CHARACTERIZATION AND ENHANCEMENT OF THE OXYGEN EVOLUTION

REACTION IN POLYMER ELECTROLYTE MEMBRANE WATER

ELECTROLYSIS

by

Jason Tai Hong Kwan

B.A.Sc., The University of British Columbia, 2010

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(CHEMICAL AND BIOLOGICAL ENGINEERING)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

December 2019

© Jason Tai Hong Kwan, 2019

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the dissertation entitled:

Characterization and Enhancement of the Oxygen Evolution Reaction in Polymer Electrolyte Membrane Water Electrolysis

submitted by	Jason Tai Hong Kwan	in partial fulfillment of the requirements for
the degree of	Doctor of Philosophy	
in	Chemical and Biological Enginee	ering
Examining C	ommittee:	
David P. Wilk	inson	
Supervisor		
Fariborz Tagh	ipour	
Supervisory C	ommittee Member	
Vladan Prodat	pović	
Supervisory C	ommittee Member	
Savvas Hatzik	iriakos	
University Exa	aminer	
Edouard Asse	lin	
University Exa	aminer	

Abstract

In this thesis, novel electrochemical methods for characterizing the oxygen reduction reaction (ORR), the oxygen evolution reaction (OER), and alternative materials for the current collector and flow field for the polymer electrolyte membrane water electrolyzer (PEMWE) are presented.

A novel modified rotating disk electrode (MRDE) apparatus used for characterizing catalyst coated membranes (CCMs) for the oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cell (PEMFC) application was demonstrated first. Cyclic voltammograms (CV) and ORR curves were obtained at room temperature for Pt foil and three commercial CCM samples. The mass activity obtained from the MRDE technique, compared to classical thin-film RDE, were in closer agreement to the PEMFC results. For the OER study, six different current collectors were tested using one commercial CCM in a half cell at 25, 40, 55, and 75°C. The MRDE was able to reach 2 A cm⁻² for commercial OER catalysts. This is a large improvement over traditional OER RDE, which seldom reaches 50 mA cm⁻². There is an improvement in performance with increasing triple contact point (TCP).

A transparent visualization cell was developed to expand the channel adjacent to the anode catalyst. This cell was designed to operate current densities higher than 2 A cm⁻², where mass transport effects are more dominant. A commercial catalyst and four Ti current collector meshes were tested at room temperature. Rapid cycling CVs and polarization curves were performed to validate this setup and rank the mesh performance. Fourier transform and bubble-ratio analysis were used to identify characteristic bubble lifetimes. Current density increases with decreasing bubble ratio in the frequency range 0.03 < f < 1 Hz.

iii

Finally, PTLs with reduced Ti content, and the concept of a no-PTL PEMWE were explored. Initial results using no PTL on the anode-side show a current density of 2 A cm⁻² at 80°C at 2.5 V when corrected for the area of the channel landing. This highlights the possibility of removing the anode PTL, and focusing the efforts on an engineered flow field, which provides the functionality of a PTL.

Lay Summary

PEMWEs are a clean energy technology that produces hydrogen, a clean burning fuel used in several applications such as fuel cell cars and chemical synthesis. Presently, the Ir-based catalyst and the Ti components are costly and have no suitable alternatives in the short-term. Current ex-situ methods to evaluate catalyst activity do not accurately represent the real conditions of a fuel cell or electrolyzer. Improvements to existing characterization methods, while adding additional testing capabilities were completed. The benefit of this will improve the design and testing of new catalysts, increasing the rate at which they are improved and lead to a reduction in testing cost. Significant reduction in Ti could reduce the total PEMWE weight and costs. This was done by exploring engineered plastic materials with thin layers of Ti. The findings in this thesis would further the commercial viability of PEMWEs by decreasing the material costs and improving performance.

Preface

All the work presented was conducted in the Applied Electrochemistry Laboratory and the Fuel Cell Laboratory at the University of British Columbia, Point Grey campus.

Chapter 1 combines the works from two published papers. Spöri, C., **Kwan, J. T. H**., Bonakdarpour, A., Wilkinson, D. P., & Strasser, P. (2017). The stability challenges of oxygen evolving catalysts: towards a common fundamental understanding and mitigation of catalyst degradation. Angewandte Chemie International Edition, 56(22), 5994-6021. I wrote half of this review paper, with my sections concerning figures of merit for electrolysis and stability protocols. Ojong, E. T., **Kwan, J. T. H.**, Nouri-Khorasani, A., Bonakdarpour, A., Wilkinson, D. P., & Smolinka, T. (2017). Development of an experimentally validated semi-empirical fullycoupled performance model of a PEM electrolysis cell with a 3-D structured porous transport layer. International journal of hydrogen energy, 42(41), 25831-25847. I performed all the RDE tests and wrote the section on the electrokinetic parameter verification.

Chapter 2 combines the works from two published papers. **Kwan, J. T. H**., Bonakdarpour, A., Afonso, G., & Wilkinson, D. P. (2017). Bridging fundamental electrochemistry with applied fuel cell testing: a novel and economical rotating disk electrode tip for electrochemical assessment of catalyst-coated membranes. Electrochimica Acta, 258, 208-219. I performed all of the experimental work and analysis, and wrote most of the paper. Kroschel, M., Bonakdarpour, A., **Kwan, J. T. H.**, Strasser, P., & Wilkinson, D. P. (2019). Analysis of oxygen evolving catalyst coated membranes with different current collectors using a new modified rotating disk electrode technique. Electrochimica Acta, 317, 722-736. I provided all the training for the MRE apparatus, collected the electrolyzer data for comparison, assisted in developing experimental protocols and edited the paper.

Table of Contents

Abstractiii
Lay Summaryv
Prefacevi
Table of Contents vii
List of Tables xii
List of Figures xiii
List of Symbols xix
List of Abbreviations xxii
Acknowledgementsxxv
Dedication xxvi
Chapter 1: Introduction1
1.1 The Hydrogen Economy and a Brief History of Water Electrolysis Technology
1.2 Fundamental Electrochemical Principles7
1.2.1 Electrochemical Thermodynamics: The Nernst Equation
1.2.2 The Anatomy of a Polarization Curve: Kinetics, Ohmic, and Mass Transport
Contributions
1.2.3 Electrochemical Kinetics: The Butler-Volmer Equation and Activation
Overpotential10
1.2.4 Electrochemical Kinetics: Electrokinetic Parameter Extraction and Limiting Cases13
1.2.5 Ohmic Losses
1.2.6 Mass Transport Losses
VII

1.3	Alkaline Water Electrolyzers	
1.3	3.1 Liquid Alkaline Water Electrolyzers	
1.3	3.2 Anion Exchange Membrane Water Electrolyzers	
1.4	Polymer Electrolyte Membrane Water Electrolyzers	
1.4	4.1 Choice of PEMWE Catalyst Material	
1.4	4.2 Choice of PEMWE Porous Transport Layer	
1.4	4.3 Figures of Merit and Key Performance Indicators (KPI)	
1.5	Solid Oxide Water Electrolyzers	
1.6	Research Objectives	
1.7	Thesis Layout	
Chapte	er 2: Development of the Modified Rotating Disk Electrode (MRDE) usi	ng the
Oxyger	n Reduction Reaction for Validation	44
2.1	Scope and Context	
2.2	Experimental	
2.3	Results and Discussion	
2.3	3.1 Cyclic Voltammogram Analysis	
2.3	3.2 Mass and Specific Activity	
2.3	3.3 Accelerated Degradation Testing	
2.4	Summary	
Chapte	er 3: Use of the Modified Rotating Disk Electrode (MRDE) to Study the	Effect of
Porous	Transport Layers on the Oxygen Evolution Reaction	63
3.1	Introduction	63
3.2	Experimental	
		viii

3.2.1	Methods and Procedures	
3.3 R	esults and Discussion	
3.3.1	Cyclic Voltammograms and Charge Quantification	
3.3.2	Resistance Measurement	
3.3.3	Polarization Curves	
3.3.4	Accelerated Degradation Testing	
3.3.5	PEMWE Comparison	
3.4 S	ummary	
Chapter 4:	Current Collector and Bubble Occupancy Characterization with a	
Visualizati	on Cell	
4.1 S	cope and Context	
4.2 E	xperimental	
4.2.1	Visualization Cell Assembly	
4.2.2	Housed Working Electrode Unit	
4.2.3	Housed Counter Electrode Unit	
4.2.4	Sample Preparation	
4.2.5	Electrochemical Testing Procedures	100
4.3 R	esults and Discussion	102
4.3.1	Demonstration of the cell using Ir Foil	102
4.3.2	CVs and Current Collector Charge	103
4.3.3	Polarization Curves for the Commercial IrO ₂ Catalyst CCM	105
4.3.4	Current Fluctuation Analysis	107
4.4 S	ummary	
		ix

Chapter 5: Methods and Materials for Titanium Reduction in the Anode Side of	the
PEWME	114
5.1 Scope and Context	114
5.2 Experimental	118
5.2.1 Materials	118
5.2.1.1 Down selection of Plastic Substrate	118
5.2.1.2 Design of the Plastic Substrate	120
5.2.1.3 Titanium Deposition	121
5.2.2 Experimental Methods	121
5.2.2.1 Through-Plane Resistance	121
5.2.2.2 PEMWE Cell Setup	122
5.2.2.3 Experimental Procedures	123
5.3 Results and Discussion	124
5.3.1 Through-Plane Resistance Screening and Remediation Strategies	124
5.3.2 PEMWE Baseline Experiments with new MEA	126
5.3.3 PEMWE Results with Ti/ABS Plastic	127
5.3.4 Diagnostic Tests for extent of CCM swelling in blank ABS samples	129
5.3.5 Blank ABS Post Mortem Analysis	131
5.4 Initial Results with No Anode PTL	133
5.5 Summary	135
Chapter 6: Conclusion	136
Chapter 7: Recommendations for Future Work	138
7.1 Future Work for the ORR studies with the MRDE	
	х

7.2	Future Work for the OER studies with the MRDE	
7.3	Future Work for the Diagnostic Cell	
7.4	Future Work for PTL Replacement	141
Bibliogr	aphy	142
Append	ices	164
Apper	ndix A	
A.1	MRDE ORR ADT Protocol	
A.2	Nernstian Correction for RDE to PEMFC Comparison	
Apper	ndix B	
B.1	Illustrative Sketch of the LWD/SWD and Characteristic Calculations	
Apper	ndix C	
C.1	Calibration Curve for Magnetic Drive Pump	
C.2	Design Progression of the Working Electrode Housing Unit	
C.3	Single-sided Amplitude Spectrum Fourier Transform Results for Current	nt Collector
Mes	shes M2 to M4	
C.4	Compiled Bubble Ratio for Frequency Ranges R ₂ and R ₃	176

List of Tables

Table 1.1: Properties of the Tokuyama A-201 AEM and AS-4 ionomer summarized from
[47,48]
Table 1.2: Summary of AEM membrane types, catalysts and reported current performance at a
specified potential. Summarized from Vincent et al. [47]
Table 1.3: Performance benchmarks for the PEMWE. Bolded entry is run at above 120°C.
Reprinted with Permission from Angewandte Chemie [5]
Table 2.1: Experimental sweep rates for CVs and ORRs for each sample. An asterix indicates
which sweep rate was taken for mass and specific activity analysis for each sample
Table 3.1: Physical properties of the six Ti-based current collectors. 66
Table 3.2: Key figures of merit for each of the current collector meshes. 79
Table 3.3: Tafel slopes of the ETS and MRDE at 25, 40, 55 and 70°C
Table 3.4: Exchange current densities of the ETS and MRDE at 25, 40, 55 and 70°C 86
Table 4.1: Cell and operating parameters for in-situ methods
Table 4.2: Current collector meshes that were down selected for testing in the visualization cell
from the two previous MRDE studies
Table 5.1: Baseline resistance for SolviCore E300 CCM with sintered Ti-PTLs. 127
Table 5.2: Resistance measurements before and after the cell is flooded for 72 hours
Table 7.1: Literature compilation of both non-invasive and direct visualization studies

List of Figures

Figure 1.1: Anodic, cathodic and migrating ion in solid polymer electrolyte for (a) AWE, (b)
PEMWE, and (c) SOEC. Reprinted with permission from Springer-Verlag [29]6
Figure 1.2: Dominant Loss Factors in a PEMWE. Y-intercept shows exchange current density, i ₀
[32]9
Figure 1.3: Resistor network model for a PEMWE. Reprinted with permission from ECS [35]. 15
Figure 1.4: A liquid alkaline electrolyzer with migration of species within [44]. Reprinted with
permission from © 2012 IEEE
Figure 1.5: Cell schematic of a zero-gap alkaline electrolyzer [46]. Reprinted with permission
from Electrochimica Acta
Figure 1.6: Electrolyer configurations using a a) unipolar, and b) bipolar cell. Reprinted with
permission from Quimica Nova [13]22
Figure 1.7: PEMWE showing the migration of species within [44]. Reprinted with permission
from © 2012 IEEE
Figure 1.8: OER Volcano plot adjusted to the ΔG_O - ΔG_{OH} descriptor. Reprinted with permission
from ChemCatChem [64]
Figure 1.9: PEMWE sketch showing the PTL and separator (or bipolar) plates. Reprinted with
permission from Elsevier [75]
Figure 1.10: Lifetime tests of a Ru _{0.8} Nb _{0.2} O ₂ (red, less steep) and the less stable RuO ₂ (black,
steeper). Reprinted with permission from Elsevier [85]
Figure 1.11: SOEC cell with migration of species in the YSZ electrolyte. Reproduced with [95]
with permission from the Royal Society of Chemistry

Figure 2.1: Modified rotating disk electrode components from an a) exploded view, and b) cross-
sectional exploded view
Figure 2.2: a) Open diameter, current collector strand width, and geometric masking of the Ti
mesh and b) CVs with and without the Ti Mesh
Figure 2.3: Cyclic voltammograms of a) Pt foil, b) 0.1 loading mg cm ⁻² CCMs, c) 0.4 loading mg
cm ⁻² CCMs, and d) a summary of ECSA before ORR (left column) and after ORR (right column)
for the CCM samples
Figure 2.4: ORR curves showing the first anodic sweep for a) Pt foil, b) JM 0.1 mg _{Pt} cm ⁻² , and c)
JM 0.4 mg _{Pt} cm ⁻²
Figure 2.5: Summary of specific and mass activity data for all CCM samples compared with the
TF-RDE and PEMFC result. Bars with hashed lines are specific activity
Figure 2.6: ADT analysis of a 0.4 mg _{Pt} cm ⁻² JM CCM. (a) Cyclic voltammogram progression
during ADT, (b) oxygen reduction reaction progression with inset showing the kinetic reaction,
and (c) loss of ECSA and mass activity during the 30,000 cycle period
Figure 3.1: a) Exploded rendering of the MRDE tip, b-g) microscope images of the Ti current
collectors. The model numbers are b) 3Ti4-031, c) 3Ti8.5-031, d) 3Ti10-031, e) 2Ti4-124, f) 10-
Ti12-125, and g) 9Ti-twill
Figure 3.2: a) OER measurement protocol, b) polarization protocol showing the current density
steps and time at each step
Figure 3.3: The 5th CV of the E300 CCM, with six different current collectors tested at a scan
rate of 50 mV s ⁻¹ at a scan range between 0.05 - 1.4 V at a) 25°C and b) 70°C. The relationship
between c) mesh coverage and average charge at 25°C, and d) average charge-temperature for all
six meshes
xiv

Figure 3.4: Sketch of the triple-contact point boundary and location of charge buildup
Figure 3.5: Resistances trends a) for all six current collectors at 25°C, and b) temperature-
resistance curve for the 3Ti4-031 current collector
Figure 3.6: a) Non-iR corrected and iR-corrected polarization curves at 25°C, and b) a condensed
polarization plot showing iR-corrected potentials corresponding to current densities of 100 mA
cm ⁻² (closed symbols) and 600 mA cm ⁻² (open symbols)
Figure 3.7: ADT at 1600 rpm in 3.5 M H ₂ SO ₄ at 40°C. In total, 15,000 square wave cycles were
performed between 0.05 - 1.4 V. a) Block diagram of the ADT protocol, b) CVs after each SWV
step, c) OER sweeps, and d) peak current density and voltammetric charge after each sequence.
Figure 3.8: PEMWE assembly of a) the baseline case with default components, and b) the
modified case with a 5 cm x 4.6 cm sheet of 3Ti4-031
Figure 3.9: Non-IR corrected polarization curves of the electrolysis test station (ETS) showing
baseline vs. tested mesh. b) iR-corrected polarization curves, c) Tafel plots of the MRDE and
ETS techniques, and d) Arrhenius plot
Figure 4.1: Diagrams showing a) true region of electrochemical activity and b) commonly
perceived electrochemical activity in a PEMWE. From [123]. Reprinted with permission from
AAAS
Figure 4.2: Overview of the visualization cell electrolysis flow cell apparatus
Figure 4.3: a) Plan view of the Ti lid, and b) exploded view of the housing unit for the working
electrode in the visualization electrolysis flow cell
Figure 4.4: Experimental block-flow diagram for a) CV characterization, and b) CA 101

Figure 4.5: Demonstration of diagnostic cell by performing AIROF growth due to rapid cycling
CVs up to 1,700 cycles 103
Figure 4.6: a) The 3 rd cyclic voltammogram for each Ti mesh used in the visualization cell,
scanned between $0.05 - 1.23$ V in 3.5 M H ₂ SO ₄ , and b) Relationship between physical coverage
from the mesh and charge 104
Figure 4.7: Polarization curves for each of the Ti meshes, iR-corrected and evaluated at 3.5 M
H ₂ SO ₄
Figure 4.8: a) 3Ti4-031 polarization, and b) Fourier transform analysis (single-sided amplitude
spectrum) for showing a lack of a defined peak 107
Figure 4.9: The bubble ratio for three frequency ranges for the different current collector meshes
used 110
Figure 4.10: Compiled bubble ratio results for frequency range R_1 (0.03 < f < 1 Hz) 112
Figure 5.1: Average 2D area porosity of a PTL using through-plane (TP), in-plane 1 (IP-1), and
in-plane 2 (IP-2) slices with a) 16 μ m pore size, and b) 60 μ m pore size. Reprinted with
permission from Energy Procedia [153]116
Figure 5.2: a) Schematic of the plastic PTL substrate, and b) as-submitted plastic PTL design
submission to Xometry.com
Figure 5.3: PEMWE component assembly for a) baseline case, b) Ti/Plastic PTL case, and c) no
anode PTL with stacked cathode PTL case
Figure 5.4: Freshly coated samples of Ti/PC (Left) and Ti/ABS (Right) 124
Figure 5.5: Real image of acetone vapour bath (left) and a labelled schematic (right) 125
Figure 5.6: Baseline polarization using setup from Figure 5.5a and a new E300E CCM 126

Figure 5.7: Performance of a SolviCore E300 CCM with a Ti/ABS anode PTL and sintered Ti-
PTL on the cathode at 2 LPM and 1 atm 128
Figure 5.8: Ti/ABS and ABS blank (no Ti coating) polarization curves compared. Both show
similar current magnitudes, despite the bare ABS not being electronically conductive
Figure 5.9: ABS blank tests before and after 72-hour hydration period
Figure 5.10: SolviCore CCM after disassembly showing the nine islands conformed to the shape
of the plastic PTL openings
Figure 5.11: Non iR-corrected baseline (dashed lines) vs non-area corrected no-anode PTL case
(solid lines)
Figure 5.12: Comparison of no anode PTL case normalized to 25 cm ² (solid line), 12.5 cm ² area
corrected no anode PTL case (dashed lines)
Figure A.1: Block-flow diagram of ADT protocol modified from Kocha et al. [111] 164
Figure B.1: Sketch of an expanded metal mesh (LWD = long way of the diamond, SWD = short
way of the diamond, TPB = triple phase boundary) 167
Figure C.1: Calibration Curve for Pan World (Model NH-15PI-Z-D)
Figure C.2: V1 working electrode assembly
Figure C.3: V2 working electrode assembly featuring sputtered Ir (100 nm) 171
Figure C.4: V3 working electrode assembly featuring screw-down Ti lid and epoxy-covered
SS316 shell
Figure C.5: Fourier transform results for 3Ti8.5-031 (M2) 174
Figure C.6: Fourier transform results for 2Ti4-125 (M3) 174
Figure C.7: Fourier transform results for 10Ti12-125 (M4) 175
Figure C.8: Bubble ratio analysis for frequency range R_2 (1 < f < 10 Hz) 176
xvii

Figure C.9: Bubble ratio analysis for frequency range R_3 (f > 10 Hz)...... 176

List of Symbols

General Symbols

А	geometric surface area of electrode (cm ²)
a	species activity
b	Tafel slope (mV dec ⁻¹)
С	concentration of species (mol L ⁻¹)
d _m	membrane thickness (mm)
E^{0}	standard potential for the redox reaction at 298K and 1 atm (V) $$
e	electron
F	Faraday's constant (96485 C mol e ⁻¹)
f	frequency (Hz)
G ⁰ _{rxn}	Gibbs free standard energy of reaction
Ι	current (A)
i	current density (A cm ⁻²)
jo	exchange current density (A cm ⁻²)
Ĵlim	limiting current density (A cm ⁻²)
L	material thickness (cm or mm)
K	Kohlarusch's Law constant (S m ^{7/2} mol ^{-3/2})
k	reaction rate constant (mol m ² s ⁻¹)
ṁ	mass flow rate of water (kg s ⁻¹)
n	number of electrons
Ox	oxidized species
Q	charge (Coulomb)

R	ideal gas constant (8.314 J mol ⁻¹ K ⁻¹)
Red	reduced species
r	molar reaction rate (mol s ⁻¹)
R _i	bubble ratio for frequency range i (dimensionless)
R _j	resistance of component j (Ω)
S	stoichiometric coefficient
S+	stoichiometric coefficient of the cation
S-	stoichiometric coefficient of the anion
ũ	ion mobility (m ² mol J ⁻¹ s ⁻¹)
Z	ion charge

Greek Symbols

α	symmetry factor
η	overpotential (V)
θ	bubble coverage (unitless)
λ	ionic molar conductivity (S $m^2 mol^{-1}$)
λ_{mem}	membrane hydration
Λ	molar conductivity (S m ² mol ⁻¹)
Λ^0	molar conductivity at infinite dilution (S m ² mol ⁻¹)
ξ	water ratio in a PEMWE
ρ	resistivity (Ω m)
σ	molar conductivity (S m ⁻¹)
σ_{m}	membrane conductivity (S m ⁻¹)

Koutecký – Levich Nomenclature (Chapter 2)

C [*] A	concentration of species A in the bulk (mol L ⁻¹)	
DA	molar diffusivity of species A (cm ² s ⁻¹)	
i _{disk}	disk current density for the RDE (A cm ⁻²)	
i _{DL}	diffusion limited current density (A cm ⁻²)	
i _k	kinetic current density (A cm ⁻²)	
n _D	number of electrons transferred	
ν	kinematic viscosity (cm ² s ⁻¹)	
ω	angular velocity (rad s ⁻¹)	
Frequency Analysis Nomenclature (Chapter 4)		
i	imaginary number	
j(t)	Current density as a function of time (A cm ⁻²)	
ĵ(ξ)	Current density in the frequency domain (A cm ⁻²)	
ξ	Frequency (Hz)	

List of Abbreviations

General Nomenclature

AC	Alternating Current
BIP	Bipolar Plate
DC	Direct Current
DI	Deionized
FPS	Frames Per Second
KPI	Key Performance Indicator
HHV	Higher Heating Value
HTM – PMBI	hexamethyl-p-terphenylene polydimethylbenzimidazolium
LHV	Lower Heating Value
LWD	Long Way of the Diamond
LPM	Liters Per Minute
PTFE	Polytetrafluoroethylene
RPM	Rotations Per Minute
STC	Standard Test Cell
SWD	Short Way of the Diamond
TOC	Total Organic Carbon
Electrochemical Nomenclature	
ACL	Anode Catalyst Layer
ADT	Accelerated Degradation Test
AIROF	Anodically Formed Iridium Oxide Film
AWE	Alkaline Water Electrolyzer

BEGV	Butler-Erdey-Grúz-Volmer
BPP	Bi-Polar Plates
C/A	Chlor-Alkali
CA	Chronoamperometry
CI	Current Interrupt
ССМ	Catalyst Coated Membrane
CCS	Catalyst Coated Substrate
CV	Cyclic Voltammogram
DFT	Dimensional Functional Theory
ECSA	Electrochemically Active Surface Area
EIS	Electrochemical Impedance Spectroscopy
ETS	Electrolysis Test Station
GDL	Gas Diffusion Layer
GEIS	Galvanostatic Electrochemical Impedance Spectroscopy
HER	Hydrogen Evolution Reaction
LGDL	Liquid Gas Diffusion Layer
MEA	Membrane Electrode Assembly
MRDE	Modified Rotating Disk Electrode
MSE	Mercury Sulphate Electrode
OCP	Open Circuit Potential
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PEM	Polymer Electrolyte Membrane

PEMFC	Polymer Electrolyte Membrane Fuel Cell
PEMWE	Polymer Electrolyte Membrane Water Electrolysis
RDE	Rotating Disk Electrode
RHE	Reversible Hydrogen Electrode
SCE	Standard Calomel Electrode
SOEC/SOWE	Solid Oxide Electrolysis Cell/Solid Oxide Water Electrolyzer
SPE	Solid Polymer Electrolyte
SWV	Square Wave Voltammetry
TF-RDE	Thin-Film Rotating Disk Electrode
ТСР	Triple Contact Point
TPB	Triple-Phase Boundary
PTL	Porous Transport Layer
Selected Material Nomenclature	
ABS	Acrylonitrile Butadiene Styrene
FDM	Fused Deposition Method
HDPE	High Density Polyethylene
LSCM	Lanthanum Strontium Chromium Manganese
PC	Polycarbonate
PEEK	Polyether Ether Keytone
PP	Polypropylene
PVD	Physical Vapor Deposition
YSZ	Yttria-Stabilized Zirconia

Acknowledgements

I would like to express my deepest gratitude towards my supervisor, Dr. David Wilkinson, for his mentorship, guidance and patience throughout my entire program. Working with him drastically improved my problem solving and diagnostic skills, especially in the face of difficult or open-ended problems. I would also like to thank my committee members Dr. Fariborz Taghipour and Dr. Vladan Prodanović for their feedback and involvement with my research. I would like to thank Dr. Arman Bonakdarpour, Dr. Amin Nouri-Khorasani, Dr. Camillo Spöri, Greg Afonso, Victor Cecon and Daniel McClement for working with me on specific aspects of my project. The support, feedback, and discussion I had with each of you have helped immensely during critical moments of my research.

Lastly, I would like to acknowledge my father and mother, Dr. Wing Cheung (Peter) Kwan and Oi Kheng (Kathy) Chin, for their financial and moral support. I would like to thank my wife, Ruby Fan Pei Kung, who provided me with the most moral support. You have stayed with me very late in the laboratory during some of my most critical scientific discoveries, made sure that I had good nutrition, and made countless sacrifices to make sure I succeeded in this program. Dedication

To my wife, family and friends.

謹獻給我的愛妻,家人及摯友

Chapter 1: Introduction

1.1 The Hydrogen Economy and a Brief History of Water Electrolysis Technology

Water electrolyzers are electrochemical conversion devices that use electrical energy to split water into hydrogen and oxygen gas. The production of hydrogen gas from such devices is critical to sustain energy demands in the future. Predictive models based on known oil reserves have shown that fossil fuels will be fully depleted by the year 2050 [1,2]. This emphasizes the need for an alternative energy carrier. Hydrogen has been considered as a solution to the future energy crisis for its low environmental impact and high energy density. When used in a fuel cell application, a major end-use application for hydrogen in the automotive industry, it acts as a clean-burning fuel with water as the only by-product of the reaction (equations 1.1 to 1.3) [3,4]. The United States Department of Energy (DOE) has reported gaseous hydrogen to have the highest gravimetric energy density (LHV of 120.2, HHV of 142.2 MJ kg⁻¹) out of all liquid and gas fuels studied [5].

Fuel Cell

Anode	$2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2$	$E^{\circ}_{ox} = 0.00$ vs. SHE	(1.1)
Cathode	$\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$	E°_{red} = -1.23 V vs. SHE	(1.2)
Overall	$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$	$E^{\circ}_{cell} = 1.23 V$	(1.3)

With the importance of hydrogen highlighted, its end use and how hydrogen is implemented must be considered. These concepts are embodied in the term "hydrogen economy", a term coined by John Bockris in 1970 [6,7]. In 2013, Bockris wrote a paper detailing his personal account on the hydrogen economy and its evolution from 1968 to 2013 [8]. In 1968, the initial thought of using a fuel that is less destructive than oil was first conceptualized during a scientific meeting in Stockholm. Preliminary discussions of transporting hydrogen through pipelines subsequently happened. In 1973, the works of Gregory, Ng, and Long analyzed the cost of carrying energy transmission and hydrogen gas as a function of piping distance. Their primary finding was that hydrogen was the cheapest to transport (assuming that the transmission of electricity in that time was 500 kV) up to distances of 400 miles. Distances farther than 400 miles require electrolysis combined with an electrical feed to decrease the piping required [9]. However, Schoots et al. provide a historical breakdown of the piping costs of CH₄, CO₂ and H₂. Their study found that average onshore piping costs (normalized to 2000 km piping length) for CH₄, CO₂ and H₂ 715,000, 788,000, and 854,000 USD respectively while factoring in region, terrain, raw material construction, and labour costs [10].

Hydrogen generation by water electrolysis had the highest feedstock (17.80 \$/GJ) and production costs (29.40 \$/GJ) out of all the fuels considered [11]. The findings from these authors have shown the importance of finding an economically viable water electrolysis process and have shaped the present-day definition of the hydrogen economy. Today, the hydrogen economy must have i) an energy conversion device, ii) a storage system, and iii) a continuous hydrogen production system at industrial scales with efficient distribution networks [5].

Water electrolyzers, in general, have a long history with continuous progress being made over the past 200 years [5,11–14]. In the 1800s, Alessandro Volta and Luigi Galvani disagreed

2

over whether electrical current in a chemical cell was a biological phenomenon. Volta then constructed an apparatus that replaced a frog's leg with brine-soaked paper and connected this to electrodes. Soon after, Volta found that zinc and silver had the largest potential difference out of all the metals investigated, and a pile of sandwiched zinc and silver discs with a brine-saturated cardboard separator was made [15]. This is what is known today as the Volta pile.

Nicholson and Carlisle discovered water electrolysis a few weeks after the Volta pile was invented [12–15]. They constructed a replica of the Volta pile using 34 alternating discs (17 zinc, 17 silver) and a moist piece of cloth or cardboard at each zinc-silver interface. When performing replicates of this experiment, Carlisle placed a drop of water on the uppermost disc to ensure electrical contact between the pile and the wire, which evolved gas [16]. In 1888, Dmitriy Lachinov developed an industrial alkaline electrolyzer for large scale production of hydrogen and oxygen [13,17,18]. By 1902, about 400 industrial water electrolyzers were in operation [12,13].

An explosion of technological growth and development for water electrolysis occurred between the years 1920 to 1980 and was called the "golden age of water electrolysis development" [13,14]. Between these years, hydrogen production capacities have been steadily increasing, and breakthroughs in cell design and architecture were achieved. In the 1920s, 100 MW capacity plants were operated in Canada to provide hydrogen feedstock for ammonia production. In 1939, the first large-scale water electrolysis plant with a capacity of 10,000 N m³ h⁻¹ was in operation in Trail, British Columbia, Canada [12,13] to supplement ammonia production. In 1948, the first pressurized electrolyzer was invented by Zdansky and Londa. A patent referencing the Zdansky/Londa process states that distilled water with KOH as a

3

supporting electrolyte is run in an electrolysis cell operating at 30 bars at a current of 6,600 A [19].

