# Developing Oil-Immersed Scanning Electrochemical Cell Microscopy for Corrosion

# Yuanjiao Li

Department of Chemistry, McGill University Montreal, Quebec, Canada May, 2022

A thesis submitted to McGill University

in partial fulfillment of the requirements of the degree of

Doctor of Philosophy

©Yuanjiao Li, 2022. All rights reserved.

"Simplicity is the ultimate sophistication."

by Leonardo da Vinci

### Abstract

Localized corrosion often initiates at the microscale due to surface microstructural features, which are hard to study using conventional macroscopic techniques. Scanning electrochemical cell microscopy (SECCM) is one of the most recently developed electrochemical scanning techniques which allows surface electrochemical measurements with a high spatial resolution by scanning a droplet cell. It can correlate corrosion-related electrochemical phenomena to surface microstructural features. However, the droplet evaporation limits the application of SECCM, especially when using NaCl electrolytes for corrosion testing. To solve this problem, we developed oil-immersed SECCM (OI-SECCM) (Chapter 2) by immersing the droplet under a layer of hydrophobic and electrochemically inert oil on the substrate surface. The droplet creates a stable electrochemical cell, allowing long-lasting surface scanning regardless of ambient humidity.

This thesis presents the OI-SECCM measurements on Al alloy AA7075-T73, analyzing the microscopic corrosion behaviors associated with microstructural features, including intermetallics (Chapter 2), grain orientations and boundaries (Chapter 5). To understand the variations in OI-SECCM measurements, this thesis also elucidated the effects of the non-isolated Ag/AgCl quasi-reference electrode (Chapter 3) and droplet landing process (Chapter 4) on the measured corrosion potentials in open circuit potential and potentiodynamic polarization. Through the optimization and interpretation of OI-SECCM measurements for corrosion, this thesis is expected to facilitate the application of SECCM in the field of corrosion, thereby promoting the understanding of corrosion mechanisms at the microscale.

### Abrégé

La corrosion localisée s'initie souvent à l'échelle microscopique en raison de la présence de caractéristiques microstructurales de surface, difficiles à étudier à l'aide des techniques macroscopiques conventionnelles. La microscopie cellulaire électrochimique à balayage (SECCM) est la technique de balayage électrochimique la plus récemment développée. Elle permet des mesures électrochimiques de surface à haute résolution spatiale grâce au balayage d'une gouttelette micrométrique. La SECCM peut corréler les phénomènes électrochimiques liés à la corrosion aux caractéristiques microstructurales de surface. Cependant, l'évaporation des gouttelettes limite l'application du SECCM, en particulier lors de l'utilisation d'électrolytes NaCl pour les tests de corrosion. Pour résoudre ce problème, nous avons développé la SECCM immergé dans l'huile (OI-SECCM) en immergeant la gouttelette sous une couche d'huile inerte hydrophobe et électrochimique à la surface du substrat (Chapitre 2). La goutte micrométrique crée une cellule de électrochimique très stable, permettant un balayage de la surface de longue durée indépendamment de l'humidité ambiante.

Cette thèse présente les mesures OI-SECCM sur l'alliage Al AA7075-T73, analysant les comportements de corrosion microscopique associés aux caractéristiques microstructurales, y compris les intermétalliques (Chapitre 2), les orientations des grains et les joints (Chapitre 5). Pour comprendre les variations des mesures de corrosion OI-SECCM, cette thèse a également élucidé les effets de la quasi-référence Ag/AgCl couramment utilisée (Chapitre 3) et du processus d'atterrissage de gouttelettes (Chapitre 4) sur les potentiels de corrosion mesurés en potentiel de circuit ouvert et en polarisation potentiodynamique. Grâce à l'optimisation et à l'interprétation des mesures OI-SECCM pour la corrosion, cette thèse devrait faciliter l'application de la SECCM dans le domaine de la corrosion, favorisant ainsi la compréhension des mécanismes de corrosion à l'échelle microscopique.

### Acknowledgements

Firstly, I would like to thank my supervisor Prof. Janine Mauzeroll for the huge encouragement and guidance over the past five years. You are always patient to teach me and give me the confidence to overcome difficulties in research. I so appreciate that you gave me chances to try different projects and finally I found this one that makes me have a wonderful research experience. Beyond that, your positive attitude to life and professionalism at work will always guide me in the future life.

I would also express my gratitude to my collaborators Dr. Alban Morel and Dr. Danick Gallant. Without you, I cannot make this thesis. Alban, thank you for guiding me in the field of corrosion. You were always patient to help me analyze and solve problems. Every time we discussed the experimental data, I can gain numerous new ideas and helpful suggestions from you. Working with you is a very enjoyable part of my PhD life. Danick, thank you for your encouragement and praise that gave me a lot of confidence in the project.

I would also like to acknowledge METALTec, NRC, Centre québécois de recherche et de développement de l'aluminium (CQRDA), Canadian Office for Energy Research and Development (OERD), NACE fellowship award, travel award. Thank you for all the financial and technical supports for the projects that make this thesis possible.

To the members of Mauzeroll group, I am so grateful to be in this harmonious group. Thank you to Isabelle Beaulieu. You make everything so organized in the lab and create a great workplace for us. To Hu Zhou, I enjoyed the time talking with you on various topics, which reduced my anxiety in both daily life and research. Thank you so much for tolerating my bad mood when I was stressed. I also feel fortunate to work on the same project with you and have so many helpful discussions. Dr. Yani Pan, I am grateful to be your labmate. I admire your decisiveness in both work and life, which is what I lack and want to learn. Shopping with you was so relaxing, but unfortunately, we do not have many chances to hang out after COVID. Dr. Emmanuel Mena, thank you for your help and encouragement when I was feeling down. I miss the time to share research ideas and snacks with you in the office. Dr. Tomer Noyhouzer, thank you for the guidance on my first electrochemical research project when I had zero electrochemical knowledge. Even though I did not continue that project, the skills I learned from you have benefited me in all projects. Jeremy Dawkins, your passion for life and research is so contagious and inspires me to think positively. Nathaniel Leslie, thank you for your generous help whenever I turned to you. Dr. Nicholas Payne, thank you for teaching me the scanning electrochemical techniques and sharing your Matlab code with me. Thank you Dr. Danny Chhin for helping me analyze and solve difficulties in the research and giving advice always on the point. To Dr. Lisa Stephens, no matter what kind of questions I asked, you can always give me useful suggestions. Changyue Du, you are such a warm-hearted and empathetic person. I feel so lucky to be meet you in my last year of Ph.D. I would also like to express my gratitude to Sarah, Dr. Lindsay Grandy, Dr. Siba Moussa, Dr. Willian Odette, Dr. Andrew Danis, Dr. Samantha Gateman, Dr. Waldemire Paschoalino, Dr. Anielli Pasqualeti, Dr. Samuel Perry, and Sebastian Skaanvik. Thank you for all the help during the past five years.

Finally, I would like to thank my family members. My husband, Zihang Qiu, always supports and believes in me no matter what I want to do. You understand all my negativity and help me overcome it. Without you, I will not have the courage to experience and complete the Ph.D. study. Thank you to my parents for supporting and understanding me through the long school life. My elder brother, thank you for taking care of our parents when I can't be with you. Also, you are always clear about what you want and bravely pursue your dream, giving me a model for my life.

# Contents

1

Abstract				
Abrégé iii				
Acknowledgements				
List of Figures				
List of Tables				
List of Equations				
List of Abbreviations				
List of Symbols				
Author Contributions				
Introduction				
Background, Motivation and Chapter Outline				
1.1    Aluminum Corrosion    3				
1.1.1 Al Alloys				
1.1.1.1 Types of Al Alloys				
1.1.1.2 Intermetallics				
1.1.1.3 Grain and Grain Boundary				
1.1.1.4 Aluminum Oxide Film				
1.1.1.4.1 Two-Layer Structure				
1.1.1.4.2 High Field Model for Oxide Growth				
1.1.1.4.3 Stability of Oxide Film				
1.1.2 Electrochemical Basis of Aluminum Corrosion				
1.1.2.1 Electrochemical Reactions				

		1.1.2.2	Corrosi	on Thermodynamics	13
		1.1.2.3	Corrosi	on Kinetics	16
		1	.1.2.3.1	Activation Energy Control	17
		1	.1.2.3.2	Potentiodynamic Polarization Curve	19
		1	.1.2.3.3	Mass Transport Control	20
	1.1.3	Types of	f Corrosi	on	24
		1.1.3.1	Uniform	n Corrosion	24
		1.1.3.2	Galvan	ic Corrosion	25
		1.1.3.3	Pitting	Corrosion	26
		1.1.3.4	Intergra	anular Corrosion	27
1.2	Scann	ing Elect	rochemic	al Cell Microscopy (SECCM)	29
	1.2.1	Advant	ages of S	ECCM over Other Scanning Electrochemical Tech-	
		niques			29
	1.2.2	Working	g Princip	le of SECCM	31
		1.2.2.1	Single-0	Channel Pipette System	32
		1.2.2.2	Double	-Channel Pipette System	33
	1.2.3	Technic	al Develo	ppment and Evolution	34
		1.2.3.1	Micro-C	Capillary Cell Technique	34
		1.2.3.2	SECCM	[ in Air	36
	1.2.4	Applica	tion of S	ECCM in Corrosion Studies	37
	1.2.5	Experin	nental Co	onsiderations for SECCM Measurement	40
		1.2.5.1	Droplet	Evaporation and Spreading	40
		1.2.5.2	Fast Sca	In Rate of PDP	41
		1	.2.5.2.1	Anodic Current Related to Oxide Film and Scan	
				Rate	41
		1	.2.5.2.2	Double Layer Capacitive Charging Current	42
		1.2.5.3	Quasi-F	Reference Counter Electrode	44
		1.2.5.4	Ohmic	Drop	45

	1.3	Thesis	Outline	47
2	Oil-Immersed Scanning Electrochemical Cell Microscopy Enabling Long-term			
	Cor	rosion	Mapping	59
	Scie	ntific C	ontributions	60
	Cha	pter Al	ostract	60
	2.1	Introd	luction	62
	2.2	Exper	imental section	63
		2.2.1	Reagents and Materials	63
		2.2.2	Fabrication of Micropipettes	64
		2.2.3	OI-SECCM Setup	64
		2.2.4	Microdroplet OCP and Polarization Measurements	65
		2.2.5	Contact angle measurements	66
	2.3	Result	ts and Discussion	66
		2.3.1	Mineral Oil Reduces Background Noise	66
		2.3.2	Droplet Wetting during the OI-SECCM	68
		2.3.3	Waiting Time for Valid Contact	72
		2.3.4	OI-SECCM Map: $E_{corr}$ (OCP) vs Time	75
		2.3.5	OI-SECCM Map: PDP	79
	2.4	Concl	usion	83
3	Ag <sup>+</sup>	Interf	erence from Ag/AgCl Wire Quasi-Reference Counter Electrode In-	
	duc	ing Co	rrosion Potential Shift in an Oil-Immersed Scanning Electrochemi-	
	cal (	Cell Mi	croscopy Measurement	90
	Scie	ntific C	Contributions	91
	Cha	pter Ał	ostract	91
	3.1	Introd	luction	93
	3.2	Exper	imental section	94
		3.2.1	Reagents and Materials	94

		3.2.2	Micropipette Fabrication	95
		3.2.3	Electrode Preparation	95
			3.2.3.1 Ag/AgCl Wire QRCE	95
			3.2.3.2 AA7075-T73	95
			3.2.3.3 Glassy Carbon	96
		3.2.4	Electrochemical Measurements	96
			3.2.4.1 OI-SECCM Measurements	96
			3.2.4.2 Corrosion Measurements on AA7075-T73	. 97
			3.2.4.3 Detection of $Ag^+$ on GC WE	97
	3.3	Resul	and Discussion	99
		3.3.1	Detection of $Ag^+$ from the $Ag/AgCl$ Wire QRCE	99
		3.3.2	Ag <sup>+</sup> Reduction at the Substrate Shifts $E_{corr}$ Positively	100
		3.3.3	Eliminating the Ag <sup>+</sup> Interference	105
	3.4	Concl	lsion	107
4	Con	trollin	Surface Contact, Oxygen Transport and Pitting of Surface Oxide	
4	Con via	trollin Single-	Surface Contact, Oxygen Transport and Pitting of Surface Oxide	112
4	Con via Scie	trollin Single- ntific C	Surface Contact, Oxygen Transport and Pitting of Surface Oxide	<b>112</b> 113
4	<b>Con</b> <b>via</b> Scie Cha	<b>itrollin</b> Single- ntific C pter Al	Surface Contact, Oxygen Transport and Pitting of Surface Oxide Channel Scanning Electrochemical Cell Microscopy Intributions	<b>112</b> 113
4	Con via Scie Cha 4.1	<b>itrollin</b> Single- ntific C pter Al Introc	Surface Contact, Oxygen Transport and Pitting of Surface Oxide Channel Scanning Electrochemical Cell Microscopy Intributions	<b>112</b> 113 113 113
4	Con via Scie Cha 4.1 4.2	<b>Single-</b> ntific C pter Al Introc Exper	Surface Contact, Oxygen Transport and Pitting of Surface Oxide Channel Scanning Electrochemical Cell Microscopy Intributions	<b>112</b> 113 113 113 114 115
4	Con via Scie Cha 4.1 4.2	ntific C pter Al Introc Exper 4.2.1	Surface Contact, Oxygen Transport and Pitting of Surface Oxide Channel Scanning Electrochemical Cell Microscopy Ontributions	<b>112</b> 113 113 114 115 115
4	Con via Scie Cha 4.1 4.2	ntific C pter Al Introc Exper 4.2.1 4.2.2	Surface Contact, Oxygen Transport and Pitting of Surface Oxide Channel Scanning Electrochemical Cell Microscopy Intributions	<b>112</b> 113 113 114 115 115 115
4	Con via Scie Cha 4.1 4.2	ntific C pter Al Introc Exper 4.2.1 4.2.2 4.2.3	Surface Contact, Oxygen Transport and Pitting of Surface Oxide         Channel Scanning Electrochemical Cell Microscopy         ontributions         ontributions         stract         uction         mental section         Chemicals and Materials         Aluminum Sample Preparation and Surface Characterization         Macro Potentiodynamic Polarization Measurements	<b>112</b> 113 113 114 115 115 115 116
4	Con via Scie Cha 4.1 4.2	ntific C pter Al Introc Exper 4.2.1 4.2.2 4.2.3 4.2.4	Surface Contact, Oxygen Transport and Pitting of Surface Oxide Channel Scanning Electrochemical Cell Microscopy Ontributions	<b>112</b> 113 113 114 115 115 116 116
4	Con via Scie Cha 4.1 4.2	ntific C pter Al Introc Exper 4.2.1 4.2.2 4.2.3 4.2.4	Surface Contact, Oxygen Transport and Pitting of Surface Oxide         Channel Scanning Electrochemical Cell Microscopy         ontributions         stract         action         mental section         Chemicals and Materials         Aluminum Sample Preparation and Surface Characterization         Macro Potentiodynamic Polarization Measurements         Oil-Immersed Single-Channel Micropipette Scanning Electrochemical Cell Microscopy	<b>112</b> 113 113 114 115 115 116 116 117
4	Con via 3 Scie Cha 4.1 4.2	Atrollin Single- Intific C Introc Exper 4.2.1 4.2.2 4.2.3 4.2.4 Result	Surface Contact, Oxygen Transport and Pitting of Surface Oxide         Channel Scanning Electrochemical Cell Microscopy         ontributions         stract         action         mental section         Chemicals and Materials         Aluminum Sample Preparation and Surface Characterization         Oil-Immersed Single-Channel Micropipette Scanning Electrochemical Cell Microscopy         Sand Discussion	<b>112</b> 113 113 114 115 115 116 116 116
4	<b>Con</b> <b>via</b> Scie Cha 4.1 4.2	Atrollin Single- Intific C Introc Exper 4.2.1 4.2.2 4.2.3 4.2.4 Result 4.3.1	Surface Contact, Oxygen Transport and Pitting of Surface Oxide         Channel Scanning Electrochemical Cell Microscopy         Intributions         Stract         Intribution         Intribution         Stract         Intribution         Intribution         Stract         Intribution         Intribution         Stract         Intribution         Intrintribution         Intributi	<b>112</b> 113 113 114 115 115 116 116 117 118 118

		4.3.3	Effect of $E_{appr}$ on $E_{corr}(PDP)$	. 125
	4.4	Concl	usion	. 131
5	Cor	relating	g Corrosion Activities to Grain Orientations of Aluminum Alloy	136
	Scie	ntific C	Contributions	. 137
	Cha	pter Ał	ostract	. 137
	5.1	Introd	luction	. 138
	5.2	Exper	imental Section	. 140
		5.2.1	Chemicals and Materials	. 140
		5.2.2	Oil-Immersed Scanning Electrochemical Cell Microscopy	. 141
		5.2.3	Surface Characterization	. 142
	5.3	Result	ts and Discussion	. 143
		5.3.1	$iR_{\Omega}$ between RE and WE	. 143
		5.3.2	Grain Orientation Dependent Cathodic Current	. 144
		5.3.3	Correlation Between Grain Orientation and Anodic Corrosion pro-	
			cesses	. 147
			5.3.3.1 Anodic current	. 147
			5.3.3.2 Pitting	. 149
		5.3.4	Corrosion Processes at Grain Boundary	. 150
	5.4	Concl	usion	. 152
6	Con	clusior	n and Future Work	158
-	6.1	Concl	usions by Chapter	. 158
	011	6.1.1	Chapter 1	. 158
		612	Chapter 2	159
		613	Chapter 3	159
		611	Chapter 4	160
		615	Chapter 5	140
	$(\mathbf{a})$	0.1.3 Eats		. 100
	0.2	ruture		. 101

	6.2.1	Understanding and Taking Advantage of Droplet Changes	. 161
	6.2.2	Further Development of SECCM	. 163
	6.2.3	Future Directions of OI-SECCM in Corrosion Field	. 163
	6.2.4	Future Direction in Corrosion Research	. 164
A	Appendix	for Chapter 2	168
B	Appendix	for Chapter 3	172
C	Appendix	for Chapter 4	174
D	Appendix	for Chapter 5	177

# **List of Figures**

1.1	Intermetallic particles	6
1.2	Grain and grain boundary	7
1.3	Face-centered-cubic crystal - low index planes	8
1.4	High field model	10
1.5	Mixed potential theory	18
1.6	Tafel plot of PDP	20
1.7	Mass transport controlled steady state current	22
1.8	Mass transport controlled corrosion kinetics	24
1.9	Galvanic corrosion	26
1.10	Metastable and stable pitting current peaks on an anodic PDP curve	27
1.11	SECCM mapping in hopping mode	32
1.12	Single-channel SECCM system	33
1.13	Double-channel SECCM system	34
1.14	Experimental setup of micro-capillary cell	35
1.15	SECCM images of surface topography and currents	37
1.16	Correlating corrosion processes to grain orientations of carbon steel by SECCM	[
	in combination with EBSD	39
1.17	Electrical double layer	43
1.18	Ohmic drop $iR_{\Omega}$	45
2.1	Schematic of the micropipette appraching to substrate under oil	66
2.2	Electric background noise in the mineral oil phase	67
2.3	SECCM experiment in a humidified cell	68

2.4	Contact angles of simulated droplet landing on Al alloy surface correspond
	to three types of PDP curves
2.5	Shortening waiting time for valid wetting
2.6	$E_{\rm corr}({\rm OCP})$ map
2.7	$E_{\rm corr}(\rm PDP)  map  \ldots  \ldots  81$
3.1	Detection of $Ag^+$ on GC in OI-SECCM
3.2	Ag <sup>+</sup> reduction induces positive shifts of $E_{corr}$
3.3	SEM image and EDS analysis of Ag deposition
3.4	Preconditioning Ag/AgCl wire in 3.5 wt% for 4 h
3.5	OI-SECCM measurement using $Ag^+$ contaminated solution $\ldots \ldots \ldots \ldots 105$
3.6	Eliminating Ag <sup>+</sup> contamination by extending distance or using leak-free RE 106
4.1	Droplet-contact landing and pipette-contact landing
4.2	$E_{\text{appr}}$ controls the magnitude of $i_{\text{trig}}$
4.3	$E_{\text{corr}}$ maps obtained by SECCM at different $E_{\text{appr}}$
4.4	Effect of $E_{appr}$ on $E_{corr}(OCP)$
4.5	Droplet-oil interface introduces additional oxygen
4.6	Effect of $E_{appr}$ on $E_{corr}(PDP)$
4.7	Effect of $E_{appr}$ on pitting
4.8	Comparison between landings with and without $E_{appr}$
5.1	Measurement of $iR_{\Omega}$ for a long WE-RE distance OI-SECCM setup 142
5.2	OI-SECCM map: cathodic current
5.3	Cathodic currents grouped by grains
5.4	Anodic current grouped by grains
5.5	The occurrence of pitting grouped by grains
5.6	Canodic and anodic currents at grain boundaries
5.7	Pitting at grain boundaries

A.1	SEM image of the micropipette
A.2	Potential stability of Ag/AgCl wire electrode over 12 h
A.3	Micropipette before after OI-SECCM experiment
A.4	Droplet evaporation and crystallization causes micropipette crush in air 169
A.5	EDS analysis of the intermetallic particle at 608
A.6	Detection of $Ag^+$ contamination
A.7	EDS analysis of the intermetallic particle at 13
B.1	SEM image of the micropipette
B.2	Reproducibility of the Ag/AgCl wire electrodes
B.3	Testing the potential stability of Ag/AgCl wire electrode with currents ap-
	plied by choronopotentiometry
B.4	Potential of leak-free Ag/AgCl electrode
C.1	PDP curve for pure Al
C.2	Trigger current of droplet and pipette contact landing
C.3	PDP curves obtained with different approach potentials
C.4	Trigger currents at -1.5 V for a 10 $\mu$ m micropipette
D.1	Misorientation angles of grains relative to three low-index planes 177
D.2	Grain size

# List of Tables

1	List of abbreviation
2	List of symbols
1.1	Series of aluminum alloys
1.2	Composition of AA7075 5
1.3	Standard Electrode Potential
4.1	Number of Pitting Locations on the Maps in Figure 4.7b
5.1	Cathodic and Anodic currents on Different Grains shown in Figure 5.3a 146

# List of Equations

1.1	Atomic planar density	8
1.11	Half-cell Nernst equation	13
1.12	Cell potential	14
1.13	Gibbs free energy	14
1.14	Gibbs free energy related to $E^0$	14
1.15	Overpotential	16
1.16	Butler-Volmer equation	17
1.17	Anodic polarization	18
1.18	Cathodic polarization	19
1.19	Anodic Tafel slope	19
1.20	Cathodic Tafel slope	19
1.21	Mass transport controlled current	20
1.22	Nernst-Planck equation	21
1.23	Fick's first law	21
1.24	Fick's second law	21
1.27	High Field Model - anodic current and electric field strength	41
1.28	High Field Model - electric field strength and scan rate	42
1.29	High Field Model - anodic current and scan rate	42
1.30	Capacitive current	44
1.31	Uncompensated potential	46
1.32	Actual potential	46

# List of Abbreviations

Abbreviation	Full Name
AFM	Atomic force microscopy
CE	Counter electrode
CV	Cyclic voltammetry
DC	Droplet contact
EBSD	Electron backscatter diffraction
EDS	Energy dispersive X-ray spectroscopy
FCC	Face-centered cubic
GC	Glassy carbon
HER	Hydrogen evolution reaction
ICP-MS	Iductively coupled plasma mass spectroscopy
ID	Inner diameter
IHP	Inner Helmholtz Plane
LEIS	Local electrochemical impedance spectroscopy
MCC	Micro-capillary cell
OCP	Open circuit potential
OD	Outer diameter
OI-SECCM	Oil-immersed scanning electrochemical cell microscopy
OI-SMCM	Oil-immersed scanning micropipette contact method
OHP	Outer Helmholtz Plane
ORR	Oxygen reduction reaction
PC	Pipette contact

**Table 1:** List of abbreviations used throughout the thesis.

Abbreviation	Full Name	
PDP	Potentiodynamic polarization	
pH <sub>pzc</sub>	pH of zero charge	
QRCE	Quasi-reference counter electrode	
RE	Reference electrode	
SCE	Saturated calomel electrode	
SECCM	Scanning electrochemical cell microscopy	
SECM	Scanning electrochemical microscopy	
SEM	Scanning electron microscope	
SHE	Standard hydrogen electrode	
SKPFM	Scanning Kelvin probe force microscopy	
SMCM	Scanning micropipette contact method	
SRET	Scanning reference electrode technique	
SVET	Scanning vibrating electrode technique	
UV-VIS	Ultraviolet-visible spectrophotometer	
WE	Working electrode	

# List of Symbols

Symbol	Usual Units	Meaning
a	-	Activity of ion
C	$mol L^{-1}$	Concentration
$\delta C_j(x,t)$	$mol \ L^{-1}$	Concentration of species $j$ at distance $x$ at
		time t
D	$\mathrm{cm}^2\mathrm{s}^{-1}$	Diffusion coefficient
$D_{\rm micropipette}$	$\mu { m m}$	Diameter of micropipette
E	V	Potential
$E^0$	V	Standard electrode potential
$E_{actual}$	V	Actual potential
$E_{anode}$	V	Oxidation half-cell potential
$E_{applied}$	V	Applied potential
$E_{appr}$	V	Approach potential
$E_{cathode}$	V	Reduction half-cell potential
$E_{\text{cell}}$	V	Full-cell potential
$E_{\rm corr}$	V	Corrosion potential
$E_{eq}$	V	Equilibrium potential
$E_{half-cell}$	V	Half-cell potential
$\Delta E_{\rm ohmic}$	V	Ohmic drop
$E_{pit}$	V	Pitting potential
F	$\rm Cmol^{-1}$	Faraday's constant
$\Delta G$	J	Gibbs free energy change

**Table 2:** List of symbols used throughout the thesis.

Symbol	Usual Units	Meaning
Н	$V m^{-1}$	Electric field strength
i	А	Current
i <sub>a</sub>	А	Anodic current
i <sub>ac</sub>	А	Alternative current
i <sub>c</sub>	А	Cathodic current
$i_{\rm cond}$	А	Conductance current
i <sub>corr</sub>	А	Corrosion current
$i_0$	А	Exchange current
$i_{ m trig}$	А	Trigger current
J	$\mathrm{mol}~\mathrm{cm}^{-2}~\mathrm{s}^{-1}$	Flux
<i>j</i> corr	$A \text{ cm}^{-2}$	Corrosion current density
ĴL	$\mathrm{A~cm^{-2}}$	Diffusion limited current density
$j_{pl}$	$A \text{ cm}^{-2}$	Anodic plateau current density
$K_{\rm sp}$	-	Solubility product constant
M	$g \text{ mol}^{-1}$	Molar mass
$R_{\Omega}$	Ω	Ohmic resistance
Т	К	Temperature
$V_{\rm bias}$	V	Bias potential
$V_m$	$m^3 mol^{-1}$	Molar volume
α	-	Transfer coefficient
ρ	g m <sub>-3</sub>	Mass density
η	V	Overpotential
v	$V s^{-1}$	Potential scan rate

## **Author Contributions**

All of the work in this thesis was performed under the supervision of Professor Janine Mauzeroll. She provided guidance on all projects and corrections on all manuscripts. All projects were carried out in collaboration with National Research Council Canada (NRC).

# Chapter 1

Yuanjiao Li wrote this chapter.

## **Chapter 2**

Yuanjiao Li performed the experiments and data analysis, and wrote the manuscript with the assistance of Dr. Alban Morel (NRC). Dr. Danick Gallant (NRC) provided guidance for the galvanic corrosion analysis and manuscript review.

## **Chapter 3**

Yuanjiao Li and Alban found the problem of Ag<sup>+</sup> contamination and designed the experiments. Yuanjiao performed the experiments and data analysis. The manuscript was written and corrected under the guidance of Dr. Alban Morel and Dr. Danick Gallant provided useful feedback.

## **Chapter 4**

Yuanjiao Li performed the experiments and data analysis, and wrote the manuscript. Dr. Alban Morel and Dr. Danick Gallant reviewed the manuscript.

# Chapter 5

Yuanjiao Li performed the experiments and wrote the manuscript. Dr. Nicolas Brodush carried out the EBSD mapping and helped with the interpretation of EBSD data. The analysis of electrochemical data correlated with EBSD map was performed with the assistance of Dr. Alban Morel.

# Chapter 6

Yuanjiao Li summarized the thesis and wrote this chapter.

### Chapter 1

### Introduction

### **Background, Motivation and Chapter Outline**

Al is a competitive metal in engineering materials due to its impressively low density, high strength, good fabricability and corrosion resistance, excellent electrical and thermal conductivity.<sup>1</sup> To satisfy the various application requirements, different types of Al alloys are made by adding alloying elements into Al, which are extensively used in aerospace and automotive industries, construction of buildings, appliances, etc.<sup>2</sup> However, the added alloying elements increase the microstructural heterogeneity, which reduces the corrosion resistance of materials.

Corrosion causes a global cost of trillions of dollars annually due to equipment maintenance, replacement and development of anti-corrosion technologies.<sup>3,4</sup> Additionally, catastrophic equipment failures due to corrosion lead to serious injury and death.<sup>5</sup> Therefore, to improve the corrosion resistance of materials, it is crucial to understand the corrosion mechanisms.

The corrosion observed at the macroscale often initiates at microscale sites related to the surface microstructure. Scanning electrochemical cell microscopy (SECCM) enables to extract microscopic electrochemical information at a high spatial resolution.<sup>6–8</sup> This thesis presents an oil-immersed SECCM to investigate the corrosion of Al alloy.

Chapter 1 will introduce and review the literature related to Al corrosion and SECCM from two sections. The first section will describe the series and microstructure of Al alloys

and the types of corrosion. The second section will focus on the working principle of SECCM and its application in field of corrosion.

### 1.1 Aluminum Corrosion

### 1.1.1 Al Alloys

#### 1.1.1.1 Types of Al Alloys

Al alloys are divided into two major categories according to their manufacturing processes: cast and wrought families. The cast family are the alloys that are melted in a furnace and poured into a mold. The wrought family are the alloys that are worked in the solid form with some specific tools. In general, wrought alloys contain a smaller percentage of alloying elements and have better tensile strength compared to cast alloys, which causes the applications and properties to vary widely between the two.

This section will focus on the wrought alloys and the research objective of the thesis, AA7075-T73, which belongs to this category. Wrought Al alloys are divided into eight series according to the principal alloying elements, which are identified by the 4-digit numerical designation system.<sup>9</sup> The first digit indicates the principal alloying element endowing the same series with the common properties. The second digit indicates a modified alloy in the series. The third and fourth digits are arbitrary numbers for the identification of specific alloys. As shown in Table 1.1, these alloying elements modify the alloys to strengthen specific properties through different treatments in Temper Designation System.<sup>10</sup>

Alloy series	Principal alloying element	Effect of alloying element	
1xxx	Minimum 99% aluminum	Excellent corrosion resistance	
2xxx	Copper (up to 6.5%)	Increase tensile, fatigue strength and hardness	
		Decrease ductility and corrosion resistance	
3xxx	Manganese (up to 1.5%)	Increase strength and hardness	
		Increase corrosion resistance	
4xxx	Silicon (up to 17%)	Improves surface hardness	
		Improves castability	
5xxx	Magnesium (up to 10%)	Good marine corrosion resistance	
		Increase strength and hardness	
6xxx	Magnesium and silicon	Improve extrudability	
		Increase strength to withstand heat treatment	
7xxx	Zinc (up to 8%)	Increase strength	
		Decrease resistance to stress corrosion cracking	
8xxx	Other elements		

Table 1.1: Series of aluminum alloys.

For AA7075-T73, 7 corresponds to Zn which is the principal alloying element. 0 represents the original alloy of 7075. If the second number is not 0, it indicates a variation of AA7075. T stands for thermal treatment and 73 designates the specific thermal treatment, which is solution heat-treated and then artificially overaged to achieve stress-corrosion resistance.

4

AA7075 are among the highest strength Al alloys available and often used in high performance applications such as aerospace, aircraft, automotive and hydraulics components. As shown in Table 1.2, apart from the intentionally added elements, Zn, Mg and Cu, trace levels of Fe, Si and others are present as impurities in alloys.<sup>11</sup> The alloying elements and impurities lead to the formation of intermetallic particles, which make AA7075 susceptible to localized corrosion.<sup>12</sup>

Component	wt%
Al	87 - 91.4
Zn	5.1 - 6.1
Mg	2.1 - 2.9
Cu	1.2 - 2
Cr	0.18 - 0.28
Fe	Max 0.5
Si	Max 0.4

 Table 1.2: Composition of AA7075

#### 1.1.1.2 Intermetallics

Excessive alloying elements precipitating during solidification will form a second phase as shown in Figure 1.1.<sup>13</sup> The second phase comprising of two or more metal elements and possessing a fixed composition and crystal structure is termed as intermetallic compound (also intermetallics, intermetallic particle, intermetallic phase, intermetallic precipitate and metallic inclusion).<sup>14</sup> If non-metallic elements like Si and C are contained in the precipitates, they are called inclusions or non-metalic inclusions, such as  $Al_4C_3$  and MgSi.<sup>15,16</sup> The second phase rich of alloying elements will have a potential very different from the matrix area, which tends to cause galvanic corrosion.<sup>17</sup> In galvanic couples, the intermetallics containing Mg and Zn work as anodes relative to the matrix in Al alloys and will experience dissolution when contacting to an electrolyte. On the other hand, intermetallics containing Fe, Cu and Mn will be the cathode and cause the dissolution of

the surrounding Al matrix. Both cases will lead to localized corrosion, which impairs the mechanical properties of alloys.<sup>18,19</sup>



Figure 1.1: SEM image shows intermetallic particles on the surface of AA7075-T73.

The intermetallics in Al alloys can be classified into three types according to their size and distribution.<sup>20</sup>

- Precipitate particles. The size ranges from Angstroms to fractions of micrometer. Their effect on localized corrosion is hard to discern when they are homogeneously dispersed. When they are concentrated at grain boundaries, they promote intergranular corrosion. Examples include MgZn<sub>2</sub>, Al<sub>2</sub>Cu, Mg<sub>2</sub>Al<sub>3</sub>.
- Constituent particles. They are relatively large, ranging from a few tenths of a micrometer up to 10 μm. Pitting is primarily associated with the constituent particles in high strength Al alloys. Examples include Al<sub>7</sub>Cu<sub>2</sub>Fe, (Al,Cu)<sub>6</sub>(Fe,Cu) and Al<sub>3</sub>Fe.
- Dispersoid particles. They are typically in small sizes ranging from 10 to 200 nm and comprise of highly insoluble elements like Mn, Cr, Ti and Zr. Example includes Al<sub>6</sub>Mn, Al<sub>3</sub>Zr and Al<sub>3</sub>Ti.

