.17 Micrographs of (a) the AA1100 electrode surface after cathodic pre-treatment (5 minutes) and (b) the electrodeposited PANI film on AA1100 one-piece electrode after cathodic pre-treatment for 5 minutes in 1 M tosylic acid with 0.16 M aniline.....162

Figure 6.18 Comparison of potentiodynamic polarisation curves (scan rate 0.2 mV/s) of PANI coated AA1100 and bare AA1100 in 0.5 M NaCl solution ($\text{pH} \approx 5.8$).....163

Figure 6.19 Comparison among (a) photograph of an AA1100 WBE after 60 minutes of potentiostatic electrodeposition at 1.25 V; (b) APC map after 20 minutes of PANI electrodeposition; (c) and (d) GC maps after 5 and 10 minutes immersion in 0.5 M NaCl solution, respectively165

Figure 6.20 OCP vs. time of the PANI coated AA1100 in aerated 0.5 M NaCl solution167

Figure 6.21 GC maps of PANI coated AA1100 WBE in 0.5 M NaCl solution after (a) 10 minutes, (b) 1 hour, (c) 3 hours, and (d) 13 hours of immersion.....168

Figure 6.22 GC maps of PANI coated AA1100 WBE in 0.5 M NaCl solution after (a) 10 minutes, (b) 1 hour, (c) 3 hours, (d) 8 hours, (e) 13 hours, and (f) 17 hours of immersion. The dotted cycles indicate the location of major anode(s)169

Figure 6.23 Comparison of (a) i_{max} and (b) i_{tot} between PANI coated and bare AA1100

WBEs	170
Figure 6.24 Schematic illustration of the anti-corrosion mechanism of PANI on AA1100 in near neutral chloride with solution	171

LIST OF TABLES

Table 2.1 Summary of experimental observation of PANI electrodeposition on stainless steel, carbon steel and aluminium alloys	41
Table 2.2 Evidence from corrosion performance and mechanism studies of PANI on stainless steel, carbon steel and aluminium alloys.....	43
Table 3.1 Composition of SS304, mild steel and AA1100	62
Table 3.2 Summary of chemical reagents used in this project.....	63
Table 3.3: Values of the anode and cathode taken from WBE galvanic mapping. Positive values represent anodes and negative values represent cathodes	75
Table 5.1 Comparison of E_{corr} , E_{pit} and i_{corr} with bare mild steel, passivated mild steel and PANI deposited mild steel in 0.5 M NaCl solution.....	125
Table 5.2 Visual observations of the metal surfaces during the salt spray testing.....	126

ABSTRACT

Polyaniline (PANI) exhibits the possibility of replacing the hazardous Cr (VI)-containing coatings as an anti-corrosion primer. This project has investigated the direct electrodeposition of an electroactive PANI coating on stainless steel 304 (SS304), mild steel and aluminium alloy (AA1100) for anti-corrosion applications using electrochemical methods, in particular, a novel wire beam electrode (WBE) method. This WBE based technique has been utilised successfully for the first time to map anodic polarisation currents (APC) during electrodeposition, and to map galvanic currents (GC) over a PANI coated surface, which was exposed to corrosion testing environments.

The APC maps have been found to be useful for monitoring, understanding and optimising PANI electrodeposition processes. The APC maps were observed to display a random anodic current distribution for uniform PANI electrodeposition, leading to a PANI coating with good coverage of electrode surface; while the APC maps were observed to show a localised anodic current distribution for non-uniform PANI electrodeposition. With the assistance of the APC maps, improvements to PANI electrodeposition and surface pre-treatment processes have been successfully achieved. A pre-treatment technique has been developed for PANI electrodeposition on mild steel by passivating the mild steel electrode. A novel pre-treatment technique was also developed for the AA1100 electrode involving the cathodic polarisation of the electrode.

The GC maps have been found to be effective for evaluating the anti-corrosion performance and for studying the anti-corrosion mechanism of electrodeposited PANI coatings. A correlation between GC maps and APC maps was discovered: APC maps measured during PANI electrodeposition correlated with the corrosion behaviour of the PANI coatings. Electrode areas with higher anodic currents in APC maps corresponded well to the cathodic sites in GC maps, suggesting that PANI deposits behaved as effective cathodes.

Potentiodynamic polarisation, open-circuit potential measurements, and salt spray testing were also carried out to study the anti-corrosion properties of the electrodeposited PANI coatings. PANI was found to offer a significant protection to localised corrosion of SS304 and AA1100 by anodic protection mechanism, although the corrosion protection provided by PANI coatings to mild steel appeared to be less significant.

Materials characterisation approaches, such as Fourier transformed infrared (FTIR) spectroscopy and scanning electron microscope (SEM), were also employed to analyse the deposited PANI coatings.

CHAPTER 1

Introduction

Chromium (VI)-containing primers and conversion coatings currently used for corrosion prevention of steels and aluminium alloys have been shown to be hazardous to the environment and to human health. Much effort has been underway to develop new coating systems with comparable anti-corrosion performance that are environmentally friendly. Polyaniline (PANI), one of the intrinsically conducting polymers (ICPs), exhibits the possibility of replacing the harmful chromium (VI)-containing coatings [Tallman *et al.* 2002a; Ahmad and MacDiarmid 1996]. PANI has also received considerable attention due to its relatively high environmental and thermal stability.

PANI can be synthesized either chemically or electrochemically from appropriate monomers. The electrodeposition of PANI is a process that involves oxidation of the monomer and generation of radical cations in acidic media. Compared to the chemical polymerisation of PANI, the electrochemical deposition of PANI is a one-step method to form coatings, and thus an effective way to control chemical and physical properties such as adhesion, molecular weight, and redox state of the deposited polymer.

It is relatively easy to electrodeposit PANI on noble metals. On stainless steels the electrodeposition of PANI can be achieved without any pre-treatments, because the metal substrate could be passivated during the PANI electrodeposition in acidic electrolyte [DeBerry 1985]. However, the electrodeposition of PANI on corrosion-susceptible metals, such as mild steel and aluminium, was found to be problematic. It is associated with the incompatibility between the properties of the metal substrate and the harsh electrodeposition condition [Camalet *et al.* 1998a; Conroy and Breslin 2003]. Firstly, the corrosion-susceptible metals are thermodynamically unstable in acidic solution and tend to be dissolved before potentials approaching the value required for PANI deposition. Secondly, the oxide film on metal surfaces, for instance on aluminium alloy surface, also has the tendency to be enhanced because of the applied anodic potential for deposition. In addition, due to the participation of nitrogen-heteroatom in the polymerisation process, the deposited PANI film is rather nonuniform, which might affect its anti-corrosion performance as a primer. Although several groups have reported their results on PANI electrodeposition on carbon steel [Camalet *et al.* 1998a; Rajagopalan and Iroh 2002], the study on the heterogeneity of the electrodeposited PANI film, and the relationship between PANI film heterogeneity and its corrosion performance are far from sufficient. As for the aluminium alloy, to the author's knowledge, there is no report about the electrodeposition of PANI on aluminium alloys with satisfactory corrosion protection performance.

Although considerable work has been carried out, the corrosion protection mechanism of PANI has not been fully understood. The most commonly accepted mechanism for

explaining the corrosion protection of PANI film on stainless steel is the anodic protection mechanism [DeBerry 1985; Wessling 1994]. This involves a shift of the corrosion potential of metal substrates from the active to passive region and thus reinforcement of its oxide film. The mechanism of anodic protection is plausible since the equilibrium potential of PANI in partially oxidised state, i.e. emeraldine (EM), is more positive than the equilibrium potential of stainless steel, mild steel and aluminium alloy. However, besides PANI's EM state, there are two other stable states, leucoemeraldine (LE) and pernigraniline (PA), representing fully reduced and oxidised states respectively. It is possible that conversions occur between these redox states of PANI at an applied positive potential, and thus the anodic protection mechanism based on EM state may be insufficient in explaining the corrosion protection provided by LE or PA states of PANI films. Other mechanisms have also been proposed to interpret the anti-corrosion behaviour of PANI on stainless steel. For instance, a mechanism has been proposed suggesting the displacement of electroactive interface from the metal / solution interface to the polymer / solution interface [Schauer *et al.* 1998].

There has also been considerable debate about the anti-corrosion mechanism of PANI on mild steel. Some experimental facts can be explained by the anodic protection mechanism [Lu *et al.* 1998; Wessling 1994]. However, recent research work has revealed that the anodic protection mechanism could not be applied to explain the behaviour of PANI on mild steels in near neutral chloride environments, where carbon steels can not be passivated [Cook *et al.* 2004]. Further study is thus necessary to clarify the electrochemical reactions

between PANI film and ferrous metals when corrosion is proceeding. As for aluminium alloys, since it is difficult to obtain samples with complete coverage of electrodeposited PANI film, a convincing theory about the anti-corrosion behaviour of electrodeposited PANI has not yet been established.

The key technique employed in this present work is an electrochemically integrated multi-electrode system, namely the wire beam electrode (WBE) [Tan *et al.* 2000; Tan *et al.* 2001 a, b, c]. WBE is specially designed to study heterogeneous electrochemical processes that usually occur if a nonuniform coating exists. The surface area of a WBE consists of 100 wires compactly bound together to simulate a conventional one-piece electrode. Each wire behaves as a corrosion substrate as well as an individual sensor to measure localised electrochemical parameters such as potential, galvanic current and corrosion resistance. For the first time, the WBE method is employed to monitor both the PANI electrodeposition process, and also the corrosion performance of PANI films.

In this project the electrodeposition of PANI and its corrosion performance has been studied using electrochemical methods, in particular, the WBE method on SS304, mild steel and AA1100.

CHAPTER 2

Literature Review: Metal Corrosion and Control by Intrinsically Conducting Polyaniline

In this chapter, three essential topics have been reviewed: the electrochemical principles of corrosion, in particular corrosion behaviours of stainless steel, carbon steel, and aluminium and its alloys; the anti-corrosion coatings, especially the intrinsically conducting polyaniline; and the electrochemical techniques for electrodeposition and corrosion evaluation with a focus on the wire beam electrode method.

2.1 The Electrochemical Principles of Metallic Corrosion

Corrosion is defined as the destruction or deterioration of materials because of their chemical or electrochemical reactions with the environment [Jones 1993]. The majority of metals, such as steel, aluminium, titanium and their alloys, except for very noble ones, are vulnerable to corrosion attacks. This is because their corrosion is a thermodynamically spontaneous process.

In aqueous systems corrosion is usually an electrochemical process that occurs in an electrochemical cell. The simplest corrosion electrochemical cell is the galvanic corrosion

cell, where the driving force for corrosion is the potential difference developed between different metals. The metal with the most negative potential behaves as an anode and the metal with the most positive potential behaves as the cathode. A net oxidation occurs on the anode and a net reduction reaction occurs on the cathode. The electrons and ionic charges go through the metal and electrolyte respectively, making the system electrically neutral. The electrochemical nature of metallic corrosion can be illustrated by the simple binary galvanic corrosion cell, as shown in Figure 2.1.

Figure 2.1 A typical dual electrode galvanic corrosion cell

In Figure 2.1, two dissimilar materials, iron and copper electrode, are electrically connected and immersed in a near neutral sodium chloride solution. Due to the lower electromotive force (emf) of iron compared to that of copper, the iron is anode and copper is cathode. The electrode reactions can be described as:

In this galvanic corrosion cell, iron is under corrosion while copper dissolution is negligible.

2.1.1 The Thermodynamics of Electrochemical Corrosion

The thermodynamics of an electrochemical corrosion cell are usually determined by the electrode potential of each half-cell reaction, which has a characteristic electrode potential when compared to a standard reference electrode. For instance, a simple reversible electrode with reaction, $\text{Red} \rightleftharpoons \text{Ox} + n\text{e}^-$, the reversible equilibrium potential, E , can be linked to the standard reversible potential of an electrode reaction, E^0 , by the Nernst equation.

$$E = E^0 - \frac{RT}{nF} \ln \frac{C_{\text{red}}}{C_{\text{ox}}} \quad \text{Equation 2.3}$$

where R is the universal gas constant; T is the absolute temperature in degrees Kelvin; n is the charge number of the electrode reaction; F is the Faraday constant (96500 C/mole); C_{ox} is the concentration of oxidised species; C_{red} is the concentration of reduced species.

In order to simplify the analysis and presentation of electrochemical corrosion thermodynamics, the Pourbaix diagram [Pourbaix 1966] was constructed through the use of the Nernst equation. The Pourbaix E-pH diagram gives the electrochemical thermodynamic behaviour of a metal in specific pH conditions, and is widely used to evaluate the thermodynamics of an electrochemical corrosion reaction. Figure 2.2 shows a typical Pourbaix diagram for the iron-water system at ambient temperature. By means of potential and pH measurements, the diagram enables the determination of whether a metal surface is in a region where the tendency for corrosion is unlikely, high, or where it may still exist but there is also a tendency for a protective or passive film to exist. Thus, by using the Pourbaix diagram, we can predict the direction of spontaneous reactions and estimate the composition of corrosion products.

Figure 2.2 Typical Pourbaix diagrams for iron at 25°C (approximate unit activity assumed for dissolved species) [Source: Verink 2000]

However, the thermodynamically derived Pourbaix diagram only provides information on corrosion tendency; it cannot be used to predict the kinetics of electrochemical corrosion, i.e. the rates of corrosion.

2.1.2 The Kinetics of Electrochemical Corrosion

The kinetics or rate of corrosion is proportional to the anodic dissolution current, as predicted by the fundamental Butler-Volmer equation, which represents current resulting from an applied potential to a specific charge-transfer reaction [Butler 1924 a and b; Volmer and Erdey-Gruz 1930].

$$i = i_0 \left[\exp\left(\frac{(1-\alpha)F(E-E_0)}{RT}\right) - \exp\left(\frac{-\alpha F(E-E_0)}{RT}\right) \right] \quad \text{Equation 2.4}$$

where E is the inner or Galvani potential of a metal in contact with an electrolyte; E_0 is the potential of charge-transfer reaction in the equilibrium; i_0 is the exchange current of the equilibrium of the charge-transfer reaction; and F , R , and T are the Faraday constant, the universal gas constant, and the absolute temperature, respectively.

In the Butler-Volmer equation, $(1-\alpha)(E-E_0)$ represents the potential through which the metal has to be ionized and $\alpha(E-E_0)$ indicates the activation barrier for the metal ions to revert back to the metallic state. By using the Butler-Volmer equation, the current is

supposed to be determined by the overpotential ($E-E_0$). However, when a metal is in contact with an aqueous solution, mixed potential must be involved, which is neither the equilibrium potential nor the overpotential in the Butler-Volmer equation. Mixed potential is generated by the combination of anodic and cathodic reactions. In order to study the kinetics of multi-electrochemical reactions, the mixed-potential theory is indispensable.

The mixed potential theory was first proposed by Wagner and Traud [Wagner and Traud 1938] to provide a solid basis for the treatment of the kinetics of electrode processes involving multi-electrochemical reactions. The theory was established based on two hypotheses: (1) any electrochemical reaction can be divided into two or more oxidation or reduction reactions, and (2) there can be no net accumulation of electrical charges during an electrochemical reaction. The significance of the mixed potential theory is that it makes it possible to describe the kinetics of electrochemical corrosion governed by the superposition of anodic and cathodic partial polarisation behaviour. For example, the equilibrium electrode potential ($E_{0\text{ (Fe/Fe}^{2+}\text{)}}$) of iron is defined by the intersection of two lines corresponding to the oxidation and reduction of iron at the charge-transfer control, as shown in Figure 2.3. Likewise, the equilibrium of electrode potential of oxygen ($E_{0\text{ (O}_2\text{/OH}^-\text{)}}$) under the charge-transfer control is also presented. If the iron electrode is in contact with oxygen containing electrolyte, an iron half-cell is formed. In order to satisfy the second hypothesis of the mixed-potential theory, the total rate of oxidation must be equal to the total rate of reduction. Therefore, the electrode is polarised to another potential between the two equilibrium potentials. The potential corresponding to this situation is the corrosion

potential E_{corr} , given by the intersection of the anodic line of the iron and the cathodic line of the oxygen. The current density at $E_{\text{corr}}(\text{Fe}/\text{Fe}^{2+})$ is corrosion current density $i_{\text{corr}}(\text{Fe}/\text{Fe}^{2+})$, which is equal to either the rate of iron dissolution or oxygen reduction.

The galvanic corrosion system can also be described by the mixed-potential theory. As introduced in Section 2.1, iron and copper are galvanically coupled (see Figure 2.1). The additional copper oxidation/reduction reactions are presented by the grey lines in Figure 2.3. The total rate of oxidation is determined by summing up the individual oxidation currents that correspond to iron, hydroxyl ion and copper, at constant potentials. Likewise, the total rate of reduction is calculated by summing up all of the reduction currents from Fe^{2+} , oxygen and Cu^{2+} . The point at which the total rate of oxidation is equal to the total rate of reduction is the corrosion potential $E_{\text{corr}}(\text{Fe-Cu})$ of the iron-copper galvanic corrosion system. It is noted that the corrosion current density $i_{\text{corr}}(\text{Fe/Cu})$ of galvanic corrosion is much larger than that of $i_{\text{corr}}(\text{Fe}/\text{Fe}^{2+})$. In general, if a less noble metal is galvanically coupled with a noble metal, the corrosion rate of the less noble metal is accelerated.

Figure 2.3 Schematically illustrated equilibrium potentials, corrosion potentials and effect of galvanic coupling of iron to copper

Based on the mixed potential theory, the original Butler-Volmer equation has been modified into a form for corrosion kinetic calculations as follows:

$$i = i_{corr} \left[\exp\left(\frac{E - E_{corr}}{\beta_M^a}\right) - \exp\left(\frac{-(E - E_{corr})}{\beta_{O_2}^c}\right) \right] \quad \text{Equation 2.5}$$

where E is the inner or Galvani potential of a metal in contact with an electrolyte; E_{corr} is the corrosion potential in contact with an electrolyte; i_{corr} is the corrosion current in contact with an electrolyte; β is equal to $2.3RT/\alpha nF$; the superscripts a and c indicate the anodic and cathodic reactions respectively; and the subscripts M and O_2 indicate the metal and oxygen, respectively.

For large anodic and cathodic overpotentials, the Butler-Volmer equation can be simplified into the Tafel equation [Tafel 1905]. For small overpotentials, the Butler-Volmer equation can be simplified into the Stern-Geary equation [Stern and Geary 1957]. However, an exception to this general Butler-Volmer model is the passivity behaviour of active-passive metals (e.g. Fe, Cr, Ni, Ti, Zr) and their alloys.

Passivity is a phenomenon which can be simply defined as a loss of chemical reactivity of metal and alloys under certain circumstances [Fontana 1986]. Due to its practical and scientific importance, passivity and passivity breakdown have been studied intensively. Numerous theories and models have been proposed to explain these phenomena [Uhlig 1978; Osterwald 1981; Okada 1985; Sharland 1987; Macdonald and Urquidi-Macdonald 1986; Dawson and Ferreira 1986; Nishimura and Kudo 1990; Szklarska-Smialowska 1999]. From the electrochemical point of view, a passive metal is one which demonstrates the typical S-shaped dissolution curve as shown in Figure 2.4. The pitting potential (E_{pit}) located between the passivation and trans-passivation states indicates a localised breakdown of the passive film. It is believed that pitting can occur only when the potential is above the pitting potential [Bohni 1967; Kaesche and Werkst 1963; Uruchurtu and Dawson 1986].

Figure 2.4 Typical anodic dissolution behaviour of an active-passive metal
[Source: Jones 1996]

If a galvanic corrosion couple includes an active-passive metal, as shown in Figure 2.5, the active metal **M** could, however, become passive when galvanically coupling with a noble metal **N** to result in less corrosion of **M**. This particular system represents the active-passive metal that can be protected by galvanically coupling with a noble metal, which is totally different from the phenomena illustrated in Figure 2.3.

Figure 2.5 Schematic illustration of the spontaneous passivation of an active-passive metal by galvanic coupling with a noble metal

2.2 Corrosion of Major Engineering Metals

Stainless steel, carbon steel and aluminium alloys are the most widely used materials for engineering metals in many industries. The corrosion prevention of stainless steel, carbon steel and aluminium is therefore an issue of engineering and economic importance.

2.2.1 Corrosion Behaviour of Stainless Steel

Stainless steel is ferrous alloy containing at least 11 wt% of chromium; they are typically low in carbon content [Smauel *et al.* 1993]. Stainless steel generally cannot be attacked by oxidising acids, aqueous solutions in the absence of halogen ions, organic and gaseous environments. This is due to the formation of metal oxides with chromium, frequently

$\text{FeO} \cdot \text{Cr}_2\text{O}_3$, through passivation. The Pourbaix diagram for iron, with the superimposed stability of Cr_2O_3 , suggests that the passive layers composing mainly Fe_2O_3 and Fe_3O_4 are stable over wide ranges of potential (-0.8 to 1.2 V vs. SHE) and pH (2 to 16) [Jones 1996]. Other elements, such as nickel, manganese, and molybdenum, can influence the effectiveness of chromium in forming or maintaining the film. If the passive film is broken or damaged due to chemical or mechanical actions, the chromium element in the steel substrate can almost instantly repair the damaged area by oxidation (re-passivation). However, under the attacks of halogen ions, the formed passive film is subjected to localised breakdown, i.e. localised corrosion.

Pitting is the most common form of localised corrosion on stainless steel and is also the root of many other forms of localised corrosion failures [Dabosi *et al.* 1994]. Pitting corrosion is due to major electrochemical heterogeneity, often as a result of a puncture in the passive film. Good correlations between E_{pit} and the resistance of Fe-Cr alloys to pitting corrosion have been reported in long-term exposure to seawater, thus the resistance to pitting corrosion of Fe-Cr alloys can be estimated by E_{pit} [Wilde and Williams 1969]. During pitting corrosion, the anode is situated in the pit and the cathode on the surrounding surface. Because of the relatively small anode area, the anodic current density is high and so is the corrosion rate. Thus, large cathode/anode area ratio is very unfavourable and pitting penetration can occur in a short period of time.

The destructive and insidious nature of pitting corrosion mainly stems from its autocatalytic

mechanism, i.e. the corrosion processes within a pit produce conditions which are stimulating and necessary for the continuing activity of the pit [Fontana 1986]. As illustrated in Figure 2.6, in a near neutral chloride containing solution, metal **M** dissolution occurs within the pit and oxygen reduction takes place on adjacent surfaces. Passive film breakdown is considered to be the first stage of pitting. There are four important conditions for the passive film breakdown to happen: critical potential, damaging species, induction time and localised sites.

Metastable pitting is considered to be the second stage of pitting corrosion, which refers to a stage when pits grow for a limited period before re-passivating. At lower potentials, pitting initiation is followed by rapid re-passivation [Baroux 1990; Böhm 2000]. Even above the pitting potential, re-passivation may still occur, showing the stochastic character of localised corrosion processes. When the active state within the pit is maintained over an extended period of time, rapid metal dissolution usually occurs. Once a pit starts to grow, major electrochemical heterogeneity is developed that further promotes pit growth. The local pit environment becomes depleted in cathodic reactant (e.g. oxygen), which shifts most of the cathodic reaction to the boldly-exposed surface where this reactant is more plentiful. The pit environment becomes enriched in metal cations and anionic species, such as chloride, which electromigrates into the pit to maintain charge neutrality. The pH in the pit is lower owing to cation hydrolysis and the absence of a local cathodic reaction [Frankel 1998; Frankel and Scully 2001]. The acidic chloride environment generated in pits is aggressive to most metals and tends to propagate the pit growth as indicated in Figure 2.6.

Figure 2.6 Autocatalytic process occurring in a corrosion pit [Source: Evens 1951]

2.2.2 Corrosion Behaviour of Carbon Steel

Carbon steel contain up to approximately 1.0 wt% carbon and the alloy content is generally less than 2 wt% [Smauel *et al.* 1993]. Carbon steel, including mild steel, generally has low resistance to corrosion and often requires protective coatings.

Carbon steel usually suffers from general corrosion. Residual carbon and other impurities in iron may migrate to grain boundaries, forming micro-alloys that may have different corrosion potential with respect to a corrosive environment [Fontana and Greene 1967].

The heterogeneity of the metallurgical microstructure results in the formation of corrosion micro-cells. General corrosion of carbon steel occurs either by the direct dissolution of

metal in the active state, or by the dissolution of the passive oxide film in the passive state. In the former case, for example, a piece of mild steel immersed in dilute sulphuric acid will normally dissolve at a uniform rate over the entire surface. The latter case can be described by the electrochemical behaviour of mild steel in a neutral sodium chloride solution, as shown in Figure 2.7. Under attacks of chloride ions, the anodic dissolution rate of metal will increase considerably even though the potential is within the passive region. Figure 2.8 illustrates the detailed corrosion process of carbon steel under a drop of seawater and outlines the composition of the “rust” i.e. $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, Fe_2O_3 and other oxides.

Figure 2.7 The effect of aggressive chloride ions in the anodic dissolution behaviour of stainless steel [Source: Jones 2005]

Figure 2.8 Schematic illustration of the corrosion reaction in a drop of seawater on carbon steel [Source: Donovan 1986]

However, under some conditions, according to the Pourbaix diagram of iron (see Figure 2.2), carbon steel surface can be passivated and shows no tendencies towards corrosion in alkaline medium due to the formation of an iron oxide film on the surface. It is known that the iron oxide film comprises of an inner layer of Fe_3O_4 (magnetite) and an outer layer of precipitated Fe_2O_3 (hematite).

2.2.3 Corrosion Behaviour of Aluminium and Its Alloys

Thermodynamically, aluminium is a very reactive metal. Its standard equilibrium potential is approximately -1.66 V vs. SHE. Passivity is the most important phenomenon that affects the behaviour of aluminium corrosion. Aluminium and its alloys owe their excellent corrosion resistance to the passivity produced by an inert and protective aluminium oxide

film (i.e. Al_2O_3), which forms almost immediately in most environments, such as aerated and de-aerated aqueous solutions. It can be seen that aluminium oxide is stable within the pH range of 4 to 8.5 from the Pourbaix diagram, as shown in Figure 2.9. Thus, except for in highly acidic or alkaline corrosive environments, such as phosphoric acid or sodium hydroxide, aluminium and its alloys usually have excellent resistance to general corrosion.

Figure 2.9 Typical Pourbaix diagrams for aluminium at 25°C (approximate unit activity assumed for dissolved species) [Source: Shreir 1994]

Although a passive film on aluminum surface can prevent to general corrosion, it is in fact an imperfect film, and thus aluminium often suffers from localised corrosion [Frankel 1998]. Pitting corrosion of aluminium and its alloys is a common and serious localised corrosion problem, especially when metallic elements are added to aluminium in order to improve its properties, such as its mechanical strength. Similar to the pitting corrosion of

stainless and carbon steel, aluminium pitting corrosion in chloride-containing solutions has an autocatalysis mechanism [Davis 1999; Wranglen 1972], as shown in Figure 2.10, displaying corrosion processes occurring 'within the pit', 'in the pit mouth' and 'around the pit' [Wranglen 1972].

Figure 2.10 The electrochemical mechanism of pit growth on aluminium, showing its autocatalytic self – stimulating nature [Source: Wranglen 1972]

Within the corrosion pit: Similar to the performance on stainless steel, the enrichment of chloride and hydrogen ions is created due to the autocatalytic properties of pitting corrosion. Moreover, O_2 supply is limited partly due to low O_2 solubility in the concentrated pit electrolyte. This process prevents re-passivation of the metastable pits.

In the pit mouth: A crust of hydrate is formed, which counteracts the dilution of the pit solution by diffusion and convection, and hence strengthens the factors listed above.