After these developments, the first solid polymer electrolyte membrane (PEM) system emerged. In 1955, the first PEMFC was developed by William Grubb during his time at General Electric [20,21]. These first membranes were made of polystyrene-divinylbenzene sulfonic acid, which was cross-linked with an inert fluorocarbon film. These films had a limited lifetime because the C-H bonds would undergo oxidative degradation under fuel cell conditions [22]. It was not until later in 1966 when perfluorosulfonic-acid membranes (trade name: NafionTM) were tested in a PEMFC. Nafion is produced by copolymerization of a perfluorinated vinyl ether comonomer with tetrafluoroethylene (TFE). The relationship between equivalent weight (EW) and repeating CF₂ chains has been explored elsewhere in a detailed investigation of the material [23]. In the mid-1980s, Yeo [24] and Eisman [25] gave positive reviews on Nafion membranes and their excellent membrane properties in an Electrochemical Society (ECS) meeting. The PEMFC was an enabler for PEMWE technology, as the operating principles are the reverse of a PEMFC [26]. Most cell designs today are based off the Zdansky/Londa alkaline electrolysis cell and the PEMWE cell designs from General Electric. The role of water electrolysis today is shaped by the present meaning of the hydrogen economy and the oil crisis in the 1970s [13,18]. The 2006 study by Bose and Malbrunot discuss the high costs associated with operation and electricity feedstock [11]. With the increase of available renewable energy harnessing systems (e.g., wind, solar, geothermal), there is interest in coupling these renewables with PEMWE systems to overcome the high electricity cost. Many renewable energy sources are highly variable in nature and unreliable sources of constant energy [27]. The viability of harnessing wind, geothermal, tidal and hydroelectric energy are highly dependent on favourable geography, while solar energy depends on when the sun is shining. Water electrolyzers coupled with renewable energy sources are a solution to addressing the intermittent nature of renewable energies by converting excess "free" energy into a storable and transportable form of energy.

There are three major types of water electrolyzers, which are i) Alkaline electrolyzers (either AEM or electrolyte-based like KOH), ii) PEMWE, and iii) Solid Oxide Water Electrolyzers (SOWE). The present-day research of these three electrolyzers was recently evaluated in a journal analytics review by Ogawa et. al [28]. According to his study, there are 1088 publications relating to alkaline water electrolysis (AWE) systems to date with the average publication year around 2004. For PEMWE systems, there are 741 to date with an average publication year around 2009. SOWE also has 741 publications to date with an average publication year of 2011. These numbers correspond with the commercial maturity of each of these technologies, with AWE being the most mature and SOWE being the least mature. Typical operating conditions, cell design, and state-of-the-art performance for these three electrolyzer technologies will be discussed in later sections. Figure 1.1 shows the main conducting ion along with the anodic and cathodic reactions for each of these electrolyzers [29].

5



Figure 1.1: Anodic, cathodic and migrating ion in solid polymer electrolyte for (a) AWE, (b) PEMWE, and (c) SOEC. Reprinted with permission from Springer-Verlag [29].

1.2 Fundamental Electrochemical Principles

Electrochemistry is the branch of science that involves a two-way exchange between electricity and chemical compounds. Parsons provides a good breakdown of the principle findings by Michael Faraday in the mid-1800s, leading to the establishment of electrochemistry as a science [30]. Faraday made a distinction between a negative charge carrier, called the electron, with a heavier charge carrier called an ion. The transfer of electrons to and from chemical species can be written as a redox (reduction-oxidation) couple in reduction form (equation 1.4):

$$\sum_{i} s_{Ox,i} Ox_{i} + ne^{-} \rightarrow \sum_{j} s_{Red,j} Red_{j}$$
(1.4)

where $s_{Ox,i}$ and $s_{Red, j}$ represent the stoichiometric coefficient of an oxidized and reduced species, respectively.

Electrochemical cells, at minimum, require an anode, a cathode, a supporting electrolyte to promote migration of ions (e.g., salt bridge, sulfuric acid), and an external power source if the reaction is non-spontaneous. Electrochemical systems are characterized by their thermodynamics, kinetics, ohmic, and mass transport contributions. The equations for each of these three subcategories will be discussed in subsequent sections.

1.2.1 Electrochemical Thermodynamics: The Nernst Equation

If the temperature, pressure, or activities of an electrochemical system are not at standard conditions, the Nernst equation must be used to calculate equilibrium cell potential ($E_{e,cell}$) at the non-standard cell conditions (equation 1.5):

$$E_{e,cell}(T,P) = E_{cell}^{0}(298K, 1atm) - \frac{RT}{nF} ln \frac{a_{red}}{a_{ox}}$$
(1.5)

where R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹), n is the moles of electrons transferred, F is the Faraday constant (96485 C mol e⁻¹), T is the temperature (K), and a_i is the activity of the species. The value of a_{red} and a_{ox} depends on the state of the species. For solids and liquids, a_i is equal to 1. For ions, the value is its concentration (typically reported in millimolar). For gases, it is the partial pressure of the gas. A full derivation of the Nernst equation from the Gibbs free energy expression can be found elsewhere [31].

1.2.2 The Anatomy of a Polarization Curve: Kinetics, Ohmic, and Mass Transport Contributions

A polarization curve represents the performance of an electrochemical system (e.g., electrolyzers) by showing current (or current density) versus potential. In electrochemical engineering, a polarization curve generally has three distinct regions: i) a kinetic region, ii) an ohmic region, and iii) a mass transport region [32] (Figure 1.2). An overpotential term, η_i , is associated with each of these three regions. A cell voltage balance for a PEMWE (equation 1.6) as a function of equilibrium cell potential and the three corresponding overpotential terms has been developed by Ojong et al. [31].

In the kinetic region, the electrochemical reaction must overcome the activation energy associated with the reaction. In the ohmic region, the behaviour observed is a straight line corresponding to Ohm's law. The resistances of all cell components (e.g., membrane, cell components) are accounted for here. In the mass transport region, mass transport resistances associated with species migration are an important factor. In the case of water electrolyzers, a major mass transport loss is oxygen bubble formation and detachment from catalytic sites.



Figure 1.2: Dominant Loss Factors in a PEMWE. Y-intercept shows exchange current density, i₀[**32**]. Details regarding the factors impacting these losses are discussed in subsequent sections (section 1.2.3 for kinetic (or activation) losses, section 1.2.4 for Ohmic losses, section 1.2.5 for mass Transport Losses).

$$E_{cell} = E_{e,cell}(T,P) + \eta_{act,a} + \eta_{act,c} + \eta_{IR} + \eta_{diff,a} + \eta_{diff,c} + \eta_{bubble,an}$$
(1.6)

1.2.3 Electrochemical Kinetics: The Butler-Volmer Equation and Activation

Overpotential

The expressions for the electrode kinetics, activation overpotential, and Tafel slopes will be developed in this section. Consider the following reversible redox reaction written in the reduction form [33]:

where Ox is the oxidant, and Red is the reductant, respectively. From this, the forward (r_f) and reverse (r_r) rate reactions can be written (equation 1.7 and 1.8, respectively). The net reaction rate is written in equation 1.9

$$r_f = \frac{dN_f}{dt} = k_f C_0(0, t)$$
(1.7)

$$r_r = \frac{dN_r}{dt} = k_r C_R(0, t)$$
(1.8)

And
$$r_{net} = r_f - r_r$$
 (1.9)

where k_f and k_r are the forward and reverse rate constants (mol m² s⁻¹), respectively. When charge is transferred across an electrified interface due to an electrochemical reaction, it is classified as a Faradaic process. If this is true, Faraday's first and second law of electrolysis applies (equation 1.10 and 1.11, respectively).

$$\frac{dq}{dt} = i \tag{1.10}$$

$$\frac{dq}{dt} = nF\frac{dN}{dt} \tag{1.11}$$

When equations 1.10 and 1.11 are combined, it yields an expression for the reaction rate as a function of current (equation 1.12).

$$i = nF\frac{dN}{dt} = nFr \tag{1.12}$$

10
Rearranging the above and ensuring that consistent reaction rate units are maintained (mol $m^2 s^{-1}$), the following expression involving current density (i) can be obtained (equation 1.13)

$$r = \frac{i}{nF}$$
(1.13)

Substituting equation 1.13 into equations 1.7 and 1.8, and if we assign the forward reaction as cathodic and the reverse reaction as anodic, we obtain an expression relating current to the concentration of reactant (equation 1.14):

$$\frac{1}{nF}(i_c - i_a) = k_f C_0(0, t) - k_r C_R(0, t)$$
(1.14)

Under equilibrium conditions (i.e., $i_c = i_a$, LHS = 0), and after taking the natural log of both sides, the following expression is obtained (equation 1.15):

$$\ln k_r - \ln k_f = \ln \left(\frac{C_0(0,t)}{C_R(0,t)} \right)$$
(1.15)

Revisiting the Nernst equation (equation 1.5) and rearranging it for the ratio of oxidant and reductant concentrations yields the following expression (equation 1.16) [34]:

$$\ln\left(\frac{c_o}{c_R}\right) = \frac{nF}{RT}(E - E^0) \tag{1.16}$$

Combining equations 1.15 and 1.16 yields an expression that has the potential, forward rate constant, and reverse rate constant (equation 1.17):

$$\ln k_r - \ln k_f = \frac{nF}{RT} (E - E^0)$$
(1.17)

Equation 1.16 can be differentiated with respect to potential to obtain Equation 1.18.

$$\frac{RT}{F} \left[\frac{d}{dE} \{ \ln k_r \} + \frac{d}{dE} \{ \ln \frac{1}{k_f} \} \right] = 1$$
(1.18)

Since the right-hand side of the equation equals 1, the two terms on the left-hand side of equation 1.18 can be characterized as two symmetry factors (equations 1.19a and 1.19b). These symmetry factors indicate the symmetry in the energy barrier when the potential is changed.

$$\frac{RT}{F}\left[\frac{d}{dE}\{\ln k_r\}\right] = 1 - \alpha \tag{1.19a}$$

$$\frac{RT}{F}\left[\frac{d}{dE}\left\{ln\frac{1}{k_f}\right\}\right] = \alpha \tag{1.19b}$$

Integrating equations 1.19a and 1.19b, using the boundary condition where $k_r = kr^0$ at $E = E_o$, $k_f = k_f^0$ at $E = E^0$, we obtain 1.20a and 1.20b, respectively (note that the forward reaction has a negative sign in the exponential term to respect the polarity of the cathode):

$$k_f = k_f^0 e^{\{-\left[\frac{\alpha F}{RT}\right](E-E^0)\}}$$
(1.20a)

$$k_r = k_r^0 e^{\{\left[\frac{(1-\alpha)F}{RT}\right](E-E^0)\}}$$
(1.20b)

In the case where concentrations of Ox and Red are equal, and potential is maintained at E^0 , then $k_r^0 = k_f^0 = k^0$. When equations 1.20a and 1.20b are combined with equation 1.17, it becomes the Butler-Volmer equation for a 1st order redox reaction (equation 1.21).

$$i = nFk^{0} [C_{0}(0,t)e^{\left\{\left[\frac{(1-\alpha)F}{RT}\right](\eta_{act,a})\right\}} - C_{R}(0,t)e^{\left\{-\left[\frac{(\alpha)F}{RT}\right](\eta_{act,c})\right\}}]$$
(1.21)

Where $\eta = E - E^0$ and is always positive for the anodic polarization, and negative for the cathodic polarization. In a kinetic-dominated region, the reactant concentration at the electrode surface will be equal to the bulk concentration, and the total electrode potential will simplify to a surface electrode potential. When both are true, the Butler-Volmer equation simplifies to the Butler-Erdey-Grúz-Volmer (BEGV) equation (equation 1.22). This form of this equation allows for extraction of electrokinetic parameters, which is discussed in section 1.2.4.

$$\frac{i}{i_o} = e^{\left\{-\left[\frac{(1-\alpha)F}{RT}\right](\eta_{act,a})\right\}} e^{\left\{\left[\frac{\alpha F}{RT}\right](\eta_{act,c})\right\}}$$
(1.22)

1.2.4 Electrochemical Kinetics: Electrokinetic Parameter Extraction and Limiting Cases

The BEGV equation allows for extraction of two important electrokinetic parameters: i) exchange current density (i_o), and ii) Tafel slope (b). The exchange current density is a measure of the intrinsic electrocatalyst activity. The Tafel slope is a characteristic parameter that indicates a reaction pathway. For electrolysis applications, the system typically operates at a high overpotential in practice (i.e., $\eta > 50$ mV). Under these conditions, the cathodic term of the BEGV equation is neglected since the contribution is small (equation 1.23).

$$\frac{i}{i_o} = e^{\left\{ \left[\frac{(1-\alpha)F}{RT} \right] \left(\eta_{act,a} \right) \right\}}$$
(1.23)

The term in the exponential preceding the anodic overpotential can be grouped as follows (equation 1.24).

$$b_{act,a} = \frac{(1-\alpha)F}{RT} \tag{1.24}$$

From this, the Tafel equation (Equation 1.25) can be shown by combining Equations 1.23 and 1.24.

$$\eta_{act,a} = b_{an} \cdot \ln\left(\frac{|i|}{|i_o|}\right) or \ \eta = b_{an} \cdot \left[\ln(i) - \ln(i_o)\right] \tag{1.25}$$

The form of equation 1.25 is in the form of the equation of a straight line (y = mx + b), where i_0 can be solved for algebraically when $\eta = 0$. The i_0 is an extrapolated parameter and provides only an order of magnitude estimate of the intrinsic electrocatalytic activity (e.g., the rate of reaction at equilibrium and at zero overpotential) [33].

1.2.5 Ohmic Losses

The ohmic overpotential term is equal to the sum of all resistances in the cell. These resistances are categorized as inhibitors of either ionic or electronic flow. Ionic resistances are typically higher for solution-based systems compared to solid polymer electrolyte-based systems, and electronic resistances depend on the bulk and interfacial contact resistances, which may change during operation (e.g., oxidation of Ti porous transport layers). For PEM-based systems, factors that contribute to total resistance are the membrane, electrolyte, flow field plates, current collectors and electrical connectors [4]. The general equation for the ohmic potential is shown in Equation 1.26:

$$\eta_{ohmic} = I \sum_{j} R_{j} = I \sum_{j} \frac{\rho_{j} L_{j}}{A_{j}} = I \sum_{j} \frac{L_{j}}{\sigma_{j} A_{j}}$$
(1.26)

Where I is the total current (A), R_j is the electronic/ionic resistance of component j (Ω), ρ_j is the resistivity of component j ($\Omega \cdot m$), σ_j is the conductivity of component j ($\Omega \cdot m$), L_j is the thickness of component j (m), and A_j is the cross-sectional area of component j.

To calculate the resistance of the cell components, resistor network models for calculating the cell resistance of cell components (e.g., porous transport layer and bipolar plates) can be used (Figure 1.3). These network models consider the resistance of the bulk material and the interfacial contact resistance between two dissimilar materials. For a breakdown of such resistance models, the works of Fritz [35] and Marangio [36] are excellent references.



Figure 1.3: Resistor network model for a PEMWE. Reprinted with permission from ECS [35].

In liquid alkaline electrolyzers, the electrolyte is responsible for ion transport. In this case, an expression for the ionic conductivity in liquid electrolytes can be used (equation 1.27):

$$\sigma = \sum_{j} z_{j}^{2} F^{2} \tilde{\mathbf{u}}_{j} C_{j} = \sum_{j} \lambda_{j} C_{j}$$
(1.27)

where σ is the conductivity of the electrolyte (S m⁻¹), z_j is the charge of ion j, \tilde{u}_j is the mobility of ion j (m² mol J⁻¹ s⁻¹), and λ_j is the ionic molar conductivity (S m² mol⁻¹).

For dilute solutions of a strong binary electrolyte which undergoes complete dissociation, the conductivity can be expressed in terms of molar conductivity, Λ (equation 1.28):

$$\sigma = \sum_{j} \lambda_{j} C_{j} = (s_{+} C_{+} + s_{-} C_{-}) = (s_{+} \lambda_{+} + s_{-} \lambda_{-}) \cdot C = \Lambda C$$
(1.28)

where Λ is the molar conductivity (S \cdot m² mol⁻¹), C is the concentration of the binary salt

(mol m⁻³), and s_+ and s_- represent the stoichiometric number of cation and anions in the salt.

Cecil et al. report that for electrolyte concentrations below 0.1 N, the expression for strong binary electrolyte poorly predicts the molar conductivity. For low concentrations of electrolyte, Kohlrausch's law is used to calculate molar conductance (equation 1.29) [37].

$$\Lambda = \Lambda^0 - K\sqrt{C} \tag{1.29}$$

where Λ^0 is the molar conductivity at infinite dilution, K is a constant, and C is the concentration of the salt. The molar conductivity at infinite dilution could be further expanded in a similar vein as equation 1.30:

$$\Lambda^{0} = (s_{+}\lambda^{0}_{+} + s_{-}\lambda^{0}_{-}) \tag{1.30}$$

where s_{+} and s_{-} are the stoichiometric coefficients of the anionic and cationic salts, and the λ_{+}^{0} and λ_{-}^{0} terms are the ionic molar conductivities of the anion and cation at infinite dilution. When the equation is in this form, the ionic molar conductivities can be found in physical chemistry databases, for example.

If a membrane is used instead of a liquid electrolyte (as in the case of PEM-based systems), equation 1.31 describes the ionic overpotential ($\eta_{ohmic, m}$) [31]:

$$\eta_{ohmic,m} = \frac{d_m}{\sigma_m} i \tag{1.31}$$

where d_m is the thickness of the membrane (m), σ_m is the conductivity of the membrane (S m⁻¹), and i is the current density (A m⁻²). Protonic conductivity of the membrane depends on the extent of membrane hydration (λ_{mem}) and operating temperature (T). The protonic conductivity of NafionTM-based membranes has been studied and the following empirical relationship has been developed by Springer et al. (equation 1.32) [38]:

$$\sigma_{membrane} = (0.005139\lambda_{mem} - 0.00326) e^{(1268\left(\frac{1}{303} - \frac{1}{T}\right))}$$
(1.32)

16

The value of λ_{mem} ranges from 14 to 25 and represents the number of water molecules per sulfonic group. For the PEMWE, the value of λ_{mem} is assumed to be 25 (i.e, fully hydrated).

1.2.6 Mass Transport Losses

Mass transport losses in water electrolyzers can be divided into two categories: i) the rate of water supply and removal of product gases from the active sites of the catalyst layer, and ii) the formation of bubbles, which block the catalyst surface.

An expression for the water feed to water removed (ξ) developed by Selamet et al. (equation 1.33) [39]:

$$\xi = \frac{\dot{m}_{in}}{\dot{m}_{cons} + \dot{m}_{eo}} \tag{1.33}$$

Where \dot{m}_{in} is the mass flow of water into the cell, \dot{m}_{cons} is the rate of water consumed by electrolysis, and \dot{m}_{eo} is the amount of water lost to electro-osmotic drag to the cathodic side

In the first category of mass transport losses, the mass transport limitations are treated as a diffusion-controlled phenomenon. At low current densities (e.g., mA cm⁻² range), the slow removal of dissolved gases from the PTL/catalyst layer interface contributes to the diffusion overpotential. Equations from the works of Fritz and Marangio have been applied for each half cell (equations 1.34 and 1.35) [35,36]:

$$\eta_{diff,an} = \frac{RT}{n_{an}F} \ln\left(\frac{C_{O2,mem}}{C_{O2,ref}}\right)$$
(1.34)

$$\eta_{diff,cat} = \frac{RT}{n_{cat}F} \ln\left(\frac{C_{H2,mem}}{C_{H2,ref}}\right)$$
(1.35)

where $C_{O2, ref}$ and $C_{H2, ref}$ are the concentrations of dissolved oxygen and hydrogen taken at the PTL/BIP interface.

At higher current densities ($\geq 0.1 \text{ A cm}^{-2}$) evolved oxygen bubbles on the anode electrode can coalesce and shield the active sites of the catalyst layer. This reduces the available active

surface area and decreases catalyst utilization. Ojong et al. derived an expression for bubble overpotential based on the BEGV equation, but modified for the mass transport region for the anode (equation 1.36) [31]:

$$\eta_{bubble,an} = \frac{RT}{\alpha_{an}Fn_{an}} \ln\left(\frac{i}{i_{lim}}\right)$$
(1.36)

where i_{lim} is the limiting current density due to bubble coverage and water starvation at high current densities (e.g., > 3 A cm⁻²). Equation 1.37 was proposed by Derhoumi to calculate j_{lim} [40]:

$$j_{lim} = j(1 - \theta) \tag{1.37}$$

where θ is a bubble coverage parameter that ranges between 0 and 1. Combining equations 1.36 and 1.37 yields equation 1.38:

$$\eta_{bubble,an} = \frac{RT}{\alpha_{an}Fn_{an}} \ln\left(\frac{1}{1-\theta}\right)$$
(1.38)

There have been empirical modifications to the above equation and to θ to capture the exponential behaviour in the mass transport region [31].

1.3 Alkaline Water Electrolyzers

Alkaline water electrolyzers are the first type of water electrolyzer to be commercialized (see section 1.1 for more details). The anodic, cathodic, and overall cell reactions are shown below (Equations 1.39 - 1.41):

Alkaline Water Electrolyzer

Overall	$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$	$E^{\circ}_{cell} = -1.23 V$	(1.41)
Cathode	$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$	$E^{\circ}_{red} = 0.83 V vs. SHE$	(1.40)
Anode	$\frac{1}{2}O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$	$E^{\circ}_{ox} = -0.40 V vs. SHE$	(1.39)

There are two types of alkaline electrolyzers: i) liquid alkaline water electrolyzers, and ii) anion exchange membrane water electrolyzers (AEMWE). Liquid alkaline electrolyzers typically use 30% KOH as the electrolyte while AEMWE use anion exchange membranes. The operation and cell structure for both liquid and AEM water electrolyzers is discussed in section 1.3.1 and 1.3.2, respectively.

1.3.1 Liquid Alkaline Water Electrolyzers

Liquid alkaline water electrolyzers are a longstanding technology that has had proven lifetimes of up to 15 years [41]. These electrolysis cells typically have Pt or Ni or Ni-alloy based catalyst on the anode, use 30 wt% KOH as the supporting electrolyte, and operate at 80°C with a maximum current density of about 0.4 A cm⁻² [14,42]. The expected stack lifetime is < 90,000 hours, with a system lifetime of about 20 to 30 years, and a degradation rate of < 3 μ V h⁻¹ [43].

Nickel is usually the anode electrocatalyst of choice because of its availability, resistance to alkali attack, good electrocatalytic activity towards the OER and low cost. The anodic and cathodic chambers are separated by a diaphragm (e.g., polyolefin spacers with 0.5 - 12 mm pore

sizes) or other similar gas separators to prevent mixing of the product gases [13]. The gas separators are typically plastic meshes which support membranes (if any), to prevent interelectrode contact (i.e., shorting), and promote turbulence (i.e., good mixing). A typical alkaline water electrolyzer system showing the migration of gaseous and ionic species is shown in Figure 1.4 [44].



Figure 1.4: A liquid alkaline electrolyzer with migration of species within [44]. Reprinted with permission from © 2012 IEEE.

Although liquid alkaline water electrolyzers use non-precious metal catalysts and have a lower cost, they have characteristics that have been criticized in the literature. For nonmembrane based technologies, some of the major criticisms include: i) a much lower maximum current density compared to the PEMWE due to the high ohmic resistances from the liquid electrolyte and across the diaphragm [42], ii) difficult to start-up/shut down, and iii) potential gas crossover leading to explosive mixtures [5,14,45]. There have been several cell architectural changes to address these shortcomings. A zerogap separator system can be used to minimize the ion transport distance between the separator and the electrodes. In this system, the anode and cathode electrodes directly contact the porous separator (igure 1.5). This reduces the ionic transport resistance in the ohmic overpotential term. Manabe et al. discuss the use of such a system adopted from the cell architecture observed in the chlor-alkali (C/A) system [46].



Figure 1.5: Cell schematic of a zero-gap alkaline electrolyzer [46]. Reprinted with permission from Electrochimica Acta.

Liquid alkaline electrolyzer cells can be operated in unipolar (parallel) or bipolar (series) configuration (Figure 1.6). In a unipolar configuration, the total voltage applied to the cell is equal to the voltage of each of the individual cells. This configuration of the electrolyzer is much easier to fabricate and requires low maintenance but have high ohmic losses. In the bipolar

configuration, the cells are connected in series and the current is the same in each cell. The anode and cathode are placed on opposite sides of a substrate (called the bipole) and are not connected to a power supply. This intricate design results in lower ohmic losses and higher currents compared to the unipolar design. However, care must be taken in maintenance and leak mitigation and it is impossible to repair without servicing the entire stack [13].



Figure 1.6: Electrolyer configurations using a a) unipolar, and b) bipolar cell. Reprinted with permission from Quimica Nova [13].

1.3.2 Anion Exchange Membrane Water Electrolyzers

AEMWE technology use a selectively permeable anion exchange membrane instead of aqueous KOH to separate hydrogen and oxygen gases while facilitating OH⁻ transfer. The advantages that an AEMWE has over liquid alkaline electrolysis are: i) the use of a low concentration of alkaline solution (e.g., 1% K₂CO₃ solution) which eliminates precipitation of K₂CO₃, which is an issue with conventional systems using KOH, ii) the quaternary ammonium ion-exchange-groups used in certain AEMs are less expensive than Nafion-based ones, and iii) avoiding the use of concentrated KOH (i.e., 1 M KOH is often used) increases ease in handling and reduces the physical footprint of the cell [47].

Many studies on the topic of AEMWEs heavily reference the Tokuyama A-201 AEM and AS-4 ionomer as classic benchmark materials. [48]. Table 1.1 shows some of the relevant properties of the A-201 membrane and AS-4 ionomer.

Table 1.1: Properties of the Tokuyama A-201 AEM and AS-4 ionomer summarized from [47,48].

	A-201 (AEM)	AS-4 (Ionomer)
Thickness (µm)	28	-
Ionic Conductivity (mS cm ⁻²)	42 (at 23°C)	13
Stability	> 200 hours (in H ₂ O at 65°C	-
Solubility	Unspecified	Insoluble in H ₂ O, MeOH, EtOH Soluble in iso-propanol

In 2017, Vincent et al. provided a brief literature summary on the types of AEMs used, the cathode catalyst, anode catalyst, and electrolyzer performance at a designated potential (Table 1.2) [47]. Acta 3030 is a CuCoO_x catalyst used for the OER, and Acta 4030 is a Ni/CeO₂-La₂O₃/C catalyst used for the HER. PSF is a polysulfone-based membrane. The mm-qPVBZ/Cl⁻ is a methylated melamine grafted poly(-vinyl benzyl chloride) based membrane. The LDPE-g-VBC is a low-density polyethylene with vinylbenzyl chloride as a graft monomer. The synthesis of, and degradation chemistry of LDPE-g-VBC membranes has been covered recently in 2018 by Espirutu et al. [49].

 Table 1.2: Summary of AEM membrane types, catalysts and reported current performance at a specified

 potential. Summarized from Vincent et al. [47].

Reference	Membrane	Anode Catalyst	Cathode Catalyst	Current Density (mA cm ⁻²)	Potential (V)
Pavel [50]	Tokuyama A-201	Acta 3030	Acta 4030	470	1.9-2.01
Leng [51]	Tokuyama A-201	IrO ₂	Pt Black	399	1.8
Parrondo [52]	PSF, In-house	Ru Perchlorate	Pt	400	1.8
Faraj [53]	LDPE-g-VBC Dabco	Acta 3030	Acta 4030	460	2.1-2.2
Cao [54]	mm-qPVBz/Cl-	Cu _{0.7} Co _{2.3} O _{4s} nanoparticles	Ni Nanopowder	100	2.05
Wu and Scott [55]	radiation grafted quaternary ammonium functional group membrane	Li _{0.21} Co _{2.79} O ₄	Ni Powder	300	2.05

The data from Table 1.2 suggests that the earlier studies on AEM is not much better compared to liquid alkaline water electrolyzers (0.2-0.4 A cm⁻² at 1.8-2.4 V quoted as a performance benchmark by Smolinka et al. [43]). One of the most critical concerns regarding AEM technology is the poor chemical stability of the membrane. Leng et al. associate the membrane degradation with the nucleophilic attack on the cationic fixed charged sites by the

OH⁻ anion. This degradation decreases the number of anion-exchange groups, and therefore decreases OH⁻ conductivity [51]. MEAs fabricated with the Tokuyama A-201 with AS-4 ionomer have shown degradation rates of about 500 μ V h⁻¹ over a 200 hour test at 500 mA cm⁻² at 60°C [47]. These degradation rates are much higher compared to the quoted 3 μ V h⁻¹ benchmark from Smolinka et al. [43].

More recent studies (e.g., within the last two years) have focused on improving the membrane stability and performance by exploring different membrane structures and fabrication methods. Cho et al. modified the fabrication process of IrO₂-based MEAs using the Tokuyama A-201 AEM by adjusting the amount of PTFE in the anode ink (5 - 20 wt %), and the temperature of the hot-pressing step (no hot press, 20, 50 and 80°C) [56]. PTFE was selected as a durability-enhancing agent because of the chemical bond strength of repeating $-[CF_2 - CF_2]$ units. They reported up to 800 mA cm⁻² from a modified MEA using 9 wt % PTFE and using hot pressing conditions of 50°C. This was a significant improvement over the 100 - 400 mA cm⁻² current densities reported from earlier studies in Table 1.2. In 2019, Park et al. performed a rigorous experimental-based AEMWE optimization study, simultaneously examining the effect of hot pressing, reactant feed concentration, cell temperature, porous transport layer (e.g., thickness) and catalyst loading using a new AEM (FAA-3-50, Fumatech Germany) [57]. They achieved 1.5 A cm⁻² at 1.9 V at 70°C using 1.0 M KOH at a flow rate of 2.5 mL min⁻¹. Park explained that the decision to use CCM-based fabrication method over a CCS-based (catalyst coated substrate) contributed to the reported performance. One of the most impressive results in the field of AEMWEs is the use of a newly-developed 2,2",4,4",6,6"-hexamethyl-p-terphenylene polydimethylbenzimidazolium (HTM-PMBI) with a plasma-sprayed Ni-based electrodes by Wang et al. [58] .They report 2 A cm⁻² at 2.1 V at 60°C using a NiAlMo catalyst, while also

25

reporting good stability within a 154-hour time frame. Overall, there has been much advancement in this field within the last two years, focusing on new types of membranes and alterations to the MEA fabrication process.

1.4 Polymer Electrolyte Membrane Water Electrolyzers

In this section, the review paper from Spöri, Kwan, et al. will be heavily referred to, as the author of this thesis made significant contributions to this review paper on OER catalyst stability.