 $Al_7Cu_2Fe$  and  $(Al,Cu)_6(Fe,Cu)$  are the most abundant and detrimental intermetallics in AA7075. They are cathodic relative to the Al matrix, leading to galvanic corrosion, which is discussed in Chapter 2.<sup>21,22</sup> The presence of Fe and Cu promotes the oxygen reduction at the particle surface,<sup>23</sup> which increases the solution pH.<sup>24</sup> This further exacerbates the potential difference and accelerates the galvanic corrosion.

### 1.1.1.3 Grain and Grain Boundary

Metal and metal alloys are polycrystalline (Figure 1.2), consisting of crystallites in different sizes and orientations. Each crystal forms one grain with grain boundaries between them. The size and number of grains are controlled by the rate of metal solidification and directly affect the mechanical properties of materials. Decreasing the grain size will increase the number of grain boundaries. Grain boundaries impede the transmission of dislocations across grains and thereby make materials harder to deform.<sup>25</sup> Since the strength of a polycrystalline is inversely proportional to the ability of plastic deformation, decreasing the grain size can increase the strength of a material.<sup>26,27</sup> A high density of grain boundaries however reduces the corrosion resistance.<sup>28,29</sup> Compared to the grain interior, grain boundaries are more susceptible to corrosion and cause intergranular corrosion because of the higher free energy,<sup>30</sup> second-phase precipitates and solute depletion in the adjacent zone.<sup>31,32</sup>



Figure 1.2: EBSD map shows the AA7075-T73 surface is made up of different grains.

Grain orientations also effect corrosion behaviors.<sup>33</sup> A densely packed crystallographic plane is thought to be less prone to corrosion than a loosely packed plane, because the

tighter atomic bonds give rise to higher binding energies that hinder atoms from leaving the bulk material.<sup>34,35</sup> Atomic planar density (eq 1.1) is used to describe the atomic packing density of one plane in a crystal.

$$Atomic planar density = \frac{Number of atoms centered on a given plane}{Area of the plane}$$
(1.1)

Al has a face-centered-cubic (FCC) crystal structure. Due to the symmetry and infinity of the equally spaced crystal lattices, the planes that have identical properties but in different Miller indices (hkl) are classified into the same plane family {hkl} as shown in Figure 1.3. For example, (100), (010) and (001) planes constitute {001} family. The three basal plane families differ in planar densities which rank in an increasing order {101} < {100} < {111} for FCC. The surface differences lead to grain orientation dependent behaviors, such as surface etching,<sup>36,37</sup> dissolution rates,<sup>38</sup> pitting,<sup>39,40</sup> and, oxide film growth and dissolution.<sup>41–44</sup>



**Figure 1.3:** Aluminum crystal structure (Face-centered cubic arrangement) and three low index families. The planes shown in grey are marked in red (hkl).

The three low-index planes (010), (101) and (111) of single crystals are often used as representatives for the study of grain dependent corrosion behaviors. It was reported that the rate of Al oxide film dissolution followed the order of (111)  $\sim$  (110) > (100) in neutral

NaCl solution,<sup>45</sup> but followed an order of (111) > (110) > (100) in NaOH solution.<sup>46</sup> G. M Tracy et al. reported the same order (111) > (110) > (100) for the onset of pitting in Cl<sup>-</sup> solutions,<sup>39</sup> but B.W. Davis found that the number of metastable pitting current peaks varied in the order of (111) > (100) > (110).<sup>40</sup> The contradiction and deviation from the planar densities may arise from the different experimental conditions and surface variations.

#### 1.1.1.4 Aluminum Oxide Film

#### 1.1.1.4.1 Two-Layer Structure

Al is a very reactive metal in air (standard electrode potential = -1.66 V vs. SHE), but, practically, Al materials are naturally passive because of the surface oxide film. When exposed to air at ambient temperature, Al is immediately oxidized to form a barrier oxide layer ( $\sim$ 2-4 nm),<sup>47–49</sup> due to the high electronegativity and strong affinity to oxygen. Even if destroyed, the oxide film can reform instantly in most environments. This renders Al materials highly resistant to corrosion.<sup>50</sup>

The natural oxide film is comprised of two layers.<sup>51</sup> The inner layer in contact with Al is formed within a few milliseconds and has a compact structure, called barrier layer. The second layer growing on the top of barrier layer is a hydrated oxide film. This layer grows much slower, and can last several weeks and even months depending on the environmental humidity and temperature. The final thickness can reach tens of nanometers.<sup>52</sup> In this thesis, the discussion of Al oxide film mainly refers to the barrier oxide layer, because the Al alloy samples were measured shortly after polishing when the second hydrated layer has not reached an appreciable thickness.

### 1.1.1.4.2 High Field Model for Oxide Growth

Al oxide film exhibits semiconducting properties with a band gap (the minimum energy required to excite an electron from valence band to conduction band) between 2.8 - 4.5 eV.<sup>53–55</sup> This allows the transport of ions and electrons through the oxide film under an electric field as shown in Figure 1.4, which was proposed as a high field model by Cabrera and Mott to explain the growth of oxide film at ambient pressures and low temperatures.<sup>56,57</sup> In the high field model, the negative oxygen anions on the surface and the positive metallic cations below the oxide create a so-called Mott potential.<sup>58</sup> Since the initial oxide film is extremely thin, the Mott potential results in a high electric field across the oxide film. Therefore, the oxide growth rate is rapid initially, but decreases as the oxide thickness increases. Finally, a limiting thickness is reached.<sup>48,59</sup>



Figure 1.4: High field model illustrates the transport of ions across the Al oxide film

#### 1.1.1.4.3 Stability of Oxide Film

The oxide film passivates Al in the pH range between 4-8.5. This range varies with the temperature and solution composition, like the concentration of  $Al^{3+}$ . Beyond the limits,

the oxide film dissolves in acidic and alkaline solutions, resulting in uniform corrosion. Thermodynamic principles to explain and predict the corrosion behavior of Al at different pH and potentials are summarised in the Pourbaix diagram, based on the electrochemical reactions of the species involved.<sup>60,61</sup> In the solutions containing aggressive anions such as Cl<sup>-</sup>, Al materials will experience localized corrosion at defective points of oxide film. This is because the Al surface has a high pH of zero charge (pH<sub>pzc</sub> = 9). As a result, the surface is positive charged in most neutral solutions, which attracts negative Cl<sup>-</sup> ions.<sup>62</sup> The adsorbed Cl<sup>-</sup> is incorporated into the oxide film and replaces oxygen in either OH<sup>-</sup> or O<sup>2-</sup> positions in the lattice.<sup>63–65</sup> In this way, the structure of oxide film is destroyed at defective points, exposing the underlying Al to the corrosive environment.

### 1.1.2 Electrochemical Basis of Aluminum Corrosion

The previous section introduced the composition and microstructure of Al alloys that determine the corrosion resistance of materials. Corrosion occurring in aqueous medium is the result of multiple electrochemical reactions at the metal/electrolyte interface. This section will provide an introduction to the electrochemical fundamentals of Al corrosion in aqueous solutions from the aspects of thermodynamics and kinetics.

#### 1.1.2.1 Electrochemical Reactions

The electrochemical reactions at the metal/electrolyte interface are in electrical equilibrium, producing equal anodic and cathodic currents in opposite directions. The basic anodic and cathodic reactions of Al corrosion are as follows:

Anodic reaction

Oxidation of Al loses electrons and produces anodic current  $i_a$ .

$$Al \longrightarrow Al^{3+} + 3e^{-}$$
(1.2)
• Cathodic reactions

Hydrogen evolution and oxygen reduction reactions take up electrons, producing cathodic current  $i_c$ .

- Reduction of H<sup>+</sup>

in acidic solutions

$$2 \operatorname{H}^{+} + 2 \operatorname{e}^{-} \longrightarrow \operatorname{H}_{2} \tag{1.3}$$

in neutral and alkaline solutions, H<sup>+</sup> comes from the dissociation of water

$$4 \operatorname{H}_2 \operatorname{O} + 4 \operatorname{e}^- \longrightarrow 2 \operatorname{H}_2 + 4 \operatorname{OH}^-$$
(1.4)

- Reduction of dissolved oxygen

in acidic solutions

$$O_2 + 4 H^+ + 4 e^- \longrightarrow 2 H_2 O \tag{1.5}$$

in neutral and alkaline solutions

$$O_2 + 2 H_2 O + 4 e^- \longrightarrow 4 O H^-$$
 (1.6)

• The corrosion of Al is the sum of oxidation and reduction reactions

- in acidic solutions

$$2 \operatorname{Al} + 6 \operatorname{H}^{+} \longrightarrow 2 \operatorname{Al}^{3+} + 3 \operatorname{H}_{2}$$

$$(1.7)$$

- in alkaline solutions

$$2 \operatorname{Al} + 6 \operatorname{OH}^{-} + 2 \operatorname{H}_2 \operatorname{O} \longrightarrow 2 \operatorname{Al}(\operatorname{OH})_4^{-} + \operatorname{H}_2$$
(1.8)

or

$$4 \operatorname{Al} + 4 \operatorname{OH}^{-} + 3 \operatorname{O}_{2} + 6 \operatorname{H}_{2} \operatorname{O} \longrightarrow 4 \operatorname{Al}(\operatorname{OH})_{4}^{-}$$
(1.9)

- in neutral solutions

$$4 \operatorname{Al} + 3 \operatorname{O}_2 + 6 \operatorname{H}_2 \operatorname{O} \longrightarrow 4 \operatorname{Al}(\operatorname{OH})_3 \tag{1.10}$$

The site where oxidation takes place is called the anode and that where reduction takes place is called the cathode. The current flows internally between anode and cathode, resulting in a zero net current. According to the locations of anode and cathode, corrosion can be classified into uniform corrosion where anode and cathode are at the same sites, and localized corrosion where anode and cathode are at separate sites associated with microstructural features, such as intermetallics, grain boundaries and pits. This is described in detail in the section Types of Corrosion.

#### 1.1.2.2 Corrosion Thermodynamics

Thermodynamics allow to determine if a metal dissolution is favorable in given circumstances. In electrochemistry, the Nernst equation calculates the equilibrium potential  $(E_{eq})$  under non-standard conditions to predict the spontaneous direction of a redox reaction as conditions change. The Nernst equation relates the equilibrium reduction half-cell potential  $(E_{half-cell})$ , to the standard electrode potential  $(E^0)$  and the activity of ion (a):

$$E_{half-cell} = E^0 - \frac{RT}{nF} ln \frac{a_{Red}}{a_{Ox}}$$
(1.11)

where *R* is the gas constant (8.314 J k<sup>-1</sup> mol<sup>-1</sup>), *T* is the absolute temperature, *F* is the Faraday constant (96485 C mol<sup>-1</sup>), *n* is the number of electron involved in the reaction.  $E^0$  refers to the standard half-cell potential as shown in Table 1.3, which is measured under standard conditions including 25 °C, 1 M concentration for each ion, partial pressure of 1 atm for each gas, metals in pure states, and with a standard hydrogen electrode (SHE) as reference by default.

For a full electrochemical cell, the full-cell potential ( $E_{cell}$ ) is the potential difference between two electrodes:

$$E_{cell} = E_{cathode} - E_{anode} \tag{1.12}$$

 $E_{\text{cell}}$  is related to the change of Gibbs free energy ( $\Delta G$ ), which is used to quantify the driving force of an electrochemical process:

$$\Delta G = -nFE_{cell} \tag{1.13}$$

Combining eq 1.13, eq 1.12 and eq 1.11, we can obtain:

$$\Delta G = nFE_{anode}^0 - nFE_{cathode}^0 + RTln\frac{a_{Red}}{a_{Ox}}$$
(1.14)

A negative  $\Delta G$  implies that the reaction can proceed spontaneously.  $E^0$  can be used to predict the oxidation tendency of metals (Table 1.3), according to eq 1.14. For a metal as an anode, the more negative the  $E^0$ , the more negative the  $\Delta G$ , so the metal is more easily oxidized. All has a highly negative  $E^0$ , -1.66 V, which is very unstable in air, and thus can immediately form an oxide film, rendering Al a passive metal in practice.

Half-Cell Reaction	$E^0$ (V)
$\operatorname{Li}_{(\operatorname{aq})}^{+} + e^{-} \rightleftharpoons \operatorname{Li}_{(\operatorname{s})}$	-3.04
$Mg^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Mg_{(s)}$	-2.37
$Al_{(aq)}^{3+} + 3e^- \rightleftharpoons Al_{(s)}$	-1.66
$Mn_{(aq)}^{2+} + 2e^{-} \Longrightarrow Mn_{(s)}$	-1.18
$Zn^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Zn_{(s)}$	-0.76
$\operatorname{Cr}^{3+}_{(\operatorname{aq})} + 3 \operatorname{e}^{-} \rightleftharpoons \operatorname{Cr}_{(\operatorname{s})}$	-0.74
$\operatorname{Fe}_{(aq)}^{2+} + 2 e^{-} \Longrightarrow \operatorname{Fe}_{(s)}$	-0.44
$2 H_2 O_{(l)} + 2 e^- \rightleftharpoons H_{2(g)} + 2 OH^{(aq)}$	-0.41
$Cd_{(aq)}^{2+} + 2e^{-} \rightleftharpoons Cd_{(s)}$	-0.40
$\operatorname{Co}_{(\operatorname{aq})}^{2+} + 2  e^{-} \rightleftharpoons \operatorname{Co}_{(\operatorname{s})}$	-0.27
$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$	-0.23
$Pb_{(aq)}^{2+} + 2e^{-} \Longrightarrow Pb_{(s)}$	-0.12
$2 H_{(aq)}^+ + 2 e^- \rightleftharpoons H_{2(g)}$	0.00
$Cu_{(aq)}^{2+} + 2e^{-} \Longrightarrow Cu_{(s)}$	+0.34
$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$O_{2(g)} + 4 H^+ + 4 e^- \Longrightarrow 2 H_2 O_{(g)}$	+0.82
$Pt^{2+}_{(aq)} + 2e^- \Longrightarrow Pt_{(s)}$	+1.2
$Au^{3+}_{(aq)} + 3e^- \Longrightarrow Au_{(s)}$	+1.52

Table 1.3: Standard Electrode Potential

#### 1.1.2.3 Corrosion Kinetics

The thermodynamic principle explains the possibility of corrosion reactions in terms of energy change, but it cannot predict the corrosion rate. Corrosion rate can be expressed by the corrosion current density ( $j_{corr}$ ) which is the corrosion current divided by surface area.

At equilibrium, the rates of cathodic and anodic reactions are equal ( $i_a = i_c$ ). The exchange current ( $i_0$ ) between them is the corrosion current ( $i_{corr}$ ). The  $E_{eq}$  of the overall system is defined as corrosion potential  $E_{corr}$ , which is a mixed potential<sup>66</sup> or open circuit potential (OCP). The mixed potential results from the equilibrium of at least two cathodic and anodic reactions proceeding simultaneously, where the net current is zero. Since the mixed potential lies between the equilibrium potentials of partial reactions, each partial reaction deviates from their own equilibrium. The deviation from equilibrium is called polarization and the potential difference is called overpotential ( $\eta$ ):

$$\eta = E - E_{eq} \tag{1.15}$$

The electron transfer rate of a reaction will increase with the increase of  $\eta$ , causing more reactants to be consumed at the electrode/electrolyte interface. When the supply of reactants is not sufficient to support the fast electron transfer, the mass transport of reactants becomes the controlling step. The controlling step determines the corrosion rate. This section will introduce the activation energy controlled and mass transport controlled corrosion.

#### 1.1.2.3.1 Activation Energy Control

Activation energy controlled corrosion occurs when an electrochemical step has a high activation energy and the resulting electron transfer rate is slower compared to the mass transport rate of reactants. Assuming a very fast mass transport rate that enables the concentrations of reactants at the electrode/electrolyte interface equal to those in the bulk solution, the departure from equilibrium at an overpotential can be expressed by the Butler-Volmer equation:

$$i = i_0 exp \left[ \frac{(1-\alpha)nF\eta}{RT} \right] - i_0 exp \left[ \frac{-\alpha nF\eta}{RT} \right]$$
(1.16)

Where  $\alpha$  is transfer coefficient ranging between 0 and 1, typically close to 0.5. It is a measure of the symmetry of the energy barrier. The first exponential term represents the anodic current (Figure 1.5, pink dashed curve) and the second term is the cathodic current (Figure 1.5, blue dashed curve). The sum of anodic and cathodic currents is the measured current in polarization measurements (Figure 1.5, black solid curve).



**Figure 1.5:** Activation energy controlled anodic and cathodic corrosion reactions. Partial reaction current changes as a function of overpotential according to eq 1.16. Pink dashed line: anodic current. Blue dashed line: cathodic current. Black solid line: net current. Corrosion potential ( $E_{corr}$ ) is a mixed potential where the rates of anodic and cathodic reactions are equal and the exchange current ( $i_a = i_c$ ) is the corrosion current ( $i_{corr}$ )

When the overpotential  $\eta$  is sufficiently large ( $|\eta| > 50mV$ ), one of the exponential terms in eq1.16 can be negligible. Butler-Volmer equation can be approximated to:

• Anodic polarization ( $\eta$  is positive)

$$i = i_a = i_0 exp\left[\frac{(1-\alpha)nF\eta_a}{RT}\right]$$
(1.17)

• Cathodic polarization ( $\eta$  is negative)

$$i = i_c = -i_0 exp\left[\frac{-\alpha n F \eta_c}{RT}\right]$$
(1.18)

Eq 1.17 and eq 1.18 can be rearranged to Tafel form:

$$\eta_a = \frac{2.3RT}{(1-\alpha)nF} logi - \frac{2.3RT}{(1-\alpha)nF} logi_0$$
(1.19)

$$\eta_c = \frac{2.3RT}{-\alpha nF} logi + \frac{2.3RT}{\alpha nF} logi_0 \tag{1.20}$$

#### 1.1.2.3.2 Potentiodynamic Polarization Curve

The kinetic parameter  $\alpha$  can be experimentally determined from Tafel slopes  $(2.3RT)/((1-\alpha)nF)$  and  $(2.3RT)/(-\alpha nF)$  of potentiodynamic polarization (PDP) measurement.<sup>67</sup> PDP is one of the most commonly used polarization methods to explore corrosion kinetics, in which a wide range of potential is linearly applied in one direction at a selected scan rate to drive the reactions. Currents are measured and plotted as a function of potentials.

Figure 1.6 depicts a PDP curve plotted as Tafel form in the absence of mass transport limit. The inverted peak points to  $E_{corr}$  on the x axis and Tafel slopes can be extracted from the linear segments of the curve far from  $E_{corr}$ . As the potential approaches  $E_{corr}$ , the curve gradually deviates from Tafel behavior (eq 1.17 and eq 1.18), because the partial reactions can no longer be negligible. Ideally, the extrapolated anodic and cathodic linear segments will intersect at  $E_{corr}$ , where the corresponding current is the  $i_{corr}$ . However, in practice, since the supply of reactants cannot support the fast electron transfer at large  $\eta$ , the mass transport of reactants will be the limitation. Therefore, the kinetics will no longer be activation controlled at large  $\eta$ , where the Butler-Volmer equation cannot be used.



**Figure 1.6:** Corrosion current ( $i_{corr}$ ) and corrosion potential ( $E_{corr}$ ) are determined by Tafel extrapolation in a slow scan rate potentiodynamic polarization measurement.

#### 1.1.2.3.3 Mass Transport Control

Corrosion is dominated by the mass transport when the rate of reactant supply is slower compared to the electron transfer of reactions, which is likely to occur at low reactant concentrations, poor agitation and large overpotentials. In such cases, the current is dependent on the number of reactants arriving to the electrode surface:

$$i = -J_j n F A \tag{1.21}$$

Where  $J_j$  is the flux of a reactant j, which represents the moles of species passing a give location per unit time and unit area. Since the concentration of reactant decreases from the bulk solution to electrode surface, the flux  $J_j$  is a negative value. i is the current. n is the number of electron involved. A is the area of electrode surface. The flux can be expressed by the Nernst-Planck equation:

$$J_j(x,t) = -D_j \frac{\partial C_j(x,t)}{\partial x} - \frac{z_j F}{RT} D_j C_j \frac{\partial \varphi(x,t)}{\partial x} + C_j \nu(x,t)$$
(1.22)

Where  $D_j$  is the diffusion coefficient,  $\delta C_j / \delta x$  and  $\delta \varphi / \delta x$  are the concentration and potential gradients at a distance x from the electrode surface,  $z_j$  is the charge,  $\nu(x)$  is the velocity of solution flow. The three terms in eq 1.22 represent the three modes of mass transport in solution: diffusion, migration and convection, which are driven by different forces.

• Diffusion occurs in response to the concentration gradient, which forms due to the consumption of reactant at the electrode surface. The region with a concentration gradient in the vicinity of electrode surface is called diffusion layer. The flux of a species in the diffusion layer at a given location at a time can be estimated in Fick's first law, which is the first term in eq 1.22.

Combining the Fick's first law equation with eq 1.21, the diffusion controlled current can be expressed as:

$$i = nFAD \left[\frac{\partial C_j(x,t)}{\partial x}\right]_{x=0}$$
(1.23)

However, Fick's first law only applies to steady state systems, where the concentration remains constant. The concentration gradient changing with time always occurs in many cases of diffusion, like the potential sweep voltammetry, which demands Fick's second law:

$$\frac{\partial C}{\partial t} = D_j \frac{\partial^2 C}{\partial x^2} \tag{1.24}$$

Diffusion controlled behaviors are encountered in most of the electrode reactions in voltammetry as overpotential increases. As an anodic PDP curve depicted in Figure 1.7, the reaction is converted to diffusion controlled at  $\eta_1$  where the thickness of diffusion layer is  $x_1$ . With the overpotential increasing, the electron transfer rate continues to increase, leading to a thicker diffusion layer. This slows down the diffusion, causing the current to decrease. When the diffusion layer reaches a limiting thickness  $x_2$  at  $\eta_2$ , the diffusion becomes constant, independent of the overpotential. This gives rise to a steady-state current.



**Figure 1.7:** (a) A steady state current is obtained in an anodic PDP as overpotential increases to a limiting value  $\eta_2$ , where the reaction rate is governed by diffusion. (b) Concentration profiles show the diffusion layer at different overpotentials.

 Migration is the movement of charged species due to the potential gradient and gives rise to the migrational ionic current. All charged species are driven by the electrostatic force and contribute to the ionic current, but the direction depends on the sign of charge, which may be the same or opposite to the diffusion direction. So, the migration will complicate the diffusion of electroactive species and is usually eliminated in practice by adding an excess of nonelectroactive supporting electrolyte. This can increase the conductivity of solution and suppress the migration of electroactive species. Since the fraction of migrational ionic current carried by one ion is proportional to its concentration, the migrational ionic current will be mainly contributed by the supporting electrolyte ions of high concentration. In this way, the migration of electroactive species can be nearly eliminated.

• Convection is caused by the action of a force in the solution including two types: natural convection and force convection. Natural convection is due to the thermal and density changes existing in any solutions. Forced convection, generally, is introduced in a solution deliberately by mechanical means to remove the other mass transport effects.

In aqueous corrosion, the mass transport of oxygen often limits cathodic reaction due to the low concentration of dissolved oxygen. The oxygen reduction reaction (ORR) tends to exhibit a diffusion-limited behavior as the green dashed curve shown in Figure 1.8.<sup>68</sup> A diffusion-limit current density of ORR ( $j_L$ ) in the range of 50-100  $\mu$ A cm<sup>-2</sup> is conventionally accepted.<sup>69</sup> However, the theoretical values for Al were not achieved in studies, because of the rate limitation of the electron transfer and mass transport through the oxide film.<sup>70</sup> Since the rates of cathodic and anodic reactions depend on each other, the diffusion controlled cathodic reaction leads to  $E_{corr}$  and  $i_{corr}$  differing from those in the activation controlled corrosion as illustrated in Figure 1.8.



Figure 1.8: The effect of the mass transport controlled cathodic process on the corrosion.

## 1.1.3 Types of Corrosion

According to the morphology of the corrosion attack, different types of corrosion are identified, which are more or less interrelated in terms of the formation mechanisms. Understanding the reasons for the formation of different types of corrosion is critical for the corrosion prevention and mitigation. This section will introduce the common types that are related to the thesis.

### 1.1.3.1 Uniform Corrosion

Uniform corrosion (general corrosion) is the most common type and causes the largest amount of material loss. This type of corrosion takes place over large visible areas and proceeds at almost the same rate at each point. This causes the metal to become thinner and eventually dissolve entirely. In highly acidic or alkaline solutions, Al experiences uniform corrosion due to the dissolution of protective oxide film (eq 1.25 and eq 1.26).<sup>71</sup>

$$Al_2O_{3(s)} + 6 H^+_{(aq)} \longrightarrow 2 Al^{3+}_{(aq)} + 3 H_2O_{(l)}$$
 (1.25)

$$Al_2O_{3(s)} + 2OH_{(aq)}^- \longrightarrow 2AlO_2^{-}_{(aq)} + H_2O_{(l)}$$
(1.26)

In practical applications, the uniform corrosion is not detrimental, because the life time of corroded material can be estimated from the corrosion rate by measuring the weight loss of a specimen immersed in a corrosive solution during a testing time.<sup>72</sup> How-ever, this method is not accurate if there is concurrent localized corrosion.

#### 1.1.3.2 Galvanic Corrosion

Galvanic corrosion occurs when two dissimilar metals are electrically connected and immersed in the same electrolyte (Figure 1.9) or when two different parts of the same metal are exposed to the electrolytes with different concentrations. The difference in  $E_{corr}$  is the driving force for galvanic corrosion. In a galvanic couple, the metal surface with a more negative  $E_{corr}$  acts as the anode and experience accelerated dissolution. The other one with a more positive  $E_{corr}$  is protected as the cathode and cathodic reactions take place on the surface. Electrons flow between them, forming a closed circuit. The galvanic corrosion is the basis for many other types of corrosion, like pitting, crevice and intergranular corrosion. In alloys, the microgalvanic corrosion between intermetallics and the surrounding matrix is often the initiation of macroscale corrosion. For example, in AA7075, the cathodic intermetallics Al<sub>7</sub>Cu<sub>2</sub>Fe and (Al,Cu)<sub>6</sub>(Fe,Cu) promote the dissolution of Al matrix,<sup>21,73</sup> forming valleys on the surface, which may evolve into pitting corrosion.



Figure 1.9: Galvanic corrosion between two dissimilar metals

#### 1.1.3.3 Pitting Corrosion

Pitting corrosion is a type of localized corrosion, characterized by the formation of irregular shaped pits on the surface of materials. As described in galvanic corrosion, the dissolution of anodic intermetallics or the Al matrix surrounding cathodic intermetallics will initiate a pit due to the galvanic corrosion.<sup>74,75</sup> Additionally, in the presence of aggressive anions in neutral electrolytes, the Al matrix area is also prone to pitting corrosion,<sup>76</sup> due to the damage of aggressive anions to the oxide film at weak points. Cl<sup>-</sup> as the constituent of seawater, is the most common aggressive anions in nature. In corrosion studies, a 3.5 wt% NaCl aqueous solution is usually used to simulate the corrosive Cl<sup>-</sup> environment in seawater.

Typically, stable pits undergo a metastable stage after the breakdown of oxide film. Metastable pits experience repassivation,<sup>77</sup> which can be characterized by the potential perturbations in the OCP measurement<sup>78</sup> and andoic current transients in the potentiometric measurement.<sup>79</sup> On an anodic PDP curve as depicted in Figure 1.10, the potential corresponding to the continuous increase of anodic current is the pitting potential ( $E_{pit}$ ) and the current peaks occurring before  $E_{pit}$  indicate metastable pitting. The pitting current peaks appearing in the thesis are mostly metastable pitting.



**Figure 1.10:** A continuous rise in anodic current on a Tafel plot represents stable pitting, where the potential is the pitting potential. Current transients before pitting potential represent metastable pitting.

Micropits propagate to large pits, which further accelerate localized corrosion through galvanic corrosion. Due to structural constraints, there will be a lower oxygen content at the bottom of pit, giving rise to a more negative  $E_{corr}$  than the outside where the oxygen content is higher. The  $E_{corr}$  difference leads to galvanic corrosion and promotes Al oxidation inside the pit. The produced Al<sup>3+</sup> cations will be neutralized by Cl<sup>-</sup> anions, because Cl<sup>-</sup> has better mobility than the OH<sup>-</sup> generated at the external cathode. The resulting AlCl<sub>3</sub> undergoes hydrolysis leading to acidification, which accelerates the pit growth.

#### 1.1.3.4 Intergranular Corrosion

Intergranular corrosion is a selective corrosion attack at grain boundaries or the adjacent zones, which is associated with the precipitation of specific elements in boundaries. The precipitates lead to a potential difference between the grain boundary regions and grain interior, causing galvanic corrosion. Anodic precipitates cause metal dissolution at boundaries. MgZn<sub>2</sub> is a typical anodic intermetallic in AA7075, usually continuous segregated at grain boundaries.<sup>80</sup> Cathodic grain boundary precipitates are usually Cu-rich intermetallics.<sup>31</sup> The segregation of Cu at boundaries results in Cu depleted anodic zone in the vicinity, inducing the matrix dissolution along grain boundaries. When the intergranular corrosion penetrates into the bulk material, it may lead to intergranular cracking in the presence of a tensile stress.

## 1.2 Scanning Electrochemical Cell Microscopy (SECCM)

The previous section has introduced the basic knowledge of Al corrosion and presents that corrosion is mostly initiated at microscale sites associated with the microstructural heterogeneity. SECCM as a powerful scanning electrochemical technique provides a direct way to monitor the microscopic corrosion related electrochemical processes. This section will introduce SECCM from the aspects of advantages, working principle, technique evolution and application in the corrosion field.

# 1.2.1 Advantages of SECCM over Other Scanning Electrochemical Techniques

Numerous scanning electrochemical techniques have been developed and successively introduced into the field of corrosion to study the corrosion related electrochemical phenomena on specific microstructural features. Representative examples include:

 Scanning reference electrode technique (SRET),<sup>81,82</sup> and the advanced successor scanning vibrating electrode technique (SVET)<sup>83,84</sup>

SVET scans potential changes above the sample surface that are caused by differences in  $iR_{\Omega}$  when encountering local current density above intermetallics during corrosion. In SVET, the probe is vibrated perpendicular to the sample, producing a higher signal-to-noise ratio compared to that in SRET which employs a stationary probe.

• Scanning Kelvin probe force microscopy (SKPFM)<sup>85,86</sup>

SKPFM maps the work function of a sample surface based on the capacitor between the surface and probe, and can produce a resolution at molecular scales based on atomic force microscopy (AFM) setup. Work function is defined as the energy needed to remove an electron from the Fermi level in a solid to vacuum, which can be used to reflect the corrosion resistance of a surface.

• Local electrochemical impedance spectroscopy (LEIS),<sup>87,88</sup>

LEIS measures the local impedance of a surface based on the potential gradient in solution generated by the ac current response from the sample surface. LEIS can be performed at a single frequency while the probe is scanned over a surface, or by varying the ac frequency to measure a full electrochemical impedance spectrum at a single location.

• Scanning electrochemical microscopy (SECM)<sup>89-91</sup>

SECM measures the currents from the redox media in the solution using a microelectrode placed close to the substrate surface. The magnitude of currents can be correlated to the reactivity of the substrate surface.

Despite these techniques having provided extensive information on localized corrosion,<sup>83,92–95</sup> they still suffer from some limitations. In SVET, LEIS and SECM, the entire sample surface is immersed under the solution, which causes the surface to change during the experiment. The inconsistent experimental conditions can result in variations on the map unrelated to the reactivity of the original surface. Furthermore, in SVET, LEIS and SECM, constant distance scan mode is used, which encounters difficulties if the substrate surface is not flat. An uneven substrate may break the probe and also leads to different distances between probe and substrate, which will give rise to misleading electrochemical data. Additionally, and most importantly, these techniques cannot provide direct local corrosion currents, thus not allowing for the study of corrosion kinetics.

In 2009, SECCM was introduction by Patrick R. Unwin et al,<sup>6</sup> opening up the avenue to directly map surface electrochemical processes. SECCM employs a (sub)micropipette filled with electrolyte to approach the sample surface at a series of pre-defined locations, which is immune to the topographic effect. A droplet cell created at the end of pipette wets the sample surface, where electrochemical measurements are performed, without affecting other areas. Due to the powerful capability in extracting spatially-resolved electrochemical information, SECCM has been extensively used to characterize battery electrode materials,<sup>96–100</sup> graphene and graphite,<sup>101–106</sup> electrochcatalyst,<sup>107–110</sup> nanoparticles,<sup>111–113</sup> etc. In 2019, SECCM was expanded to the field of corrosion,<sup>114</sup> opening up the prospect to elucidate the microstructure related microscopic corrosion based on the direct surface electrochemical measurements.

## 1.2.2 Working Principle of SECCM

A (sub)micropipette filled with electrolyte solution is used as the probe. The diameter of the pipette tip opening determines the size of droplet cell, which defines the spatial resolution of mapping. The diameter of pipette is selected according to the dimension of target. For example, the studies of electrochemical activities at nanoscale features, such as grain boundaries, edge structure and nanoparticles, employed nanopipettes, <sup>101,102,111,115,116</sup> whereas the measurements that need to scan a large area, like the grain-dependent electrochemical phenomena, used micropipettes.<sup>117-119</sup> A miniaturized non-isolated wire electrode serves as the quasi-reference counter electrode (QRCE), inserted from the top to the pipette as shown in Figure 1.11. The pipette is approached to sample surface with an approach potential  $(E_{appr})$  applied. Upon the droplet contact with the sample surface, a feedback current will be generated that exceeds the set current threshold, causing the pipette to stop moving. Simultaneously,  $E_{appr}$  is removed and local electrochemical measurements are performed. Afterwards, the pipette is retracted and laterally moved to the next location repeating the approach process, which is called hopping mode as illustrated in Figure 1.11. Using hopping mode, the substrate topography will not affect the electrochemical measurements and a synchronous topographic map can be achieved.<sup>108,111,120</sup>



Figure 1.11: Schematic of a single-channel pipette SECCM mapping in hopping mode.