Around the pit: Cathodic protection is generated by the corrosion current. Passivation is caused by the formation of alkali in the cathode reaction, particularly in the presence of

calcium hydrogen carbonate. More noble metals, such as copper, are deposited on local cathodes so that the cathode potential within the pit has to be in the active region, which is facilitated by the pit.

2.3 Corrosion Prevention Technologies and Protective Coatings

Since metal corrosion is a thermodynamically spontaneous process, corrosion control strategies are focused on controlling the kinetics of corrosion, i.e. slowing the corrosion kinetics and/or altering corrosion mechanisms. A variety of strategies have been developed to prevent corrosion on metal structures. The most commonly applied anti-corrosion methods include cathodic/anodic protection, corrosion inhibitors, and anti-corrosion coatings.

Cathodic protection is achieved by supplying electrons to the metal structure to be protected [Fontana 1986]. In practice, cathodic protection is usually applied by employing either a sacrificial anode or an external power supply to negatively polarise a metal surface, which reduce the rate of corrosion. In the latter case, the sacrificial anode is consumed during protection and needs to be replaced after a certain period.

Anodic protection is based on the anodic polarisation of a metal surface in order to form a passive film on the metal by externally applied anodic currents. To be suitable for anodic protection, an active-passive metal should exhibit a broad range of passivity and a low

protection current. In the case of the anodic protection of aluminium, a passive layer can form on its surface if it is anodically polarised in a medium at pH between 2 and 9. The anodic polarisation curve can be used to evaluate anodic protection as shown in Figure 2.11. The corrosion current of case one, $i_{\text{corr}}(M_1)$, is much smaller than that of case two, $i_{\text{corr}}(M_2)$, and anodic protection is therefore more suitable for the former case.

Figure 2.11 Schematic illustration of the effect of anodic dissolution current on the anodic protection of an active-passive metal

An inhibitor is a substance that, when added in small concentration to an environment, decreases the corrosion rate [Fontana 1986]. Among commonly used inhibitors, chromate-containing inhibitors are one of the oxidisers primarily used to inhibit corrosion on active-passive transition metals, such as steel and aluminium alloys. Like all oxidisers, chromate ions accelerate corrosion at low concentrations. The critical minimum chromate concentration for passivation at 25°C is approximately $10^{-3} \text{ mol L}^{-1}$ [Wicks *et al.* 1999].

Organic coatings are the most widely used method for corrosion prevention. Conventional organic coatings are complex mixtures of chemical substances, including binders, volatile components, pigments, and additives. Organic coatings can be classified in terms of application methods, such as electrodeposition coatings, radiation cure coatings, dip coatings and so on. Anti-corrosion coatings reduce the rate of corrosion by reducing the rate of transportation of essential ingredients (e.g. water, oxygen, or aggressive ions) to the metal surface, and also by preventing the operation of electrochemical cell located at the coating/metal interface. According to the work of Funke [Funke 1979, 1983 and 1985], wet adhesion is regarded as a critical factor for the anti-corrosion performance of organic coatings. If perfect wet adhesion could be achieved in all areas of the metal-coating interface, the organic coating that covers the metal on both microscopic and macroscopic scales would protect the metal indefinitely from corrosion [Wicks *et al.* 1999]. A common ingredient for coatings, especially in primers, is chromium (VI)-containing inhibitors and surface conversion coatings. The main effect of the chromium (VI)-containing inhibiting pigments is believed to promote the formation of a passive layer on the active-passive metal surface. However, chromium (VI) has been shown to be hazardous to both the environment and to human health. A major topic in anti-corrosion coating studies is to find replacements for the harmful Cr (VI)-containing coatings.

Conventional electrodeposition of organic coatings is widely used in situations where primers or single-layer coatings on metal surface under mass-production conditions are needed, especially on articles with a complex shape where coating application by other

methods is difficult. It should be noted that neither oxidation nor reduction is involved in the conventional electrodeposition of organic coatings. In simple terms, conventional electrodeposited organic coatings are created by the electrolysis of polyelectrolyte along with the electrolysis of water. The necessity for anodic electrodeposition occurs when there is a lower solubility of organic ions at a higher concentration of H^+ in the vicinity of the metal subjects. As for cathodic electrodeposition, it takes place when there is a lower solubility of organic ions at a higher concentration of OH^- . As shown in Figure 2.12, the formula for polymers used for anodic and cathodic deposition can be described as R_nCOOA and $R_nX^+Z^-$, respectively [Krylova 1984]. Since neither oxidation nor reduction occurs during the conventional electrodeposition of organic coatings, it is completely different from the electrodeposition of intrinsically conducting polymers (ICPs as introduced in Section 2.4) in terms of the deposition mechanism.

Figure 2.12 Schematic illustrations of the electrochemical cells of anodic and cathodic electrodeposition

In practice, to be suitable for the electrodeposition process, the resin must be held in a stable particulate or micelles dispersed by connection with hydrophilic ionic groups, which provide colloidal stabilisation. Non-ionically sterically stabilised dispersion, however, may also be electrodeposited [Schweitzer 2001]. Both anodic and cathodic electrodepositing methods now exist. The anti-corrosion performance of organic coatings by deposition on the cathode is of better quality than that of the anode.

2.4 Intrinsically Conducting Polymers

Intrinsically conducting polymers (ICPs) are a relatively new class of materials. Since the discovery of electrically conducting polyacetylene in 1977, ICPs have attracted enormous interest from both applied science and fundamental research. ICPs have conjugated polymer backbones that display unusual electronic properties. The electroactivity and conductivity (or semi-conductivity) of ICPs have changed the concept of polymers dramatically. The impact is significant and was recognised in 2000 by the award of the Nobel Prize for Chemistry to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, the scientists who discovered the first ICP--polyacetylene [Heeger 2001; MacDiarmid 2001; Shirakawa 2001].

2.4.1 Key Features of ICPs

The most prominent polymers of ICPs are PANI, polypyrrole (PPY), and polythiophene (PT), as shown in Figure 2.13. They possess electronic conductivity in their “doped” state.

Doped ICPs are good conductors for two reasons [Heeger and Smith 1991]:

- i) Doping leads to the injection of carriers into the π -electron system. Since every monomer is a potential redox site, conjugated polymers can be doped (n-type or p-type) to a relatively high density of charge carriers.

ii) The π -bonding leads to π -electron delocalization along polymer chains, and thereby, results in the possibility of charge carrier mobility (intra-chain). The mobility can be extended into three dimensional transports by the inter-chain electron transfer interactions, allowing electrons to "hop" from one position to another (inter-chain). Thus, the basic intrinsically conducting frame has been formed. In principle, the broad π -electron bandwidth (often several electron-volts) can lead to relatively high carrier mobilities.

The doping process in ICPs is reversible and controllable. The electric conductivity of ICPs now range from that typical of insulators ($< 10^{-10}$ S/cm) to that typical of semiconductors such as silicon ($\sim 10^{-5}$ S/cm), even to a value greater than 10^4 S/cm (nearly the conductivity of copper, 5×10^5 S/cm) [Heeger and Smith 1991; MacDiarmid 2001].

Figure 2.13 Typical conducting polymer structures (in un-doped form) [Source: Tallman *et al.* 2002a]

Another common feature to all ICPs is that they can exist in different stable redox states by

p-doping and/or n-doping. The p-doping or n-doping is partial oxidation or reduction of the π -backbone of the organic polymer, respectively [Smela 1999]. By using doping, de-doping, and re-doping methods, it is possible to reversibly switch the polymer structure and obtain the desired electrochemical, optical, chemical and mechanical properties of these polymers. It is worthwhile to note that all the final products of ICPs are environmentally friendly and much more biodegradable than conventional polymers.

Generally, due to the interesting properties of ICPs, they have been used in many applications. These include electrochromic devices [Akhtar *et al.* 1988; Gao *et al.* 1999], anti-corrosion primers [Lu *et al.* 1998; Tallman *et al.* 2002b; Camalet *et al.* 1998; Ahmad and MacDiarmid 1996], biochemical capacitors [Huang *et al.* 1992], rechargeable batteries [Karami *et al.* 2003; MacDiarmid 2001], electrochemical actuators [Lu *et al.* 2004], electromagnetic shielding [Lee *et al.* 1999], and membrane separation [Su *et al.* 1996; Stolarczyk and Lapkowski 2001]. In addition to a wide range of applications, ICPs can be altered to tailor their properties and blended with other polymers, leading to potentially diversified applications.

2.4.2 Structure and Properties of PANI

PANI is an old polymer, which has been used as a so-called “Prussian Blue” dye since the 1860s. After the investigations by MacDiarmid in the mid-1980’s [MacDiarmid *et al.* 1986], the high electronic conduction of PANI was found. A considerable amount of

research has been focused on studying the structure, properties and synthesis of PANI.

PANI can be differentiated by its oxidation states combining with protonation levels. The general polymeric structure of PANI as proposed by MacDiarmid is shown in Figure 2.14 [MacDiarmid 2001]. When PANI is partially oxidised to the emeraldine (EM) state ($y=0.5$), i.e. amine ($-NH-$) sites are in equal proportions to imine ($=N-$) sites, PANI is a conjugated polymer. Besides the EM state, there are two other stable states, leucoemeraldine (LE) ($y=1$) and pernigraniline (PA) ($y=0$), representing fully reduced and oxidised states, respectively. In addition, each redox state of PANI also undergoes non-redox doping (so-called “protonation”) by treating it with acids. Each redox state (the same y value in the general formula) of PANI includes two forms i.e. the salt (protonated) form and base (un-protonated) form, as shown in Figure 2.15. The only electrically conducting form is the emeraldine salt. The other forms are either insulator or semiconductor, depending on the doping level [Wallace *et al.* 2003]. In general, all of these forms can reversibly convert through redox doping and protonation, as illustrated in Figure 2.16. Therefore, each form of PANI can be achieved by two completely different routes — redox doping and protonation.

Figure 2.14 General structure of PANI; $y=1$ (leucoemeraldine), 0.5 (emeraldine) and 0 (pernigraniline) [Source: MacDiarmid 2001]

Figure 2.15 Three basic oxidation states including the base and salt forms of PANI [Source: Tallman *et al.* 2002a]

Figure 2.16 The reversible protonation and electron transfers of PANI in emeraldine and leucoemeraldine state. [Source: Tallman *et al.* 2002a]

PANI is ready to undergo electrochemical redox reactions. An approximate range of the electroactive potential of PANI in the EM state is around +0.4 to +1.0 V (vs. SHE at pH 7), and the actual reduction potential depends on the dopant (counterions), doping level, the electrolytes and other experimental variables [Tallman *et al.* 2002a]. In the field of anti-corrosion coatings, DeBerry found that PANI can stabilise the potential of stainless steel electrodes in the passive region in 0.5 M H_2SO_4 solutions [DeBerry 1985]. Since then,

many studies have shown that PANI can provide corrosion protection on stainless steel [Ahmad and MacDiarmid 1996], carbon steel [Kinlen *et al.* 1999], aluminium and its alloys [Cogan 2000] and copper [Wessling 1994]. The potential range of PANI is much higher than that of active-passive metals, such as stainless steel and aluminium (refer to Section 2.2), and similar to the potential of chromium (VI) ($\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_3$; +0.42 V vs. SHE). It is therefore possible that the potential range of PANI benefits the anti-corrosion performance of stainless steel and aluminium. PANI has received considerable attention in the field of corrosion due to its relatively high environmental and thermal stability.

As noted above, PANI can also be typically protonated by protonic acids. Once PANI is protonated, counter anions from the acid will also be incorporated into the polymer backbone for overall electronic neutrality. However, if PANI is in a neutral or alkaline solution, the dopant acid attached in the polymer would be released [MacDiarmid 2001]. There is an exception, which is called “self-doped” (or sulphonated) PANI. If PANI is protonated by sulphonic acids (e.g. p-toluenesulphonic acid), electronic protonation is achieved from a covalently attached acid group. If the acid functionality is sufficiently strong, the dopant acid would not be released and the protonation of the polymer backbone occurs; in some cases even up to pH approaching 14 [Deore *et al.* 2004]. The reaction is illustrated in Figure 2.17.

Figure 2.17 A self-doped (or sulphonated) PANI redox scheme showing cation (C⁺) incorporation upon reduction [Source: Tallman *et al.* 2002a]

The structure of PANI is also unique among ICPs, in that nitrogen heteroatom rather than the carbonium ion of other p-doped polymers (e.g. PPY and PT) determines the conjugation structure. Due to the nitrogen heteroatom, the heterogeneous polymers formed are generally neither soluble in most common solvents, nor do they possess a melting point or other softening behaviour when heated. Nevertheless, the processibility of PANI can be improved by its protonation with functionalised acids, such as camphor-sulfonic acids, dodecylbenzene sulfonic acid (DBSA), or bis (2-ethylhexyl) phosphate. The resulting PANI-EM salt by such protonation agents is soluble in m-cresol, NMP, DMSO, and xylene [Heeger and Smith 1991].

2.4.3 Synthesis of PANI Coatings

A range of techniques have been developed for the polymerisation of PANI, including electrochemical, chemical, photochemcially initiated, enzyme-catalysed and electron acceptors polymerisation [Wallace *et al.* 2003]. The most widely used methods are electrochemical and chemical polymerisation of PANI from appropriate monomers in

acidic solutions. The mechanism of chemical polymerisation is by oxidising aniline in acidic solution by agents such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and FeCl_3 . Compared to the chemical polymerisation of PANI, the electrochemical deposition of PANI is a one-step method of forming PANI coatings, and thus is an efficient way of controlling its chemical and physical properties such as adhesion, molecular weight, and redox state of the deposited PANI coating. A further advantage is that the electrodeposition of PANI coating could be carried out on irregular shaped objects [Breslin *et al.* 2005; Iroh *et al.* 2003].

The electrodeposition of PANI is a completely different process from the conventional electrodeposition of organic coatings. It involves oxidation of the monomer and generation of radical cations in acidic media [Shim *et al.* 1990]. It is generally accepted that the electropolymerisation can be divided into two stages: an electrochemical initiation and subsequent chemical and electrochemical reactions for polymer propagation [Tallman *et al.* 2002a]. The following chemical and electrochemical reactions can be repeated without any other initiation reactions due to the auto-catalysing properties of PANI polymerisation, i.e. the more PANI deposited, the higher the rate of polymer formation. The detailed electropolymerisation, involving four steps of reactions, is as follows [Wallace *et al.* 2003]:

Step1. Oxidation of monomer:

Equation 2.6

This is the rate determining step.

Step 2. Radical coupling and re-aromatisation

the reaction energy in the formation of radical cations, and to generate the EM salt [Wallace *et al.* 2003]. It is relatively easier to electrodeposit PANI on noble metals, such as gold and platinum [Shim *et al.* 1990; Hatchett *et al.* 1999], and inert materials, such as indium tin oxide and graphite [Jelle *et al.* 1993; Li *et al.* 2004]. However, the electrodeposition of PANI on corrosion-susceptible metals such as mild steel [Camalet *et al.* 1998] and aluminium [Eftekhar 2001] was found to be problematic.

2.5 Electrodeposition and Corrosion Protection by PANI Coatings

2.5.1 Difficulties of PANI Electrodeposition

The major problem of electrodeposition of PANI on alloys of iron and aluminium originates from the mismatch between the required deposition condition ($\text{pH} < 4$, $E_{\text{deposition}} > 0.9 \text{ V vs. SHE}$) [Wallace *et al.* 2003] and the properties of the metal substrate. Thermodynamics as illustrated by the Pourbaix diagrams (see Figures 2.2 and 2.9), predicts that iron and aluminium will undergo corrosion in an acidic environment ($\text{pH} < 4$) before the electropolymerisation potential ($> 0.9 \text{ V vs. SHE}$) of monomers is reached. Moreover, the nature of the passive oxide film formed on active-passive metals under anodic electrodeposition conditions could act as another crucial factor in the formation of a uniform PANI film.

The electrodeposition of PANI on stainless steel is relatively easy because of the better

anti-corrosion capability of stainless steel. In addition, the passive film on stainless steel essentially follows the same basic properties as the metal [Kaesche and Werkst 2000], thus, allowing anodic electrochemical deposition in the presence of the passive film. The major concern is to keep the potential of electropolymerisation at the range that reduces the extent of over-oxidation of the resulting PANI as further discussed at the end of this section.

However, the electrodeposition of PANI on corrosion susceptible carbon steel has been found to be much more difficult. In order to overcome the incompatibility between the electrode properties and required deposition conditions, different electrolytes such as *p*-toluene-sulfonic acid [Camalet *et al.* 1998] and oxalic acid [Iroh *et al.* 2003; Camalet *et al.* 1998] have been employed. Oxalic acid has been commonly used for the electrodeposition of PANI on carbon steel due to its properties in enabling the formation of a passive film with iron, which decreases metal dissolution without preventing the nucleation of the polymer. Iroh and co-workers [Iroh *et al.* 2003] have studied the electrodeposition process of PANI on low carbon steel in oxalic acid. Three stages have been described for the formation of the polymer composite, namely (1) electroadsorption of monomers and initiation of passive film, (2) growth and subsequent impingement of the passive film, and (3) formation of composite coatings. Although much work has been carried out to study the electrodeposition process as a function of time, little has been explored of the distribution of PANI deposits on the electrode surface, i.e. the heterogeneity of the electrodeposited PANI on the metal surface and its effects on

corrosion resistance has not been understood.

The difficulties of the electrodeposition of PANI on aluminium and its alloys result from two aspects. On the one hand, aluminium and its alloys are corrosion-susceptible metals, and thus, metal substrate could experience dissolution during PANI deposition. On the other hand, aluminium and its alloys belong to the valve metals (see Section 2.2.3) [Fontana 1986]. The oxide film on aluminium and its alloys acts as an insulator, possessing asymmetrical conductivity, which could impede the anodic current for PANI initiation. Actually, besides PANI, the properties of the oxide film can result in non-uniform electrodeposition of other ICPs on aluminium alloys, for instance polypyrrole [Tallman *et al.* 2002b]. In order to overcome these problems, pre-treatment and modification of the metallic surface are crucial processes for the successful electrodeposition of PANI on aluminium alloys.

The direct electrodeposition of PANI on aluminium alloys was first reported by Runge-Marchese and McNallan [Runge-Marchese and McNallan 2001]. PANI was electrodeposited with simultaneous aluminium anodising in sulphuric solution, resulting in a non-protonated and ring-sulfonated PANI aluminium salt with no electroactivity. One researcher group has demonstrated that enzyme-modified PANI could be electrodeposited on the aluminium electrode by galvanostatic and potentiostatic methods [Aftekhari 2001] in the presence of a uniform and hollow oxide film. However, the formation of this special oxide film needs voltages typically in the range of ~ 100 V in 4% phosphoric acid [Miller

and Majda 1986], which makes this method impractical as the replacement of Cr (VI)-containing conversion coatings.

A pre-treatment approach was reported by Huerta-Vilca *et al.* [Huerta-Vilca *et al.* 2004]. An aluminium alloy AA1050 was first anodised in 0.1 M HNO₃ solution with 0.1 M aniline using the galvanostatic method before the electrodeposition of PANI from H₂SO₄ solution using cyclic voltammetry. In this study, anodising broke the oxide film and created spots for PANI initiation, and at the same time, anodising also produced defects on the metal surface and thus decreased the anti-corrosion performance of the deposited PANI. To author's knowledge, there is no literature about the electrodeposition of PANI on aluminium alloys with satisfactory corrosion protection performance. Further studies are important to better understand the PANI electrodeposition processes on aluminium and its alloys, in order to explore the possibility of developing the PANI film into a primer with a satisfactory anti-corrosion performance.

Another problem of the electrodeposition of PANI is associated with the electropolymerisation and polymer degradation affecting all metal substrates. The potential for the initiation of electrodeposition should be no less than 0.9 V *vs.* SHE [Wallace *et al.* 2003]. In most cases, the applied potential is larger than this value due to a concern about kinetics. However, it has been reported that if PANI is exposed to a potential more positive than *ca.* ~ 0.70 V *vs.* SHE, PANI could undergo over-oxidation and degradation. This is probably due to a chain scission by the hydrolysis of amine groups to form insoluble

benzoquinone and acrylamine terminations [Su *et al.* 1996; Shim *et al.* 1990; Hatchett *et al.* 1999]. Since this kind of problem is inevitable, attempts have been made to minimise the extent of degradation, for instance, by using cyclic voltammetry or dividing the electrodeposition process into two steps [Bernard *et al.* 2001]. Table 2.1 summarises the relevant studies and experimental details of PANI electrodeposition on stainless steel, carbon steel and aluminium alloys.

Table 2.1 Summary of experimental observation of PANI electrodeposition on stainless steel, carbon steel and aluminium alloys

Substrate	Solvent/Doping agents	Electrodeposition method	Observation	Reference
SS 430, 410	HClO ₄ (pH=1)+ 1.0 M aniline	cyclic voltammetry: -0.2 ~ 1.1 V (vs.SCE); 20 mV/s	SS430:Active-passive transition from -0.27 V (1 st cycle); 1 st oxidation peak 0.12 V	Deberry 1985
SS 316	0.5 M H ₂ SO ₄ +0.5 M aniline	cyclic voltammetry: -0.4 ~ 1.2 V (vs. SCE); 100 mV/s	1 st oxidation peak recoded at ~ 1.2 V, followed by reduction peak at ~ 0.4 V	Prasad and Munichandrai -ah 2001
SS 304	0.5 M H ₂ SO ₄ (pH=1)+0.2 M aniline	cyclic voltammetry: -0.2 ~ 1.0 V (vs. Ag/AgCl); 50 mV/s	SS304 was passivated in the electrolyte, PANI deposited at 0.9 V; two anodic peaks at 0.22,0.76 V	Hermas 2005
Mild steel	1 M tosylic acid +0.3 M aniline	cyclic voltammetry: potential range is not claimed chronopotentiometry: ~ 1.8 V (vs. SCE)(300s)	Between 0.2 ~ 1.2 V an electroactive and electrochromic film was deposited	Camalet 1998a
Mild steel	0.3 M oxalic acid+0.1 M aniline	(1) cyclic voltammetry: -0.5 ~ 1.7 V(based on figure) (2) Galvanostatic: 1 ~ 20 mA/cm ² (3)Potnetiostaitc: two steps involving -0.5 ~ -0.2 V (vs.SCE) and increase to1.6-1.9 V	Similar morphology was obtained by the three methods, but the current efficiency in oxalic acid is low	Camalet 1998b
Iron plate	2 M LiClO ₄ +0.2 M aniline	Galvanostat: 5 or 10 mA/cm ²	No induction period indicating passivation of metal is readily obtained. A homogeneous, strong adhesion PANI film	Nguyen 1998
Cold mild steel	20 vol% CH ₃ OH+0.13 M H ₂ SO ₄ +0.3 M aniline 0.1 M HNO ₃ +0.3 M	Potentiokinetic:0.8 ~ 1.5 V (vs.SCE) Potentiostat: at 1.1 V, 4	The deposited films are brittle and powdery	Troch-Nagels 1992

	aniline	minutes		
Mild steel	1.7H ₃ PO ₄ +0.1 Metanilic acid+0.3aniline (pH ~ 0.5); 0.5 M H ₂ SO ₄ + 0.2 M aniline; 0.25 M oxalic acid +0.1 M aniline	In H ₃ PO ₄ Step1:potentiodynamic -0 ~ 0.9 V(vs.SSE) (time:20s); Step2: potentiostatic 0.3 V (vs.SSE) (time:3h)	If the thickness is more than 500nm, adhesion decreases.	Bernard 2001
AA 2024-T3	Oxalic acid+0.1 M aniline	cyclic voltammetry:-1.0 ~ 3.0 V (vs. SCE)	Anodic current peak at 0.3 V responds to emeraldine form	Iroh 2003
Aluminium	H ₂ SO ₄ , pH2.4 concentration used regarding to the solution pH+0.1 M aniline	Galvanostatic: 3.0, 5.0, 8.0 mA/cm ² Potentiostatic: not shown	Pre-treated the electrode in 4% H ₃ PO ₄ at 100 V; as a result, the growth rate of PANI on Al is two times faster than on Pt	Eftekhari 2001; Miller and Majda 1986

2.5.2 PANI Coatings for Corrosion Prevention

PANI, particularly in EM state including emeraldine base (EB) and emeraldine salt (ES), has been found to possess the ability to protect metals from electrochemical corrosion. As suggested in the Pourbaix diagram (in Figure 2.18), the superimposed potential of PANI-EM (either PANI-ES or PANI-EB), is more positive than the respective potential of bare iron, and is mainly located in the passive region of iron. Many studies have shown that PANI-EM coating can also reduce the corrosion rate of stainless steel, mild steel and aluminium alloys, as summarised in Table 2.2. To date, there is a general agreement that PANI provides corrosion protection to metals such as stainless steel, mild steel and aluminium alloys.

Figure 2.18 Pourbaix diagram of PANI and iron in water; (a) and (b) represent the reduction potential for oxygen and hydrogen ions, respectively
[Source: Dominis *et al.* 2003]

Table 2.2 Evidence from corrosion performance and mechanism studies of PANI on stainless steel, carbon steel and aluminium alloys

Substrate	Type of polymer coating(s)	Test method	$\frac{\Delta E_{\text{corr}}^*}{\Delta E_{\text{pit}}^* / i_{\text{corr}}^*}$	Observation/Suggestion	Reference
SS 430	Electrodeposited PANI (HClO_4)	open-circuit potential in 1 M H_2SO_4 Potentiodynamic in 0.2 M H_2SO_4 +0.2 M NaCl	$> \Delta 0.4 \text{ V} / \Delta 0.2 \text{ V}$ (according to figures)	open-circuit potential shows unusual oscillation over 30h. In acid chloride solution, oscillation occurs between pitting potential and protective potential	Deberry 1985
SS430	PANI-EB was cast from NMP;	open-circuit potential in 1 M H_2SO_4 : parts of PANI film was removed during testing	$\sim \Delta 0.7 \text{ V} / - / -$	open-circuit potential shows drop and recover process, suggests that not all of the metal surface was covered to obtain passivation	Gašparac and Martin 2002a
SS 430	PANI- EB was cast from NMP solution;	cyclic voltammetry in various concentrations of H_2SO_4 solution such as 1.0 M, 10 M, 100 M	open-circuit potential: 1.0 M $\Delta 0.65 \text{ V}$ 10 M $\Delta 0.9 \text{ V}$ /- / -	PANI- EB was partially doped in 1-100 MM H_2SO_4 and the corrosion protection to metal surface is independent of doping level.	Gašparac and Martin 2002b
Mild steel	PANI- ES (DNNSA/TA/PMS A) sprayed to the substrate from xylene;	Ranking the total Fe (lost) analysis in 3.5% NaCl of various coating compositions	—	PANI- EB provides superior corrosion protection to PANI- ES due to “residual alkalinity”	Dominis 2003

	Dedoping/redoping used to exchange counterions, amine-cured epoxy and polyurethane topcoats				
Mild steel	PANI- EB and PANI- ES (CSA) blended into epoxy binder	open-circuit potential and potentiodynamic polarisation in 0.6 M NaCl or 0.1 M HCl	0.4 ~ 0.6 V /-/ i_{corr} reduce 5 orders	In presence of PANI, a grey protective layer was observed, suggesting PANI enhance in formation of protective interlayer	Talo 1999
Mild steel	PANI- ES (oxalic) was electrodeposited; no topcoat; scratched	Measure Fe^{2+} by spectrophotometry using an o-phenanthroline method	–	After 2 days, disbanding occurred near the scratches; after 1 week, the extent of Fe^{2+} in Fe/PANI solution is half as much as bare Fe metal	Camalet 1998a
AA 2024-T3	As-received Zipperling Corrpasiv 900226/19; PANI- EB; screen-printed	Cu rotating disk electrode (RDE) in 5% NaCl, compare PANI coatings with inhibitors Cr(VI), Ce(III) by current density vs. diffusion layer thickness & observation	–	Galvanic coupling of doped PANI coating to Al substrate provides the energy to release the inhibitor which stops the corrosion within the scribe.	Kendig 2003
AA 2024-T3	Chemical synthesis in HCl $(NH_4)_2S_2O_8$; dedoped EB and redoped ES (CSA) no topcoat	Poteniodynamic polarisation in 3.5% NaCl with O_2 or Ar	E_{corr} & E_{pit} no change/ slightly reduced $i_{corr}(< 8)$	Metal substrate dominates the mixed potential between PANI (CSA) and metal system.	Cogan 2000

The most common mechanism for explaining the effects of PANI film on active-passive metals is anodic protection, which is developed from Deberry's findings in 1985 [Deberry 1985]. This mechanism involves the shifting of corrosion potential of the metal substrate from the active to passive region and thus reinforcing its oxide film. McAndrew proposed the electrochemical reactions responsible for the mechanism of anodic protection of ICPs in his review article, as shown in Equations 2.10 and 2.11 [McAndrew *et al.* 1993]. In particular PANI on steels, these equations can be re-written as shown in Equations 2.12, 2.13 [Wessling 1994].