PEMWEs are a more recent water electrolysis technology with increasing global interest and research activities (see Section 1.1 on Ogawa's journal analytics) [28]. PEMWEs use a gastight solid-phase polymer membrane (≤ 0.2 mm thickness) with H⁺ as the charge carrier. Commercially available MEAs for PEMWE (e.g., Solvicore E300E) generally use an unsupported nanoparticulate Ir or IrO₂-based anode (mass loadings of 0.05 – 2 mg cm⁻²), and Pt on carbon support (mass loadings of 0.3 – 0.4 mg_{Pt} cm⁻²) for the cathode. The equations for the PEMWE are shown below (equations 1.42 – 1.44):

PEMWE

Anode	$\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$	$E^{\circ}_{ox} = -1.23 V vs. SHE$	(1.42)
Cathode	$2H^+ + 2e^- \leftrightarrow H_2$	$E^{\circ}_{red} = 0.00V$ vs. SHE	(1.43)
Overall	$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$	$E^{\circ}_{cell} = -1.23 V$	(1.44)

A general schematic of a PEMWE showing the migration of ions and product gases is shown in Figure 1.7. Water splits into oxygen, H⁺, and e⁻ on the anode side (oxygen evolution reaction, or OER). The H⁺ migrates across the membrane and reduces to hydrogen gas on the cathode side (hydrogen evolution reaction, or HER). PEMWEs typically operate at a cell temperature of 50-80°C, a cell pressure of 30 barg, at 0.6 - 2.0 A cm⁻², and at stack efficiencies of about 77%.



Figure 1.7: PEMWE showing the migration of species within [44]. Reprinted with permission from © 2012 IEEE.

Some of the operational advantages that the PEMWE has over alkaline electrolysis are: i) the ability to operate at higher current densities (therefore higher gas production rates), ii) low hydrogen crossover rates (safer operation), and iii) the ability to electrochemically compress the gas prior to discharge into a storage unit (e.g., gas cylinder). A common figure of merit in PEMWE literature is to report the potential at a current density of 2 A cm⁻², which is much higher than the maximum allowable current density of 0.4 A cm⁻² for many alkaline water electrolyzers. MEAs made with Nafion® 117, a commercial membrane product, have a low hydrogen permeability (< 1.25×10^{-4} cm³ s⁻¹ cm⁻², 1 atm, 80°C, 2 mA cm⁻²) [59]. PEMWEs can operate at high pressure (which is dependent on the thickness of the membrane) or differential pressure mode. Operating at high pressures (e.g., 30 barg) electrochemically compresses the

product gases. This decreases the amount of additional work required to further compress gases to meet storage requirements.

The PEMWE also has several disadvantages: i) high activation overpotential for the oxygen evolution reaction, ii) the dependence on noble metal catalysts for the oxygen evolution reaction, and iii) relatively lower durability ($\approx 20,000$ hrs) compared to liquid alkaline electrolyzers ($\approx 90,000$) hours). These disadvantages with respect to the PEMWE cell components are discussed in the upcoming sections.

1.4.1 Choice of PEMWE Catalyst Material

The choice of PEMWE catalyst material must meet several important criteria: i) it must be active towards the rate-determining reaction, ii) it must be stable under typical cell operating conditions, and iii) it must be economical. A fuel cells and hydrogen joint undertaking (FCHJU) study in 2014 has shown that electricity accounts for 70-90% of the production cost of hydrogen on a per mass basis [60]. It has been established that the anodic OER is the rate-determining step (RDS). Therefore, reducing the activation overpotential of the reaction is of extreme importance. A review article by Dau et al. shows a current density disparity of 11 orders of magnitude between the anodic ($\approx 10^{-9}$ A cm⁻²) and cathodic ($\approx 10^2$ A cm⁻²) exchange current densities in a PEMWE using a Pt-based catalyst [61]. Carmo reports current density disparities for a PEMWE operating at 80°C ranging from 1 to 9 orders of magnitude between the Pt-Ir anode and a Pt cathode [42].

OER reaction mechanisms have faded in and out of popularity over the past century. Smolinka et al. give a detailed account on the progression of OER mechanisms within the past century, starting from Bockris (1956) to Rossmeisl (2007) [62]. Currently, the Rossmeisl

29

mechanism is one of the most widely accepted mechanisms for the OER [63]. This mechanism consists of four single-electron transfer steps (equations 1.45 - 1.48):

$$2H_2O \rightarrow OH_{(ads)} + H^+ + e^- + H_2O$$
 (1.45)

$$OH_{(ads)} + H^+ + e^- + H_2 O \rightarrow O_{(ads)} + 2H^+ + 2e^- + H_2 O$$
 (1.46)

$$O_{(ads)} + 2H^{+} + 2e^{-} + H_2 O \rightarrow OOH_{ads} + 3H^{+} + 3e^{-}$$
(1.47)

$$00H_{ads} + 3H^{+} + 3e^{-} \rightarrow 0_{2} + 4H^{+} + 4e^{-}$$
(1.48)

For surfaces where oxygen binds too weakly, step 2 is the RDS (equation 1.46). For surfaces where oxygen binds too strongly to the catalyst, step 3 is the RDS (Equation 1.47) [64]. Mom et al. used a Dimensional Function Theory (DFT) approach to calculate the thermodynamic overpotential by taking the higher binding energy from either step 2 or 3 into account (equation 1.49) [65]:

$$\eta_{thermo} = \max(\Delta G_0 - \Delta G_{OH}, \Delta G_{OOH} - \Delta G_0) - 1.23$$
(1.49)

The difference in binding energies (e.g., $\Delta G_0 - \Delta G_{OH}$) is called a descriptor (e.g., x-axis of volcano plot) [64–66]. The choice of descriptor is based on the expected RDS. Volcano plots exhibit pyramidal-like trends for electrocatalysts, and single crystal metals or metal oxides found closer to the top of the volcano have the lowest thermodynamic overpotential. A volcano plot generated from Man et al. [64] show that the Co₃O₄, RuO₂, IrO₂ and PtO₂ oxides that exhibit the lowest thermodynamic overpotential for step 2 (Figure 1.8).



Figure 1.8: OER Volcano plot adjusted to the ΔG_0 - ΔG_{OH} descriptor. Reprinted with permission from ChemCatChem [64].

OER catalysts must have excellent Pourbaix stability in addition to having a low thermodynamic overpotential for the RDS. Many of the non-noble transition metal oxides shown in Figure 1.8 would degrade severely in the harsh operating conditions of PEMWE (e.g., potentials between 1.4 - 2.0 V, temperatures of about 80°C). This severely limits the choice of catalyst used for the PEMWE.

The activities of Ru, Ir and Pt-based catalysts are three of the most frequently reported in the literature [5,67,68]. In general, Ru has the worst stability out of the three catalysts. The degradation of Ru at potentials 200 mV above the equilibrium cell potential in acidic electrolysis has been discussed by Izgorodin et al. [69]. Ru changes into the soluble RuO_4^{2-} species under

these conditions. Reier et al. show rapid deterioration of cyclic voltammogram features of both bulk and nanoparticulate Ru [68]. Pt forms a poorly conducting oxide at OER potentials. Damjanovic et al. found that the growth of a Pt oxide film, even 10-15 Å thick, changes the electron tunneling dynamics and decreases conductivity [70]. The activity of Ir is slightly worse than Ru, but it has better stability (i.e., lower dissolution rates). One of the earliest studies characterizing Ir, Ru, Pt and their respective alloys was performed by Miles et al [67]. They reported the oxygen evolution potential (vs. SCE) at 2 mA cm⁻² for Ru, Ir and Pt to be 1.16, 1.28 and 1.60 V, respectively. Iridium oxides (e.g., IrO₂) are the preferred anode catalyst for the OER due to their high conductivity [71]. Commercial catalysts are usually unsupported IrO₂ nanoparticles, which have a low electrochemical surface area (ECSA) and are expensive. Current research efforts are aimed towards using reduced precious metal loading tertiary catalysts (e.g., RuIrCoO_x) or using new catalyst structures (i.e., core-shell nanoparticles) to improve ECSA [72,73].

1.4.2 Choice of PEMWE Porous Transport Layer

The PTL plays multiple roles in the PEMWE: i) good electrical connection between electrode and the bipolar plate, ii) efficient mass transport of water and evolved gases between electrode and channel landing, and iii) provide mechanical support to the membrane, especially under compression [42]. The current collector must also be stable in the harsh operating conditions of a PEMWE (i.e., acidic conditions, high overpotentials). Currently, the state-of-theart materials for PEMWE PTLs are Ti-based for the anode side, and Ti or carbon paper on the cathode side (Figure 1.9). Passivation of the Ti to TiO₂ in the PTL leads to significant increases in ohmic resistances. Lohoff et al. report a voltage degradation rate of 194 μ V h⁻¹ after a period of 1000 hours, concluding that 78% of the degradation can be explained by the passivation of the anodic PTL [74].



Figure 1.9: PEMWE sketch showing the PTL and separator (or bipolar) plates. Reprinted with permission from Elsevier [75].

Several notable experimental and modelling studies on the role of a Ti-PTL in a PEMWE focus on the physical characteristics such as PTL wettability, pore size, PTL thickness, and porosity. Currently, the reported optimum PTL properties vary wiedely in the literature. Grigoriev et al. performed an experimental optimization study of in-house made sintered Ti-PTLs in a 7 cm² (active area) PEMWE by testing 11 different samples of varying pore size and porosity. They concluded that the optimal pore size is 12-13 microns and the optimal spherical powder size is 50 to 75 microns [76]. Li et al. performed an anode and cathode current collector study on titanium meshes and found that the best performing mesh (1.69 V at 100°C at 2 A cm⁻²) had an average pore diameter of 21 um and an overall PTL thickness of 0.2 mm [77]. The optimal porosity reported in the literature ranges from 50-75% according to two individual

studies by Ito et al [78,79]. Current collector property optimization is an ongoing study in this field due to the varied reported results in the literature.

Given the variability in reported optimal PTL characteristics in the literature, modelling studies in more recent years have attempted to determine desirable PTL characteristics on a fundamental level. The PTL must first facilitate unhindered water access to the anode catalyst layer while ejecting evolved bubbles in a facile manner. Nouri et al. performed a modelling study on bubbles evolving from pores in a PEMWE. They concluded that tuning the PTL to reduce the number of coalescence host sites (e.g., sites at the PTL-channel interface where bubbles join a larger growing bubble) will reduce the anodic overpotential [80]. Ito et al. performed a wettability study on current collectors and emphasized PTL hydrophilicity to pull water in towards the catalyst from the pores [81]. In addition to these models, PEMWE visualization studies starting from 2014 have provided insight on bubble nucleation and detachment [39,75,82,83]. To further narrow down current collector selection and selection, the major findings from PEMWE models coupled with such visualization studies are needed to make progress in this area.

1.4.3 Figures of Merit and Key Performance Indicators (KPI)

The importance of common figures of merit in the literature provides a common guide to compare electrolyzer performance between research laboratories. For fundamental kinetic studies (i.e., RDE), the onset potential of OER/HER catalysts have been reported by Reier, Spöri and Wang [5,18,68]. This can be done qualitatively by reporting the potential when the current is non-zero or reported at a fixed low current density $(0.5 - 1 \text{ mA cm}^{-2})$. The closer the onset potential is to the equilibrium cell potential, the more energy efficient the system is. The

34

exchange current density and Tafel slope are also frequently reported parameters. The exchange current density of state of the art Ir-based catalysts ranges from 10^{-7} to 10^{-9} A cm_{geo}⁻² [31,42].

Figures of merit for stability are challenging as these have not been developed as rigorously compared to PEMFCs. McCrory was one of the first authors to emphasize the lack of standardized tests in OER stability results [84]. In the literature, researchers have reported arbitrary runtimes and cell conditions for degradation tests. If a catalyst was unstable, the time for a sudden voltage spike to occur was reported (Figure 1.10) [85]. Spöri, Kwan et al. have attempted to generalize these stability figures of merit by suggesting a general stability protocol. A preliminary stability test should reflect the most commonly reported test conditions in the literature. For preliminary catalyst screening, this was determined to be a 1 A cm⁻² test for 24 hours at 80°C and 1 atm [5]. A more thorough catalyst degradation study would be a 2 A cm⁻² test for 100 hours. These numbers were selected based on the capabilities of most single-cell electrolyzer hardware (e.g., Greenlight E20 Electrolyzer), and the DOE targets of sustained operation (e.g., 50,000 hours runtime or longer until failure) at 2 A cm⁻² as recommended by Ayers et al. [86].



Figure 1.10: Lifetime tests of a Ru_{0.8}Nb_{0.2}O₂ (red, less steep) and the less stable RuO₂ (black, steeper). Reprinted with permission from Elsevier [85].

Key performance indicators (KPI) of an electrolysis system reflect the figures of merit in a stack environment. These were summarized by Smolinka et al. [62]:

- Hydrogen production rate [N m³ h⁻¹]
- Electrical power consumption
- Hydrogen pressure after purification and drying
- Hydrogen purity (SAE J2719 standards is 99.998%)
- Faradaic efficiency
- Lifetime
- Stability/Degradation [mV per 1000 hours, or $\mu V h^{-1}$]

The hydrogen production rate and electrical power consumption are consequences of catalyst performance. Spöri, Kwan et al. compiled figures of merit (Table 1.3) from several PEMWE studies (lifetimes and catalyst performance).

 Table 1.3: Performance benchmarks for the PEMWE. Bolded entry is run at above 120°C. Reprinted with

 Permission from Angewandte Chemie [5].

E versus	j	Voltage Degradation	PGM Loading	Runtime [h]	Ref.
RHE		$[mV h^{-1}]$	$[mg cm^{-2}]$		
[V]			-		
-	10 A g ⁻¹	-	-	-	Fabbri [66]
-	10 mA cm^{-2}	-	-	2	McCrory [84]
1.65	1.6 A cm ⁻²	0.006	-	60,000-80,000	Colella [87]
1.7	1 A cm ⁻²	< 0.02	< 0.5	-	Xu [88]
1.5	2 A cm ⁻²	-	2	50,000	Ayers [86]
1.55	1 A cm ⁻²	20	2	5,000	WELTEMP [89]
-	-	-	-	40,000	NEXPEL [90]
-	-	< 0.015	0.5	40,000	NOVEL [91]

1.5 Solid Oxide Water Electrolyzers

Solid oxide water electrolyzers or solid oxide electrolysis cell (SOWE or SOEC) operate at high temperatures (600°C to 1000°C), use relatively inexpensive raw ceramic materials (not including processing of materials) for ion transport, and have higher faradic efficiencies (100% current efficiency achievable) compared to alkaline and PEM water electrolyzers [92]. The advantage of using SOECs is that they can be repurposed from solid oxide fuel cell (SOFC) infrastructures, and operate at high temperatures to reduce the thermodynamic potential required to split water [93]. The first SOEC was the HotElly project, where a 7-cell stack operated at a temperature of 1003°C, a current density of 0.3 A cm⁻² and at a potential of 1.07 V [94]. The reactions involved in a SOEC are in equations 1.50 - 1.52.

Anode	$\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}$		(1.50)
Cathode	$H_2O + 2e^- \leftrightarrow H_2 + O^{2-}$		(1.51)
Overall	$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$	$E^0 = 1.23V$	(1.52)

SOEC

State-of-the-art SOECs use an yttria-stabilized zirconia (YSZ) as the electrolyte, lanthanum strontium manganese (LSM) as the anode, and Ni-YSZ or lanthanum strontium chromium manganese (LSCM) doped perovskites as the cathode. A diagram of a typical SOEC cell is shown in Figure 1.12 [95].



Figure 1.11: SOEC cell with migration of species in the YSZ electrolyte. Reproduced with [95] with permission from the Royal Society of Chemistry.

SOECs are currently in the R&D phase and are the least mature out of the three major types of electrolysis systems. A recent journal metrics study has shown that the average publication year for SOEC is 2011, compared to 2004 for alkaline electrolysis and 2009 for the PEMWE [28]. Two of the most important early SOECs experimental studies performed by Brisse [92] and Schiller [96] highlighted the importance of steam content in the feed. Brisse et al. reported an increase in current density (0.4 to 1.1 A cm⁻² at 1.3V) when increasing the absolute humidity from 30 to 80 vol%. Schiller reported cell performance increases with an increase in steam content from 43% to 92%, but commented on this effect being more pronounced at 800°C and less so at 850°C.

In recent years (from 2016 to present), there is a growing interest co-electrolysis of water and carbon dioxide into hydrogen and syngas, respectively. However, this introduces additional complications, such as the composition of the feedstock. Cinti et al. studied the effect of three different feed compositions with different $CO_2/H_2/CO$ mol% (e.g., 20/70/10, 30/60/10, and 40/50/10) on SOEC performance [97]. Although all three feedstocks had similar polarization curves, Cinti reported that the 40/50/10 feed had the largest molar % reduction (molar dry concentration reduction of 80% to 32% at 500 mA cm⁻²). A major criticism of SOEC technology is the poor performance and stability. Current densities are rarely reported above 800 mA cm⁻², since LSM degradation has been reported between the range of 500 to 1000 mA cm⁻² [97]. Galvanostatic durability tests performed by Hauch et al. have shown 100 – 200 mV increases in 100 hours or less [93]. Jensen [98] and Liu [99] have discovered silicon-based impurities at the Ni-YSZ anode in their experiments, which originated from the YSZ feedstock. A possible reason for this cell potential increase is that the Si-buildup at the anode interface layer impacts the diffusion path length for O²⁻.

1.6 Research Objectives

The objective of this research is to develop new characterization tools for the oxygen evolution reaction half reaction. The project research is divided into the following components: 1) Develop a novel modified rotating disk electrode (MRDE) analytical method capable of testing catalyst coated membranes (CCM)

- Demonstrate the viability of this tool by testing fuel cell catalysts first, as the benchmarks are more established in this field
- Screen commercial PEMWE catalysts and CCMs with different current collectors more effectively than existing RDE methods

2) Characterize bubble nucleation and detachment in a modified visualization cell that does not have the disadvantages (e.g., prone to water starvation at current densities of 2 A cm⁻² or greater) of current state-of-the-art visualization cells.

- Demonstrate the ability to achieve current densities up to 2 A cm⁻²
- Identify trends in bubble nucleation using modelling analysis (i.e., bubble detachment periodicity, formation of primary and secondary bubbles)

3) Explore different thin-film Ti current collectors deposited on various substrates, and investigate any other possible PEMWE cell configurations that could decrease the amount of Ti used.

- Identify a Ti deposition technique suitable for PEMWE
- Test low-loading Ti-deposited porous transport layers in the PEMWE hardware
- Examine the effect of no PTL on the anode side

1.7 Thesis Layout

In Chapter 1, much of the material pertaining to catalyst stability and electrokinetic parameter estimation came from the author's contribution to a review paper and a modelling paper, respectively. In the catalyst stability review paper, there was a lack of standards in addressing OER catalyst stability. An experimentally validated semi-empirical model used electrokinetic parameters calculated by the author. The material in this chapter has been published in the following works:

- Ojong, E. T., Kwan, J. T. H., Nouri-Khorasani, A., Bonakdarpour, A., Wilkinson, D. P., & Smolinka, T. (2017). Development of an experimentally validated semi-empirical fully-coupled performance model of a PEM electrolysis cell with a 3-D structured porous transport layer. International Journal of Hydrogen Energy, 42(41), 25831-25847.
- Spöri, C., Kwan, J. T. H., Bonakdarpour, A., Wilkinson, D. P., & Strasser, P. (2017). The stability challenges of oxygen evolving catalysts: Towards a common fundamental understanding and mitigation of catalyst degradation. Angewandte Chemie International Edition, 56(22), 5994-6021.

Chapter 2 has two parts. In the first part, a modified rotating disk electrode (MRDE) tool was designed for the evaluation of fuel cell catalysts. In the literature, there is a discrepancy between classic RDE and PEMFC data, and the MRDE was a tool designed to partially address these discrepancies. Rigorous testing of industry standard catalyst coated membranes (e.g., Johnson-Matthey, Solvicore, Fuel Cells Earth) in the MRDE showed good agreement between fuel cell testing and the MRDE. The material in this section has been published:

Kwan, J. T. H., Bonakdarpour, A., Afonso, G., & Wilkinson, D. P. (2017).
 Bridging Fundamental Electrochemistry with Applied Fuel Cell Testing: A Novel and Economical Rotating Disk Electrode Tip for Electrochemical Assessment of Catalyst-Coated Membranes. Electrochimica Acta, 258, 208-219.

Chapter 3 focuses on the application of the MRDE for oxygen evolution catalysts. Current collector characterization with CCMs could be performed on a benchtop scale, which allows high-throughput testing of current collectors and different CCMs. This provides insight on the combination of current collector properties (e.g., triple contact point, porosity) that lead to improved electrolyzer performance. The material in this section of the chapter is published:

Kroschel, M., Bonakdarpour, A., Kwan, J. T. H., Strasser, P., & Wilkinson, D. P. (2019). Analysis of oxygen evolving catalyst coated membranes with different current collectors using a new modified rotating disk electrode technique. Electrochimica Acta, 317, 722-736.

In Chapter 3, sintered Ti current collectors and expanded metal Ti meshes were tested in a visualization flow cell. The flow cell has a large channel landing, removing the possibility of reactant starvation at high current densities. The effect of catalyst masking and current collector choice was tested in the cell. The chronoamperometric (CA) results were analyzed for trends in bubble detachment, such as bubble periodicity, and primary and secondary bubble formation and detachment patterns. The paper is currently in preparation, where the author of this thesis is the first author.

In Chapter 4, exploratory work concerning the use of thin-film heat barriers was used in a PEMWE test cell in an attempt to decrease the activation overpotential of the OER. A screening

of thermally insulative, but electronically conductive materials was performed to down-select samples of Ti sputtered onto polycarbonate sheets or 3D-printed porous slabs that mimic the physical properties of state of the art PTLs.

Chapter 2: Development of the Modified Rotating Disk Electrode (MRDE) using the Oxygen Reduction Reaction for Validation

2.1 Scope and Context

The rotating disk electrode (RDE) technique is a catalyst characterization method used for many electrochemical applications, including fuel cells, and to a lesser extent, water electrolysis. Dalton provides a brief overview of the physical assumptions that led to the development of the Levich equation, and later the Koutecký –Levich equation [100]. The Levich equation calculates a limiting current density (i_{DL}) as a function of rotation rate, with the key assumption being that mass transport at the rotating disk is well-defined (i.e., does not change with radial distance from axis of rotation). The Koutecký –Levich equation expresses the overall disk current (i_{disk}) as the sum of two individual current contributions: a kinetic current (i_k), and a diffusion i_{DL} . These are shown in equations 2.1 and 2.2, respectively.

$$i_{DL} = 0.62 n_D F A C_A^* D_A^{2/3} v^{-1/6} \omega^{1/2}$$
(2.1)

$$\frac{1}{i_{disk}} = \frac{1}{i_k} + \frac{1}{i_{DL}}$$
(2.2)

In the above set of equations, n is the number of electrons transferred, F is the Faraday Constant (96485 C per mol e⁻), A is the geometric surface area, C_A^* is the concentration of species A in the bulk (mol L⁻¹), D_A is the molar diffusivity of species A (cm² s⁻¹), v is the kinematic viscosity (cm² s⁻¹), and ω is the rotation rate (RPM).

The RDE technique is commonly used for characterizing catalysts that facilitate the ORR half-cell reaction, which is the rate-determining reaction for the PEMFC and of great interest for fuel cell studies [101]. This is done using the thin-film RDE (TF-RDE) technique, which is a variant of RDE involving drop-casting a catalyst ink onto a glassy carbon surface and has been

used since the 1990's [102–104]. The catalyst inks used in the TF-RDE involve small amounts of precious metal catalysts ($0.15 - 0.20 \ \mu g_{Pt} \ cm^{-2}$). The lower capital cost ($\approx 2000 - 3000 \ USD$), ease of handling, and lower precious metal catalyst loading used in the TF-RDE technique make it a more economical testing method compared to fuel cell test stations (capital cost of about $\approx 20,000 - 50,000 \ USD$). The membrane electrode assembly (MEAs) used in these test stations have platinum metal loadings of about $0.3 - 0.4 \ mg_{Pt} \ cm^{-2}$. Established protocols for good TF-RDE technique (e.g., three-electrode cell cleanliness, purity of electrolyte, anion absorption) [101], and impact of ink preparation (with emphasis on catalyst film preparation quality) [105] are present in the literature .

A contentious topic in the ORR research field is the comparability of the TF-RDE result with the PEMFC (or fuel cell test station) result, which has been discussed more in recent years (2014 onwards). In 2005, Gasteiger published an impactful review article benchmarking Ptbased ORR catalysts, and comments on the agreement between PEMFC and the TF-RDE technique. He shows some agreement for specific and mass activity ranges for Pt/C-based catalysts with the PEMFC ($0.07 - 0.16 \text{ A mg}_{Pt}^{-1}$; 110-330 µA cm_{Pt}⁻²) and the TF-RDE ($0.069 - 0.16 \text{ A mg}_{Pt}^{-1}$; 190-230 µA cm_{Pt}⁻²) [3]. However, more recent works have shown a lack of agreement between the two techniques, with differences reported as high as $30 - 100 \times$ between the RDE and PEMFC for Fe-N-C catalysts [106]. In 2014, Kocha et al. presented a Department of Energy (DOE) talk that examined test protocols and testing methods for TF-RDE for studying the ORR. He listed key differences including oxygen delivery to the electrocatalyst, the use of liquid vs. solid polymer electrolyte (SPE), and electrode thicknesses ($\approx 10 \text{ um for PEMFC}$, 0.3-4µm for TF-RDE) [107]. The oxygen in a PEMFC is often high (e.g., equivalent stoichiometry of 10), whereas with RDE systems the amount of dissolved oxygen in a three-electrode cell system

45

is dependent on the diffusivity limit of oxygen in the electrolyte (e.g., $D_{02} = 1.93 \times 10-5 \text{ cm}^2\text{s}^{-1}$ at 25°C [108]. Kriston et al. examine the effect of Pt loading (i.e., loadings of 0.05, 0.1, 0.2, 0.3, and 0.4 mg_{Pt} cm⁻²) on an MEA and evaluated the mass and specific activity in a PEMFC. When the Pt catalyst loading was increased from 0.05 to 0.4 mg_{Pt} cm⁻², they reported a decrease in catalyst utilization (82% to 48%), electrochemical surface area (ECSA of 70.18 to 41.08 m² g⁻¹), specific activity (328 to 209 μ A cm⁻²), and mass activity (240 to 87.5 mA mg⁻¹) when comparing the lowest and highest loading samples [109]. This is an argument against the TF-RDE technique, as thin-film catalysts have very good oxygen diffusion into the catalyst, leading to an overestimation of the catalyst activity when compared to the thicker catalysts used in PEMFCs.

In ORR studies, the activities are normalized to a real surface area, which accounts for porosity and roughness. A standardized method for calculating the real surface area involves determining the ECSA experimentally, integrating the hydrogen under-deposition peak (H_{UPD}) peak, and converting it to a real surface area using the conversion factor of 210 μ C cm⁻² (the charge corresponding to a monolayer of H₂ adsorbed onto platinum) [110].

To summarize, the discrepancy between TF-RDE and PEM-based results for the ORR and OER are attributed to different factors. For the ORR, the extent of oxygen diffusion is lower in thicker catalyst layers, leading to decreased catalyst utilization. Thin-film ORR catalysts will have higher catalyst utilization since the extent of O_2 diffusion is higher, but would overestimate the specific and mass activity and not be representative of its performance in a PEMFC. This is important as the ability to characterize the mass transport region cannot be achieved at the TF-RDE level due to the limited maximum current density achieved by current thin-film catalysts.

The main goal of the MRDE technique is to establish a new method that addresses the catalyst thickness discrepancy in the TF-RDE method resulting in an overestimation of activity
in the conventional RDE technique, while being cheaper than PEMFC hardware. A key feature of this technique is that CCMs are tested instead of using deposited thin-film inks used in conventional RDE setups. This removes the need to prepare these inks, and reduces the issues with non-uniform catalyst dispersion from drop casting. In addition, the MRDE head can accommodate other types of catalyst-coated substrates (e.g., metal foils, gas diffusion electrodes), which provides added utility over conventional RDE setups.

This chapter will cover the research concerning the modified rotating disk electrode (MRDE) applied for ORR studies. A new MRDE tip was developed that uses CCMs instead of thin-film drop casted catalyst films. Performance benchmarks for fuel cell catalysts are rigorously standardized, so the MRDE for the ORR was tested first to verify the functionality of the technique. After the MRDE technique was proven for the ORR, it was applied to characterize PTLs for the OER (Chapter 3).

2.2 Experimental

Much of the MRDE design focused on the construction of the tip. Figure 2.1 shows an a) exploded view and b) a cross-sectional rendering of the MRDE tip. The MRDE head has an exposed area of 0.785 cm² and can hold samples (e.g., CCM, metal foils, and conductive ceramics) up to 10 mm outer diameter. The sample is sandwiched between a current collector (expanded Ti, 0.0508 mm nominal original thickness, Microgrid® model 2 Ti 4-125FA × 9", Dexmet Corporation) and a stepped Teflon back-piece. The tip must secure the sample in place, while providing an electrical pathway to the shaft. Two Ti-wire threading holes were drilled in the sides of the tip. Ti-wire (0.25 mm thickness, 99.7% metals basis, Alfa Aeser) is carefully threaded through this hole, with the ends of the wires slightly extended over the MRDE face to allow contact with the Ti current collector.



Figure 2.1: Modified rotating disk electrode components from an a) exploded view, and b) cross-sectional exploded view.

The three samples used in the ORR investigation and to prove the validity of the MRDE measurement were: i) Pt foil (0.02 mm thickness, 99.9+%, Sterngold Dental), ii) unsupported hand-painted half CCMs (0.1 and 0.4 mg_{Pt}cm⁻², FuelCellsEarth (FCE)), and iii) carbon-supported Pt (Pt/C) half-CCMs (Johnson-Matthey (JM) and Solvicore GmbH & Co. KG (SC) now known as Greenerity GmbH (GR)). Kapton (0.0015-inch adhesive thickness, Matrix Technology Ltd.) was used to mask one side of the Pt foil sample and the inactive side of the CCM sample. This was done to ensure that the other side of the Pt foil sample would not be electrochemically active and not introduce an artifact into the experimental data. The Kapton on the CCM samples provided additional rigidity to the sample, making it easier to assemble and less susceptible to curling when exposed to moisture. All samples were cut into 10 mm diameter disks and were flattened with an applied pressure of ≈ 4 MPa using a hydraulic press (MTI Corporation).

The MRDE tests were performed in a three-electrode cell (125 mL, 5 neck, Ace Glass Products Ltd.), with the MRDE loaded with the sample as the working electrode, a Pt-flag counter electrode (Radiometer Analytical), a Cl⁻ free Hg/Hg₂SO₄ reference electrode (REF621, Radiometer Analytical), and 0.1 M HClO₄ electrolyte (made from 70%, Veritas Double Distilled HClO₄, GFS Chemicals Inc.). The electrolyte was purged with either Ar (99.999%, UHP, Praxair Canada Inc.) for ECSA characterization, or O₂ (99.993%, UHP, Praxair Canada Inc.) for ORR studies.