The use of current as the positional signal is called chronogalvanometric mode. By contrast, a chronopotentiometric mode was reported recently, in which the potential is adopted as the positional feedback signal by applying current during the pipette approach,<sup>108,121</sup> satisfying the need for galvanostatic techniques. Currently, the chronopotentiometric mode remains the dominant approach and is divided into two systems based on the type of pipette.

#### 1.2.2.1 Single-Channel Pipette System

A single-channel pipette SECCM setup is shown in Figure 1.12, where  $E_{appr}$  is applied between substrate working electrode (WE) and QRCE. As the electric circuit is open prior to the droplet landing, opposite charges are aligned on the surface of droplet and substrate. Upon the droplet landing on the substrate, the electric circuit is closed, when opposite charges flow through the external electric circuit like the discharging process of a capacitor, resulting in a transient capacitive current. At the same time, reactions take place at the droplet/substrate interface driven by  $E_{appr}$ , giving rise to a transient faradaic current. The capacitive and faradaic currents compose the feedback current and the ratio of these two components depends on the conductivity of substrate and the composition of electrolyte.



**Figure 1.12:** (a) Schematic of the approaching principle of a single-channel pipette SECCM. (b) Approach potential ( $E_{appr}$ ) is applied during the pipette approach to the substrate and a rapid increase in the current is detected upon the droplet landing on the substrate.

#### 1.2.2.2 Double-Channel Pipette System

Double-channel pipette SECCM has two QRCEs that are inserted in the two separate channels of pipette as shown in Figure 1.13a. Different from the single-channel pipette system, a bias potential ( $V_{\text{bias}}$ ) is applied between the two QRCEs during the pipette approaching, producing an ionic conductance current ( $i_{\text{cond}}$ ) flow across the droplet. Meanwhile, the pipette is periodically oscillated perpendicular to the substrate, generating an alternating current ( $i_{\text{ac}}$ ) component from  $i_{\text{cond}}$ . Once the droplet contacts the substrate, it will experience reversible deformation at the same frequency with the oscillation. This leads to an increase in  $i_{\text{ac}}$  because  $i_{\text{ac}}$  is sensitive to the droplet morphology. Therefore,  $i_{\text{ac}}$  can be used as the droplet positional feedback signal. Because the magnitude of  $i_{\text{ac}}$  is independent of the conductivity of substrate surface, the double-channel SECCM can be used

for insulators and semiconductors,<sup>122</sup> but so far still mainly for conductive substrates. Notably, Paulose Nadappuram et al. reported a quad-channel pipette used as a multifunctional probe that combines the double-channel SECCM and SECM with the other two diagonal channels deposited with carbon as microelectrodes.<sup>123</sup> This work shows the prospect of integrating SECCM with other functions, such as local pH measurement.



**Figure 1.13:** (a) Schematic of the approaching principle of a double-channel pipette SECCM. A bias potential ( $V_{\text{bias}}$ ) is applied between two QRCEs, resulting in a conductance current  $i_{\text{cond}}$ .  $i_{\text{cond}}$  gives rise to an alternative current  $i_{\text{ac}}$  due to the periodic oscillation of pipette. (b) The droplet contact with the substrate results in an increase in  $i_{\text{ac}}$ , which is used as the positional feedback current. Adapted with permission from Reference 124. Copyright © 2017 Elsevier B.V.

## **1.2.3** Technical Development and Evolution

#### 1.2.3.1 Micro-Capillary Cell Technique

SECCM was developed as an advanced scanning version of micro-capillary cell (MCC) technique, but used smaller pipettes.<sup>6</sup> MCC was introduced by T. Suter et al. in the nineties to measure the electrochemistry of single microstructural heterogeneities of metal

materials using capillaries ranging from 1 to 1000  $\mu$ m.<sup>124,125</sup> In fact, the spatial resolution of MCC is limited by the current resolution of potentiostat rather than the capillary size.<sup>126,127</sup> Taking advantage of the direct local electrochemical measurement, MCC was extensively used to study the localized corrosion related to intermetallics and inclusions, passive film and pitting susceptibility of stainless steel,<sup>125,128,129</sup> duplex stainless steel,<sup>130–132</sup> and Al alloys.<sup>133–135</sup> Compared to SECCM, MCC is primarily a stationary local technique, with a silicon rubber gasket at the end of capillary to enclose the droplet cell (Figure 1.14).<sup>125,136</sup> Free droplet was also used to scan the substrate surface in a continuous mode, instead of hopping mode, which can be regarded as the early version of SECCM.<sup>126,137,138</sup> Since large free droplets tend to leak, substrate surfaces are required to be not-wetting, like most of the electropolished metals. This produces a large contact angle preventing droplet spreading and decreases the friction when scanning the droplet on the substrate surface. By contrast, the silicone gasket sealed droplet can be applicable to more versatile substrates including rough and hydrophilic surfaces.



**Figure 1.14:** Schematic of experimental setup of micro-capillary cell. Adapted with permission from Reference 129. Copyright © 2001 ECS - The Electrochemical Society Different from the SECCM setup, a typical MCC setup is usually in a three-electrode arrangement, with reference electrode (RE) and counter electrode (CE) connected to WE through a holder as shown in Figure 1.14. The holder enables the flow of electrolyte and thereby allows the analysis of corrosion products by coupling MCC with other techniques, such as ultraviolet-visible spectrophotometer (UV-VIS)<sup>139–141</sup> and inductively coupled plasma mass spectroscopy (ICP-MS).<sup>142,143</sup> In an alternative arrangement, the RE is directly inserted in a metal capillary or glass capillary with metallized inner surface which serves as the CE. This is similar to the two-electrode arrangement of SECCM, decreasing the distance between WE and RE, and hence the Ohmic drop.<sup>126,137,144,145</sup>

#### 1.2.3.2 SECCM in Air

Based on the working principle of MCC and SECM, Unwin group developed the singlechannel pipette SECCM in 2009, and named it as scanning micropipette contact method (SMCM).<sup>6</sup> They used micropipettes with diameters of 300 nm to 1  $\mu$ m to map the highly oriented pyrolytic graphite and aluminum alloy AA1050, based on the reactions of redox mediates in the electrolyte. This is similar to the SECM measurement that relies on indirect currents associated to the substrate conductivity, but SMCM does not require the whole surface to be immersed in the solution, thus avoiding the effect of other areas. Built on SMCM, double-channel pipette SECCM was reported in 2010,<sup>7</sup> which has a more precise tip position control with the conductance alternative current. This was tested on 25  $\mu$ m wide gold bands separated on a glass slide. Electrochemical and topographical maps were obtained as shown in Figure 1.15. Since then, SECCM was formally used to describe both single- and double-channel pipette systems. SMCM only refers to the single-channel pipette SECCM.



**Figure 1.15:** SECCM images of gold bands on glass. (a) 3D topography of the sample. (b) Plane fitted topographical data. (c) Surface current maps of the gold band structure. (c) Surface current in 2 mM FcTMA<sup>+</sup>, 20 mM KCl. The substrate was biased at +500 mV with respect to the Ag/AgCl quasi-reference electrode. Adapted with permission from Reference 7. Copyright © 2010, American Chemical Society.

## 1.2.4 Application of SECCM in Corrosion Studies

SECCM was applied to corrosion studies since 2019 and over the past three years, there are total eight papers reporting for carbon steel,<sup>114,146,147</sup> zinc,<sup>148</sup> copper,<sup>121</sup> silver,<sup>149</sup> aluminum alloys (chapter 2 and chapter 3).<sup>150,151</sup>

The first application of SECCM on corrosion was to probe the local electrochemical phenomena on carbon steel in a 10 mM KNO<sub>3</sub> neutral solution with a 2  $\mu$ m diameter

double-channel pipette.<sup>114</sup> A 17 x 17 matrix of droplet landing points were achieved with PDP measurement (scan rate: 50 mV/s) at each (Figure 1.16a). Tafel plots exhibited spikes on the anodic branches at MnS inclusions, indicating metastable pitting, agreeing with the previous studies by MCC on pitting initiation at MnS sites..<sup>127,129,152</sup> Moreover, in conjunction with the electron backscatter diffraction (EBSD) map (Figure 1.16b), Tafel plots on (100), (101) and (111) grains were extracted and displayed similar cathodic branches, but larger anodic currents on (101) grains (Figure 1.16d), indicating the dependence of anodic passive film growth on the grain orientations. Most importantly, this work firstly demonstrates the capability of SECCM in investigating the structure-activity relationship in corrosion science. However, due to the limited number of droplet landing points, it is difficult to gain more detailed information on grain dependent corrosion behaviors.



**Figure 1.16:** (a) SEM image of the low carbon steel surface that was characterized with SECCM, with EBSD map superimposed and (b) the corresponding EBSD map. The droplet footprints are clearly visible on the SEM image. (c) Grains deemed close enough to the low index planes of (100), (101) and (111), respectively. (d) Representative Tafel plots obtained on the (100) (red trace), (101) (green trace) and (111) (blue trace) grains. The plots were obtained by averaging the i-E data collected during PDP measurements made with SECCM. 15, 12 and 26 individual measurements were averaged on the (100), (101) and (111) grains, respectively. The highlighted section is magnified. The dashed lines included above and below the traces represents the standard error of the data. Adapted with permission from Reference 114. Copyright © 2019 Elsevier.

The following works performed by the same group on carbon steel obtained 1600 and 3600 droplet landings with a 150 nm diameter single-channel pipette, significantly improving the spatial resolution and the number of local electrochemical measurements. The cathodic reaction HER and anodic iron dissolution of carbon steel in the 5 mM H<sub>2</sub>SO<sub>4</sub> acidic solution were analyzed and correlated to grain orientations in two separate works. The study of HER performed a chronoamperometric program at each point, consisting of a 10 ms anodic potential to form the passive film and a 10 ms cathodic potential to drive HER.<sup>146</sup> The following work carried out cyclic voltammetry at a fast scan rate of 2 V/s to visualize the grain-dependence of anodic iron dissolution.<sup>147</sup> In both cases, short times spent at each location greatly reduced the total imaging time. This allows to gain a large quantity of droplet landing points, ensuring the validity of grain-dependence analyses. More specific grain dependence trends of the cathodic HER and anodic iron dissolution were extracted, decreasing in the order of (100) > (111) > (101). Furthermore, the high resolution SECCM map allows to visualize the promoted HER activities at the nanoscale grain boundaries.

However, in neutral solutions, electrochemical measurements cannot be completed in such short times, especially OCP and PDP, because the establishment of steady state is not as rapid as that in acidic solutions. This is bound to take a long time for mapping, which requires a long-term stable droplet. Although the number of SECCM applications in corrosion is limited so far, SECCM has proven to be a powerful tool for identifying the electrochemical differences between small structural variations.

#### **1.2.5** Experimental Considerations for SECCM Measurement

#### 1.2.5.1 Droplet Evaporation and Spreading

Small droplets suffer from evaporation due to the large surface-to-volume ratio.<sup>153</sup> This was usually solved by creating a humidified cell using a solution moat or wet gas flow

to increase the environmental humidity,<sup>115,154–156</sup> especially when KCl was used as the supporting electrolyte, making solution readily evaporate. In corrosion studies, the commonly used NaCl solutions are also subject to serious evaporation in atmospheric air, which hinders the application of SECCM. By contrast, the studies of lithium battery materials and electrocatalysis for electrocatalytic hydrogen evolution reaction (HER) usually do not need humidified cells, because the used lithium saline electrolytes<sup>96–98,157</sup> and acidic solutions<sup>107,110,112,158,159</sup> are invulnerable to evaporation. In addition, to prevent pipette breakage due to the spread of droplet on the pipette glass, the outer wall of micropipette tip needs to be silanized to make it hydrophobic, usually using dichlorodimethyl-silane.<sup>114,160</sup>

#### 1.2.5.2 Fast Scan Rate of PDP

In corrosion science, PDP is often carried out at a low scan rate of 0.167 mV/s recommonded by ASTM standard,<sup>161</sup> in which the electrochemical processes can remain steady state at each potential. However, 0.167 mV/s is not realistic for a SECCM map consisting of hundreds and even thousands of PDP measurements. Thus, a fast potential scan rate is usually applied, but it will accelerate the anodic process within the oxide film, and introduce capacitive charging current.

#### 1.2.5.2.1 Anodic Current Related to Oxide Film and Scan Rate

The formation of anodic barrier oxides on passive metals, like Al, Ti, Nb, Zr and Hf<sup>162</sup> depends on the migration of ions through the oxide film driven by an electric field according to the high field model:<sup>56,57</sup>

$$j = A \exp BH \tag{1.27}$$

Where j is oxide formation density, A and B are temperature dependent constants (kinetic parameters of the oxide growth), H is the electric field strength defined as the potential drop across the oxide film divided by the film thickness.

The thickness of oxide film is determined by the applied anodizing potential. D. Hasenay et al.<sup>163</sup> reported that *H* can be related to the potential scan rate (v) and anodic plateau current density ( $j_{pl}$ ) of PDP measurement for Al:

$$H = \frac{zFv}{V_m j_{pl}} \tag{1.28}$$

Where *z* is the number of electrons used in anodizing process, *F* is the Faraday constant (96 485 C mol<sup>-1</sup>),  $V_{\rm m}$  is the molar volume of oxide layer and equal to the molar mass (M) divided by the mass density ( $\rho$ ).

A relationship between the anodic plateau current density and scan rate can be achieved by combining eq 1.27 and eq 1.28:<sup>163</sup>

$$log j_{pl} = log A + B \frac{zF\upsilon}{2.3V_m j_{pl}}$$
(1.29)

According to eq 1.29, a fast potential scan rate will lead to a higher anode current, resulting in a distorted PDP curve, which was demonstrated by the study of H. Zhou et al. on Al alloy AA7075.<sup>164</sup>

#### 1.2.5.2.2 Double Layer Capacitive Charging Current

The charging process of WE always contributes a nonfaradaic capacitive charging current to the external current, due to the separation of charges in the electrode/solution interfacial region. The potential applied at WE causes a charge imbalance at the electrode/solution interface, which is neutralized by the rearrangement of charged species in the solution. Those charged species form a so-called double layer structure with three regions separated by two planes as depicted in Figure 1.17. The innermost layer consists of water molecules and specifically adsorbed ions, the center of which is called Inner Helmholtz Plane (IHP). The second layer is composed of nonspecifically adsorbed solvated ions, the center of which is called Outer Helmholtz Plane (OHP). The final region, called diffuse layer, extends from OHP to bulk solution. Beyond the diffuse layer, ions are not subject to the electrostatic attraction of the charged electrode surface.



**Figure 1.17:** Depiction of the electrical double layer that is composed of Inner Helmholtz Plane (IHP), the Outer Helmholtz Plane (OHP), and diffuse layer.

The separation of opposite charges at the electrode/solution interface and the double layers in the solution can be analogized to the plates of multiple tandem capacitors. During a PDP, the linearly scanned potential leads to a continuous change in the charges stored in the interfacial regions, producing a capacitive charging current which distorts the PDP curve. Because the capacitive current is proportional to the potential scan rate (eq 1.30), a fast scan rate will increase the capacitive charging current and aggravates the distortion of PDP curve.

Capacitive current = 
$$C \frac{\partial E}{\partial t}$$
 (1.30)

Where *C* is the capacitance and  $\partial E/\partial t$  can represent the scan rate in PDP. The direction of charging current depends on the direction of potential sweep. In a positive PDP where the potential increases in the positive direction, electrons flow from WE to external circuit, producing a charging current in the direction of anodic faradaic current. The increase of anodic current will shift the zero-net-current potential ( $E_{corr}$ ) to a more negative value where the a larger cathodic current can neutralize the increased anodic current. Nevertheless, the extent of shift depends on the ratio of charging current to faradaic current.

#### 1.2.5.3 Quasi-Reference Counter Electrode

In a tyipcal SECCM setup, RE serves as the CE because the passage of small currents (between  $10^{-9}$  and  $10^{-15}$  A) does not change the potential of RE. RE is a nonpolarizable electrode whose reaction is infinitely fast having a very large  $i_0$  so that small current flow does not change the equilibrium potential. Commercially available REs are usually isolated from the sample solution using a glass frit or salt bridge to eliminate the contamination from inner solution to outer sample solution, but they are not suited for small electrochemical cells due to the bulky size. In SECCM, a non-isolated miniaturized metal wire is used as a QRCE directly inserted in the micropipette. Because the potential of QRCE is dependent on the composition of sample solution, QRCE needs to be calibrated with respect to an isolated RE in the sample solution before use.

Ag/AgCl wire electrode is the most commonly used QRCE in neutral solutions,<sup>96,102,104,105</sup> and some acidic solutions such as H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>.<sup>148,159,165</sup> It is fabricated from a silver wire by oxidation forming an outer layer of AgCl through electrochemical deposition or chemical chlorization in chloride containing solutions.<sup>166,167</sup> The potential of Ag/AgCl is determined by the reversible redox reaction between the solid Ag<sub>(s)</sub> and AgCl<sub>(s)</sub>. Due to the dissociation of AgCl ( $K_{sp} = 1.8 \times 10^{-10}$ ), there will be Ag<sup>+</sup> ions near the Ag/AgCl

wire. In alkaline solutions, Ag<sup>+</sup> forms AgOH precipitates ( $K_{sp} = 2.0 \times 10^{-8}$ ) and therefore Ag/AgCl wire cannot be used. Ag/AgO<sub>x</sub> wire and Pt wire have been reported to be used as QRCE in KOH solutions.<sup>109,168</sup> In acidic solutions, Pd/H<sub>2</sub> is the mostly employed,<sup>111,112,169</sup> which is fabricated by hydrogenerating a Pd wire in H<sup>+</sup> containing solutions.<sup>112,158</sup> Untreated noble metal wires can also serve as QRCE if there is a stable ionic activity of the related ions. For example, Pt wire serves as QRCE in the 1 mM K<sub>2</sub>[PtCl<sub>4</sub>] solution, whose potential is determine by the redox reaction between Pt<sup>2+</sup> and Pt.<sup>170</sup> Some studies employed a commercial leak-free Ag/AgCl as RE to eliminate the leakage of interfering ions.<sup>115,171</sup> A leak-free RE is in ionic contact with the electrolyte via a pipette holder, which is presented in chapter 3.

#### 1.2.5.4 Ohmic Drop

The current flow between CE and WE leads to a potential drop (Ohmic drop <sub>ohmic</sub>) as depicted in Figure 1.18, which is affected by the distance between RE and WE, and electrolyte conductivity.



**Figure 1.18:** Schematic of Ohmic drop  $iR_{\Omega}$  in the micropipette based electrochemical cell.

Due to the use of QRCE, CE and RE are placed at the same distance away from WE. The current between CE and WE is equivalent to that between RE and WE. According to Ohm's law, <sub>ohmic</sub> is the product of current (*i*) and Ohmic resistance ( $R_{\Omega}$ ) between RE and WE:

$$\Delta E_{ohmic} = iR_{\Omega} \tag{1.31}$$

Since the applied potential ( $E_{applied}$ ) is referenced to RE, the actual potential ( $E_{actual}$ ) applied on WE is:

$$E_{actual} = E_{applied} - \Delta E_{ohmic} = E_{applied} - iR_{\Omega}$$
(1.32)

Since  $R_{\Omega}$  increases with the distance between RE and WE, RE should be placed close to WE when the electrolyte is not highly conductive. Normally, supporting electrolyte, an electroinactive salt like KCl, is intentionally added to increase the solution conductivity.

The evaluation of  $\Delta E_{\text{ohmic}}$  can be done by current interruption technique or impedance spectroscopy. Birbilis et al. demonstrated that  $R_{\Omega}$  is geometry dependent with respect to the diameter of micropipette ( $D_{\text{micropipette}}$ ).<sup>172</sup> L.C. Yule et al. reported that currents up to 100 pA was not subject to a significant  $\Delta E_{\text{ohmic}}$  in a 10 mM KNO<sub>3</sub> solution for a 2  $\mu$ m diameter double channel micropipette.<sup>114</sup> However, PDP measurements above  $E_{\text{pit}}$  generate large currents, which may lead to a high  $\Delta E_{\text{ohmic}}$ . Simultaneously, extensive corrosion products will be produced, probably blocking the micropipette. Therefore, it is suggested to terminate the potential sweep during PDP before pitting.

## **1.3 Thesis Outline**

The application of SECCM in corrosion studies remains challenging due to the serious droplet evaporation of most Cl<sup>-</sup> containing electrolytes. This thesis strives to make the single-channel SECCM (SMCM) applicable to corrosion experimental conditions by developing an oil-immersed SECCM (OI-SECCM) and clarifying the influence of SECCM related experimental parameters on electrochemical measurements. OI-SECCM was applied to study the microscopic corrosion of Al alloy AA7075-T73 in relation to intermetallics, oxide film, grain, and grain boundary. OI-SECCM is expected to facilitate direct electrochemical measurements of localized corrosion phenomena, which is the significance of this thesis.

Chapter 2 describes the development of OI-SECCM to solve the problem of droplet evaporation of 3.5 wt% NaCl electrolyte. This allows to perform a long-term scan in which the time-consuming OCP and PDP measurements can be conducted. Galvanic corrosion between intermetallics and Al matrix was analyzed.

Chapter 3 uncovers the interference of Ag<sup>+</sup> contaminants from Ag/AgCl wire QRCE on measurements of  $E_{\text{corr}}$ . Solutions are proposed to eliminate the  $E_{\text{corr}}$  drifts.

Chapter 4 clarifies the effect of  $E_{appr}$  on the droplet landing process and structure of surface Al oxide, resulting in variations in OCP and PDP measurements. This provides a strategy to control the surface oxide conductivity by adjusting the value of  $E_{appr}$ .

Chapter 5 investigates the correlations of multiple corrosion related electrochemical processes to grain orientations and boundary, based on the large quantity of PDP measurements obtained by OI-SECCM and the colocated EBSD mapping.
## References

- Rana, R.; Purohit, R.; Das, S. International Journal of Scientific and Research Publications 2012, 2, 1–7.
- 2. Davis, J. R. et al., *Aluminum and Aluminum Alloys*; ASM international: 1993.
- Hou, B.; Li, X.; Ma, X.; Du, C.; Zhang, D.; Zheng, M.; Xu, W.; Lu, D.; Ma, F. *npj Materials Degradation* 2017, 1, 1–10.
- Koch, G. H.; Brongers, M. P.; Thompson, N. G.; Virmani, Y. P.; Payer, J. H., et al. Corrosion Cost and Preventive Strategies in the United States; tech. rep.; United States. Federal Highway Administration, 2002.
- Malomo, D.; Scattarreggia, N.; Orgnoni, A.; Pinho, R.; Moratti, M.; Calvi, G. M. Journal of Performance of Constructed Facilities 2020, 34, 04020044.
- 6. Williams, C. G.; Edwards, M. A.; Colley, A. L.; Macpherson, J. V.; Unwin, P. R. *Analytical Chemistry* **2009**, *81*, 2486–2495.
- Ebejer, N.; Schnippering, M.; Colburn, A. W.; Edwards, M. A.; Unwin, P. R. *Analyt*ical Chemistry 2010, 82, 9141–9145.
- 8. Ebejer, N.; Güell, A. G.; Lai, S. C.; McKelvey, K.; Snowden, M. E.; Unwin, P. R. *Annual Review of Analytical Chemistry* **2013**, *6*, 329–351.
- 9. Cayless, R. 2013.
- Kaufman, J. G., Introduction to Aluminum Alloys and Tempers; ASM international: 2000.
- 11. Taylor, J. A. Procedia Materials Science 2012, 1, 19–33.
- 12. Andreatta, F.; Terryn, H.; De Wit, J. Electrochimica Acta 2004, 49, 2851–2862.
- 13. Ebhota, W. S.; Jen, T.-C. Intermetallic Compounds-Formation and Applications, IntechOpen **2018**, 21–41.

- 14. Ebhota, W. S.; Jen, T.-C. Intermetallic Compounds-Formation and Applications, IntechOpen **2018**, 21–41.
- Samuel, A.; Doty, H.; Valtierra, S.; Samuel, F. International Journal of Metalcasting 2018, 12, 625–642.
- Eckermann, F.; Suter, T.; Uggowitzer, P. J.; Afseth, A.; Schmutz, P. Electrochimica Acta 2008, 54, 844–855.
- 17. Buchheit, R. Journal of the Electrochemical Society 1995, 142, 3994.
- Lourenço, J. C.; Robin, A. L. M.; Faria, M. I. S. T.; Prisco, L. P.; Puccini, M. C.; Oliveira, L. D. d. *Materials Research* 2019, 22.
- 19. Zhu, Y.; Sun, K.; Frankel, G. Journal of the Electrochemical Society 2018, 165, C807.
- 20. Birbilis, N.; Buchheit, R. G. Journal of the Electrochemical Society 2005, 152, B140.
- 21. Birbilis, N.; Cavanaugh, M. K.; Buchheit, R. G. Corrosion Science 2006, 48, 4202–4215.
- 22. Ayer, R.; Koo, J.; Steeds, J.; Park, B. Metallurgical Transactions A 1985, 16, 1925–1936.
- 23. Birbilis, N.; Cavanaugh, M. K.; Buchheit, R. G. Corrosion Science 2006, 48, 4202–4215.
- Ambat, R.; Davenport, A. J.; Scamans, G. M.; Afseth, A. Corrosion Science 2006, 48, 3455–3471.
- 25. Van Swygenhoven, H. Science 2002, 296, 66–67.
- Gianola, D.; Van Petegem, S.; Legros, M.; Brandstetter, S.; Van Swygenhoven, H.; Hemker, K. Acta Materialia 2006, 54, 2253–2263.
- Balasubramanian, N.; Langdon, T. G. Metallurgical and Materials Transactions A 2016, 47, 5827–5838.
- Zeiger, W.; Schneider, M.; Scharnweber, D.; Worch, H. Nanostructured Materials 1995, 6, 1013–1016.
- 29. Soleimani, M.; Mirzadeh, H.; Dehghanian, C. *Materials Research Express* 2020, 7, 016522.

- 30. Bulatov, V. V.; Reed, B. W.; Kumar, M. Acta Materialia 2014, 65, 161–175.
- 31. Ramgopal, T.; Gouma, P.; Frankel, G. Corrosion 2002, 58, 687–697.
- 32. Larsen, M. H.; Walmsley, J. C.; Lunder, O.; Mathiesen, R. H.; Nisancioglu, K. *Journal of the Electrochemical Society* **2008**, 155, C550.
- 33. Schreiber, A.; Rosenkranz, C.; Lohrengel, M. *Electrochimica Acta* 2007, *52*, 7738–7745.
- 34. Song, G.-L.; Mishra, R.; Xu, Z. Electrochemistry Communications 2010, 12, 1009–1012.
- 35. Lüth, H., Solid Surfaces, Interfaces and Thin Films; Springer: 2001; Vol. 4.
- 36. Koroleva, E.; Thompson, G.; Skeldon, P.; Noble, B. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2007**, *463*, 1729–1748.
- Holme, B.; Ljones, N.; Bakken, A.; Lunder, O.; Lein, J. E.; Vines, L.; Hauge, T.;
   Bauger, Ø.; Nisancioglu, K. *Journal of the Electrochemical Society* 2010, 157, C424.
- 38. Wang, S.; Wang, J. Corrosion Science **2014**, 85, 183–192.
- 39. Treacy, G. M.; Breslin, C. B. *Electrochimica Acta* **1998**, *43*, 1715–1720.
- 40. Davis, B.; Moran, P.; Natishan, P. Corrosion Science 2000, 42, 2187–2192.
- 41. Flötotto, D.; Wang, Z.; Jeurgens, L. P.; Mittemeijer, E. *Applied Physics Letters* **2014**, 104, 091901.
- 42. Lee, S.; White, H. S. Journal of the Electrochemical Society 2004, 151, B479.
- 43. Ng, C. K.; Ngan, A. H. Chemistry of Materials 2011, 23, 5264–5268.
- Nguyen, L.; Hashimoto, T.; Zakharov, D. N.; Stach, E. A.; Rooney, A. P.; Berkels, B.; Thompson, G. E.; Haigh, S. J.; Burnett, T. L. ACS Applied Materials & Interfaces 2018, 10, 2230–2235.
- 45. Lee, S.; White, H. S. Journal of the Electrochemical Society **2004**, 151, B479.
- 46. Miadoková, M.; Plchová, M.; Halaša, I. Collection of Czechoslovak Chemical Communications **1987**, 52, 88–92.
- 47. Barrie, A. Chemical Physics Letters **1973**, 19, 109–113.

- Evertsson, J.; Bertram, F.; Zhang, F.; Rullik, L.; Merte, L.; Shipilin, M.; Soldemo, M.; Ahmadi, S.; Vinogradov, N.; Carlà, F., et al. *Applied Surface Science* 2015, 349, 826– 832.
- 49. Strohmeier, B. R. Surface and Interface Analysis 1990, 15, 51–56.
- 50. Dunlop, H.; Benmalek, M. Le Journal de Physique IV 1997, 7, C6–163.
- 51. Davis, J. R., Corrosion of Aluminum and Aluminum Alloys; Asm International: 1999.
- 52. Godard, H. P. Journal of the Electrochemical Society **1967**, 114, 354.
- 53. Virtanen, S.; Wojtas, H.; Schmuki, P.; Böhni, H. *Journal of the Electrochemical Society* **1993**, 140, 2786.
- Tuccio, G.; Piazza, S.; Sunseri, C.; Di Quarto, F. *Journal of the Electrochemical Society* 1999, 146, 493.
- 55. Menezes, S.; Haak, R.; Hagen, G.; Kendig, M. Journal of the Electrochemical Society **1989**, 136, 1884.
- 56. Mott, N. Transactions of the Faraday Society **1947**, 43, 429–434.
- 57. Cabrera, N.; Mott, N. F. Reports on Progress in Physics 1949, 12, 163.
- 58. Cai, N.; Zhou, G.; Müller, K.; Starr, D. E. Applied Physics Letters 2012, 101, 171605.
- 59. Baran, J. D.; Grönbeck, H.; Hellman, A. Physical Review Letters 2014, 112, 146103.
- 60. Pourbaix, M. NACE 1974, 307.
- 61. Deltombe, E.; Pourbaix, M. Corrosion 1958, 14, 16–20.
- 62. Natishan, P.; O'grady, W. Journal of the Electrochemical Society 2014, 161, C421.
- 63. Nguyen, T.; Foley, R. Journal of the Electrochemical Society **1980**, 127, 2563.
- 64. Yu, S.; O'grady, W.; Ramaker, D.; Natishan, P. Journal of the Electrochemical Society 2000, 147, 2952.
- O'Grady, W. E.; Roeper, D. F.; Natishan, P. M. *The Journal of Physical Chemistry C* 2011, 115, 25298–25303.

- 66. Frankel, G. Active Protective Coatings **2016**, 17–32.
- 67. Guidelli, R.; Compton, R. G.; Feliu, J. M.; Gileadi, E.; Lipkowski, J.; Schmickler, W.; Trasatti, S. *Pure and Applied Chemistry* **2014**, *86*, 245–258.
- 68. Vukmirovic, M.; Vasiljevic, N.; Dimitrov, N.; Sieradzki, K. *Journal of the Electrochemical Society* **2002**, 150, B10.
- 69. Fontana, M. G.; Greene, N. D. **1967**.
- 70. Ilevbare, G.; Scully, J. Corrosion 2001, 57.
- 71. Draley, J.; Ruther, W. Corrosion **1956**, *12*, 31–38.
- 72. On Corrosion of Metals, A. C. G.-1., *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens;* ASTM International: 2003.
- 73. Andreatta, F.; Terryn, H.; De Wit, J. Corrosion Science 2003, 45, 1733–1746.
- 74. Seri, O.; Furumata, K. *Materials and Corrosion* **2002**, *53*, 111–120.
- 75. Kakinuma, H.; Muto, I.; Oya, Y.; Kyo, Y.; Sugawara, Y.; Hara, N. Journal of the Electrochemical Society **2019**, 166, C19.
- 76. Szklarska-Smialowska, Z. Corrosion Science 1999, 41, 1743–1767.
- 77. Frankel, G. Journal of the Electrochemical Society **1998**, 145, 2186.
- 78. Pride, S.; Scully, J.; Hudson, J. Journal of the Electrochemical Society **1994**, 141, 3028.
- Tang, Y.; Zuo, Y.; Wang, J.; Zhao, X.; Niu, B.; Lin, B. Corrosion Science 2014, 80, 111– 119.
- Svenningsen, G.; Larsen, M. H.; Walmsley, J. C.; Nordlien, J. H.; Nisancioglu, K. Corrosion Science 2006, 48, 1528–1543.
- 81. Kinlen, P. J.; Menon, V.; Ding, Y. Journal of the Electrochemical Society 1999, 146, 3690.
- Trethewey, K.; Sargeant, D.; Marsh, D.; Tamimi, A. *Corrosion Science* **1993**, *35*, 127–134.

- 83. Bastos, A.; Quevedo, M.; Karavai, O.; Ferreira, M. *Journal of the Electrochemical Society* **2017**, 164, C973.
- 84. Isaacs, H. Journal of the Electrochemical Society **1988**, 135, 2180.
- 85. Melitz, W.; Shen, J.; Kummel, A. C.; Lee, S. Surface Science Reports 2011, 66, 1–27.
- 86. Rohwerder, M.; Turcu, F. *Electrochimica Acta* **2007**, *53*, 290–299.
- Huang, V. M.; Wu, S.-L.; Orazem, M. E.; Pébère, N.; Tribollet, B.; Vivier, V. *Electrochimica Acta* 2011, 56, 8048–8057.
- Mouanga, M.; Puiggali, M.; Tribollet, B.; Vivier, V.; Pébère, N.; Devos, O. *Electrochimica Acta* 2013, *88*, 6–14.
- 89. Payne, N. A.; Stephens, L. I.; Mauzeroll, J. Corrosion 2017, 73, 759–780.
- Martinez-Lombardia, E.; Gonzalez-Garcia, Y.; Lapeire, L.; De Graeve, I.; Verbeken,
   K.; Kestens, L.; Mol, J.; Terryn, H. *Electrochimica Acta* 2014, 116, 89–96.
- 91. Izquierdo, J.; Nagy, L.; Varga, Á.; Santana, J. J.; Nagy, G.; Souto, R. M. *Electrochimica Acta* **2011**, *56*, 8846–8850.
- 92. Guillaumin, V.; Schmutz, P.; Frankel, G. Journal of the Electrochemical Society 2001, 148, B163.
- Baril, G.; Blanc, C.; Keddam, M.; Pébère, N. Journal of the Electrochemical Society 2003, 150, B488.
- 94. Lister, T.; Pinhero, P. *Electrochemical and Solid-State Letters* **2002**, *5*, B33.
- 95. Bard, A. J.; Fan, F. R. F.; Kwak, J.; Lev, O. Analytical Chemistry 1989, 61, 132–138.
- Takahashi, Y.; Kumatani, A.; Munakata, H.; Inomata, H.; Ito, K.; Ino, K.; Shiku, H.; Unwin, P. R.; Korchev, Y. E.; Kanamura, K., et al. *Nature Communications* 2014, 5, 1–7.
- Snowden, M. E.; Dayeh, M.; Payne, N. A.; Gervais, S.; Mauzeroll, J.; Schougaard,
   S. B. *Journal of Power Sources* 2016, 325, 682–689.