ICP reduction/metal oxidation:

ICP oxidation by molecular oxygen:

PANI reduction/steel oxidation:

PANI oxidation by molecular oxygen:

Equation 2.12 describes the reduction process of the partially oxidised state EM to LE, which oxidises the steel surface and reinforces the oxide film on the metal. This assumption was further tested by X-ray photoelectron spectroscopy (XPS) and Auger measurements [Camalet *et al.* 1998]. Equation 2.13 shows the fact that the LE is re-oxidised back to EM again by O₂ reduction. The cathodic oxygen reduction on the polymer film replenishes the polymer charge consumed by metal dissolution, thereby stabilising the potential of the exposed metal in the passive regime and minimizing the rate of metal dissolution. The electrochemical reactions can occur reversibly. By this kind of anodic protection, PANI-EM film has also shown tolerance for coating defects such as pinholes, scratches and even incomplete coverage. Gašparac and co-workers [Gašparac and Martin 2001] reported that not all of the metal surface must be coated in order to obtain passivation. In their studies, half of the PANI film was removed, which resulted in a dip in

OCP, but as the EM salt form of PANI held the potential of underlying SS430 in the passive region, the OCP was recovered again.

However, from the definition, the requirement of anodic protection is a constant potential supply [Fontana 1986]. If the potential of a corroding system drops into the activity region instead, a possible bad-effect of anodic protection could be the acceleration of the corrosion rate. As introduced in Table 2.2, many groups have observed that the open-circuit potential (OCP, i.e. E_{corr}) of PANI coated stainless steel have experienced a drop-and-increase process [Ahmad and MacDiarmid 1996; DeBerry 1985]. Kraljić and colleagues [Kraljić *et al.* 2003] suggesting that the timing of the OCP drop-and-increase is dependent upon the rate of reaction in Equations 2.8, 2.9 and the ratio of LE/EM. Therefore, a complication arises from the redox properties of PANI in the corrosion protection mechanism [Dominis *et al.* 2003; Lu *et al.* 1998; Spinks *et al.* 2002]. Further study is needed to achieve a more comprehensive understanding of the anti-corrosion performance of PANI on stainless steel.

Like the corrosion protection behaviours on stainless steel, an anodic protection mechanism has been proposed to explain the anti-corrosion mechanism of PANI on carbon steel. Nevertheless, it is known that carbon steel do not usually passivate in near neutral or acidic environments and the equilibrium potential of carbon steel is also lower than that of stainless steel. There are diversified interpretations to the anti-corrosion mechanism of PANI on carbon steel. Kinlen and co-workers [Kinlen *et al.* 1999] suggested that the potential of the pinholes was shifted positively to the passive regime when they studied the

corrosion protection mechanism of PANI-ES blends on carbon steel in tap water, using the scanning reference electrode (SRET) technique. In addition, they also pointed out that the released dopant species also played an important role, because it was observed that the PANI-ES doped by phosphonic anions exhibited greater corrosion resistance than PANI-ES doped by sulfonic acids. However, since the equilibrium potential and the anti-corrosion properties of carbon steel are lower compared to stainless steel, recent research by Cook and co-workers [Cook *et al.* 2004] revealed that the anodic protection mechanism could not be applied to explain the anti-corrosion mechanism of PANI on mild steel. Alternatively, only polymer's dopant anions, released during the reduction of PANI-ES, protected mild steel from corrosion. Further study is therefore necessary to clarify the corrosion protection mechanism of PANI on mild steel.

There are diverse interpretations of the anti-corrosion mechanism of PANI on aluminium and its alloys, mainly originating from the fact that the equilibrium potential of aluminium and its alloys is much lower than that of stainless steel. Tallman and co-workers [Tallman *et al.* 1998] studied the anti-corrosion properties of PANI-EM salt on AA7075-T6 in dilute Harrison solution (0.35% $(\text{NH}_4)_2\text{SO}_4$, 0.05% NaCl). The OCP of PANI-EM salt-coated AA7075-T6 was found to be shifted to 0.2 V vs. SCE, which suggested PANI may oxidise the metal substrate and ennoble the metals by reducing and de-doping itself. Other studies, however, have shown that PANI coatings offer only barrier function rather than anodic protection [Cogan *et al.* 2000; Kendig *et al.* 2003]. Cogan and co-workers studied the polarisation behaviours of a PANI-EM salt-coated AA2024-T3 in 3.5% NaCl solution

[Cogan *et al.* 2000]. It was found that AA2024-T3 dominated the mixed potential of the PANI/2024-T3 galvanic coupling in polarisation tests and reduced the conducting EM salt form into a non-conducting LE state. Since the prerequisite of the anodic protection mechanism is that the equilibrium potential of EM state PANI is more positive than that of metals [Ahmad and MacDiarmid 1996], the absence of EM state PANI on AA2024-T3 made this mechanism inapplicable. Alternatively, the reduced LE form was believed to prevent O₂ reduction at the cathodic sites of corrosion, thus, the mechanism of PANI anti-corrosion on Al alloys could be attributed to the barrier properties of PANI in LE state rather than the anodic protection from the EM salt form.

2.6 Electrochemical Methods for Electrodeposition of PANI Films

Electrochemical methods in the synthesis of PANI include cyclic voltammetry, potentiostatic and galvanostatic deposition. Among these methods, cyclic voltammetric and potentiostatic electrodeposition are the most widely used techniques.

2.6.1 Potentiostatic Electrodeposition

Potentiostatic electrodeposition is carried out using potentiostatic method, which usually refers to an approach that electrode potential is held constant; the current is monitored as a function of time and the result is presented in chronoamperograms. Potentiostatic method has a feedback circuit that monitors the potential of a working electrode against the

reference electrode [Caro *et al.* 2003]. As shown in Figure 2.19, in order to measure the potential of a working electrode with regards to the reference electrode, the potentiostat employs an electrometer. If the measured potential value of the working electrode deviates from a pre-selected value, a current is applied between the working and counter electrodes. The voltage drop of the working electrode is increased until the measured potential of the working electrode (vs. the reference electrode) returns to the pre-selected value.

Figure 2.19 Schematically illustrated principle of potentiostat (can also serve as principle of cyclic voltammetry) [Source: Ramanarayanan 2003]

Potentiostatic does not only be applied to materials-characterisation, such as studying metallic corrosion behaviour and the electronic performance of semiconductors, but also to the electrochemical synthesis of materials, especially chemical modified electrodes (CMEs). The synthesis of ICPs by electrodeposition has attracted much attention recently. As shown in Table 2.2, some research groups employed potentiostat to deposit PANI on different metals since the electrodeposition parameters of this method are more controllable

compared to other electrochemical methods, for instance cyclic voltammetry. It has been reported that a short-term increase of the applied potential to 0.9 to 1.1 V vs. Ag/AgCl, followed by potentiostatic deposition can produce a better adherent PANI film [Bernard *et al.* 2001].

2.6.2 Cyclic Voltammetric Electrodeposition

Cyclic voltammetry technique is based on varying the applied potential at a working electrode in both forward and reverse directions at a certain scan rate while monitoring the current. As shown in Figure 2.20 (a), a triangular potential $E(t)$ signal is applied to the working electrode and the current response is obtained from an ideal, reversible one-electron redox couple as shown in Figure 2.20 (b). Cyclic voltammetry has many applications as a versatile electroanalytical technique for studying conducting polymers [Rajendra and Munichandraiah 2001], redox produced crystalline inorganic [Runde *et al.* 2002], the electrocatalytic nature of various metallic systems [Caro *et al.* 2003; Ebadi *et al.* 2001], and the photoelectrochemical properties of semi-conducting junctions [Massiani *et al.* 1987]. It is also widely used for the qualitative study of redox processes, for understanding reaction kinetics and intermediates, and for evaluating the stability of reaction products.

Figure 2.20 (a) Triangular $E(t)$ signal of a cyclic voltammetric scan and (b) Cyclic voltammetric current vs. potential for an ideal, reversible one-electron redox couple
[Source: Bocarsly 2002]

Cyclic voltammetry can be used to study more complex reaction mechanisms in which chemical reactions are coupled to charge transfer processes, known as “non-reversible charge-transfer reactions”. This kind of mechanism is also relevant to the polymerisation mechanism of PANI. The simplest EC reactions (i.e. electrochemical step, followed by a chemical step) are as follows:

Equation 2.14

where A and B refer to electroactive species and C refers to non-electroactive reaction products.

When the scan rate is fast, A can be converted to B and B back to A before any appreciable

C is formed. Under this condition, as shown in Figure 2.21 (a), the cyclic voltammetric response appears “reversible”. On the other hand, when the scan rate reduced, the redox couple will spend a longer time in the B state and thus the formation of C will reduce the amount of B. Therefore, at a slow scan rate the ratio of peak i_a/i_c will increase, as shown in Figure 2.21 (b).

Figure 2.21 Schematic cyclic voltammograms for EC reactions ($K_s = 10 \text{ s}^{-1}$) at scan rates of (a) 10 V/s and (b) 1 V/s, current in amperes and potential in voltage [Source: Bocarsly 2002]

As for electrochemical studies on electroactive PANI film, cyclic voltammetry can be used to electrodeposit of PANI, and also to provide qualitative diagnosis of the redox process, stability of the intermediates and kinetics of electrochemical reactions. A typical cyclic voltammogram of PANI in HCl solution is shown in Figure 2.22. Two pairs of distinct peaks illustrate the two redox processes. The first oxidation peak represents the conversion of dimers, oligomers, and polymers between their neutral state and the radical cation (polaron) state, i.e. leucoemeraldine (LE) to emeraldine (EM) state. The second oxidation peak indicates further oxidation to quinoid (bipolaron) state, i.e. pernigraniline (PA) state,

and the reduction peaks indicate the vice versa process. The redox reactions during cyclic voltammetry will also cause the chromatic change of the PANI film. As shown at the lower part of Figure 2.22, the colour of PANI changes from yellow to green, then to violet according to the oxidation level and each state appears different in colour depending on the doping level.

Figure 2.22 Cyclic voltammograms of PANI on a glassy carbon electrode, including the potentials at which structural and colour changes occur, doped by 1 M HCl (pH=0), scan rate 50 mV/s [Source: Wallace *et al.* 2003]

If a PANI film is exposed to potentials greater than the second oxidation potential, the third voltammetric potential peak will appear. The third peak is believed to be associated with polymer degradation and the polymerisation process [Wallace *et al.* 2003], although this interpretation has not been generally accepted. Detailed study of the electrodeposition of

PANI using cyclic voltammetry is therefore necessary to further understand the electrochemical properties of PANI film.

2.7 Electrochemical Methods for Evaluating of Protective Coatings

2.7.1 Conventional Electrochemical Methods

Conventional electrochemical methods for corrosion evaluation can be classified as involving: (i) large perturbations such as Tafel technique; (ii) small perturbations, such as linear polarisation resistance (LPR) and electrochemical impedance spectroscopy (EIS); (iii) no perturbations, such as open-circuit potential (OCP), electrochemical noise analysis (ENA). The Tafel technique belongs to the first class, which involves large perturbations.

In principle, the Tafel technique involves the determination of the intersection point of the major anodic and the major cathodic reaction curves, in order to determine the corrosion current i_{corr} as introduced in mixed-potential in Section 2.1.2 [Tafel 1905]. A larger perturbation voltage is required by the Tafel technique. Practically, the potential-current response of a typical corroding electrode is usually called the potentiodynamic polarisation curve, as shown in Figure 2.23. Within a small region (typically ~ 0.05 V) on either side of E_{corr} , corrosion is under charge transfer control. Hence, the corrosion current is proportional to the exponential of the potential and presented as linear in a semi-logarithmic plot. Extrapolation or curve fitting over this region can be used to determine E_{corr} , i_{corr} and

other kinetic parameters. Since this technique involves larger perturbation voltage that can cause irreversible damage to the electrode surface, it is not recommended for on-line corrosion rate measurement.

Figure 2.23 A Classic Tafel Analysis [Source: Ramanarayanan 2003]

2.7.2 A Novel Technique for Studying Coating Performance — Wire Beam Electrode (WBE)

Conventional electrochemical methods including open-circuit potential, potentiodynamic polarisation, electrochemical impedance spectroscopy (EIS) are all based on a uniform corrosion mechanism, and therefore can only detect mixed or averaged electrochemical parameters over the one-piece of electrode surface. However, corrosion in reality is a heterogeneous process [Fontana 1986]. A relatively new method, i.e. the wire beam electrode (WBE), has been developed in an attempt to overcome the limitations of

conventional electrochemical methods. It is designed to measure electrochemical parameters from a chosen location of the electrode surface.

The WBE divides a one-piece electrode into many small parts. It is most commonly made by binding a large number of metal wires together (usually 100 metal wires). Each wire in the WBE is insulated from its neighbours with a very thin epoxy layer, acting as both a mini-electrode (i.e. mini-sensor) and a corrosion substrate. The array of addressable wires is electrochemically integrated by connecting all wire terminals [Tan 1998; 1999; 2000; Tan *et al.* 2001 a, b, c].

The key ideas of the WBE concept are (i) to simulate a one-piece electrode using an electrochemically integrated electrode array, and (ii) to assume each wire surface is electrochemically uniform even though the whole electrode surface is electrochemically non-uniform [Tan *et al.* 2001 a, b, c]. The assumptions are reasonable because the surface area of each wire is so small compared to the whole electrode, and allows traditional electrochemical theories and techniques may be applied to each individual wire in a WBE [Tan 1998; 1999; 2000; Tan *et al.* 2001 a, b, c]. Based on the concept of WBE, the traditional electrochemical kinetics method (e.g. Butler-Volmer formulations) can be applied to study non-uniform electrochemical processes.

In practice, currents (either galvanic or polarisation currents) in different directions can be easily measured by inserting an ammeter into the WBE system, since all the wire terminals

are connected together, as shown in Figure 2.24 (a). As external voltage is applied, all the currents produced from WBE are polarisation currents, either positive or negative according to the potential above or below the E_{corr} . For corrosive media without external voltage perturbation, each individual wire 'k' behaves either as anode or as cathode and is differentiated by the direction of galvanic currents (i.e. I_g) through the ammeter. Based on the mixed-potential theory, at conditions without external voltage perturbation, the sum of galvanic current approaches zero:

$$\sum_{k=1}^z I_{gk} = 0 \quad \text{Equation 2.15}$$

where $z = 100$ for the WBEs used in this work; k is the number of the wires.

This design also reflects a multi-electrode system, where every wire is polarised by other wires, and an overall system potential (E_{sys}) is achieved. E_{sys} can be measured using a voltammeter via a reference electrode (RE) (see Figure 2.24 (b)) [Tan 1998, 2001 a, b, c].

Figure 2.24 Experimental setup showing measurements of (a) galvanic corrosion currents and (b) corrosion potential of individual wires of the WBE

This design enables the WBE method to map anodic/cathodic polarisation current distribution, galvanic current distribution, potential distribution, and corrosion rate distribution over the WBE surface. Typical contour maps of galvanic current, potential and localised corrosion rates over the WBE surface together with actual corrosion profile are shown in Figure 2.25. On the galvanic current maps (Figure 2.25 (c)), the regions with positive galvanic current densities indicate the anodic sites, while regions with negative values denote cathodic sites. The larger the anodic galvanic current density, the more severe the corrosion is. The WBE in conjunction with the electrochemical noise method has been successfully applied to study several electrochemical processes [Tan 1998; 1999; 2000; Tan *et al.* 2001 a, b, c; Tan *et al.* 2002a].

Figure 2.25 Typical results of WBE measurements; (a) corrosion profile, (b) potential (V), (c) galvanic current (mA/cm^2) and (d) corrosion rate (mm/year) maps [Source: Tan *et al.* 2001b]

In corrosion evaluation of organic coatings, the results of WBE on organic coatings showed good correlation with others' work such as those by Mayne [Mayne 1964] and visual observation. Using the individual resistance of the mini-sensors within a WBE rather than the overall resistance, the WBE technique overcame the problem of poor reproducibility and reliability of conventional electrochemical measurements of corrosion under organic coatings.

The WBE was utilised previously to characterise the uniformity of metallic electrodeposition/electroplating. The conventional methods of controlling the current

distribution of electrodeposition/electroplating are largely performed on trial-and-error bases by adjusting bath parameters. The industrial practices rely upon personnel experience, and sometimes the assistance of the Hull cell test [Hull 1943] and mathematical modelling. However, the Hull cell and mathematical modelling methods suffer from some drawbacks. In previous work, the WBE surface was employed to measure the distribution of metallic electroplating currents for generating a current distribution map over the electroplated surface at any point on the metal surface, as illustrated in Figure 2.26. Based on the current distribution maps measured instantaneously as the reaction proceeds, WBE method provide real time relationships between the characteristics of electroplated metallic coating and electroplating bath parameters, such as bath concentration, temperature and electrolyte flow [Tan and Lim 2003; Tan and Lim 2004]. For example, in Watts' nickel plating bath, the most common pattern observable in electroplating current distribution maps was the 'secondary' current distribution type, a pattern that shows higher currents along the electrode edges with the magnitude decreasing in a contour-like manner towards the centre of the WBE surface. When bath concentration decreased, the electrodeposition current pattern was found to change into the 'primary' current distribution type, a pattern that shows higher currents at locations in proximity to the anode and lower at regions further away. The reproducible results demonstrate that WBE is a new tool for monitoring, characterising, and optimising electroplating and electrodeposition processes, and also for verifying the accuracy and completeness of mathematical modelling of electroplating and electrodeposition [Tan and Lim 2003; Tan and Lim 2004].

Figure 2.26 Electroplating current (mA/cm^2) distribution maps measured in Watts' nickel bath after 30 minutes (a) the thickness profile of nickel deposit at -40 mV for ~ 5 hours, (b) -120 mV, (c) -80 mV and (d) -40 mV cathodic polarisation [Source: Tan and Lim 2004]

In summary, the WBE has been experimentally proven to be a convenient new tool in monitoring localised electrochemical processes and recording patterns, such as localised corrosion. However, the WBE method has not yet been used to study the electrodeposition of intrinsically conducting PANI under anodic polarisation and the corrosion processes beneath PANI films.

CHAPTER 3

Experimental

3.1 Materials

Metals: Stainless steel 304, mild steel (UNS No.G10350) and commercial pure aluminium, AA1100 were utilised in this project. Their compositions are listed in Table 3.1.

Table 3.1 Composition of SS304, mild steel and AA1100

Stainless Steel SS304						
<i>Elements</i>	<i>C</i>	<i>Mn</i>	<i>P</i>	<i>S</i>	<i>Si</i>	
<i>Wt %</i>	<0.03	<2.00	<0.045	<0.03	<1.00	
<i>Elements</i>	<i>Cr</i>	<i>Ni</i>	<i>Mo</i>	<i>Fe</i>		
<i>Wt %</i>	18.00-20.00	8.00-12.00	<0.02	Balance		
Mild Steel (UNS No. G10350)						
<i>Elements</i>	<i>C</i>	<i>Mn</i>	<i>P</i>	<i>S</i>	<i>Fe</i>	
<i>Wt %</i>	0.31 - 0.38	0.6 - 0.9	<0.04	<0.05	Balance	
Aluminium Alloy AA1100						
<i>Elements</i>	<i>Si</i>	<i>Fe</i>	<i>Cu</i>	<i>Mn</i>	<i>Zn</i>	<i>Al</i>
<i>Wt %</i>	<1.0 (Si + Fe)		0.05-0.20	0.05	0.10	Balance

Chemicals: All of the chemicals used in this project are reagents or of a higher grade, as listed in Table 3.2. Except for aniline, which was distilled before use, the other chemicals were used as received. Deionised water was used for the preparation of electrolyte solutions.

Table 3.2 Summary of chemical reagents used in this project

<i>Reagent</i>	<i>Purity</i>	<i>Grade</i>	<i>Company</i>
Aniline	99.5+%	A.C. S. Reagent	Aldrich®
Tetrafluoroboric Acid (HBF ₄)	32%	A.C. S. Reagent	Riedel-deHaën ®
Perchloric Acid (HClO ₄)	70%	A.C. S. Reagent	KANTO CHEMICAL CO.INC
Phosphoric Acid (H ₃ PO ₄)	85%	Analytical Reagent	Asia Pacific Chemical Limited
Ammonium Hydroxide	28 ~ 30%	A.C. S. Reagent	BAKER Analysed ®
Sulfuric Acid (H ₂ SO ₄)	98%	A.C. S. Reagent	BAKER Analysed ®
<i>p</i> - toluenesulfonic acid (tosylic acid)	98.5%	A.C.S. Reagent	Sigma-Aldrich Chemie GmbH, Germany
Oxalic Acid	99%	A.C. S. Reagent	BAKER Analysed ®
Sodium chloride (NaCl)	99.5%	A.C. S reagent	Merck
Nitric acid (HNO ₃)	69 ~ 70%	A.C. S. reagent	BAKER Analysed ®
Poly(Acrylic acid)	M _w ca.2000 (GPC)	A.C. S. reagent	Aldrich®

3.2 Electrode Preparation

One-piece electrode – As shown in Figure 3.1, one-piece electrodes were prepared by cutting each sample of SS304, mild steel and AA1100 into 1.0 cm × 1.0 cm coupons. The coupons were mounted with epoxy and polished up to 1000-grit SiC paper, degreased with ethanol, rinsed with deionised water, and dried in the air.

Figure 3.1 (a) Side view, (b) top view of the one-piece electrode and (c) photograph of the one-piece electrode

Wire Beam Electrode (WBE) – In this project, WBEs were fabricated from 100 identical wires. As shown in Figure 3.2, the 100 wires in a WBE were mounted together in 10×10 array, and insulated from each other by the epoxy resin. The two-component-epoxy resin (the ratio of the resin and hardener is 10:4) used for specimen mounting was provided by Chemicrete Enterprises Pte. Ltd., Singapore. The working surfaces (the area occupied by the wire beam) of SS304, G10350, and AA1100 WBE (in Figure 3.3) were approximately 1.96 cm^2 ($1.40 \times 1.40 \text{ cm}$), 3.24 cm^2 ($1.8 \text{ cm} \times 1.8 \text{ cm}$) and 1.44 cm^2 ($1.2 \times 1.2 \text{ cm}$), respectively. The total metallic areas fabricated from each material were approximately 1.13 cm^2 , 1.77 cm^2 and 1.10 cm^2 , respectively. Before each experiment, the WBE specimen was polished using 180, 320, 600, and 1000-grit SiC paper, degreased with ethanol, rinsed with deionised water, and dried in the air.

Figure 3.2 Schematic of the design of WBE

Figure 3.3 Photographs of the (a) SS304 (b) mild steel and (c) AA1100 WBE surfaces

3.3 Electrodeposition of PANI on One-Piece Electrodes and WBEs

3.3.1 Electrodeposition of PANI on One-Piece Electrodes

The electrodeposition of PANI on one-piece electrodes was performed with a

three-electrode electrochemical cell (as shown in Figure 3.4) with a saturated calomel electrode (SCE) as the reference electrode, and a high purity graphite rod as the auxiliary electrode. The working electrodes were SS304, mild steel G10350 and AA1100. All of the reported potential values were *vs.* SCE reference electrode. A PANI film was electrodeposited using cyclic sweep (i.e. a type of potentiodynamic method) and potentiostat methods with a GillAC device (AutoAC, ACM Instruments, UK).

Figure 3.4 Schematic diagram of experimental setup for the electrode position, including cyclic voltammetry and potentiostatic methods on SS304, G10530 and AA1100 electrodes

On SS304, the electrolyte used for the electrodeposition of PANI was 0.75 M H_2SO_4 solution containing 0.1 M aniline. In cyclic voltammetry, the potential was started from corrosion potential (E_{corr}) in a particular electrolyte to a more positive direction (the potential range will be specified in Chapter 4). In order to obtain PANI in a partially oxidised EM state, the deposition process was terminated at the most positive potential. In the potentiostatic deposition method, after initiating the electropolymerisation reaction by

potentiodynamic sweep (20 mV/s) for half a cycle from 0 to 0.85 V *vs.* SCE, the potential was fixed at lower potentials in order to reduce the damage to the metal substrate during electrodeposition. In order to study the corrosion behaviour of an incompletely covered PANI film, a small part of the electrode was intentionally covered by scotch tape before the electrodeposition, so that this small area ($\sim 1.5 \times 10^{-2} \text{ cm}^2$) was free of PANI deposition.

The electrolyte used for the electrodeposition of PANI on the mild steel G10530 was a 0.3 M oxalic acid solution containing 0.1 M aniline. The sweep rate of cyclic voltammetry applied on mild steel is 20 mV/s, which is same as what used on SS304. The difference from the deposition on SS304 is that before the electrodeposition of PANI, the mild steel electrode was passivated in oxalic acid using the potentiodynamic method for one cycle from -0.54 ~ 1.8 V at a sweep rate of 50 mV/s, with the purpose of protecting mild steel substrate from dissolution during electrodeposition of PANI. In the potentiostatic method, metal substrate was also pre-treated before the PANI deposition. Then, the voltage was fixed at 0.75, 0.85 and 0.95 V, and the time of electrodeposition was around 60 minutes. Similar to what had been carried out on SS304, a small part of mild steel electrode was intentionally covered by scotch tape before the electrodeposition so that this small area ($\sim 1.5 \times 10^{-2} \text{ cm}^2$) was free of PANI deposition. The electrolyte used for the electrodeposition of PANI on AA1100 was 1 M tosylic acid solution containing 0.16 M aniline. Before electrodeposition, cathodic pre-treatment was carried out at around -0.9 V *vs.* SCE in the same electrolyte as the electrodeposition. The cyclic voltammetry was performed at a potential range of -0.2 - 1.2 V subsequently. The sweep rate of cyclic voltammetry applied

on AA1100 is 20 mV/s, which is same as what used on SS304 and mild steel. PANI was also electrodeposited using the potentiostatic method at 1.25 V for around 30 minutes after the cathodic pre-treatment introduced above.

3.3.2 Electrodeposition of PANI on WBEs

The WBE system used in this project mainly consisted of an AutoSwitch v2 (custom made), a computer, and a measurement instrument — AutoAC, namely GillAC (ACM instruments, England), as shown in Figure 3.5.

AutoSwitch –A computer controlled automatic switch (custom made) is used to connect the measurement instrument (AutoAC) to all the wires of the WBE.

GillAC – This can function as a potentiostat to provide current for both cyclic voltammetry and the potentiostatic method for PANI deposition.