Prior to testing each sample, an electrochemical cleaning step (i.e., conditioning) was performed by sweeping the potential between 0 and 1.30 V vs. RHE at 500 mV s⁻¹ until steady state CVs were obtained. Once conditioning was completed, performance CVs were collected at some or all of the following sweep rates depending on the sample: 50, 20, 10, 5 and/or 2 mV s⁻¹ both before and after the ORR measurements. The ORR measurements for each sample were swept between 0 V vs. RHE and open circuit potential (OCP) in an oxygen saturated electrolyte, which corresponds to 1.1V vs. RHE (onset of ORR). The scan rates for these samples were 50, 5 and 2 mV s⁻¹ for the Sterngold Pt foil, the 0.1 mg_{Pt}cm⁻² and 0.4 mg_{Pt}cm⁻² CCM samples, respectively. The rotator speeds chosen were 225, 400, 625, 900, and 1225 RPM for the ORR characterization. Initially, the material strength of the thin Ti wire was a potential issue, so the chosen rotation speeds were lower than the benchmark standard of 1600 RPM to prevent potential wire entanglement or breaking. However, it was discovered later that the wires were suitable for the previously mentioned rotation rates. For the accelerated degradation test (ADT), was performed at 1600 RPM in order to be comparable with the US DOE protocol.

Table 2.1 summarizes the experiments performed for each sample, with the box containing an asterix showing the chosen sweep rate reported for the mass and specific activities.

49

The sweep rates of 5 and 2 mV s⁻¹ were chosen to minimize the capacitive response from the carbon-rich sample, while being able to complete the experiment in a timely manner.

 Table 2.1: Experimental sweep rates for CVs and ORRs for each sample. An asterix indicates which sweep

 rate was taken for mass and specific activity analysis for each sample.

	Experiment Sweep Rate (mV s ⁻¹)							
Sample	50	20	10	5	2			
Pt Foil	*							
0.1 mg cm ⁻² CCM				*				
0.4 mg cm ⁻² CCM					*			

For the accelerated degradation tests (ADT), the protocol was adopted from the US DOE protocol [111]. The protocol alternates between rapid cycling CVs collected at 50 mV s⁻¹ between 0.6 - 1 V vs. RHE, and a full CV collected between 0.05 - 1.2V vs. RHE using a sweep rate of 2 mV s⁻¹ instead of the 50 mV s⁻¹ in the DOE protocol. Choosing this slower sweep rate reduces the contribution of capacitive currents (< 4% at 0.9 V), which are significant for high surface area Pt/C catalysts [3]. A description of the full ADT protocol is shown in Appendix A.1, Figure A.1.

Classical TF-RDE and PEMFC experiments were also performed and compared with the MRDE result. A JM Pt/C catalyst ink was drop-casted on top of the tip of a 5.0 mm OD mirror polished glassy carbon RDE (AFE5T050GCPK, Pine Research Instrumentation Inc.) cleaned in DI water and ethanol. The composition of the ink mixture was 5 mg catalyst (Pt/carbon black, 20 wt % Pt, Alfa Aeser, HiSPEC® 3000), 1.99 mL DI water, 0.5 mL isopropanol (Sigma Aldrich Corporation), and 10 µL Nafion ® D-521 dispersion (5% w/w in water and 1-propanol. Alfa Aeser). The deposited ink was air dried and visually checked for uniform catalyst coverage (e.g.,

50

the existence of agglomerates or the characteristic coffee ring structure) on the glassy carbon disk, yielding a loading of 0.0204 mg_{Pt}cm⁻². For the fuel cell test, a Ballard standard test cell (STC, Ballard Power System) with an active area of 45 cm² and a compression pressure of 60 psi (413 kPa) was used. An MEA was fabricated in house using the JM 0.4 mg_{Pt}cm⁻² CCM and hot pressed with a perfluorosulpohnic acid-based membrane (17 μ m, Johnson-Matthey). A conditioning step was performed galvanostatically at 500 mA cm⁻², 100 kPag, anode flow rate of 0.235 NLPM (equivalent stoichiometry of 1.5), and cathode flow rate of 3.74 NLPM (equivalent stoichiometry of 10) at 80°C for 12 hours. The polarization measurements were performed at 100 kPag, 80°C, 100% RH, with anode stoichiometry of 1.5, and a cathode stoichiometry of 5. The current density at each step was held for 180s, and the steady-state potential was the average of the last 90 seconds of each current hold.

The Pt loading (mg cm_{Pt}⁻²) in the CCMs (for as-received and post-ADT samples) was assessed by X-ray fluorescence spectroscopy (XRF, Fischerscope X-Ray XDV-SDD, Fischer Technology Inc.). The XRF used a micro focus tube with beryllium window X-ray source, 1000 μ m Al filter, 200 μ A anode current, 1 mm collimator diameter and a 50 kV beam voltage. Baseline substrate correction scans were performed using an uncoated Nafion membrane (Johnson Matthey) and Kapton film (Matrix Technologies Ltd.). XRF scans were performed in raster mode on a 4 mm x 4 mm grid of 16 evenly-spaced points with a counting time of 60 s per point.

2.3 **Results and Discussion**

The results are reported in the following order: i) Results with an ideal platinum foil sample and the effect of geometric area masking by the Ti current collector, ii) measurements of ORR activity with comparisons to TF-RDE and PEMFC, and iii) durability studies using a modified US DOE protocol for the CCMs. The results are organized in this order to demonstrate the MRDE technique in three stages. The Pt foil results demonstrate the viability of the MRDE technique with what is considered the most ideal sample. ORR curves are obtained with three commercial CCM samples and are compared with each other. The ADT demonstrates an additional MRDE capability that can provide degradation data in an accelerated time frame (e.g., equal to a one-month PEM fuel cell test bench runtime)

2.3.1 Cyclic Voltammogram Analysis

The current collector used to provide an electrical pathway from the CCM to the potentiostat slightly masks the sample (Figure 2.2a). The ECSA between the masked and unmasked case was quantified by integrating the charge of the hydrogen adsorption and desorption peaks (Figure 2.2b). The integrated charge for the H_{ads} region was 203 and 215 μ C for the MRDE loaded with and without the mesh, respectively. The integrated charge for the H_{des} region was 213 and 225 μ C for the MRDE loaded with and without the mesh, respectively. The integrated charge for the H_{des} region was 213 and 225 μ C for the MRDE loaded with and without the mesh, respectively. The ECSA loss due to the Ti mesh masking for both the H_{ads} and H_{des} regions is about 6%. The loss of geometric area due to the projected physical coverage is about 16%. This difference could be explained by some regions under the Ti wire being electrochemically active. The electrochemical contribution of the Ti current collector is small, with Kroschel et al. reporting charges of about 0.02 mC cm⁻² to 0.16 mC cm⁻² for similar types of Ti current collectors [112].



Figure 2.2: a) Open diameter, current collector strand width, and geometric masking of the Ti mesh and b) CVs with and without the Ti Mesh.

The specific activity of the Pt foil using the MRDE was $1.55 \text{ mA}_{\text{kinetic}} \text{ cm}_{\text{Pt}}^{-2}$ at 0.9 V vs. RHE and at 900 RPM. This value agrees with the $1.2 - 2 \text{ mA}_{\text{kinetic}} \text{ cm}_{\text{Pt}}^{-2}$ specific activity range for polycrystalline platinum RDE and demonstrates the validity of the MRDE approach.

The CVs of the Johnson Matthey (JM) and Greenerity (SC) for 0.1 and 0.4 mg_{Pt}cm⁻² loading are compared with the Pt foil baseline (Figures 2.3a – 2.3c). All the CVs for the CCMs show the typical features for Pt (i.e., Pt-H oxidation, Pt-OH formation, Pt-O reduction, and Pt-H formation). These CVs show that the MRDE is free of issues (e.g., leakage, contamination, poor electrical contact) and functions like a proper standard RDE). The ECSAs for all the CCM samples were calculated after the 3rd cycle of each CV, before and after the ORR polarizations (Figure 2.3d). The JM CCM sample had the highest ECSA (75-80 m² g_{pt}⁻¹) out of all samples. The FuelCellsEarth CCM had the lowest ECSA out of all samples investigated (15-20 m² g_{pt}⁻¹), likely due to the inhomogeneous Pt-black distribution from the hand painted procedure used.



Figure 2.3: Cyclic voltammograms of a) Pt foil, b) 0.1 loading mg cm⁻² CCMs, c) 0.4 loading mg cm⁻² CCMs, and d) a summary of ECSA before ORR (left column) and after ORR (right column) for the CCM samples.

2.3.2 Mass and Specific Activity

The CCM ORR activities for JM, SC, and FCE were obtained using rotational speeds ranging from 225 to 1225 RPM. The 0.1 mg_{Pt}cm⁻² and 0.4 mg_{Pt}cm⁻² JM samples for both loadings compared to the Pt foil are shown in Figures 2.4a – 2.4c. The Pt foil sweeps were performed at 50 mV s⁻¹. An issue with electrocatalysts with low roughness factors (e.g., rf \approx 1) is that contamination of the active sites becomes prominent at sweep rates lower than 5 mV s⁻¹ [3]. For polycrystalline Pt, 20 mV s⁻¹ and 50 mV s⁻¹ sweep rates are equally popular choices. The latter sweep rate was chosen to decrease the experimental runtime.

The presence of carbon support in the CCM samples results in large capacitive CV loops that appear in the range of 0 to 0.8 V unless CV-corrected, and the size of these loops scale with increased catalyst loading. Lower sweep rates 5 mV s⁻¹ and 2 mV s⁻¹ were chosen for the 0.1 mg_{Pt}cm⁻² and 0.4 mg_{Pt} cm⁻² samples, respectively, to minimize the capacitive current contribution. For each sample at a given rotation speed, the current density reaches a plateau at the 0 – 0.6 V vs. RHE region. This plateau represents a diffusion limited current, and corresponds to expected values as calculated by the Levich equation. The curves at each rotation rate show coincident currents of about 0 mA at high potentials (e.g., > 0.9 V vs. RHE), indicating complete background correction is performed for the kinetic region.



Figure 2.4: ORR curves showing the first anodic sweep for a) Pt foil, b) JM 0.1 mg_{Pt} cm⁻², and c) JM 0.4 mg_{Pt} cm⁻².

Before discussing the specific and mass activities of the MRDE, TF-RDE and PEMFC, a Nernstian temperature/pressure correction must be applied to the MRDE and TF-RDE result to account for the differences in testing conditions compared to the PEMWE. A method similar to the one used by Pinaud et al. for comparing the half-cell and PEMFC catalytic activities was used [113]. Equation 2.3 was used, where $\Delta E = 0.0078$ V, thus the specific and mass activity measurements for the TF-RDE and MRDE were taken at 0.892 V vs. RHE to compare with the PEMFC data at 0.9 V (Figure 2.5). The full Nernstian calculation is in Appendix A.2 $E_{RDE}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = E_{RDE}(20^{\circ}C, a_{H_2} = 1, a_{O_2} = 1.26 \times 10^{-3}) + \Delta E$ (2.3)

The FCE Pt black CCM sample has relatively high specific activity but low mass activity. There have been literature reports of this trend (high specific activity, but lower mass activity) compared to supported Pt/C CCMs. This is likely due to the inhomogeneous catalyst distribution and poor adhesion of the hand-painted sample with Pt black.



Figure 2.5: Summary of specific and mass activity data for all CCM samples compared with the TF-RDE and PEMFC result. Bars with hashed lines are specific activity.

The key comparison is the JM samples as tested in the TF-RDE ($0.4 \mu g_{Pt} cm^{-2}$), MRDE, and PEMFC method (denoted with a JM-FC). The mass activities reported for the 0.1 mg_{Pt}cm⁻² JM CCM are 111 and 133 mA mg_{Pt}⁻¹ for the MRDE and PEMFC, respectively. The mass activities reported for the 0.4 mg_{Pt}cm⁻² JM CCM are 58 and 86 mA mg_{Pt}⁻¹ for the MRDE and PEMFC, respectively. The MRDE and PEMFC are in closer agreement compared to the TF-RDE result of 227 mA mg_{Pt}⁻¹. This is a factor of 2-3 greater than the mass activity determined by the MRDE or PEMFC techniques. Catalyst loadings exceeding 20 ug_{Pt}cm⁻² have decreasing ECSA with increasing loading, leading to decreased catalyst utilization. This phenomenon was observed by Kriston et al., where the ECSA for 0.05, 0.10, 0.20, 0.30 and 0.40 mg_{Pt}cm⁻² Pt/Cbased MEAs (as measured by H₂/O₂ PEMFC measurements) were 70.2, 67.9, 49.5, 47.6, and 41.1 m²g_{Pt}⁻¹, respectively [109]. This highlights the advantage of testing CCMs with the MRDE, as the catalyst thickness is a constant variable between these two testing techniques (e.g., MRDE and PEMFC), and avoids overestimation of kinetic data with the TF-RDE.

2.3.3 Accelerated Degradation Testing

The 30,000-cycle accelerated degradation test (ADT) experiments and the progression of the ORR curve taken at specific cycles as shown in Figures 2.6a to 2.6c. As a convention, rapid CVs performed between 0.6 - 1.0 V vs. RHE are defined as "ADT cycles", and the CVs between 0 - 1.2 V vs. RHE are defined as "Full CVs". Figure 2.6 shows full CVs collected after 0, 1,000, 5,000, 10,000, 20,000, and 30,000 ADT cycles. It is apparent that considerable changes have occurred in the shape of the full CVs in several regions. The Pt-H and Pt-OH peaks diminish in size with increasing cycle number, indicating a decrease in electrochemically active Pt surface sites for ORR. Both the Pt-H and Pt-OH peak vertexes also shift in the positive direction (e.g., to the right). The onset of the P_{ox} formation shifts to higher potentials (as seen by the sharp incline in the 30,000th cycle at around 1 - 1.2 V), and the formation of a new P_{red} peak is also observed after the 30,000th cycle. The most pronounced changes in the full CVs were observed between the 10,000 and 20,000 cycle period. As a side note, each full CV was performed three times, with no major changes observed between the three replicates.

Figure 2.6b shows the cathodic ORR curves at the same cycle cutoffs as Figure 2.6a (e.g., after 0, 1,000, 5,000, 10,000, 20,000, and 30,000 cycles). The changes in the ORR are easier to discern in the graph inset, where the impact of longer ADT cycling shifts the curve towards the left. Up to and including the 10,000th cycle, the ORR curves nearly overlap. The most visible ORR activity change occurs between the 10,000th and the 20,000th cycle interval, which corresponds to the most visible full CV change which also occurs in this cycle interval. Fang et

59

al. reported similar ECSA degradation trends between the 5,000th and 10,000th cycle interval for carbon black Vulcan XC-72R (VC)-supported Pt hollow nanospheres [114].

The ECSA and mass activity losses were quantified over the entire 30,000 cycle range using linear regression (Figure 2.6c). The ECSA and mass activity losses normalized to cycle number are $1.0 \times 10^{-3} \text{ m}^2\text{g}_{\text{Pt}}^{-1}$ cycle⁻¹, and $1.8 \times 10^{-6} \text{ A mg}_{\text{Pt}}^{-1}$ cycle⁻¹, respectively.

XRF grid scans were performed on the 0.4 mg_{Pt} cm⁻² JM CCM (both the as-received sample and the post-ADT sample). The averaged catalyst loadings over the entire grid were 0.451 ± 0.016 mg_{Pt}cm⁻² and 0.436 ± 0.019 mg_{Pt}cm⁻² for the as-received sample and the post-ADT sample, respectively. Based on these two grid scans, the Pt loss was about 3.3 wt% after the ADT cycling protocol. ICP-OES analysis of the 3-electrode cell electrolyte (i.e., 0.1 M HClO₄) after the ADT experiment showed a mass of 9.39 µg of Pt, corresponding to a 2.74 wt% Pt mass loss from the CCM sample. These experiments show the efficacy of the MRDE for direct ADT testing of fuel cell CCMs.



Figure 2.6: ADT analysis of a 0.4 mg_{Pt}cm⁻² JM CCM. (a) Cyclic voltammogram progression during ADT, (b) oxygen reduction reaction progression with inset showing the kinetic reaction, and (c) loss of ECSA and mass activity during the 30,000 cycle period.

2.4 Summary

The MRDE is a newly developed tool that may have significant impact in electrochemical science as a general testing method for electroactive samples. This tool was first tested with Pt foil to understand the effect of the Ti current collector mesh. The Ti mesh had a projected geometric coverage of 16%, but the change in the H_{ads} and H_{des} peaks was 6%. The 0.1 mg_{Pt}cm⁻² Johnson-Matthey commercial sample had the best performance out of all three commercial samples evaluated in the MRDE (i.e., specific activity of 111 μ A cm_{Pt}⁻², mass activity of 133 mA mg_{Pt}⁻¹). The mass activities of CCM samples measured by the MRDE are in better agreement with the PEMFC results compared to the TF-RDE approach. This indicates that the MRDE is better at predicting catalyst activity in a PEMFC than the current RDE method.

Using a 30,000 cycle ADT protocol on the 0.1 mg_{Pt}cm⁻² Johnson Matthey, degradation was most pronounced between the 10,000th and 20,000th cycle. The ECSA and mass activity losses were calculated using linear regression, and are found to be 1.0×10^{-3} m²g_{Pt}⁻¹ cycle⁻¹, and 1.8×10^{-6} A mg_{Pt}⁻¹ cycle⁻¹, respectively. However, to further improve the MRDE comparability to the PEMFC method at higher current densities, direct delivery of gaseous O₂ to the electrode is suggested so that the concentration of O₂ is not limited to the solubility of the electrolyte.

Chapter 3: Use of the Modified Rotating Disk Electrode (MRDE) to Study the Effect of Porous Transport Layers on the Oxygen Evolution Reaction

3.1 Introduction

The TF-RDE technique could also be applied to studying OER electrocatalysts for water electrolysis studies. However, the literature for TF-RDE for the OER is less prevalent compared to ORR. The reasons for this include: i) lack of a facile way to calculate real surface area (ECSA) for IrO₂-based catalysts (an important and commonly explored OER catalyst), and ii) large performance dependency on IrO_x loading. These two factors for less benchmarking data on OER TF-RDE are briefly discussed below.

Currently, there is no standardized way to calculate ECSA for IrO₂-based catalysts because the H_{UPD} is absent in the 0 – 1.4 V_{SHE} potential window. Alternate methods to determine real surface area have been proposed, but are currently not standardized. In 2012, Reier et al. determined the number of surface sites using a CO stripping experiment [68]. Zhao soaked IrO_x electrodes in a zinc solution, and correlated the pseudocapaciative charge of both electrodeposited and powder-based IrO_x electrodes yielding a proposed universal constant of 596 (\pm 21) μ C cm⁻² [115]. The most commonly used method of understanding the real surface area is the use of total voltammetric charge (Q*) averaged from the anodic and cathodic sweeps [116]. This is an uncomplicated and popular method that does not require the use of additional reagents (e.g., CO, zinc solution), but the nature of the surface reactions is not precisely known [117]. The voltammetric charge is useful, at best, when compared with other catalysts. Ir-based catalysts for TF-RDE studies are typically unsupported in nature. Baseline bulk or nanoparticulate Ir profiling have been performed by Reier [68] and Alia [118]. Typical loadings for OER TF-RDE studies are about $10 - 50 \ \mu g \ cm^{-2}$ [42,72,119,120], and reach current densities no larger than 50 mA cm_{geo}^{-2} [42,116]. These loadings and current densities are different from those encountered in PEM electrolyzer setups, where Ir catalyst loadings are about 2 mg cm_{geo}^{-2} and reach current densities of about 2 A cm_{geo}^{-2} and higher at 2 V. Rozain et al. observed an increase in performance when the loading was increased from 0.1 to 0.71 mg cm⁻² in a PEM electrolyzer [117]. The OER catalyst performance at TF-RDE may not necessarily predict performance in a PEMWE due to these loading differences. Also, mass transport losses are more prevalent beyond 2 A cm_{geo}^{-2} in the form of bubble accumulation, a phenomenon not encountered at the low current densities typically explored by a TF-RDE setup.

The goal of this chapter is to use the MRDE developed in chapter 2 to evaluate the performance of six PTL grid meshes using a Greenerity E300 commercial catalyst. Current densities of 2 A cm⁻² or higher are explored, which has never been previously documented in the literature. Favourable physical parameters are generalized to provide insight on future PTL design for PEMWE.

3.2 Experimental

The MRDE apparatus used for investigating the OER performance in this work is the same one used in the ORR work outlined in section 2.2. However, the focus of the OER work is on verifying the MRDE approach for OER-relevant CCMs, and characterizing current collector meshes. Figure 3.1a reintroduces the MRDE apparatus from section 2.2, with Figures 3.1b - 3.1g showing images of the six different current collector meshes tested in this work.



Figure 3.1: a) Exploded rendering of the MRDE tip, b-g) microscope images of the Ti current collectors. The model numbers are b) 3Ti4-031, c) 3Ti8.5-031, d) 3Ti10-031, e) 2Ti4-124, f) 10-Ti12-125, and g) 9Ti-twill.

Expanded metal samples (Figures 3.1b - 3.1f) were obtained from Dexmet Corporation, and the sample depicted in Figure 3.1g is sourced from Unique Wire Weaving Co., Inc. Table 3.1 summarizes the geometrical characteristics of the six Ti current collectors used. The first, second, and third numbers in the index correspond to the nominal thickness, strand width, and length along the diamond shape in thousandths of an inch, respectively. The openings per cm², coverage and triple-contact point (TCP) length were calculated based on the short way of the

diamond (SWD) and long way of the diamond (LWD). Appendix B.1 has more details on the calculations, and an illustration of the SWD and LWD (Figure B.1). All meshes were cut to 12 mm diameter disks using a hollow punch and flattened with a hydraulic press (YLJ-24, MTI Corporation) up to 10 MPa to ensure planar geometry. The flattened meshes were sonicated for 5 minutes in 18M Ω Millipore deionized water (DI, 18.2 M Ω , < 5 ppb TOC water, Milli-Q Integral 5, Fisher Scientific International Inc.), then a 50/50 vol% DI water/ethanol solution mixture (ethanol is \geq 99.5% ACS Plus, Fisher Scientific Company), then DI water again.

Thickness ^a (µm)	Openings / cm ²	Projected	TCP (mm)
		Coverage (%)	
76	534	48	56
76	433	78	35
76	437	77	34
50	38	20	20
254	42	39	18
228	558	51 ^b	40
	Thickness ^a (μm) 76 76 76 50 254 228	Thickness ^a (μm) Openings / cm ² 76 534 76 433 76 437 50 38 254 42 228 558	Thickness ^a (µm) Openings / cm ² Projected 76 534 48 76 433 78 76 437 77 50 38 20 254 42 39 228 558 51 ^b

Table 3.1: Physical properties of the six Ti-based current collectors.

^a specified by manufacturer

Only one type of CCM was investigated (GreenerityTM Generation E300, SolviCore GmbH & Co. KG), with about 2.0 mg cm⁻² IrO₂ on the anode and 0.3 mg cm⁻² Pt/C on the cathode. The as-received CCM had the cathode side masked with Kapton (0.0015-inch adhesive thickness, Matrix Technology Ltd.) to prevent any electrochemical activity from occurring on the Pt. A 10 mm diameter hollow punch was used to cut out circular CCM disks that were assembled in the MRDE head with the mesh.

The electrochemical tests were performed with the assembled MRDE (working electrode), a Pt-flag counter electrode (M241Pt, Radiometer Analytical), and a Cl⁻ free K₂SO₄saturated Hg/Hg₂SO₄ (MSE) reference electrode (REF621, Radiometer Analytical) inserted in a Luggin capillary. The electrolyte was prepared by diluting concentrated H₂SO₄ (96.8 %, Sigma-Aldrich, LOT#SHBG0974V) down to 3.5 M with $18M\Omega$ Millipore deionized water. H₂SO₄ was chosen as the electrolyte instead of HClO₄ (from the ORR experiments), as Ir-based catalysts reduce perchloric ions to chloride ions below 1 V which poison the Ir catalyst [68,121]. The electrolyte was purged with N₂ (99.998 %, Praxair Canada Inc.) through a porous gas dispersion tube (Ace dispersion tube, porosity D, Sigma-Aldrich Corporation) for about 15 minutes prior to the first CV characterization measurements. The rotator setup consists of commercial rotator with control unit (AFMSRCE, Pine Instrument Company) and an RDE shaft (AFE3M, Pine Instrument Company). A multichannel potentiostat with a 5 A current booster (VMP3, Bio-Logic Science Instruments) and accompanying software (EC-Lab software V11.02, Bio-Logic Science Instruments) were used to perform all half-cell experiments. A jacketed electrochemical cell (500 mL, CANSCI Glass Products Ltd., Surrey, Canada) with an in-house machined polyetherimide lid (Ultem 1000, Polymer Plastics Company, LC) was used as the electrochemical half-cell.

3.2.1 Methods and Procedures

The experiments performed included: i) initial parametric influence on current collector charge (e.g., current collector geometry), ii) current interrupt (CI) and electrochemical impedance spectroscopy (EIS) for resistance measurements, iii) OER polarization tests for activity comparison, and iv) ADT. The details of each experiment are explained as follows.

The ohmic resistance was measured in two different ways: i) galvanostatic electrochemical impedance spectra (GEIS), and ii) current interrupt (CI). The GEIS was performed at a frequency range of 100 Hz - 15 Hz with AC amplitude equal to 5% of the DC current. The total GEIS time was 14 seconds, with 10 points per decade averaged over three measurements. CI measurements had a current stimulus maintained for 0.1 s followed by an immediate switch to open circuit potential for 0.1 s. This was performed 10 times and the average resistance was used by calculating the rising and falling edges of each step.

The OER measurement protocol is shown in a protocol flow chart (Figure 3.2a). Much of the development of this OER protocol was inspired by the suggested protocol for OER catalyst benchmarking by Spöri, Kwan et al. The OER protocol has four major subroutines: five CVs (Figure 3.2a, Step 1), a chronoamperometric potential hold (Figure 3.2a, Step 2), a galvanostatic polarization curve (Figure 3.2a, Step 3), and a final five CVs (Figure 3.2a, Step 4). These measurements were done for 25, 40, 55 and 70°C. All OER measurements were performed at a rotation speed of 1600 rpm. For Step 1 and 4, the CVs were swept between 0.05 and 1.4 V vs. RHE at a sweep rate of 50 mV s⁻¹. The reported charge was the average of the integrated charge of the anodic and cathodic sweep. Step 2 involves a potential hold at 1.4 V vs. RHE for 1.5 minutes to accelerate double layer charging. Step 3 is the galvanostatic polarization and the

68

details of each current step and time held are shown in Figure 3.2b. The first polarization step (i.e., 0.2 mA cm⁻²) was recorded for five minutes to obtain more data in the kinetic region, with subsequent current steps recorded for one minute.



Figure 3.2: a) OER measurement protocol, b) polarization protocol showing the current density steps and time at each step.

The ADT protocol was performed at 40°C and at 1600 rpm. Three initial CV scans were performed between 0.05 - 1.4 V vs. RHE at a sweep rate of 50 mV s⁻¹, followed by a single OER sweep at 5 mV s⁻¹. Resistance was determined using the CI method at 100 mA cm⁻². Square wave voltammetry (SWV) was performed between 0.05 - 1.4 V for 1000 cycles, with each potential held for 3 s. The experimental sequence of SWV – CV – OER – CI was performed 15 times for a total of 15,000 SWV cycles, with the ADT protocol concluding with a final CV – OER – CI measurement sequence.

A Greenlight electrolyzer test station (E20 in E40 frame, Greenlight Innovations) with automated pressure/flow/temperature control/monitoring system coupled with an 850 W power

supply (Sorenson XG 6-110, AMETEK Programmable Power, Inc.) was used for the PEMWE measurements. A 25 cm² active area electrolysis cell (Fraunhofer ISE) with two gold-plated parallel flow fields machined in the Ti end plates was used for the electrolysis cell testing. The porous transport layer (40 % porosity, grade 2, MOTT Corp.) had an area of 23 cm², a thickness of 1 mm, and was made from sintered Ti particles. The MEA used with the cell (25 cm², Greenerity Generation E300, SolviCore GmbH & Co. KG) has a loading of about 2.0 mg cm⁻² IrO₂ on the anode and 0.3 mg cm⁻² Pt/C on the cathode. The cell was torqued to 17.16 Nm, and uniform pressure distribution was confirmed using a pressure sensitive film (Prescale, 73 – 363 psig range, 5.0 – 25.0 barg, Fujifilm) placed between a bare membrane and the PTLs.

The test station measurements were performed at 25, 40, 55 and 70°C at ambient pressure (1 barg). The galvanostatic testing protocol consist of 15 current steps ranging from 5 mA cm⁻² to 2 A cm⁻², with the first step applied for five minutes and each subsequent step applied for one minute. The reported potential at each step is the average over the last 10 seconds. Flow rates of 250 mL min⁻¹ and 2 L min⁻¹ were chosen for the experiments testing the baseline (PTL only) case and the PTL with a current collector expanded metal (3Ti4-031), respectively. A lower flow rate was initially chosen because there were issues with the cathode mass flow meters when the flow rate was set to 2 L min⁻¹, which prematurely shut down the test before the polarization could be completed. However, the impact of the PEMWE flow rate (between 250 mL min⁻¹ and 2 L min⁻¹) on performance was previously studied by a summer student in 2015. There was negligible difference in performance up to 2 A cm⁻², which is in agreement with the combined modelling and experimental study using a channel-less PEMWE of similar dimensions by Ojong, Kwan et al [31]. The resistance was measured using an LCR-meter (GWinstek LCR-821, Good Will Instrument Co., Ltd.) at a frequency of 0.5 kHz with an AC voltage amplitude of 200 mV.

3.3 Results and Discussion

3.3.1 Cyclic Voltammograms and Charge Quantification

The major findings of the first set of CV experiments are summarized in Figures 3.3a – 3.3d. Figures 3.3a and 3.3b show the CVs for all the meshes tested with the E300 CCM at the lowest and highest bulk electrolyte temperatures investigated (e.g., 25° C and 70° C). For both temperatures investigated, broad redox peaks can be identified between 0.45 - 1.2 V vs. RHE for the anodic sweep, and 1.4 - 0.5 V vs. RHE for the cathodic sweep. The bulky rectangular CV shape is characteristic of IrO₂ CVs and has been reported previously [68].

It is important to note that there is currently no standardized method for calculating an ECSA for Ir-based catalysts for the OER reaction. Integrating the hydrogen underpotential deposition peak is an accepted method for ECSA determination for Pt-based catalysts performing ORR, but there is currently no equivalent for the OER with Ir-based catalysts. Active surface sites for oxide-based catalysts can be related to the adsorbed charge [117,122], and may be of interest to determine relationships between charge, coverage, and bulk temperature for the E300 CCM in the MRDE. For the purposes of this discussion, the term *charge* will refer to the averaged adsorbed and desorbed charge from CV measurements in the voltage range before hydrogen or oxygen evolution occurs (e.g., 0.05 to $1.4 V_{RHE}$).



Figure 3.3: The 5th CV of the E300 CCM, with six different current collectors tested at a scan rate of 50 mV s⁻¹ at a scan range between 0.05 - 1.4 V at a) 25°C and b) 70°C. The relationship between c) mesh coverage and average charge at 25°C, and d) average charge-temperature for all six meshes.

Figures 3.3a and 3.3b show that the size of the CV rectangles depends on the type of current collector used. Before examining the charge contribution of the CCM and current collector, a blank CV test was performed with a Nafion NRE 211 membrane and all six current collectors. The charge from the current collectors alone (as measured from the blank test) varied between 0.02 mC cm⁻² (2Ti-125) to 0.16 mC cm⁻² (9Ti-twill). This contribution is negligible compared to the charges reported in Figure 3.3c. Figure 3.3c shows an attempt to correlate charge with a uniquely defining characteristic of the current collectors (i.e., physical geometric coverage) is presented. Charge is shown to exhibit a linear ($R^2 = 0.98$) relationship with current

collector coverage. Sample 3Ti10-031 was excluded from this fit analysis, as poor catalyst layer and current collector contact was suspected in that experimental run. The current collector that had the lowest geometric coverage (2Ti4-125, 20%) results in the lowest charge (27.3 mC cm⁻²), and the current collector with the highest geometric coverage (3Ti8.5-031, 72%) results in the highest charge (90.4 mC cm⁻²). The regression analysis shows a 1.2 mC per increase in percentage coverage. There are two major findings from this linear relationship: i) the catalyst layer covered by the current collector is accessible by the electrolyte (mainly the H⁺) and contributes to the total charge, and ii) open areas of a CCM (i.e., CCM not covered by mesh) may not contribute significantly to the adsorbed charge.