- 98. Kang, M.; Wilson, P.; Meng, L.; Perry, D.; Basile, A.; Unwin, P. R., et al. *Chemical Communications* 2018, 54, 3053–3056.
- 99. Inomata, H.; Takahashi, Y.; Takamatsu, D.; Kumatani, A.; Ida, H.; Shiku, H.; Matsue,
  T. *Chemical Communications* 2019, *55*, 545–548.
- 100. Takahashi, Y.; Yamashita, T.; Takamatsu, D.; Kumatani, A.; Fukuma, T. *Chemical Communications* **2020**, *56*, 9324–9327.
- 101. Kumatani, A.; Miura, C.; Kuramochi, H.; Ohto, T.; Wakisaka, M.; Nagata, Y.; Ida,
  H.; Takahashi, Y.; Hu, K.; Jeong, S., et al. *Advanced Science* 2019, *6*, 1900119.
- 102. Lai, S. C.; Patel, A. N.; McKelvey, K.; Unwin, P. R. *Angewandte Chemie International Edition* **2012**, *51*, 5405–5408.
- 103. Güell, A. G.; Cuharuc, A. S.; Kim, Y.-R.; Zhang, G.; Tan, S.-y.; Ebejer, N.; Unwin, P. R. ACS nano 2015, 9, 3558–3571.
- 104. Patel, A. N.; Collignon, M. G.; O'Connell, M. A.; Hung, W. O.; McKelvey, K.; Macpherson, J. V.; Unwin, P. R. *Journal of the American Chemical Society* **2012**, *134*, 20117–20130.
- 105. Patel, A. N.; Tan, S.-y.; Unwin, P. R. Chemical Communications 2013, 49, 8776–8778.
- 106. Unwin, P. R.; Guell, A. G.; Zhang, G. *Accounts of Chemical Research* **2016**, *49*, 2041–2048.
- 107. Choi, M.; Siepser, N. P.; Jeong, S.; Wang, Y.; Jagdale, G.; Ye, X.; Baker, L. A. *Nano Letters* **2020**, *20*, 1233–1239.
- 108. Daviddi, E.; Gonos, K. L.; Colburn, A. W.; Bentley, C. L.; Unwin, P. R. *Analytical Chemistry* **2019**, *91*, 9229–9237.
- 109. Tarnev, T.; Aiyappa, H. B.; Botz, A.; Erichsen, T.; Ernst, A.; Andronescu, C.; Schuhmann, W. *Angewandte Chemie International Edition* **2019**, *58*, 14265–14269.
- 110. Tao, B.; Unwin, P. R.; Bentley, C. L. Journal of Physical Chemistry C 2019, 124, 789–798.
- 111. Bentley, C. L.; Kang, M.; Unwin, P. R. Journal of the American Chemical Society 2017, 139, 16813–16821.

- 112. Lai, S. C.; Dudin, P. V.; Macpherson, J. V.; Unwin, P. R. *Journal of the American Chemical Society* **2011**, 133, 10744–10747.
- 113. Kang, M.; Perry, D.; Kim, Y.-R.; Colburn, A. W.; Lazenby, R. A.; Unwin, P. R. *Journal* of the American Chemical Society **2015**, 137, 10902–10905.
- Yule, L. C.; Bentley, C. L.; West, G.; Shollock, B. A.; Unwin, P. R. *Electrochimica Acta* 2019, 298, 80–88.
- 115. Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. Science 2017, 358, 1187–
   1192.
- Byers, J. C.; Güell, A. G.; Unwin, P. R. *Journal of the American Chemical Society* 2014, 136, 11252–11255.
- 117. Aaronson, B. D.; Chen, C.-H.; Li, H.; Koper, M. T.; Lai, S. C.; Unwin, P. R. *Journal of the American Chemical Society* **2013**, *135*, 3873–3880.
- Patten, H. V.; Lai, S. C.; Macpherson, J. V.; Unwin, P. R. *Analytical Chemistry* 2012, 84, 5427–5432.
- Patten, H. V.; Meadows, K. E.; Hutton, L. A.; Iacobini, J. G.; Battistel, D.; McKelvey, K.; Colburn, A. W.; Newton, M. E.; Macpherson, J. V.; Unwin, P. R. *Angewandte Chemie International Edition* 2012, *51*, 7002–7006.
- 120. Bentley, C. L.; Unwin, P. R. Faraday Discussions 2018, 210, 365–379.
- 121. Daviddi, E.; Shkirskiy, V.; Kirkman, P. M.; Robin, M. P.; Bentley, C. L.; Unwin, P. R. *Chemical Science* **2021**, *12*, 3055–3069.
- 122. Kinnear, S. L.; McKelvey, K.; Snowden, M. E.; Peruffo, M.; Colburn, A. W.; Unwin,
   P. R. *Langmuir* 2013, 29, 15565–15572.
- 123. Paulose Nadappuram, B.; McKelvey, K.; Byers, J. C.; Güell, A. G.; Colburn, A. W.; Lazenby, R. A.; Unwin, P. R. *Analytical Chemistry* **2015**, *87*, 3566–3573.
- 124. Böhni, H.; Suter, T.; Schreyer, A. *Electrochimica Acta* **1995**, *40*, 1361–1368.
- 125. Suter, T.; Böhni, H. Electrochimica Acta 1997, 42, 3275–3280.

- Lohrengel, M.; Moehring, A.; Pilaski, M. Fresenius' Journal of Analytical Chemistry 2000, 367, 334–339.
- 127. Suter, T.; Böhni, H. *Electrochimica Acta* **2001**, *47*, 191–199.
- Suter, T.; Webb, E.; Böhni, H.; Alkire, R. Journal of the Electrochemical Society 2001, 148, B174.
- 129. Webb, E.; Suter, T.; Alkire, R. C. Journal of the Electrochemical Society 2001, 148, B186.
- 130. Vignal, V.; Delrue, O.; Heintz, O.; Peultier, J. *Electrochimica Acta* **2010**, *55*, 7118–7125.
- 131. Krawiec, H.; Vignal, V.; Akid, R. *Electrochimica Acta* 2008, *53*, 5252–5259.
- Vignal, V.; Mary, N.; Oltra, R.; Peultier, J. Journal of the Electrochemical Society 2006, 153, B352.
- 133. Birbilis, N.; Buchheit, R. G. Journal of the Electrochemical Society 2005, 152, B140.
- 134. Birbilis, N.; Buchheit, R. Journal of the Electrochemical Society 2008, 155, C117.
- Schneider, M.; Liebmann, T.; Langklotz, U.; Michaelis, A. *Electrochimica Acta* 2017, 249, 198–205.
- Andreatta, F.; Lohrengel, M.; Terryn, H.; De Wit, J. *Electrochimica Acta* 2003, 48, 3239– 3247.
- 137. Lohrengel, M. *Electrochimica Acta* **1997**, *42*, 3265–3271.
- 138. Hassel, A.; Lohrengel, M. *Electrochimica Acta* **1997**, *42*, 3327–3333.
- 139. Lohrengel, M.; Rosenkranz, C. Corrosion Science 2005, 47, 785–794.
- 140. Klemm, S. O.; Schauer, J.-C.; Schuhmacher, B.; Hassel, A. W. *Electrochimica Acta* 2011, *56*, 4315–4321.
- 141. Arjmand, F.; Adriaens, A. Journal of Solid State Electrochemistry 2014, 18, 1779–1788.
- Ulrich, A.; Ott, N.; Tournier-Fillon, A.; Homazava, N.; Schmutz, P. Spectrochimica Acta Part B: Atomic Spectroscopy 2011, 66, 536–545.

- 143. Homazava, N.; Ulrich, A.; Krähenbühl, U. Spectrochimica Acta Part B: Atomic Spectroscopy **2008**, 63, 777–783.
- 144. Lohrengel, M.; Moehring, A.; Pilaski, M. Electrochimica Acta 2001, 47, 137–141.
- 145. Lohrengel, M.; Heiroth, S.; Kluger, K.; Pilaski, M.; Walther, B. *Electrochimica Acta* 2006, *51*, 1431–1436.
- 146. Yule, L.; Shkirskiy, V.; Aarons, J.; West, G.; Bentley, C.; Shollock, B.; Unwin, P. *The Journal of Physical Chemistry C* **2019**, 123, 24146–24155.
- 147. Yule, L.; Shkirskiy, V.; Aarons, J.; West, G.; Shollock, B.; Bentley, C.; Unwin, P. *Electrochimica Acta* **2020**, *332*, 135267.
- 148. Shkirskiy, V.; Yule, L.; Daviddi, E.; Bentley, C.; Aarons, J.; West, G.; Unwin, P. *Journal of the Electrochemical Society* **2020**, *167*, 041507.
- 149. Liu, S.; Shi, M.; Zhou, Y.; Li, R.; Xie, Z.; Hu, D.; Zhang, M.; Hu, G. *Journal of Cultural Heritage* **2020**, *46*, 176–183.
- 150. Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J. Analytical Chemistry 2020, 92, 12415– 12422.
- 151. Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J. Analytical Chemistry 2021, 93, 9657–9662.
- 152. Suter, T.; Böhni, H. *Electrochimica Acta* **1998**, *43*, 2843–2849.
- 153. Morsali, S.; Daryadel, S.; Zhou, Z.; Behroozfar, A.; Qian, D.; Minary-Jolandan, M. *Journal of Applied Physics* **2017**, *121*, 024903.
- 154. Snowden, M. E.; Güell, A. G.; Lai, S. C.; McKelvey, K.; Ebejer, N.; O'Connell, M. A.; Colburn, A. W.; Unwin, P. R. *Analytical Chemistry* 2012, *84*, 2483–2491.
- 155. Chen, C.-H.; Jacobse, L.; McKelvey, K.; Lai, S. C.; Koper, M. T.; Unwin, P. R. *Analytical Chemistry* **2015**, *87*, 5782–5789.
- 156. Bentley, C. L.; Perry, D.; Unwin, P. R. Analytical Chemistry 2018, 90, 7700–7707.
- 157. Kumatani, A.; Takahashi, Y.; Miura, C.; Ida, H.; Inomata, H.; Shiku, H.; Munakata,
  H.; Kanamura, K.; Matsue, T. *Surface and Interface Analysis* 2019, *51*, 27–30.

- Takahashi, Y.; Kobayashi, Y.; Wang, Z.; Ito, Y.; Ota, M.; Ida, H.; Kumatani, A.; Miyazawa,
  K.; Fujita, T.; Shiku, H., et al. *Angewandte Chemie International Edition* 2020, *59*, 3601–3608.
- 159. Liu, D.-Q.; Tao, B.; Ruan, H.-C.; Bentley, C. L.; Unwin, P. R. *Chemical Communications* 2019, 55, 628–631.
- 160. Martin-Yerga, D.; Costa-Garcia, A.; Unwin, P. R. ACS sensors 2019, 4, 2173–2180.
- 161. Standard, A. Annual Book of ASTM Standards 2004.
- 162. Lohrengel, M. Materials Science and Engineering: R: Reports 1993, 11, 243–294.
- 163. Hasenay, D.; Šeruga, M. Journal of Applied Electrochemistry 2007, 37, 1001–1008.
- 164. Zhou, H.; Chhin, D.; Morel, A.; Gallant, D.; Mauzeroll, J. *npj Materials Degradation* 2022, *6*, 1–11.
- 165. Bentley, C. L.; Kang, M.; Maddar, F. M.; Li, F.; Walker, M.; Zhang, J.; Unwin, P. R. *Chemical Science* 2017, *8*, 6583–6593.
- 166. Mechaour, S. S.; Derardja, A.; Oulmi, K.; Deen, M. *Journal of the Electrochemical Society* **2017**, *164*, E560.
- 167. Barlag, R.; Nyasulu, F.; Starr, R.; Silverman, J.; Arthasery, P.; McMills, L. *Journal of Chemical Education* **2014**, *91*, 766–768.
- 168. Lu, X.; Li, M.; Peng, Y.; Xi, X.; Li, M.; Chen, Q.; Dong, A. Journal of the American Chemical Society 2021, 143, 16925–16929.
- 169. Chen, C.-H.; Meadows, K. E.; Cuharuc, A.; Lai, S. C.; Unwin, P. R. *Physical Chemistry Chemical Physics* **2014**, *16*, 18545–18552.
- 170. Ornelas, I. M.; Unwin, P. R.; Bentley, C. L. Analytical Chemistry 2019, 91, 14854– 14859.
- 171. Wang, Y.; Gordon, E.; Ren, H. Analytical Chemistry 2020, 92, 2859–2865.
- 172. Birbilis, N.; Padgett, B. N.; Buchheit, R. G. Electrochimica Acta 2005, 50, 3536–3544.

## Chapter 2

# Oil-Immersed Scanning Electrochemical Cell Microscopy Enabling Long-term Corrosion Mapping



## **Scientific Contributions**

The droplet evaporation seriously limits the application of SECCM, especially in the field of corrosion using highly evaporated NaCl electrolytes. Chapter 2 presents an OI-SECCM, in which a droplet cell is immersed under a layer of hydrophobic and electrochemical inert oil on the substrate surface. A highly stable droplet cell can thus be obtained regardless of ambient humidity, allowing to map a large area of substrate surface over a long time. The development of OI-SECCM will greatly expand the application of SECCM and promote the study of microscopic corrosion.

## **Chapter Abstract**

The micropipette based technique SECCM suffers from the droplet evaporation and crystallization, which limits its application in the study of metal corrosion at the microscale due to the readily evaporative NaCl electrolyte solutions. This chapter presents an oilimmersed SECCM, where a thin layer of hydrophobic and insulating mineral oil was overlaid on the surface of the substrate. The droplet was immersed under the oil throughout the experiment, significantly increasing the droplet stability, thus allowing for prolonged mapping and the use of highly evaporative saline solutions regardless of ambient humidity levels.

This systematic mapping technique was used to conduct a detailed investigation of localized corrosion taking place at the surface of an AA7075-T73 aluminum alloy in a 3.5 wt% NaCl electrolyte. Maps of corrosion potentials and corrosion currents extracted from potentiodynamic polarization curves showed good correlations with the chemical composition of surface features and known galvanic interactions at the microscale level. This demonstrates the viability of OI-SECCM and opens up the avenue to mechanistic

corrosion investigations at the microscale level using aqueous solutions that are prone to evaporation under non-controlled humidity levels.

### **Publication**

The work presented in this chapter is reproduced from:

Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J., Oil-Immersed Scanning Micropipette Contact Method Enabling Long-term Corrosion Mapping. *Analytical Chemistry*. **2020**, 92 (18), 12415-12422.

## 2.1 Introduction

SECCM<sup>1-4</sup> is a robust technique for direct high-resolution electrochemical activity mapping. The local electrochemical activities of electrocatalytic materials,<sup>5-7</sup> battery cathode materials,<sup>3,8-10</sup> polycrystalline electrodes,<sup>11-14</sup> graphite<sup>15-17</sup> and other materials<sup>18-21</sup> with heterogeneous microstructural features have been successfully investigated using SECCM. Compared to other scanning probe techniques,<sup>22-25</sup> SECCM enables localized electrochemical measurements to be performed on a sample surface area of the scale of the micropipette size. Moreover, the integrated positional feedback of the micropipette with respect to the substrate surface enables synchronous topographical imaging.<sup>3,5,26</sup>

In the SECCM, because the movable droplet formed at the end of the micro- or nanopipette is directly exposed to ambient air, its evaporation leads to crystallization for most of saline solutions,<sup>27</sup> often resulting in breakage of the glass micropipette. This evaporation phenomenon especially becomes a thorny issue when performing large area mapping over prolonged experimental times, thus seriously limiting the application scope of SECCM. As a result, concentrated electrolyte solutions with high vapor pressure, although more realistic from a corrosion engineering testing purpose, are typically not used in SECCM experiments.<sup>28</sup> In certain domains, such as SECCM studies of battery cathode materials, high concentrations of LiCl solutions<sup>3,9,29</sup> employed as electrolytes possess low evaporation rates.<sup>30,31</sup> For the same reason, the acid and alkaline electrolytes (HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, KOH)<sup>5,6,18,32</sup> used for the exploration of electrocatalytic materials do not suffer from the crystallization problem. In cases employing easily evaporating saline solutions, the concentrations are usually low,<sup>28,33,34</sup> thereby reducing the evaporation related issues. Several studies have shown that droplet evaporation can also be minimized by working under controlled humidity.<sup>2,13,32,35–37</sup> By placing an electrolyte solution around the sample as a moat can increase the air humidity to some extent, but not sufficient for highly evaporative solutions. The humidified cell produced by flowing water saturated air provides sufficiently high humidity to prevent evaporation. However, it significantly increases the background noise level, thus raising the risk of micropipette crash.

To overcome the challenges of applying SECCM to a corrosion initiation tracking study while limiting droplet evaporation and extending imaging time to 20 h, an oil immersed variant of SECCM was developed in this chapter. In the oil immersed-SECCM (OI-SECCM), the sample surface is covered by a thin layer of mineral oil acting as an insulating protection layer preventing droplet evaporation and enclosing the droplet to prevent its spreading over a corroding substrate.<sup>38</sup> The hydrophobicity and chemical stability of the mineral oil prevents mixing and contamination of the immersed microdroplet.<sup>39,40</sup> Herein, OI-SECCM provides electrochemical maps of the surface of AA7075-T73 aluminum alloy, locally measuring the heterogeneous corrosion response across microstructural second phase particles. Importantly, the OI-SECCM measurements are carried out in a 3.5 wt% NaCl solution, which is recognized as the standard corrosion media<sup>41–44</sup> but nonetheless difficult to employ during long-lasting SECCM mapping. It is anticipated that the development of OI-SECCM under such a realistic corrosive condition will provide a better understanding of microscale corrosion phenomena occurring at the surfaces of engineering alloys and complex architectures such as welds or fractured samples.

## 2.2 Experimental section

#### 2.2.1 Reagents and Materials

Sodium chloride (NaCl, anhydrous, 99.8%) and mineral oil (M5310) were purchased from Sigma-Aldrich. AA7075-T73 aluminum alloy samples were supplied by NRC (National Research Council Canada, Saguenay). The samples were ground with a 320 grit SiC paper (Struers, Canada), subsequently polished on a MD Chem cloth (Struers, Canada) using 9  $\mu$ m and 3  $\mu$ m colloidal diamond suspensions (Struers, Canada) and finally polished using a colloidal silica suspension (Struers, Canada) on the MD Chem cloth until mirrorlike surface was obtained. The polished samples were subsequently sonicated with anhydrous ethanol and Milli-Q water (Milli-Q, Millipore, 18.2 M $\Omega$  cm resistivity at 25 °C) to remove the residue of suspensions before drying. All the polishing procedures were conducted on a TegraPol-25 polishing wheel by mounting the samples in an automated TegraForce-5 polishing arm (Struer, USA). The electrolyte solution (3.5 wt% NaCl) was prepared from Milli-Q water.

#### 2.2.2 Fabrication of Micropipettes

Quartz capillaries of 0.3/1.0 mm ID/OD (Sutter Instrument, Novato, CA) were pulled to form two symmetrical micropipettes with apertures of ~1.65  $\mu$ m diameter (Figure A.1) using a P-2000 CO<sub>2</sub> laser puller (Sutter Instrument) operated from a single line heating and pulling program (Heat = 585; Fil = 2; Vel = 30; Del = 130; Pul = 30).

#### 2.2.3 OI-SECCM Setup

The OI-SECCM experiments were performed over a polished Al alloy 7075-T73 covered with a thin layer of mineral oil ( $\sim$  5 mm thickness) that was mounted into an in-house electrochemical cell. A micropipette was filled with 3.5 wt% NaCl solution. Using an established procedure,<sup>45,46</sup> an Ag/AgCl QRCE as labeled in Figure 2.1, was fabricated by soaking an Ag wire (0.125 mm diameter, Goodfellow Metals, Huntingdon, England) in bleach where the surface of Ag wire was oxidized to AgCl, subsequently rinsed in deionized water and then wiped clean. The wire was then inserted into the back of the micropipette and kept at a constant distance ( $\sim$ 1.5 cm) from the micropipette tip. The potential of Ag/AgCl QRCE was found to be stable versus a saturated calomel electrode (SCE) monitored upon open circuit potential (OCP) measurement immersed in a 3.5 wt% NaCl solution. Only a small drift of -2.5 mV was observed over 12 h (Figure B.3). All potentials below are reported versus Ag/AgCl QRCE.

#### 2.2.4 Microdroplet OCP and Polarization Measurements

The droplet at the end of the micropipette was immersed under the oil and positioned near the Al alloy surface. With the AA7075-T73 acting as the working electrode (WE) and the Ag/AgCl QRCE immersed into the back of the electrolyte-filled micropipette, when the droplet at the end of the tip comes in contact with the substrate, the two-electrode system is completed (Figure 2.1). All potentiodynamic polarization (PDP) and OCP measurements were performed using an ElProScan3 system (HEKA, Germany; bipotentiostat model PG340) within a Faraday cage positioned on a vibration isolating table to minimize noise. An approach potential (-1.4 V) was applied as the micropipette was lowered under the mineral oil. Upon the droplet contact with the sample surface, the measured current spiked above the set threshold (threshold = 2 pA in OI-SECCM, 6 pA in humidified cell, 3 pA in ambient air), immediately halting the z-movement. Subsequently, the micropipette moved down further to squeeze the droplet (depicted in Figure 2.1) followed by a waiting time to ensure the formation of a stable electrolyte-wetted area for reliable electrochemical measurements (OCP and PDP) to be performed. The micropipette was then retracted and hopped to the next predefined location (hopping mode).<sup>47</sup> The separation distance between landing points was conservatively set to 5  $\mu$ m to avoid overlap between droplets. The micropipette was scanned in a snake mode, with a movement to the left in the first row. Typical OCP measurements were carried out over 60 s. During the PDP, the potential was scanned at a rate of 100 mV/s, from -1.0 V to -0.3 V, or until the current exceeds the set limit of 100 pA. The droplet was under the oil throughout mapping.

After completion of a matrix scan, the mineral oil on the sample surface was removed using acetone and Milli-Q water. The scanned area was first imaged using optical microscopy and its chemical characterization was carried out using a scanning electron microscope (FEI Helios Nanolab 660 dual beam SEM, 5 kV) coupled with energy dispersive X-ray spectroscopy (TEAM 3D EDS analysis system).



**Figure 2.1:** Schematic of the micropipette approaching to, landing, and wetting the substrate surface in the mineral oil. Red arrows represent downward motion of the micropipette.

#### 2.2.5 Contact angle measurements

The contact angle of a 3.5 wt% NaCl solution droplet ( $\sim$ 10 µL) on the polished sample surface was measured in air and mineral oil respectively using the Contact Angle System (Dataphysics). AA7075-T73 was immersed in oil to create the same condition as that in OI-SECCM. A simulated landing of a droplet in OI-SECCM was performed using a 3.5 wt% solution filled steel needle (0.5 mm diameter) to study the droplet wetting dynamics.

## 2.3 **Results and Discussion**

#### 2.3.1 Mineral Oil Reduces Background Noise

Although all experiments were performed with caution to prevent noise, pA fluctuations in current were still present due to background and instrumental noises. The noise amplitude determines the value of current threshold that is used to stop the vertical movement of the micropipette during the approach. Because the threshold value has to be higher than the noise amplitude and lower than the current spike generated upon contact, increased noise leads to a higher current threshold, thus increasing the risk of micropipette breakage. In ambient air (Figure 2.2, black), the recorded noise amplitude was low (2.2 pA), but significant challenges were still encountered during SECCM operation (Figure A.4) because of the rapid evaporation of droplet in low ambient humidity.



**Figure 2.2:** Background noise current measured over time upon the droplet approaching the surface before landing in mineral oil, humidified cell (relative humidity ~85%) and ambient air (relative humidity 30-60%).

Under humidified conditions (Figure 2.2, red), the amplitude of the noise increased to 5.2 pA due to air flow, resulting in micropipette break after only 169 landings (Figure 2.3a). Measurements using the broken micropipette were inaccurate as shown by the mismatch between the scanned surface and corresponding  $E_{corr}$  (PDP) map (in the red boxes of Figure 2.3a and 2.3b). When the sample is covered by mineral oil (Figure 2.2, blue), a lower noise amplitude (1.35 pA) was observed, thus allowing to lower the current threshold to be lowered to 2 pA and consequently enabling a long lifetime of the micropipette to acquire large area maps on the Al alloy surface.



**Figure 2.3:** SECCM experiment in a humidified cell. (a) Optical micrograph of a  $75 \times 75$   $\mu$ m<sup>2</sup> scanned area (16 × 16, 256 landings) and (b) the corresponding  $E_{corr}$  (PDP) map. PDP measurements were performed at 100 mV/s after a wait time of 30 s at each landing point. The red box marks the area scanned following the breakage of the micropipette. This breakage is thought to have happened at landing 170 marked by the white circle, as points following the 169th landing (right side of the white circle), showed abnormalities in both their footprints on the sample surface and their  $E_{corr}$  (OCP) values. (c) Amplified image of the area in the orange box in (a). (d) The PDP curves (averaged smoothed every 30 data points) at three points 106, 107, 108.

#### 2.3.2 Droplet Wetting during the OI-SECCM

Changing the droplet electrolyte-air interface to an electrolyte-oil interface influences the contact angle of the free droplet on the alloy surface during OI-SECCM measurements.

In air, the contact angle is 27.2° (Figure 2.4a, left), showing a strong electrolyte solutionsurface interaction. In mineral oil, the contact angle increases to 73.3° (Figure 2.4a, right), indicating a decreased wettability. Therefore, the presence of the mineral oil helps to enclose the droplet, preventing its spreading,<sup>38</sup> which is essential for time consuming measurements as well as the use of larger micropipettes. To observe and simulate the droplet/sample interaction during OI-SECCM, a droplet was formed at the end of a large steel needle during contact angle measurements (Figure 2.4b). Upon contact with the mineral oil covered AA7075-T73 sample, the droplet did not immediately wet the sample, as the surface is covered by the hydrophobic and viscous oil. Effective wetting to the surface is slow in absence of an applied external force needed to displace the oil from the surface. By pushing down the droplet towards mineral oil covered AA7075-T73, a threestage wetting process was observed based on contact angle measurements. Similarly, PDP curves recorded in OI-SECCM experiments can be classified into three types (Figure 2.4b(i), (ii), (iii)) which are likely related to these three wetting stages.



**Figure 2.4:** (a) The contact angle of a 3.5 wt% NaCl solution droplet on AA7075-T73 surface measured in air and in mineral oil. (b) A droplet of 3.5 wt% NaCl at the end of a steel needle with a diameter of 0.5 mm is approached to the Al alloy surface in mineral oil (blue: 3.5 wt% NaCl; light yellow: mineral oil; dark gray: AA7075-T73). Three stages of droplet-sample wetting (steel needle delivered) and three types of PDP curves obtained in OI-SECCM (1.65  $\mu$ m diameter micropipette opening) can be associated. The current spikes over 10 pA in (b(ii)) and (b(iii)) were due to the pitting corrosion. (c) Polarization measurements recorded to investigate the micropipette lowering distance (0.5 and 1.0  $\mu$ m) after its z-movement was stopped by the set current threshold.

The first stage involves the droplet landing on AA7075-T73 with an invalid electrical contact. At this stage of the downward motion, the droplet's contact angle was  $\sim 180^{\circ}$  due to the presence of the mineral oil layer. A zero-current PDP curve (Figure 2.4b (i)) measured in the microdroplet cell in OI-SECCM may result from this situation.

In the second stage, a non-equilibrium wetting transition was observed. As the needle was lowered further into the mineral oil, the droplet started to wet the surface and spread with an advancing contact line. The contact area is the result of the balance between the electrolyte-surface attraction and the confinement of oil to the droplet shape. At the non-equilibrium wetting transition stage without additional downward force, only small wetted areas were produced. A 1 pA-current (at -1.0 V) polarization curve (Figure 2.4b (ii)) observed in OI-SECCM may arise from this type of wetting. The current spike at ~-0.55 V due to the pitting corrosion proves that the alloy surface was wetted, but on the other hand, the cathodic current indistinguishable from the noise suggests a small wetted area. Small wetted areas were also observed in SECCM conducted in the humidified cell (Figure 2.3d, landing point 107 and 108). Abnormal current peaks occurring on such PDP curves, as well as the absence of clear anodic and cathodic branches, prevent the extraction of corrosion potential ( $E_{corr}$ ) and yield to unreliable corrosion data.

In a third stage, further downward movement of the steel needle reduces the contact angle to ~90° and shifts the wetting process to a mechanical equilibrium state where a larger area is wetted. Figure 2.4b (iii), exhibiting a higher current polarization curve, illustrates the kind of PDP measurement is obtained from such wetting during OI-SECCM measurements. However, unlike the macrodroplet that can immediately remove the oil from the alloy surface after a further downward movement, it takes time for the micro-droplet to generate an equilibrium wetting state that can produce a high current polarization curve as shown in Figure 2.4b(iii). For Al alloy, the equilibrium wetting state for the generation of high current polarization curve has two implications herein. Firstly, a large wetting area is acquired in this state, ensuring a higher current. Secondly and importantly, for the Al alloy possessing a passive oxide layer on the surface, the Cl<sup>-</sup> ions in

the electrolyte solution need to break the oxide layer for the initiation of the metastable pitting.<sup>48,49</sup> To satisfy these two points, a waiting time is required for the establishment of equilibrium wetting state. As shown in Figure 2.4c, lowering the micropipette distances by -0.5 and -1.0  $\mu$ m after the z-movement had been stopped by the current threshold did not lead to higher current polarization curves but stable pitting current spikes were observed. This is because only a small area of the alloy was wetted, or the Cl<sup>-</sup> ions do not have time to initiate sufficient metastable pits for higher anodic currents before the pitting current spike. The waiting time is discussed in detail in the following paragraph.

#### 2.3.3 Waiting Time for Valid Contact

A waiting time before electrochemical measurements is necessary for effective wetting of the droplet on the AA7075-T73. Prior to droplet landing, the time dependence of the OCP and its derivative (Figure 2.5a) is asymptotic and a sub-pA background noise is recorded in PDP curve. Upon droplet contact with the sample, the OCP was monitored for 100 s (Figure 2.5b). The OCP and its derivative remain asymptotic, but a measurable current spike was observed in the subsequent PDP curve at -0.4V (Figure 2.5b), which can be linked to pitting corrosion and thus indicates that the droplet is partially wetting the sample (non-equilibrium wetting). As the waiting time was extended to 200 s (Figure 2.5c), a transient response can be observed in the OCP derivative plot, implying the establishment of a large wetted contact area, which was verified by the subsequent polarization curve that displayed a -10 pA current under large cathodic polarization (Figure 2.5c) compared to the 0 pA (Figure 2.5a) and -1 pA (Figure 2.5b) measured under the same polarization condition. However, a 200 s waiting time at a single location is far too long for SECCM experiments aiming to land hundreds of times on a sample. It was thus found that lowering the micropipette by 0.5  $\mu$ m towards the sample after droplet contact (Figure 2.5d) makes the transient point in the OCP derivative plot observable after only 10 s. An effective wetting was confirmed by the following PDP measurement after the 100 s OCP monitor in Figure 2.5d.



**Figure 2.5:** OI-SECCM experiments for which the time dependence of the OCP (left, blue trace) and its derivative (left, orange trace) and polarization curves (right) are reported at three positions where the micropipette (a) stopped in the mineral oil before landing; (b), (c) z-movement was stopped by the current threshold; (d) was lowered by 0.5  $\mu$ m after reaching the current threshold. (e) Polarization curves of a landed micropipette that was further lowered by 0.5  $\mu$ m with different waiting times (2, 5 and 10 s) prior to electrochemical measurements. The three curves were smoothed using the 30-point moving averaging method.

In order to confirm whether the peak at 10 s (Figure 2.5d) is indicative of the transition from the nonequilibrium wetting state to the equilibrium state, PDP measurements were conducted after waiting times of 2, 5, and 10 s (Figure 2.5e). For 2 and 5 s, the PDP curves display low-current characteristics of invalid and nonequilibrium wetting. PDP curves with high currents were observed after a waiting time of 10 s (Figure 2.5e, yellow). Therefore, all subsequent OI-SECCM experiments consistently used the optimized 0.5  $\mu$ m push down distance after reaching the current threshold and 10 s equilibration time after the final droplet downward movement.

#### 2.3.4 OI-SECCM Map: *E*<sub>corr</sub>(OCP) vs Time

The time dependence of  $E_{\rm corr}(\rm OCP)$  (i.e., the corrosion potential measured under opencircuit conditions) is commonly used to investigate the susceptibility of materials to corrosion.<sup>50,51</sup>  $E_{corr}(OCP)$  measurements are rarely adopted in SECCM studies because the experimental time required to obtain a stable  $E_{\rm corr}(\rm OCP)$  at a single location is in the order of tens to hundreds of seconds, compared to that of voltammetric methods used in the conventional SECCM, that are acquired on ms to s timescales.<sup>32,37,52,53</sup> However, by increasing the droplet stability, the OI-SECCM method is able to conduct time-consuming measurements at each landing location. In Figure 2.6a, the micropipette was scanned over an area of  $150 \times 150 \ \mu m^2$ , landing 961 times in a total time of  $\sim 20$  h without breaking the micropipette (Figure A.3). Such time-extended scans are typically difficult to achieve in conventional SECCM performed under ambient air owing to the droplet evaporation. Cross-correlating the  $E_{corr}(OCP)$  map (Figure 2.6b) to the optical micrograph (Figure 2.6a) of the scanned area, with landing sites revealed by footprints of the micropipette, clearly identifies the locations of more noble sites (yellow points with higher  $E_{\rm corr}(\rm OCP)$  values), which can be assigned to intermetallic particles. Indeed, based on the  $E_{\rm corr}(\rm OCP)$  map, the constituent particles exhibit cathodic behaviors relative to the material matrix, which is in agreement with the corresponding EDS maps revealing the presence of Fe-rich constituent phases  $(Al_7Cu_2Fe \text{ and } (Al,Cu)_7(Fe,Cu)$  are the most abundant intermetallic particles in Al alloy 7075 series  $)^{54-57}$  and the Al matrix (Figures 2.6c, d). This observation confirms the ability of OI-SECCM to reveal the microscale electrochemical heterogeneities at the surface of a complex alloy.