Figure 3.5 Photograph of experimental setup for PANI electrodeposition on WBE

Electrodeposition was carried out on WBEs following the same method as for corresponding one-piece electrodes. Figure 3.6 shows the experimental setup for PANI

electrodeposition on WBE, which incorporates a three-electrode electrochemical cell with WBE as the working electrode and a platinum sheet (1.50×1.50 cm) as the AE. The AE was placed facing towards the working surface of the WBEs in order to ensure the uniformity of the applied current. The anodic electrodeposition of PANI on WBE was realised by connecting all the wire terminals of the WBE through an auto-switch device to the WBE terminal of a GillAC device functioning as a potentiostat. During the electrodeposition, the impressed anodic polarisation current for each wire was measured by connecting another GillAC device, which performed as a zero resistance ammeter (Auto ZRA), in sequence between a chosen wire terminal and all the other terminals shorted together using the computer controlled auto-switch device. This was repeated for all 100 wires over a short period (50 Hz with 2 seconds for each wire), so that an electrodeposition current, distribution data set could be generated. The raw data was then compiled with the Mathcad software (Mathcad Professional 7, MathSoft, Inc., Massachusetts, USA), from which a map representative of the current distribution over the WBE surface was obtained.

Figure 3.6 Schematic diagram of experimental setup for PANI electrodeposition on WBE

3.4 Corrosion Testing Using Potentiodynamic Polarisation and Open-Circuit Potential

Potentiodynamic polarisation techniques were also used to study the corrosion prevention of PANI coated electrodes. The setup of the polarisation experiment is schematically illustrated in Figure 3.7. It consists of a computer, an AutoAC, a salt bridge, an auxiliary electrode, a reference electrode (SCE), an electrochemical cell, and a single piece electrode. The procedure of potentiodynamic polarisation was generally in accordance with the standard ASTM Designation G61.

Figure 3.7 Schematic diagram of the experimental setup for potentiodynamic polarisation experiments on electrodes including PANI coated SS304, MS G10530 and AA1100

Before initiating polarisation, the specimen was immersed in the electrolyte for about 0.25 hour. The potential scan began at the E_{corr} and scanned in the more noble direction at a rate of 10 mV/min (or 0.2 mV/s). The onset of localised corrosion was usually marked by a sharp increase in the anodic current at potentials below the oxygen-evolution potential. In addition, the open-circuit potential (OCP) of PANI coated one-piece electrodes was measured to record the E_{corr} variation as a function of time in 0.5 M NaCl solution. These experiments were always carried out at air-conditioned temperature ($\sim 22^\circ\text{C}$).

3.5 Corrosion Testing Using the Wire Beam Electrode

The experimental setup for the corrosion evolution of PANI coated wire beam electrodes (WBEs) mainly consisted of an AutoSwitch v2 (custom made), a computer, and a measurement instrument — AutoAC, namely GillAC (ACM instruments, England), as

shown in Figure 3.8.

Figure 3.8 Photograph of experimental setup for corrosion testing in 0.5M NaCl solution (pH ~ 5.8) of PANI coated WBE

AutoSwitch –A computer controlled automatic switch is used to connect the measurement instrument (AutoAC) with one or more chosen wires.

GillAC – This can function as a voltameter to record the corrosion potential of each wire, as shown in Figure 3.9 (a). It can also as an auto zero resistance ammeter to measure the current flowing between each wire and the rest of the wires in the whole wire bundle, as shown in Figure 3.9 (b).

AutoAC enables current and voltage to be measured accurately and to be recorded automatically from a WBE surface through pre-programmed systematic measurements. The corrosion potential distribution is obtained by sequentially measuring the open-circuit potential of each wire against the reference electrode (SCE) using the AutoAC and AutoSwitch. The galvanic currents flowing between each individual wire and the wire beam system are measured by sequentially inserting the AutoAC between a chosen wire terminal and all other terminals, shorted together using the AutoSwitch. Current or

potential values measured from each wire of WBE (I_k and E_k , $k = 1 - 100$) are plotted using the professional software MathCAD 2000, to produce a WBE galvanic current distribution or a WBE potential distribution map.

Figure 3.9 Schematic illustrations of the measurement of potential and galvanic current of each wire of a WBE specimen

The corrosion evaluation test on PANI deposited SS304, G10530, and AA1100 WBEs was performed in aerated 0.5 M NaCl solution under a free corrosion condition. Without pre-exposure time, the OCP of PANI coated WBE was measured by a GillAC device which performed as an automatic voltmeter (Auto-Voltmeter). All the terminals of WBE were connected and the corrosion potential was measured. Since the wire terminals were connected together during the corrosion evaluation, as shown in Figure 3.10, galvanic currents flowed between wires of the WBE in different directions. This reflects a

multi-electrode system, where every wire is polarised by other wires. The directions of galvanic currents ($I_{g1}, I_{g2} \dots I_{gk}$) indicate how a wire behaves; some of the wires in a WBE behave as anodes and others behave as cathodes, and

$$\sum_{K=1}^z I_{gk} = 0 \quad \text{Equation 3.1}$$

where $z = 100$ for the WBEs used in this work; k is the number of the wires.

Figure 3.10 Schematic diagram illustrating the experimental setup for the corrosion evaluation of PANI deposited WBE in 0.5 M NaCl solution

In the experiment, the galvanic current of each wire (e.g. I_{gk} for wire k) was measured by sequentially inserting the Gill AC functioning as AutoZRA between a chosen individual wire terminal and all other terminals, shorted together using the computer controlled automatic switch. Due to the fast data collection rate (2 second intervals at each wire) and

the Gill AC enabling current from 325 mA to 10 pA being measured accurately, the current distribution map can reflect the actual galvanic activity without interfering with the corrosion process. These experiments were always carried out in air-conditioned temperature ($\sim 22^\circ\text{C}$).

Experimentally obtained raw data was transferred to software written under Mathcad software to generate galvanic current distribution maps. In addition, the software will generate a data table including the galvanic current density of each wire as shown in Table 3.3. Based on this data table, the total anodic current density (i_{tot}) can be obtained from the sum of the total positive current in the table. Since the i_{max} indicates the largest anodic current from a single wire in this table, it suggests the intensity of localised corrosion. On the contrary, the i_{tot} suggests the anodic current from all types of corrosion including both localised and general corrosion. By comparing the i_{max} and i_{tot} , the type and extent of the corrosion over the WBE surface can be qualitatively determined.

Table 3.3: Values of the anode and cathode taken from WBE galvanic mapping. Positive values represent anodes and negative values represent cathodes

	Coulmn 1	Coulmn 2	Coulmn 3	Coulmn 4	Coulmn 5	Coulmn 6	Coulmn 7	Coulmn 8	Coulmn 9	Coulmn 10
Row 1	-2.67E-3	-0.03	-5.747E-3	-1.755E-3	-2.347E-3	-1.835E-3	-7.503E-3	-4.075E-3	-2.523E-3	0.054
Row 2	-1.834E-3	0.012	-6.429E-3	-2.224E-3	-2.042E-3	-1.873E-3	-1.63E-3	4.419E-3	-0.03	0.046
Row 3	-2.308E-3	-1.615E-3	-1.503E-3	-1.47E-3	-1.33E-3	-1.502E-3	7.29E-04	-0.034	-1.997E-3	-1.859E-3
Row 4	-1.499E-3	-1.512E-3	-1.446E-3	-4.409E-3	-1.381E-3	-1.394E-3	-1.52E-3	-0.028	-1.758E-3	-1.463E-3
Row 5	-1.347E-3	-1.373E-3	-1.385E-3	-1.364E-3	-1.67E-3	-0.015	-0.048	-1.373E-3	-1.568E-3	0.026
Row 6	-2.073E-3	-1.609E-3	-3.641E-3	-1.413E-3	-2.784E-3	-1.649E-3	-2.580E-3	-3.825E-3	-1.520E-3	-3.282E-3
Row 7	-1.876E-3	-1.264E-3	-1.285E-3	-0.012	-1.34E-3	-2.023E-3	-1.473E-3	-1.758E-3	-3.006E-3	-1.559E-3
Row 8	-1.558E-03	-1.431E-3	-3.641E-3	1.323E-3	-3.551E-3	0.029	-2.267E-3	-1.984E-3	3.184E-6	-3.159E-3
Row 9	1.481E-03	-2.111E-3	-3.292E-3	-0.017	-3.15E-3	-1.763E-3	-3.638E-3	1.514E-3	-5.419E-3	0.038
Row 10	0.038	0.038	0.054	-1.923E-3	-1.648E-3	-0.024	-1.554E-6	0.027	0.034	-1.974E-3

i_{max}

3.6 Microscopic and Surface Analysis

A Fourier transformed infrared (FTIR) spectrum was recorded on a FTIR spectrometer (Perkin-Elmer FTIR spectrum GX) to identify the chemical structure of the electrodeposited PANI film. The resolution of the spectrometer is 0.01 cm^{-1} and the wavelength range is $400 - 4000\text{ cm}^{-1}$. The KBr method was used to prepare FTIR samples.

The thickness of the electrodeposited PANI films was measured by surface profiler (Alpha-step 500, Tencor). The average thickness of a neat deposited PANI on the SS304, mild steel and AA1100 electrodes was determined over a length of $2000\text{ }\mu\text{m}$ at a speed of $200\text{ }\mu\text{m/s}$. Since the electrodeposition conditions of PANI on WBEs are exactly the same as on the one-piece electrode, the thickness of PANI is correspondingly similar.

After each experiment, the specimen surface was analysed by visual and microscopic examination. The visual observation images were mainly recorded using a digital camera, i.e. Canon PowerShot A95, and other models of optical microscopes, i.e. Nikon Epiphot 2000 (magnification from $0.63\times$ to $4\times$). Surface observation was further carried out using a scanning electron microscope (SEM, JEOL JSM 5310, Japan) and field emission scanning electron microscope (FESEM JEOL JSM 6340F, Japan) to examine the morphology of the electrodeposited PANI film.

3.7 Salt Spray (Fog) Testing

Salt spray (fog) testing according to ASTM G85-02^{e1} was performed to evaluate the anti-corrosion performance of electrodeposited PANI as a primer on mild steel with the cooperation of acrylic (R.J London Chemicals) and anti-rust oil (Hobbycraft E88, USA) as top coats. For salt spray exposure, the ASCOTT Model S120t salt spray cabinet was used, as shown in Figure 3.11. The salt fog environment is fixed at 50 ± 5 g/l NaCl at a temperature of 35 ± 2 °C. The air pressure was 15 ± 1 ksi, and the flow rate was 15 ± 1 ml/min.

Figure 3.11 Salt spray test machine

With additional top coats, average thickness of the coating system on mild steel for salt spray testing was around $42 \sim 45$ μm by surface profiler (Alpha-step 500, Tencor). For example, the thickness of PANI/anti-corrosion oil coating system was determined at the positions indicated in Figure 3.12 (a) over a length of 5000 μm at a speed of 200 $\mu\text{m/s}$. An average thickness around 42.8 μm was obtained after scanning for 60 cycles as shown in

Figure 3.12 (b) and (c).

Figure 3.12 (a) Photograph illustrating the positions of thickness measurement, (b) and (c) data obtained from the thickness measurement by the surface profiler

3.8 Experimental Procedures

Studies of the electrochemical properties of a PANI film on different metals during electrodeposition and corrosion testing were conducted on both one-piece electrodes and WBEs. With the purpose of understanding the effect of metal substrate on the PANI film, experiments on the one-piece electrode and WBEs were carried out following almost the same procedure for SS304, G10530, and AA1100, as illustrated in Figure 3.13. Each issue has been studied using at least two kinds of methods. When interesting phenomena as well as unsolved problems were observed on the one-piece electrode, the WBE was employed to further study the electrodeposition and anti-corrosion performance of PANI on metal

substrates. At the same time, the conclusion or assumptions made from the WBE were verified on the one-piece electrode in order to improve the performance of PANI film on metals.

Note: **a**, Cyclic sweep; **b**, Potentiostatic; **c**, Scanning Electron Microscope; **d**, Fourier Transform Infrared; **e**, Potentiodynamic polarisation; **f**, Salt spray testing, specific on PANI with top coats on mild steel; **g**, Open-circuit potential.

Figure 3.13 Routes presenting the experimental procedures on one-piece electrodes and WBEs involving different materials (SS304, MS G10530, AA1100)

CHAPTER 4

Results and Discussion I: Electrodeposition of Polyaniline (PANI) on Stainless Steel 304 (SS304)

As described in Section 2.2, stainless steel has excellent resistance to many corrosive environments due to the formation of a passive layer. However, the passive film is subjected to localised breakdown under the attack of halogen ions, resulting in rapid pitting corrosion. It is important to improve the resistance of stainless steel to localised corrosion. The possibility of using electrodeposited PANI to prevent localised corrosion of SS304 in halogen ions containing media is investigated in this work.

4.1 Electrodeposition of PANI on SS304 Using Cyclic Voltammetry in Various Electrolytes

The first series of experiments were carried out to study the influence of electrolytes on the electrodeposition of PANI. Since the anions in electrolyte participate in the protonation process of dimmer, oligomer and polymer to maintain electroneutrality [Wallace *et al.* 2003; Aykanat and Iroh 2002], they could affect PANI electrodeposition and the anti-corrosion performance of PANI coating. The electrodeposition of PANI was first carried out in H₂SO₄ electrolyte using cyclic voltammetry (CV), a widely used electrochemical method that has been reviewed in Section 2.6.2, in order to understand the

basic mechanism of the polymer growth and redox reactions.

Figure 4.1 shows the first cycle of CV on SS304 one-piece electrode in 0.75 M H_2SO_4 , both with and without the presence of aniline. When aniline is added to electrolyte, as shown in Figure 4.1, a small peak **A'** at approximately 0.4 V was detectable during the reverse scan. This peak should be attributed to the reduction from the polaron state to the neutral state as a result of the radical cation polymerisation mechanism of PANI [Shim *et al.* 1990], i.e. presence of this current peak indicates the deposition of PANI. Within the potential range of 0.0 - 1.1 V, the current remained at a rather small value, suggesting only a small amount of PANI was deposited and low dissolution rate of metal. Large increase in current at the noble end of the potential range were attributed to the transpassivation behaviour of stainless steel in the acidic electrolyte [Fontana 1986].

Figure 4.1 Comparison of cyclic voltammograms on one-piece SS304 electrode in 0.75 M H_2SO_4 with and without 0.1 M aniline monomer

Figure 4.2 shows cyclic voltammograms obtained during the following 8.5 cycles of the CV. With the increase in CV scan cycle numbers PANI deposition current increased steadily, as shown in Figure 4.2.

Figure 4.2 Cyclic voltammogram of the 2nd to 9.5th cycles during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H₂SO₄ solution with 0.1 M aniline

Electrochemical reactions associated with the peaks shown in Figure 4.2 can be identified by directly comparing these reaction peaks with those for dimmers, oligomers and polymers, which were obtained from inert electrodes as presented in Figure 2.22 [Wallace *et al.* 2003]. Peaks **A/A'** at approximately 0.21/0.11 V were due to the conversion of dimmers, oligomers, and polymers between their neutral state and the radical cation (polaron) state i.e. leucoemeraldine (LE) state to emeraldine (EM) state [Wallace *et al.* 2003]. Peak **B** at approximately 0.7 V was due to the second oxidation reaction, indicating the further oxidation to quinoid (bipolaron) states i.e. pernigraniline (PA) state. The

reduction peak **B'** indicates the process and vice versa. The peaks **C/C'** at approximately 0.5/0.4 V were closely related to the redox reactions of some degradation products, such as p-aminophenol/p-benzoquinone and/or p-benzoquinone/hydroquinone redox pairs as shown in Equations 4.1 and 4.2.

The appearance of peaks **C/C'** can be eliminated by reducing the scan potential range. As shown in Figure 4.3, when the potential range was decreased from 0.0 - 1.1 V to -0.1 - 0.8 V, the middle voltammetric response peaks **C/C'** could not be observed. More precisely, the current from the electroactive degradation products was overlapped by the current of PANI propagation. Thus, controlling the scan potential range properly was a method to avoid PANI degradation. The characteristic potentials, either **A/A'** or **B/B'**, were found to be similar under the two conditions. It was also noted that the current values for peaks **A/A'** were quite comparable for two kinds of scan ranges, indicating a similar PANI growth rate in spite of the reduced potential range for the latter case. It is probable that the potential range of -0.1 - 0.8 V is favourable for the formation of PANI with better uniformity. For the purpose of minimising PANI degradation, this potential range was used in subsequent experiments.

Figure 4.3 Cyclic voltammogram of 9.5 cycles during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H_2SO_4 solution with 0.1 M aniline

The second series of PANI electrodeposition experiments were carried out in oxalic acid based electrolytes. Oxalic acid was selected on the assumption that it will reduce polymer degradation and accelerate PANI deposition simultaneously. Oxalic acid is also extensively used for the passivation of steel [Iroh et al 2003]. In order to initiate the polymerisation of PANI at a higher rate, anodic polarisation to a more positive potential of 1.8 V was conducted prior to the PANI electrodeposition in the same solution (see Figure 4.4 (a)). As shown in Figure 4.4 (b), the electrochemical behaviours of PANI in oxalic acid were similar to those in H_2SO_4 electrolyte with three pairs of redox peaks at similar characteristic potentials. Figure 4.4 (b) also shows that both the PANI growth and degradation rates decreased in oxalic acid, as indicated by the measured current scale. The middle current peaks $\text{C/C}'$ mainly from the degradation products were still observable, even though the actual current values were much smaller than those obtained in H_2SO_4 .

(a)

(b)

Figure 4.4 (a) Potentiodynamic polarisation of SS304 and (b) voltammogram of 9.5 cycles during the electrodeposition of PANI on one-piece SS304 electrode in 0.3 M oxalic acid with 0.1 M aniline

The third series of PANI electrodeposition experiments were performed in *p*-toluenesulfonic (tosylic) acid based electrolytes. The main reason for selecting it as an electrolyte is its catalytic properties in the formation of polymers [Camalet *et al.* 1998b]. In addition, tosylic acid is also known for its self-doping effect on PANI films [Deore *et al.*

2004]. As shown in Figure 4.5, two pairs of redox peaks appear in the CV diagram from tosylic acid. After checking the characteristic potentials carefully, it was found that the reduction peak, at approximately 0.4 V, was actually due to the reduction of degradation products instead of reduction from the PA (bipolaron) state. Hence, two current peaks, i.e. peak **C** and **B'** were indistinguishable in the CV diagram. More importantly, the absence of the middle peak **C** indicated that the oxidation from the degradation products was less significant when compared to the oxidation in the formation of PANI. The deposition current in tosylic acid was at least two times higher compared to the other two acids, probably due to its high acidity and catalytic property. In addition, the potentials of all the redox peaks shifted forward according to the direction of the potential scan. This phenomenon may be associated with the benzene ring in tosylic acid, which retards the electrochemical reaction, but facilitates the formation of H-bonds [Aykanat and Iroh 2002].

Figure 4.5 Cyclic voltammogram of 9.5 cycles during the electrodeposition of PANI on one-piece SS304 electrode in 1.0 M tosylic acid with 0.17 M aniline

Based on the comparison between the CV diagrams of H_2SO_4 , oxalic and tosylic acid, it seems that tosylic acid is a more suitable electrolyte for the electrodeposition of PANI, because the growth rate of PANI film is higher with a relatively smaller proportion of degradation. The growth rate in oxalic acid is the lowest. However, from the practical application point of view, H_2SO_4 is still an attractive candidate to deposit PANI as a primer for the purpose of anti-corrosion because of its cheap price, minimised polymer degradation, as well as the acceptable PANI growth rate under carefully controlled experimental conditions.

4.2 Electrodeposition of PANI Using Potentiostatic (PS) Method

In order to minimise the polymer degradation during PANI polymerisation because of the higher initiation potential, and obtain PANI film with satisfying properties, potentiostatic (PS) method was considered for the deposition of PANI. An additional purpose is to identify a more suitable approach for effective deposition of PANI. An anodic scan from -0.1 to 0.85 V with the scan rate of 20 mV/s prior to the PS method was applied in order to initiate the radical cation reaction of aniline. Low potentials at 0.60 V, 0.70 V, 0.75 V and 0.80 V of the PS method were adopted to avoid the degradation of the PANI formed. At the potential of 0.60 V, as shown in Figure 4.6, there was no indication of PANI electrodeposition by visual inspection and the anodic current was also as low as 0.0035 mA/cm^2 , confirming that no electroactive species were deposited on the electrode at this potential.

Figure 4.6 Chronoamperogram during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H₂SO₄ with 0.1 M aniline

When the PS deposition potential was increased to 0.7 V and above, as shown in Figure 4.7, PANI was electrodeposited successfully on the SS304 electrode. Due to the radical polymerisation mechanism, the current densities at potentials of 0.70, 0.75, and 0.80 V increased exponentially with time after the very short initial reduction. There was a clear increment in the deposition current as the applied potentials increased from 0.70 to 0.80 V. For all three PS potentials, deposition currents stabilised as the deposition rate approached saturation point at which a balance was reached among the radical cation initiation, the polymer degradation, and the reactant diffusion. It took more than 30 minutes for the current stabilisation to happen at the potential of 0.70 V, in contrast to less than 20 minutes and 10 minutes at 0.75 and 0.80 V, respectively. Considering the possibility that a potential of 0.85 V could cause a higher degree of polymer degradation and a potential of 0.70 V resulted in fewer PANI deposits, potentiostatic deposition at 0.75 V was adopted for PANI

electrodeposition in this work. The thickness of electrodeposited PANI film at the potential of 0.75 V was approximately 30 μm measured by the surface profiler and was suitable thickness for the anti-corrosion study.

Figure 4.7 Chronoamperogram during the electrodeposition of PANI on one-piece SS304 electrode in 0.75 M H_2SO_4 with 0.1 M aniline at various potentials

4.3 Characterisations of Electrodeposited PANI on SS304

A field emission scanning electron microscope (FESEM) and a Fourier transformed infrared (FTIR) spectroscopy were employed to characterise the electrodeposited PANI film. As shown in Figure 4.8 (a), the electrodeposited PANI at a fixed potential of 0.75 V has a granular structure. Additionally, the electrodeposited PANI film was not uniform, consisting of clusters of deposits and micropores. Thus, the porous PANI film allowed corrosive electrolytes to penetrate into the metal substrate. Figure 4.8 (b) presents PANI film obtained by cyclic voltammetry at a potential range of -0.1 - 0.8 V in 0.75 M H_2SO_4

with 0.1 M aniline (see Figure 4.3). It can be seen that the deposited PANI films using the CV method also have a granular structure, indicating that the morphologies of deposited PANI films from the two methods were similar. The only distinct difference between Figures 4.8 (a) and (b) is that elongated particles appeared on the top of the granular structure when PANI was deposited by cyclic voltammetry, suggesting a higher growth rate. Usually, the PANI film electrodeposited using cyclic voltammetry possesses a better quality than that produced from the potentiostatic approach [Wallace *et al.* 2003]. However, by controlling the deposition potential properly, the deposited PANI film using the potentiostatic method can also possess a similar morphology to the one deposited using cyclic voltammetry.

Figure 4.8 Micrographs of electrodeposited PANI film on one-piece SS304 using (a) cyclic voltammetry and (b) potentiostatic methods in 0.75 M H_2SO_4 with 0.1 M aniline

As shown in Figure 4.9, the peaks of the FRIT spectrum at around 1493 cm^{-1} , 1572 cm^{-1} could be due to C=C and C-C stretching modes for the benzenoid (B) and quinoid (Q) rings, respectively. The almost equal intensities of these two peaks suggest that the deposited

PANI could be in a conjugated EM state, in contrast to a very low intensity ratio of the $1600\text{ cm}^{-1}/1500\text{ cm}^{-1}$ peaks exhibited by the LM state [Neoh *et al.* 1993; Kang *et al.* 1998]. Another informative peak at 1135 cm^{-1} was assigned to the electronic-like absorption of the $\text{N}=\text{Q}=\text{N}$ structure by MacDiarmid and co-workers, indicating that the electrodeposited PANI film could be EM salt [MacDiarmid *et al.* 1986]. The peak at 1326 cm^{-1} in the FTIR spectrum can be attributed to the C-N stretching absorption in QBQ, QBB or BBQ units, and LM does not have this characteristic absorption peak at this frequency, while EM does [Lu *et al.* 2002]. Based on these observations, we could draw the conclusion that the electrodeposited PANI is in the EM state. The other peaks at about the 504, 800, 2932, and 3214 cm^{-1} frequencies were assigned to the N-H out-of plane bending, C-H bending, C-H stretching and N-H stretching of aromatic amine, respectively [Kang *et al.* 1998].

4.4 Corrosion Evaluation of Electrodeposited PANI Film

4.4.1 Potentiodynamic Polarisation Measurement

The PANI coated SS304 one-piece electrode was tested using potentiodynamic polarisation (sweep rate of 10 mV/min) after being immersing in an aerated 0.5 M NaCl solution for about 15 minutes. The bare SS304 electrode was also tested under the same conditions for comparison. As shown in Figure 4.10, the corrosion potential (E_{corr}) and pitting potential (E_{pit}) of PANI deposited SS304 shifted to the noble direction by about 0.145 V (from 0.045 to 0.19 V) and 0.18 V (from 0.28 to 0.46 V), respectively. In addition, the corrosion current (i_{corr}) decreased almost 10 times (from 0.001 to 0.0001 mA/cm²) compared to the bare metal. The results suggest that the electrodeposited PANI film provides significant corrosion protection to the stainless steel, which were in good agreement with findings by other researchers [Hermas *et al.* 2005; DeBerry 1985]. As discussed in the previous section, a PANI film has a porous structure as observed by SEM. Thus, the high permeability of PANI suggests that PANI cannot function as a barrier film. It is worthwhile to note that the cathodic polarisation current of PANI coated SS304 was much larger than that of bare metal, indicating that the PANI film could facilitate the cathodic reaction i.e. oxygen reduction in this circumstance.

Figure 4.10 Comparison of potentiodynamic polarisation of PANI coated SS304 and bare SS304 electrodes in an aerated 0.5 M NaCl solution ($\text{pH} \approx 5.8$)

4.4.2 Open-Circuit Potential Measurement

Open-circuit potential (OCP) measurement was also carried out to investigate how the corrosion potential (E_{corr}) of PANI coated electrode changes in the presence of chloride ions. In order to study the corrosion performance under non-uniformly coated PANI film, an electrode incompletely coated with PANI film was prepared by intentionally covering a small part of the electrode surface with scotch tape before the electrodeposition, so that this small area was free of PANI deposition. The photographs in Figure 4.11 show electrodes with complete and incomplete PANI coverage before the OCP testing. The OCPs of SS304 electrodes with complete and also incomplete PANI coverage were measured in 0.5 M NaCl solution for one week using the method described in Section 3.3. As shown in Figure 4.12, the OCPs from both complete and incomplete PANI coated SS304 electrodes presented drop-and-increase cycles. The OCPs cycled within a potential range between

-0.015 and 0.12 V, which primarily locates them within the passive region of SS304 [Ahmad and MacDiarmid 1996]. It was further confirmed that the electrodeposited PANI in the EM state shifted the mixed potential of the metal-PANI system towards positive direction.

Figure 4.11 Photographs of (a) a complete PANI coated and (b) an incomplete PANI coated SS304 electrode before OCP testing

These results are in agreement with reports by other researchers [Ahmad and MacDiarmid 1996; DeBerry 1985; Gašparac and Martin 2002a]. Similar OCP drop-and-increase behaviours have also been found by other researchers for PANI coated steel, either chemically or electrochemically synthesised, in various solutions, such as NaCl + H₂SO₄ [DeBerry 1985], H₂SO₄ [Gašparac and Martin 2002a], H₃PO₄ [Kraljic *et al.* 2002] and HCl [Kraljic *et al.* 2002]. The explanation of this phenomenon was that the electrons released from the localised corrosion induced the conversion from PANI-EM to LE, which resulted in a sudden decrease of the mixed potential of the whole polymer-metal system. This was followed by the oxidation by oxygen reproduced PANI-EM and led to a rise of the OCP. However, the galvanic activities at the metal-PANI interface during the variation of OCP have not yet been fully understood, probably due to the difficulties encountered by conventional electrochemical apparatus in investigating the electrochemical processes under the coverage of organic coatings.