The triple contact point (TCP) is a parameter describing the catalyst utilization of active surfaces (referred to as triple-phase boundary in corresponding reference) [123]. Three conditions must be met for a TCP to exist: i) adequate protonic conductivity at the catalytic surface, ii) electrical conductivity at the catalytic surface, and iii) unhindered mass transport of reactants and products to and from the catalytic surface. The edges of the current collector contacting the CCM and exposed to the acidic electrolyte meet these three conditions simultaneously (Figure 3.4). Maximizing this TCP-length is an important parameter in optimizing catalyst utilization in OER applications.



Figure 3.4: Sketch of the triple-contact point boundary and location of charge buildup.

Revisiting Figures 3.3a and 3.3b, a side-by-side comparison of CV shapes can be made by looking at the two extreme temperatures (i.e., 25°C and 70°C). The features of the anodic sweep (from about 0.1 V to 0.5 V) are less pronounced at 70°C and the hydrogen evolution tail (0.05 to 0.10 V) is sharper. The sharpness of the hydrogen evolution tail skews the current density scale range of the CVs between -15 to 10 mA cm⁻² at 70°C, while the current density range at 25°C is reported as 6 to -6 mA cm⁻². The CVs at 70°C appear to be more block-shaped compared to the 25°C case, this resembling a capacitive response. This suggests that the CV charge at 70°C is mainly caused by the formation of the electrochemical double layer and not by changes of the redox state. Figure 3.3d shows the charge trends for all current collectors and temperatures. All current collectors exhibit an exponential relationship between temperature and charge. This behavior could be described by faster diffusion processes at higher temperatures, which can be explained by an Arrhenius-type activation process [124]. The exponential increases in charge have been attributed to a decreasing apparent activation energy of charging at higher temperatures [125,126]. The apparent activation energy for porous electrodes likely refers to the proton diffusion. The activation energy has also been found to decrease with scan rate, suggesting that pore diffusion is the limiting process [126]. More details on the influence of scan rate on CVs are in the original journal publication by Kroschel, Kwan et al. [112].

3.3.2 Resistance Measurement

Resistance of the assembled MRDE was measured using three different techniques: i) current interrupt (CI), ii) electrochemical impedance spectroscopy (EIS), and iii) slope calculation (ohmic region) from the polarization curves. Figure 3.5a summarizes the resistances for all combinations of CCM and current collectors at 25°C. Figure 3.5b shows the resistance trends of the best performing current collector (3Ti4-031). In addition, the resistance of the electrolyte (3.5 M H₂SO₄) is also presented. The exponential decrease for the electrolyte resistance is related to the dynamic viscosity, where temperature dependency exhibits an Arrhenius-type behavior [127].

From Figure 3.5a, the method-dependent resistance ranking is as follows: $R_{slope} > R_{CI} > R_{EIS}$. The slope method could potentially overestimate the resistance, as the potential during galvanostatic experiments can increase slightly at each current step like in Figure 3.2b. For all measurements, the R_{CI} values are higher than the R_{EIS} values, an observation also reported by Cooper et al. [128]. The resistance deviation between CI and EIS methods could be attributed to

75

the time scale differences between the measurements. Impedance spectroscopy uses a small perturbation at high frequencies to obtain ohmic resistance, while the CI method uses the potential change (i.e., rise or drop) after a sudden current stimulus. The current interrupt technique was used for iR corrections of the OER polarization curves as a conservative measure to prevent over or underestimation of cell resistance.



Figure 3.5: Resistances trends a) for all six current collectors at 25°C, and b) temperature-resistance curve for the 3Ti4-031 current collector.

3.3.3 Polarization Curves

Figure 3.6a shows the non-iR corrected (dashed lines) and iR-corrected (solid lines) CCM performance at 25°C with the six current collectors. It is important to note the spread of the data for the non-iR corrected curves, stressing the importance of current collector optimization. The potential for the best and worst performing meshes (evaluated at 2 A cm⁻²) is 1.97 V for the 3Ti4-031 sample and 2.54 V for the 9Ti-Twill, respectively.

Figure 3.6b is a condensed plot of all the current collector polarization curves, showing the iR-corrected potential corresponding to a current density of 100 mA cm⁻² (kinetic region) and 600 mA cm⁻² (ohmic region). The Ti meshes studied can be divided into three performance classifications based on their non iR-corrected performance: i) 3Ti4-031 is the best performing mesh, ii) 10Ti12-125 is the worst performing mesh, and ii) the intermediate performing meshes, 3Ti10-031, 3Ti8.5-031, 2Ti4-125 and 9Ti-twill. From Figure 2.12b, the 10Ti12-125 current collector consistently performed the worst, and the 3Ti4-031 was consistently the best performing for the temperatures explored. 10Ti12-125 sample has two undesirable current collector properties that may explain its poor performance: i) it has the highest through-plane thickness (254 μ m), and ii) it has the lowest TCP-length (18 mm). This means that the catalyst layer paired with this current collector would have the worst catalyst utilization. Note that the ranking in these current collectors matches the resistance ranking (lowest to highest).



Figure 3.6: a) Non-iR corrected and iR-corrected polarization curves at 25°C, and b) a condensed polarization plot showing iR-corrected potentials corresponding to current densities of 100 mA cm⁻² (closed symbols) and 600 mA cm⁻² (open symbols).

A summary of the Tafel parameters and the corresponding reported potentials (both iR and non-iR corrected) corresponding to 1 A cm⁻² is shown in Table 3.2. The linear region between 2 - 5 mA cm⁻² was used for the linear regression analysis. The Tafel slopes reported range from 57 - 68 mV dec⁻¹, which are in close agreement to the literature value of 60 mV dec⁻¹ [119].

Mesh	R _{CI, 1A/cm2} (Ω)	E _{1A/cm2} (V) (no iR- correction)	E _{1A/cm2} (V _{iR}) (iR corrected)	b (mV dec ⁻¹)	j ₀ (A cm ⁻²)
3Ti4-031	1.37	3.03	1.95	57	7.5 ×10 ⁻⁹
3Ti8.5-031	1.74	3.46	2.09	55	5.8 × 10 ⁻⁹
3Ti10-031	1.82	3.95	2.16	57	8.8×10^{-9}
2Ti4-125	1.69	3.42	2.10	66	1.1 × 10 ⁻⁸
10Ti12-125	2.37	3.99	2.13	61	1.5×10^{-8}
9Ti-twill	1.70	3.53	2.19	68	5.2×10^{-8}

 Table 3.2: Key figures of merit for each of the current collector meshes.

A value of 60 mV dec⁻¹ may indicate that Eq. 3.2 is the rate-determining step (RDS), where the OH surface species is rearranged due to a surface reaction [129]. One such mechanism that fits this description is the Krasil Schchikov mechanism (equations 3.1 - 3.4) where S denotes a surface substrate [130]. The exchange current densities are in the order of around 10^{-8} to 10^{-9} A cm⁻², and are within the expected ranges for the OER on Ir-based CCMs [42].

$$S + H_2 0 \rightleftharpoons S - 0H_{ads} + H^+ + e^-$$
(3.1)

$$S - OH_{ads} \rightleftharpoons S - O^- + H^+$$
(3.2)

$$S - 0^{-} \rightleftarrows S - 0 + e^{-} \tag{3.3}$$

$$S - 0 \rightleftharpoons S + 1/2 O_2 \tag{3.4}$$

3.3.4 Accelerated Degradation Testing

Figure 3.7a shows the ADT protocol used for degradation characterization using rapid CV cycling followed by OER polarizations. For discussion of the ADT results, the term "sequence" refers to one iteration of steps 2 through 5. The potential domain of the rapid SWV (0.05 - 1.4 V for 1000 times, Figure 3.7a, step 2) was suggested by a catalyst stability review by Spöri, Kwan et al [5]. The shape of the CV broadens with each successive cycle and has the characteristic redox bumps described previously (Figure 3.7b). The OER polarizations (step 4 in Figure 3.7a) taken after step 3 show a slight performance increase up to the 4th sequence, then the performance steadily decays. Figure 3.7d shows the charge and peak current density (identified as the apex in the OER polarization) as the sequence progresses. The highest current density is reached after the second sequence. This could indicate a break-in or conditioning period during the first two cycles. There is a resistance decrease when comparing sequence 1 (1.40 Ω) to sequence 2 (1.37 Ω), then the resistance steadily increases up to the end of the ADT test. This momentary resistance decrease is likely due to the conformation of the MEA to the current collector. Rakousky et al. also observed similar trends and concluded MEA conformation to the current collector as the main cause of resistance decrease in their degradation studies [131,132]. The increasing resistance starting after sequence 2 could be explained by titanium passivation over time. The peak current density stays relatively constant starting from sequence 2 to sequence 4, then slowly decays linearly after each sequence. The decline in catalyst activity from sequence 4 and onwards is possibly caused by catalyst degradation, or increasing resistance by titanium oxidation, or both.

81



Figure 3.7: ADT at 1600 rpm in 3.5 M H₂SO₄ at 40°C. In total, 15,000 square wave cycles were performed between 0.05 - 1.4 V. a) Block diagram of the ADT protocol, b) CVs after each SWV step, c) OER sweeps, and d) peak current density and voltammetric charge after each sequence.
3.3.5 **PEMWE** Comparison

The last set of experiments tested the best performing current collector mesh in the MRDE (3Ti4-031) in PEMWE hardware. Figure 3.8a shows the components in the baseline PEMWE case. In Figure 3.8b, a 5 cm x 4.6 cm (length by width) square cutout of the mesh was positioned between the CCM and the PTL to approximate the placement conditions in the MRDE.



Figure 3.8: PEMWE assembly of a) the baseline case with default components, and b) the modified case with a 5 cm x 4.6 cm sheet of 3Ti4-031.

Figure 3.9a compares the non-iR corrected polarization curves of the baseline case (PTL only) with the best mesh from the MRDE study (PTL + Mesh). The influence of stacking the mesh on top of the sintered PTL may have decreased the accessibility of the liquid electrolyte (e.g., water) to the CCM under cell compression. The potentials in the kinetic region (e.g., 0.2 A cm⁻² or below) and ohmic region are lower for the baseline case. Ti PTLs are generally optimized for PEMWE use and have more homogeneous contact with the catalyst layer compared to a current collector mesh. Steen et al. compared Ti meshes and Ti felts in a PEMWE and commented on the improved performance of the latter. The Ti felt is a more homogeneous

structure with some compressibility to the material leading to better CCM conformity. Figure 3.9b shows the iR-corrected polarization curves obtained with the MRDE and electrolysis test station (ETS). There is roughly a 200 to 300 mV difference between two methods when comparing point-to-point in the ohmic region. The ETS result has lower overpotentials compared to the MRDE. Owe et al. showed the dependence of activity on liquid electrolyte in a three-electrode cell using a flag electrode, and was ranked in the following order with regards to performance: 0.5 M H₃PO₄ < 0.5 M H₂SO₄ < 0.5 M HClO₄ [133]. This activity difference could also be attributed to the difference in liquid electrolyte vs. solid polymer electrolyte, since neutral water was used for the electrolysis test cell.

Table 3.3 summarizes the Tafel slopes both the ETS and the MRDE at 25, 40, 55 and 70°C using linear regression analysis (Figure 3.9c). For both experimental methods, the Tafel slope does not change with temperature, indicating that the RDS does not change with temperature. The Tafel slopes obtained from the MRDE is in good agreement with the ETS. **Table 3.3: Tafel slopes of the ETS and MRDE at 25, 40, 55 and 70°C.**

	$b_{,25\ ^{\circ}C}$ (mV dec ⁻¹)	b, 40 °C (mV dec ⁻¹)	b, 55 °C (mV dec ⁻¹)	b, 70 °C (mV dec ⁻¹)
ETS	50	51	50	50
MRDE	57	58	58	60



Figure 3.9: Non-IR corrected polarization curves of the electrolysis test station (ETS) showing baseline vs. tested mesh. b) iR-corrected polarization curves, c) Tafel plots of the MRDE and ETS techniques, and d) Arrhenius plot.

The exchange current densities of the ETS and MRDE using the 3Ti4-031 mesh are shown in Table 3.4. Although the exchange current densities are generally higher in the ETS, both testing methods yield numbers in the 10^{-7} to 10^{-9} A cm⁻² range, which is the commonly reported in the literature for Ir-based catalysts as mentioned previously.

Table 3.4: Exchange current densities of the ETS and MRDE at 25, 40, 55 and 70°C.

	j0, 25 °C (A cm ⁻²)	j _{0, 40 °C} (A cm ⁻²)	j0, 55 °C (A cm ⁻²)	j0, 70 °C (A cm ⁻²)
ETS	1.3×10^{-8}	7.3×10^{-8}	1.9×10^{-7}	5.4×10^{-7}
MRDE	$7.5 imes 10^{-9}$	2.4×10^{-8}	8.9×10^{-8}	4.1×10^{-7}

Figure 3.9d shows the Arrhenius plot of the two measurement methods. The calculated activation energies for the ETS and MRDE are 75 and 68 kJ mol⁻¹, respectively. These numbers are consistent with the 67 kJ mol⁻¹ reported by Suermann et al. for a commercial GreenerityTM MEA [134].

3.4 Summary

The use of the MRDE for characterizing OER catalysts proved to be a better application of the tool compared to the ORR. Both the PEMWE and conventional RDE setups have water as the reactant and have no gas solubility issues as in the ORR case. The importance of current collector studies was highlighted, with emphasis on the quantification of the TCP. A detailed electrochemical and physicochemical study of six different Ti-based current collectors was performed with the MRDE. The first half of this study focused on charge quantification, as there is a lack of a standardized method to calculate ECSA for Ir-based catalysts. It was found that the voltammetric charge increased 1.2 mC with each % increase of the projected coverage of the current collector.

The MRDE tool was successful in demonstrating high current densities (> 2 A cm⁻²) in a 3-electrode cell, which is a commonly explored current density in PEMWE hardware. Six current collector meshes with different geometric properties were tested, with 3Ti4-031 performing the best and 10Ti12-125 performing the worst. The 3Ti4-031 mesh had the highest TCP length (56 mm), and large openings per cm⁻² for liquid and gas to move freely.

ADT data shows performance degradation after the fourth sequence (4000 rapid square wave voltammetry cycles) and a break-in period of roughly two sequences (2000 rapid square wave voltammetry cycles) before peak performance was achieved. The MRDE and PEMWE have comparable Tafel slopes (60 vs 50 mV dec⁻¹), exchange current densities (10⁻⁷ to 10⁻⁹ vs. 10⁻⁷ A cm⁻²), and activation energies (75 vs 68 kJ mol⁻¹). The differences in these results are attributed to interactions found in solution-based environments, particularly anion adsorption.

Chapter 4: Current Collector and Bubble Occupancy Characterization with a Visualization Cell

4.1 Scope and Context

The porous transport layer (PTL) is a vital component of the PEMWE that must provide good current collection, facilitate unhindered water and gas transport to and from the electrode, and have the mechanical strength to withstand compression. Ti was discussed in section 1.4.2 as the material of choice for current collectors. In the OER region (e.g., $> 1.4 V_{RHE}$), bubbles formed on the anode catalyst can persist on this surface. This shields the catalyst layer from the reactant water, reducing its electrochemical activity. Therefore, favourable tuning of the current collector properties reduces the tendency of bubbles to stick to catalyst surfaces and block active area.

Current collector design involves two key parameters that are inversely related: porosity and physical coverage. Consider the extreme case where porosity is 100%. In this case, bubbles can freely detach from the catalyst surface. However, there is no electrical pathway from the catalyst layer to the flow field, which means that the catalyst is not electrochemically active. In the other case where the physical coverage is 100%, the catalyst is fully active but inaccessible by water. Studies that explore these two extremes are of critical interest in current collector design. A brief review of impactful literature on current collector performance, design, and selection is covered in this chapter.

There are three classifications of PTLs: i) screen or mesh type, ii) felt type, and iii) sintered particle types [135]. Screen-type current collectors are low-cost and are appropriate for electrolyzers with large active areas (> 1 m²). These typically have narrow strand diameters (e.g.,

100 µm) and have large pores (e.g., ~150 µm). The physical parameters of mesh type PTLs (i.e., thickness, pore size and porosity) are easier to control and fabricate (e.g., expanded metal processes such as Dexmet). However, depending on the rigidity of the mesh, it can embed itself into the catalyst when the PEMWE is compressed causing irreversible damage (e.g., slicing). Felts (or unwoven fabrics) are softer structures that have pore sizes in the range of 60 to 100 μ m. The catalyst layer is less susceptible to slicing or deformation from this type of current collector. Ito et al. examined the effect of pore size and porosity of Ti felts experimentally in a PEMWE. His work concluded that porosities exceeding 50% had no significant effect on PEMWE performance, and that performance increased with decreasing mean pore diameter (MPD) to a minimum of 10 µm [78]. Sintered Ti PTLs are made very rigid structures that can withstand the compression requirements of PEMWEs, while not being damaging to the MEA. They are typically made from Ti powder and are highly influenced by the temperature and duration of the sintering process. Bogart et al. studied the effect of power type (i.e., spherical and irregular powders) using sintering temperatures ranging from $800 - 1200^{\circ}$ C to produce PTLs with a film thickness ranging from 235-526 µm and subjected them to pressure tests. Samples with the lowest porosity (e.g., around 8 - 10 %) could withstand around 200 - 250 bar before breaking, whereas the samples with the highest porosity (e.g., around 30 - 50 %) could only withstand up to 10-25 bar with the powders used in this study. This type of PTL is considered state-of-the-art in PEMWEs, and has been used in numerous experimental studies including the impact of flow fields with no channel landings [31], effect of IrO_x catalyst loading on performance [117], and in high pressure electrolysis applications [134]

Although sintered Ti PTLs are the current collector of choice for electrolyzers, they currently are a costly component due to the machining and material costs. The studies mentioned so far in this section are plug-and-play experiments that only examine the effect of performance from a specific current collector (i.e., examining the polarization curve and observing any changes in overpotential). Although this method tests these current collectors under real conditions, the limited insight gained from these studies is attributed to physical properties of the current collector (e.g., pore size, porosity, etc.). In addition to these performance studies, the problem of designing cost effective and high performing current collectors could be tackled in two additional ways: i) fundamental analysis via modelling, and ii) visualization of the PEMWE anode side.

There are very few fundamental studies on pore-scale bubble nucleation and detachment dynamics in the PTL confinement of the PEMWE anode. Earlier modelling studies (2012-2016) by García-Valverde et al. [136] and Han et al. [137] assumed a continuously dispersed oxygen phase, which do not account for the PTL shape and geometry. The modelling study on PEMWE bubble evolution in pores by Nouri-Khorasani et al. presented a force balance on evolved oxygen bubbles at the PTL pore exit/flow field interface [80]. His work introduced the idea of bubble overpotential as an additional loss term in the voltage balance. He concluded that ACL wettability was the most influential factor in this overpotential term, a physical parameter that is not commonly explored in experimental PEMWE studies.

Visualization of the anode side of the PTL-flow field interface may provide additional information that regular PEMWE experimentation cannot provide. For example, the bubble periodicity (i.e., when do bubbles detach from pores), area obstructed by bubbles, and bubble diameter can be quantified using image analysis. Visualization methods for the PEMWE are

categorized either as: i) direct visualization methods (e.g., high-speed optical cameras that can range from 3000 – 7500 FPS), or ii) by in-situ or in-operando characterization (e.g., neutron spectroscopy, x-ray, fluorescence spectroscopy). Before 2014, the value of direct optical imaging in PEMWEs was not as recognized compared to the fuel cell application according to Dedigama et al. [138].

Direct visualization methods involve modification to the PEMWE hardware to accommodate a transparent observation window viewing the anode-side channel landing. Observation windows can be made from glass [81], fused silica glass [39], or PerspexTM (or other acrylic-based resins) [138]. The difference between true electrochemical activity, and the misconceptions with the commonly perceived electrochemical activity in a PEMWE using the triple contact point (TCP) concept has been described by Mo et al. [123]. To date, he arguably performed the most impactful work in this space using this method (optical window and high-speed camera). The catalyst is only active where the porous transport layer (in this case, the liquid/gas diffusion layer) and water are all in contact at once (Figure 4.1).



Figure 4.1: Diagrams showing a) true region of electrochemical activity and b) commonly perceived electrochemical activity in a PEMWE. From [123]. Reprinted with permission from AAAS.

They were able to demonstrate an OER mass activity 17 times more active than conventional PTLs using a tuned liquid-gas diffusion layer (LGDL) where the catalyst layer is directly deposited on the LGDL itself.

In-situ characterization methods reported in the literature include synchrotron x-ray spectroscopy, neutron spectroscopy, or micro-computed tomography (micro CT) visualization. Synchrotron x-ray spectroscopic methods have been used mainly to analyze operating cells, and have mainly examined mainly the regions under the anode channel landings. Hoeh et al. used xray radiography to profile in-plane and through-plane bubble formation as a function of time [75]. The average bubble diameter before detachment at 10 mA cm⁻², 75 mA cm⁻², and 100 mA $cm^{\text{-}2}$ are 60-80, 50-70, and 40-60 $\mu m,$ respectively. Neutron spectroscopy has been used primarily to look at water-gas distribution. Panchenko et al. used neutron spectroscopy to profile the PEMWE under water-starved conditions, and concluded that stoichiometric water flow rates less than 1 mL min⁻¹ for a 1.5 cm² active area cell [139]. Arbabi et al. used microfluidic CT chips to compared the extent of bubble entrapment in the GDL for sintered Ti, foam, and felt GDLs [140]. The results showed that the felt GDL had the least amount of air entrapment out of the three PTLs examined, but the authors also mentioned the need for more rigorous studies in this area. Table 4.1 summarizes the conditions of the experiment for the above three in-situ experiments.

Author	Cell Temperature (°C)	Channel Dimensions, L x W (mm x mm)	Flow Rate (mL min ⁻¹)	Current Density (mA cm ⁻²)
Hoeh [75]	80	1.4 x 0.4	0.6 - 1.5	10 - 200
Panchenko [139]	80	0.8 x 3	0.5	1000
Arbabi [140]	20	Unspecified	0.001	1400

Table 4.1: Cell and operating parameters for in-situ methods.

Based on the reported literature in this field, there are several observations relating to the value of the data obtained. It is clear there is an emphasis on examining the oxygen bubble formation and ejection on the anode-side channels. Typically, these channels are within the mm width range. If bubbles fully develop into a slug-flow regime in these narrow channels, there could be local starvation of reactant water for the anode catalyst. This introduces a potential second source of noise, which may mask the true bubble signal. Because of this, many cells use low flow rates (low end of mL min⁻¹ range) and do not reach current densities in the 2 A cm⁻² (the most commonly reported benchmark for PEMWE systems). Secondly, an analysis coupling the capability of visualization and fundamental approaches (i.e., modelling) could provide additional metrics for in-situ evaluation aside from activation over potentials. However, for this coupled analysis to be meaningful, a cell must be developed to address the issues associated with narrow channels and the inability to reach current densities of 2 A cm⁻².

This chapter presents the development of a fully-transparent visualization cell with an adaptable head assembly which can test multiple types of PTLs at current densities higher than 2 A cm⁻². The cell is designed to accommodate a large volume of electrolyte flowing above the anode catalyst, which avoids the problem of local reactant starvation from accumulated slug-flow bubbles at high current densities. This allows a more accurate study of performance loss

due to bubble coverage of the active area alone, and explore the effect of physical coverage of the current collector on the OER.

4.2 Experimental

4.2.1 Visualization Cell Assembly

The components of the visualization cell body are shown in Figure 4.2. The visualization cell was glass blown by Cansci Glass Products, Ltd. There are dedicated openings on the top and bottom of the cell, where the working and counter electrode assemblies are positioned parallel to each other. The inlet and outlet ports of this cell are connected to the reservoirs using chemical resistant tubing (5/8" OD, TygonTM tubing, Fisherbrand). The electrolyte was circulated using a magnetic drive pump (NH-15PI-ZD, Pan World Co., Ltd.) connected to the inlet of the cell. The electrolyte reservoirs (1 L Erlenmeyer flasks) were connected to the outlet of the cell. The electrolyte used was 3.5M H₂SO₄ made with double distilled sulfuric acid stock solution (Assay 95 - 98%, Veritas® Double Distilled, GFS Chemicals Inc.). The pump was driven by a DC power supply (Sorenson DLM 150-4 600W, 0-150 V, 0-4 A, Signal Test, Inc.). The flowrate and Reynolds number were determined by changing the DC power and measuring the time required to fill a 100 mL graduated cylinder. The trials were performed three times, and the data was averaged to calculate an average flow rate (Appendix C.1, Figure C.1).



Figure 4.2: Overview of the visualization cell electrolysis flow cell apparatus.

4.2.2 Housed Working Electrode Unit

Figure 4.3 shows the working electrode assembly and its components. Details regarding the design of this unit and previous iterations are explained in Appendix C.2 (Figures C.2 to C.4) The working electrode assembly had four major parts: i) a Ti casing that holds down the sample, ii) the catalyst component sample and auxiliary parts, iii) a threaded titanium core, and iv) a threaded screw facilitating a connection to the potentiostat. All parts of the working electrode assembly (except the catalyst samples) were fabricated or provided by Core Tool and Mold Manufacturing Ltd., North Vancouver, Canada.



Figure 4.3: a) Plan view of the Ti lid, and b) exploded view of the housing unit for the working electrode in the visualization electrolysis flow cell.

The Ti lid (Ti Grade 2) has a 0.375-inch O.D. opening with a cross-shaped bar (1 mm width) spanning the entire opening. This cross bar secures the catalyst sample down against the 0.5-inch O.D. silicone platform. The silicone platform provides back pressure equal to or exceeding 365 psig as confirmed by two-part pressure paper tests (73 – 365 psig range, Fujifilm Global). The main body is a polyether ether ketone (PEEK) shell (1-inch O.D. top portion, 1.625-inch O.D. base) with a fiberglass gasket (Garlock 9900 Hi-Temperature Gasket, McMaster Carr) which rests on the step near the base. The sample and silicone platform disc (1460N14, 1/8-inch thickness, 50 A durometer, McMaster Carr) was placed in the center on top of the

threaded titanium core, which screws into the PEEK shell. The screw connector threads into a hole on the other side of the Ti core and protrudes from the bottom of the PEEK casing. The exposed screw was connected to the Bio-Logic potentiostat using an alligator clip.

Two types of samples were examined: i) Ir foil (99.9% purity, 0.0508 mm thickness, efilaments, LLC), and ii) a commercial full CCM (E300, anode catalyst loading of ca. 2.0 mg cm⁻² IrO₂, Greenerity GmbH) cut to a 0.71 cm² geometric area. The cathode catalyst layer of the CCM was covered with Kapton film (Model CR2345-1 Model, 0.0025-inch total thickness, Matrix Technologies-Ltd.) to prevent the cathode side from reacting with the electrolyte.

4.2.3 Housed Counter Electrode Unit

A custom-designed Teflon housing unit (Core Tool and Mold Manufacturing Ltd., North Vancouver, Canada) holds the i) counter electrode (CE), ii) leak-free Ag/AgCl reference electrode (LF-2 model, Warner Instruments, LLC), and iii) an endoscope inspection camera (720P digital USB endoscope, Shenzhen Changsai Te Technology Co., Ltd) protected by a quartz sheath (Cansci Glass Products Ltd., Surrey, Canada). Three holes extend through the housing unit with O-rings embedded in the middle of the openings, holding the above parts in place. The CE was an expanded metal (3Ti4-125FA, Dexmet Corporation) with a titanium wire (10388-BU, 1.0 mm O.D., annealed, 99.9% metals basis, Alfa Aeser) laser welded onto the mesh (Welding services provided by Expert Castings, Vancouver, Canada). A Ti mesh was used instead of Pt foil due to two reasons: i) the geometric area of the CE must be three times the geometric area of the WE to avoid current limitations, and ii) the foil needed to have a minimum thickness of 0.3 mm to be properly welded onto Pt wire by Expert Castings. For a Pt foil to satisfy these requirements, the costs could be within the 1,000 to 2,000 USD range.

4.2.4 Sample Preparation

The Solvicore E300 CCM was used as-received and stored dry to avoid membrane swelling prior to assembly. The Ti lid with crossbeam and CE were immersed in a beaker of DI (DI, 18.2 M Ω cm, < 5 ppb TOC water, Milli-Q Integral 5, Fisher Scientific International Inc.) water, and cleaned in an ultrasonic bath (Ultrasonic Cleaner B1510, Branson Ultrasonics) prior to every experiment. The counter electrode assembly and the glass cell were rinsed with DI water before and after every experiment. No isopropanol or other organic solvent was used to clean these components, as epoxy-cured silicone was used to seal some of the holes. The silicone would shrink or crack when exposed to these solvents.

Four different Ti Meshes (Table 4.2) were used in this study: 3Ti4-031, 3Ti85.-031, 2Ti4-125 and 10Ti12-125 (Dexmet Corporation). These four meshes were specifically chosen to cover a porosity spread from 20 to 80%, and the two worst performing ones from Chapter 3 were rejected. The 3Ti8.5-031 was used as a current collector in a first demonstration of the modified rotating disk electrode (MRDE) used in studying the electrokinetics and stability of commercial oxygen reduction reaction (ORR) catalysts (Chapter 2) [141]. The 3Ti4-031 current was reported as the best performing mesh (ranked 1 out of 6) in a recent current collector screening study using an MRDE by Kroschel et al. (Chapter 3) [112]. Two other meshes with different coverages and porosities were chosen to understand the effect of physical coverage on bubble formation and detachment. These four meshes were hole-punched into 3/8-inch diameter circles and flattened using an applied pressure of \approx 10 MPa using a hydraulic press (MTI Corporation).

Index	Thickness (µm)	Openings /	Coverage	TCP (mm)
		cm ²	(%)	
3Ti4-031	76	534	48	56
3Ti8.5-031	76	433	78	35
2Ti4-125	50	38	20	20
10Ti12-125	254	42	39	18

 Table 4.2: Current collector meshes that were down selected for testing in the visualization cell from the two

 previous MRDE studies.

4.2.5 Electrochemical Testing Procedures

All the experiments were performed with a potentiostat (VMP3 potentiostat with a 5 A booster, Bio-Logic Science Instruments) and dedicated software interface (EC-Lab V11.02, Bio-Logic Science Instruments). All potentials reported are relative to the reference hydrogen electrode (RHE). The power supply was set to 11.7 V and 7.1 A (\approx 83 W). At this power, the pump circulated electrolyte at a flowrate of 1.7 L min⁻¹, and a Reynolds number of 870 was calculated for the system. The cell was operated at room temperature (21 ± 0.5 °C) and at ambient pressure (1 atm). A calibration plot is in Appendix C.1 (Figure C.3).