**Figure 2.6:** (a) Optical micrograph of the scanned area  $(31 \times 31 \text{ landings on } 150 \times 150 \ \mu\text{m}^2)$  of the AA7075-T73 sample after OISECCM measurements and (b) corresponding OI-SECCM map. At each landing point,  $E_{\text{corr}}(\text{OCP})$  was monitored for over 60 s. The white spots in the OI-SECCM map represent failed droplet landings due to external noise interference. EDS maps for the elements (c) Al and (d) Fe. (e) SEM image of the amplified region in the red box [in (a)] and (f)  $E_{\text{corr}}(\text{OCP})$  vs time plots for two representative landing points.

At the microscale, galvanic couplings are expected to form between cathodic particles and the surrounding Al matrix.<sup>58,59</sup> From a thermodynamic standpoint, as the an-

ode, Al should be oxidized and electrons flow towards the electrically contacted cathodic particles where oxygen reduction takes place, thus promoting dissolution of the Al matrix.<sup>60–62</sup> Figures 2.6e and f present two landing sites (608 and 610) representative of this galvanic coupling and corresponding  $E_{\rm corr}$  (PDP) curves, respectively. EDS analyses (Figure A.5) conducted at site 608 revealed the  $(Al,Cu)_6$  (Fe,Cu) nature of the particle, that sits to a more positive  $E_{\rm corr}$  (PDP) value relative to point 610 on the Al matrix (by ~200 mV). The recording of the OCP at these two locations exemplifies how efficient are the electrochemical measurements in OI-SECCM to track the differences in microstructures and tightly map them in two dimensions. It should be noted that the  $E_{corr}(PDP)$  drift shown by the progressive color change on the map (Figure 2.6b) along the Y coordinate (especially visible between 0 to  ${\sim}20~\mu\text{m}$ ) is primarily due to the Ag^+ contamination in the micropipette electrolyte from the QRCE Ag/AgCl wire.<sup>63,64</sup> Ag<sup>+</sup> ions leaked from the Ag/AgCl wire transported to the droplet during the OI-SECCM experiment. At the droplet-alloy interface, the Ag<sup>+</sup> was reduced, generating additional cathodic current to the system. Because the Ag<sup>+</sup> reduction increased the total cathodic current, a higher anodic current at a more positive potential was required to ensure a zero net current at the  $E_{\text{corr}}$ . As a result, the recorded  $E_{\text{corr}}$  drifted to positive. With more Ag<sup>+</sup> diffused to the droplet over time, a positively increased  $E_{\rm corr}$  gradient was observed. In the micropipette after the OI-SECCM scanning, the Ag<sup>+</sup> was detected by CV in Figure A.6. As suggested by Unwin group,<sup>65</sup> careful placement of the Ag/AgCl wire QRCE at a far distance from the tip of micropipette can sufficiently remove the Ag contamination. Because the diffusion time of Ag<sup>+</sup> at the distance of 1.5 cm was shorter than that expected in the 3.5 wt% NaCl solution, Ag $^+$  can arrived at the droplet during experiment in spite of careful placement of the Ag/AgCl wire. Another reason that may account for the  $E_{corr}$  drift is the corrosion products contaminating the micropipette tip as previously reported in the microcapillary cell.<sup>58,66,67</sup> However, during the most part of experiment, it does not affect the identification of intermetallic particles and the matrix based on variations of electrochemical potentials. Improvements of the technique are currently underway to counter

the contamination issues and use the polarization curves with appropriate positioning of  $E_{\rm corr}({\rm OCP})$  values as modeling inputs in the development of predictive corrosion models.<sup>68</sup> Such approach would contribute to bridge the gap between microgalvanic corrosion and the observed macroscale corrosion of Al alloys.

#### 2.3.5 OI-SECCM Map: PDP

The  $E_{\rm corr}(\rm OCP)$  map presented in Figure 2.6b displays the thermodynamic activity associated to different metallurgical features, thus revealing the areas apparently susceptible to galvanic corrosion on the surface. In order to determine whether or not this thermodynamic coupling can induce corrosion, kinetics measurements must be conducted at the microscopic level. To this end, PDP measurements were carried out after equilibrium wetting was established at each point (10 s after the final 0.5  $\mu$ m downward pushing, the droplet was kept in OCP for an extra 50 s before the polarization starts at -1.0V). Corrosion currents ( $i_{corr}$ ) were obtained by extrapolating the linear portion of cathodic branch of the Tafel plot back to the zero-current-density potential, that is,  $E_{\rm corr}(PDP)$  (Figures 2.7c, d). Even though  $i_{corr}$  values extracted from 100mV/s PDPs should be used with care due to likely high capacitive current contributions, the  $i_{corr}$  map (Figure 2.7b) extracted by scanning a  $100 \times 100 \ \mu m^2$  area can display a semi-quantitative view of the corrosion kinetics at the microscale. Interestingly, the  $i_{\rm corr}$  map presented in Figure 2.7b reveals that the constituent phases are characterized by higher corrosion currents than the Al matrix. Based on the galvanic corrosion couplings tentatively deduced from thermodynamics measurements (Figure 2.6), this observation seems contradictory. In order to clarify the nature of the corrosion phenomena taking place in the vicinity of intermetallic particles, two of them were magnified (Figure 2.7c, d) for the discussion of specific PDP curves. In the amplified area in the blue box, the PDP measurements display that points 13 and 30, located on a (Al,Cu)<sub>7</sub>(Fe,Cu) particle (EDS analysis in Figure A.7), are characterized by more positive  $E_{\text{corr}}$  (PDP) and higher  $i_{\text{corr}}$  values compared to points 12 and 29 which represent the Al matrix. Therefore, at the microscopic level, a faster corrosion kinetics (higher  $i_{corr}$ ) was observed on (Al,Cu)<sub>6</sub>(Fe,Cu) particles than that on the Al matrix. This is due to a dense and inert oxide layer at the surface of the Al matrix that prevents the electrolyte and oxygen from interacting with the underlying Al,<sup>69,70</sup> which is consistent with the passive behavior observed on the anodic branches of PDP curves recorded at point 12 and 29. However, as seen in Figure 2.7d, Al matrix point 76 and 93 present a reduced passive zone length (between  $E_{corr}$ (PDP) and the passive film breakdown potential), followed by a steep current increase attributable to pitting corrosion. Such pitting corrosion behavior is expected due to the high chloride concentration in the electrolyte penetrating the defective sites on the passive film at the surface of the Al matrix.



**Figure 2.7:** (a) Optical micrograph of a  $21 \times 21$  (441) landings on the AA7075-T73 surface after OI-SECCM scan and (b) the corresponding  $i_{corr}$  map of the scanned area. At each landing location, PDP measurements were carried out at scan rate of 100 mV/s after a waiting time of 10 s plus 50 s OCP monitoring. SEM images and PDP curves of the corresponding landing sites in the areas enclosed by the (c) blue and (d) red boxes in (a).  $i_{corr}$  was extracted by extrapolation of the linear portion of cathodic curve with the vertical line at  $E_{corr}$ (PDP).

In order to judge the galvanic corrosion intensity at the microscale level that eventually leads to macroscopic and engineering failures, the relative surface area of contacting surface features must be considered. Should a thin and highly conductive electrolyte cover a much larger Al surface than Fe-rich particles, which is expected to happen in a real-life scenario, the Al polarization curve will shift upward on the current axis to a larger extent than the intermetallic particle polarization curve (e.g., in a 10:1 surface area ratio scenario). Although the overall anodic current will be distributed on a large Al matrix surface, the meeting point between Al anodic and Fe-rich particle cathodic branches of PDP curves shows that a high current density will be found at the faying line between the two phases, as expected from the PDP curves measured at points 76 and 77 in Figure 2.7d. Under this situation, the oxygen reduction reaction occurring at the surface of (Al,Cu)<sub>6</sub>(Fe,Cu) particles will promote the Al matrix dissolution in its vicinity, thus sustaining a galvanic corrosion action. It is worthy to mention that in the absence of pitting corrosion with a steep current increase in the cathodic potential range of the adjacent intermetallic particles, the anodic branch characterizing the passive state of the Al matrix would cross the cathodic portion of the (Al,Cu)<sub>7</sub>(Fe,Cu) particles PDP at a current value virtually equal to the corrosion current of the Al matrix. Thus, under this circumstance, no significant galvanic contribution to the corrosion process would be observed due to the protection of the Al matrix by a pitting-resistant passive film.

Ongoing work is currently aiming to extract quantitative data from each PDP measurement with the objective to turn this analysis, based on point to point comparison, into quantitative modeling of micro-galvanic corrosion. This model would then take into account reaction kinetics as well as geometries of the various features present at the investigated surface.<sup>71-73</sup> In addition, the effect of the potential scan rate on the passive-topitting transition will be determined.<sup>74</sup> Preliminary results indicate that the passive zone tends to disappear as the potential scan rate is lowered, thus favoring the pitting process of the Al matrix next to the Fe-rich particles.

## 2.4 Conclusion

OI-SECCM has proven powerful in imaging the localized corrosion at the surface of an aluminum alloy. The hydrophobic and insulating oil significantly increases the stability of the droplet at the end of the micropipette by preventing its evaporation, allowing highly evaporative electrolyte solutions like 3.5 wt% NaCl to be used notwithstanding the ambient relative humidity. This improved stability also enables OI-SECCM to map a larger surface area, as well as perform time-consuming measurements at each landing point. OI-SECCM has successfully probed the local electrochemical activities of AA7075-T73, revealing the cathodic behavior of the Fe-rich constituent phases on the surface as well as their faster corrosion kinetics, which makes the Al areas that contains the Ferich particles more susceptible to galvanic corrosion when immersed under an electrolyte solutions. Moreover, given that the wetting area at each landing point has been manifested by the footprints of the micropipette on the substrate surface in OI-SECCM, the corrosion current density  $(j_{corr})$  can be calculated in the future work, which may enable OI-SECCM to quantify the microscopic corrosion rate once the PDP curve can be corrected for the effect of high scan rates. The development of OI-SECCM has considerably increased the availability and feasibility of SECCM, making it accessible to more laboratories with low local humidity, and promoting the electrochemical exploration at the microscale. Noteworthily, quantitatively understanding the microscopic corrosion and its relationship with the macroscopic corrosion may be achieved using OI-SECCM in the future, advancing the microscopic quantitative techniques and supporting the industry.
# References

- Bentley, C. L.; Edmondson, J.; Meloni, G. N.; Perry, D.; Shkirskiy, V.; Unwin, P. R. Analytical Chemistry 2019, 91, 84–108.
- Ebejer, N.; Schnippering, M.; Colburn, A. W.; Edwards, M. A.; Unwin, P. R. *Analyt*ical Chemistry 2010, 82, 9141–9145.
- Takahashi, Y.; Kumatani, A.; Munakata, H.; Inomata, H.; Ito, K.; Ino, K.; Shiku, H.; Unwin, P. R.; Korchev, Y. E.; Kanamura, K., et al. *Nature Communications* 2014, 5, 1–7.
- 4. Williams, C. G.; Edwards, M. A.; Colley, A. L.; Macpherson, J. V.; Unwin, P. R. *Analytical Chemistry* **2009**, *81*, 2486–2495.
- Bentley, C. L.; Kang, M.; Unwin, P. R. Journal of the American Chemical Society 2017, 139, 16813–16821.
- Lai, S. C.; Dudin, P. V.; Macpherson, J. V.; Unwin, P. R. *Journal of the American Chemical Society* 2011, 133, 10744–7.
- 7. Tarnev, T.; Aiyappa, H. B.; Botz, A.; Erichsen, T.; Ernst, A.; Andronescu, C.; Schuhmann, W. *Angewandte Chemie International Edition* **2019**, *58*, 14265–14269.
- Dayeh, M.; Ghavidel, M. R. Z.; Mauzeroll, J.; Schougaard, S. B. *ChemElectroChem* 2019, 6, 195–201.
- Kumatani, A.; Takahashi, Y.; Miura, C.; Ida, H.; Inomata, H.; Shiku, H.; Munakata, H.; Kanamura, K.; Matsue, T. *Surface and Interface Analysis* 2019, *51*, 27–30.
- Snowden, M. E.; Dayeh, M.; Payne, N. A.; Gervais, S.; Mauzeroll, J.; Schougaard, S. B. *Journal of Power Sources* 2016, 325, 682–689.
- 11. Aaronson, B. D.; Chen, C. H.; Li, H.; Koper, M. T.; Lai, S. C.; Unwin, P. R. *Journal of the American Chemical Society* **2013**, 135, 3873–80.

- 12. Chen, C. H.; Meadows, K. E.; Cuharuc, A.; Lai, S. C.; Unwin, P. R. *Physical Chemistry Chemical Physics* **2014**, *16*, 18545–52.
- Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. Science 2017, 358, 1187– 1192.
- Patten, H. V.; Lai, S. C.; Macpherson, J. V.; Unwin, P. R. Analytical Chemistry 2012, 84, 5427–32.
- 15. Lai, S. C.; Patel, A. N.; McKelvey, K.; Unwin, P. R. *Angewandte Chemie International Edition* **2012**, *51*, 5405–8.
- 16. Patel, A. N.; Collignon, M. G.; O'Connell, M. A.; Hung, W. O.; McKelvey, K.; Macpherson, J. V.; Unwin, P. R. *Journal of the American Chemical Society* **2012**, *134*, 20117–30.
- 17. Unwin, P. R.; Guell, A. G.; Zhang, G. Accounts of Chemical Research 2016, 49, 2041–8.
- Bentley, C. L.; Andronescu, C.; Smialkowski, M.; Kang, M.; Tarnev, T.; Marler, B.; Unwin, P. R.; Apfel, U. P.; Schuhmann, W. *Angewandte Chemie International Edition* 2018, 57, 4093–4097.
- Bentley, C. L.; Kang, M.; Maddar, F. M.; Li, F.; Walker, M.; Zhang, J.; Unwin, P. R. Chemical Science 2017, 8, 6583–6593.
- Kumatani, A.; Miura, C.; Kuramochi, H.; Ohto, T.; Wakisaka, M.; Nagata, Y.; Ida, H.; Takahashi, Y.; Hu, K.; Jeong, S.; Fujita, J. I.; Matsue, T.; Ito, Y. *Advance Science* 2019, 6, 1900119.
- 21. Martin-Yerga, D.; Costa-Garcia, A.; Unwin, P. R. ACS Sensors 2019, 4, 2173–2180.
- 22. Chen, C.-C.; Zhou, Y.; Baker, L. A. Annual Review of Analytical Chemistry 2012, 5, 207–228.
- 23. Bard, A. J.; Fan, F. R. F.; Kwak, J.; Lev, O. Analytical Chemistry 1989, 61, 132–138.
- 24. Payne, N. A.; Stephens, L. I.; Mauzeroll, J. Corrosion 2017, 73, 759–780.
- Takahashi, Y.; Kumatani, A.; Shiku, H.; Matsue, T. Analytical Chemistry 2017, 89, 342–357.

- 26. Bentley, C. L.; Unwin, P. R. Faraday Discussions 2018, 210, 365–379.
- Morsali, S.; Daryadel, S.; Zhou, Z.; Behroozfar, A.; Qian, D.; Minary-Jolandan, M. *Journal of Applied Physics* 2017, 121, 024903.
- Yule, L. C.; Bentley, C. L.; West, G.; Shollock, B. A.; Unwin, P. R. *Electrochimica Acta* 2019, 298, 80–88.
- Inomata, H.; Takahashi, Y.; Takamatsu, D.; Kumatani, A.; Ida, H.; Shiku, H.; Matsue, T. *Chemical Communications* 2019, 55, 545–548.
- 30. Kuznetsov, G. V.; Feoktistov, D. V.; Orlova, E. G.; Misyura, S. Y.; Morozov, V. S.; Islamova, A. G. *International Journal of Heat and Mass Transfer* **2018**, 126, 161–168.
- Ponomarev, K. O.; Feoktistov, D. V.; Marchuk, I. In MATEC Web of Conferences. Vol. 91: Smart Grids 2017.—Les Ulis, 2017. 2017; Vol. 912017, p 1029.
- Yule, L. C.; Shkirskiy, V.; Aarons, J.; West, G.; Bentley, C. L.; Shollock, B. A.; Unwin,
   P. R. *the Journal of Physical Chemistry C* 2019, 123, 24146–24155.
- 33. Byers, J. C.; Guell, A. G.; Unwin, P. R. *Journal of the American Chemical Society* **2014**, 136, 11252–5.
- Patten, H. V.; Meadows, K. E.; Hutton, L. A.; Iacobini, J. G.; Battistel, D.; McKelvey, K.; Colburn, A. W.; Newton, M. E.; Macpherson, J. V.; Unwin, P. R. *Angewandte Chemie International Edition* 2012, *51*, 7002–6.
- 35. Day, T. M.; Unwin, P. R.; Macpherson, J. V. Nano Letters 2007, 7, 51–57.
- Snowden, M. E.; Guell, A. G.; Lai, S. C.; McKelvey, K.; Ebejer, N.; O'Connell, M. A.;
   Colburn, A. W.; Unwin, P. R. *Analytical Chemistry* 2012, 84, 2483–91.
- 37. Yule, L.; Shkirskiy, V.; Aarons, J.; West, G.; Shollock, B.; Bentley, C.; Unwin, P. *Electrochimica Acta* **2020**, 332, 135267.
- Shkirskiy, V.; Yule, L.; Daviddi, E.; Bentley, C.; Aarons, J.; West, G.; Unwin, P. Journal of the Electrochemical Society 2020, 167, 041507.

- 39. Rodolfa, K. T.; Bruckbauer, A.; Zhou, D.; Schevchuk, A. I.; Korchev, Y. E.; Klenerman, D. *Nano Letters* **2006**, *6*, 252–257.
- 40. Rouse, T. O. Elecrical Inslulation Magazine **1998**, 14, 6–16.
- 41. Gateman, S. M.; Stephens, L. I.; Perry, S. C.; Lacasse, R.; Schulz, R.; Mauzeroll, J. *npj Materials Degradation* **2018**, *2*, 1–8.
- 42. Man, H.; Kwok, C.; Yue, T. Surface and Coatings Technology 2000, 132, 11–20.
- Reda, Y.; Abdel-Karim, R.; Elmahallawi, I. Materials Science and Engineering: A 2008, 485, 468–475.
- Shi, Y.; Yang, B.; Xie, X.; Brechtl, J.; Dahmen, K. A.; Liaw, P. K. Corrosion Science 2017, 119, 33–45.
- 45. Barlag, R.; Nyasulu, F.; Starr, R.; Silverman, J.; Arthasery, P.; McMills, L. *Journal of Chemical Education* **2014**, *91*, 766–768.
- Da Silva, E. T. S. G.; Miserere, S.; Kubota, L. T.; Merkoçi, A. *Analytical chemistry* 2014, 86, 10531–10534.
- 47. Daviddi, E.; Gonos, K. L.; Colburn, A. W.; Bentley, C. L.; Unwin, P. R. *Analytical Chemistry* **2019**, *91*, 9229–9237.
- 48. Pride, S.; Scully, J.; Hudson, J. Journal of the Electrochemical Society 1994, 141, 3028.
- 49. Szklarska-Smialowska, Z. Corrosion Science 1999, 41, 1743–1767.
- 50. Bommersbach, P.; Alemany-Dumont, C.; Millet, J.-P.; Normand, B. *Electrochimica Acta* **2005**, *51*, 1076–1084.
- 51. Roberge, P. R., Corrosion Inspection and Monitoring; John Wiley Sons: 2007; Vol. 2.
- Takahashi, Y.; Kobayashi, Y.; Wang, Z.; Ito, Y.; Ota, M.; Ida, H.; Kumatani, A.; Miyazawa, K.; Fujita, T.; Shiku, H., et al. *Angewandte Chemie International Edition* 2020, 59, 3601–3608.
- 53. Tao, B.; Unwin, P. R.; Bentley, C. L. *The Journal of Physical Chemistry C* 2019, 124, 789–798.

- 54. Andreatta, F.; Terryn, H.; de Wit, J. H. W. Corrosion Science 2003, 45, 1733–1746.
- 55. Ayer, R.; Koo, J.; Steeds, J.; Park, B. J Metallurgical Transactions A 1985, 16, 1925–1936.
- 56. Birbilis, N.; Cavanaugh, M. K.; Buchheit, R. G. Corrosion Science 2006, 48, 4202–4215.
- 57. Birbilis, N.; Buchheit, R. G. Journal of the Electrochemical Society **2005**, 152, B140–B151.
- Andreatta, F.; Lohrengel, M. M.; Terryn, H.; de Wit, J. H. W. *Electrochimica Acta* 2003, 48, 3239–3247.
- 59. Otani, K.; Sakairi, M.; Sasaki, R.; Kaneko, A.; Seki, Y.; Nagasawa, D. Journal of Solid State Electrochemistry **2013**, 18, 325–332.
- 60. Mansfeld, F. Corrosion **1971**, 27, 436–442.
- 61. Oldfield, J. W. In *Galvanic Corrosion*; ASTM International: 1988.
- 62. Zhang, X. G. Uhlig's Corrosion Handbook 2011, 51, 123.
- 63. Perera, R. T.; Rosenstein, J. K. *Scientific Reports* **2018**, *8*, 1–10.
- 64. Yakushenko, A.; Mayer, D.; Buitenhuis, J.; Offenhäusser, A.; Wolfrum, B. *Lab on a Chip* **2014**, *14*, 602–607.
- 65. Bentley, C. L.; Perry, D.; Unwin, P. R. Analytical Chemistry 2018, 90, 7700–7707.
- 66. Andreatta, F.; Fedrizzi, L. *Electrochimica Acta* **2016**, *203*, 337–349.
- 67. Arjmand, F.; Adriaens, A. Journal of Solid State Electrochemistry **2014**, 18, 1779–1788.
- 68. Laycock, N. J.; C., R. Corrosion Science **1997**, 39, 1771–1790.
- 69. Strohmeier, B. R. Surface and Interface Analysis 1990, 15, 51–56.
- Yu, S.; O'grady, W.; Ramaker, D.; Natishan, P. Journal of the Electrochemical Society 2000, 147, 2952.
- 71. Deshpande, K. B. Electrochimica Acta 2011, 56, 1737–1745.
- Wang, Y.; Yin, L.; Jin, Y.; Pan, J.; Leygraf, C. Journal of the Electrochemical Society 2017, 164, C1035–C1043.

- Yin, L.; Jin, Y.; Leygraf, C.; Birbilis, N.; Pan, J. Journal of the Electrochemical Society 2017, 164, C75–C84.
- Zhang, X. L.; Jiang, Z. H.; Yao, Z. P.; Song, Y.; Wu, Z. D. Corrosion Science 2009, 51, 581–587.

**Chapter 3** 

Ag<sup>+</sup> Interference from Ag/AgCl Wire Quasi-Reference Counter Electrode Inducing Corrosion Potential Shift in an Oil-Immersed Scanning Electrochemical Cell Microscopy Measurement



# **Scientific Contributions**

The effect of  $Ag^+$  ions from Ag/AgCl wire QRCE on the electrochemical measurements of corrosion during SECCM experiments was elucidated for the first time. The trace amount of  $Ag^+$  contaminants are usually ignored, but proved to produce considerable interfering current upon its reduction on Al alloy, causing the corrosion potential to shift to positive with time. Given the widespread use of Ag/AgCl wire RE, the clarification of  $Ag^+$  interference is of great importance for various fields in interpreting the measured currents and potentials.

# **Chapter Abstract**

 $E_{\rm corr}$  was observed to shift toward positive values over the number of landings in Chapter 2, which was attributed to the Ag<sup>+</sup> ions from the Ag/AgCl wire QRCE. Chapter 3 reveals that the reduction of these Ag<sup>+</sup> species at WE generated a faradaic current, which significantly affects the low magnitude currents inherently measured in the OI-SECCM. We demonstrated that the cathodic current of the microscopic corrosion of AA7075-T73 was increased by the Ag<sup>+</sup> reduction, which caused the positive shifts of corrosion potentials. The use of a leak-free Ag/AgCl electrode or an extended distance between the Ag/AgCl wire and micropipette tip droplet eliminated the Ag<sup>+</sup> contamination, making it possible to measure accurate corrosion potentials during the OI-SECCM measurements.

### Publication

The work presented in this chapter is reproduced from:

Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J., Ag<sup>+</sup> Interference from Ag/AgCl Wire Quasi-Reference Counter Electrode Inducing Corrosion Potential Shift in an Oil-Immersed Scanning Micropipette Contact Method Measurement. *Analytical Chemistry*. **2021**, 93 (28), 9657-9662.

# 3.1 Introduction

The silver/silver chloride (Ag/AgCl) electrode is one of the most commonly used reference electrodes (REs) in electrochemical measurements.<sup>1–3</sup> The potential of Ag/AgCl associated with the redox reaction between Ag and AgCl (eq 3.1) is controlled by the activity of Cl<sup>–</sup> in the solution according to eq 3.2.<sup>4–6</sup>

$$AgCl_{(s)} + e^{-} \rightleftharpoons Ag_{(s)} + Cl^{-}_{(aq)}$$
 (3.1)

$$E_{Ag/AgCl} = E^0_{Ag/AgCl} - \frac{RT}{F} \ln a_{Cl^-}$$
(3.2)

In eq 3.1,  $E_{(Ag/AgCl)}$  is the equilibrium potential (V);  $E^{0}_{(Ag/AgCl)}$  is the standard electrode potential (V); R is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>); T is the temperature (K); F is the Faraday's constant (96485 C mol<sup>-1</sup>);  $a_{Cl^-}$  is the activity of Cl<sup>-</sup>.

In a conventional Ag/AgCl RE, an Ag/AgCl wire is immersed in a KCl solution with a constant Cl<sup>-</sup> activity and isolated from the test solution with a porous frit to limit the sample contamination,<sup>2</sup> whereas the non-isolated Ag/AgCl wire serves as QRCE in SECCM<sup>7-14</sup> which is the advanced version of scanning droplet cell technique.<sup>15–17</sup> Singleand double-channel pipettes are the most commonly used in SECCM, with one and two Ag/AgCl wires inserted respectively. Herein, we explored the behavior of Ag/AgCl wire QRCE in the single-channel micropipette SECCM, which is also called SMCM.<sup>13,18–20</sup> Although the potential stability of Ag/AgCl QRCE has been confirmed under SECCM experimental conditions,<sup>14,21–25</sup> the effect of Ag<sup>+</sup> originating from the Ag/AgCl wire QRCE (AgCl<sub>(s)</sub>  $\Rightarrow$  Ag<sup>+</sup><sub>(aq)</sub> + Cl<sup>-</sup><sub>(aq)</sub>)<sup>26,27</sup> on the currents (pA levels) measured in a SECCM experiment has not been elucidated.

In most macroscale electrochemical measurements, the Ag<sup>+</sup> contamination is negligible because of the limited solubility of AgCl in water ( $K_{sp} = 1.8 \times 10^{-10} \text{ M}^2$ ).<sup>5,28</sup> However, a measurable impact can be observed in silver sensitive systems even when using a commercial single-junction Ag/AgCl RE.<sup>27,29–31</sup> Low currents of the electrochemical measurements at the microscale make SECCM experiments susceptible to trace amounts of contaminants that have amplified effects considering the small volume of electrolyte contained in a micropipette. In this study, Ag<sup>+</sup> was detected in the micropipette tip droplet using a glassy carbon working electrode (WE). The study was then extended to an aluminum alloy WE since its dense oxide film further reduced the currents recorded in SECCM, thus making the system even more sensitive to trace Ag<sup>+</sup> contaminants. The corrosion potentials ( $E_{corr}$ ) of aluminum alloy AA7075-T73 were extracted from microscale areas using oil-immersed SECCM (OI-SECCM) which prevents the evaporation of the 3.5 wt% NaCl solution droplet.<sup>24,32,33</sup> We report the deleterious effects of Ag<sup>+</sup> contamination on the measured  $E_{corr}$ , which globally drift towards positive values over time, and experimental solutions to eliminate such effects during OI-SECCM mapping. Given that Ag/AgCl wire QRCE is the most commonly used in the micropipette-based techniques, the understanding of Ag<sup>+</sup> interference is key to correctly interpreting the measured currents and potentials, paving the way for the quantitative analysis and long-term mapping.

# 3.2 Experimental section

#### 3.2.1 Reagents and Materials

Sodium chloride (NaCl, anhydrous, 99.8%) and mineral oil (M5310) were purchased from Sigma-Aldrich. AA7075-T73 aluminum alloy was supplied by NRC (National Research Council Canada, Saguenay). The electrolyte solution (3.5 wt% NaCl solution) was prepared from ultrapure water (Milli-Q Reference Water Purification System, Millipore, 18.2  $M\Omega$  cm resistivity at 25 °C). Ag<sup>+</sup> contaminated solution was prepared by soaking Ag/AgCl wires in a 3.5 wt% NaCl solution in the dark for 3 days. The micropipette holder (MEW-M10U) and leak-free Ag/AgCl electrode (2 mm OD, ET-072) were purchased from Warner Instruments.

### 3.2.2 Micropipette Fabrication

Micropipettes were obtained by pulling a quartz capillary of 0.3/1.0 mm ID/OD (Sutter Instrument, Novato, CA) with a P-2000 CO<sub>2</sub> laser puller (Sutter Instrument) using the single line heating and pulling program (Heat = 585; Fil = 2; Vel = 30; Del = 130; Pul = 30). The tip diameter of micropipette is ~1.6  $\mu$ m, as estimated from a scanning electron microscope (SEM) image (Figure B.1).

### 3.2.3 Electrode Preparation

#### 3.2.3.1 Ag/AgCl Wire QRCE

Ag/AgCl wire QRCE was prepared by soaking a 0.125 mm diameter Ag wire (Goodfellow Metals, Huntingdon, England) in household bleach for 15-30 min.<sup>34–36</sup> An AgCl film was formed by oxidation, giving rise to an Ag/AgCl wire. After rinsing with deionized water, the Ag/AgCl wire was used as a QRCE in the OI-SECCM measurements. The bleach oxidized Ag/AgCl wire is reported to have the same performance as the electrochemically generated Ag/AgCl wire.<sup>26</sup> To verify the reproducibility of the bleach oxidized Ag/AgCl electrode, eight Ag/AgCl wires were measured versus saturated calomel electrode (SCE) in a 3.5 wt% NaCl solution, showing a maximal variation of only ~3.5 mV (Figure B.2).

#### 3.2.3.2 AA7075-T73

AA7075-T73 aluminum alloy supplied by NRC (National Research Council Canada, Saguenay) was mounted in an automated TegraForce-5 polishing arm (Struers, USA). It was ground with a 320 grit SiC paper (Struers, Canada) and subsequently polished by 9 and 3  $\mu$ m colloidal diamond suspensions (Struers, Canada), on a MD Chem cloth (Struers, Canada), using a TegraPol-25 polishing wheel (Struers, USA). The final step employed a colloidal silica suspension (Struers, Canada) on the MD Chem cloth to polish the samples until mirror-like surfaces were obtained. The samples were then sonicated with anhydrous ethanol and ultrapure water to remove residuals of silica suspensions before drying in air.

#### 3.2.3.3 Glassy Carbon

Glassy carbon (GC) substrate was successively polished with 1, 0.3, 0.1, and 0.05  $\mu$ m diameter alumina powder (Struers, USA) on polishing clothes (Struers, Canada), followed by sonication in ultrapure water before drying in air.

#### 3.2.4 Electrochemical Measurements

#### 3.2.4.1 OI-SECCM Measurements

The OI-SECCM experiments were carried out as previously reported<sup>33</sup> with an EIProScan 3 system (HEKA, Germany; bipotentiostat model PG340) in a Faraday cage (Acoustic Isolation Novascan Ultracube, Ames, IA, USA) mounted on a vibration isolating unit (Micro 60 Halcyonics Active Vibration Isolation Platform, Novascan, Ames, IA, USA). The micropipette was filled with a 3.5 wt% NaCl solution, and an Ag/AgCl wire was inserted from the top, which has a 5 mV difference versus a SCE in the 3.5 wt% NaCl solution. The WE substrate was covered with a layer of mineral oil where the droplet at the end of micropipette was immersed throughout the experiment, thus preventing the droplet evaporation and crystallization. The hopping mode protocol was carried out during which the micropipette was lowered to the substrate under oil at a rate of 1  $\mu$ m/s with 1 nm data sampling. A bias voltage of -1.4 V was applied until the droplet contacted the WE surface. Upon contact, a current spike exceeded the set current threshold (2 pA for AA7075-T73, 4 pA for GC), thus triggering the system to stop the micropipette approach. At this moment, an electrochemical cell in the two-electrode configuration was established.

#### 3.2.4.2 Corrosion Measurements on AA7075-T73

The OI-SECCM electrochemical measurement on the AA7075-T73 WE at each landing point includes a 60 s OCP measurement, followed by a PDP measurement at a scan rate of 100 mV/s from -1.0 V to -0.3 V or to the potential where the current exceeded the set limit of 100 pA.

### 3.2.4.3 Detection of Ag<sup>+</sup> on GC WE

The detection of Ag<sup>+</sup> was carried out with a GC electrode serving as the WE (Figure 3.1ai). At each landing point, a potential of -0.6 V was applied for 5 s to reduce  $Ag^+_{(aq)}$  to  $Ag_{(s)}$  which was subsequently oxidized in cyclic voltammetry (CV) (-0.6 to 0.4 V) at a scan rate of 100 mV/s (Figure 3.1a-ii).



**Figure 3.1:** (a-i) Schematic of the micropipette in contact with the GC substrate under the mineral oil in an OI-SECCM setup. (a-ii) E - t waveform applied to the GC substrate at each landing. -1.4 V before 0 s represents the approach potential when the micropipette is moving down. CV was run at a scan rate of 100 mV/s between -0.6 and 0.4 V. (a-iii) A representative CV at the landing point 1681 shows the Ag oxidation peak. (b) Forward scan of CV from -0.1 to 0.1 V that contains an Ag oxidation peak at landings 1, 100, 150, 200, and 300. Thirty minutes passed between the time of Ag/AgCl wire insertion in the micropipette and the first landing. (c) Areas of Ag oxidation peaks extracted from the i - t plot for each of the 1681 landings on GC.