Figure 4.13 shows both the completely and incompletely coated PANI electrode surfaces after one week of corrosion testing in a 0.5 M NaCl solution. It can be seen in Figure 4.13 (a) that the corrosion products on the completely coated PANI SS304 were mainly located at the edge of the sample, indicating the heterogeneity of the corrosion on PANI coated SS304. Interestingly, the exposed metal surface in Figure 4.13 (b) did not show any corrosion products on visual inspection. Instead, it was the PANI film around the exposed metal that showed brown corrosion products. This phenomenon, i.e. the uncovered metal area which was visually free of corrosion products, is reproducible. If the testing time is

sufficiently long, both the coated and the exposed metal will be corroded eventually.

Figure 4.13 Photographs of the corroded SS304 electrodes with (a) a complete PANI coverage and (b) an incomplete PANI coverage after being exposed in 0.5 M NaCl solution for one week

4.5 Studying PANI Electrodeposition and Anti-Corrosion on SS304 Using the WBE

The SS304 WBE was introduced to monitor how the heterogeneity of the electrodeposited PANI film influences its anti-corrosion performance and mechanism for complete and incomplete PANI coverage using the experimental setup illustrated in Figure 3.10, under exactly the same conditions as for the one-piece electrodes.

4.5.1 Anodic Polarisation Current Mapping over the SS304 WBE

At the fixed potential of 0.75 V, the chronoamperogram from the SS304 WBE, displayed in Figure 4.14, was similar to that observed with the one-piece electrode (see Figure 4.7). The dotted lines indicate the time of the measurement of anodic polarisation current (APC)

distribution maps during PANI deposition.

Figure 4. 14 Chronoamperogram during the electrodeposition of PANI at 0.75 V on SS304 WBE in 0.75 M H_2SO_4 with 0.1 M aniline

After about 40 minutes of electrodeposition, a dark-green colored PANI film was coated on the SS304 WBE surface, as shown in Figure 4.15 (a). Figures 4.15 (b)-(d) illustrate the APC maps measured at 20, 30, and 40 minutes of deposition (as indicated by the dotted line in Figure 4.14), respectively. Under the anodic deposition conditions, all of the currents were positive. It was observed that the APC distributed non-uniformly over the WBE surface. The first APC map (see Figure 4.15 (b)) had no clear similarity to the following maps because the deposition current had not yet reached saturation at 20 minutes of electrodeposition, as indicated in Figure 4.14. Once the deposition was stabilised after 25 minutes, as shown in both Figure 4.15 (c) and (d), the non-uniformly distributed current pattern began to show a certain consistence, where the higher currents were concentrated in

the centre of the WBE surface. The highest anodic current was found to be around 10.1-11.5 mA/cm². The non-uniform current distribution in Figures 4.15 (c) and (d) reflected a non-uniform PANI deposition on SS304 in a H₂SO₄ based electrolyte, which is difficult to monitor on a conventional one-piece electrode.

Figure 4.15 (a) Photograph of a PANI coated SS304 WBE; (b)-(d) corresponding APC maps (mA/cm²) measured at 20, 30 and 40 minutes, respectively

4.5.2 Galvanic Current Mapping over SS304 WBE

The PANI coated WBE was then immersed in a 0.5 M NaCl solution for corrosion testing, and galvanic current (GC) distributions were measured using an experimental setup shown

in Figure 3.10 and the procedure described in Section 3.5. It could be found that the corrosion product variations observed over one-piece electrodes (in Figure 4.13) were also observed on the WBE (in Figure 4.16 (a)). The GC maps were measured after 0.5, 72, and 100 hours of immersion when the OCP was in plateau i.e. at a more positive potential level.

Figure 4.16 (a) Photograph of corroded SS304 WBE after one week's OCP testing in 0.5 M NaCl solution; (b)-(d) GC (mA/cm^2) maps measured at 0.5, 72 and 100 hours, respectively; major cathodic area was labelled by dotted cycles

A large current density was observed in Figure 4.16 (b), as indicated by the scale of the GC map, indicating that galvanic activities between PANI and the metal substrate occurred at the initial stage of testing. However, in the subsequent GC mapping, the current density was observed to keep decreasing. After 72 hours of immersion the consistence among the GC distribution patterns, electrodeposition current, and the corrosion products became more distinguishable, as shown in Figure 4.16 (c). In contrast to the anodes at the edges with more corrosion products, the cathodes were located in the centre of the GC map during the remaining corrosion process, and corresponded to the areas with larger electrodeposition currents (Figure 4.16 (c) and (d)) and fewer corrosion products. This kind of correlation continued until 100 hours, as shown in Figure 4.16 (d), i.e. better corrosion protection properties were observed at locations where higher electrodeposition currents were registered.

The rate-controlling step of PANI polymerisation is the oxidation of the aniline monomers, which is proportional to the applied current [Wallace *et al.* 2003]. The current density on the WBE should reflect the polymerisation rate of the PANI film and thus, the distribution of PANI on the WBE surface after the electrodeposition reached a stable stage. Therefore, the correlations that exist between the APC and GC mapping, and the real corrosion products, suggested that the heterogeneity caused by non-uniform PANI deposition was also a major factor affecting the subsequent corrosion protection properties. In fact, as shown in Figure 4.17, between the APC maps during PANI deposition and GC maps during corrosion testing, it was found that at locations with larger deposition currents, the metal

substrate beneath the PANI film could behave as the cathodes and ultimately suffer less corrosion.

Figure 4.17 Comparison between the SS304 WBE APC maps measured at (a) 30 minutes and (b) 40 minutes of PANI electrodeposition with GC maps measured at (c) 72 hours and (d) 120 hours

4.5.3 Anti-Corrosion Performance and Mechanism of PANI on SS304

An additional benefit of the WBE method is that it could provide the maximum current density ($i_{\max}$) and the total anodic current (i_{tot}), as a function of time. During the GC mapping, it was noted that the intensity of the major anode decreased continuously. As

shown in Figure 4.18, in spite of the high initial galvanic current density, both i_{tot} and i_{max} values of PANI covered SS304 WBE decreased rapidly and remained at a much lower level than the current density produced by bare metal. It could also be observed that with applied PANI, the localised corrosion current as indicated by the i_{max} remained at a very low level, down to 10^{-5} mA/cm² over 72 hours of corrosion testing. However, the total current from all types of corrosion as indicated by the i_{tot} does not seem very low, suggesting that in the presence of PANI film, the corrosion of SS304 was more like general corrosion rather than localised corrosion.

(a)

Figure 4.18 Comparison of the (a) i_{max} and (b) i_{tot} of PANI coated SS304 WBE with bare SS304 WBE in an aerated 0.5 M NaCl solution

Since the findings of Deberry that the electrodeposited PANI film provided corrosion protection to stainless steel [Deberry 1985], many studies have been carried out using traditional methods such as potentiodynamic polarisation [Tan and Blackwood 2003], electrochemical impedance spectroscopy (EIS) [Santos *et al.* 1998] and OCP measurement [Gasparac *et al.* 2000]. However, these research did not provide specific information on the corrosion prevention mechanism of PANI.

Based on the galvanic current characteristics described above, it is believed that PANI improves the corrosion resistance of SS304, especially to localised corrosion through enhancement of the passive film. From the electrochemical view point, this enhancement of the passive film was realised by the galvanic coupling of PANI with the metal substrate, and shifting the mixed potential to a more noble direction. The correlation between the

deposition current, the galvanic current and the actual corrosion products distribution provides solid experimental evidence of this passive film enhancement to further confirm this postulation. In addition, during potentiodynamic polarisation, the larger cathodic current obtained with PANI coated SS304 when compared with that of bare metal (see Figure 4.10) suggests that PANI could catalyse the cathodic reduction of oxygen.

The anti-corrosion mechanism of PANI on SS304 could be illustrated using the mixed-potential theory. Based on this theory, any electrochemical reaction can be divided into two or more oxidation or reduction reactions. As illustrated in Figure 4.19, in the case of stainless steel in near neutral NaCl solution, the electrochemical reactions are oxygen reduction and iron oxidation that shows an active-passive behaviour. It is known that stainless steel is under protection by the passive film, however, the passive film on stainless steel is defective under chloride containing circumstance [Fontana 1986]. With the presence of PANI, another reduction reaction sets in because the reduction potential of PANI (around 0.4 - 1.0 V) [Tallman *et al.* 2004] is close to the oxygen reduction potential (typically at ~ 1.23 V) [Jones 1996]. Consequently, the reduction current is increased and the mixed potential of the PANI-metal system is shifted more positive. By this means, the passive film is enhanced, which leads to the reduction of subsequent corrosion current, especially the currents from major anodic sites. It should be noted that instead of the simple combination of the PANI and oxygen reduction currents, it is more likely that PANI accelerates the oxygen reduction on stainless steel. This effect could also contribute to the enhancement of the passive film on stainless steel.

Figure 4.19 Schematic illustration of the anti-corrosion mechanism of PANI on stainless steel in near neutral chloride containing solution

4.5.4 Anti-Corrosion Behaviour of Incomplete PANI Film on the SS304 WBE

The SS304 WBE was employed to understand how the heterogeneity in PANI coating affects its anti-corrosion performance. An incomplete coating was made by disconnecting one wire (wire no.95) during the electrodeposition of PANI on the WBE. This PANI coated SS304 WBE thus had one PANI-free location. The WBE was then immersed in 0.5 M NaCl solution for corrosion evaluation. The OCP was monitored and galvanic current maps were recorded simultaneously.

As shown in Figure 4.20, the OCP of the WBE with partial PANI coverage decreased from 0.2 V and stabilised at around 0.13 V, which is similar to the plateau potential value

obtained from the one-piece electrode (see Figure 4.12), during the first 8.5 hours in step I. Then, the OCP suddenly dropped to -0.012 V and fluctuated at this potential range for about 1.5 hours, as labelled in step II. Next, the OCP increased slowly, as labelled in step III. OCP oscillation was frequently observed, but the current study only focused on the first cycle. WBE GC measurements were carried out and left sharp spikes on the OCP curves, which did not interfere with the corrosion process.

Figure 4.20 OCP vs. time for incompletely PANI coated SS304 WBE in 0.5 M NaCl solution

Figure 4.21 (a) shows the corroded SS304 WBE with applied PANI film after one week of corrosion testing. It was noted that the exposed metal at wire no. 95 was visually free of corrosion products, similar to the result on one-piece electrodes (see Figure 4.13). The edge of the SS304 WBE suffered more severe corrosion than the central region, which is similar to the observations for the complete coverage situation. GC distribution maps were measured during the three steps of the OCP drop-and-increase process, and are shown in

Figure 4.21 (b)-(d). Figure 4.21 (b) was recorded 10 minutes after the immersion. It was observed that the anodic area occupied most of the WBE surface including the exposed metal surface with the current density of 0.006 mA/cm^2 , probably due to the oxidation of the metal surface by oxygen. However, the GC values decreased rapidly in the following measurements, indicating that the passive film on the metal substrate was reinforced. The current density at wire no.95 was also observed to decrease from 0.006 mA/cm^2 to very small current density values in the order of 10^{-4} mA/cm^2 , suggesting a lower corrosion rate.

Figure 4.21 (a) Photograph of the corroded SS304 WBE after one week's OCP testing; (b)-(d) GC maps (mA/cm^2) over the three steps at 0.2, 7.1 and 11.5 hours of OCP change. The location of the exposed metal area (at wire no.95) was indicated by a dotted circle

However, in step II, when the OCP was at a low level, the GC maps exhibited quite different behaviour. During this step, the anodic sites were observed to shift randomly over the WBE surface, which is reproducible on both complete and incomplete PANI coverage, but more significantly on the electrode with an incomplete PANI film. A possible explanation to this phenomenon stems from PANI reduction: PANI-LE became the predominant compound due to the reduction of PANI-EM, as shown in Equation 4.3 [Wessling 1994], which resulted in a drop of the OCP [DeBerry 1985; Gašparac and Martin 2002a; Kraljic *et al.* 2002].

More importantly, during this period, the potential difference between the metal and PANI film significantly reduced. As a result, the anodic and cathodic sites shifted frequently over the WBE surface until they reached equilibrium potential. Thus, during step II, GC distribution showed no consistence with the GC maps in the other two stages. It was also observed that the exposed wire could even behave as the cathode with a current density of $-7.815 \times 10^{-3} \text{ mA/cm}^2$ at a certain period, as shown in Figure 4.21 (c).

The GC map in Figure 4.21 (d), measured after 11.5 hours of testing, indicates that galvanic currents activate in step III of the OCP. The resemblance between GC maps and real corrosion product distribution shown in Figure 4.21 (a) was more obvious in step III. At this stage, the amount of PANI-EM increased because PANI-LE was re-oxidised

continuously to the PANI-EM state by oxygen as shown in Equation 4.4 [Wessling 1994].

The maximum current density value was reduced to the order of 10^{-4} mA/cm², suggesting that the corrosion on the SS304 WBE surface became negligible. It is evident that the anode was located at the exposed metal area again with the current density of 8.9×10^{-4} mA/cm². The current density of the galvanic map reduced even more in the following measurement, leading to a continuous recovery of the OCP.

In summary, the OCP of PANI coated stainless steel experienced drop-and-increase processes. When the OCP was at a low level, the GC distribution patterns were different from those corresponding to the OCP at a high level, which was probably associated with the PANI reduction, reducing the potential difference between metal and PANI films. It was also evident that the anodic current density of the exposed metal surface was always at a relatively low level, which could result to the fact that no visually detectable corrosion products could be found on the exposed metal surface. This could be attributed to the anodic protection mechanism of PANI film.

CHAPTER 5

Results and Discussion II: Electrodeposition of Polyaniline (PANI) on Low Carbon Steel

As described in Section 2.2.2, carbon steel can suffer from general and localised corrosion. Under the attack of aggressive chloride ions, the anodic dissolution rate of low carbon steel, usually called mild steel, increases even though the potential is within the passive region. The possibility of using electrodeposited PANI to prevent localised corrosion of mild steel in chloride ions containing media is investigated in this work.

5.1 The Electrodeposition of PANI on Mild Steel Using Cyclic Voltammetry in Various Conditions

The electrodeposition of PANI on mild steel has been found to be much more difficult than on stainless steel. The first series of experiments were carried out in a H_2SO_4 in order to understand the influence of electrolytes on PANI electrodeposition on mild steel. It was not successful since severe corrosion occurred on the mild steel even before anodic polarisation reached electrodeposition potential. As shown in Figure 5.1, a large anodic current up to 350 mA was produced over the mild steel electrode at potential (~ 0.4 V) far below that

required for PANI polymerisation. Vigorous gas evolution was observed. It was thus believed that H_2SO_4 acid was not suitable for the electrodeposition of PANI on mild steel due to its high acidity.

Figure 5.1 Cyclic voltammogram of a one-piece mild steel electrode in 0.8 M H_2SO_4 acid with 0.1 M aniline

In order to overcome the difficulties associated with the H_2SO_4 acid based electrolyte and the properties of mild steel substrate, oxalic acid was chosen as electrolyte for the electrodeposition of PANI on mild steel. This was mainly because oxalic acid is able to ‘passivate’ carbon steel by forming a protective ferric oxalic salt film under anodic polarisation [Rajagopalan and Iroh 2001]. Although similar research efforts have been reported before [Camalet *et al.* 1998a; Rajagopalan and Iroh 2001], little study on the passivation and initiation of PANI electrodeposition has been carried out. The current work

has focused on the study of PANI electrodeposition in oxalic acid based electrolytes, in particular, (i) the passivation of a mild steel electrode; (ii) the initiation of electropolymerisation using potentiodynamic polarisation and (iii) the electrodeposition of PANI using the cyclic voltammetry (CV) method.

5.1.1 Passivation of a Mild Steel Electrode in Oxalic Acid Based Electrolyte

As shown in Figure 5.2, a mild steel electrode was polarised by applying a potentiodynamic scan from -0.54 to 1.0 V (*vs.* SCE) in 0.3 M oxalic acid electrolyte (pH=0.8). In the forward scan, an anodic current peak 'a' was observed around -0.1 V, probably due to the formation of the insoluble Fe (II) oxalate dehydrate passive film [Camalet *et al.* 1998a]. A small anodic current of about 1.08×10^{-4} mA/cm² indicates negligible metal dissolution between 0.2 and 1.0 V, which also suggests that the potential window for PANI deposition in oxalic acid is sufficiently wide. At potentials beyond 1.0 V, the current density began to increase due to the transpassivation behaviour of the mild steel in the acidic electrolyte. In the reverse scan, however, a large anodic current peak 'b' at a potential of ~ 0.3 V was observed. This observation, which is inconsistent with that reported in the literature [Camalet *et al.* 1998a; Rajagopalan and Iroh 2001], could be associated with the reactions at the oxide/solution interface as suggested by Camalet. The Fe (II) oxalate dehydrate tends to decompose at potentials above 0.6 V and forms more soluble Fe (III) species at the

top of the Fe (II) oxalate; the resulting Fe (III) species further transforms into Fe_2O_3 [Camalet *et al.* 1998a]. Thus, the passive film on mild steel in oxalic acid consists of two components, i.e. the Fe (II) oxalate dehydrate (insulator) and Fe_2O_3 (n-type semiconductor). Although this passive film cannot provide full protection to the mild steel substrate because of its insulating/semiconducting properties, it can still provide certain degree of protection to the metal substrate.

Figure 5.2 Passivation of one-piece mild steel electrode using potentiodynamic polarisation in 0.3 M oxalic acid (pH $\approx$ 0.8)

5.1.2 Initiation of PANI Electrodposition on a Mild Steel Electrode

Electrodposition was then conducted on the passivated mild steel electrode, following similar procedures for PANI electrodposition on stainless steel as reported in Chapter 3. However, it was noticed that neither PANI deposition nor obvious corrosion occurred on

the metal substrate if the potential range was limited to -0.45 - 1.0 V, as shown in Figure 5.3. The current peak 'a' indicating the formation of Fe (II) oxalate dehydrate was only observed in the 1st cycle at a potential around -0.4 – -0.2 V. The current peak 'b' at a potential of ~ 0.2 V suggests the decomposition of the resulting passive film. None of the electrochemical responses led to PANI formation. This could be due to the passive film formed during passivation in oxalic acid. On the one hand, the pre-existence of a passive film protected the mild steel from corrosion in the acidic electrolyte. On the other hand, due to the insulating properties of Fe (II) oxalate, as well as the semiconducting properties of Fe₂O₃, the passive film could prevent the electrodeposition of PANI.

Figure 5.3 Four cycles of potentiodynamic polarisation for the one-piece mild steel electrode in 0.3 M oxalic acid with 0.1 M aniline

In order to initiate the polymerisation of PANI, a larger potential range was scanned on a mild steel electrode. Figure 5.4 shows the potentiodynamic polarisation of the passivated mild steel at a larger potential range (-0.5 - 1.8 V). The actual potential scan was terminated at the upper potential limits and the reverse scan (as shown in the dotted line) is also presented for reference. It was observed that the current peak 'a' was more significant and the current from peak 'b' in the reverse scan was much less, which could be attributed to the anti-corrosion properties of PANI species formed on the metal surface. The purpose of ending the potential scan at a more positive value of 1.8 V was to initiate PANI formation by partially thinning the passivated film on mild steel, since the potential was in the transpassivation region of mild steel. A sharp rise of the current at a potential beyond 1.2 V indicated both the initiation of polymerisation and corrosion of the metal substrate. But for a short time (less than 10 seconds), the corrosion of the metal substrate was negligible.

Figure 5.4 Potentiodynamic polarisation of the passivated mild steel in 0.3 M oxalic acid with 0.1 M aniline

5.1.3 The Electrodeposition of PANI on Mild Steel at Different Potentials

After passivation of the electrode and initiation of PANI polymerisation at a wider potential range using potentiodynamic polarisation, PANI can be electrodeposited using the CV method under similar conditions as on stainless steel (see Figure 4.4). As shown in Figure 5.5 (a), at a potential range of 0.05 - 0.8 V, it was observed that both of the forward and backward scans were affected by the electrochemical reactions from the metal substrate. For example, in the forward scan, current from the oxidation of leucoemeraldine (LE) to emeraldine (EM) state appeared to be a big hump 'A', instead of a distinct current peak of the PANI deposition on SS304 (see Figure 4.4). This was probably associated with the interference from the current peak 'a' (i.e. the current response 'a' in Figures 5.2, 5.3 and 5.4). In the reverse scan, the PANI reduction peak 'A' was also overlapped by the sharp

current peak 'b' at a potential between 0.05 and 0.2 V. Thus, in this CV, only current peaks B/B' (0.5 - 0.75 V) from the conversion between EM and pernigraniline (PA) states indicated PANI formation. Similar PANI electrodeposition behaviour using the CV method has also been reported [Camalet *et al.* 1998].

(a)

(b)

Figure 5.5 Cyclic voltammograms of electrodeposition of PANI on mild steel electrodes at potentials of (a) 0.05 - 0.8 V and (b) 0.3 - 0.85 V in 0.3 M oxalic acid with 0.1 M aniline.

For the purpose of optimising the electrodeposition process, PANI was electrodeposited at different potential ranges. It was found that when the potential range was reduced to 0.3 - 0.85 V, the current responses presented two pairs of distinct peaks. As shown in Figure 5.5 (b), with a narrowed potential range, the current peaks **A/A'** (0.0 - 0.2 V) were absent. Peaks **B/B'** indicated the conversion between EM and PA and peaks **C/C'** resulted from the electroactive degradation products. The current from the metal substrate became indistinguishable, indicating that the redox reactions from the metal substrate were effectively minimised by this narrowed potential range. Comparing the current responses on mild steel with the ones on SS304 (see Figure 4.4), it was found that the characteristic potentials (peaks **B/B'** and **C/C'**) were almost the same for the two ferrous metals, suggesting that the positive shift in potential would not affect the electrodeposition of PANI. It was noticed from visual observation that the deposited PANI at the latter potential range appeared to be more dense and uniform. Since the latter potential range of CV (0.3 - 0.85 V) avoided electrochemical interference (current peaks '**a**' and '**b**') from the metal substrate, the current responses mainly represented the electrochemical formation of PANI. It is believed that the potential range of 0.3 - 0.85 V is favourable to increase the uniformity of the deposited PANI on mild steel.

5.2 Electrodeposition of PANI Using the Potentiostatic Method

Although CV is useful for the electrodeposition of PANI on a mild steel electrode, due to the low growth rate in oxalic acid, it usually takes a long time to deposit a PANI film of sufficient thickness. The Potentiostatic (PS) method was applied in order to find a more suitable method for the effective electrodeposition of PANI. The electrodeposition of PANI using the PS method was carried out after the passivation of the mild steel electrode and the initiation of PANI polymerisation using potentiodynamic polarisation, as described in Section 5.1.

Figure 5.6 shows the electrodeposition currents on mild steel at the applied potentials of 0.95 V, 0.85 V and 0.75 V, respectively. Similar to the electrodeposition current responses in the initial stage on stainless steel, the currents became stabilised after an initial decrease, indicating the deposition of an electroactive polymer. It was observed that the growth rate of PANI film on mild steel in oxalic acid was much lower compared to that on stainless steel in H_2SO_4 acid, probably associated with the pre-treatment of mild steel. As a result, the deposition time had to be prolonged to one hour to obtain a PANI film with a similar thickness to the one on the stainless steel. It was evident that the deposition currents rose with the increased potentials from 0.75 V to 0.95 V. By visual observation, however, the PANI film deposited under 0.95 V was coarser and non-uniform when compared to the ones deposited at lower potentials. This could be attributed to the larger extent of polymer

degradation and metal dissolution at 0.95 V accompanied by a higher growth rate of PANI. Therefore, it could be considered that the potential of around 0.85 V was the appropriate potential for PANI electrodeposition with an acceptable growth rate and PANI film properties.

Figure 5.6 Chronoamperogram obtained during the electrodeposition of PANI on one-piece mild steel electrodes in 0.3 M oxalic acid with 0.1 M aniline at various potentials

5.3 Characterisations of the Electrodeposited PANI on Mild Steel

A scanning electron microscope (SEM) was employed to observe the morphology of the PANI film on mild steel deposited using the PS method. As shown in Figure 5.7 (a), the PANI deposits are an assembly of equal-axis grains with an average size of about 500 nm. They appear to be dense and pore free when observed with 5,000 times magnification,

which could be attributed to the relatively slow growth rate in the oxalic acid. As shown in the cross-section image (Figure 5.7 (b)), the electrodeposited PANI film on mild steel has a laminated structure. The PANI deposits were laid down over the metal surface layer by layer. This kind of morphology is considered favourable for the barrier function of a coating. However, the results of salt spray testing (in Section 5.4.2) suggested that the barrier function was only a minor contributor to the corrosion prevention of PANI film.

(a)

(b)

Figure 5.7 Micrographs of (a) the top view and (b) a cross-section of the electrodeposited PANI film obtained at a fixed potential of 0.85 V on one-piece mild steel electrodes in 0.3 M oxalic acid with 0.1 M aniline

Fourier transformed infrared (FTIR) spectroscopy was employed to identify the electrodeposited PANI on mild steel after the sample was placed in ambient air for three weeks. As shown in Figure 5.8, like the spectrum of PANI on SS304, four distinct peaks occurred at 1570, 1469, 1295 and 1118 cm^{-1} , respectively. It was noted that the

characteristic peaks were shifted to a lower wavenumber, compared to the ones on SS304, i.e. 1578 cm^{-1} , 1491 cm^{-1} , 1302 cm^{-1} and 1137 cm^{-1} . Based on the fact that PANI was doped by oxalic acid instead of H_2SO_4 acid, as for the SS304, this is probably due to the low bond strength of oxalic anions, which resulted in a lower electron density of the polymer. This observation also corroborated well with reports by other researchers [Aykanat and Iroh 2002]. The peak at the higher wavenumber of 3461 cm^{-1} is probably associated with oxalic anionic dopants trapped in the polymer. The additional large peak at 1118 cm^{-1} is most likely due to the electronic-like band [Salaneck *et al.* 1986]. The almost equal intensity of the 1570 and 1496 cm^{-1} peaks indicate that the electrodeposited PANI film remained in EM state [Neoh *et al.* 1993] even after three weeks' contact with the mild steel substrate.

Figure 5.8 FTIR spectrum of the electrodeposited PANI at a fixed potential of 0.85 V on a mild steel electrode in 0.3 M oxalic acid with 0.1 M aniline

5.4 Corrosion Evaluation of the Electrodeposited PANI Film

5.4.1 Potentiodynamic Polarisation Measurements

The electrodeposited PANI on the mild steel electrode was tested using potentiodynamic polarisation at a sweep rate of 1 mV/s in aerated 0.5 M NaCl solutions (see Figure 5.9). Bare mild steel electrode and the passivated mild steel in oxalic acid were also tested under the same conditions for the purposes of comparison. Polarisation was started after 0.25 hours of immersion in order to stabilise the electrochemical system. The corrosion potentials (E_{corr}), pitting potential (E_{pit}) and corrosion current densities (i_{corr}) were evaluated using Tafel extrapolations and were summarised in Table 5.1. According to Figure 5.9 and Table 5.1, it can be seen that the E_{corr} of PANI coated mild steel shifted positively by approximately 0.07 V (i.e. from -0.84 V to -0.77 V). With additional PANI film, the E_{corr} was further ennobled by about 0.12 V, indicating that the applied PANI film could shift the mixed potential of the metal-PANI system in the noble direction. In addition, with the protection of PANI film, E_{pit} was also observed to be ennobled from -0.41 V of the passivated metal to -0.30 V, which suggested that the applied PANI film could enhance the passive film of mild steel. The i_{corr} values of both the passivated and PANI coated mild steel were generally smaller than those of bare metal. The fact that E_{pit} increased and i_{corr} decreased suggested that the electrodeposited PANI provided some extent of protection to the localised and general corrosion of mild steel. It was also noticed that the cathodic

current of PANI deposited mild steel was much larger than those of both bare metal and passivated metal. This suggests that the PANI film could accelerate the cathodic reaction, which is also inconsistent with the results obtained from the potentiodynamic polarisation of PANI coated stainless steel. It should be noted that in order to initiate PANI polymerisation, the passive film was damaged (as outlined in Section 5.1.2), which could serve as the reason to explain why the i_{corr} of the applied PANI increased slightly when compared to passivated mild steel.