The cell resistance was determined before every set of experiments using EC-Lab's potentio-electrochemical impedance spectroscopy function (ZIR). ZIR point scans were performed using 20 mV AC amplitude, and at 50 kHz frequency. Using the real (ohmic) component of the impedance, the cell resistance was between $0.10 - 0.15 \Omega$ on average for each run. IR correction was performed on measured potentials (85% correction level in-situ, remaining 15% correction accounted for after data collection).

Figure 4.4 summarizes the testing protocol used to collect data for the CCM. There are two main testing subroutines: i) a CV scan before and after a CV conditioning step (Figure 4.4a), and ii) a series of CA steps to characterize bubble periodicity and activity (Figure 4.4b). The preand post-conditioning CVs were recorded between $0.05 - 1.4 V_{RHE}$ at a sweep rate of 50 mV s⁻¹. The reported charge is the average of the last post-conditioning anodic and cathodic sweep. The potentials were recorded between $1.61 - 3.79 V_{RHE}$.



Figure 4.4: Experimental block-flow diagram for a) CV characterization, and b) CA.

4.3 **Results and Discussion**

4.3.1 Demonstration of the cell using Ir Foil

The first experimental run done with this apparatus was with Ir foil in 1.0 M H₂SO₄ to check the response of the system using an ideal sample. Iridium foil has excellent lateral conductivity, so there should be less performance dependence on electrical contact and compression. The process of forming an anodically formed iridium oxide films (AIROF) involved rapid cycling at 500 mV s⁻¹ between 0.05 and 1.4 V_{RHE} until the peak shape and amplitude reached a steady state. Figure 4.5 shows the continuous growth of the oxide layer with the anodic and cathodic peaks increasing in size and shifting towards the scanning direction with increasing cycle number (i.e., anodic peak slowly shifting to a more positive potential, and the cathodic peak slowly shifting towards a more negative potential). The CVs are centered about the x-axis with symmetric anode and cathodic peaks. The growth in the cathodic and anodic peaks between cycle 1,000 and cycle 1,700 is small, indicating that it is reaching a steady state at close to 1,700 cycles. The CV shape and growth patterns are similar to those reported by Burke [142] and Geiger [143], where oxide growth scans were performed up to 120 and 500 cycles, respectively.



Figure 4.5: Demonstration of diagnostic cell by performing AIROF growth due to rapid cycling CVs up to 1,700 cycles.

4.3.2 CVs and Current Collector Charge

In the case of the ORR in fuel cells, the ECSA can be estimated from integrating the H_{ads}^+ peak and using the 210 μ C cm⁻²_{Pt} conversion factor for polycrystalline Pt. The absence of this peak (and thus a universally agreed upon conversion factor for Ir-based catalysts for OER) has led to some researchers using adsorbed charge to quantify the number of active sites. We used this metric as a measure of finding the relative ECSA in different tests.



Figure 4.6: a) The 3rd cyclic voltammogram for each Ti mesh used in the visualization cell, scanned between 0.05 - 1.23 V in 3.5 M H₂SO₄, and b) Relationship between physical coverage from the mesh and charge. Figure 4.6 shows the 3rd post-conditioning CV scan for each of the four meshes in the visualization cell. All three CV scans for each sample closely superimposed each other, therefore the standard error (i.e., $\sigma n^{-1/2}$) is very small. Therefore, the only error associated with the analysis is attributed to the error of the Biologic instrument (± 50 pA) or the error associated with the integration of the CVs (which is about 0.067 % using conservative a priori error estimates). A blank test (no sample) with the titanium cap screwed down onto the titanium core was tested to check the current contribution of these components. The current densities from the blank test CVs were in the range of 0.02 mA cm⁻²_{geo} for the anodic sweep. This result verifies that the current contribution from the titanium components alone and the electrochemical activity of the Ti core do not contribute much to the total charge of the CCM. The shape of the CVs are broad, rounded parallelograms with broad redox peaks from 0.4 - 1.23 V on the anodic sweep, and at 1.23 - 0.5 V for the cathodic sweep, respectively. The shapes of these CVs resemble anhydrous IrO₂ electrodes [144,145]. Figure 4.6b is a charge-coverage plot that shows the averaged charge for each mesh. There is a general linear trend, with increasing charge (about 1.3 mC per %

coverage, like chapter 3) with increasing physical coverage. The meshes used in the visualization cell can be ranked from lowest charge to highest charge: 2Ti4-125, 10Ti12-125, 3Ti4-031, 3Ti8.5-031. These ranking of charges is the same ranking as seen in Chapter 3.3.1, Figure 3.3c.

4.3.3 Polarization Curves for the Commercial IrO₂ Catalyst CCM

Figure 4.7 shows the iR-corrected polarization curves for each of the Ti meshes (Table 4.1). Each point on the plot is the current average of the last 30 seconds for each current step. Between the first point and up to 2 V_{RHE} , the potential was ramped up in 100 mV increments to better capture the polarization trends at this potential range. For convenience, each mesh was assigned a shorthand naming convention (i.e., M1 through M4) to easily distinguish performance ranking of these meshes. Using this convention, mesh M1 is the best performing current collector, and M4 is the worst performing current collector.



Figure 4.7: Polarization curves for each of the Ti meshes, iR-corrected and evaluated at 3.5 M H₂SO₄.

The test run with the M4 mesh had the worst performance out of all four meshes tested. In the case of testing this exact same CCM catalyst and mesh combination in the MRDE, it was mentioned that the high nominal thickness and lowest TCP length were reasons for its poor performance [112]. The best performing mesh (M1) reached 2.5 A cm⁻² at 3.4 V_{RHE} at 298K and 1 atm in the visualization cell. The performance ranking of meshes corresponds with the charge ranking of meshes from Figure 4.6. For future experiments, it would be worth exploring temperatures up to 80°C.

4.3.4 Current Fluctuation Analysis

The last 60 seconds of each polarization curve was analyzed using single-sided amplitude spectrum Fourier transform analysis. The best performing mesh (Solvicore E300, 3Ti4-031 mesh, 3.5 M H₂SO₄, 293 K, 1 atm) is shown in Figure 4.8a. The result shows no distinct peaks; therefore, a characteristic bubble lifetime could not be determined using Fourier transform analysis (Figure 4.8b). The Fourier transform analysis on the other three meshes is in Appendix C.3 (Figure C.5 to Figure C.7). This observation was previously made by Zeradjanin et al. [146], and Paul et a.1 [147]. They attribute the reason to the presence of many surface facets and interface conditions on the active catalyst layer surface.



Figure 4.8: a) 3Ti4-031 polarization, and b) Fourier transform analysis (single-sided amplitude spectrum) for showing a lack of a defined peak.

Even though a characteristic peak was not observed (Figure 4.8b) in the Fourier transform results, the frequency ranges were analyzed where one would expect the effects of different kinds of bubbles to appear. The fluctuation with frequencies above 50 Hz can be attributed to the mass flow controllers, rotameters, and the environmental noise within the laboratory. Therefore, an upper cutoff limit of 50 Hz was established to limit the Fourier transform analysis to only the phenomenon occurring inside the visualization cell (i.e., periodic nucleation, growth and detachment of oxygen bubbles from the anode).

Since the Fourier transform results did not yield any meaningful result (i.e., no distinct peak), a new method called the "bubble ratio" analysis was developed. The bubble ratio is a fraction that represents the bubbles that are present at a given frequency range, and at a fixed current density. The sum of the bubble ratio at any current density must equal to 1. In this study, the three selected frequency ranges to represent different bubble phenomenon were: i) 0.03 < f < 1 Hz, ii) 1 < f < 10 Hz, and iii) f > 10 Hz. An average current density (j) for the whole frequency range is shown in equation 4.1

$$\hat{j}(\xi) = \int_{-\infty}^{\infty} j(t) e^{-2\pi i t \xi} dt$$
(4.1)

where j(t) is current density as a function of time, ξ is the frequency and i in this context is an imaginary number. The CA experiments recorded 90 seconds of data, but the first 30 seconds were excluded from the analysis. Therefore, any bubble that persisted longer than 60 seconds would not be observed in the Fourier transform analysis. A theoretical bubble lifetime of 60 seconds is equal to 0.017 Hz. This number was doubled (i.e., 0.03 Hz) and was set as the lower bound frequency limit. Nouri et al.[148] predicted the presence of nucleation-driven and drag-driven bubbles with lifetimes around 1-10 ms and 10-100 ms at typical operating conditions. These bubble lifetimes could be roughly attributed to the current fluctuations at 108 above 10 Hz from nucleation-driven bubbles, and current fluctuation between 1-10 Hz from drag-driven bubbles. From this, Nouri [149] developed three equations calculating the bubble ratio (R_i) for these three frequency ranges (equations 4.2 - 4.4).

$$R_1 = \int_{0.03}^1 \hat{j}(\xi) \, d\xi \tag{4.2}$$

$$R_2 = \int_1^{10} \hat{j}(\xi) \, d\xi \tag{4.3}$$

$$R_3 = \int_{10}^{50} \hat{j}(\xi) \, d\xi \tag{4.4}$$



Figure 4.9: The bubble ratio for three frequency ranges for the different current collector meshes used.

Figure 4.9 shows the bubble ratio plots for each current collector mesh for all three frequency ranges (in Hz). Each 0.03 < f < 1 Hz curve from each of the samples (M1 through M4) from Figure 4.9 is compiled in Figure 4.10. The compiled bubble ratio results for the other two frequency ranges (1 < f < 10 Hz, and f > 10 Hz) did not have any noteworthy trends and are shown in the Appendix C.4 (Figure C.8 and Figure C.9, respectively). In theory, a lower bubble ratio implies that more catalyst surface area is available to react with the electrolyte. In other words, a lower bubble ratio should mean the performance is better. However, the best performing current collector (M1) has the largest bubble ratio which is initially counter-intuitive. An potential explanation is that the presence of gas at the interface may have resulted in an intermittent and local temperature increase at the interface. A similar phenomenon exists for fuel cells, with Zhou et al. [150] reporting an 8°C increase in temperature in the case of no microporous layer from a thin layer of water near the GDL/CL interface.



Figure 4.10: Compiled bubble ratio results for frequency range R₁ (0.03 < f < 1 Hz).

4.4 Summary

A diagnostic flow-cell was developed to study the OER performance and current fluctuations from bubble growth and detachment. The cell was initially tested with Ir foil, with rapid cycling CV data matched literature results for the growth of the oxide up to 1700 cycles. The selection of four Ti current collector meshes for use with the cell was based on two previous MRDE studies (Chapter 2 and Chapter 3). The increasing charge with physical mesh coverage and the improvement of OER performance based on TCP coverage matches the trends found from the MRDE work in Chapter 2.

The Fourier transform analysis was inconclusive as there was no distinct peak found between 1 < f < 50 Hz. A new figure of metric, the bubble ratio, considered the fraction of bubbles that existed on the catalyst surface for three defined frequency ranges. The frequency ranges were divided into three ranges, based on the dominance of buoyancy and drag driven bubbles in each respective region as determined from a previous modelling study. There is an increasing bubble ratio with increasing current density observed for the bubbles found between 0.03 < f < 1 Hz past 700 mA cm⁻². This was attributed to local temperature increases on the surface of the catalyst, where a similar phenomenon exists in PEMFCs.

Future work could consider a reorientation of the cell such that fluid flow fights against gravity, ensuring that there are no air pockets trapped in regions of interest (e.g., camera lens, current collector). A comparison between cameras used in the literature has been discussed in section 7.3

Chapter 5: Methods and Materials for Titanium Reduction in the Anode Side of the PEWME

5.1 Scope and Context

Porous transport layers (PTLs) serve an important role in the PEMWE and must have the following: i) The anode PTL must have good Pourbaix stability (i.e., not corrode or dissolve) up to about 2 V, ii) function as a low-resistance current collector, iii) provide unhindered water transport to the catalyst (to prevent reactant water starvation), iv) allow evolved gases (especially oxygen) to be easily transported away from the catalyst, and v) have good mechanical properties and withstand the compression of the cell. Point i applies only to the anode current collector, but points ii-iv apply to both the anode and cathode PTLs. Section 1.4.2 (Introduction) of this thesis has covered similar requirements for current collectors, and reported desirable physical property values (e.g., pore size, thickness) for PEMWE. A more detailed discussion is provided in this chapter, expanding on the physical characteristics and addressing challenges associated with state-of-the-art current collectors. The term "current collector" and PTL can be used interchangeably, but PTL will be used throughout this chapter for consistency and is focused on the anode PTL.

Ti is one of the few materials that can withstand the electrochemical conditions of the cell. The high electrochemical potential (i.e., up to at least 2 V), and the acidic environment in the PEMWE limits the choice of PTL material to Ti. At potentials above 0 V_{SHE} and 0 pH, the Ti oxidizes to TiO₂ [151]. Rakousky et al. used an in-house device to measure through-plane resistance of both a fresh Ti-PTL, and a spent Ti-PTL after 1009 hours of operation at 80°C and 2 A cm⁻² [131]. The reported resistances were 49 m Ω cm² (new PTL) and 238 m Ω cm², but this

information is qualitative as the conditions of this ex-situ measurement are different compared to the in-situ measurement. Mitigation strategies such as sputtering the sintered Ti-PTL with 200 nm of Pt have been mentioned by Qi et al. in a review article [152]. However, this strategy would not be viable for commercial PEMWE stacks with active areas ranging in the m² because of the costs associated with Pt.

Points iii and iv are linked to the physical classification of the PTL. Ito et al. has classified PTLs into 3 categories: i) Mesh or screen types, ii) Sintered Powder Types, and iii) Felts or unwoven fabrics [135]. Mesh or screen-type PTLs have a low material cost, but imprint themselves in the catalyst layer when the cell is compressed during assembly. Although mesh/screen type PTLs have a larger porosity (i.e., ability for water to access the catalyst), these types of PTLs lead to low catalyst utilization. Since meshes have inherently high porosity (e.g., open area), much of the catalyst is not electrochemically active. If the mesh strands are fine enough, the CCM could incur permanent damage. These types of PTLs are avoided because of the above reasons.

Sintered powder types PTLs are formed from thermal sintering of Ti powder. These are the most widely adopted, as PTLs provide mechanical support under compression and have high TCP coverage. Important characteristics of sintered Ti-PTLs are pore size distribution, average pore size, porosity, and thickness. Grigoriev et al performed an experimental optimization study of Ti current collectors of various porosities, powder size, and thickness [76]. His study found that a pore size of 12-13 μ m and a spherical Ti powder size of 50-75 μ m yielded the best PEMWE performance for his system. Majasan et al. [153] illustrate the importance of pore size (both through-plane and two in-plane 2D slices) of two PTLs with a pore size of 16 μ m (Figure

4.2a) and 60 um (Figure 4.2b), respectively. There is less variation in area porosity seen with the PTL with the 16 μ m pore size diameter (Figure 5.1).

Although the 60 µm PTL sample had larger pores, the average pore volume was smaller, facilitating larger bubbles being formed at the PTL | anode catalyst layer interface. The consequence of larger bubbles formed at this interface causes increased slug formation of bubbles in the flow channels [154]. Felts or unwoven fabrics are an intermediate option when compared to sintered materials and meshes. Ti felts have a lower material cost compared to sintered Ti PTLs, and a reduced likelihood of embedding in or piercing the CCM. However, the pore size distribution and porosity of these felt materials is not well controlled, and can exacerbate the problem of increased slug flow in the flow channels.



Figure 5.1: Average 2D area porosity of a PTL using through-plane (TP), in-plane 1 (IP-1), and in-plane 2 (IP-2) slices with a) 16 μm pore size, and b) 60 μm pore size. Reprinted with permission from Energy Procedia [153].

The discussion of important PTL characteristics and types has highlighted two challenges: i) the lack of a proper substitute for Titanium as the anodic PTL, and ii) the high costs associated with sintered Ti PTL fabrication, the most widely used type of PTL. Unlike research in new PEMWE catalyst materials, there does not seem to be much in the literature with regards to alternative PTL materials. Aside from the mentioned coating with Pt or Au, the use of a microporous layer to reduce interfacial contact resistance has also been considered [134]. However, no substitute for a base substrate material or engineered PTL involving thin-film metals on plastic substrates has been reported in the literature.

The goals of this chapter are to reduce the need for a solid Ti-based current collector on the anode side, since the machining of Ti is costly. Two experiments were performed: i) using a 3D printed plastic material coated with a thin layer of Titanium (e.g., 500 nm) using physical vapour deposition methods, and ii) exploratory work by using no PTL on the anode side and relying solely on CCM to channel contact.

5.2 Experimental

5.2.1 Materials

5.2.1.1 Down selection of Plastic Substrate

Given the challenge of replacing Ti as a current collector in the short term, the adhesion strength of Ti onto various plastics was investigated first. Calcagno et al. investigated the adhesion strength between Ti foil (99%, 0.127 mm thick) onto polycarbonate (PC), polypropylene (PP) and high-density polyethylene (HDPE) using a cold-rolling process to physically combine the metal and the plastic substrate. They reported the adhesion force required to cause Ti debonding over the strip surface was about 4.5, 2.2, and 1.8 N mm⁻² for PC, PP and HDPE respectively [155]. Although the method of combining these two is purely physical (whereas fabrication of Ti/PC PTLs could be done chemically), Calcagno's work illustrates interfacial adhesion differences between Ti and different plastic substrates.

The Ti/PC or TiO₂/PC composite system is well-known in the literature, with applications in aerospace, artificial organ replacement, car manufacturing, photocatalysis and sensor development [156,157]. Polycarbonate is a readily available engineered plastic that is reported as lightweight, strong, chemically resistant material that is commonly used in 3D printing. It has a glass transition temperature of 152°C and a melting point of 267°C [158], which meets the temperature requirements of the PEMWE since the highest commonly reported operating temperature is 80°C. Polycarbonate is resistant to acid attack, although vulnerable to alkali solutions [159]. Although the PEMWE uses an acidic solid polymer electrolyte (SPE), a component's resistance to sulfuric acid is commonly used as a metric for evaluating acid resistance. There are currently no reported publications on metallic thin-film plastics being used
as PTLs for the PEMWE. As such, there is a need for research to be done on the Ti/PC PTL for the PEMWE application.

The customizability of the Ti/PC system has been demonstrated by a few research groups. Tomizawa et al. have shown the use of a homogenous low energy electron beam irradiation (HLEBI) at 30 MGy to improve Ti adhesion [156]. Average peeling loads of 1.25 N and 0.3 N were reported for the Ti/PC sample treated with the HLEBI and without, respectively (Figure 4.3a-b). The HLEBI irradiation created active terminated atoms with dangling bonds, improving the chemical bond between the Ti and the plastic polymer [160].

Yaghoubi et al. showed the change of hydrophobicity with surface treatment of the PC using concentrated H₂SO₄, K₂Cr₂O₇, and DI water respectively. The contact angles of an untreated PC layer and a fully treated PC layer were 88° and 20°, respectively [157]. Hydrophilicity is a desired property for PTLs (e.g., to draw water towards the PTL, and by association towards the catalyst) [80]. Given the large design space of the use of Ti/PC for PEMWE applications, this research focused on Ti/PC as an alternative PTL approach, and the future work required to make this a competitive PTL.

5.2.1.2 Design of the Plastic Substrate

The dimensions of the plastic substrate were 5 cm x 4.6 cm x 0.1 cm (length, width, thickness), with a total area of 23 cm² (Figure 5.2a). These dimensions were specified as such, so that the plastic-based PTL could fit into the dedicated anode PTL-slot in the PEMWE hardware as specified in Chapter 3 (Fraunhofer electrolyzer cell). The plastic substrate was designed on SolidworksTM (Figure 5.2b), and was submitted to a 3D printing company (Xometry.com). Two types of plastic substrates were made: i) Accura 25 (Acrylonitrile butadiene styrene) using the Stereolithography method, and ii) PC using the Fused Deposition Modeling (FDM) method. The highest resolution possible was specified for the Solidworks file, meaning that the surface roughness of these two plastic substrates was minimized. The two plastic substrates used were acrylonitrile butadiene styrene (ABS) and PC, respectively.



Figure 5.2: a) Schematic of the plastic PTL substrate, and b) as-submitted plastic PTL design submission to Xometry.com.

From the literature review, the porosity of sintered Ti-PTLs range from 30 to 50%. There are nine holes with a diameter of 1 cm and a depth of 0.1 cm. Based on these dimensions, the porosity of these plastic PTLs is 30.71%, which falls within the typical porosity range.

5.2.1.3 Titanium Deposition

The as-received ABS and PC samples were cleaned individually with a 50/50 vol% mixture of isopropanol /18 M Ω deionized water and sonicated for 5 minutes. They were dried with Kimwipes and stored in a petri dish until ready for the coating process. The plastic substrates were coated with Ti using an 18" O.D. chamber sputtering system (ATC-1800-HY, AJA International Inc.) with a Labview-based computer system (Phase II J, AJA International Inc.) at the Advanced Materials Process Engineering Laboratory (AMPEL). Titanium (Purity Grade 4.5N, Kurt J. Lesker) was evaporated at a rate of 0.5 nm s⁻¹ in a vacuum chamber with a base pressure of 6×10^{-8} torr. The plastic substrate was mounted to a sample holder using carbon tape. The sample holder was tilted at a 30-degree angle to coat the inner circles and edges of the plastic substrates. The final thickness of the Ti coating on front and back surface was around 500 nm.

5.2.2 Experimental Methods

5.2.2.1 Through-Plane Resistance

Through-plane resistance was measured using an in-house compression device with an air cylinder (Humphrey 5-SHP-1, Humphrey Automation Inc.) and two gold-plated plates. A multichannel potentiostat with a 5 A current booster (VMP3 and VMP3B-5, Bio-Logic Science Instruments) was used to perform the through-plane resistance measurement. An impedance scan was performed for each sample at 10 mV AC amplitude and a frequency range of 1 Hz to 1000 kHz.

121

5.2.2.2 PEMWE Cell Setup

A 23 cm² active area PEMWE cell was used as-received from Fraunhofer ISE. The cell architecture and components have been previously described under "Test setup and rig" section by Ojong, Kwan et al [31]. The endplates, bipolar plates (BIP), flow field, and current collector were made from Ti Grade 2 (e.g., commercially pure Ti).

An electrolysis test station (E20 in E40 frame, Greenlight Innovation) with an 850 W power supply (Sorensen XG 6-110, AMETEK Programmable Power, Inc.) was used. The CCM (E300 Series, 25 cm², Greenerity Generation E300, SolviCore GmbH & Co. KG) has unsupported IrO₂ on the anode and Pt black on the cathode. The cell was compressed to about 0.6 MPa using 12 bolts and tightened with an applied torque of 17.16 Nm. The resistance measurements were performed using an LCR-meter (GWistek LCR 821, Good Will Instrument Co., Ltd.) at a frequency of 0.5 kHz with an AC voltage amplitude of 200 mV.

For the Ti thin-film plastic experiments, the standard Ti cathode PTL was used (Figure 5.3a) while the anode was replaced with either Ti/ABS or Ti/PC (Figure 5.3b). The no-PTL experiment removes the anode PTL and positions it on top of the cathode PTL. This pushes the CCM down towards the flow field channel, facilitating good contact between the ACL and flow field channels (Figure 5.3c)



Figure 5.3: PEMWE component assembly for a) baseline case, b) Ti/Plastic PTL case, and c) no anode PTL with stacked cathode PTL case.

5.2.2.3 Experimental Procedures

Three experiments were performed for the thin-film plastic PTL: i) Baseline setup with Ti PTL on the anode and cathode, ii) a Ti-coated plastic on the anode, Ti/PTL on the cathode, and 3) a blank plastic substrate on the anode, Ti/PTL on the cathode. Polarization tests using the galvanostatic protocol from Kroschel, Kwan et al. [112] were run at 25, 40, 60, 80 and back to 25°C at 2 LPM and at 0 barg for each of the three experiments. The CCMs were conditioned by cycling between 1.0 and 1.7 V for a period of 2 hours at 25°C. For each subsequent use, the cell was hydrated by having DI water flow at 2 LPM for 30 minutes prior to polarizations. The LCR was used to measure the resistance before and after each polarization.

5.3 Results and Discussion

5.3.1 Through-Plane Resistance Screening and Remediation Strategies

The through-plane conductivity of the Ti/ABS and Ti/PC samples were 535 k Ω and 18 M Ω , respectively. Although both samples were coated with a film of 500 nm Ti under the exact same deposition method, the surface homogeneity of the PC and ABS samples were quite different. The PC surface is mostly comprised of thick diagonal striations. The nature of this rough and electronically disconnected surface likely limited the conductive pathways between the two large faces of this PTL. The ABS plastic had the appearance of a smooth sheet metal. The Ti coating appeared uniform on the ABS substrate, which likely explains the lower resistance compared to the Ti/PC sample (Figure 5.4).



Figure 5.4: Freshly coated samples of Ti/PC (Left) and Ti/ABS (Right).

To improve the surface uniformity of the Ti/PC sample, a method suggested by AMPEL was used to expose the surface of the PC to vaporized acetone in a closed environment. The use of "cracking solvents" (e.g., acetone, benzene) on the material properties of ABS was explored by Mai et al [161]. 60 mL of acetone was heated in a 500 mL beaker over a hotplate. The bare

PC was suspended over the boiling acetone and a larger beaker covered the PC and beaker. The combination of all the glassware and the hotplate is be referred to as the "acetone vapour bath" (Figure 5.5).



Figure 5.5: Real image of acetone vapour bath (left) and a labelled schematic (right).

The sample was taken out of the acetone vapour bath and inspected visually every 30 seconds. For the first 30 seconds, minor dissolution of the PC striations was observed but the surface was not homogenized. The sample was placed in the acetone vapour bath for another 30 seconds, but this caused irreversible warping and flaking of the plastic. The PC plastic at this point was also more brittle, and snapped when a modest amount of pressure was applied to the edge. For these reasons, the Ti/ABS plastic was selected for evaluation in the PEMWE.

5.3.2 PEMWE Baseline Experiments with new MEA

Since a new, unconditioned MEA was used, the purpose of these baseline experiments was to confirm the stability of the setup and reproducibility of data. At 2 A cm⁻², the non-iR corrected potential reported for 25, 40, 60 and 80°C was 2.32, 2.20, 2.08 and 1.92 V respectively. A duplicate run of the 25°C run shows an increase of about 40 mV (Figure 5.6).



Figure 5.6: Baseline polarization using setup from Figure 5.5a and a new E300E CCM.

The resistance of the cell was measured before and after the polarization (Table 5.1) at each temperature. The aggregated resistance (m Ω cm²) can be obtained from equation 5.1. The area resistance ranges from 312 - 460 m Ω cm², depending on operating temperature.

Area resistance
$$[m\Omega \ cm^2] = Resistance [\Omega] \times Area [23 \ cm^2] \times \frac{1000 \ m\Omega}{1 \ \Omega}$$
 (5.1)

Run (°C)	Before Polarization (Ω)	After Polarization (Ω)
25	2.0E-02	2.0E-02
40	1.7E-02	1.7E-02
60	1.5E-02	1.5E-02
80	1.4E-02	1.4E-02
25R	2.3E-02	2.1E-02

Table 5.1: Baseline resistance for SolviCore E300 CCM with sintered Ti-PTLs.

5.3.3 PEMWE Results with Ti/ABS Plastic

The first test with the Ti/ABS PTL tested the maximum current of the PEMWE in this configuration. At 25°C, a maximum of 1.15 A, and 5.9073 V was attained before the test station safety limits were reached using the protocol from chapter 3 (Figure 3.2a). Only four data points were acquired: 0.115, 0.23, 0.46, and 1.15 A. Therefore, the protocol from Figure 3.2a was modified to obtain more data points, which will be called the *ABS protocol* from now on. The polarization is performed at the following currents: 0.115, 0.1725, 0.23, 0.345, 0.46, 0.805, and 1.15 A. The additional current set points were selected based on the average between neighboring current set points in the previous protocol (e.g., 0.1725 is the average between 0.115 and 0.23).

Figure 5.7 shows the polarization curves using the ABS protocol for the Ti/ABS at 25°C, 40°C, 60°C and then 25°C again as a replicate test (denoted as R2). 80°C was not performed for this experiment because the deflection temperature of ABS is about 72°C. Current is reported instead of current density, as the true active geometric surface area is unknown (more on this in section 5.3.4). The currents were very low, only reaching about 1.2 A at 3.5 V for 60°C. However, there is a large difference in the 25°C polarizations, which may indicate that CCM

swelling was enough to protrude through the nine holes of the PTL to directly contact the flow field. If this is what is occurring in the cell, then the Ti/ABS PTL is not serving its intended purpose as a current collector. Section 5.3.4 will examine the effect of the blank ABS PTL alone.



Figure 5.7: Performance of a SolviCore E300 CCM with a Ti/ABS anode PTL and sintered Ti-PTL on the cathode at 2 LPM and 1 atm.

5.3.4 Diagnostic Tests for extent of CCM swelling in blank ABS samples

To validate that the current response was a result of the Ti/ABS providing sufficient electrical contact instead of the swelled CCM contacting the flow field, the same tests were performed with the ABS plastic with no Ti coating (Figure 5.8). Although the Ti/ABS sample performed better than the ABS blank, in theory the blank ABS sample should show no current or activity (i.e., an incomplete circuit with a plastic separator). In both cases, the results are better with an increase in temperature. This is likely due to increased volume expansion and protrusion making increased contact with the channel landings.



Figure 5.8: Ti/ABS and ABS blank (no Ti coating) polarization curves compared. Both show similar current magnitudes, despite the bare ABS not being electronically conductive

Figure 5.9 shows the effect of increased hydration on the PEMWE polarization with an ABS blank PTL. After the first blank test, the assembled PEMWE with the ABS PTL was left flooded for 72 hours before a second polarization run. The extent of CCM swelling should have reached a steady state after this time. There was a significant improvement in cell performance at lower temperatures in the second blank test (0.5-1V improvement for 25 and 40°C), but only a marginal improvement at 60°C. The marginal improvement observed at higher temperatures is possibly due to the heat accelerating the swelling, allowing the CCM contact in both the 72-hour case and the blank case to be similar.



Figure 5.9: ABS blank tests before and after 72-hour hydration period.

The cell resistances for the Ti/ABS, ABS blank with 30-minute initial hydration, and ABS blank with 72-hour hydration are summarized in Table 5.2. The resistances reported are 3-4 times larger in magnitude compared to the baseline case (Table 5.1), showing poor electrical contact in general. The difference between the 25°C resistances of blank 1 and blank 2 indicate that the catalyst protrusion through the PTL is a major contributing factor to resistance. The similarity in resistances for all three experiments for 40°C and 60°C indicate that the main conductive pathway is through the CCM contacting the flow field, and not through the Titanium on the ABS.

	Before Polarization (Ω)				After Polarization (Ω)		
Run (°C)	Ti/ABS	Blank 1 (30 min hydration)	Blank 2 (72-hour flood)	Ti/ABS	Blank 1 (30 min hydration)	Blank 2 (72-hour flood)	
25	3.38	10.9	3.84	2.46	10.3	3.70	
40	2.77	5.42	2.82	NR	4.32	2.85	
60	1.75	2.44	2.08	1.66	2.16	2.14	

Table 5.2: Resistance measurements before and after the cell is flooded for 72 hours.

5.3.5 Blank ABS Post Mortem Analysis

Upon immediate disassembly of the cell after testing, the CCM had nine "protruding islands" corresponding to the holes in the plastic PTL (Figure 5.10). There is a bar in the middle of each island, corresponding to where contact was made with the channel landings. The real surface area of this catalyst is likely the total area of the CCM contacting these gold-covered bars.