# 3.3 **Results and Discussion**

### 3.3.1 Detection of Ag<sup>+</sup> from the Ag/AgCl Wire QRCE

Trace amounts of contaminants can greatly affect the pA level currents during OI-SECCM measurements. As the Ag/AgCl wire QRCE is directly exposed to the electrolyte solution in an OI-SECCM setup, the dissolution of the AgCl film can release Ag<sup>+</sup> to the surrounding solution. To investigate whether these Ag<sup>+</sup> can reach the micropipette tip droplet during OI-SECCM mapping, CVs were performed at each landing site on the GC WE (Figure 3.1a-i, ii). The end of Ag/AgCl wire was placed at a 1.5 cm distance from the tip of micropipette. Ag<sup>+</sup> was reduced and subsequently oxidized during the anodic scan, thus exhibiting a positive current peak in CV (Figure 3.1a-iii). The areas under the Ag oxidation peaks indicated the amount of Ag<sup>+</sup> accumulated in the droplet at the end of micropipette.

An area of  $200 \times 200 \ \mu m^2$  GC surface was mapped with 1681 landings during ~14 h. At the first landing, no Ag oxidation peak was detected on the CV (Figure 3.1b), indicating the absence of Ag<sup>+</sup> in the droplet. After 100 landings, an Ag oxidation peak was detected at -0.04 V and gradually grew over time, as landing events accumulated. The increasing integrated peak areas suggest the accumulation of Ag<sup>+</sup> over time in the droplet (Figure 3.1c). Thus, Ag<sup>+</sup> reached the tip droplet between the moment of insertion of the Ag/AgCl wire in the micropipette and the 100th landing, which took 80 min. If the mass transport was exclusively governed by the diffusion mechanism, ~19 h would be required for a diffusion distance of 1.5 cm according to the diffusion coefficient of Ag<sup>+</sup> in water ( $1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).<sup>37,38</sup> Hence, other factors must contribute to the accelerated mass transport detected. The WE surface was negatively charged during 68 % of the time while the droplet wetted the surface, during which electrical migration may speed up the movement of Ag<sup>+</sup>.<sup>21</sup> Additionally, the 3.5 wt% NaCl solution may promote the dissolution of AgCl by forming soluble [AgCl<sub>n</sub>]<sup>-(n-1)</sup> complexes,<sup>39–42</sup> which would accelerate the

flux of silver ion species. Perera and Rosenstein reported an Ag oxidation peak 40 min after the insertion of Ag/AgCl wire into a micropipette containing a 0.1 M LiCl solution at a distance of 2.5 cm away from the tip,<sup>26</sup> whereas Unwin's group reported that the silver contamination did not occur in the 0.1 M HClO<sub>4</sub> solution during a 6 h SECCM experiment by extending the distance between the Ag/AgCl wire and the micropipette tip to 3 cm.<sup>21</sup> They attributed the observation of  $\mathrm{Ag}^+$  to detached AgCl fragments that would find their way close to the pipette tip when inappropriately inserting the Ag/AgCl wire. However, no solid fragments were observed in the micropipettes before and after our OI-SECCM experiments. Therefore, we conclude that the presence of high concentration of Cl<sup>-</sup> could be one of the reasons that led to the observation of silver contamination in the droplet in such a short time (80 min). The presence of the unwanted electrochemically active Ag<sup>+</sup> at the droplet-substrate interface will interfere with the electrochemical measurements, leading to misinterpretation of the measured currents in OI-SECCM. For example, in local corrosion measurements, where one seeks to delineate microstructure reactivity, additional current contributions from Ag<sup>+</sup> reduction will lead to incorrect measurements of corrosion potential,  $E_{\rm corr}$ , and will overestimate the extent of cathodic reactions at the local scale.

### 3.3.2 Ag<sup>+</sup> Reduction at the Substrate Shifts $E_{corr}$ Positively

Ag<sup>+</sup> migrating from the Ag/AgCl wire to the micropipette tip droplet during OI-SECCM mapping is expected to be reduced under cathodic potentials, thus interfering with electrochemical measurements. This was especially true when studying aluminum alloys (AA7075-T73, Figure 3.2a), where a 200 mV  $E_{corr}$  shift was observed over the first 200 landings of OI-SECCM measurements within the first 4 h. As the potential stability of Ag/AgCl wire QRCE in the 3.5 wt% NaCl solution has been confirmed by chronopotentiometry (Figure B.3), and the alloy surface was fresh for each landing, the  $E_{corr}$  shift was attributed to changes within the droplet's solution.  $E_{corr}$  is a mixed potential (Figure 3.2b,

black point), where the cathodic current (negative) equals the anodic current (positive).<sup>43</sup> For the corrosion of AA7075-T73 in a 3.5 wt% NaCl solution, the cathodic current arises from the reduction of the dissolved oxygen and the anodic current from the aluminum oxidation.<sup>44</sup> While using an Ag/AgCl wire QRCE, Figure 3.2c shows that the cathodic currents measured at -0.9 V during the PDP scan increase with the number of landings. This is consistent with the Ag<sup>+</sup> accumulation in the droplet, as deduced from Figure 3.1c. The reduction of Ag<sup>+</sup> increases cathodic currents. As  $E_{corr}$  is the potential at which a zero-net current is measured, this potential will shift toward a new value for which the anodic current equals the now increased cathodic current (Figure 3.2b). As a result, a more positive  $E_{corr}$  (Figure 3.2b, red point) was recorded at the re-established balance between the cathodic and anodic currents.



**Figure 3.2:** OI-SECCM mapped the surface of AA7075-T73 with a 0.125 mm diameter Ag/AgCl wire as the QRCE in a 3.5 wt% NaCl solution. (a)  $E_{corr}$  extracted from the 60 s OCP measurement at each landing site. (b) Mixed potential theory explains the  $E_{corr}$  shift induced by the Ag<sup>+</sup>/Ag reduction reaction. (c) Cathodic currents at -0.9 V from the PDP measurement at each landing.

To confirm the reduction of  $Ag^+$  on the AA7075-T73 alloy surface, the scanned areas were characterized by SEM imaging and EDS analyses. Two landing sites were selected from the scanned areas enclosed by the yellow and green boxes (Figure 3.3a), between which  $E_{corr}$  shifted by ~250 mV (Figure 3.3b). On the landing area in the yellow box, only elements present in the Al alloy (i.e., Al, Zn, Mg, Cu) were detected (Figure 3.3c), whereas, in the green box, some precipitates containing Ag were observed (Figures 3.3d), demonstrating that Ag<sup>+</sup> originating from the Ag/AgCl wire contaminated the droplet during OI-SECCM mapping. Also, the oxygen to aluminum ratio increased compared with that in Figure 3.3c. Our results suggest that the precipitates may also contain corrosion products (aluminum oxides, hydroxide and/or oxyhydroxide species) implied by the higher oxygen content, suggesting that both corrosion products and Ag<sup>+</sup> accumulated in the droplet.



**Figure 3.3:** (a) SEM image of the scanned areas  $(21 \times 19 \text{ landings on } 100 \times 90 \ \mu\text{m}^2)$ . (b) OI-SECCM  $E_{\text{corr}}(\text{OCP})$  map of the scanned area. Energy dispersive X-ray spectroscopy (EDS) analyses of the surfaces pointed by the arrows in one landing location selected from (e) the yellow box and (f) green box in (a).

To reduce the possible contribution from the corrosion product on the  $E_{corr}$  shift, an Ag/AgCl wire QRCE was preconditioned by immersion in a micropipette containing 3.5 wt% NaCl for 4 h. Since no contact was established with the AA7075-T73 alloy, no corrosion products were generated during preconditioning. Once contacted to the AA7075-T73 alloy, the  $E_{corr}$  obtained (Figure 3.4a) using the preconditioned Ag/AgCl wire QRCE did not drift as seriously between landings (Figure 3.2a), but these measured  $E_{corr}$  values were more positively shifted when compared to the first landings observed without preconditioning, because Ag<sup>+</sup> had diffused to the tip droplet during preconditioning. This was verified by CVs on a GC surface, in which an Ag oxidation peak was observed at the

first landing (Figure 3.4b, inset). Also, the Ag<sup>+</sup> amount linearly increased with increasing landing (Figure 3.4b) as more Ag<sup>+</sup> was released into the micropipette.



**Figure 3.4:** Ag/AgCl wire QRCE was preconditioned in the micropipette containing 3.5 wt% NaCl for 4 h prior to the experiments in (a) and (b). (a)  $E_{corr}$  extracted from OCP measurements during the OI-SECCM measurements at the surface of the AA7075-T73 alloy. (b) Areas under the Ag oxidation peaks of 1681 landings in the OI-SECCM measurement on GC.

To further confirm that the  $E_{corr}$  shift was induced by Ag<sup>+</sup>, an Ag<sup>+</sup> contaminated 3.5 wt% NaCl solution was used in the micropipette, which was obtained by equilibrating 3.5 wt% NaCl solution with Ag/AgCl wires for 3 days (Figure 3.5a). The Ag<sup>+</sup> was measured with the method presented in Figure 3.1a. A leak-free Ag/AgCl QRCE was used to make sure that the detected Ag<sup>+</sup> originated from the contaminated solution rather than Ag/AgCl QRCE. A large Ag oxidation peak with an area of 17.24 pC (Figure 3.5b) was observed, which was almost twice that measured at the last landing (9.73 pC) in Figure 3.4b. The concentration of Ag<sup>+</sup> in the contaminated solution (Figure 3.5a) was thus high such that the dissolution of AgCl on the wire QRCE quickly reached equilibrium during OI-SECCM scanning. As expected, the solution gave rise to highly stable  $E_{corr}$  values (Figure 3.5c). Importantly, even though the  $E_{corr}$  did not drift, their values do not inform on the corrosion properties of AA7075-T73 in the 3.5 wt% solution because they are tainted from the Ag<sup>+</sup> interference.



**Figure 3.5:** (a) Ag/AgCl wires were immersed in a 3.5 wt% NaCl solution for 3 days to obtain the Ag<sup>+</sup> contaminated solution. (b) The Ag<sup>+</sup> in the contaminated 3.5 wt% NaCl solution was detected on the surface of GC in the setup of OI-SECCM shown in Figure 3.1a. A leak-free Ag/AgCl electrode served as the QRCE. (c) OI-SECCM mapping of the AA7075-T73 surface using the Ag<sup>+</sup> contaminated solution without preconditioning the Ag/AgCl wire QRCE.

### **3.3.3** Eliminating the Ag<sup>+</sup> Interference

To avoid  $Ag^+$  interference, one must balance the time needed for  $Ag^+$  to arrive at the tip droplet and the overall mapping time. When the distance between the Ag/AgCl wire QRCE and the micropipette tip was increased to 6 cm (Figure 3.6a), 14 h of SECCM mapping was achieved where no Ag<sup>+</sup> was detected on the CVs (Figure 3.6b). Alternatively, the use of an electrode preventing Ag<sup>+</sup> leakage from the Ag/AgCl QRCE would be more generalizable and remove the constant requirement to optimize mapping time with the Ag<sup>+</sup> contamination.



**Figure 3.6:** (a) The distance between Ag/AgCl wire and micropipette tip was extended to 6 cm. (c) A leak-free Ag/ AgCl electrode exposed to the electrolyte solution via a holder connected to the micropipette. OI-SECCM measurements were carried out on GC substrate using (b) Ag/AgCl wire and (d) a leak-free Ag/AgCl electrode as the QRCE. The color bar indicates the number of landings. At each landing, the *E* - *t* waveform shown in Figure 3.1a was performed for the detection of Ag<sup>+</sup>. The scanning lasted ~14 h.

The commonly used commercial Ag/AgCl RE with a single junction frit can prevent the leakage of Ag<sup>+</sup> to a large extent, but not completely, as it has been detected in the CO<sub>2</sub> reduction experiment by Leung and McCrory<sup>30</sup> and electrocatalytic hydrogen evolution by Roger and Symes.<sup>31</sup> The double-junction Ag/AgCl RE was proposed to mitigate the Ag<sup>+</sup> leakage,<sup>30,31</sup> but it is not suitable for the micropipette due to the difficulty of miniaturization. A leak-free Ag/AgCl electrode, which uses a highly conductive but not porous junction to prevent the solution migration in either direction, would be one choice for OI-SECCM measurements.<sup>45–48</sup> The leak-free Ag/AgCl used here has a potential difference of 1.7 mV versus SCE in the 3.5 wt% NaCl solution (Figure B.4), which is close to the potential of Ag/AgCl wire. The setup shown in Figure 3.6c presents one configuration to connect the leak-free Ag/AgCl QRCE to a micropipette with a holder.<sup>49,50</sup> Other configurations could be developed on the basis of various types of commercial and homemade holders. No Ag oxidation peaks were observed over 14 h of landing (Figure 3.6d), indicating the successful elimination of interfering Ag<sup>+</sup>.

# 3.4 Conclusion

The Ag<sup>+</sup> contaminant arising from the use of an Ag/AgCl wire QRCE can be electrochemically reduced at the substrate, thus contributing to additional cathodic currents measured during the investigation of the AA7075-T73 corrosion mechanism. The results demonstrate that trace amounts of Ag<sup>+</sup> from an Ag/AgCl wire QRCE will lead to the misinterpretation of currents and potentials, especially for the systems measuring small currents for which the  $E_{corr}$  drifts are more pronounced. Extending the distance between the Ag/AgCl wire and the tip end droplet in accordance with the scan duration or using a leak-free Ag/AgCl electrode as QRCE, can eliminate the Ag interference. This chapter thus reveals the precautions to be taken when employing the most commonly used Ag/AgCl wire QRCE in SECCM and proposes strategies to make possible accurate quantification of underlying corrosion processes at the microscopic level during a long-term OI-SECCM scan.

# References

- 1. East, G. A.; Del Valle, M. Journal of Chemical Education 2000, 77, 97.
- Inzelt, G.; Lewenstam, A.; Scholz, F., Handbook of Reference Electrodes; Springer: 2013, pp 86–98.
- Zhou, J.; Ren, K.; Zheng, Y.; Su, J.; Zhao, Y.; Ryan, D.; Wu, H. Electrophoresis 2010, 31, 3083–9.
- 4. Cranny, A.; Harris, N. R.; Nie, M.; Wharton, J. A.; Wood, R. J. K.; Stokes, K. R. Sensors and Actuators A: Physical **2011**, 169, 288–294.
- 5. Ha, H.; Payer, J. Electrochimica Acta 2011, 56, 2781–2791.
- Suzuki, H.; Hirakawa, T.; Sasaki, S.; Karube, I. J Sensors Actuators B: Chemical 1998, 46, 146–154.
- Bentley, C. L.; Kang, M.; Unwin, P. R. Journal of the American Chemical Society 2017, 139, 16813–16821.
- 8. Choi, M.; Siepser, N. P.; Jeong, S.; Wang, Y.; Jagdale, G.; Ye, X.; Baker, L. A. *Nano Letters* **2020**, *20*, 1233–1239.
- 9. Kang, M.; Perry, D.; Kim, Y.-R.; Colburn, A. W.; Lazenby, R. A.; Unwin, P. R. *Journal* of the American Chemical Society **2015**, 137, 10902–10905.
- 10. Lai, S. C.; Patel, A. N.; McKelvey, K.; Unwin, P. R. *Angewandte Chemie International Edition* **2012**, *51*, 5405–5408.
- 11. McKelvey, K.; O'Connell, M. A.; Unwin, P. R. Chemical Communications 2013, 49, 2986–2988.
- Takahashi, Y.; Kumatani, A.; Munakata, H.; Inomata, H.; Ito, K.; Ino, K.; Shiku, H.; Unwin, P. R.; Korchev, Y. E.; Kanamura, K., et al. *Nature Communications* 2014, *5*, 1–7.

- 13. Williams, C. G.; Edwards, M. A.; Colley, A. L.; Macpherson, J. V.; Unwin, P. R. *Analytical Chemistry* **2009**, *81*, 2486–2495.
- Yule, L. C.; Bentley, C. L.; West, G.; Shollock, B. A.; Unwin, P. R. *Electrochimica Acta* 2019, 298, 80–88.
- 15. Hassel, A.; Lohrengel, M. *Electrochimica Acta* **1997**, *42*, 3327–3333.
- Lohrengel, M.; Moehring, A.; Pilaski, M. Fresenius' Journal of Analytical Chemistry 2000, 367, 334–339.
- 17. Lohrengel, M.; Moehring, A.; Pilaski, M. Electrochimica Acta 2001, 47, 137–141.
- Dayeh, M.; Ghavidel, M. R. Z.; Mauzeroll, J.; Schougaard, S. B. *ChemElectroChem* 2019, *6*, 195–201.
- 19. Gateman, S. M.; Georgescu, N. S.; Kim, M.-K.; Jung, I.-H.; Mauzeroll, J. *Journal of the Electrochemical Society* **2019**, *166*, C624–C630.
- Snowden, M. E.; Dayeh, M.; Payne, N. A.; Gervais, S.; Mauzeroll, J.; Schougaard, S. B. *Journal of Power Sources* 2016, 325, 682–689.
- 21. Bentley, C. L.; Perry, D.; Unwin, P. R. Analytical Chemistry 2018, 90, 7700–7707.
- 22. Ebejer, N.; Schnippering, M.; Colburn, A. W.; Edwards, M. A.; Unwin, P. R. *Analyt-ical Chemistry* **2010**, *82*, 9141–9145.
- 23. Payne, N. A.; Mauzeroll, J. ChemElectroChem 2019, 6, 5439–5445.
- 24. Shkirskiy, V.; Yule, L.; Daviddi, E.; Bentley, C.; Aarons, J.; West, G.; Unwin, P. *Journal of the Electrochemical Society* **2020**, *167*, 041507.
- Tao, B.; Unwin, P. R.; Bentley, C. L. the Journal of Physical Chemistry C 2019, 124, 789– 798.
- 26. Perera, R. T.; Rosenstein, J. K. *Scientific Reports* **2018**, *8*, 1–10.
- 27. Yakushenko, A.; Mayer, D.; Buitenhuis, J.; Offenhäusser, A.; Wolfrum, B. *Lab on a Chip* **2014**, *14*, 602–607.

- 28. Polk, B. J.; Stelzenmuller, A.; Mijares, G.; MacCrehan, W.; Gaitan, M. Sensors and *Actuators B: Chemical* **2006**, *114*, 239–247.
- 29. Ansuini, F. J.; Dimond, J. R. Materials Performance **1994**, 33, 14–17.
- 30. Leung, K. Y.; McCrory, C. C. L. ACS Applied Energy Materials 2019, 2, 8283–8293.
- 31. Roger, I.; Symes, M. D. ACS Applied Materials and Interfaces **2017**, *9*, 472–478.
- 32. Daviddi, E.; Shkirskiy, V.; Kirkman, P. M.; Robin, M. P.; Bentley, C. L.; Unwin, P. R. *Chemical Science* **2021**, *12*, 3055–3069.
- 33. Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J. Analytical Chemistry 2020, 92, 12415– 12422.
- 34. Barlag, R.; Nyasulu, F.; Starr, R.; Silverman, J.; Arthasery, P.; McMills, L. *Journal of Chemical Education* **2014**, *91*, 766–768.
- Da Silva, E. T. S. G.; Miserere, S.; Kubota, L. T.; Merkoçi, A. *Analytical Chemistry* 2014, *86*, 10531–10534.
- Rohaizad, N.; Mayorga-Martinez, C. C.; Novotný, F.; Webster, R. D.; Pumera, M. Electrochemistry Communications 2019, 103, 104–108.
- 37. Heyrovsky, J.; Kuta, J. Instrumental Techniques in Electrochemistry., 1966.
- Johans, C.; Clohessy, J.; Fantini, S.; Kontturi, K.; Cunnane, V. J. Electrochemistry Communications 2002, 4, 227–230.
- 39. Fritz, J. J. Journal of Solution Chemistry **1985**, 14, 865–879.
- 40. Jonte, J. H.; Martin Jr, D. S. Journal of the American Chemical Society **1952**, 74, 2052–2054.
- 41. Katan, T.; Szpak, S.; Bennion, D. N. Journal of the Electrochemical Society 1974, 121, 757–764.
- 42. Zelyanskii, A.; Zhukova, L.; Kitaev, G. Inorganic Materials 2001, 37, 523–526.

- 43. Zhang, X. G. In *Corrosion and Electrochemistry of Zinc*; Springer US: Boston, MA, 1996, pp 125–156.
- 44. Davis, J. R., Corrosion of Aluminum and Aluminum Alloys; ASM International: 1999.
- Arán-Ais, R. M.; Scholten, F.; Kunze, S.; Rizo, R.; Roldan Cuenya, B. *Nature Energy* 2020, *5*, 317–325.
- Ding, M.; Zhong, G.; Zhao, Z.; Huang, Z.; Li, M.; Shiu, H.-Y.; Liu, Y.; Shakir, I.; Huang, Y.; Duan, X. ACS Central Science 2018, 4, 590–599.
- 47. Hirano, Y.; Kodama, M.; Shibuya, M.; Maki, Y.; Komatsu, Y. *Analytical Biochemistry* 2014, 447, 39–42.
- 48. Kuttiyiel, K. A.; Sasaki, K.; Choi, Y.; Su, D.; Liu, P.; Adzic, R. R. Energy & Environmental Science **2012**, 5, 5297–5304.
- 49. Wang, Y.; Gordon, E.; Ren, H. Analytical Chemistry **2020**, *92*, 2859–2865.
- Yu, Y.; Sundaresan, V.; Bandyopadhyay, S.; Zhang, Y.; Edwards, M. A.; McKelvey, K.; White, H. S.; Willets, K. A. ACS Nano 2017, 11, 10529–10538.

**Chapter 4** 

Controlling Surface Contact, Oxygen Transport and Pitting of Surface Oxide via Single-Channel Scanning Electrochemical Cell Microscopy



# **Scientific Contributions**

Chapter 4 reveals the effect of the potential controlled droplet landing process on subsequent electrochemical measurements in the single-channel pipette SECCM, which has important implications for understanding variations between SECCM measurements. Additionally, the applied potential during the pipette approach to substrate was found to damage the surface oxide upon droplet landing. By controlling the value of approach potential, this work provides a strategy to increase the surface conductivity without destroying the surface heterogeneity. This method is specifically useful for the oxide-covered metals to increase the measured currents in SECCM, thereby facilitating the use of small (sub)micropipettes to resolve small surface differences.

# **Chapter Abstract**

In the single-channel pipette SECCM, the applied potential during the approach of micropipette to the substrate, generates a transient current upon droplet contact with the substrate. Once the transient current exceeds a set threshold, the micropipette is automatically halted. Currently, the effect of the approach potential on the subsequent electrochemical measurements, such as the OCP and PDP, is considered to be inconsequential. In this chapter, we demonstrate that the applied approach potential does impact the extent of probe to substrate interaction and subsequent microscale electrochemical measurements on Al alloy AA7075-T73.

### 4.1 Introduction

SECCM enables direct electrochemical measurements at microscopic sites by scanning a droplet cell over a substrate surface.<sup>1–3</sup> Single-channel SECCM is often used to record the spatially resolved electrochemical activities across metal surfaces to investigate corrosion at the (sub)microscale.<sup>4–8</sup> In single-channel pipette systems, the contact of the droplet with the substrate produces a transient current  $(i_{trig})$  triggering the stop of pipette movement once a set current threshold is exceeded.<sup>9,10</sup>  $i_{trig}$  must have a higher magnitude than the background noise which is the minimal threshold, otherwise the micropipette will not stop until it touches the substrate. For a given micropipette diameter, the magnitude of  $i_{trig}$  depends on the conductivity of substrate, the composition of electrolyte and the approach potential  $(E_{appr})$  applied during the micropipette approach to the substrate. Since the substrate and electrolyte are often experimentally fixed, the magnitude of  $i_{trig}$ is primarily controlled by  $E_{appr}$ . For conductive substrates or electrolytes containing active redox species, such as carbon-based materials,<sup>11,12</sup> battery materials,<sup>10,13–17</sup> Au<sup>18–20</sup> and Pt,<sup>10,21</sup> and Fc/Fc<sup>+</sup>,<sup>22</sup> [Fe(CN)<sub>6</sub>]<sup>2+/3+</sup>,<sup>3</sup> [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>2+/3+</sup>,<sup>9,23</sup> it is easy to achieve a  $i_{trig}$  higher than the current threshold despite applying a small  $E_{appr}$ . For example, an  $E_{appr}$  of 0.65 V (vs. Ag/AgCl) applied to a LiFePO<sub>4</sub> composite electrode gave rise to a  $i_{trig}$  up to 9 pA (threshold = 2 pA).<sup>10</sup> An  $E_{appr}$  of -200 mV (vs. RHE) applied on a conductive noble graphene substrate generated a capacitive current high enough to trigger a 70 nm diameter pipette to stop upon contact to form a graphene-0.5 M H<sub>2</sub>SO<sub>4</sub> interface.<sup>12</sup>

When studying corroding alloys, the electrolytes typically do not contain added active redox species since they will influence the corrosion mechanism.  $i_{trig}$  is mainly dependent on corrosion reactions such as metal dissolution, oxygen reduction and hydrogen evolution reactions, which are typically low in concentration compared to other systems.<sup>10,12,15,19</sup> Additionally,  $i_{trig}$  is expected to have a lower magnitude compared to conductive substrates due to the presence of surface oxides. As such, a larger  $E_{appr}$  is needed to obtain an  $i_{trig}$  higher than the current threshold.

 $E_{appr}$  is a decisive parameter for successful SECCM investigation of Al alloys, and we revisit the common assumption that it is innocuous to subsequent microscale electrochemical measurements. We systematically analyzed the effects of  $E_{appr}$  on the microscale open circuit potential (OCP) and potentiodynamic polarization (PDP) measurements on an Al alloy AA7075-T73 in oil-immersed single SECCM.<sup>4,6,24</sup> We demonstrate that  $E_{appr}$  controls the extent of micropipette substrate interactions, impacting subsequent microscale measurements of corrosion potential ( $E_{corr}$ ) and the pitting density.

# 4.2 **Experimental section**

#### 4.2.1 Chemicals and Materials

Sodium chloride (NaCl, anhydrous, 99.8%) and mineral oil (M5310) were used as purchased from Sigma-Aldrich. AA7075-T73 Al alloy was supplied by NRC (National Research Council Canada, Saguenay). 3.5 wt% NaCl electrolyte solution was prepared using ultrapure water (Milli-Q Reference Water Purification System, Millipore, 18.2 M $\Omega$  cm resistivity at 25 °C).

Single channel micropipettes were fabricated from quartz glass capillaries (Sutter Instrument, Novato, CA) with dimensions of (o.d. × i.d.)  $1.0 \times 0.3$  mm, using a CO<sub>2</sub>-laser puller (P-2000, Sutter Instruments, U.S.A.). Pulling parameters for the diameter of ~2  $\mu$ m opening pipette: Line 1: heat = 585, filament = 2, velocity = 30, delay = 130, pull = 30. Pulling parameters for diameter ~10  $\mu$ m opening pipette: Line 1: heat = 750, filament = 4, velocity = 10, delay = 130, pull = 4.

An Ag/AgCl wire was prepared by chemically coating a 0.125 mm diameter Ag wire (Goodfellow Metals, Huntingdon, England) with AgCl film in household bleach.<sup>25–28</sup>

Note that, unless specified otherwise, all potentials reported below have been calibrated to the Ag/AgCl wire in the 3.5 wt% NaCl solution, which has a 5 mV difference with respect to the saturated calomel electrode (SCE).

Glassy carbon (GC) was successively polished with 1, 0.3, 0.1, 0.05  $\mu$ m diameter alumina powder (Struers, USA) on polishing clothes (Struers, Canada), followed by a sonication in ultrapure water before drying in air.

#### 4.2.2 Aluminum Sample Preparation and Surface Characterization

AA7075-T73 Al was polished with a 320 grit SiC paper (Struers, Canada), followed by 9  $\mu$ m and 3  $\mu$ m colloidal diamond suspensions (Struers, Canada), on a MD Chem cloth pad (Struers, Canada), using a TegraPol-25 polishing wheel (Struers, USA). A mirror-like surface was achieved after the final polishing step employing a colloidal silica suspension (Struers, Canada) on the MD Chem cloth. The sample surface was then rinsed with anhydrous ethanol and sonicated in ultrapure water for the removal of the residuals of silica suspensions before drying in air. The surfaces were imaged by optical microscope and scanning electron microscopy (SEM, FEI Helios Nanolab 660 dual beam, 5 keV). The surface topography was scanned by atomic force microscopy (AFM) with a molecular force probe controller (Asylum Research-an Oxford Instruments Company, Santa Barbara, CA) equipped on an MFP3D microscope working in alternating contact mode in air. The cantilevers were model ACTA (AppNano, Mountain View, CA).

#### 4.2.3 Macro Potentiodynamic Polarization Measurements

Macro electrochemical measurements were conducted with a multi-channel VSP-300 potentiostat (BioLogic Science Instruments, USA). The polished samples were mounted in a corrosion cell (K0235 Flat Cell, Princeton Applied Research, AMETEK<sup>®</sup> Scientific Instruments) with an area of 1 cm<sup>2</sup> exposed to the 3.5 wt% NaCl electrolyte solution. A SCE and platinum mesh were used as the reference and counter electrodes. Prior to the PDP measurement, OCP was measured allowing the corrosion system to reach a stationary state where  $E_{corr}(OCP)$  was obtained. The PDP measurement was carried out in the range of  $E_{corr}(OCP) \pm 250$  mV at a scan rate of 0.167 mV/s in the anodic direction (from negative to positive potentials). A current exceeding the set current limit (10 mA) ended the potential sweep.

# 4.2.4 Oil-Immersed Single-Channel Micropipette Scanning Electrochemical Cell Microscopy

Since the 3.5 wt% NaCl solution evaporates easily in air, SECCM was carried out under mineral oil as previously reported to prevent the crystallization of droplet at the end of micropipette.<sup>4</sup> All electrochemical measurements were performed using an EIProScan 3 system (HEKA, Germany; bipotentiostat model PG340) in a Faraday cage (Acoustic Isolation Novascan Ultracube, Ames IA, USA) on a vibration isolation table (Micro 60 Halcyonics Active Vibration Isolation Platform, Novascan, Ames IA, USA). A micropipette filled with a 3.5 wt% NaCl solution was inserted with an Ag/AgCl wire from the top that served as the quasi-reference counter electrode (QRCE). The substrate surface was covered with a thin layer of mineral oil, sufficient to submerge the droplet at the end of micropipette throughout the experiment. The micropipette was approached to the working electrode (WE) substrate under oil at a rate of 1  $\mu$ m/s with 1 nm data sampling with  $E_{appr}$  applied. Once the movement of the micropipette was triggered to stop, OCP (30 s) followed by PDP (-1.3 to -0.3 V at a scan rate of 100 mV/s) measurements were carried out in the established droplet cell.

# 4.3 **Results and Discussion**

### **4.3.1** *E*<sub>appr</sub> Determines the Type of Landing

Depending on the choice of  $E_{appr}$ , two types of landing were observed, droplet contact (DC) landing and pipette contact (PC) landing as shown in Figure 4.1a and b.  $E_{appr}$  was selected in the cathodic region, more negative than  $E_{\rm corr}$ , to prevent the significant metal dissolution and morphological changes during SECCM. The  $E_{\rm corr}$  of pure Al (-1.329 V, Figure C.1) was used as an approximation for the Al alloy matrix area. DC-landings were obtained at an  $E_{appr}$  of -2.5 V. Figure 4.1a shows that white particles were left on the alloy surface, assigned to the corrosion products, that identified the area of DC-landing. PClandings obtained at an  $E_{appr}$  of -1.5 V display dark circles on the alloy surface (Figure 4.1b), which agree with the size of 2  $\mu$ m diameter micropipette tip opening. This implies the pipette indentations, which were confirmed by AFM mapping (Figure 4.1c and d). A line scan over three landings was displayed in Figure 4.1d to quantify the indentation depth. At location 0 and 2, the depths are 13.24 and 13.23 nm, exceeding the usual oxide film thickness ( $\sim$  2-4 nm),<sup>29,30</sup> which indicates that the pipette physically damaged the oxide film. Most of the indentations in Figure 4.1c are actually not full circles and crescent shape in some cases. This is attributed to the tilt of the micropipette opening with respect to the alloy surface.



**Figure 4.1:** On the SECCM scanned surface of AA7075-T73, (a) droplet contact left corrosion products as the landing traces and (b) pipette contact left indentation (c) The topographic map of the alloy surface with pipette contact landings made by AFM. (d) Line scan across three pipette contact landings shows the indentation depths. The middle unlabelled two depths correspond to the second pipette indentation on the line scan in (c).

The formation of DC and PC landings was tied to the magnitude of  $i_{trig}$  which determined when the approach of micropipette was stopped. Positive and negative  $i_{trig}$  were observed for PC and DC respectively (Figure 4.2a and C.2). To elucidate the landing process,  $i_{trig}$  was measured at different  $E_{appr}$  with chronoamperometry carried out on the Al alloy using a 2  $\mu$ m diameter micropipette. The first current point on the chronoamperogram curve was approximated to be  $i_{trig}$ . For PC landings obtained with -1.5 V  $E_{appr}$ , the current was positive at the first point (red arrow in Figure 4.2b) and then progressively became negative with time. Theoretically, the cathodic potential of -1.5 V should produce a negative current. The positive current could be the current noise made by the physical contact between the micropipette and alloy, or an anodic current of the oxidation of the freshly exposed underlying Al due to the pipette contact damaging the oxide film. We infer that the DC generated  $i_{trig}$  was smaller than the current threshold and thus could not stop the micropipette movement. Consequently, the micropipette to stop. Accord-
ingly, to obtain DC-landings, a more negative  $E_{appr}$  is needed to generate a larger  $i_{trig}$ . Figure 4.2c shows the increase of  $i_{trig}$  with  $E_{appr}$  from -2 to -2.5 V. With respect to a current threshold of 2 pA shown by the amplitude of the background noise in Figure 4.2b, the  $i_{trig}$  values at -2 to -2.5 V  $E_{appr}$  are sufficient to produce DC-landings.



**Figure 4.2:** (a) The currents recorded during the process of the micropipette approach to the substrate for the pipette contact (upper curve) and droplet contact landings (lower curve). (b) Chronoamperometry was carried out at the approach potential of -1.5 V for 10 ms immediately after the micropipette contacted the Al alloy AA7075-T73. The first recorded current point was approximated to be  $i_{trig}$ . The black trace represents the background noise under the experimental conditions at that time. (c) First current points measured upon landing ( $i_{trig}$ ) in chronoamperometry were plotted as a function of approach potentials.