Figure 5.9 Potentiodynamic polarisation of (a) bare mild steel, (b) passivated mild steel in 0.3 M oxalic acid, and (c) PANI electrodeposited mild steel in 0.5 M NaCl solution

Table 5.1 Comparison of E_{corr} , E_{pit} and i_{corr} with bare mild steel, passivated mild steel and PANI deposited mild steel in 0.5 M NaCl solution

	E_{corr} (V)	E_{pit} (V)	i_{corr} (mA/cm ²)
Bare mild steel	-0.84	-0.63	4.53E-3
Passivated mild steel	-0.77	-0.41	1.55E-4
PANI deposited mild steel	-0.65	-0.30	3.58E-4

5.4.2 Salt Spray (Fog) Tests

Salt spray (fog) testing according to ASTM G85-02 ^{e1} was performed to evaluate the electrodeposited PANI as a primer on mild steel with acrylic and anti-rust oil as top coats. Neat PANI coated mild steel and bare mild steel were also tested and displayed for the purposes of comparison. The thickness of the top and primer coatings was around 40 μm as determined by the surface profiler described in Section 3.7. The descriptions of the surface conditions of metals with testing times are summarised in Table 5.2.

As shown in Figure 5.10 (b), without protection from top coats, the PANI coated mild steel was severely corroded after 12 hours, which was similar to the corrosion performance of the bare mild steel tested under the same conditions. Therefore, the results suggested that PANI film itself could not provide sufficient corrosion protection to mild steel in corrosive environments. However, with the assistance of the top coats, PANI has shown a better corrosion protection performance. Neither acrylic/PANI nor acrylic coatings showed any

sign of corrosion in the first 36 hours. After testing for 108 hours, the acrylic coating suffered rusting and blistering (see Figure 5.10 (c)), which was more severe than that appeared on the acrylic/PANI coating (see Figure 5.10 (d)).

When the acrylic coating was changed to anti-rust oil, as illustrated in (e) and (f), the corrosion protection from the PANI primer was more effective than that from the mere anti-rust oil. In general, the electrodeposited PANI film can slow down the corrosion rate, especially when it interacts with top coats with good barrier functions.

Table 5.2 Visual observations of the metal surfaces during the salt spray testing

Coating Systems		Cumulative Number of Hours				
		12	36	60	84	108
I	No coating	whole rust area	-	-	-	-
	PANI	whole rust area	-	-	-	-
II	Acrylic	not affected	not affected	not affected	small blister area	small rust area moderate blister area
	PANI/ Acrylic	not affected	not affected	small rust area	small rust and blister area	small rust and blister area
III	Oil	whole rust area	-	-	-	-
	PANI/Oil	small rust area	-	-	-	-

Figure 5.10 Photographs of (a) bare mild steel and (b) PANI primer on mild steel after salt spray for 12 hours; (c) Acrylic coating and (d) PANI primer/Acrylic on mild steel after salt spray for 108 hours; (e) anti-rust oil and (f) PANI primer /anti-rust oil on mild steel after salt spray for 12 hours

5.4.3 Open-Circuit Potential Measurements

Open-circuit potential (OCP) was monitored to study the E_{corr} variation of PANI coated and bare mild steel in 0.5 M NaCl solution. Incomplete PANI coated mild steel was also tested with the expectation of understanding how the heterogeneity affects the electrochemical behaviour of PANI films. Photographs of the two samples before the OCP testing are shown in Figure 5.11.

Figure 5.11 Photographs of (a) a complete PANI and (b) an incomplete PANI coated one-piece mild steel electrode in 0.3 M oxalic acid with 0.1 M aniline, before OCP testing

During OCP testing, it was observed that the pale green PANI coating became transparent, indicating the conversion from the EM to the LE state [Huang and MacDiarmid 1993]. This conversion occurred on both the completely and incompletely coated PANI films after 1 hour and 0.4 hour of immersion, respectively. Recent research by Cook [Cook *et al.* 2004] revealed that PANI could be reduced by the mild steel substrate to the LE state immediately upon exposure to the aqueous environment. Our results were in agreement with their observations, but the duration of conversion was one hour after the testing electrode was immersed into the 0.5 M NaCl solution. This was probably due to the different application method: they used a chemical application method instead of electrodeposition. The prolonged reduction from the EM to the LE state could be attributed to the passivation process in oxalic acid before the electrodeposition of PANI, which retarded the electrochemical reactions at the metal/coating interface.

As shown in Figure 5.12, OCPs of the complete and incomplete PANI coated mild steel electrodes are more positive than those of bare metal, suggesting that the PANI film could shift the corrosion potential of mild steel positively. The OCP of incomplete PANI coverage was observed to decrease continuously with time, whereas the OCP for a fully PANI covered electrode was observed to slightly increase between 6 and 10 hours of testing from -0.63 V to -0.61 V, and to approach -0.62 V after 12 hours. This behaviour is very different from the OCP change of PANI coated SS304, where the OCP experienced a drop-and-increase for more than 0.1 V (see Figure 4.12). This is probably due to the low equilibrium potential of mild steel compared to that of stainless steel. As suggested in the Section 2.4.2, it is possible that PANI-LE state is oxidised in contact with stainless steel and, more importantly with the presence of oxygen [Ahamd and MacDiarmid 1996]. However, the oxidation potential of the mild steel is much lower than that of the PANI-LE state. In contact with mild steel in chloride containing aqueous, the PANI in LE state could be the stable oxidation state of PANI. Indeed, the drop-and-increase process of OCP was only reported on stainless steel substrates [Gasparac and Martin 2001; Ahamd and MacDiarmid 1996; Kraljic *et al.* 2003].

Corrosion products were observed to be randomly distributed over both the completely and incompletely coated metal surface, indicating that the corrosion pattern of PANI coated mild steel could be general corrosion. After immersion in 0.5 M NaCl solution for 12 hours,

the exposed metal area was corroded before the metal surface being covered by PANI film, as shown in Figure 5.13 (b). This behaviour was also different from the behaviours of the PANI film on SS304 (see Section 4.4.2).

Figure 5.12 OCP vs. time for a PANI coated one-piece mild steel electrode and a bare mild steel electrode without PANI in aerated 0.5 M NaCl solution

Figure 5.13 Photographs of (a) a complete PANI and (b) an incomplete PANI coated mild steel one-piece electrodes after exposed in aerated 0.5 M NaCl solution for about 24 hours and 12 hours, respectively

5.5 Studying PANI Electrodeposition and Anti-Corrosion on Mild Steel Using the WBE

5.5.1 Anodic Polarisation Current Measurements over Mild Steel WBE

In order to understand the relationship between electrodeposition and corrosion, a mild steel WBE was utilised to monitor the electrodeposition and the corrosion process of the PANI coated electrode under exactly the same conditions as those on the one-piece electrodes. It was also anticipated that this would help understand how the heterogeneity of the electrodeposited PANI film influenced its anti-corrosion performance on both complete and incomplete PANI coverage. The chronoamperogram obtained from the mild steel WBE, as shown in Figure 5.14, is similar to what happened on the one-piece electrode (see Figure 5.11), and the dotted line indicates the time of the anodic polarisation current (APC) measurement following the experiment setup shown in Figure 3.5.

Figure 5.14 Chronoamperogram during the electrodeposition of PANI at 0.85 V on a mild steel WBE in 0.3 M oxalic acid with 0.1 M aniline

As shown in the Figure 5.15 (a), the electrodeposited PANI film with a dark-green colour covered the mild steel WBE surface, similar to what happened to the one-piece electrodes (see Figure 5.11 (a)). Figures 5.15 (b)-(d) show APC maps that were measured after 30, 40 and 50 minutes of electrodeposition. Under anodic deposition conditions, all the electrodeposition currents were positive and stabilised at about 0.78 mA/cm^2 . It was observed that the anodic polarisation currents distributed non-uniformly over the WBE surface. However, this non-uniformity was smaller than that on the SS304 in Figure 4.15, since the ratio of the maximum/minimum current values was smaller. The similarity among the three APC maps, recorded at different times, also indicated the consistency of this non-uniformity over the electrodeposition process.

Figure 5.15 (a) Photograph of a mild steel WBE with PANI deposits; (b)-(d) APC maps (mA/cm^2) measured at the times of 30, 40 and 50 minutes, respectively

5.5.2 Galvanic Current Map Measurements over a Mild Steel WBE

This PANI coated mild steel WBE was then immersed in an aerated 0.5 M NaCl solution for corrosion evaluation under free corrosion conditions according to the experimental setup shown in Figure 3.8. Figure 5.16 (a) shows a photograph of the electrode corroded with PANI film after 30 hours of immersion. From the photograph, it can be clearly seen that the majority of the area of the electrode surface shows corrosion products, except for the lower and upper right corners, indicating that the corrosion of PANI coated mild steel in

0.5 M NaCl solution was mainly general corrosion. Galvanic current (GC) maps were measured at 0.5, 2 and 30 hours of corrosion testing. As shown in Figure 5.16 (b), both the anodic and cathodic currents were very large (up to 0.284 mA/cm² and -0.426 mA/cm²) at the initial stage, indicating highly active galvanic interactions between the PANI film and the metal substrate. After 1.5 hours, the PANI film became transparent, indicating the reduction from PANI-EM to PANI-LE state. GC maps showed that the current density decreased significantly and the anode/cathode shifted over the WBE surface frequently. Within 15 hours, both the anodic and cathodic currents continuously decreased and no obvious corrosion products on the WBE surface were observed. As the corrosion testing approached the end of 30 hours, however, the anodic current began to increase gradually and the anodes and cathodes became localised in the current maps, indicating localised corrosion. Figure 5.16 (d) was recorded immediately before the WBE was taken out of the solution after 30 hours. Comparison of this galvanic current map with the actual corroded WBE surface in Figure 5.16 (a) shows a good correlation between galvanic current and the corrosion product distribution was evident. The anodic area corresponded to the area with more corrosion products, and the cathodic areas were correlated with the PANI film in a dark-blue colour and with fewer corrosion products. This result suggests that the WBE method can be used to monitor the corrosion process and estimate corrosion product distribution on a PANI coated mild steel. Similar experiments were repeated and the characteristics in the results were reproduced.

Figure 5.16 (a) Photograph of corroded mild steel WBE after 30 hours' OCP testing in 0.5 M NaCl solution; (b)-(d) GC maps(mA/cm^2) measured at 0.5, 2, and 30 hours, respectively

A comparison of the GC map and APC map shows that the major cathodes in the GC map are mainly located at the areas with higher deposition current in the APC map, as shown in Figure 5.17. Accordingly, areas with lower deposition current in APC map behaved as anodes in the GC map. This suggests that PANI film behaved as a cathode when the WBE was immersed in corrosive solution. The heterogeneity caused by non-uniform PANI deposition influenced the subsequent anti-corrosion properties. This suggests that the corrosion behaviour of a PANI coated mild steel surface can be predicted from its APC maps.

Figure 5.17 Comparison between (a) the APC map measured at 50 minutes of PANI electrodeposition on mild steel WBE and (b) the GC map measured at 0.5 hour during OCP testing in 0.5 M NaCl solution

Similar to the behaviour on the one-piece electrode (see Figure 5.12), the simultaneously recorded OCP with the GC measurements also showed a more positive potential than the potential of bare metals. This is shown in Figure 5.18, where the OCP continuously decreased and stabilised at the potential of -0.65 V. Based on the galvanic current and OCP measurements, it is believed that the noble potential of the PANI-metal system resulted from the galvanic coupling between the metal and PANI film in which PANI behaved as cathode.

Figure 5.18 OCP vs. time for the PANI coated mild steel in 0.5 M NaCl solution.

5.5.3 Anti-Corrosion Performance and the Mechanism of PANI Film on Mild Steel

The maximum anodic current ($i_{\max}$) and total anodic current (i_{tot}) as a function of time are plotted in Figure 5.19 based on the WBE GC maps. Compared to the $i_{\max}$ and i_{tot} of bare mild steel in 0.5 M NaCl solution, both the $i_{\max}$ and i_{tot} of PANI coated mild steel were much lower than those of bare metal. Whereas, it was also noted that the first two i_{tot} values measured within 0.5 hours of immersion were more than 3 times larger than the i_{tot} produced by the bare metal, but the maximum current of PANI coated mild steel was still comparable to that of bare metal. This observation may be explained by the large passive currents required in the initiation of the passive film on the metal surface. It is most likely that PANI enhanced the passive film on the mild steel at the initiation phase of corrosion.

The decreasing i_{tot} was also consistent with the visual observation of the colour changes of the PANI film, indicating that dramatic galvanic reactions occurred and resulted in the reduction of the PANI. Through this galvanic coupling, a more corrosion protective passive film could be formed on mild steel surfaces and provide corrosion protection to the metal substrate. However, it was found that both the i_{max} and i_{tot} increased after 20 hours of testing, indicating that the corrosion may become more active after 20 hours.

(a)

Figure 5.19 Comparison of the (a) i_{max} and (b) i_{tot} between PANI coated mild steel WBE and a bare mild steel WBE

Based on these results, it is evident that the electrodeposited PANI film provided some corrosion protection to mild steel. The good correlation between the APC and GC maps indicated that PANI behaved as a cathode and the more PANI deposits, the better the corrosion prevention performance in the subsequent corrosion testing. A reasonable interpretation of these phenomena is that at initial stage, the PANI in the EM state shifted the mixed potential of the PANI-metal system to a noble direction and oxidised the mild steel substrate, resulting in the formation of a protective film on the metal surface. Moreover, PANI is likely to accelerate the oxygen reduction (based on the results from potentiodynamic polarisation), which also facilitates the formation of a protective oxide film on mild steel. The proposed mechanism based on the mixed potential theory is illustrated in Figure 5.20. Other mechanisms, such as the inhibitory process of releasing

dopant anions during PANI reduction as reported by Cook [Cook *et al.* 2004], may also contribute to the anti-corrosion properties of PANI.

Figure 5.20 Schematic illustration of the anti-corrosion mechanism of PANI on mild steel in near neutral chloride containing solution

5.5.4 Anti-Corrosion Behaviour of Incomplete PANI Film on a Mild Steel

WBE

In order to further understand the mechanism of PANI corrosion protection, in particular, how incomplete PANI coverage affects corrosion on mild steel, an incomplete coating was made by disconnecting one wire (at wire No. 95) from the WBE during the electrodeposition. After corrosion testing in 0.5 M NaCl solution for about 30 hours, the WBE was examined, as shown in Figure 5.21 (a). Including the area without coating, the mild steel surface showed general corrosion. The area without coating acted as an anode

during the whole galvanic current measurement. As shown in Figure 5.21 (b)-(d), the area without coating behaved as an anode at currents of 0.126 , 1.31×10^{-4} and 2.37×10^{-5} mA/cm², respectively. This was expected since the equilibrium potential of mild steel was lower than that of PANI in the LE state, the occurrence of passivation on PANI coated SS304 could not be repeated on the PANI coated mild steel surface. It has been reported that the pinhole can be corrosion protected by a PANI coating in tap water [Kinlen *et al.* 1999]. However, in more corrosive 0.5 M NaCl solution, the anti-corrosion capability of PANI seemed insufficient to protect the pinhole from corrosion.

Figure 5.21 (a) Photograph of corroded mild steel WBE with a pinhole after 30 hours' OCP testing in 0.5 M NaCl solution; (b)-(d) GC maps of PANI coated mild steel WBE measured at 0.5 hour, 3.5 hours, and 30 hours, respectively

CHAPTER 6

Results and Discussion III: Electrodeposition of Polyaniline (PANI) on Aluminium Alloy

As described in Section 2.2.3, aluminium and its alloys owe their excellent corrosion resistance to the passivity produced by an inert and protective aluminium oxide film, which forms almost immediately in most environments, such as aerated and de-aerated aqueous solutions. However, the passive film on aluminium surface is in fact an imperfect film and thus aluminium often suffers from localised corrosion. Pitting corrosion of aluminium and its alloys is a common and serious localised corrosion problem, especially when metallic elements are added to aluminium in order to improve its properties, such as its mechanical strength. The possibility of using electrodeposited PANI for preventing the localised corrosion of aluminium in halogen ions containing media has been investigated in this work.

6.1 Electrodeposition of PANI on AA1100 Using Cyclic Voltammetry in Various Conditions

The electrodeposition of PANI on aluminium has been found to be even more difficult than on mild steel. Indeed, few reports exist on the successful electrodeposition of PANI on

aluminium alloys [Conroy and Breslin 2003], although many attempts have been made including those with various electrolytes, different electrodeposition potentials, and surface pre-treatments. Besides the commonly used candidate acids, H_2SO_4 , oxalic and *p*-toluenesulfonic (tosylic) acids, others such as HNO_3 and poly(acrylic acid) (average molecular weight 2000 g/mol) have also been tested for PANI electrodeposition on aluminium [Huerta-Vilca 2004; Kinlen *et al.* 2004]. However defects on the aluminium surface and the required high voltage (up to 100 V) is impractical to be used in industryent of Cr (VI)-containing conversion coatings. Pre-treatment methods, such as degreasing AA1100 electrode ultrasonically with hexadecane for about 15 minutes [Iroh *et al.* 2003], passivation of the AA1100 electrode in oxalic acid and H_3PO_4 [Iroh *et al.* 2003; Eftekhari 2001] have also been explored. However none of these methods can result in PANI electrodeposition with satisfactory corrosion resistance.

In this present workw the first seriesof experiments were carried out in a H_2SO_4 in order to understand the influences of electrolytes on the PANI electrodeposition on aluminium. This was not successful, as shown in the cyclic voltammogram (CV) obtained during the electrodeposition of PANI on the AA1100 electrode using 1 M H_2SO_4 electrolyte in Figure 6.1. After the first half cyclew the currentdecreased with the increasing cycle numbers. There was no indication of PANI electrodeposition in the CV and the AA1100 electrode was visually free of PANI deposits.

Modification of the aluminium surface was carried out before electrodeposition, similar to the pre-treatment of mild steel. An AA1100 electrode was passivated in oxalic acid at a potential of $-0.5 \sim 2.25$ V using potentiodynamic polarisation, as shown in Figure 6.2 (a). However, as shown in Figure 6.2 (b), the current indicating the electrodeposition of electroactive PANI at potentials from 0.0 to 2.0 V was extremely small. Figure 6.3 shows the CV diagram obtained from the AA1100 electrode in a tosylic acid based electrolyte. The AA1100 electrode was ultrasonically degreased in hexadecane. Obviously no PANI electrodeposition occurred.

(a)

(b)

Figure 6.2 (a) and (b) Cyclic voltammograms of a Pt electrode in 0.25 M oxalic acid with 0.01 M BA. The scan rate is 10 mV/s.

Figure 6.3 Cyclic voltammogram of 9.5 cycles electrodeposition of PANI on the AA1100 electrode in 1 M tosylic acid with 0.16 M aniline

Since PANI could not be electrodeposited on AA1100 using the CV method, the potentiostat (PS) method was used to apply a more consistent current. An improvement that PANI could be electrodeposited on the AA1100 electrode was observed. But even in the best situation, PANI could only partially cover the metal surface. Figure 6.4 shows the currents at a fixed potential of 1.25 V in H_2SO_4 , oxalic acid, and tosylic acid, respectively. It was observed that the currents from H_2SO_4 and oxalic acid decreased with time after the initial current variations, indicating that the growth rate of PANI decreased with electrodeposition proceeding. It was noticeable that the current produced in tosylic acid stabilised at about 0.6 mA/cm^2 after half an hour, indicating the growth of the electroactive polymers. Figure 6.5 shows the corresponding PANI deposits from H_2SO_4 , oxalic and tosylic acids, respectively. It is obvious that PANI deposited from H_2SO_4 and oxalic acid is inferior to that from tosylic acid. Thus, tosylic acid was chosen as the electrolyte in the

electrodeposition of PANI on AA1100 in the subsequent studies.

Figure 6.4 Chronoamperogram during the electrodeposition of PANI on the AA1100 one-piece electrodes at a fixed potential of 1.25 V in 0.75 M H₂SO₄ containing 0.1 M aniline, 0.3 M oxalic acid with 0.1 M aniline, and 1 M tosylic acid with 0.16 M aniline

Figure 6.5 Photographs of one-piece AA1100 electrode surfaces with PANI deposits from (a) 1 M H₂SO₄ with 0.16 M aniline, (b) 0.25 M oxalic acid with 0.1 M aniline, and (c) 1 M tosylic acid with 0.16 M aniline

In summary, the best result of electrodeposition on the AA1100 one-piece electrode was achieved using the PS method in tosylic acid. However, this preliminary work only

resulted in an incomplete PANI electrodeposition.

6.2 Studying the Electrodeposition of PANI on AA1100 Using the WBE

No further improvements were achieved in the electrodeposition of PANI on AA1100 electrodes until the WBE method was employed to better understand the electrodeposition processes. The WBE was used to investigate the reason for the incomplete PANI electrodeposition and to investigate possible approaches to improve the uniformity of the PANI deposits.

PANI was electrodeposited on the WBE following exactly the same conditions and procedures as on one-piece electrodes, as described in Section 6.1. As shown in Figure 6.6 (a), the pattern of PANI distribution over the WBE is similar to that on the one-piece electrode shown in Figure 6.5 (c). This suggests that the WBE effectively simulated electrodeposition behaviour on the one-piece electrode. Figure 6.6 (b)-(d) show the corresponding anodic current distribution (APC) maps measured during the electrodeposition of PANI. It is evident that the APC maps, as presented by the positive current, correspond well with the area with more PANI deposits, as shown in the photograph of Figure 6.6 (a). Anodic current densities on the lower half of the WBE surface were three or four orders of magnitude lower than those on the upper part, which also agreed with the fact that few PANI deposits were visible on these regions. These results demonstrate clearly that the WBE APC maps correlated with the distribution of the

actual PANI deposits, and thus can be employed as a means for monitoring and studying the electrodeposition of PANI coating.

Figure 6.6 (a) Photograph of an AA1100 WBE with PANI deposits after 60 minutes of potentiostatic electrodeposition (1.25 V vs. SCE); (b)-(d) corresponding APC maps (mA/cm^2) of PANI electrodeposition in 1 M tosylic acid with 0.16 M aniline after 30, 40 and 50 minutes, respectively

After examining the WBE APC maps, a possible explanation to this incomplete PANI coverage was assumed that the insulating oxide film formed on certain portions of the

AA1100 WBE surface was thicker than that at other locations. A thicker oxide layer could block the anodic polarisation current at these portions of the electrode. It is recognised that oxide layers on an aluminium surface could dissolve in an acidic solution [Conroy and Breslin 2003], however, in the electrodeposition experiment reported here, aluminium was under anodic polarisation. Anodic polarisation may have acted to actively repair and maintain the oxide layer. When anodic polarisation was applied during the electrodeposition of PANI on an aluminium alloy surface, the oxide film could have been enhanced continuously. Actually, as shown in Figure 6.6 (d), the anodic current density values recorded over the WBE surfaces areas without deposits was as low as 3.5×10^{-5} mA/cm². The PANI deposit could be much more difficult to initiate over these low-current areas. Hence, the insulating properties of the oxide film appeared to be the predominant factor that impedes the electrodeposition of PANI on AA1100 electrodes.

Based on this result and analysis, a cathodic pre-treatment of the aluminium surface was proposed to improve the uniformity of PANI electrodeposition. It was believed that cathodically polarising an aluminium surface could remove or thin the oxide layer when an AA1100 electrode is immersed in the acidic electrolyte, by the following reactions:

Indeed, after pre-treatment by cathodically polarising an AA1100 WBE at a static potential of -0.9 V for 5 minutes in the same electrolyte used for the electrodeposition (see Figure 6.7), a PANI film was successfully deposited on the AA1100 WBEs with a complete coverage.

Figure 6.7 Cathodic pre-treatment of the AA1100 WBE at a fixed potential of -0.9 V for 5 minutes in 1 M tosylic acid with 0.16 M aniline

As shown in Figure 6.8 (a), the WBE was completely coated with a PANI film after cathodic pre-treatment. The anodic polarisation current values shown in Figure 6.8 (b)-(d) are much larger (maximum approximately 10 mA/cm²) than those shown in Figure 6.6 (maximum approximately 0.5 mA/cm²), suggesting that the pre-treatment made the electrodeposition on AA1100 surfaces significantly more efficient. Due to an improved current efficiency, the required electrodeposition time was shortened to 30 minutes. It is also interesting to note that higher current regions, as indicated by the brighter spots in

Figure 6.8 (b)-(d), distributed randomly over the WBE surface and their locations shifted frequently, leading to a more uniform distribution of PANI deposits over the WBE surface. The random distribution of anodic polarisation currents appears to be a characteristic pattern to produce a PANI film that covers an electrode surface completely.

Figure 6.8 (a) Photograph of an AA1100 WBE with PANI deposits after 30 minutes of electrodeposition; (b)-(d) APC maps (mA/cm^2) after 20, 25 and 30 minutes of PANI electrodeposition at 1.25 V in 1 M tosylic acid with 0.16 M aniline

To understand and confirm the effects of cathodic pre-treatment on the electrodeposition of PANI, galvanic current (GC) maps were measured from the WBE before and after cathodic polarisation treatment in the same electrolyte. From the scale bars shown in Figures 6.9 (a)

and (b), it can be seen that the anodic current density was slightly larger after the cathodic pre-treatment. Since the anodic current density indicates the corrosion rate in a specific solution, the increased anodic current density indicates a thinner oxide layer on a metal surface after cathodic pre-treatment. Compared to the relatively smaller cathodic area (see Figure 6.9 (a)), cathodic sites after pre-treatment (see Figure 6.9 (b)) increased significantly (about ~ 1.5 times by counting of the cathodic wires over a WBE surface) and distributed more evenly on the electrode surface. Moreover, these cathodic sites primarily corresponded to the major APC sites measured during PANI electrodeposition, as compared in Figures 6.9 (b) and (c). This result suggests that cathodic polarisation indeed contribute to removing or thinning the oxide layer.

Figure 6.9 Comparison of the GC maps of the AA1100 electrode (a) before, (b) after the cathodic pre-treatment in 1 M tosylic acid with 0.16 M aniline, and (c) the corresponding APC map after electrodeposition for 20 minutes at a fixed potential 1.25 V in the same electrolyte

After confirming the efficiency of surface treatment using the cathodic polarisation of aluminium electrodes, further work was carried out to explore better cathodic pre-treatment conditions. One parameter investigated was the duration of the cathodic pre-treatment. When cathodic polarisation of the aluminium electrode was extended to 8 minutes at the same applied potential, as shown in Figure 6.10, the uniformity of PANI electrodeposition deteriorated, as shown in Figure 6.11 (a). Certain parts of the metal surface were exposed, and the result was certainly not as good as that in Figure 6.8 (a). The corresponding APC

maps obtained during the electrodeposition process are illustrated in Figure 6.11 (b)-(d).