Figure 5.10: SolviCore CCM after disassembly showing the nine islands conformed to the shape of the plastic PTL openings.

The blank PTL also had catalyst impressions after disassembly, and show black markings on the PTL from catalyst delamination (Figure 5.10). However, for the performance of the PEMWE to decrease as a result of catalyst loss, the loading would have to fall below 1.71 mg_{IrO2} cm⁻² before any appreciable effect would occur according to Rozain et al. [117].

Based on these observations and testing results, this engineered Ti/Plastic PTL has not demonstrated that it can provide sufficient electrical contact. The expansion of the hydrated CCM contacting the flow field made it difficult to identify if the Ti/ABS plastic was accomplishing its intended purpose. This is consistent with the low through-plane and in-plane conductivity measured as well.

5.4 Initial Results with No Anode PTL

Figure 5.11 shows how the no anode PTL case (CCM in contact directly with the flow field, as shown in Figure 5.5c) compares with the baseline case (Figure 5.5a). Unlike the Ti/ABS PTL case (Figure 5.5b), the no anode PTL case was able to reach 2 A cm⁻², however at very large overpotentials. The current for the no PTL case was normalized to the 25 cm² active area of the CCM (e.g., the area equal to the front face of a sintered Ti PTL), and is called the non-area corrected polarization.



Figure 5.11: Non iR-corrected baseline (dashed lines) vs non-area corrected no-anode PTL case (solid lines).

The raised flow field in the PEMWE contact half the active CCM face area, which is 12.5 cm². Therefore, a more useful comparison would be to normalize it to this real contact area. Figure 5.12 compares the 80°C runs for the PTL-less 25 cm² area with the PTL-less 12.5 cm² area. This data shows that without the PTL, current densities up to 2 A cm⁻² are achievable with almost twice the potential. The anode porous transport layer (PTL) is important in order to reach good performance in a PEMWE. However, the possibility of having no anode PTL, or a PTL with reduced Ti content, reduced machining and assembly would reduce costs for the PEMWE.



Figure 5.12: Comparison of no anode PTL case normalized to 25 cm² (solid line), 12.5 cm² area corrected no anode PTL case (dashed lines).

5.5 Summary

The short-term irreplaceability of Ti as the PTL and endplates for PEMWE remains a financial challenge. This chapter explores two scenarios: i) Ti/Plastic as a replacement anode PTL, and ii) no anode PTL. The through-plane resistance of the Ti/ABS and Ti/PC samples were 535 k Ω and 18 M Ω , respectively. The PC samples had a poor surface finish with bumpy lateral striations which affected the coating uniformity. Using the Ti/ABS as the anode PTL in the PEMWE, the maximum current obtained was just slightly below 1.2 A. An ABS blank PTL with no Ti showed that the performance was similar to the Ti/ABS, indicating that the observed current was from the swelled CCM extruding through the PTL holes contacting the flow field.

In the no anode PTL case, the cell was carefully assembled to ensure that the CCM would fit in the recess previously occupied by the anode PTL. At 80°C, the reported potential was 3.5 V at 2 A cm⁻², a much better result compared to the Ti/ABS case. However, in both cases performance is inferior to the Ti mesh anode PTLs studied in chapter 3, and the sintered Ti anode PTL.

Chapter 6: Conclusion

Two new electrochemical testing methods were developed for the OER, and exploratory work on Ti meshes, Ti coated plastic and no PTL were completed in this work. The two electrochemical testing methods are the MRDE, and the diagnostic cell. The purpose of this work is to accelerate catalyst and CCMdevelopment by improving existing testing methods while increasing the testing capabilities, to provide more insight into catalyst research.

The MRDE tests CCMs instead of thin film inks, which has never been performed before. This tool was rigorously tested for ORR activity using Pt foil and three commercial CCMs. The Johnson-Matthey CCM had the highest mass activity out of the three commercial CCMs. The mass activity of the Johnson-Matthey CCM was in better agreement with the PEMFC result. This tool could be used to screen catalysts at an earlier stage of catalyst development, saving time and money. However, the solubility of oxygen in the electrolyte is a reason that the MRDE will not duplicate the PEMFC result.

The MRDE was then used to assess six current collectors with a state-of-the-art commercial CCM for the OER. Currents of 2 A cm⁻² and higher were reported, which was never achieved with the TF-RDE technique for the OER. The challenge with current collectors is that the catalyst is only active where the current collector contacts the catalyst. This means that much of the catalyst is inactive, and effectively unused. The results showed a clear link between TCP and OER performance.

The utility of the MRDE can be used for other electrochemical applications, including battery testing and molten electrolysis. An invention disclosure was filed describing the additional testing capabilities and improved accuracy when using CCMs over catalyst inks (UILO #17-092 USP).

136

A visualization cell with a large flow channel was designed to mitigate the noise associated with bubble slugs at high current densities. Four current collectors were chosen: one from the MRDE ORR study and three from the MRDE OER study. The performance ranking of the four meshes was the exact same as found from the MRDE OER study. Fourier transform analysis and bubble ratio methods were applied to understand the distribution of bubbles. Most bubbles had a lifetime of 1 s or lower. The bubble ratio was increasing with increasing current density, and this trend was prominent after 700 mA cm⁻².

The need to substitute Ti as the preferred PTL and BPP material is a financial challenge for PEMWE systems. A 3D printed PTL made from PC and ABS plastics were selected for sputtering of Ti. This 3D printed alternative could decrease Ti (on a mass basis) by a factor of at least 50. The through-plane resistivity in the k Ω to M Ω range, suggesting that the structure needs to be modified for improved through-plane conductivity. The case where the anode PTL was removed showed that a current density of 2 A cm⁻² was obtained at 80°C at 2.5 V (area corrected). This shows that the PEMWE can function without an anode PTL. The only means of electrical contact was from the CCM directly in contact with the elevated flow field channels.

The main contributions from this thesis are to catalyst R&D and exploratory work at Ti reduction of PTL and BPP. The intent was to bring additional scientific value to current testing methods, and serve as a foundation for future PEMWE work in the hopes to springboard widespread commercialization.

137

Chapter 7: Recommendations for Future Work

Suggestions for future exploration for each of the chapters (i.e., MRDE for the ORR, OER, diagnostic cell and PTL replacement) are suggested in this chapter. In general, the work for the MRDE (Chapter 2 and Chapter 3) was complete with few recommended suggestions. However, there are some suggestions for the diagnostic cell (Chapter 4) and the PTL replacement (Chapter 5).

7.1 Future Work for the ORR studies with the MRDE

For the work concerning the MRDE for the ORR, improvements to the MRDE apparatus to facilitate oxygen delivery to the catalyst sample from behind (e.g., the shaft itself serves as a means of delivering oxygen to the catalyst). This was suggested in the invention disclosure (UILO #17-092 USP). Also, using an electrolyte with a higher solubility of oxygen could also be studied.

7.2 Future Work for the OER studies with the MRDE

For the work concerning the MRDE for the OER, it is clear how important the TCP parameter is and should be considered in future PTL designs. Development and testing of high surface area electrodes (e.g., catalyst-coated PTLs) and testing these in the MRDE would be an important next step in improving the disadvantage of state-of-the-art low surface area IrO₂ catalysts.

7.3 Future Work for the Diagnostic Cell

The camera was inserted in a quartz sheath and suspended in the head space of the cell. At potentials above 2 V_{RHE} , the bubbles generated from the catalyst would rise and many would be swept away from the flow. However, some of these bubbles would stick and persist on the

quartz sheath, blocking the camera's view. The flow rate was varied (up to 2x) in an attempt to prevent the rising bubbles from accumulating in the above head space, but this did not work

To mitigate this, having the cell tilted 90° with the direction of flow from bottom to top would prevent bubble accumulation in their relative head spaces. Any evolved bubbles would rise with the direction of flow and away from the camera. Secondly, it may be worth considering modifying the cell such that the camera views the catalyst area by a dedicated port on the side of the glass body rather than have the camera integrated with the lid.

If the suggestion above does not result in obtaining better video footage, changing the type of camera could be considered. The camera selected for this work was an endoscopic camera with 30 frames per second (FPS) and a resolution of 1024 x 800 (30 USD). Table 7.1 is a summary of other cameras used in this work. This should only be considered if reorientation of the cell does not resolve the bubble accumulation of the quartz sheath, and if there is interest in performing an in-depth study on bubble size distribution and lifetime.

Author	Flow Rate (mL min ⁻¹)	Current Density	Channel Dimensions	Camera	Resolution (Pixels)	Frames per second
Kwan, Nouri (this work)	1700	2 – 2.5 A cm ⁻²	2.54 inch x 2.54	USB Endoscope	1024 x 800	30
Hoeh [75]	0.6 to 1.5	10 - 200 mA cm ⁻²	1.4 mm wide x 0.4 mm deep	N/A, camera was not used		used
Panchenko [82]	1-5	1.5 A cm ⁻² , 3V	2mm width	Andor Neo 5.5 sCMOS camera	2562 × 2160	N/A
Mo [123]	20-40	2 A cm ⁻²	1 mm width	Phantom v711	1280 x 800	7520
Selamet [39]	175-300	0.1 A cm ⁻²	Channel width of 0.8 mm	Canon Rebel T2i	-	N/A
Degidama [83]	1-10	Up to 1 A cm ⁻²	2.5 mm	Photron SA-5	1024 x 1024	7000
Ito [81]	80 and 150	0.065 A cm ⁻²	1 mm width	VW-9000 camera	-	6000
Degidama [138]	1, 3 and 5	0.5 A cm ⁻²	0.3 cm x 8.5 cm	Photron SA-5	1024 x 1024	2000
Arbabi [140]	0.01	1.4 A cm ⁻²	Fluidic Chip	pco. 1600 monochrome	800 x 600	31.62
Kobayashi [162]	Oª	2 A cm ⁻² , 10 cell stack	No channels	N/A, ca	mera was not	used

^a cell was circulated naturally via differences in buoyancy

Table 7.1: Literature com	pilation of both no	n-invasive and direct	visualization studies.
---------------------------	---------------------	-----------------------	------------------------

7.4 Future Work for PTL Replacement

Future experiments with Ti-coated plastic PTLs should demonstrate the viability of this alternative technology:

• Use a smaller PTL hole diameter, to prevent CCM contacting the flow field. This will determine the PTL is performing its intended function

Optimization of these plastic PTLs is challenging due to the added complexity the Ti/Plastic system. The quality of the Ti coating and plastic structure are two areas for improvement. Other suggested improvements in this area include:

- Using different Ti-deposition methods, such as electrodeposition of Ti onto the plastic PTL.
- Improve the surface finish of polycarbonate by making the surface more homogeneous. Other, more sophisticated, 3D-printing services/methods could be considered (for example, a finer plastic dispersing nozzle would lead to better quality structures)
- Introduce a conductive intermediate embedded in the plastic to improve through-plane conductivity
- Use more complex plastic structures that provide more conductive pathways from the CCM to the flow field when coated with titanium

Bibliography

- S. Shafiee, E. Topal, When will fossil fuel reserves be diminished?, Energy Policy. 37 (2009) 181–189. doi:10.1016/j.enpol.2008.08.016.
- B.R. Singh, O. Singh, Global Trends of Fossil Fuel Reserves and Climate Change in the 21st Century, 2012. doi:10.5772/38655.
- [3] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, Appl. Catal. B Environ. 56 (2005) 9–35. doi:10.1016/j.apcatb.2004.06.021.
- [4] A.B. Ilicic, Investigation of a Direct Liquid Redox Fuel Cell with Design Simplification, University of British Columbia, 2010.
 https://open.library.ubc.ca/cIRcle/collections/ubctheses/24/items/1.0058853.
- [5] C. Spöri, J.T.H. Kwan, A. Bonakdarpour, D.P. Wilkinson, P. Strasser, The Stability Challenges of Oxygen Evolving Catalysts: Towards a Common Fundamental Understanding and Mitigation of Catalyst Degradation, Angew. Chemie - Int. Ed. 56 (2017) 5994–6021. doi:10.1002/anie.201608601.
- [6] N.P. Brandon, Z. Kurban, Clean energy and the hydrogen economy, Philos. Trans. R. Soc.
 London A Math. Phys. Eng. Sci. 375 (2017) 1–17. doi:10.1098/rsta.2016.0400.
- [7] G. Miley, Dr. John O'M. Bockris 1923 2013, Infin. Energy. 19 (2013) 26–30.
- [8] J.O.M. Bockris, The hydrogen economy: Its history, Int. J. Hydrogen Energy. 38 (2013)
 2579–2588. doi:10.1016/j.ijhydene.2012.12.026.
- [9] D.P. Gregory, D.Y.C. Ng, G.M. Long, The electrochemistry of cleaner environments, 1st ed., Plenum Press, New York, 1972. doi:10.15713/ins.mmj.3.
- [10] K. Schoots, R. Rivera-Tinoco, G. Verbong, B. van der Zwaan, Historical variation in the

capital costs of natural gas, carbon dioxide and hydrogen pipelines and implications for future infrastructure, Int. J. Greenh. Gas Control. 5 (2011) 1614–1623. doi:10.1016/j.ijggc.2011.09.008.

- [11] T. Bose, P. Malbrunot, Hydrogen: Facing the Energy Challenges of the 21st Century, John Libby Euro Texts, UK, 2006.
- [12] W. KREUTER, Electrolysis: The important energy transformer in a world of sustainable energy, Int. J. Hydrogen Energy. 23 (1998) 661–666. doi:10.1016/S0360-3199(97)00109-2.
- [13] D.M.F. Santos, C.A.C. Sequeira, J.L. Figueiredo, Hydrogen production by alkaline water electrolysis, Quim. Nova. 36 (2013) 1176–1193. doi:10.1590/S0100-40422013000800017.
- K. Zeng, D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, Prog. Energy Combust. Sci. 36 (2010) 307–326.
 doi:10.1016/j.pecs.2009.11.002.
- [15] S. Trasatti, Water electrolysis: who first?, J. Electroanal. Chem. (1999) 90–91. doi:PSO-F&U 2006-1-6287.
- [16] W.M. Sudduth, The Voltaic Pile and Electro-Chemical Theory in 1800, Ambix. 27 (1980)26–35. doi:10.1179/amb.1980.27.1.26.
- [17] K. Fujii, Electrochemical Water Splitting Coupled with Solar Cells, in: 2016: pp. 229–245. doi:10.1007/978-3-319-25400-5_14.
- J. Wang, F. Xu, H. Jin, Y. Chen, Y. Wang, Non-Noble Metal-based Carbon Composites in Hydrogen Evolution Reaction: Fundamentals to Applications, Adv. Mater. 29 (2017). doi:10.1002/adma.201605838.

- [19] R. Kruppa, B. Rohland, H. Schuldzig, F. Adolf, B. Roth, US 2002/0187020 A1, 2004.
- [20] W.T. Grubb, L.W. Niedrach, Batteries with Solid Ion-Exchange Membrane Electrolytes,J. Electrochem. Soc. 107 (1960) 131. doi:10.1149/1.2427622.
- [21] W.T.J. Grubb, U.S. Patent No. 2,913,511, 1959.
- [22] M.L. Perry, T.F. Fuller, A Historical Perspective of Fuel Cell Technology in the 20th Century, J. Electrochem. Soc. 149 (2002) S59. doi:10.1149/1.1488651.
- [23] K.A. Mauritz, R.B. Moore, State of understanding of Nafion, Chem. Rev. 104 (2004)
 4535–4585. doi:10.1021/cr0207123.
- [24] R.S. Yeo, Intrinsic Conducitivity of Perfluorosulfonic Acid Membranes and its Implication to the Solid Polymer Electrolyte (SPE) Technology, in: R.S. Yeo, T. Katan,
 D.-T. Chin (Eds.), Proc. Symp. Transp. Process. Electrochem. Syst., The Electrochemical Society, 1982: pp. 178–204.
- [25] G.A. Eisman, The Physical and Mechanical Properties of a New Perfluorosulfonic Acid Ionomer for use as a Separator/Membrane in Proton Exchange Processes, in: J.W. Van Zee, R.E. White, K. Kinoshita, H.S. Burney (Eds.), Proc. Symp. Diaphragms, Separators, Ion-Exchange Membr., The Electrochemical Society, Pennington, 1986: pp. 156–171.
- [26] P.W.T. Lu, S. Srinivasan, Advances in water electrolysis technology with emphasis on use of the solid polymer electrolyte, J. Appl. Electrochem. 9 (1979) 269–283.
 doi:10.1007/BF01112480.
- [27] M.Z. Ibrahim, K. Sopian, W.R.W. Daud, Experimental performance of PV-wind-battery hybrid system for hydrogen production in tropical climatic condition through water electrolysis: A case study for Terengganu state, Malaysia, Int. Energy J. 10 (2009) 11–18.
- [28] T. Ogawa, M. Takeuchi, Y. Kajikawa, Analysis of Trends and Emerging Technologies in

Water Electrolysis Research Based on a Computational Method: A Comparison with Fuel Cell Research, Sustainability. 10 (2018) 478. doi:10.3390/su10020478.

- [29] P. Corbo, F. Migliardini, O. Veneri, Hydrogen Fuel Cells for Road Vehicles, 2011. doi:10.1007/978-0-85729-136-3.
- [30] R. Parsons, Electrochemistry in Research and Development, Springer US, Boston, MA, 1985. doi:10.1007/978-1-4684-5098-9.
- [31] E.T. Ojong, J.T.H. Kwan, A. Nouri-Khorasani, A. Bonakdarpour, D.P. Wilkinson, T. Smolinka, Development of an experimentally validated semi-empirical fully-coupled performance model of a PEM electrolysis cell with a 3-D structured porous transport layer, Int. J. Hydrogen Energy. 42 (2017) 25831–25847. doi:10.1016/j.ijhydene.2017.08.183.
- [32] B. Bladergroen, H. Su, S. Pasupathi, V. Linkov, Overview of Membrane Electrode Assembly Preparation Methods for Solid Polymer Electrolyte Electrolyzer, in: Electrolysis, InTech, 2012: pp. 45–60. doi:10.5772/52947.
- [33] Vijay Ramani, Electrode Kinetics, (2018).
 http://www.engr.uconn.edu/~jmfent/CHEG320_electrode kinetics lectures.pdf (accessed September 8, 2018).
- [34] M. Dudukovic, Chapter 16: Electrochemical Processes, (n.d.) 10–18.
 https://classes.engineering.wustl.edu/che503/che471-08/Electrochemical_Notes.pdf (accessed September 8, 2018).
- [35] D.L. Fritz, J. Mergel, D. Stolten, PEM Electrolysis Simulation and Validation, ECS Trans.
 58 (2014) 1–9. doi:10.1149/05819.0001ecst.
- [36] F. Marangio, M. Santarelli, M. Calì, Theoretical model and experimental analysis of a

high pressure PEM water electrolyser for hydrogen production, Int. J. Hydrogen Energy. 34 (2009) 1143–1158. doi:10.1016/j.ijhydene.2008.11.083.

- [37] B.Y. Cecil, W. Davies, C.W. Davies, The Conductivity of Electrolytes, J. Phys. Chem. 29 (1924) 473–481. doi:10.1021/j150250a011.
- [38] T.E. Springer, Polymer Electrolyte Fuel Cell Model, J. Electrochem. Soc. 138 (1991)2334. doi:10.1149/1.2085971.
- [39] O.F. Selamet, U. Pasaogullari, D. Spernjak, D.S. Hussey, D.L. Jacobson, M.D. Mat, Twophase flow in a proton exchange membrane electrolyzer visualized in situ by simultaneous neutron radiography and optical imaging, Int. J. Hydrogen Energy. 38 (2013) 5823–5835. doi:10.1016/j.ijhydene.2013.02.087.
- [40] Z. Derhoumi, P. Mandin, R. Wuthrich, H. Roustan, Experimental and numerical investigations of two-phase electrolysis processes - Electrical energy conversion in hydrogen production, J. Appl. Fluid Mech. 4 (2011) 81–87.
- [41] J. Ivy, Summary of Electrolytic Hydrogen Production Milestone Completion Report, 2004. doi:10.1126/science.1066771.
- [42] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis, Int. J. Hydrogen Energy. 38 (2013) 4901–4934.
 doi:10.1016/j.ijhydene.2013.01.151.
- [43] T. Smolinka, M. Günther, J. Garche, Stand und Entwicklungspotenzial der
 Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien, Freiburg, 2011.
- [44] A. Ursua, L.M. Gandia, P. Sanchis, Hydrogen Production From Water Electrolysis: Current Status and Future Trends, Proc. IEEE. 100 (2012) 410–426.

doi:10.1109/JPROC.2011.2156750.

- [45] L. Chen, X. Dong, Y. Wang, Y. Xia, Separating hydrogen and oxygen evolution in alkaline water electrolysis using nickel hydroxide, Nat. Commun. 7 (2016) 1–8. doi:10.1038/ncomms11741.
- [46] A. Manabe, M. Kashiwase, T. Hashimoto, T. Hayashida, A. Kato, K. Hirao, I.
 Shimomura, I. Nagashima, Basic study of alkaline water electrolysis, Electrochim. Acta.
 100 (2013) 249–256. doi:10.1016/j.electacta.2012.12.105.
- [47] I. Vincent, A. Kruger, D. Bessarabov, Development of efficient membrane electrode assembly for low cost hydrogen production by anion exchange membrane electrolysis, Int. J. Hydrogen Energy. 42 (2017) 10752–10761. doi:10.1016/j.ijhydene.2017.03.069.
- [48] Y. Leng, C.-Y. Wang, Electrochemical Energy, CRC Press, Boca Raton, 2018. doi:10.1201/9781351228756.
- [49] R. Espiritu, B.T. Golding, K. Scott, M. Mamlouk, Degradation of radiation grafted anion exchange membranes tethered with different amine functional groups via removal of vinylbenzyl trimethylammonium hydroxide, J. Power Sources. 375 (2018) 373–386. doi:10.1016/j.jpowsour.2017.07.074.
- [50] C.C. Pavel, F. Cecconi, C. Emiliani, S. Santiccioli, A. Scaffidi, S. Catanorchi, M. Comotti, Angewandte Highly Efficient Platinum Group Metal Free Based Membrane-Electrode Assembly for Anion Exchange Membrane Water Electrolysis, Angew. Chemie - Int. Ed. 53 (2014) 1378–1381. doi:10.1002/anie.201308099.
- [51] Y. Leng, G. Chen, A.J. Mendoza, T.B. Tighe, M.A. Hickner, C.Y. Wang, Solid-state water electrolysis with an alkaline membrane, J. Am. Chem. Soc. 134 (2012) 9054–9057. doi:10.1021/ja302439z.

- [52] J. Parrondo, C.G. Arges, M. Niedzwiecki, E.B. Anderson, K.E. Ayers, V. Ramani, RSC Advances Degradation of anion exchange membranes used for hydrogen production by ultrapure water electrolysis [†], RSC Adv. 4 (2014) 9875–9879. doi:10.1039/c3ra46630b.
- [53] M. Faraj, M. Boccia, H. Miller, F. Martini, S. Borsacchi, M. Geppi, A. Pucci, New LDPE based anion-exchange membranes for alkaline solid polymeric electrolyte water electrolysis, Int. J. Hydrogen Energy. 37 (2012) 14992–15002. doi:10.1016/j.ijhydene.2012.08.012.
- [54] Y. Cao, X. Wu, K. Scott, A quaternary ammonium grafted poly vinyl benzyl chloride membrane for alkaline anion exchange membrane water electrolysers with no-noble-metal catalysts, Int. J. Hydrogen Energy. 37 (2012) 9524–9528. doi:10.1016/j.ijhydene.2012.03.116.
- [55] X. Wu, K. Scott, CuxCo3-xO4 (0 < x < 1) nanoparticles for oxygen evolution in high performance alkaline exchange membrane water electrolysers, J. Mater. Chem. 4 (2011) 12344–12351. doi:10.1039/c1jm11312g.
- [56] M.K. Cho, H.Y. Park, S. Choe, S.J. Yoo, J.Y. Kim, H.J. Kim, D. Henkensmeier, S.Y. Lee,
 Y.E. Sung, H.S. Park, J.H. Jang, Factors in electrode fabrication for performance
 enhancement of anion exchange membrane water electrolysis, J. Power Sources. 347
 (2017) 283–290. doi:10.1016/j.jpowsour.2017.02.058.
- [57] J.E. Park, S.Y. Kang, S.H. Oh, J.K. Kim, M.S. Lim, C.Y. Ahn, Y.H. Cho, Y.E. Sung,
 High-performance anion-exchange membrane water electrolysis, Electrochim. Acta. 295
 (2019) 99–106. doi:10.1016/j.electacta.2018.10.143.
- [58] L. Wang, T. Weissbach, R. Reissner, A. Ansar, A.S. Gago, S. Holdcroft, K.A. Friedrich,High Performance Anion Exchange Membrane Electrolysis Using Plasma-Sprayed, Non-

Precious-Metal Electrodes, ACS Appl. Energy Mater. 2 (2019) 7903–7912. doi:10.1021/acsaem.9b01392.

- [59] F. Barbir, PEM electrolysis for production of hydrogen from renewable energy sources, Sol. Energy. 78 (2005) 661–669. doi:10.1016/j.solener.2004.09.003.
- [60] L. Bertuccioll, A. Chan, D. Hart, F. Lehner, B. Madden, E. Standen, Study on development of water electrolysis in the EU, 2014. http://www.fchju.eu/sites/default/files/study electrolyser_0-Logos_0.pdf.
- [61] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, The Mechanism of Water Oxidation: From Electrolysis via Homogeneous to Biological Catalysis, ChemCatChem. 2 (2010) 724–761. doi:10.1002/cctc.201000126.
- [62] T. Smolinka, E.T. Ojong, T. Lickert, Fundamentals of PEM Water Electrolysis, in: D. Bessarabov, H. Wang, H. Li, N. Zhao (Eds.), PEM Electrolysis Hydrog. Prod. Princ. Appl., 2015: pp. 11–34.
- [63] P. Liao, J.A. Keith, E.A. Carter, Water oxidation on pure and doped hematite (0001) surfaces: Prediction of Co and Ni as effective dopants for electrocatalysis, J. Am. Chem. Soc. 134 (2012) 13296–13309. doi:10.1021/ja301567f.
- [64] I.C. Man, H.Y. Su, F. Calle-Vallejo, H.A. Hansen, J.I. Martínez, N.G. Inoglu, J. Kitchin, T.F. Jaramillo, J.K. Nørskov, J. Rossmeisl, Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces, ChemCatChem. 3 (2011) 1159–1165. doi:10.1002/cctc.201000397.
- [65] R. V. Mom, J. Cheng, M.T.M. Koper, M. Sprik, Modeling the oxygen evolution reaction on metal oxides: The infuence of unrestricted DFT calculations, J. Phys. Chem. C. 118 (2014) 4095–4102. doi:10.1021/jp409373c.

- [66] E. Fabbri, A. Habereder, K. Waltar, R. Kötz, T.J. Schmidt, Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction, Catal. Sci. Technol. 4 (2014) 3800–3821. doi:10.1039/c4cy00669k.
- [67] M.H. Miles, E. a. Klaus, B.P. Gunn, J.R. Locker, W.E. Serafin, S. Srinivasan, The oxygen evolution reaction on platinum, iridium, ruthenium and their alloys at 80°C in acid solutions, Electrochim. Acta. 23 (1978) 521–526. doi:10.1016/0013-4686(78)85030-0.
- [68] T. Reier, M. Oezaslan, P. Strasser, Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and pt catalysts: A comparative study of nanoparticles and bulk materials, ACS Catal. 2 (2012) 1765–1772. doi:10.1021/cs3003098.
- [69] A. Izgorodin, O. Winther-Jensen, D.R. MacFarlane, On the stability of water oxidation catalysts: Challenges and prospects, Aust. J. Chem. 65 (2012) 638–642.
 doi:10.1071/CH12024.
- [70] A. Damjanovic, V.I. Birss, D.S. Boudreaux, Electron Transfer Through Thin Anodic
 Oxide Films during the Oxygen Evolution Reactions at Pt Electrodes, J. Electrochem. Soc.
 138 (1991) 2549. doi:10.1149/1.2086015.
- [71] C. Sung, C. Liu, Short communication A novel micro protective layer applied on a simplified PEM water electrolyser, Int. J. Hydrogen Energy. 38 (2013) 10063–10067. doi:10.1016/j.ijhydene.2013.06.034.
- [72] H.N. Nong, L. Gan, E. Willinger, D. Teschner, P. Strasser, IrOx core-shell nanocatalysts for cost- and energy-efficient electrochemical water splitting, Chem. Sci. 5 (2014) 2955–2963. doi:10.1039/c4sc01065e.
- [73] J.L. Corona-Guinto, L. Cardeño-García, D.C. Martínez-Casillas, J.M. Sandoval-Pineda, P. Tamayo-Meza, R. Silva-Casarin, R.G. González-Huerta, Performance of a PEM

electrolyzer using RuIrCoOxelectrocatalysts for the oxygen evolution electrode, Int. J. Hydrogen Energy. 38 (2013) 12667–12673. doi:10.1016/j.ijhydene.2012.12.071.

- [74] A.S. Lohoff, L. Poggemann, M. Carmo, M. Müller, D. Stolten, Enabling High Throughput Screening of Polymer Electrolyte Membrane (PEM) Water Electrolysis Components via Miniature Test Cells, J. Electrochem. Soc. 163 (2016) F3153–F3157. doi:10.1149/2.0211611jes.
- [75] M.A. Hoeh, T. Arlt, I. Manke, J. Banhart, D.L. Fritz, W. Maier, W. Lehnert, In operando synchrotron X-ray radiography studies of polymer electrolyte membrane water electrolyzers, Electrochem. Commun. 55 (2015) 55–59. doi:10.1016/j.elecom.2015.03.009.
- [76] S.A. Grigoriev, P. Millet, S.A. Volobuev, V.N. Fateev, Optimization of porous current collectors for PEM water electrolysers, Int. J. Hydrogen Energy. 34 (2009) 4968–4973. doi:10.1016/j.ijhydene.2008.11.056.
- [77] H. Li, T. Fujigaya, H. Nakajima, A. Inada, K. Ito, Optimum structural properties for an anode current collector used in a polymer electrolyte membrane water electrolyzer operated at the boiling point of water, J. Power Sources. 332 (2016) 16–23. doi:10.1016/j.jpowsour.2016.09.086.
- [78] H. Ito, T. Maeda, A. Nakano, C.M. Hwang, M. Ishida, A. Kato, T. Yoshida, Experimental study on porous current collectors of PEM electrolyzers, Int. J. Hydrogen Energy. 37 (2012) 7418–7428. doi:10.1016/j.ijhydene.2012.01.095.
- [79] H. Ito, T. Maeda, A. Nakano, A. Kato, T. Yoshida, Influence of pore structural properties of current collectors on the performance of proton exchange membrane electrolyzer, Electrochim. Acta. 100 (2013) 242–248. doi:10.1016/j.electacta.2012.05.068.