Although the pipette contact damages the oxide film, the  $E_{corr}(OCP)$  map (-1.5 V  $E_{appr}$ ) can still qualitatively display the correlation between the electrochemical activities and the alloy surface microscopic features similarly to the maps acquired with DC-

landings at  $E_{appr}$  of -2.0 and -2.5 V (Figure 4.3). Moreover, the pipette indentation provides a way to mark the scanned area for post characterizations by adjusting the value of  $E_{appr}$ . However, from a semiquantitative perspective, the difference in the types of landings and values of  $E_{appr}$  leads to variations in the electrochemical measurements, which will be discussed below by comparing the  $E_{corr}$ (OCP) and  $E_{corr}$ (PDP) extracted from the three maps in Figure 4.3.



**Figure 4.3:** The  $E_{corr}(OCP)$  maps obtained using SECCM with different  $E_{appr}$  were superimposed on optical microscopic images of the scanned surfaces.

### **4.3.2** Effect of $E_{appr}$ on $E_{corr}$ (OCP)

The  $E_{\text{corr}}(\text{OCP})$  collected from SECCM maps exhibit a dependence on  $E_{\text{appr}}$  (-1.5, -2.0 and -2.5 V) because of the differences between PC- and DC-landings (Figure 4.4a). PC-landings with  $E_{\text{appr}}$  at -1.5 V gave rise to more negative  $E_{\text{corr}}(\text{OCP})$  compared to DC-

landings obtained at  $E_{appr}$  of -2.0 and -2.5 V. According to the mixed potential theory,<sup>31</sup>  $E_{corr}$  shifting more negative is due to the anodic current increase (Figure 4.4b) or cathodic current decrease (Figure 4.4c). In DC-landings, the presence of droplet-oil interface allows for additional oxygen flux diffusing from the mineral oil to the droplet (Figure 4.4d, red arrows).<sup>6,32</sup> While, in PC-landings, the oxygen is entirely supplied by the flux along the micropipette in the bulk solution (Figure 4.4d, blue arrow). Because of the higher oxygen content in mineral oil,<sup>33–35</sup> the presence of the droplet-oil interface serves as a reservoir that enhances the mass transport of oxygen to the metal-electrolyte surface, leading to higher cathodic currents.<sup>6</sup>



**Figure 4.4:** (a) Histograms of  $E_{corr}$  (OCP) obtained from the SECCM maps in Figure 4.3 at different  $E_{appr}$ . (b) Anodic current increase or (c) cathodic current decrease induce the negative shift of  $E_{corr}$  according to the mixed potential theory. (d) The presence of droplet-oil interface in the droplet contact landing brings additional oxygen flux from the oil phase to the droplet (red arrows). In the pipette contact landing, the oxygen flux only comes from the bulk solution along the micropipette (bule arrows).

To verify the enhancement of oxygen reduction reaction (ORR) in the presence of droplet-oil interface, linear sweep voltammetry (LSV) was performed in the negative direction on a GC working electrode confined by the droplet size in SECCM.<sup>36,37</sup> A 10  $\mu$ m diameter micropipette was used to generate a larger droplet convenient for adjusting the height of droplet to change the area of droplet-oil interface. The first polarization curve of ORR was recorded upon droplet landing. The micropipette was then moved down by 1  $\mu$ m three times in succession to reduce the area of droplet-oil interface as depicted

in Figure 4.5a. After each descent, a polarization curve was recorded to show the effect of the reduced area of droplet-oil interface on the ORR current (Figure 4.5b). The absolute current decreased with the descent of micropipette, indicating the reduction in mass transport of oxygen. For comparison, LSV was repeated four times upon the droplet landing without moving the micropipette down further. The polarization curves did not exhibit significant changes except for the first curve where the oxygen concentration was expectedly higher at the beginning (Figure 4.5c). This proves that the presence of the droplet-oil interface indeed contributes to an increase in the cathodic current, leading to the variations of  $E_{corr}$ (OCP) between the PC- and DC-landings.



**Figure 4.5:** (a) A 3.5 wt% NaCl solution filled 10  $\mu$ m diameter micropipette landed on the surface of GC in SECCM. Droplet contact landing was obtained at -1.5 V  $E_{appr}$  (Figure C.4). Then, the pipette was moved down to change the area of oil-droplet interface. (b) The cathodic polarization measurement of oxygen reduction reaction (ORR) was carried out at a scan rate of 100 mV/s. After the first ORR curve, the micropipette was moved down 1  $\mu$ m for three consecutive times to diminish the droplet-oil interface followed by an ORR measurement each time. (c) ORR measurements were repeated four times without the further lowering the micropipette once the droplet landed on GC. The arrow shows the sequence of ORR measurements.

#### 4.3.3 Effect of $E_{appr}$ on $E_{corr}$ (PDP)

For a large area SECCM map consisting of hundreds to thousands of landings, the applied potentiodynamic methods at each landing point are performed at high potential scan rates.<sup>38–40</sup> For example, SECCM maps of AA7075-T73 using anodic PDPs were acquired with a swept rate of 100 mV/s. The increase of total anodic current in the high-scan-rate PDP leads to negative shift of  $E_{corr}$ (PDP) relative to the  $E_{corr}$ (OCP) (Figure 4.6a). The anodic current related processes involve electron transfer at the metal-oxide interface

and the migration of metal cations within the oxide film that is regarded as the limiting step.<sup>41–44</sup> The migration of metal cations is driven by the high electric strength within the oxide film, which is determined by the thickness of the oxide film and the Mott potential generated by the adsorbed oxygen ions at the oxide-electrolyte interface and the positive metallic cations at the oxide-metal interface.<sup>45</sup> Since the time for the anodic growth of oxide film during PDP is less at a high scan rate, the oxide film would be thinner compared to that at a low scan rate. The electric field strength is therefore stronger during a high-scan-rate PDP, which facilitates the migration of cations within the oxide film, and as a result, the anodic current is predicted to be higher. Moreover, the potential scanned at a high rate will generate capacitive charging current that also contributes to the increase of anodic current.<sup>46</sup> The high potential scan rate induced anodic current increase leads to the  $E_{corr}$ (PDP) shifting to more negative values as shown in Figure 4.4b.



**Figure 4.6:** (a) The histograms of  $E_{corr}$  show that the negative shift of  $E_{corr}(PDP)$  relative to  $E_{corr}(OCP)$  varies with  $E_{appr}$  in PDP measurements at a high scan rate of 100 mV/s. (b) The anodic currents at -0.7 V extracted from PDP measurements (Figure C.3) of 25 landing locations increased as the  $E_{corr}$  became more cathodic. (c) An increase in the anodic current causes  $E_{corr}$  to shift to more negative values according to the mixed potential theory.

The negative shift of  $E_{corr}(PDP)$  relative to the  $E_{corr}(OCP)$  was found to increase as  $E_{appr}$  increased to more negative values (Figure 4.6a). This resulted from the increase of anodic currents at more negative  $E_{appr}$  (Figure 4.6b). The Al alloy surface experienced a transient cathodic polarization at  $E_{appr}$  upon the droplet contact.<sup>47,48</sup> As  $E_{appr}$  increased to sufficiently negative values, the hydrogen evolution occurred, increasing the concentration of OH<sup>-</sup> ion at the oxide-electrolyte interface that accelerates the hydration of oxide film.<sup>49–51</sup> This will lead to a more porous structure and decrease the resistance of oxide film to the ion transport.<sup>52,53</sup> The decrease in the resistance will promote the migration of cations through the oxide film, thus enhancing the effect of high scan rate that increase the anodic current.

The hydration and increased porosity of oxide film renders it more susceptible to Cl<sup>-</sup> attack, promoting pitting to occur. During PDP, a current transient was produced when pitting occurred that exceeded the set current limit of 100 pA, ending the potential sweep (Figure 4.7a, pink curve). In the absence of pitting, the current was lower than 20 pA throughout the anodic potential range (Figure 4.7a, cyan curve). Thereby, the magnitudes of the anodic currents at the end of potential sweep can be used to distinguish the pitting (pink) and non-pitting (cyan) locations on the SECCM map (Figure 4.7b). At  $E_{\mathrm{appr}}$  from -1.5 to -2.0 V, there was a small increase in the frequency of pitting, whereas at  $E_{appr}$  of -2.5 V, pitting occurred at a much higher frequency (Table 4.1). This implies that the  $E_{appr}$  damaged the oxide film, but the breakdown potential of the oxide film is likely between -2.0 and -2.5 V under the SECCM experimental conditions.  $E_{appr}$  of -2.5 V may have reached the breakdown potential so that pitting was readily to occur during PDP. The breakdown potential of oxide film is not constant, which varies with the anions and pH of solution, the thickness, alloying elements of oxide film, and so on.<sup>52,54,55</sup> This highlights that we can promote the anodic processes by controlling the values of  $E_{appr}$ , which increases the anodic current and the frequency of pitting. This is meaningful for the microscopic measurement of the oxide covered metal surfaces, that produce extremely low currents, making it difficult to discriminate small changes of the surface

structure. Controlling  $E_{appr}$  to appropriately increase the conductivity of surface oxides allows to increase the magnitude of current without removing the surface heterogeneity.



**Figure 4.7:** (a) PDP curves at 100 mV/s show the locations with (pink) and without (cyan) pitting occurrence. (b) SECCM maps show the incidence of pitting at different  $E_{appr}$  values.

$E_{\mathrm{appr}}$	Number of Pitting Locations	Number of Pitting Locations Excluding Intermetallics
-1.5 V	41	40
-2.0 V	81	62
-2.5 V	200	196

Table 4.1: Number of Pitting Locations on the Maps in Figure 4.7b

To visualize the impact of  $E_{appr}$  on the electrochemical measurements more directly, the PDP measurements at the landings with and without  $E_{appr}$  are compared. To facilitate the approach of micropipette without  $E_{appr}$ , a 10  $\mu$ m diameter micropipette was used. As shown in Figure 4.8a, an  $E_{appr}$  of -2.0 V was applied at one location for the approach and the micropipette was moved up a distance of 15  $\mu$ m after the PDP measurement. At the subsequent location, the micropipette was moved down 15  $\mu$ m to obtain a droplet landing without the effect of  $E_{appr}$ . Without  $E_{appr}$  applied, the  $E_{corr}$  (PDP) values are more positive (Figure 4.8b, points on the grid lines) and have negligible shifts with respect to  $E_{corr}$  (OCP) (Figure 4.8c, red points). Additionally, the anodic currents were extremely low (Figure 4.8d, red points) compared to those with  $E_{appr}$ , suggesting the insulating property of oxide film, that limits electrochemical measurements at the microscale. By contrast, the application of -2.0 V  $E_{appr}$  increased the oxide conductivity reflected by the relatively large anodic current (Figure 4.8d, blue points), which can amplify the small current differences between the microstructural variations, that are otherwise hard to distinguish between low currents.



**Figure 4.8:** (a) Schematic of the movement of a 10  $\mu$ m diameter micropipette in the SECCM measurement with  $E_{appr}$  applied every other landing. The micropipette was approached to the AA7075-T73 surface at an  $E_{appr}$  of -2 V. After OCP and PDP measurements, the micropipette was moved up a distance of d = 15  $\mu$ m, and then laterally moved to next spot where the micropipette was moved down d = 15  $\mu$ m without  $E_{appr}$  applied. (b)  $E_{corr}$ (PDP) maps from the alternately  $E_{appr}$  applied SECCM measurement. The points on the grid lines represent the landings without  $E_{appr}$  applied. Comparison between the landings with and without  $E_{appr}$  applied: (c) the difference between  $E_{corr}$ (PDP) and  $E_{corr}$ (OCP); (d) anodic currents at -0.7 V of PDPs.

## 4.4 Conclusion

This work demonstrates that  $E_{appr}$  in SECCM affects the droplet substrate interaction and the microscale OCP and PDP measurements of Al alloy AA7075-T73.  $E_{appr}$  controls the magnitude of  $i_{trig}$ . A large cathodic  $E_{appr}$  generated a high  $i_{trig}$ , giving rise to a droplet contact landing, while a small  $E_{appr}$  resulted in the pipette contact landing due to the presence of passive oxide film of the Al alloy. In droplet contact landing, the droplet-oil interface enhanced the cathodic reaction by introducing additional oxygen flux to droplet from the oil phase, resulting in more negative  $E_{\rm corr}(OCP)$ . Additionally,  $E_{\rm corr}(PDP)$  values obtained from the anodic PDP at 100 mV/s shifted from  $E_{\rm corr}(\rm OCP)$  more seriously as the  $E_{appr}$  increased to more negative values. This is due to prior cathodic degradation of the oxide film at Eappr, which also account for the higher pitting density at more negative  $E_{appr}$  values. The clarification of the effect of  $E_{appr}$  on the microscale OCP and PDP measurements of Al alloy in the single-channel micropipette SECCM provides a strategy to control the electrochemical processes on the metal surface oxides. Controlling  $E_{\rm appr}$  to increase the conductivity of the metal surface oxides will increase the magnitudes of currents, but not make significant changes in the surface structure. This will facilitate the use of small probes to reveal small electrochemical differences on the metal surface, such as between grain orientations.

## References

- Ebejer, N.; Schnippering, M.; Colburn, A. W.; Edwards, M. A.; Unwin, P. R. *Analytical Chemistry* 2010, *82*, 9141–9145.
- Takahashi, Y.; Kumatani, A.; Shiku, H.; Matsue, T. Analytical Chemistry 2017, 89, 342–357.
- 3. Williams, C. G.; Edwards, M. A.; Colley, A. L.; Macpherson, J. V.; Unwin, P. R. *Analytical Chemistry* **2009**, *81*, 2486–2495.
- Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J. Analytical Chemistry 2020, 92, 12415– 12422.
- 5. Liu, S.; Shi, M.; Zhou, Y.; Li, R.; Xie, Z.; Hu, D.; Zhang, M.; Hu, G. *Journal of Cultural Heritage* **2020**, *46*, 176–183.
- Shkirskiy, V.; Yule, L.; Daviddi, E.; Bentley, C.; Aarons, J.; West, G.; Unwin, P. Journal of The Electrochemical Society 2020, 167, 041507.
- Yule, L. C.; Shkirskiy, V.; Aarons, J.; West, G.; Bentley, C. L.; Shollock, B. A.; Unwin, P. R. *The Journal of Physical Chemistry C* 2019, 123, 24146–24155.
- 8. Yule, L.; Shkirskiy, V.; Aarons, J.; West, G.; Shollock, B.; Bentley, C.; Unwin, P. *Electrochimica Acta* **2020**, *332*, 135267.
- 9. Daviddi, E.; Gonos, K. L.; Colburn, A. W.; Bentley, C. L.; Unwin, P. R. *Analytical Chemistry* **2019**, *91*, 9229–9237.
- Takahashi, Y.; Kumatani, A.; Munakata, H.; Inomata, H.; Ito, K.; Ino, K.; Shiku, H.;
   Unwin, P. R.; Korchev, Y. E.; Kanamura, K., et al. *Nature Communications* 2014, 5, 1–7.
- 11. Bentley, C. L.; Unwin, P. R. Faraday Discuss 2018, 210, 365–379.

- Kumatani, A.; Miura, C.; Kuramochi, H.; Ohto, T.; Wakisaka, M.; Nagata, Y.; Ida,
   H.; Takahashi, Y.; Hu, K.; Jeong, S., et al. *Advanced Science* 2019, *6*, 1900119.
- Dayeh, M.; Ghavidel, M. R. Z.; Mauzeroll, J.; Schougaard, S. B. *ChemElectroChem* 2019, *6*, 195–201.
- Inomata, H.; Takahashi, Y.; Takamatsu, D.; Kumatani, A.; Ida, H.; Shiku, H.; Matsue,
  T. *Chemical Communications* 2019, *55*, 545–548.
- Kumatani, A.; Takahashi, Y.; Miura, C.; Ida, H.; Inomata, H.; Shiku, H.; Munakata,
  H.; Kanamura, K.; Matsue, T. *Surface and Interface Analysis* 2019, *51*, 27–30.
- Snowden, M. E.; Dayeh, M.; Payne, N. A.; Gervais, S.; Mauzeroll, J.; Schougaard, S. B. *Journal of Power Sources* 2016, 325, 682–689.
- 17. Takahashi, Y.; Yamashita, T.; Takamatsu, D.; Kumatani, A.; Fukuma, T. *Chemical Communications* **2020**, *56*, 9324–9327.
- 18. Bentley, C. L.; Kang, M.; Unwin, P. R. Analytical Chemistry 2020, 92, 11673–11680.
- Liu, D.-Q.; Tao, B.; Ruan, H.-C.; Bentley, C. L.; Unwin, P. R. *Chemical Communications* 2019, 55, 628–631.
- Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. Science 2017, 358, 1187– 1192.
- 21. Wang, Y.; Gordon, E.; Ren, H. Analytical Chemistry **2020**, *92*, 2859–2865.
- 22. Payne, N. A.; Mauzeroll, J. ChemElectroChem 2019, 6, 5439–5445.
- 23. Ornelas, I. M.; Unwin, P. R.; Bentley, C. L. Analytical Chemistry 2019, 91, 14854– 14859.
- Daviddi, E.; Shkirskiy, V.; Kirkman, P. M.; Robin, M. P.; Bentley, C. L.; Unwin, P. R. Chemical Science 2021, 12, 3055–3069.
- 25. Barlag, R.; Nyasulu, F.; Starr, R.; Silverman, J.; Arthasery, P.; McMills, L. Journal of *Chemical Education* **2014**, *91*, 766–768.

- Da Silva, E. T. S. G.; Miserere, S.; Kubota, L. T.; Merkoçi, A. *Analytical Chemistry* 2014, *86*, 10531–10534.
- 27. Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J. Analytical Chemistry 2021, 93, 9657–9662.
- Rohaizad, N.; Mayorga-Martinez, C. C.; Novotný, F.; Webster, R. D.; Pumera, M. Electrochemistry Communications 2019, 103, 104–108.
- 29. Barrie, A. Chemical Physics Letters **1973**, 19, 109–113.
- 30. Strohmeier, B. R. Surface and Interface Analysis **1990**, 15, 51–56.
- 31. Power, G.; Ritchie, I. *Electrochimica Acta* **1981**, *26*, 1073–1078.
- 32. Chen, C.-H.; Meadows, K. E.; Cuharuc, A.; Lai, S. C.; Unwin, P. R. *Physical Chemistry Chemical Physics* **2014**, *16*, 18545–18552.
- 33. Becerra, H. Q.; Retamoso, C.; Macdonald, D. D. Corrosion Science 2000, 42, 561–575.
- 34. Martins, M. A. G. IEEE Electrical Insulation Magazine 2010, 26, 7–13.
- Owrang, F.; Mattsson, H.; Olsson, J.; Pedersen, J. *Thermochimica Acta* 2004, 413, 241– 248.
- 36. Kruusenberg, I.; Alexeyeva, N.; Tammeveski, K. Carbon 2009, 47, 651–658.
- 37. Tammeveski, K.; Kontturi, K.; Nichols, R. J.; Potter, R. J.; Schiffrin, D. J. Journal of *Electroanalytical Chemistry* **2001**, *515*, 101–112.
- Bentley, C. L.; Andronescu, C.; Smialkowski, M.; Kang, M.; Tarnev, T.; Marler, B.; Unwin, P. R.; Apfel, U.-P.; Schuhmann, W. *Angewandte Chemie International Edition* 2018, 57, 4093–4097.
- Takahashi, Y.; Kobayashi, Y.; Wang, Z.; Ito, Y.; Ota, M.; Ida, H.; Kumatani, A.; Miyazawa, K.; Fujita, T.; Shiku, H., et al. *Angewandte Chemie International Edition* 2020, 59, 3601–3608.
- Yule, L. C.; Bentley, C. L.; West, G.; Shollock, B. A.; Unwin, P. R. *Electrochimica Acta* 2019, 298, 80–88.

- Boxley, C. J.; Watkins, J. J.; White, H. S. *Electrochemical and Solid State Letters* 2003, 6, B38.
- 42. Ghez, R. The Journal of Chemical Physics 1973, 58, 1838–1843.
- 43. Seyeux, A.; Maurice, V.; Marcus, P. *Journal of The Electrochemical Society* **2013**, *160*, C189–C196.
- 44. Verwey, 1. E. *Physica* **1935**, *2*, 1059–1063.
- 45. Cabrera, N.; Mott, N. F. Reports on progress in physics 1949, 12, 163–184.
- Zhang, X. L.; Jiang, Z. H.; Yao, Z. P.; Song, Y.; Wu, Z. D. Corrosion Science 2009, 51, 581–587.
- 47. Lin, C.; Hebert, K. R. Journal of the Electrochemical Society **1990**, 137, 3723.
- 48. Takahashi, H.; Kasahara, K.; Fujiwara, K.; Seo, M. *Corrosion Science* **1994**, *36*, 677–688.
- Despić, A.; Radošević, J.; Dabić, P.; Kliškić, M. *Electrochimica Acta* 1990, 35, 1743– 1746.
- 50. Lin, C.; Porter, M. D.; Hebert, K. R. Journal of the Electrochemical Society 1994, 141, 96.
- 51. Moon, S.-M.; Pyun, S.-I. *Corrosion Science* **1997**, *39*, 399–408.
- Gudić, S.; Radošević, J.; Smoljko, I.; Kliškić, M. *Electrochimica Acta* 2005, 50, 5624– 5632.
- 53. Nişancioğlu, K.; Holtan, H. *Electrochimica Acta* **1979**, *24*, 1229–1235.
- 54. Hassel, A. W.; Lohrengel., M. M. Electrochimica Acta 1995, 40, 433–437.
- 55. Sato, N. Electrochimica Acta **1971**, *16*, 1683–1692.

Chapter 5

# Correlating Corrosion Activities to Grain Orientations of Aluminum Alloy

## **Scientific Contributions**

Chapter 5 uncovers the correlations of multiple corrosion related electrochemical processes with grain orientations of a practical polycrystalline Al alloy. A large number of microscopic PDP measurements were performed on numerous grains using OI-SECCM, allowing to carry out statistical analyses. This ensures the reliability of results. Previous studies of grain dependent behaviors mostly relied on macro electrochemical measurements of single crystals, to eliminate the influence of other surface features. However, single crystals are not realistic for practical polycrystalline metals. Alternatively, a limited number of microscopic corrosion tests were performed on individual grains, but this may not reflect the average properties due to surface variations. This work using OI-SECCM measurements to analyze grain dependent behaviors will provide a benchmark for the study of polycrystalline surfaces.

## **Chapter Abstract**

The study of grain-dependent corrosion behaviors of practical polycrystalline metals remains challenging due to the difficulty in eliminating the influence of other microstructural features, like intermetallics and grain boundaries. In this chapter, we took advantage of the spatially resolved OI-SECCM measurement to perform multiple microscopic PDP measurements on individual grains of Al alloy AA7075-T73. Data can be extracted only from grain interior areas, eliminating the interference of intermetallics and grain boundaries. Based on the statistical analyses of thousands of PDP measurements, the small differences between grains were revealed. Cathodic currents exhibited a strong grain orientation dependence, decreasing in the order of  $\{101\} > \{001\} > \{111\}$ . By contrast, the dependence of anodic currents on grain orientation is weak, and pitting is independent of grain orientation, which may be due to the limited mass transport of ions and electrons within the surface oxide. This work highlights the capability of OI-SECCM in resolving small electrochemical differences, which will greatly promote the study of grain dependent behaviors of polycrystalline samples.

## 5.1 Introduction

Alloys are composed of numerous grains in different sizes and orientations with grain boundaries between them, which are critical in determining the properties of materials. The crystallographic orientations of grains influence the growth of oxide film,<sup>1,2</sup> surface treatment,<sup>3,4</sup> and tensile strength.<sup>5,6</sup> However, the effect of grain orientations on corrosion behaviors is still poorly understood. Most previous studies were performed on single crystals to eliminate the influence of intermeatllics and grain boundaries,<sup>7–11</sup> which are nevertheless not realistic for practical applications. However, the study of polycrystalline metals lacks a scanning electrochemical technique that enables direct microscopic corrosion measurements of individual grains.

The emergence of single-channel pipette SECCM<sup>12</sup> and the following double-channel pipette SECCM<sup>13</sup> open up the prospect of spatially resolved measurements of corrosion related electrochemical processes. In SECCM, a droplet cell is created at the end of electrolyte filled micropipette used to scan the substrate surface and perform microscopic electrochemical measurements. OI-SECCM mapping allows to reveal electrochemical differences related to surface microstructures.

In 2019, LC. Yule et al. performed SECCM on low carbon steel, revealing the dependence of anodic passive film on grain orientations based on the comparison between PDP curves.<sup>14</sup> However, the limited number of measurements cannot provide more specific information. A larger quantity of measurements of more grains is required. This can be realized by performing short-time measurements at each droplet landing,<sup>15–17</sup> but not applicable for the time-consuming OCP and PDP measurements of corrosion in neutral solutions. Moreover, since grain orientations are randomly distributed, a large surface area needs to be mapped to include diverse grain orientations. This necessitates a highly stable droplet cell capable of long-term scanning. In 2020, OI-SECCM was reported, in which the droplet was immersed under a thin layer of hydrophobic and inert oil on the substrate surface.<sup>18,19</sup> This protects the droplet from evaporation and significantly increases the stability of droplet.<sup>17,18,20</sup>

Taking advantage of OI-SECCM, this work explored the corrosion behaviors of Al alloy AA7075-T73 correlated to grain orientations. For Al, the presence of passive oxide film reduces the conductivity and reactivity of surface,<sup>21,22</sup> resulting in extremely low currents in microscopic electrochemical measurements. Low currents make it difficult to discriminate small electrochemical differences between grains. By controlling the value of approach potential of single-channel pipette SECCM applied during the micropipette approach to the substrate, the conductivity of surface oxide can be appropriately increased by the destruction of oxide film upon droplet landing, which is discussed in Chapter 4. This will not destroy the surface microstructure, allowing the study of grain dependent behaviors.

The PDP measurements of multiple grains revealed a clear dependence of cathodic currents on grain orientations, which decreased in the order of  $\{101\} > \{001\} > \{111\}$ . Furthermore, the OI-SECCM maps showed enhanced cathodic activity and pitting preference at grain boundaries, reflecting the higher reactivity of grain boundaries. In contrast, anodic currents and pitting were less correlated with grain orientations. The statistical analyses based on the large number of measurements ensure the reliability of results. This will promote the study of grain dependent electrochemical behaviors directly on polycrystalline samples.

## 5.2 Experimental Section

#### 5.2.1 Chemicals and Materials

Sodium chloride (NaCl, anhydrous, 99.8%) and mineral oil (M5310) were used as purchased from Sigma-Aldrich. Quartz glass capillaries (Sutter Instrument, Novato, CA) with dimensions of (o.d. × i.d.)  $1.0 \times 0.3$  mm were pulled (P-2000 CO2-laser puller, Sutter Instruments, U.S.A.) to produce two single-channel micropipettes with a tip diameter of ~ 2  $\mu$ m.

AA7075-T73 Al alloy was provided by NRC (National Research Council Canada, Saguenay) and fixed in cold mounting epoxy (Epofix-Struers). AA7075-T73 was ground using a 320 grit SiC paper (Struers, Canada), and polished using 9  $\mu$ m, 3  $\mu$ m colloidal diamond suspensions and finally a colloidal silica suspension (Struers, Canada) on a MD Chem cloth (Struers, Canada) to obtain a mirror-like surface. The sample surface was then rinsed using anhydrous ethanol and sonicated in ultrapure water to remove the residue of silica suspension before drying in air.

Ag/AgCl reference electrode (RE) was made using an Ag wire (0.5 mm diameter, Goodfellow Metals, Huntingdon, England) immersed in household bleach.<sup>20,23–25</sup> Ag was oxidized in the bleach to form a AgCl outer layer on the wire. The potential stability and reproducibility of the Ag/AgCl electrode have been verified in our previous work,<sup>20</sup> which has a 5 mV difference with respect to SCE. All potentials have been calibrated to Ag/AgCl wire RE in 3.5 wt% NaCl solution.

All electrochemical measurements were performed using an EIProScan 3 system (HEKA, Germany; bipotentiostat model PG340) in a Faraday cage (Acoustic Isolation Novascan Ultracube, Ames IA, USA) on a vibration isolation table (Micro 60 Halcyonics Active Vibration Isolation Platform, Novascan, Ames IA, USA).

#### 5.2.2 Oil-Immersed Scanning Electrochemical Cell Microscopy

OI-SECCM was carried out as previously reported.<sup>18</sup> Briefly, a 2  $\mu$ m diameter micropipette was filled with 3.5 wt% NaCl aqueous solution, creating a droplet cell at the end of tip. The droplet was immersed under a layer of mineral oil on the surface of substrate WE to prevent the droplet evaporation. A three-electrode arrangement was used as shown in Figure 5.1a, where a non-isolated Ag/AgCl wire and Pt wire served as RE and CE, respectively. The distance between the end of Ag/AgCl wire and micropipette tip was extended to 50 cm with a PVC (polyvinyl chloride) plastic tube (Inner diameter 0.76 mm), similar to the microcapillary cell setup,<sup>26</sup> but, in this work, it is to eliminate the interference of Ag<sup>+</sup> ions from Ag/AgCl wire on electrochemical measurements (discussed in Chapter 3).<sup>20,27</sup> The tube connected the micropipette to a more open syringe, where both RE and CE were immersed in the electrolyte. The more open space allows to use a commercial isolated RE in OI-SECCM experiments, but we still employed the non-isolated Ag/AgCl wire in this work to be consistent with our previous works.<sup>18,20</sup> The micropipette was approached to WE under the mineral oil with an approach potential of -2.5 V applied. Upon the droplet landing on WE, the electrochemical circuit was closed giving rise to a current spike which triggered the micropipette to stop moving. Meanwhile, the approach potential was removed, and OCP was measured for 30 s followed by a PDP measurement. PDP was carried out at 100 mV/s from -1.35 to -0.3 V. After that, the micropipette was retracted and laterally moved to the next location in a hopping mode with a separation of 5  $\mu$ m between locations.



**Figure 5.1:** (a) Schematic of OI-SECCM setup using a 41 cm long PVC tube (inner diameter: 0.76 mm), extending the distance between Ag/AgCl RE and WE to 50 cm. A Pt wire serves as CE. (b) Chronopotentiograms show the potential changes in response to the applied currents. Glassy carbon was used as WE.

#### 5.2.3 Surface Characterization

The Al alloy surface scanned by OI-SECCM was imaged by optical microscope and scanning electron microscope (SEM), and mapped with electron backscattered diffraction (EBSD) at an acceleration voltage of 20 keV with a step size of 0.7  $\mu$ m. EBSD was performed with an Oxford SDD EBSD detector on Hitachi SU3500 variable pressure-SEM. The alloy surface was tilted 70° to the EBSD detector. Inverse Pole Figure (IPF) coloring maps were obtained showing the grain orientations of Al alloy. The EBSD maps and electrochemical data obtained by OI-SECCM was analyzed using MATLAB® R2020a.

## 5.3 **Results and Discussion**

#### **5.3.1** $iR_{\Omega}$ between RE and WE

The long distance between RE and WE designed in the OI-SECCM setup (Figure 5.1a) eliminated the interference of RE contaminants on the electrochemical measurements of WE, but could lead to a high  $iR_{\Omega}$  drop between RE and WE. Our previous study<sup>20</sup> found that the commonly used non-isolated Ag/AgCl wire QRCE leaked Ag<sup>+</sup> into electrolyte, which diffused to the tip of micropipette in a prolonged experiment. The reduction of interfering Ag<sup>+</sup> ions on WE generated a considerable cathodic current, that will make the small current differences between grains undetectable.<sup>20</sup> Therefore, in this work, we extended the distance between Ag/AgCl wire RE and WE to 50 cm to ensure the droplet cell free of Ag<sup>+</sup> throughout the experimental time. However, the extended distance will increase the uncompensated potential, ( $iR_{\Omega}$ ), which decreases the actual potential (E<sub>actual</sub>) applied to the WE.<sup>28</sup>

$$E_{actual} = E_{app} - iR_{\Omega} \tag{5.1}$$

Where  $E_{app}$  is the potential applied to the system and *i* is the current flowing between WE and RE. Current interruption technique<sup>29,30</sup> was used to calculate the value of  $iR_{\Omega}$  in 3.5 wt% NaCl solution, by performing chronopotentiometry on glassy carbon WE. Potentials were monitored in response to currents 100, 0 and -100 pA (Figure 5.1b). An average of 2.75 mV potential change was recorded, when a current change of 100 pA occurred. As the current range measured in OI-SECCM was 100 pA, 2.75 mV has been the maximal  $iR_{\Omega}$  drop, which can be negligible during experiments. Thus, the OI-SECCM setup can be used for a long time scan. PDP measurements were performed at 2511 droplet landing points, providing a wealth of information on multiple corrosion related electrochemical processes. Figure 5.2a presents the reproducibility of 26 randomly selected PDP curves that are dispersed over 2511 locations. This demonstrates the stability of OI-SECCM measurement over the long time.

#### 5.3.2 Grain Orientation Dependent Cathodic Current

To visualize the dependence of cathodic process on grain orientations, cathodic currents were extracted from PDP curves at -1.3 V (Figure 5.2a) to construct a current map. The cathodic current map was superimposed on grain boundaries as shown in Figure 5.2b, displaying a clear contrast between currents. This is consistent with the grain distribution in Figure 5.2c. More specifically, the currents on (101) grains (green color in Figure 5.2c) are higher than others, indicating the enhanced cathodic reactions. To quantitatively present the dependence of corrosion processes on grain orientations, grains were categorized into three groups based on their misorientation angles to the three low-index grains families {001}, {101} and {111} (Figure D.1b and c).



**Figure 5.2:** (a) 26 PDP curves randomly selected from the 2511 locations on OI-SECCM maps. (b) Cathodic current map superimposed on the grain boundary map, in which the cathodic currents were extracted from PDP curves at -1.3 V. The currents were confined between -70 and -25 pA to remove the higher currents on intermetallics sites. (c) EBSD IPF coloring map showing the grain orientations with respect to the sample normal direction (ND).

To spatially correspond the current map to grain orientations point by point, the grain orientation map was filtered (Figure D.1a) to the same density as the cathodic current map. Since the misorientation angle is the angle between normal directions of two grains, the smaller the misorientation angle, the closer the properties of two grains. We collected the grains with misorientation angles less than 20° to represent the three low-index families, {001}, {101} and {111}, shown in Figure 5.3a. The currents on theses grains are extracted for the analyses of grain orientation dependence.



**Figure 5.3:** (a) Filtered grain orientation map containing the grains with misorientation angles less than 20 degrees relative to the {101}, {111}, {001} family planes. (b) Statistical distribution of cathodic currents (at -1.3 V) on the three groups of grains.