Figure 6.10 Cathodic pre-treatment of the AA1100 WBE at -0.9 V for 8 minutes in 1 M tosylic acid with 0.16 M aniline

In contrast to what was revealed in Figure 6.6, the exposed metal area shows a correlation with the larger cathodic polarisation current, instead of the PANI deposits. Larger currents were observed in the APC maps, which are even larger than those found in Figure 6.6, and correspond primarily to the exposed metal areas without PANI deposition. It is possible that the metal substrate could be dissolved during PANI deposition. This study between the PANI deposits distribution and the APC maps suggested that if the AA1100 electrode was under cathodic polarisation for too long, the oxide film could be damaged too much and lead to a rapid metal dissolution during the subsequent PANI electrodeposition. Therefore, it is critical to control the formation of the oxide layer and its thickness very carefully, in order to achieve uniform PANI electrodeposition. The oxide layer cannot be too thick to

block the electrodeposition current, and the existence of the oxide film cannot be too thin to prevent the metal from dissolution in the acidic electrolyte. Neither situation would lead to uniform PANI deposition. These experiments also demonstrated the benefits of the WBE method in the investigation of the electrodeposition of PANI on aluminium alloys.

Figure 6.11 (a) Photograph of an AA1100 WBE with PANI deposits after 30 minutes of electrodeposition; (b)-(d) APC maps (mA/cm²) after 20, 25 and 30 minutes of PANI electrodeposition at a fixed potential of 1.25 V in 1 M tosylic acid with 0.16 M aniline

6.3 Electrodeposition and Characterisations of PANI on AA1100

After cathodic pre-treatment at -0.9 V for 5 minutes, it was found that PANI could also be electrodeposited on the AA1100 electrode using both the CV and PS methods. The corresponding CV diagram is shown in Figure 6.12. Compared to the one without PANI electrodeposition (see Figure 6.3), the current increased with increasing number of cycles, suggesting the continuous growth of the electroactive polymer on the AA1100 surface. It is interesting to note that there was only one pair of current peaks at 0.57 V and 0.15 V, instead of two pairs of oxidation and reduction peaks on ferrous metals in tosylic acid (see Figure 4.5). The absence of the other pair of redox current peaks indicated that the electrodeposited PANI film may not have been protonated EM salt, which is probably associated with electrochemical reactions between PANI and the oxide film on the aluminium electrode. It has also been reported that the electrodeposited PANI could form a non-protonated PANI aluminium salt in the pores of the aluminium oxide film [Runge-Marchese and McNallan 1998].

Figure 6.12 Cyclic voltammogram of 15.5 cycles of the electrodeposition of PANI on a one-piece AA1100 electrode in 1 M tosylic acid with 0.16 M aniline

Figure 6.13 Photograph of the electrodeposited PANI film using cyclic voltammetry on the AA1100 one-piece electrode in 1 M tosylic acid with 0.16 M aniline after cathodic pre-treatment for 5 minutes

PANI was also deposited on a one-piece electrode using the PS method. As presented in Figure 6.14 (a), the negative current responses of cathodic polarisation at a static potential of -0.9 V increased as a function of time, probably due to the hydrogen evolution. After cathodic pre-treatment for 5 minutes, PANI was electrodeposited on the AA1100 electrode in the same electrolyte. The current of the electrodeposition increased from 0.6 mA/cm² to

3 mA/cm², which further confirmed the effectiveness of the cathodic pre-treatment. The electrodeposited PANI on the AA1100 electrode was an even, dark-green film without any exposed metal substrate, as shown in Figure 6.15. By using a surface profiler, the thickness of the deposited PANI film was found to be around 30 μ m.

Figure 6.14 (a) The cathodic pre-treatment for 5 minutes in 1 M tosylic acid with 0.16 M aniline and (b) chronoamperogram during electrodeposition at a fixed potential of 1.25 V in 1 M tosylic acid with 0.16 M aniline

Figure 6.15 Photograph of the PANI film on the AA1100 one-piece electrode deposited in 1 M tosylic acid with 0.16 M aniline after cathodic pre-treatment for 5 minutes

Figure 6.16 exhibits the FTIR transmission spectroscopy obtained from the electrodeposited PANI using the PS method in tosylic acid after the sample was placed in ambient air for four weeks. The peaks at about 1481 cm^{-1} and 1575 cm^{-1} are due to the quinoid (Q) and bensenoid (B) ring stretch. A strong band at around 1117 cm^{-1} in the PANI was related to the delocalisation of electron [Salaneck *et al.* 1986]. The almost equal intensity of these two peaks indicated that deposited PANI could be in the EM state [Neoh *et al.* 1993; Kang *et al.* 1998]. Another informative peak at 1299 cm^{-1} could be due to the C-N stretching absorption in QBQ units, further suggesting that the deposited PANI should be in the conducting EM state. The peaks at 802 and 2941 cm^{-1} are due to aromatic C-H bending [Lu *et al.* 2002]. In general, it was found that the characteristic peaks of electrodeposited PANI on AA1100 were similar to the ones on stainless steel 304 (SS304) and mild steel, indicating the identical structure of PANI, i.e. in the EM state on the three different metal substrates in ambient air.

Figure 6.16 FTIR spectrum of the electrodeposited PANI at 1.25 V on one-piece AA1100 electrode in 1 M tosylic acid with 0.16 M aniline after cathodic pre-treatment for 5 minutes

The SEM images shown in Figure 6.17 exhibit the AA1100 electrode after cathodic pre-treatment and PANI electrodeposition. As shown in Figure 6.17 (a), after the cathodic pre-treatment for 5 minutes, the metal was slightly damaged as indicated by the particles on the surface, probably due to the formation of $\text{Al}(\text{OH})_3$, or the second phase containing Al_6Fe , Al_3Fe , and $\text{Al}_{12}\text{Fe}_3\text{Si}_2$. The electrodeposited PANI film on the AA1100 electrode (see Figure 6.17 (b)) was observed to be of a dense, laminated structure, arranged regularly in the direction of the scratches on the metal surface.

Figure 6.17 Micrographs of (a) the AA1100 electrode surface after cathodic pre-treatment (5 minutes) and (b) the electrodeposited PANI film on AA1100 one-piece electrode after cathodic pre-treatment for 5 minutes in 1 M tosylic acid with 0.16 M aniline

6.4 Corrosion Evaluation Testing of the Electrodeposited PANI Film

6.4.1 Corrosion Testing of Electrodeposited PANI on a One-Piece AA1100 Electrode

Anti-corrosion properties of the electrodeposited PANI film on the AA1100 one-piece electrode were evaluated using potentiodynamic polarisation. As shown in Figure 6.18, the AA1100 electrode with complete PANI coverage was polarised in aerated 0.5 M NaCl solution at a scan rate of 0.2 mV/s. The bare AA1100 electrode was also tested under the same conditions for comparison. With the existence of a PANI film, the AA1100 substrate exhibited obvious passive behaviour and the pitting potential E_{pit} was -0.52 V, which is 0.13 V more positive than the corresponding E_{pit} of the bare AA1100 alloy (-0.65 V). In addition, the current density approached 1.2×10^{-4} mA/cm² in the passive region and this current density is 20 times less than that of the bare AA1100 alloy. This suggests

that the PANI film significantly improves protection to localised corrosion of AA1100. It was also found that the PANI coated AA1100 produces a larger cathodic current than the bare AA1100 electrode, which is similar to a phenomenon reported by Conney *et al.* [Conroy and Breslin 2003]. This result suggests that PANI could have enhanced passivation of the aluminium by behaving as an effective cathode.

Figure 6.18 Comparison of potentiodynamic polarisation curves (scan rate 0.2 mV/s) of PANI coated AA1100 and bare AA1100 in 0.5 M NaCl solution (pH $\approx$ 5.8)

6.4.2 Anti-Corrosion Performance and Mechanism of the Electrodeposited PANI Film on an AA1100 WBE

A WBE coated with incomplete PANI using an electrodeposition process, as described in Figure 6.6, was also studied in aerated 0.5 M NaCl solution to test its anti-corrosion performance under free corrosion conditions. Figure 6.19 shows both the APC maps of an incomplete PANI coverage and the corresponding galvanic current (GC) maps, in order to

study the relationship between the PANI deposits and its corrosion performance. When the photo (Figures 6.19 (a)) and the APC map (Figures 6.19 (b)) were carefully examined and compared with the GC maps (Figures 6.19 (c) and (d)), it was observed that the cathodic areas were mainly locations with more deposits. This suggests that the PANI deposits behaved as cathodes over the WBE surface. The major anodic areas on the WBE are mainly located at areas with fewer PANI deposits, for instance the anodes shown in Figures 6.19 (c) and (d) are located at neighbouring wires next to the cathodes. The anodic current values decreased with the extension of electrode exposure, as indicated in Figures 6.19 (c) and (d), the maximum anodic current value decreased from 0.321 mA/cm^2 to 0.168 mA/cm^2 . This result suggests that the aluminium electrode with the PANI deposit underwent a passivation process, in which the PANI behaved as an effective cathode.

Figure 6.19 Comparison among (a) photograph of an AA1100 WBE after 60 minutes of potentiostatic electrodeposition at 1.25 V; (b) APC map after 20 minutes of PANI electrodeposition; (c) and (d) GC maps after 5 and 10 minutes immersion in 0.5 M NaCl solution, respectively

A WBE covered completely with a PANI layer was tested in aerated 0.5 M NaCl solution under free corrosion conditions. The open-circuit potential (OCP) was recorded continuously, along with galvanic current measurements; the latter were performed without any interfering with the corrosion process. Thus, both the galvanic activities on the electrode surface and the resulting potential changes could be monitored. Figure 6.20

shows the OCP variation. The parallel lines are the equipment noise left by the galvanic current measurements with no influence on the corrosion process. The OCP was initially found to be around -0.68 V and dropped to -0.72 V within 10 minutes, then, it increased quickly to -0.71 V after another 15 minutes. After the brief drop-and-increase process, the OCP decreased gradually in the following 24 hours. It was also found that the OCP of the PANI coated AA1100 was more noble than the OCP of bare AA1100. After 17 hours, the OCP of the PANI coated AA1100 decreased continuously and became lower than the OCP of the bare metal. It is possible that PANI-EM was reduced within 17 hours to a non-electroactive LE state by the metal substrate. The PANI-LE state behaved in a similar manner to a barrier layer and prevented the access of oxygen to the metal surface. According to the work of Cogan *et al.*, aluminium alloys dominated the mixed potential of the PANI-metal system, and quickly reduced the PANI into LE state [Cogan *et al.* 2000]. These results are basically in agreement with their reports, but due to the different application method, the passive film formed during the anodic electrodeposition of PANI could retard PANI's reduction from the EM to LE states.

Figure 6.20 OCP vs. time of the PANI coated AA1100 in aerated 0.5 M NaCl solution

Figure 6.21 shows the galvanic current maps during the OCP measurement. Large anodic and cathodic currents were recorded with the maximum anodic current value reaching 0.183 mA/cm^2 , indicating highly active galvanic reactions between the PANI film and the aluminium substrate. With the extension of the corrosion exposure to 1 hour, followed by 3 and 16 hours, the anode currents decreased rapidly. For instance, the current density of the major anode as indicated in Figure 6.21 (b) decreased, as indicated in Figure 6.21 (c), and was later replaced by new anodes with less current density, as shown in Figure 6.21 (d).

Figure 6.21 GC maps of PANI coated AA1100 WBE in 0.5 M NaCl solution after (a) 10 minutes, (b) 1 hour, (c) 3 hours, and (d) 13 hours of immersion

By analysing additional GC maps, as illustrated in Figure 6.22, it was found that the corrosion process appeared to be more general since the distribution of anodes was random and changed with time. It was interesting to observe from these GC maps that, once a certain area behaved as an anode, this area would not act as a major anode in the following testing. Since the electrodeposited PANI film was found to be in the EM state by FTIR, this observation could suggest that the corrosion protection of PANI on the AA1100 could be achieved by the conversion of PANI from the EM to the LE state, which enhanced the passive film on the metal surface. As a result, the metal with the enhanced passive film would not behave as a major anode(s) over a long period of corrosion testing.

Figure 6.22 GC maps of PANI coated AA1100 WBE in 0.5 M NaCl solution after (a) 10 minutes, (b) 1 hour, (c) 3 hours, (d) 8 hours, (e) 13 hours, and (f) 17 hours of immersion. The dotted cycles indicate the location of major anode(s)

Figure 6.23 illustrates the variations of maximum current ($i_{\max}$) and total current (i_{tot}) over a PANI coated AA1100 WBE and also over a bare AA1100 WBE. It can be seen clearly that with the extension of exposure, the i_{tot} and $i_{\max}$ values over the PANI coated WBE surface decreased rapidly. It was observed that after 10 hours, the $i_{\max}$ value from the PANI coated WBE became smaller than that from a bare AA1100 WBE. This suggests that the PANI coating minimises localised corrosion on the AA1100 surface, which is indicated by the $i_{\max}$ value. However, with PANI coating, general corrosion rates, which are reflected by the i_{tot} values, are higher than those without PANI coating. This result suggests that the corrosion pattern of AA1100 with a PANI film is more like general rather than localised corrosion.

(a)

(b)

Figure 6.23 Comparison of (a) $i_{\max}$ and (b) i_{tot} between PANI coated and bare AA1100 WBEs

Therefore, based on the GC measurement, $i_{\max}$, and i_{tot} monitoring, it is believed that the corrosion protection properties of PANI could be attributed to its capability to enhance the passive film on aluminium surfaces through galvanic coupling with the aluminium

substrate. The passive film of aluminium alloy is defective (compared to SS304, AA1100 would show a passivation at lower potential), especially under attacks of chloride ions. With the help of the PANI film, the mixed potential of the PANI-metal system is shifted to positive, as illustrated by Figure 6.24. Additionally, oxygen reduction is accelerated on the metal surface, as suggested by the cathodic polarisation curve results shown in Figure 6.18. By these two means, the PANI film enhances the passive film on the aluminium alloy surface, and consequently, the existence of the PANI film reduces the corrosion currents in both the polarisation and OCP measurements. This passive film enhancement mechanism is also supported by the decreasing current density of the major anode recorded by the GC map during the first 17 hours of corrosion testing in 0.5 M NaCl solution. On the other hand, the enhancement of the passive film could also cause PANI reduction to the non-electroactive LE state, which only behaves as a barrier layer that could only have minor effect for reducing corrosion.

Figure 6.24 Schematic illustration of the anti-corrosion mechanism of PANI on AA1100 in near neutral chloride with solution

The results reported above indeed suggested that the PANI layer, without a top coating, could lead to an increase in the general corrosion of aluminium. However, the most serious concern for aluminium is localised corrosion, not the general form of corrosion. This is because general aluminium corrosion is very slow and can be easily overcome by applying a layer of top coating. This investigation has clearly shown that PANI coating could help overcome the most destructive form of aluminium corrosion i.e. localised corrosion.

CHAPTER 7

Conclusions & Future Work

7.1 Conclusions

This project has investigated the direct electrodeposition of an electroactive PANI coating on stainless steel 304 (SS304), mild steel and aluminium alloy (AA1100) for anti-corrosion applications. Key results and findings are:

- WBE has been demonstrated to be an electrochemical method to understand the PANI electrodeposition and anti-corrosion mechanism on ferrous and aluminium alloys. Good correlation has been found between the anodic polarisation current (APC) mapping during electrodeposition, galvanic current (GC) mapping during the corrosion testing, and the actual PANI deposits / corrosion products distribution. WBE can reliably reproduce the electrochemical behaviours of a PANI coating on one-piece electrode.
- The APC maps have been proven to be useful in monitoring, understanding, and optimising PANI electrodeposition processes. If an AA1100 electrode was not pre-treated, APC maps measured by WBE method would show a localised anodic

current distribution pattern, which corresponds well with the actual non-uniform PANI deposits. After pre-treatments, however, APC maps would display a more random anodic current distribution, leading to PANI coatings with full coverage of the electrode surface. With the assistance of the APC maps, improvements to surface pre-treatment processes have been successfully made. A pre-treatment technique developed for mild steel involved electrode passivation in an aniline free oxalic acid solution at potentials between -0.4 and 1.0 V. The subsequent initiation of electrodeposition was performed at 1.8 V, a potential more positive than the necessary potential (usually at ~ 0.9 V) for PANI deposition. A novel pre-treatment technique developed for AA1100 involved cathodic polarisation of the AA1100 electrode in p-toluenesulfonic (tosylic) acid. This new pre-treatment technique has been found to improve both electrodeposition uniformity and electrodeposition efficiency. After pre-treatments, both mild steel and AA1100 surfaces were successfully electrodeposited with PANI coatings that fully covered the electrode surfaces.

- The GC maps have been found to be effective for evaluating the anti-corrosion performance and for studying the anti-corrosion mechanism of electrodeposited PANI coatings. A correlation between GC and APC maps was discovered: APC maps measured during PANI electrodeposition correlated with the corrosion behaviour of the PANI coating. Electrode areas with higher anodic currents in APC maps corresponded

well with the cathodic sites in GC maps, suggesting that PANI deposits behaved as effective cathodes. Electrode areas with lower anodic currents in APC maps corresponded well with the anodic sites in GC maps, suggesting that PANI-free areas behaved as corrosion anodes.

- Potentiodynamic polarisation and open-circuit potential (OCP) measurements were also carried out to study the anti-corrosion properties of electrodeposited PANI coatings.

It has been found that PANI offers significant protection to localised corrosion of SS304 and AA1100 by ennobling the pitting potential of PANI coated electrodes for about 0.18 V and 0.13 V, respectively, although the corrosion protection provided by PANI coatings to mild steel appeared to be less significant. It is believed that PANI coating provided corrosion protection to stainless steel, mild steel, and aluminium alloys by an anodic protection mechanism. In addition, SS304 / mild steel one-piece electrodes and WBEs with incomplete PANI coverage were investigated in order to further understand the anti-corrosion mechanism of PANI coatings.

- Fourier transformed infrared (FTIR) spectroscopy has indicated that the electrodeposited PANI using potentiostatic method is emeraldine(EM) state on SS304, mild steel and AA1100. Other material characterisation methods involve scanning electron microscope / field emission scanning electron microscope (SEM / FESEM). It

is evident that the electrodeposited PANI coating using cyclic voltammetric and potentiostatic method has a similar micro-structure when PANI was deposited on SS304 in H_2SO_4 acid. It was observed that the deposited PANI coatings on the mild steel and AA1100 in different electrolytes both possess laminated structures.

7.2 Future Work

- The WBE method has been proven to be an effective tool for monitoring, characterising and optimising the electrodeposition processes and anti-corrosion performance of PANI coatings. The current work has been completed in terms of the corrosion behaviour of non-uniformly electrodeposited PANI coating. However, there are a few possible areas which could also contribute to understanding the anti-corrosion performance of the electrodeposited PANI coating.
- Although it is experimentally evident that the exposed metal surface of SS304 was free of corrosion products, the explanation of this phenomenon requires further confirmation from other evidences, such as potential distribution mapping by WBE and *in-situ* FTIR. In addition, the galvanic activities of the stainless steel with incomplete PANI coverage when the OCP was in a low level has not been fully understood.

- The corrosion performance of the electrodeposited PANI coating on stainless steel, mild steel and aluminium alloys caused by the dopant effect has not been fully studied. Since the electrolytes act not only as electrochemical media, but also as doping agents during the electrodeposition of PANI on metal substrates, the electrolytes could have a significant effect on the structure of PANI coating as well as its growth rate. The corrosion performance could thus be affected by the entrapped electrolyte in the polymers.
- PANI has been found to offer a significant localised corrosion protection to AA1100. From a practical point of view, however, the electrodeposition of PANI on aluminium alloy 2024-T3 (AA2024-T3) is more useful, since this alloy is widely used in industries with an unsatisfactory anti-corrosion performance. Preliminary work indicates that PANI can be efficiently electrodeposited on AA2024-T3 in tosylic acid (omitted in this thesis for consistency). The anti-corrosion mechanism of PANI coated AA2024-T3 is also of importance and originality because of the challenges encountered in the complex interaction between PANI and the AA2024-T3 substrate.

- Other future work might involve the optimisation of the WBE based technique. The surface area of the WBE probe can be further reduced, so that the WBE based method could be used in conjunction with other material characterisation techniques such as SEM and XRD. The studies of electrochemical reactions could also be investigated at a micro-scale level.

LIST OF PUBLICATIONS

Journals:

1. Wang, T., and Tan, Y-J., “Understanding electrodeposition of polyaniline coatings for corrosion prevention applications using the wire beam electrode method”, *Corros. Sci.*, **48** (2006) 2274.
2. Wang, T., and Tan, Y-J., “Electrodeposition of polyaniline on aluminium alloys for corrosion prevention — a study using the wire beam electrode (WBE)”, *Mater. Sci. Eng.: B*, **132** (2006) 48.
3. Tan, Y-J., Wang, T., Liu, T., and Aung N-N., “Studying and Evaluating Anti-Corrosion Coatings and Inhibitors Using the Wire Beam Electrode Method in Conjunction with Electrochemical Noise Analysis”, *Anti-Corrosion Method and Materials*, **53** (2006) 30.
4. Wang, T., and Tan, Y-J., “A New Method for Characterising and Evaluating Anodically Electrodeposited Anti-Corrosion Polymer Coatings Using the Wire Beam Electrode”, *J. Appl. Electrochem.*, (accepted for publication, July 2006).

International Conference:

1. Wang, T., Liew S. C., and Tan, Y-J., “Electrodeposition of Polyaniline Coatings for Corrosion Prevention Application”, **2nd International Conference on Advances of Thin Films and Coatings**, 13th~17th July 2004, Singapore.
2. Wang, T., and Tan, Y-J., “Electrodeposition of polyaniline on aluminum alloys for corrosion prevention — a study using the wire beam electrode”, **3rd ICMAT**, 3rd~8th July 2005, Singapore.

REFERENCE

- Ahmad, N. and MacDiarmid, A. G. (1996). "Inhibition of Corrosion of Steels with the Exploitation of Conducting Polymers" *Synth. Met.* **78**: 103-110.
- Akhtar, M., Weakliem, H. A., Paiste, R. M. and Gaughan, K. (1988). "Polyaniline Thin Film Electrochromic Devices" *Synth. Met.* **26**: 203-208.
- Aung, N. N. and Tan, Y.-J. (2004). "A New Method of Studying Buried Steel Corrosion and Its Inhibition Using the Wire Beam Electrode" *Corros. Sci.* **46**: 3057-3067.
- Aykanat, A. and Iroh, J. O. (2002). "Carbon Fiber-Polyaniline Composites: Kinetics of Electrodeposition of Polyaniline onto Carbon Fibers by Cyclic Voltammetry" *Journal of Adhesion* **78**: 629-643.
- Barbero, C., Kotz, R., Kalaji, M., Nyholm, L. and Peter, L. M. (1993). "Ion Exchange and Memory Effects in Polyaniline" *Synth. Met.* **55**: 1545-1551.
- Bernard, M. C., Joiret, S., Goff, A. H.-L. and Phong, P. V. (2001). "Protection of Iron against Corrosion Using a Polyaniline Layer. I. Polyaniline Electrodeposit" *J. Electrochem. Soc.* **148**: 12-16.
- Boehni, H. and Uhlig, H. H. (1969). "Environmental Factors Affecting the Critical Pitting Potential of Aluminum" *J. Electrochem. Soc.* **116**: 906-910.
- Breslin, C. B., Fenelon, A. M. and Conroy, K. G. (2005). "Surface Engineering: Corrosion Protection Using Conducting Polymers" *Materials and Design Tribology* **26**: 233-237.
- Butler, J. A. V. (1924a). "Studies in Heterogeneous Equilibria I".
- Camalet, J. L., Lacroix, J. C., Aeiyaeh, S., Chane-Ching, K. and Lacaze, P. C. (1996). "Electrodeposition of Protective Polyaniline Films on Mild Steel" *J. Electroanal. Chem.* **416**: 179-182.
- Camalet, J. L., Lacroix, J. C., Aeiyaeh, S., Chane-Ching, K. and Lacaze, P. C. (1998a). "Electrosynthesis of Adherent Polyaniline Films on Iron and Mild Steel in Aqueous Oxalic Acid Medium" *Synth. Met.* **93**: 133-142.
- Camalet, J. L., Lacroix, J. C., Aeiyaeh, S. and Lacaze, P. C. (1998b). "Characterization of Polyaniline Films Electrodeposited on Mild Steel in Aqueous P-Toluenesulfonic Acid Solution" *J. Electroanal. Chem.* **445**: 117-124.

Reference

- Camalet, J.-L., Lacroix, J.-C., Nguyen, T. D., Aeiyaich, S., Pham, M. C., Petitjean, J. and Lacaze, P.-C. (2000). "Aniline Electropolymerization on Platinum and Mild Steel from Neutral Aqueous Media" *J. Electroanal. Chem.* **485**: 13-20.
- Caro, C. A., Zagal, J. H. and Bedioui, F. (2003). "Electrocatalytic Activity of Substituted Metallophthalocyanines Adsorbed on Vitreous Carbon Electrode for Nitric Oxide Oxidation" *J. Electrochem. Soc.* **150**: 95-103.
- Cogan, S. F., Gilbert, M. D., Holleck, G. L., Ehrlich, J. and Jillson, M. H. (2000). "Galvanic Coupling of Doped Polyaniline and Aluminum Alloy 2024-T3" *J. Electrochem. Soc.* **147**: 2143-2147.
- Conroy, K. G. and Breslin, C. B. (2003). "The Electrochemical Deposition of Polyaniline at Pure Aluminium: Electrochemical Activity and Corrosion Protection Properties" *Electrochem. Acta* **48**: 721-732.
- Cook, A., Gabriel, A. and Laycock, N. (2004). "On the Mechanism of Corrosion Protection of Mild Steel with Polyaniline" *J. Electrochem. Soc.* **151**: 529-535.
- Dao, L. H., Nguyen, M. T., Chevalier, J. W., Do, T. N., Bergeron, J. Y. and Paynter, R. (1991). "Processible, Stable Conducting Polymers for Electrochromic Display and Window Applications". 49th Annual Technical Conference -ANTEC '91, May 5-9 1991, Montreal, Que, Can. **37**: 861-863.
- Davis, J. R. (1999). "Understanding the Corrosion Behavior of Aluminum", ASM international: 25-43.
- Dawson, J. L. and Ferreira, M. G. S. (1986). "Electrochemical Studies of the Pitting of Austenitic Stainless Steel." *Corros. Sci.* **26**: 1009-1026.
- DeBerry, D. W. (1985). "Modification of the Electrochemical and Corrosion Behavior of Stainless Steels with an Electroactive Coating" *J. Electrochem. Soc.* **132**: 1022-1026.
- Deore, B. A., Hachey, S. and Freund, M. S. (2004). "Electroactivity of Electrochemically Synthesized Poly(Aniline Boronic Acid) as a Function of Ph: Role of Self-Doping" *Chemistry of Materials* **16**: 1427-1432.
- Dominis, A. J., Spinks, G. M. and Wallace, G. G. (2003). "Comparison of Polyaniline Primers Prepared with Different Dopants for Corrosion Protection of Steel" *Prog. Org. Coat.* **48**: 43-49.
- Donovan, P. D. (1986). "Protection of Metals from Corrosion in Storage and Transit". John Wiley & Sons, London.