- [80] A. Nouri-Khorasani, E. Tabu Ojong, T. Smolinka, D.P. Wilkinson, Model of oxygen bubbles and performance impact in the porous transport layer of PEM water electrolysis cells, Int. J. Hydrogen Energy. 42 (2017) 28665–28680. doi:10.1016/j.ijhydene.2017.09.167.
- [81] K. Ito, T. Sakaguchi, Y. Tsuchiya, A. Inada, H. Nakajima, R. Saito, Gas crossover suppression by controlling wettability of cathode current collector, ECS Trans. 75 (2016) 1107–1112. doi:10.1149/07514.1107ecst.
- [82] O. Panchenko, E. Borgardt, W. Zwaygardt, F.J. Hackemüller, M. Bram, N. Kardjilov, T. Arlt, I. Manke, M. Müller, D. Stolten, W. Lehnert, In-situ two-phase flow investigation of different porous transport layer for a polymer electrolyte membrane (PEM) electrolyzer with neutron spectroscopy, J. Power Sources. 390 (2018) 108–115. doi:10.1016/j.jpowsour.2018.04.044.
- [83] I. Dedigama, P. Angeli, K. Ayers, J.B. Robinson, P.R. Shearing, D. Tsaoulidis, D.J.L.
 Brett, In situ diagnostic techniques for characterisation of polymer electrolyte membrane water electrolysers Flow visualisation and electrochemical impedance spectroscopy, Int.
 J. Hydrogen Energy. 39 (2014) 4468–4482. doi:10.1016/j.ijhydene.2014.01.026.
- [84] C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction, J. Am. Chem. Soc. 135 (2013) 16977– 16987. doi:10.1021/ja407115p.
- [85] V.K. Puthiyapura, S. Pasupathi, S. Basu, X. Wu, H. Su, N. Varagunapandiyan, B. Pollet,
 K. Scott, RuxNb1–xO2 catalyst for the oxygen evolution reaction in proton exchange
 membrane water electrolysers, Int. J. Hydrogen Energy. 38 (2013) 8605–8616.
 doi:10.1016/j.ijhydene.2013.04.100.

- [86] K.E. Ayers, C. Capuano, E.B. Anderson, Recent Advances in Cell Cost and Efficiency for PEM-Based Water Electrolysis, in: 2012: pp. 15–22. doi:10.1149/1.3684798.
- [87] B.D. Colella, Witney GJames, J.M. Moton, Techno-economic Analysis of PEM Electrolysis for Hydrogen Production, Electrolytic Hydrog. Prod. Work. (2014). https://www.energy.gov/sites/prod/files/2014/08/f18/fcto_2014_electrolytic_h2_wkshp_c olella1.pdf (accessed August 25, 2019).
- [88] H. Xu, High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis, (2014) 1–24.
 https://www.hydrogen.energy.gov/pdfs/progress17/ii_b_2_xu_2017.pdf (accessed August 18, 2019).
- [89] N.J. Bjerrum, WELTEMP Executive Summary, (n.d.) 1–29.
 https://cordis.europa.eu/docs/publications/1405/140538141-8_en.zip (accessed August 22, 2019).
- [90] M.S. Thomassen, NEXPEL Final Report Summary, (n.d.).
 https://www.fch.europa.eu/sites/default/files/nexpel%5B1%5D.pdf (accessed August 22, 2019).
- [91] M.S. Thomassen, NOVEL Project Final Report, (2006) 1–30.
 https://cordis.europa.eu/docs/results/303/303484/final1-novel-final-reports-publishablesummary-report.pdf (accessed August 22, 2019).
- [92] A. Brisse, J. Schefold, M. Zahid, High temperature water electrolysis in solid oxide cells,
 Int. J. Hydrogen Energy. 33 (2008) 5375–5382. doi:10.1016/j.ijhydene.2008.07.120.
- [93] A. Hauch, S.H. Jensen, S. Ramousse, M. Mogensen, Performance and Durability of Solid
 Oxide Electrolysis Cells, J. Electrochem. Soc. 153 (2006) A1741. doi:10.1149/1.2216562.

- [94] M. a. Laguna-Bercero, Recent advances in high temperature electrolysis using solid oxide fuel cells: A review, J. Power Sources. 203 (2012) 4–16. doi:10.1016/j.jpowsour.2011.12.019.
- [95] Q. Fu, M. Corentin, M. Zahid, A. Brisse, L. Gautier, Energy & Environmental Science, Energy Environ. Sci. 3 (2010) 1382–1397. doi:10.1039/c0ee00092b.
- [96] G. Schiller, A. Ansar, M. Lang, O. Patz, High temperature water electrolysis using metal supported solid oxide electrolyser cells (SOEC), J. Appl. Electrochem. 39 (2009) 293–301. doi:10.1007/s10800-008-9672-6.
- [97] G. Cinti, G. Discepoli, G. Bidini, A. Lanzini, M. Santarelli, Co-electrolysis of water and CO 2 in a solid oxide electrolyzer (SOE) stack, (2016) 207–215. doi:10.1002/er.
- [98] K. Vels Jensen, R. Wallenberg, I. Chorkendorff, M. Mogensen, Effect of impurities on structural and electrochemical properties of the Ni-YSZ interface, Solid State Ionics. 160 (2003) 27–37. doi:10.1016/S0167-2738(03)00147-4.
- [99] Y.L. Liu, C. Jiao, Microstructure degradation of an anode/electrolyte interface in SOFC studied by transmission electron microscopy, Solid State Ionics. 176 (2005) 435–442.
 doi:10.1016/j.ssi.2004.08.018.
- [100] F. Dalton, ECS Classics: Historical Origins of the Rotating Ring-Disk Electrode, Electrochem. Soc. Interface. 25 (2016) 50–59. doi:10.1149/2.F03163if.
- [101] K. Shinozaki, J.W. Zack, R.M. Richards, B.S. Pivovar, S.S. Kocha, Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique: I. Impact of Impurities, Measurement Protocols and Applied Corrections, J. Electrochem. Soc. 162 (2015) F1144–F1158. doi:10.1149/2.1071509jes.

[102] W. Sheng, H.A. Gasteiger, Y. Shao-Horn, Hydrogen Oxidation and Evolution Reaction
Kinetics on Platinum: Acid vs Alkaline Electrolytes, J. Electrochem. Soc. 157 (2010) B1529–B1536. doi:10.1149/1.3483106.

- [103] D. Chu, S. Gilman, The Influence of Methanol on O[sub 2] Electroreduction at a Rotating Pt Disk Electrode in Acid Electrolyte, J. Electrochem. Soc. 141 (1994) 1770–1773. doi:10.1149/1.2055002.
- [104] U.A. Paulus, T.J. Schmidt, H.A. Gasteiger, R.J. Behm, Oxygen reduction on a high-surface area Pt/Vulcan carbon catalyst: A thin-film rotating ring-disk electrode study, J. Electroanal. Chem. 495 (2001) 134–145. doi:10.1016/S0022-0728(00)00407-1.
- [105] Y. Garsany, J. Ge, J. St-Pierre, R. Rocheleau, K.E. Swider-Lyons, Analytical Procedure for Accurate Comparison of Rotating Disk Electrode Results for the Oxygen Reduction Activity of Pt/C, J. Electrochem. Soc. 161 (2014) F628–F640. doi:10.1149/2.036405jes.
- [106] F. Jaouen, V. Goellner, M. Lefèvre, J. Herranz, E. Proietti, J.P. Dodelet, Oxygen reduction activities compared in rotating-disk electrode and proton exchange membrane fuel cells for highly active FeNC catalysts, Electrochim. Acta. 87 (2013) 619–628. doi:10.1016/j.electacta.2012.09.057.
- [107] S. Kocha, Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique, in: DOE Annu. Prog. Rep., 2014: pp. 215–218.
- [108] A. Bonakdarpour, R.T. Tucker, M.D. Fleischauer, N.A. Beckers, M.J. Brett, D.P. Wilkinson, Nanopillar niobium oxides as support structures for oxygen reduction electrocatalysts, Electrochim. Acta. 85 (2012) 492–500.
 doi:10.1016/j.electacta.2012.08.005.
- [109] A. Kriston, T. Xie, P. Ganesan, B.N. Popov, Analysis of the Effect of Pt Loading on Mass and Specific Activity in PEM Fuel Cells, J. Electrochem. Soc. 160 (2013) F406–F412.

doi:10.1149/2.075304jes.

- [110] T.J. Schmidt, P.N. Ross, N.M. Marko, Surface segregation effects in electrocatalysis : kinetics of oxygen reduction reaction on polycrystalline Pt 3 Ni alloy surfaces, 555 (2003) 191–199. doi:10.1016/S0022-0728(03)00177-3.
- [111] S.S. Kocha, Y. Garsany, D. Myers, Testing Oxygen Reduction Reaction Activity with the Rotating Disc Electrode Technique, DOE Webinar. (2013). http://energy.gov/eere/fuelcells/downloads/testing-oxygen-reduction-reaction-activityrotating-disc-electrode.
- [112] M. Kroschel, A. Bonakdarpour, J.T.H. Kwan, P. Strasser, D.P. Wilkinson, Analysis of oxygen evolving catalyst coated membranes with different current collectors using a new modified rotating disk electrode technique, Electrochim. Acta. 317 (2019) 722–736. doi:10.1016/j.electacta.2019.05.011.
- [113] B.A. Pinaud, A. Bonakdarpour, L. Daniel, J. Sharman, D.P. Wilkinson, Key Considerations for High Current Fuel Cell Catalyst Testing in an Electrochemical Half-Cell, 164 (2017) 321–327. doi:10.1149/2.0891704jes.
- [114] B. Fang, B.A. Pinaud, D.P. Wilkinson, Carbon-Supported Pt Hollow Nanospheres as a Highly Efficient Electrocatalyst for the Oxygen Reduction Reaction, Electrocatalysis.
 (2016) 336–344. doi:10.1007/s12678-016-0311-4.
- [115] S. Zhao, H. Yu, R. Maric, N. Danilovic, C.B. Capuano, K.E. Ayers, W.E. Mustain, Calculating the Electrochemically Active Surface Area of Iridium Oxide in Operating Proton Exchange Membrane Electrolyzers, J. Electrochem. Soc. 162 (2015) 1292–1298. doi:10.1149/2.0211512jes.
- [116] M. Bernicke, E. Ortel, T. Reier, A. Bergmann, J. Ferreira De Araujo, P. Strasser, R.

Kraehnert, Iridium oxide coatings with templated porosity as highly active oxygen evolution catalysts: Structure-activity relationships, ChemSusChem. 8 (2015) 1908–1915. doi:10.1002/cssc.201402988.

- [117] C. Rozain, E. Mayousse, N. Guillet, P. Millet, Influence of iridium oxide loadings on the performance of PEM water electrolysis cells: Part I-Pure IrO2-based anodes, Appl. Catal. B Environ. 182 (2016) 153–160. doi:10.1016/j.apcatb.2015.09.013.
- [118] S.M. Alia, B. Rasimick, C. Ngo, K.C. Neyerlin, S.S. Kocha, S. Pylypenko, H. Xu, B.S. Pivovar, Activity and Durability of Iridium Nanoparticles in the Oxygen Evolution Reaction, J. Electrochem. Soc. 163 (2016) F3105–F3112. doi:10.1149/2.0151611jes.
- [119] T. Reier, M. Oezaslan, P. Strasser, Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and pt catalysts: A comparative study of nanoparticles and bulk materials, ACS Catal. 2 (2012) 1765–1772. doi:10.1021/cs3003098.
- [120] S. Lee, K. Ito, T. Ohshima, S. Noda, K. Sasaki, In Situ Measurement of Temperature Distribution across a Proton Exchange Membrane Fuel Cell, (2009) 126–130. doi:10.1149/1.3152331.
- [121] M. Wasberg, G. Horanyi, The reduction of ClO4- ions on Rh electrodes, J. Electroanal. Chem. 385 (1995) 63–70. doi:10.1093/isle/ist137.
- [122] M. Bernt, H.A. Gasteiger, Influence of Ionomer Content in IrO 2 /TiO 2 Electrodes on PEM Water Electrolyzer Performance, J. Electrochem. Soc. 163 (2016) F3179–F3189. doi:10.1149/2.0231611jes.
- [123] J. Mo, Z. Kang, S.T. Retterer, D.A. Cullen, T.J. Toops, J.B. Green, M.M. Mench, F.Y. Zhang, Discovery of true electrochemical reactions for ultrahigh catalyst mass activity in water splitting, Sci. Adv. 2 (2016). doi:10.1126/sciadv.1600690.

- [124] S. Umino, Temperature Dependence of the Diffusion Coefficient of Sulfuric Acid in Water, J. Electrochem. Soc. 144 (1997) 1302. doi:10.1149/1.1837588.
- [125] E.. Tsai, K. Rajeshwar, Influence of temperature on the voltammetric response of thermal ruthenium oxide electrodes, Electrochim. Acta. 36 (1991) 27–30. doi:10.1016/0013-4686(91)85175-7.
- [126] S. Fierro, L. Ouattara, E.H. Calderon, C. Comninellis, Influence of temperature on the charging/discharging process of IrO2coating deposited on p-Si substrate, Electrochem. Commun. 10 (2008) 955–959. doi:10.1016/j.elecom.2008.04.026.
- [127] D. Arrigan, Electrochemistry, in: Electrochemistry, 2nd ed., Wiley-VCH Verlag GmbH & Co. KGaA, 2010: pp. 351–351. doi:10.1365/s10337-009-1435-y.
- K.R. Cooper, M. Smith, Electrical test methods for on-line fuel cell ohmic resistance measurement, J. Power Sources. 160 (2006) 1088–1095.
 doi:10.1016/j.jpowsour.2006.02.086.
- [129] L.A. Faria, J.F.C.F.C. Boodts, S. Trasatti, L.A. De Faria, J.F.C.F.C. Boodts, S. Trasatti, Electrocatalytic properties of ternary oxide mixtures of composition
 Ru0.3Ti(0.7-x)CexO2: Oxygen evolution from acidic solution, J. Appl. Electrochem. 26 (1996) 1195–1199. doi:10.1007/BF00243745.
- [130] P. Millet, PEM Water Electrolysis, in: Hydrog. Prod. By Electrolysis, 2015: pp. 63–116. doi:10.1002/9783527676507.ch3.
- [131] C. Rakousky, U. Reimer, K. Wippermann, M. Carmo, W. Lueke, D. Stolten, An analysis of degradation phenomena in polymer electrolyte membrane water electrolysis, J. Power Sources. 326 (2016) 120–128. doi:10.1016/j.jpowsour.2016.06.082.
- [132] C. Rakousky, U. Reimer, K. Wippermann, S. Kuhri, M. Carmo, W. Lueke, D. Stolten,

Polymer electrolyte membrane water electrolysis : Restraining degradation in the presence of fluctuating power, J. Power Sources. 342 (2017) 38–47. doi:10.1016/j.jpowsour.2016.11.118.

- [133] L.E. Owe, M. Tsypkin, S. Sunde, The effect of phosphate on iridium oxide electrochemistry, Electrochim. Acta. 58 (2011) 231–237. doi:10.1016/j.electacta.2011.09.043.
- [134] U. Babic, M. Suermann, N.B. Felix, L. Gubler, T.J. Schmidt, Review Identifying Critical Gaps for Polymer Electrolyte Water, 164 (2017) 387–399.
 doi:10.1149/2.1441704jes.
- [135] H. Ito, Current Collectors (GDLs) and Materials, in: D. Bessarabov, H. Wang, H. Li, N. Zhao (Eds.), PEM Electrolysis Hydrog. Prod. Princ. Appl., n.d.: pp. 147–157.
- [136] R. García-Valverde, N. Espinosa, A. Urbina, Simple PEM water electrolyser model and experimental validation, 7 (2011). doi:10.1016/j.ijhydene.2011.09.027.
- [137] B. Han, J. Mo, Z. Kang, F. Zhang, Effects of membrane electrode assembly properties on two-phase transport and performance in proton exchange membrane electrolyzer cells, Electrochim. Acta. 188 (2016) 317–326. doi:10.1016/j.electacta.2015.11.139.
- [138] I. Dedigama, P. Angeli, N. Van Dijk, J. Millichamp, D. Tsaoulidis, P.R. Shearing, D.J.L. Brett, Current density mapping and optical flow visualisation of a polymer electrolyte membrane water electrolyser, J. Power Sources. 265 (2014) 97–103. doi:10.1016/j.jpowsour.2014.04.120.
- [139] O. Panchenko, E. Borgardt, W. Zwaygardt, F.J. Hackemüller, M. Bram, N. Kardjilov, T. Arlt, I. Manke, M. Müller, D. Stolten, W. Lehnert, In-situ two-phase flow investigation of different porous transport layer for a polymer electrolyte membrane (PEM) electrolyzer

with neutron spectroscopy, J. Power Sources. 390 (2018) 108–115. doi:10.1016/j.jpowsour.2018.04.044.

- [140] F. Arbabi, A. Kalantarian, R. Abouatallah, R. Wang, J.S. Wallace, A. Bazylak, Feasibility study of using microfluidic platforms for visualizing bubble flows in electrolyzer gas diffusion layers, J. Power Sources. 258 (2014) 142–149. doi:10.1016/j.jpowsour.2014.02.042.
- [141] J.T.H. Kwan, A. Bonakdarpour, G. Afonso, D.P. Wilkinson, Bridging Fundamental Electrochemistry with Applied Fuel Cell Testing: A Novel and Economical Rotating Disk Electrode Tip for Electrochemical Assessment of Catalyst-Coated Membranes, Electrochim. Acta. 258 (2017) 208–219. doi:10.1016/j.electacta.2017.10.087.
- [142] L.D. Burke, R.A. Scannell, Electrochromic Iridium Oxides: Preparation and Properties of Hydrous Films, Platin. Met. Rev. 28 (1984) 56–61.
- [143] S. Geiger, O. Kasian, B.R. Shrestha, A.M. Mingers, K.J.J. Mayrhofer, S. Cherevko, Activity and Stability of Electrochemically and Thermally Treated Iridium for the Oxygen Evolution Reaction, J. Electrochem. Soc. 163 (2016) F3132–F3138. doi:10.1149/2.0181611jes.
- [144] S. Ardizzone, A. Carugati, S. Trasatti, Properties of Thermally Prepared Irridium Dioxide Electrodes, J Electroanal Chem. 126 (1981) 287–292. doi:10.1016/S0022-0728(81)80437-8.
- [145] A. Marshall, B. Børresen, G. Hagen, M. Tsypkin, R. Tunold, Electrochemical characterisation of IrxSn1–xO2 powders as oxygen evolution electrocatalysts, Electrochim. Acta. 51 (2006) 3161–3167. doi:10.1016/j.electacta.2005.09.004.
- [146] A.R. Zeradjanin, Efficiency of Electrocatalytic Gas Evolution on Transition Metal-Oxides

 from Spatial Distribution of Morphological Pattern Towards Understanding of Electrocatalysis as Resonance Phenomenon Efficiency of Electrocatalytic Gas Evolution on Transition Metal, Ruhr-Universität Bochum, 2012. https://hssopus.ub.rub.de/opus4/frontdoor/index/index/docId/241.

- [147] M.T.Y. Paul, B.B. Yee, D.R. Bruce, B.D. Gates, Hexagonal Arrays of Cylindrical Nickel Microstructures for Improved Oxygen Evolution Reaction, ACS Appl. Mater. Interfaces. 9 (2017) 7036–7043. doi:10.1021/acsami.6b14129.
- [148] A. Nouri-Khorasani, E. Tabu Ojong, T. Smolinka, D.P. Wilkinson, Model of oxygen bubbles and performance impact in the porous transport layer of PEM water electrolysis cells, Int. J. Hydrogen Energy. 42 (2017) 28665–28680. doi:10.1016/j.ijhydene.2017.09.167.
- [149] A. Nouri-Khorasani, Structure-Property Modeling and Testing of Transport Layers for PEM Fuel Cells and Water Electrolysis Cells, University of British Columbia, 2019. https://open.library.ubc.ca/cIRcle/collections/ubctheses/24/items/1.0380614.
- [150] J. Zhou, S. Shukla, A. Putz, M. Secanell, Analysis of the role of the microporous layer in improving polymer electrolyte fuel cell performance, Electrochim. Acta. 268 (2018) 366– 382. doi:10.1016/j.electacta.2018.02.100.
- [151] M. Pourbaix, Altas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed., Houston, 1974.
- [152] Q. Feng, X.A. Zi, G. Liu, B. Wei, Z. Zhang, H. Li, H. Wang, Review article A review of proton exchange membrane water electrolysis on degradation mechanisms and mitigation strategies, J. Power Sources. 366 (2017) 33–55. doi:10.1016/j.jpowsour.2017.09.006.
- [153] J.O. Majasan, F. Iacoviello, P.R. Shearing, D. Jl, Effect of Microstructure of Porous

Transport Layer on Performance in Polymer Electrolyte Membrane Water Electrolyser, in: Energy Procedia, Elsevier B.V., 2018: pp. 111–119. doi:10.1016/j.egypro.2018.09.035.

- [154] C.M. Hwang, M. Ishida, H. Ito, T. Maeda, Influence of properties of gas diffusion layers on the performance of polymer electrolyte-based unitized reversible fuel cells, 6 (2010). doi:10.1016/j.ijhydene.2010.10.091.
- [155] B.O. Calcagno, K.R. Hart, J.C. Springmann, G.G. Antoun, W.C. Crone, Deformation and fracture of polymer / metal composites subjected to cold rolling, 72 (2012) 1344–1351. doi:10.1016/j.compscitech.2012.05.004.
- [156] M. Tomizawa, M.C. Faudree, C. Kubo, M. Kanda, I. Jimbo, Y. Nishi, Adhesive Force of Laminations of Titanium Untreated and Polycarbonate Homogeneously Irradiated by Low Potential Electron Beam Prior to Assembly and Hot-Press, Mater. Trans. 58 (2017) 457– 464.
- [157] H. Yaghoubi, N. Taghavinia, E. Keshavarz, Surface & Coatings Technology Self cleaning TiO2 coating on polycarbonate : Surface treatment, photocatalytic and nanomechanical properties, 204 (2010) 1562–1568. doi:10.1016/j.surfcoat.2009.09.085.
- [158] H.A. Wittcoff, B.G. Reuben, J.S. Plotkin, Industrial Organic Chemicals, (2013). https://app.knovel.com/hotlink/toc/id:kpIOCE0011/industrial-organicchemicals/industrial-organic-chemicals (accessed August 20, 2019).

[160] A. Minegishi, T. Okada, M. Kanda, M.C. Faudree, Y. Nishi, Tensile Shear Strength

 ^[159] L.L. Shreir, R.A. Jarman, G.T. Burstein, Corrosion (3rd Edition) Volumes 1-2 - Polymers with Enhanced Heat Resistance, (1994) 18:74.
 https://app.knovel.com/hotlink/pdf/id:kt002ZBM6B/corrosion-3rd-edition/polymers-with-enhanced (accessed August 20, 2019).

Improvement of 18-8 Stainless Steel / CFRP Joint Irradiated by Electron Beam Prior to Lamination Assembly and Hot-Pressing, 56 (2015) 1169–1173.

- [161] Y.W. Mai, Fracture initiation and crack propagation of acrylonitrile-butadiene-styrene(ABS) in organic solvents, J. Mater. Sci. 11 (1976) 303–316. doi:10.1007/BF00551442.
- [162] Y. Kobayashi, K. Kosaka, T. Yamamoto, Y. Tachikawa, K. Ito, K. Sasaki, A solid polymer water electrolysis system utilizing natural circulation, Int. J. Hydrogen Energy. 39 (2014) 16263–16274. doi:10.1016/j.ijhydene.2014.07.153.

Appendices

Appendix A

A.1 MRDE ORR ADT Protocol





Figure A.1 describes the ADT protocol used. As a convention, rapid CVs performed between 0.6 - 1.0 V vs. RHE are defined as "ADT cycles", and the CVs between 0 - 1.2 V vs. RHE are defined as "Full CVs". There is a total of 30,000 ADT cycles, with three full CVs after each loop counter (e.g., $n \rightarrow n + 1$).

A.2 Nernstian Correction for RDE to PEMFC Comparison

Given:

 $C_{O2, 20^{\circ}C} = 1.26 \times 10^{-3} \text{ M}$ $a_{H2} = 1 \text{ (RHE conditions)}$ $E_{o} = 1.23 \text{ V}$ <u>Reaction (Important to note that n = 2 for the MRDE):</u>
Anode: $H_{2}(g) + 0^{2-} = H_{2}0 + 2e^{-}$ Cathode: $2e^{-} + \frac{1}{2}O_{2}(g) = 0^{2-}$ Overall: $H_{2} + \frac{1}{2}O_{2} = H_{2}O$ <u>Using the relation from Pinaud et. al [113]:</u>

 $E_{PEMFC}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = E_{MRDE}(20^{\circ}C, a_{H2} = 1, c_{O2} = 1.26 \times 10^{-3}M) + \Delta E$ Calculate <u>E_{PEMFC</u>

$$E_{PEMFC}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = E^{\circ} - \frac{RT}{nF} \ln\left(\frac{a_{H2O}}{a_{H2} \times a_{O2}^{0.5}}\right)$$
$$E_{PEMFC}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = 1.18 - \frac{(8.314)(273 + 80)}{(2)(96485)} \ln\left(\frac{1}{2 \times 2^{0.5}}\right)$$

 $E_{PEMFC}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = 1.18 - (0.01509)(\ln(0.3535))$

 $E_{PEMFC}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = 1.18 - (-0.01581)$

 $E_{PEMFC}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = 1.19581$

Calculate E_{MRDE}

$$E_{MRDE}(20^{\circ}C, a_{H2} = 1, c_{02} = 1.26 \times 10^{-3}M) = E^{\circ} - \frac{RT}{nF} \ln\left(\frac{a_{H20}}{a_{H2} \times a_{02}^{0.5}}\right)$$
$$E_{MRDE} = 1.23 - \frac{(8.314)(273 + 20)}{(2)(96485)} \ln\left(\frac{1}{1 \times (1.26 \times 10^{-3})^{0.5}}\right)$$

165

 $E_{MRDE} = 1.23 - (0.01262)(\ln(28.171))$

 $E_{MRDE} = 1.23 - 0.04213$

 $E_{MRDE} = 1.18787V$

<u>Calculate ΔE </u>

 $E_{PEMFC}(80^{\circ}C, 2 \text{ bar } H_2, 2 \text{ bar } O_2) = E_{MRDE}(20^{\circ}C, a_{H2} = 1, c_{O2} = 1.26 \times 10^{-3}M) + \Delta E$

 $1.1958 V = 1.18787V + \Delta E$

 $\Delta E = 0.00793 V \text{ or } 8 mV$

Appendix **B**



B.1 Illustrative Sketch of the LWD/SWD and Characteristic Calculations

Figure B.1: Sketch of an expanded metal mesh (LWD = long way of the diamond, SWD = short way of the diamond, TPB = triple phase boundary).

The open area and the perimeter were determined by approximating a polygon to the openings, with the result averaged over ten openings. The total open area was found by multiplying the number of openings per MEA area (0.785 cm²) with the averaged open area (equation B1).

Total open area (cm²) =
$$\frac{\text{\#openings}}{\text{cm}^2} \times \frac{\text{open area}(\text{cm}^2)}{\text{\#opening}} \times A_{\text{electrode}}(\text{cm}^2)$$
 (B1)

The total open area divided by the MEA area gives the open area as a percentage (equation B2).

Open area (%) =
$$\frac{\text{Total open area (cm^2)}}{A_{\text{electrode (cm^2)}}}$$
 (B2)

The projected coverage (%) was determined by taking the difference of the open area from 100 % (equation B3)

Coverage
$$(\%) = 100 - 0$$
 pen area $(\%)$ (B3)

The twilled Ti mesh has a unique geometric structure consisting of woven wires, therefore it is not completely flat. Equation B3 cannot be used to calculate the coverage of a twilled mesh, because the coverage corresponds to the projected contact face. Therefore, assuming a certain elasticity of the swollen MEA, a correction factor of 2/3 is applied in case of the 9Ti-twill current collector to the calculated contact area.

The TCP length is the total inner perimeter of the openings, and is the product of the perimeter and the number of openings per MEA area (equation B4). The coverage depends on the number of openings and the perimeter per opening, and is not related to the TCP length.

TCP length (cm) =
$$\frac{\text{#openings}}{\text{cm}^2} \times \frac{\text{perimeter (cm)}}{\text{#opening}} \times A_{\text{electrode}}(\text{cm}^2)$$
 (B4)

Appendix C



C.1 Calibration Curve for Magnetic Drive Pump

Figure C.1: Calibration Curve for Pan World (Model NH-15PI-Z-D).

C.2 Design Progression of the Working Electrode Housing Unit

The final working electrode assembly presented (referred to as V4) was the result after three other conceptual designs (which will be named V1, V2, and V3 respectively) had been previously tested for their compatibility in the diagnostic cell. A brief discussion of the three design iterations and the flaws of each are as follows.

Version V1 was composed of a singular stainless steel 304 hollow cylinder (or shell) with a solid cap (Figure C.2). This was financially the cheapest option, and stainless steel is easy to machine. A copper wire was attached to the back of the cylinder using a two-part silver epoxy. The catalyst sample (e.g., foil, CCM) would be placed on top of the elevated stainless steel portion. Within minutes, the electrolyte would change from colourless to a light yellow, likely due to stainless steel corrosion.



Figure C.2: V1 working electrode assembly.

Version V2 had the same shell geometry as Version V1, but was machined from stainless steel 316 instead of 304 (Figure C.3). A copper wire was attached to the back of the cylinder with silver epoxy like the previous version. There was no detectable change in the electrolyte colour, but the entire shell casing was electrochemically active (e.g., bubbles were forming on the stainless steel shell at OER potentials). With this version, a 100 nm layer of Ir (the thickest possible that the UBC Pharmacy could deposit with sputtering) was sputtered onto the surface of the elevated Ti. The purpose behind sputtering Ir was that there was no way to secure a sample (e.g., Ir foil) down to the elevated stainless steel core, ensuring proper contact. However, even at low overpotentials (e.g., $> 1.3 V_{RHE}$), bubble evolution from the sputtered surface caused the iridium to crack and delaminate from the stainless steel substrate.



Figure C.3: V2 working electrode assembly featuring sputtered Ir (100 nm).

Version V3 (Figure C.4), unlike V1 and V2, showcased a threaded elevated portion for a cap to secure down the sample. The main body was covered with a 1 mm coating of high temperature silicone to prevent the main body from being electrochemically active. However, the maximum current density attained with this setup was roughly 300 mA cm⁻² at 2 V_{RHE} using Solvicore CCMs. Using pressure paper tests, it was confirmed that the contact between the catalyst and the Ti screw-on cap was poor. In addition, the protective silicone coating would peel off after one experiment.



Figure C.4: V3 working electrode assembly featuring screw-down Ti lid and epoxy-covered SS316 shell.

Version V4 (Figure 4.3b, Chapter 3) was the first design iteration to feature a separate body and a Titanium core that the catalyst component could be placed upon. The body was made of PEEK, so no external silicone coating was required to electrochemically inactivate the metal and shield from potential acidic attack. The Ti core had a small step machined into the disk to improve contact between the sample and the lid. The first tests using Iridium foil used an ULTEM cross-beam lid, but later tests using commercial CCM and Ti current collector meshes used a Ti lid with the same geometry. The results reported in Chapter 3 are based off version V4 of the apparatus.

C.3 Single-sided Amplitude Spectrum Fourier Transform Results for Current Collector





Figure C.5: Fourier transform results for 3Ti8.5-031 (M2).



Figure C.6: Fourier transform results for 2Ti4-125 (M3).



Figure C.7: Fourier transform results for 10Ti12-125 (M4).



C.4 Compiled Bubble Ratio for Frequency Ranges R₂ and R₃

Figure C.8: Bubble ratio analysis for frequency range R₂ (1 < f < 10 Hz).



Figure C.9: Bubble ratio analysis for frequency range R₃ (f > 10 Hz).