Grai	{101}	{001}	{111}	
Number of SECCM I	1003	201	598	
Atomic Planar Der	0.177	0.25	0.289	
Cathodic Currents	Mean	-43.8106	-42.0062	-38.8822
(pA) at -1.3 V	Standard Deviation	5.3288	6.2214	5.2769
Anodic Currents (pA)	Mean	4.0944	4.0166	3.9115
at -0.7 V	Standard Deviation	0.3770	0.3897	0.3576

Table 5.1: Cathodic and Anodic currents on Different Grains shown in Figure 5.3a

Note: r is the radius of atom.

The cathodic currents grouped by grain orientations show a decreasing trend {101} > {001} > {111} (Figure 5.3b and Table 5.1). This can be explained by the difference in surface energy,<sup>31-33</sup> which is inversely related to the order of atomic planar density {101} < {001} < {111}. A loosely packed plane has less atoms and thus the less satisfied atomic bonds, resulting in higher surface energy.<sup>34,35</sup> The higher surface energy planes can offer more sites for oxygen and water adsorption, thus facilitating the cathodic oxygen reduction and hydrogen evolution reactions.<sup>36</sup> This accounts for the higher cathodic currents on {101} grains. However, a macro study of single-crystal Al reported a higher rate of cathodic reactions on (001) plane in 0.5 M NaCl.<sup>8</sup> The contradiction could stem from the difference in the materials and number of measurements. Since the current differences between grains are small, inadequate repetitions of measurements may not reflect the current trend. The advantage of SECCM is to allow multiple measurements on the same grain of a real polycrystalline sample, which can provide a statistical analysis for the current trend, ensuring the validity of results.

## 5.3.3 Correlation Between Grain Orientation and Anodic Corrosion processes

#### 5.3.3.1 Anodic current

Anodic currents were extracted from PDP curves at -0.7 V (Figure 5.4a) to represent the anodic corrosion process, Al dissolution. The anodic current distribution (Figure 5.4b) presents a weaker grain orientation dependence compared with the cathodic currents. As shown in Table 5.1, the anodic currents also show a decreasing order of  $\{101\} > \{001\} > \{111\}$ , consistent with the prediction from the order of atomic planar density.  $\{101\}$  grains possess a smaller planar density, 0.177 atoms/ $r^2$ , which facilitates the escape of Al atoms from bulk material.<sup>37</sup> In combination with the higher cathodic currents on the



 $\{101\}$  grains, it can be inferred that the corrosion rate on  $\{101\}$  grains is higher than that on  $\{001\}$  and  $\{111\}$ .

**Figure 5.4:** (a) Anodic currents were extracted from the anodic plateau of PDP curves at -0.7 V, excluding the pitting peak current. (b) Statistical distribution of anodic currents on the three groups of grains {101}, {111} and {001}. Currents were confined between 2.5 and 5.5 pA to remove the high currents on intermetallics. (c) Schematic of the migration of ions and electrons within the oxide film and the breakdown of oxide film inducing pitting.

Compared to the Al grain orientation, the surface oxide film may play a more important role in determine the magnitude of anodic current. The generation of anodic current involves the Al oxidation at the metal-oxide interface, and the migration of Al<sup>3+</sup> within the oxide,<sup>38-40</sup> which considered to be the limiting step of anodic process.<sup>41</sup> Therefore, the anodic current could be more related to the structure of oxide film rather than the underlying Al crystal structure. However, the relationship between the growth of natural oxide film and grain orientation is still unclear, and most studies were performed under unrealistic conditions, such as high oxygen pressures.<sup>2,42,43</sup>

#### 5.3.3.2 Pitting

The breakdown of oxide film exposed the underlying Al to electrolyte, giving rise to current transient peaks on PDP curves as shown in Figure 5.4a, which represented pitting or metastable pitting as depicted in Figure 5.4c.<sup>44-46</sup> Figure 5.5a shows the distribution of pitting on grains in different orientations represented by different color points. On an anodic PDP curve, a more negative onset potential of pitting (pitting potential) indicates a higher pitting susceptibility,<sup>45</sup> suggesting a more defective oxide film structure. So, the number of pitting locations was presented as a function of pitting potential and categorized into the three groups of {001}, {101} and {111} to reveal the relationship between pitting and grain orientations. Figure 5.5b shows that pitting and grain orientations are not related in terms of both the number of pitting locations and E<sub>pit</sub>. Moreover, the density of pitting (Figure 5.5c) shows little difference between grain orientations. It could be due to the dependence of pitting on the structure of oxide film. H Krawiec et al. reported that a high density of dislocations caused by plastic deformation affected the properties of oxide film, leading to an increase in the pitting susceptibility, which was not influenced by grain orientations.<sup>47</sup> It implies that when the defectiveness of oxide film is dominant, pitting will be independent of the underlying grain orientations. To check if the pitting locations indicate more defective oxide film,<sup>44</sup> which can produce higher currents, the anodic currents at pitting and non-pitting locations are compared. Figure 5.5d shows a diminutive but observable trend that pitting locations tend to generate higher anodic currents, implying the correlation between the structure of oxide film and pitting.



**Figure 5.5:** (a) Pitting occurred on different grains. (b) Statistical distribution of pitting occurring at different potentials on the three groups of grains  $\{101\}$ ,  $\{111\}$  and  $\{001\}$ . (c) The density of pitting on  $\{101\}$ ,  $\{111\}$  and  $\{001\}$  grains. (d) Anodic current (at -0.7 V) distribution on the locations with and without pitting.

#### 5.3.4 Corrosion Processes at Grain Boundary

Grain boundary (GB) is more prone to corrosion compared to the grain interior due to the microstructural heterogeneity<sup>48,49</sup> and second-phase precipitates,<sup>50</sup> like MgZn<sup>2</sup> in 7xxx series alloys that dissolves as an anode relative to the adjacent Al matrix.<sup>51,52</sup> To prove the high reactivity of grain boundaries, larger cathodic and anodic currents were collected (Figure 5.6a and b: black bars) to see if they were located at grain boundaries. The large currents were highlighted as black points on OI-SECCM maps. Most of large cathodic current points reside near the boundaries (Figure 5.6a), suggesting enhanced cathodic reactions at the boundaries. This is because of the less dense atomic packing and higher energy of grain boundaries,<sup>53</sup> that facilitate the oxygen reduction and hydrogen evolution reactions.<sup>15,54</sup> By contrast, the large anodic currents (black points in Figure 5.6b) do not



show a strong preference for grain boundaries. They tend to be on {101} grains (green), as discussed above.

**Figure 5.6:** Maps and histograms of (a) cathodic currents at -1.3 V, (b) anodic currents at -0.7 V on different grains. Intermetallic particles were removed leaving empty points on the maps. The larger points on the maps indicate the cathodic and anodic currents larger than arbitrarily selected thresholds. The black points in (a-i) and (b-i) are values in black bins of the histograms (a-ii) and (b-ii).

To check if pitting preferentially occurred at grain boundaries, locations with pitting potentials more negative than -0.6 V were displayed in Figure 5.7. -0.6 V is arbitrarily selected as a dividing line. In more positive potential ranges of PDP, pitting is easier to occur because of the large electric driving force, which is however hard to reflect the influence of surface structure. To stress the influence of surface structure on pitting, the locations with pitting negative than -0.6 V (Figure 5.7a) were collected, exhibited as large points in Figure 5.7b. Pitting occurred at potentials positive than -0.6 V was removed.

On the grains labeled A-E, pitting shows a boundary preference. While on other grains, pitting is irregularly distributed, which could be the defective points in the grain interior. Due to the large grain size (average 60  $\mu$ m wide, Figure D.2), we used a 2  $\mu$ m diameter micropipette with a 5  $\mu$ m separation between droplet landings to map more grains. Although the diameter of micropipette is large relative to the nanoscale grain boundaries, we can still glimpse the distinctive properties of grain boundaries.



**Figure 5.7:** (a) Histogram of pitting occurring at different potentials. Black bins correspond to the pitting points in (b), showing the pitting occurring at potentials negative than -0.6 V. The smaller color points in (b) display grains in different orientations.

## 5.4 Conclusion

This work has explored the effects of grain orientations on cathodic, anodic corrosion processes and pitting of a polycrystalline Al alloy sample. Numerous measurements were performed on each grain, enabling statistical analyses of electrochemical differences between grains. The cathodic currents exhibited a strong grain dependence, decreasing in the order of  $\{101\} > \{001\} > \{111\}$ , inversely related to the atomic planar density. Larger cathodic currents were found in grain boundary regions, proving the enhanced cathodic reactions at grain boundaries. However, the anodic currents and pitting did not show a clear grain dependence, because the anodic corrosion processes are more dependent on the properties of oxide film. This work highlights the powerful capability of OI-SECCM in identifying microstructure-induced differences in corrosion processes and will facilitate the electrochemical study of grain orientations of practical polycrystalline samples.

## References

- 1. Ng, C. K.; Ngan, A. H. Chemistry of Materials 2011, 23, 5264–5268.
- Nguyen, L.; Hashimoto, T.; Zakharov, D. N.; Stach, E. A.; Rooney, A. P.; Berkels, B.; Thompson, G. E.; Haigh, S. J.; Burnett, T. L. ACS Applied Materials & Interfaces 2018, 10, 2230–2235.
- Holme, B.; Ljones, N.; Bakken, A.; Lunder, O.; Lein, J. E.; Vines, L.; Hauge, T.; Bauger, O.; Nisancioglu, K. *Journal of The Electrochemical Society* 2010, 157.
- Yuan, Y.; Zhang, D.; Zhang, F.; Yang, C.; Gan, Y. Journal of the Electrochemical Society 2020, 167, 113505.
- 5. Liu, Q.; Jensen, D. J.; Hansen, N. Acta Materialia **1998**, 46, 5819–5838.
- Stoudt, M. R.; Levine, L. E.; Creuziger, A.; Hubbard, J. B. Materials Science and Engineering: A 2011, 530, 107–116.
- 7. Seo, J. H.; Ryu, J. H.; Lee, D. N. *Materials Science Forum* **2002**, 408-412, 1037–1042.
- 8. Treacy, G. M.; Breslin, C. B. Electrochimica Acta 1998, 43, 1715–1720.
- Yasuda, M.; Weinberg, F.; Tromans, D. Journal of the Electrochemical Society 1990, 137, 3708.
- 10. Gartland, P. Surface Science 1977, 62, 183–196.
- 11. Lee, S.; White, H. S. Journal of the Electrochemical Society **2004**, 151, B479.
- 12. Williams, C. G.; Edwards, M. A.; Colley, A. L.; Macpherson, J. V.; Unwin, P. R. *Analytical Chemistry* **2009**, *81*, 2486–2495.
- 13. Ebejer, N.; Schnippering, M.; Colburn, A. W.; Edwards, M. A.; Unwin, P. R. *Analyt-ical Chemistry* **2010**, *82*, 9141–9145.
- Yule, L. C.; Bentley, C. L.; West, G.; Shollock, B. A.; Unwin, P. R. *Electrochimica Acta* 2019, 298, 80–88.

- Yule, L. C.; Shkirskiy, V.; Aarons, J.; West, G.; Bentley, C. L.; Shollock, B. A.; Unwin,
   P. R. *The Journal of Physical Chemistry C* 2019, 123, 24146–24155.
- 16. Yule, L.; Shkirskiy, V.; Aarons, J.; West, G.; Shollock, B.; Bentley, C.; Unwin, P. *Electrochimica Acta* **2020**, 332, 135267.
- Daviddi, E.; Shkirskiy, V.; Kirkman, P. M.; Robin, M. P.; Bentley, C. L.; Unwin, P. R. Chemical Science 2021, 12, 3055–3069.
- 18. Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J. Analytical Chemistry 2020, 92, 12415– 12422.
- 19. Shkirskiy, V.; Yule, L.; Daviddi, E.; Bentley, C.; Aarons, J.; West, G.; Unwin, P. *Journal* of *The Electrochemical Society* **2020**, *167*, 041507.
- 20. Li, Y.; Morel, A.; Gallant, D.; Mauzeroll, J. Analytical Chemistry 2021, 93, 9657–9662.
- Habib, K.; Al-Muhanna, K.; Al-Sabti, F.; Al-Arbeed, A. In *Defect and Diffusion Forum*, Trans Tech Publ; Vol. 268, pp 1–13.
- 22. Nguyen, T.; Foley, R. Journal of the Electrochemical Society 1980, 127, 2563.
- 23. Barlag, R.; Nyasulu, F.; Starr, R.; Silverman, J.; Arthasery, P.; McMills, L. *Journal of Chemical Education* **2014**, *91*, 766–768.
- Da Silva, E. T. S. G.; Miserere, S.; Kubota, L. T.; Merkoçi, A. *Analytical Chemistry* 2014, *86*, 10531–10534.
- Rohaizad, N.; Mayorga-Martinez, C. C.; Novotný, F.; Webster, R. D.; Pumera, M. Electrochemistry Communications 2019, 103, 104–108.
- 26. Andreatta, F.; Fedrizzi, L. *Electrochimica Acta* **2016**, *203*, 337–349.
- 27. Bentley, C. L.; Perry, D.; Unwin, P. R. Analytical Chemistry 2018, 90, 7700–7707.
- 28. Myland, J. C.; Oldham, K. B. Analytical Chemistry 2000, 72, 3972–3980.
- 29. Baruzzi, A.; Ühlken, J. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **1990**, 282, 267–273.
- 30. Birbilis, N.; Padgett, B. N.; Buchheit, R. G. Electrochimica Acta 2005, 50, 3536–3544.
- 31. Wen, Y.-N.; Zhang, J.-M. Solid State Communications 2007, 144, 163–167.
- 32. Fu, B.; Liu, W.; Li, Z. Applied Surface Science 2010, 256, 6899–6907.
- 33. Jinlong, L.; Hongyun, L. Surface and Coatings Technology **2013**, 235, 513–520.
- 34. Lüth, H., Solid Surfaces, Interfaces and Thin Films; Springer: 2001; Vol. 4.
- 35. Song, G.-L.; Mishra, R.; Xu, Z. Electrochemistry Communications 2010, 12, 1009–1012.
- 36. Dwivedi, D.; Lepková, K.; Becker, T. RSC advances 2017, 7, 4580–4610.
- 37. Zhang, L.; Szpunar, J. A.; Dong, J.; Ojo, O. A.; Wang, X. Metallurgical and Materials Transactions B **2018**, 49, 919–925.
- 38. Cabrera, N.; Mott, N. F. Reports on progress in physics 1949, 12, 163–184.
- 39. Cai, N.; Zhou, G.; Müller, K.; Starr, D. E. Applied Physics Letters 2012, 101, 171605.
- 40. Verwey, 1. E. *Physica* **1935**, *2*, 1059–1063.
- 41. Hasenay, D.; Seruga, M. Journal of Applied Electrochemistry 2007, 37, 1001–1008.
- 42. Martinson, C.; Flodstrom, S. Surface Science **1979**, *80*, 306–316.
- 43. Flötotto, D.; Wang, Z.; Jeurgens, L. P.; Mittemeijer, E. *Applied Physics Letters* **2014**, 104, 091901.
- 44. Szklarska-Smialowska, Z. Corrosion Science 1999, 41, 1743–1767.
- 45. Gupta, R.; Sukiman, N.; Cavanaugh, M.; Hinton, B.; Hutchinson, C.; Birbilis, N. *Electrochimica Acta* **2012**, *66*, 245–254.
- 46. Natishan, P.; O'grady, W. Journal of the Electrochemical Society 2014, 161, C421.
- 47. Krawiec, H.; Szklarz, Z. Electrochimica Acta 2016, 203, 426–438.
- 48. Tucker, G. J.; McDowell, D. L. International Journal of Plasticity **2011**, 27, 841–857.
- 49. Ye, W.; Kumar, P.; Misra, M.; Mushongera, L. T. Materials Letters 2021, 300, 130153.
- 50. Galvele, J.; de De Micheli, S. Corrosion Science 1970, 10, 795–807.

- 51. Ramgopal, T.; Gouma, P.; Frankel, G. Corrosion 2002, 58, 687–697.
- 52. Sha, G.; Cerezo, A. Acta Materialia 2004, 52, 4503–4516.
- 53. Rohrer, G. S. Journal of Materials Science **2011**, *46*, 5881–5895.
- 54. Zhu, E.; Xue, W.; Wang, S.; Yan, X.; Zhou, J.; Liu, Y.; Cai, J.; Liu, E.; Jia, Q.; Duan, X., et al. *Nano Research* **2020**, *13*, 3310–3314.

## Chapter 6

## **Conclusion and Future Work**

## 6.1 Conclusions by Chapter

#### 6.1.1 Chapter 1

Chapter 1 first introduced the classification of Al alloys for the understanding of different types of alloys, and then focused on the microstructures that are related to corrosion mechanism. Corrosion is divided into uniform and localized corrosion. The mechanisms of three types of localized corrosion, galvanic, pitting and intergranular corrosion were described in Chapter 1. Chapter 1 also presented the corrosion thermodynamics and kinetics from the electrochemical perspective to provide basics for the analysis of Al corrosion in electrochemical measurements. Microscopic electrochemical measurements using SECCM can reveal the correlation between corrosion mechanisms and surface microstructures. Chapter 1 gave a literature review on the advantages, working principle and development of SECCM. To facilitate the understanding of SECCM measurements in the field of corrosion, several experimental considerations were discussed. As the most recently developed scanning electrochemical technique, SECCM is on the rise as an important tool for mapping local electrochemical phenomena, providing opportunities to directly study corrosion mechanisms at the (sub)microscale.

### 6.1.2 Chapter 2

OI-SECCM was developed to address the longstanding problem of droplet evaporation in SECCM. Droplet evaporation is detrimental to SECCM experiments, because the resulting droplet electrolyte crystal will cause pipettes to break. Although humidified cells created by wet gas flow have been used to prevent droplet evaporation, the resulting high background noise and moisture that damages electronic components make it impractical, especially for the low current systems. OI-SECCM uses a layer of oil on the substrate surface to submerge the droplet cell. A highly stable droplet is created, which is particularly useful for corrosion studies using highly evaporated NaCl solutions.

Long-term OI-SECCM measurements using a 3.5 wt% NaCl solution were performed on Al alloy AA7075-T73 with OCP followed by PDP measurements at each droplet landing location. An area of  $150 \times 150 \ \mu m^2$  was mapped during ~ 21 h. Based on the obtained  $E_{corr}$  and  $i_{corr}$  maps, and PDP curves, the galvanic corrosion between intermetallics and the surrounding matrix Al was analyzed, demonstrating the accelerated Al dissolution around the Fe-rich intermetallics.

### 6.1.3 Chapter 3

Chapter 3 revealed that the commonly used non-isolated Ag/AgCl wire QRCE in SECCM introduced Ag<sup>+</sup> contaminants into electrolyte, leading to  $E_{corr}$  shifting to positive with time. Ag<sup>+</sup> originated from the dissociation of AgCl film on the Ag/AgCl wire QRCE, which diffused to the micropipette tip and was reduced on the Al alloy WE. The generated interfering cathodic current led to the  $E_{corr}$  positive shift. This will affect the quantitative analysis and identification of potential and current changes associated with surface structure. The presence of Ag<sup>+</sup> in droplet was demonstrated by the oxidation peak of Ag on CV and Ag signal on EDS spectrum. To eliminate the Ag<sup>+</sup> interference, the distance between Ag/AgCl wire and micropipette tip was extended to prolong the diffusion time

when the droplet was free of Ag<sup>+</sup>, or a leak-free Ag/AgCl electrode was used to replace the non-isolated wire QRCE.

### 6.1.4 Chapter 4

Chapter 4 demonstrated that the droplet landing process was governed by  $E_{appr}$ , which influenced the subsequent electrochemical measurements in the single-channel pipette SECCM. For a semiconductive surface, like the oxide covered Al,  $E_{appr}$  determines the magnitude of  $i_{trig}$  and hence when the micropiptte is stopped during the pipette approach to substrate. This leads to two types of landings, droplet-contact and pipettecontact observed on the Al alloy AA7075-T73 at different  $E_{appr}$ . At droplet-contact landing, the presence of droplet-oil interface introduced additional oxygen from the oil phase to droplet, enhancing the ORR cathodic reaction. This resulted in more positive  $E_{corr}$  compared to that at pipette-contact landing. Furthermore,  $E_{corr}$  damaged the oxide film upon the droplet landing, increasing the surface conductivity. This led to an increase in the anodic current and pitting frequency during PDP measurement. In conclusion, this work explains the variations of SECCM measurements at different  $E_{appr}$  and, more importantly, provides a strategy to increase the conductivity of surface oxide, which facilitates the use of small pipettes in SECCM and identification of small electrochemical differences.

### 6.1.5 Chapter 5

The development and optimization of OI-SECCM technique in Chapter 2, 3 and 4 enables to obtain highly stable electrochemical measurements during long-term scans. This allows the study of small electrochemical differences caused by more subtle microstructures over large surface areas. Taking advantage of OI-SECCM, Chapter 5 revealed the effects of grain orientations and boundaries on anodic, cathodic currents, and pitting by performing numerous PDP measurements on a practical polycrystalline Al alloy AA7075-T73.

The statistic distribution of cathodic currents measured at 2511 locations shows an increasing order on grains  $\{111\} < \{001\} < \{101\}$ , agreeing with the opposite order of atomic planar density  $\{111\} > \{001\} > \{101\}$ . A smaller atomic planar density indicates less satisfied atomic bonds, resulting in higher surface energy. The planes with higher surface energy can offer more sites for oxygen and water adsorption and thus generate larger cathodic currents. By contrast, anodic currents exhibited a weak dependence on grain orientations and pitting showed a grain independence. This is probably because the limiting steps of the two anodic processes are more dependent on the structure of oxide film. Moreover, OI-SECCM maps demonstrated the higher electrochemical activities at grain boundaries. This work highlights the ability of OI-SECCM in discriminating small surface differences and promotes the study of grain dependent corrosion behaviors directly on practical polycrystalline samples.

## 6.2 Future Work

### 6.2.1 Understanding and Taking Advantage of Droplet Changes

Given the small currents measured in SECCM, any external and internal changes may lead to different electrochemical results for the same sample, as described in Chapter 3 and 4. Therefore, understanding variations in SECCM measurements is critically important for the correct interpretation of the obtained electrochemical data. This is the first step towards quantitative analysis of SECCM measurements in the future. Most of the variations stem from droplet changes. In Chapter 2, due to the lack of understanding of the effect of  $E_{appr}$  on droplet changes, the pipette was moved down further when it has contacted the substrate. Therefore, we provided a clear explanation for the influence of  $E_{appr}$  to highlight the importance of droplet changes for SECCM measurements. The presence of droplet-air or droplet-oil interface makes a great contribution to the oxygen mass transport. Variation in the interfacial area is one of the reasons for the difference in electrochemical measurements. Apart from  $E_{appr}$  discussed in Chapter 4, other factors that affect droplet height would cause differences in the oxygen flux.<sup>1</sup> For example, the pressures on the top of micropipette, especially when using a pipette holder,<sup>2</sup> will control the droplet height. Inconsistent pressures will result in different areas of interface and droplet contacting the substrate. Thus, the pipette holders or others added on the top of pipette should be used with caution. In addition, the background noise is also a factor that could cause the droplet height to change. Since the micropipette is stopped by a current spike that exceeds the current threshold, a different droplet heights. The current threshold is usually set based on the amplitude of background noise, which varies with the environmental and instrumental conditions.

With respect to OI-SECCM, the oils or liquids that are hydrophobic and electrochemically inert can be used theoretically. However, the differences in the polarity, viscosity and oxygen content of oils will affect the oxygen mass transport through the droplet-oil interface and the extent of the interaction between the oil and substrate, leading to inconsistent results for the same samples. Therefore, elucidating the effects of oils on OI-SECCM measurements would be meaningful for the further development of OI-SECCM. This could be used to customize OI-SECCM for different purposes by selecting different oils. For example, controlling the droplet-oil interface allows to perform oxygen-controlled experiments,<sup>3,4</sup> especially those requiring high oxygen content. Additionally, adding chemicals to the oil phase could be a strategy to change or counteract the changes of droplet accumulated during the multiple local measurements. Overall, OI-SECCM provides opportunities to control and manipulate the droplet cell by changing the surrounding hydrophobic phase. Additionally, since the difference in the polarity of oils could affect electrochemical measurements of different surface microstructural features, such as grain boundaries, studying a variety of oils in OI-SECCM would help select the appropriate oil for different properties.

### 6.2.2 Further Development of SECCM

The incorporation of other functions into SECCM platform and co-located measurements with complementary techniques to obtain correlative information have been the trend of SECCM applications. For example, SECCM combined with EBSD are usually used to map polycrystalline substrate surfaces, like platinum electrode,<sup>1,5,6</sup> Au,<sup>2</sup> etc. for the correlation of electrochemical activities to grain orientations and boundaries. Future work could be done by coupling MS, UV-VIS and ICP-OES with SECCM. The electrolyte can be extracted by connecting the pipette with a holder like the one shown in Figure 1.14 for analysis. Furthermore, quad-probe has been reported to incorporate SECM and SECCM functions.<sup>7,8</sup> This is a promising direction to take advantage of the powerful positioning ability of SECCM to assist the local measurement of microelectrode. For example, incorporating a pH sensor into multiple-channel SECCM could monitor pH changes during electrochemical processes at one location and pH response to the surface microstructure and composition.

### 6.2.3 Future Directions of OI-SECCM in Corrosion Field

OI-SECCM has been optimized and proved stable during long-term measurement of Al alloy corrosion by eliminating the RE contaminants and elucidating the effects of  $E_{appr}$ . This provides directions for optimizing OI-SECCM to measure other metals under different experimental conditions. So far, OI-SECCM has been applied for Zn,<sup>9</sup> Cu,<sup>10</sup> and Al on the subjects of intermetallics and grain orientations and boundaries. Future studies can be extended to steels, Mg, Au, Pt, etc. Besides the localized microstructural features, the more general surface structures, like oxide films and the surfaces with different treat-

ments, like heating, rolling and coating, can be analyzed at the microscale to explore their influences on the corrosion initiation.

Furthermore, the high stability of OI-SECCM measurements allows for the comparison of different samples, which would be an advance over previous studies in which SECCM was mainly used to analyze differences within a single sample. This can be applied to compare the same series of alloys that have common properties but extremely small differences in either composition or surface treatment. The comparable OI-SECCM measurements could make a great contribution to the corrosion science, opening up avenues to discern small microscopic electrochemical difference between samples.

The application of SECCM in the corrosion field not only suffers from the droplet evaporation, but also corrosion products and pH changes. Whether the corrosion products are deposited on the metal surface or accumulate in the droplet, and whether the corrosion products and pH significantly change the droplet, are questions that need to be clarified, especially when using highly aggressive electrolytes and mapping large areas. Post analysis of droplet composition after OI-SECCM mapping by either SEM, EDS and ICP-OES could be solutions to check the existence of corrosion products. pH may have a very local change at the droplet-substrate interface and the change could be diluted by the bulk solution at the next droplet landing location. Whether the pH change significantly affects measurements can be analyzed by modelling. The elucidation of droplet electrolyte changes during the continuous measurements of multiple locations will be helpful to promote the OI-SECCM application in the field of corrosion and others with substrate involved reactions.

#### 6.2.4 Future Direction in Corrosion Research

This thesis presents the powerful capability of OI-SECCM in analyzing the microscopic corrosion, which is an advance in the corrosion field using local and scanning electrochemical techniques to understand the corrosion mechanism. Understanding the corrosion mechanism can provide a theoretical basis for corrosion prevention, material selection and design. However, the conventionally used corrosion tests mostly rely on the bulk scale techniques, making it difficult to detect corrosion phenomena at the (sub) microscale. In the future, investment should be increased in the development and application of microscale electrochemical techniques in the corrosion industry. This promotes the study of corrosion mechanism which will greatly benefit corrosion control and prevention. Mitigating and preventing corrosion could reduce the global corrosion cost which reaches astonishing trillion dollars (US) annually.<sup>11,12</sup> Efforts to prevent corrosion can not only reduce economic losses, but also save lives and injuries in corrosion disasters and reduce the impact of corrosion on the environment.

## References

- 1. Chen, C.-H.; Meadows, K. E.; Cuharuc, A.; Lai, S. C.; Unwin, P. R. *Physical Chemistry Chemical Physics* **2014**, *16*, 18545–18552.
- Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. Science 2017, 358, 1187– 1192.
- Zana, A.; Wiberg, G. K.; Deng, Y.-J.; Østergaard, T.; Rossmeisl, J.; Arenz, M. ACS Applied Materials & Interfaces 2017, 9, 38176–38180.
- Ustarroz, J.; Ornelas, I. M.; Zhang, G.; Perry, D.; Kang, M.; Bentley, C. L.; Walker, M.; Unwin, P. R. ACS Catalysis 2018, 8, 6775–6790.
- 5. Aaronson, B. D.; Chen, C.-H.; Li, H.; Koper, M. T.; Lai, S. C.; Unwin, P. R. *Journal of the American Chemical Society* **2013**, *135*, 3873–3880.
- 6. Chen, C.-H.; Jacobse, L.; McKelvey, K.; Lai, S. C.; Koper, M. T.; Unwin, P. R. *Analytical Chemistry* **2015**, *87*, 5782–5789.
- Byers, J. C.; Paulose Nadappuram, B.; Perry, D.; McKelvey, K.; Colburn, A. W.; Unwin, P. R. *Analytical Chemistry* 2015, 87, 10450–10456.
- 8. Paulose Nadappuram, B.; McKelvey, K.; Byers, J. C.; Güell, A. G.; Colburn, A. W.; Lazenby, R. A.; Unwin, P. R. *Analytical Chemistry* **2015**, *87*, 3566–3573.
- 9. Shkirskiy, V.; Yule, L.; Daviddi, E.; Bentley, C.; Aarons, J.; West, G.; Unwin, P. *Journal of the Electrochemical Society* **2020**, *167*, 041507.
- Daviddi, E.; Shkirskiy, V.; Kirkman, P. M.; Robin, M. P.; Bentley, C. L.; Unwin, P. R. Chemical Science 2021, 12, 3055–3069.
- 11. Koch, G. Trends in Oil and Gas Corrosion Research and Technologies 2017, 3–30.

 Koch, G. H.; Brongers, M. P.; Thompson, N. G.; Virmani, Y. P.; Payer, J. H., et al. *Corrosion Cost and Preventive Strategies in the United States*; tech. rep.; United States. Federal Highway Administration, 2002.

## Appendix A



**Figure A.1:** SEM image of the micropipette (diameter =  $\sim$ 1.65  $\mu$ m)



**Figure A.2:** Schematic of the setup used to measure the potential of the Ag/AgCl wire QRCE vs. saturated calomel electrode (SCE) in 3.5 wt% NaCl electrolyte solution based on open circuit potential (OCP) measurement. The potential of a freshly prepared Ag/AgCl QRCE was monitored over 12 h. Only a small shift (~2.5 mV) was observed.



**Figure A.3:** The optical microscopic images of the micropipette before and after landing 961 times during a ~20 h OI-SECCM experiment



**Figure A.4:** (a) NaCl crystal formed at the end of a broken micropipette used in SECCM conducted in air. (b) The micropipette crashed, leaving electrolyte on the surface. (c) After removing the electrolyte from the surface using water, the corrosion spots were exposed. The white dashed circles represent the locations where the droplet did not land because of the interference of external noise.



**Figure A.5:** EDS point analysis of the constituent phase at point 608 in Figure 2.6e. The Atomic Cu/Fe ratio is 0.44, which is defined as  $(Al,Cu)_6$ (Fe,Cu) according to literature.



**Figure A.6:** A micropipette filled with 3.5 wt% NaCl solution was landed on a glassy carbon working electrode. Ag/AgCl wire served as the QRCE. CVs were run from -0.6 to 0.4 back to -0.6 V at a scan rate of 100 mV to detect Ag<sup>+</sup>. (a) In a freshly filled micropipette, no peak was detected. (b) In the micropipette after a long time OI-SMCM scanning, a peak representing Ag oxidation was observed. This indicates the presence of Ag<sup>+</sup> in the droplet at the end of micropipette.



**Figure A.7:** EDS point analysis of the constituent phase at point 13 in Figure 2.7c. The Atomic Cu/Fe ratio is 0.34, which is defined as  $(Al,Cu)_6$  (Fe,Cu) according to literature.

# Appendix **B**



**Figure B.1:** SEM image of the micropipette (diameter =  $\sim$ 1.6  $\mu$ m)



**Figure B.2:** The open circuit potentials of eight Ag/AgCl wires were monitored for 1000 s in a 3.5 wt% NaCl aqueous solution versus SCE.



**Figure B.3:** a) Schematic of the electrochemical cell in a three-electrode configuration with a SCE as the RE and a Pt wire as the CE to monitor the potential of a 0.125 mm diameter Ag/AgCl wire (WE) in 3.5 wt% NaCl solution. (b) The potential of Ag/AgCl wire was recorded for 25 h via chronopotentiometry with 100 pA (blue) and -100 pA (orange) currents applied.



**Figure B.4:** The potential of leak-free Ag/AgCl electrode was measured versus a SCE in a 3.5 wt% NaCl solution via OCP mode for 1000 s. Black trace: raw data, red trace: 500-point averaged data.

# Appendix C



**Figure C.1:** PDP measurement of pure Al at the scan rate of 0.167 mV/s. The potential was referred to SCE during the experiment. To be consistent with the potentials in SECCM, the potential was converted to be referred to the Ag/AgCl wire electrode in a 3.5 wt% NaCl solution.



**Figure C.2:** Currents recorded during the 2  $\mu$ m diameter micropipette approach to the surface of aluminum alloy AA7075-T73 at a cathodic approach potential of (a) -1.5 V and (b) -2.5 V vs. Ag/AgCl.



**Figure C.3:** (a) PDP curves at the landing locations with different approach potentials applied. (b) Anodic currents at -0.7 V were extracted.



**Figure C.4:** Currents recorded during the 10  $\mu$ m diameter micropipette approach to the surface of aluminum alloy AA7075-T73 at a cathodic approach potential of -1.5 V. Negative trigger currents ( $i_{trig}$ ) were produced giving rise to droplet contact landing.

# Appendix D



**Figure D.1:** (a) Diluted crystallographic orientation map generated using MATLAB, which has the same density with OI-SECCM map. (b) Misorientation angles of grains relative to {001}, {101} and {111} planes. The color bars on the right side indicate the degree of misorientation angle. (c) Grains with misorientation angle ( $\theta$ ) less than 20 degrees were classified into groups: {001}, {101} and {111}.



**Figure D.2:** (a) Grain size map showing the mean grain widths in the horizontal, vertical and two diagonal directions using point-sampled linear intercept method. (b) The mean grain size in the horizontal direction.