Reference

- Du, G., Avlyanov, J., Wu, C. Y., Reimer, K. G., Benatar, A., MacDiarmid, A. G. and Epstein, A. J. (1997). "Inhomogeneous Charge Transport in Conducting Polyaniline" *Synth. Met.* **85**: 1339-1340.
- Dung Nguyen, T., Camalet, J.-L., Lacroix, J.-C., Aeiyaeh, S., Pham, M. C. and Lacaze, P.-C. (1999). "Polyaniline Electrodeposition from Neutral Aqueous Media: Application to the Deposition on Oxidizable Metals" *Synth. Met.* **102**: 1388-1389.
- Ebadi, M., Alexiou, C. and Lever, A. B. P. (2001). "The Reduction of Oxygen and Hydrogen Peroxide on Dinuclear Ruthenium Phthalocyanine Electrocatalytic Surfaces" *Canadian Journal of Chemistry* **79**: 992-1001.
- Eftekhari, A. (2001). "Aluminum as a Suitable Substrate for the Deposition of Conducting Polymers: Application to Polyaniline and Enzyme-Modified Electrode" *Synth. Met.* **125**: 295-300.
- Evans, U. R. (1951). "Stress Corrosion: Its Relation to Other Types of Corrosion" *Corrosion* **7**: 238-244.
- Evans, U. R. (1981). "An Introduction to Metallic Corrosion,". Edward Arnold, London.
- Fontana, M. G. (1986). "Corrosion Engineering". McGraw-Hill Book Company, NY, USA.
- Frankel, G. S. (1998). "Pitting Corrosion of Metals: A Review of the Critical Factors" *J. Electrochem. Soc.* **145**: 2186-2198.
- Frankenthal, R. P. and Kuger, J. (1978). "Passivity of Metals". Princeton, N.J., The Electrochemical Society.
- Funke, W. and Haagen, H. (1978). "Empirical or Scientific Approach to Evaluate the Corrosion Protective Performance of Organic Coatings." *Industrial & Engineering Chemistry, Product Research and Development* **17**: 50-53.
- Funke, W., Leidheiser, H. J., Dickie, R. A., Dinger, H., Fischer, W., Haagen, H., Herrmann, K., Mosle, H. G., Oechsner, W. P., Ruf, J., Scantlebury, J. S., Svoboda, M. and Sykes, J. M. (1986). "Unsolved Problems of Corrosion Protection by Organic Coatings: A Discussion." *Journal of Coatings Technology* **58**: 79-86.
- Gao, J., Heeger, A. J., Campbell, I. H. and Smith, D. L. (1999). "Direct Observation of Junction Formation in Polymer Light-Emitting Electrochemical Cells" *Physical Review B (Condensed Matter)* **59**: 2482-2485.

Reference

- Gasparac, R. and Martin, C. R. (2001). "Investigations of the Mechanism of Corrosion Inhibition by Polyaniline. Polyaniline-Coated Stainless Steel in Sulfuric Acid Solution" *J. Electrochem. Soc.* **148**: B138-B145.
- Gasparac, R. and Martin, C. R. (2002). "The Effect of Protic Doping Level on the Anticorrosion Characteristics of Polyaniline in Sulfuric Acid Solutions" *J. Electrochem. Soc.* **149**: 409-413.
- Gasparac, R., Martin, C. R., Stupnisek-Lisac, E. and Mandic, Z. (2000). "In Situ and Ex Situ Studies of Imidazole and Its Derivatives as Copper Corrosion Inhibitors II. Ac Impedance, Xps, and Sims Studies" *J. Electrochem. Soc.* **147**: 991-998.
- Grzeszczuk, M. (1994). "Electrochemical Study of Polyaniline Film Electrodes and Their Modifications - Impedance Spectroscopy Measurements on Hydrogen Evolution Reaction" *Electrochem. Acta* **39**: 1809-1816.
- Hatchett, D. W., Josowicz, M. and Janata, J. (1999). "Comparison of Chemically and Electrochemically Synthesized Polyaniline Films" *J. Electrochem. Soc.* **146**: 4535-4538.
- He, J., Gelling, V. J., Tallman, D. E., Bierwagen, G. P. and Wallace, G. G. (2000). "Conducting Polymers and Corrosion III. A Scanning Vibrating Electrode Study of Poly(3-Octyl Pyrrole) on Steel and Aluminum" *J. Electrochem. Soc.* **147**: 3667-3672.
- Heeger, A. J. (1991). "Conducting Polymers: The Route from Fundamental Science to Technology". Science and Applications of Conducting Polymers. Papers from the 6th European Physical Society Industrial Workshop, 28-31 May 1990, Lofthus, Norway. 1-12.
- Heeger, A. J. (2001). "Disorder-Induced Metal-Insulator Transition in Conducting Polymers" *Journal of Superconductivity* **14**: 261-268.
- Hermas, A. A., Nakayama, M. and Ogura, K. (2005). "Enrichment of Chromium-Content in Passive Layers on Stainless Steel Coated with Polyaniline" *Electrochem. Acta* **50**: 2001-2007.
- Huang, S.-C., Huang, S.-M., Ng, H. and Kaner, R. B. (1993). "Polyaniline Capacitors" *Synth. Met.* **57**: 4047-4052.
- Huang, W. S. and MacDiarmid, A. G. (1993). "Optical Properties of Polyaniline" *Polymer* **34**: 1833-1845.
- Huerta-Vilca, D., de Moraes, S. R. and de Jesus Motheo, A. (2004). "Anodic Treatment of Aluminum in Nitric Acid Containing Aniline, Previous to Deposition of Polyaniline and Its Role on Corrosion" *Synth. Met.* **140**: 23-27.

Reference

- Huerta-Vilca, D., De Moraes, S. R. and De Jesus Motheo, A. (2005). "Aspects of Polyaniline Electrodeposition on Aluminium" *J. Solid State Electrochem.* **9**: 416-420.
- Hull, R. O. (1943). "What Electrodeposited Surfaces Offer, Today and Tomorrow" *Electrical Manufacturing* **32**: 100-102.
- Iroh, J. O., Zhu, Y., Shah, K., Levine, K., Rajagopalan, R., Uyar, T., Voevodin, N. N., Donley, M., Mantz, R., Johnson, J., Balbyshev, V. N. and Khramov, A. N. (2003). "Electrochemical Synthesis: A Novel Technique for Processing Multi-Functional Coatings" *Prog. Org. Coat.* **47**: 365-375.
- Jelle, B. P., Hagen, G., Hesjevik, S. M. and Odegard, R. (1993). "Reduction Factor for Polyaniline Films on Ito from Cyclic Voltammetry and Visible Absorption Spectra" *Electrochem. Acta* **38**: 1643-1647.
- Johnson, B. J. and Park, S.-M. (1996). "Electrochemistry of Conductive Polymer" *J. Electrochem. Soc.* **143**: 1269-1276.
- Jones, D. A. (1996). "Principles and Prevention of Corrosion". Upper Saddle River, NJ, Prentice Hall.
- Kaesche, H. (1963). "Investigation of Uniform Dissolution and Pitting of Aluminum Electrodes" *Werkst, Koros.*, **14**: 557-564.
- Kang, E. T., Neoh, K. G. and Tan, K. L. (1998). "Polyaniline: A Polymer with Many Interesting Intrinsic Redox States" *Progress in Polymer Science (Oxford)* **23**: 277-324.
- Karami, H., Mousavi, M. F. and Shamsipur, M. (2003). "A New Design for Dry Polyaniline Rechargeable Batteries" *Journal of Power Sources* **117**: 255-259.
- Kendig, M., Hon, M. and Warren, L. (2003). "'Smart' Corrosion Inhibiting Coatings" *Prog. Org. Coat.* **47**: 183-189.
- Kilmartin, P. A., Trier, L. and Wright, G. A. (2002). "Corrosion Inhibition of Polyaniline and Poly(O-Methoxyaniline) on Stainless Steels" *Synth. Met.* **131**: 99-109.
- Kinlen, P. J., Lawless, I. M. and Menon, V. (2004). "Anodically Formed Intrinsically Conductive Polymer-Aluminum Oxide Composite as a Coating on Aluminum". USA, McDonnell Douglas Corporation: 40.
- Kinlen, P. J., Menon, V. and Ding, Y. (1999). "A Mechanistic Investigation of Polyaniline Corrosion Protection Using the Scanning Reference Electrode Technique" *J. Electrochem. Soc.* **146**: 3690-3695.
- Kitani, A., Kaya, M., Yano, J., Yoshikawa, K. and Sasaki, K. (1986). "'Polyaniline': Formation Reaction and Structure." *Synth. Met.* **18**: 341-346.

Reference

- Kraljic, M., Mandic, Z. and Duic, L. (2002). "Inhibition of Steel Corrosion by Polyaniline Coatings" *Corros. Sci.* **45**: 181-198.
- Krylova, I. A. and Zubov, P. I. (1984). "Formation and Properties of Coatings Produced by Electrodeposition of Paints." *Prog. Org. Coat* **12**: 129-141.
- Lacroix, J.-C., Camalet, J.-L., Aeiyaeh, S., Chane-Ching, K. I., Petitjean, J., Chauveau, E. and Lacaze, P.-C. (2000). "Aniline Electropolymerization on Mild Steel and Zinc in a Two-Step Process" *J. Electroanal. Chem.* **481**: 76-81.
- Lee, C. Y., Song, H. G., Jang, K. S., Oh, E. J., Epstein, A. J. and Joo, J. (1999). "Electromagnetic Interference Shielding Efficiency of Polyaniline Mixtures and Multilayer Films" *Synth. Met.* **102**: 1346-1349.
- Leidheiser, H. J., Mills, D. J. and Bilder, W. (1987). "Permeability of a Polybutadiene Coating to Ions, Water and Oxygen." Proceedings of the Symposium on Corrosion Protection by Organic Coatings. **87-2**: 23-36.
- Li, W., Johnson, C. L. and Wang, H.-L. (2004). "Preparation and Characterization of Monolithic Polyaniline-Graphite Composite Actuators" *Polymer* **45**: 4769-4775.
- Lifka, B. W., Schweitzer, w. ed. "Corrosion of Aluminum and Aluminum Alloys". Marcel Dekker, Inc.
- Lim, K. S. (1995). "Preparation and Characterisation of Conductive Polyaniline Film". School of Applied Science. Singapore, Nanyang Technological University: 1 v. (various pagings).
- Lin, L. F., Chao, C. Y. and Macdonald, D. D. (1981). "A Point Defect Model for Anodic Passive Films. II. Chemical Breakdown and Pit Initiation" *J. Electrochem. Soc.* **128**: 1194-1198.
- Lu, W., Smela, E., Adams, P., Zuccarello, G. and Mattes, B. R. (2004). "Development of Solid-in-Hollow Electrochemical Linear Actuators Using Highly Conductive Polyaniline" *Chemistry of Materials* **16**: 1615-1621.
- Lu, W.-K., Elsenbaumer, R. L., Chen, T. and Kulkarni, V. G. (1998). "Corrosion Protection of Metals by Conductive Polymers. III. Improved Performance and Inhibition in NaCl". Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV. Symposium, 1-5 Dec. 1997, Boston, MA, USA. 653-658.
- Lu, X., Ng, H. Y., Xu, J. and He, C. (2002). "Electrical Conductivity of Polyaniline-Dodecylbenzene Sulphonic Acid Complex: Thermal Degradation and Its Mechanism" *Synth. Met.* **128**: 167-178.

Reference

- MacDiarmid, A. G. (2001). "Nobel Lecture: "Synthetic Metals": A Novel Role for Organic Polymers" *Reviews of Modern Physics* **73**: 701-712.
- MacDiarmid, A. G. (2001). "Synthetic Metals: A Novel Role for Organic Polymers" *Synth. Met.* **125**: 11-22.
- MacDiarmid, A. G., Chiang, J. C., Richter, A. F. and Epstein, A. J. (1986). "Polyaniline: A New Concept in Conducting Polymers." *Synth. Met.* **18**: 285-290.
- MacDonald, D. D. and Urquidi-MacDonald, M. (1986). "Distribution Functions for the Initiation of Pitting Attack on Passive Alloys." *Indian Journal of Technology* **24**: 485-491.
- Malik, M. A., Galkowski, M. T., Bala, H., Grzybowska, B. and Kulesza, P. J. (1999). "Evaluation of Polyaniline Films Containing Traces of Dispersed Platinum for Protection of Stainless Steel against Corrosion" *Electrochem. Acta* **44**: 2157-2163.
- Massiani, Y., Crousier, J., Picq, G. and Vennereau, P. (1987). "Role of the Structure and of the Chromium Content in the Electrochemical and Photo Electrochemical Behaviours of the (44-X)Fe-6b-36ni-14p-Xcr Alloys." *Electrochem. Acta* **32**: 1343-1351.
- Mayne, J. E. O. (1964). "Mechanism of Protection by Organic Coatings" *Institute of Metal Finishing -- Transactions* **41**: 121-126.
- Mayne, J. E. O. and Scantlebury, J. D. (1970). "Ionic Conduction on Polymer Films. II. Inhomogeneous Structure of Varnish Films" *British Polymer Journal* **2**: 240-243.
- McAndrew, T. P. and Miller, S. A. (1993). "Reduction of Aqueous Fluid Drag with Poly(Vinylamine)". Proceedings of the American Chemical Society Division of Polymeric Materials - Science and Engineering, Apr 18-23 1993, Denver, CO, USA. **68**: 195-196.
- Miller, C. J. and Majda, M. (1984). "Microporous Aluminum Oxide Films as Matrices for Immobilization of Electroactive Polymers at Electrodes." International Society of Electrochemistry 35th Meeting - Program., Berkeley, CA, USA. 963-965.
- Nernst, W. and Bose, E. (1898). "Osmotic Theory of the Galvanic Cell" *Zeitschrift fur Elektrochemie* **5**: 233-235.
- Niu, L., Latonen, R.-M., Kvarnstrom, C. and Ivaska, A. (2004). "Influence of Charged Tail Groups of Self-Assembled Monolayers on Electrodeposition of Polyaniline" *Electrochem. Acta* **49**: 4455-4460.
- Nishimura, R. and Kudo, K. (1990). "Effects of Passive Films Formed on Iron, Nickel and Austenitic Stainless Steels (SS 304 and SS 316) on Pitting Corrosion" *Corros. Sci.* **31**: 479-484.

- Okada, T. (1985). "Theory of Perturbation-Initiated Pitting." *J. Electrochem. Soc.* **132**: 537-544.
- Osterwald, J. (1981). "Contribution to the Theory of Anodic Pitting." Proceedings of an International Symposium Honoring Professor H. H. Uhlig on his 75th Birthday: Corrosion and Corrosion Protection., Denver, CO, USA. **81-8**: 112-119.
- Pourbaix, M. (1970). "Significant of Protection Potential in Pitting and Intergranular Corrosion" *Corrosion* **26**,: 431-438.
- Pourbaix, M., Klimzack-Mathieu, L. and Mertens, C. (1963). "Potentiokinetic and Corrosimetric Investigations of Corrosion Behaviour of Alloy Steels" *Corros. Sci.* **3**: 239-259.
- Prasad, K. R. and Munichandraiah, N. (2002). "Electrocatalytic Efficiency of Polyaniline by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy Studies" *Synth. Met.* **126**: 61-68.
- Rajagopalan, R. and Iroh, J. O. (2001). "Development of Polyaniline-Polypyrrole Composite Coatings on Steel by Aqueous Electrochemical Process" *Electrochem. Acta* **46**: 2443-2455.
- Rajagopalan, R. and Iroh, J. O. (2002). "Corrosion Performance of Polyaniline-Polypyrrole Composite Coatings Applied to Low Carbon Steel" *Surface Engineering* **18**: 59-63.
- Rajagopalan, R. and Iroh, J. O. (2002). "A One-Step Electrochemical Synthesis of Polyaniline-Polypyrrole Composite Coatings on Carbon Fibers" *Electrochem. Acta* **47**: 1847-1855.
- Rajendra Prasad, K. and Munichandraiah, N. (2001). "Potentiodynamic Deposition of Polyaniline on Non-Platinum Metals and Characterization" *Synth. Met.* **123**: 459-468.
- Ramanarayanan, T. A. (2003). "Electrochemical Techniques for Corrosion Quantification". *Characterization of Materials*. New Jersey, USA, John Wiley & Sons, Inc.
- Runde, W., Conradson, S. D., Efur, D. W., Lu, N., VanPelt, C. E. and Tait, C. D. (2002). "Solubility and Sorption of Redox-Sensitive Radionuclides (Np, Pu) in J-13 Water from the Yucca Mountain Site: Comparison between Experiment and Theory" *Applied Geochemistry* **17**: 837-853.
- Runge-Marchese, J. M. and McNallan, M. J. (1998). "Electrochemical Formation of a Composite Polymer - Aluminum Oxide Film". Proceedings of the 1998 56th Annual Technical Conference, ANTEC. Part 2 (of 3), Apr 26-30 1998, Atlanta, GA, USA. **2**: 1392-1396.

Reference

- Salaneck, W. R., Lundstrom, I., Huang, W.-S. and MacDiarmid, A. G. (1986). "Two-Dimensional-Surface 'State Diagram' for Polyaniline." *Synth. Met.* **13**: 291-297.
- Santos, J. R. J., Mattoso, L. H. C. and Motheo, A. J. (1998). "Investigation of Corrosion Protection of Steel by Polyaniline Films" *Electrochem. Acta* **43**: 309-313.
- Sato, N. and Notoya, T. (1967). *J. Electrochem. Soc.* **114**: 585.
- Schauer, T., Joos, A., Dulog, L. and Eisenbach, C. D. (1998). "Protection of Iron against Corrosion with Polyaniline Primers" *Prog. Org. Coat.* **33**: 20-27.
- Schweitzer, P. A., Ed. "Corrosion-Resistant Linings and Coatings". New York., Marcel Dekker, Inc.
- Scotto, V., Traverso, E. and Ventura, G. (1979). "Influence of Non-Metallic Inclusion Nature and Shape on the Pitting Corrosion Susceptibility of 18cr9ni and 17cr11ni2mo Austenitic Stainless Steels." **19**: 237-250.
- Shah, K., Zhu, Y., Akundy, G. S., Iroh, J. O. and Popoola, O. (2001). "Corrosion and Bonding Behaviors of Intrinsically Conductive Polymers on Aluminum (Al 2024-T3)" *Key Engineering Materials* **197**: 111-119.
- Shah, K., Zhu, Y., Iroh, J. O. and Popoola, O. (2001). "Corrosion Protection Properties of Polyaniline-Polypyrrole Composite Coatings on Al 2024" *Surface Engineering* **17**: 405-412.
- Sharland, S. M. (1987). "Review of the Theoretical Modelling of Crevice and Pitting Corrosion." *Corros. Sci.* **27**: 289-323.
- Shim, Y.-B., Won, M.-S. and Park, S.-M. (1990). "Electrochemistry of Conductive Polymers VIII. In Situ Spectroelectrochemical Studies of Polyaniline Growth Mechanisms" *J. Electrochem. Soc.* **137**: 538-544.
- Shirakawa, H. (2001). "Nobel Lecture: The Discovery of Polyacetylene Film-the Dawning of an Era of Conducting Polymers" *Reviews of Modern Physics* **73**: 713-718.
- Shreir, L. L. (1994). "Corrosion". *Corrosion*. Shreir, L. L., Jarman, R. A. and Burstein, G. T. London, Butterworths-Heinemann, Ltd. **4**: 15.
- Smela, E. (1999). "Microfabrication of Ppy Microactuators and Other Conjugated Polymer Devices" *Journal of Micromechanics and Microengineering* **9**: 1-18.
- Spinks, G. M., Dominis, A. J., Wallace, G. G. and Tallman, D. E. (2002). "Electroactive Conducting Polymers for Corrosion Control. Part 2. Ferrous Metals" *J. Solid State Electrochem.* **6**: 85-100.

- Stern, M. and Geary, A. L. (1957). "Electrochemical Polarization" *J. Electrochem. Soc.* **104**: 56-63.
- Stolarczyk, A. and Lapkowski, M. (2001). "Investigation of Gas Separation on Polyaniline Laminar Composite Membranes" *Synth. Met.* **121**: 1385-1386.
- Stoychev, D., Papoutsis, A., Kelaidopoulou, A., Kokkinidis, G. and Milchev, A. (2001). "Electrodeposition of Platinum on Metallic and Nonmetallic Substrates - Selection of Experimental Conditions" *Materials Chemistry and Physics* **72**: 360-365.
- Su, T. M., Kwon, A. H., Lew, B. M. and Kaner, R. B. (1996). "Synthesis and Gas Separation Studies of Substituted Polyaniline Membranes". Proceedings of the 1996 ACS New Orleans Meeting, Mar 24-29 1996, New Orleans, LA, USA. **37**: 670-671.
- Szklarska-Smialowska, Z. (1999). "Pitting Corrosion of Aluminium" *Corros. Sci.*: 1743-1767.
- Tallman, D. E., Pae, Y. and Bierwagen, G. P. (2000). "Conducting Polymers and Corrosion. II. Polyaniline on Aluminum Alloys" *Corrosion* **56**: 401-410.
- Tallman, D. E., Pae, Y., Chen, G., Bierwagen, G. P., Reems, B. and Gelling, V. J. (1998). "Studies of Electronically Conducting Polymers for Corrosion Inhibition of Aluminum and Steel". Proceedings of the 1998 56th Annual Technical Conference, ANTEC. Part 2 (of 3), Apr 26-30 1998, Atlanta, GA, USA. **2**: 1234-1237.
- Tallman, D. E., Spinks, G., Dominis, A. and Wallace, G. G. (2002a). "Electroactive Conducting Polymers for Corrosion Control. Part 1. General Introduction and a Review of Non-Ferrous Metals" *J. Solid State Electrochem.* **6**: 73-84.
- Tallman, D. E., Vang, C., Wallace, G. G. and Bierwagen, G. P. (2002b). "Direct Electrodeposition of Polypyrrole on Aluminum and Aluminum Alloy by Electron Transfer Mediation" *J. Electrochem. Soc.* **149**: 173-179.
- Tallman, D. E. and Wallace, G. G. (1997). "Preparation and Preliminary Characterization of a Poly(4-Vinylpyridine) Complex of a Water-Soluble Polyaniline" *Synth. Met.* **90**: 13-18.
- Talo, A., Forsen, O. and Ylasaari, S. (1999). "Corrosion Protective Polyaniline Epoxy Blend Coatings on Mild Steel" *Synth. Met.* **102**: 1394-1395.
- Tan, C. K. and Blackwood, D. J. (2003). "Corrosion Protection by Multilayered Conducting Polymer Coatings" *Corros. Sci.* **45**: 545-557.
- Tan, Y.-J. (1998). "Monitoring Localized Corrosion Processes and Estimating Localized Corrosion Rates Using a Wire-Beam Electrode" *Corrosion* **54**: 403-413.

- Tan, Y.-J. (2002). "Studying Non-Uniform Electrodeposition Using the Wire Beam Electrode Method" *International Journal of Modern Physics B* **16**: 144-150.
- Tan, Y. J., Bailey, S., Kinsella, B. and Lowe, A. (2000). "Mapping Corrosion Kinetics Using the Wire Beam Electrode in Conjunction with Electrochemical Noise Resistance Measurements" *J.Electrochem. Soc.* **147**: 530-539.
- Tan, Y.-J., Bailey, S. and Kinsella, B. (2001a). "Mapping Non-Uniform Corrosion Using the Wire Beam Electrode Method. I. Multi-Phase Carbon Dioxide Corrosion" *Corros. Sci.* **43**: 1905-1918.
- Tan, Y.-J., Bailey, S. and Kinsella, B. (2001b). "Mapping Non-Uniform Corrosion Using the Wire Beam Electrode Method. II. Crevice Corrosion and Crevice Corrosion Exemption" *Corros. Sci.* **43**: 1919-1929.
- Tan, Y.-J., Bailey, S. and Kinsella, B. (2001c). "Mapping Non-Uniform Corrosion Using the Wire Beam Electrode Method. III. Water-Line Corrosion" *Corros. Sci.* **43**: 1931-1937.
- Tan, Y.-J., Bailey, S. and Kinsella, B. (2002). "Studying the Formation Process of Chromate Conversion Coatings on Aluminium Using Continuous Electrochemical Noise Resistance Measurements" *Corros. Sci.* **44**: 1277-1286.
- Tan, Y.-J. and Lim, K. Y. (2003). "Understanding and Improving the Uniformity of Electrodeposition" *Surface & Coatings Technology* **167**: 255-262.
- Tan, Y.-J. and Lim, K. Y. (2004). "Characterising Nonuniform Electrodeposition and Electrodissolution Using the Novel Wire Beam Electrode Method" *J. Appl. Electrochem.* **34**: 1093-1101.
- Tan, Y.-J. and Shiti, Y. (1991). "Effects of Inhomogeneity in Organic Coatings on Electrochemical Measurements Using a Wire Beam Electrode. Part Ii" *Prog. Org. Coat.* **19**: 257-263.
- Theophilou, N., MacDiarmid, A. G., Djurado, D., Fischer, J. E. and Epstein, A. J. (1989). "Highly Conducting Polyanilines and Polyacetylene/Polyaniline Composites". Electronic Properties of Conjugated Polymers III. Basic Models and Applications. Proceedings of an International Winter School, 11-18 March 1989, Kirchberg, Austria. 29-33.
- Troch-Nagels, G., Winand, R., Weymeersch, A. and Renard, L. (1992). "Electron Conducting Organic Coating of Mild Steel by Electropolymerization" *J. Appl. Electrochem.* **22**: 756-764.
- Uhlig, H. H. (1979). "Passivity in Metals and Alloys" *Corros. Sci.* **19**: 777-791.
- Uruchurtu, J. and Dawson, J. L. (1986). "Noise Analysis of Pure Aluminum under

Different Pitting Conditions" *Materials Sci. Forum* **8**: 113-124.

Wallace, G. G., Spinks, G. M., Kane-Maguire, L. A. P. and Teasdale, P. R. (2003). "Conductive Electroactive Polymers : Intelligent Materials Systems". Publisher: CRC Press, Boca Raton, Florida.

Wessling, B. (1994). "Passivation of Metals by Coating with Polyaniline: Corrosion Potential Shift and Morphological Changes" *Adv. Mater.* **6**: 226-228.

Wessling, B. (2003). "Progress in Science and Technology of Polyaniline and Poly-Ethylenedioxythiophene" *Synth. Met.* **135-136**: 265-267.

Wessling, B. and Posdorfer, J. (1999). "Corrosion Prevention with an Organic Metal (Polyaniline): Corrosion Test Results" *Electrochem. Acta* **44**: 2139-2147.

Wicks, Z. W., Jones, F. N. and Pappas, P. S. (1999). "Organic Coatings : Science and Technology". Wiley-Interscience, New York.

Wilde, B. E. and Williams, E. (1969). "On the Breakdown of Passivity on Stainless Steels in Halide Media" *J. Electrochem. Soc.* **116**: 1539-1540.

Wojkewicz, J.-L., Fauveaux, S. and Miane, J.-L. (2003). "Electromagnetic Shielding Properties of Polyaniline Composites" *Synth. Met.* **135-136**: 127-128.

Wu, C.-l., Zhou, X.-j. and Tan, Y.-j. (1995). "Study on the Electrochemical Inhomogeneity of Organic Coatings" *Prog. Org. Coat.* **25**: 379-389.

Yang, C. Y., Cao, Y., Smith, P. and Heeger, A. J. (1993). "Morphology of Polyaniline in Solution Processed Blends with Poly(Methyl Methacrylate)" *Polymer Preprints, American Chemical Society* **34**: 790.

Yang, Y., Westerweele, E., Zhang, C., Smith, P. and Heeger, A. J. (1995). "Polyaniline Network Electrodes: Enhanced Performance of Polymer Light-Emitting Diodes". Proceedings of the 1995 IS&T's 48th Annual Conference, May 7-11 1995, Washington, DC, USA. 401-405.

Yonezawa, S., Kanamura, K. and Takehara, Z.-i. (1995). "Effects of the Solvent for the Electropolymerization of Aniline on Discharge and Charge Characteristics of Polyaniline" *J. Electrochem. Soc.* **142**: 3309-3313.

Yuxian, S., Hongli, W. and Yuansuo, Z. (2002). "Electric and Electromagnetic Shielding Properties of Highly Conducting Polyaniline Films". Proceedings of International Symposium on Electromagnetic Compatibility, 21-24 May 2002, Beijing, China. 582-585.