

ELECTRIC TERMINAL PERFORMANCE AND CHARACTERIZATION OF
SOLID OXIDE FUEL CELLS AND SYSTEMS

by

Peter Allan Lindahl

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

April, 2013

© COPYRIGHT

by

Peter Allan Lindahl

2013

All Rights Reserved

APPROVAL

of a dissertation submitted by

Peter Allan Lindahl

This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to The Graduate School.

Dr. Steven R. Shaw

Approved for the Department of Electrical and Computer Engineering

Dr. Robert C. Maher

Approved for The Graduate School

Dr. Ronald W. Larsen

STATEMENT OF PERMISSION TO USE

In presenting this dissertation in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this dissertation is allowable only for scholarly purposes, consistent with “fair use” as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this dissertation should be referred to ProQuest Information and Learning, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted “the exclusive right to reproduce and distribute my dissertation in and from microform along with the non-exclusive right to reproduce and distribute my abstract in any format in whole or in part.”

Peter Allan Lindahl

April, 2013

ACKNOWLEDGEMENTS

The great number of individuals who's support and encouragement provided me with the strength to complete this project deserve their recognition. First, I would like to thank my advisor, Dr. Steven R. Shaw for allowing me to participate in this research project. His willingness to share his immense knowledge and acute insights certainly helped make this project successful.

Of course, I would also like to thank my committee members, Dr. Stephen Sofie, Dr. Robert Maher, Dr. Kevin Repasky and my Graduate School representative, Dr. David McKenzie. Their questions, suggestions and overall general guidance helped this project gain shape.

I want to thank the other graduate and undergraduate students who helped in various aspects of my research. In particular, I want to thank those within Dr. Shaw's research group: Joshua Wold, Eric Moog, Eric Seger, Matthew Cornachione, Aric Litchy, and Christopher Miller, and those within Dr. Sofie's group: Adam Weisenstein, David Driscoll and Clay Hunt.

I would like to acknowledge the various agencies who provided financial support for this research: the Boeing Company, the National Science Foundation grant 0547616, the William Benjamin Fellowship, the McLeod Family Graduate Student Support, and the Electrical and Computer Engineering Department here at Montana State University.

Finally, I want to express my appreciation to my family and friends for their unrelenting support through this arduous journey.

TABLE OF CONTENTS

1. INTRODUCTION	1
Fuel Cell Technologies	1
Fuel Cell Advantages	2
Fuel Cell Disadvantages	4
Scope of this Research Project	5
Previous Contributions from the Scientific Community	7
Fuel Cell Stack Simulation and Hardware-in-the-Loop Testing.....	7
Electrochemical Impedance Spectroscopy Based Diagnostics	10
Fuel Cell Degradation Mechanisms and Performance	13
Fuel Cell Degradation Mitigation	15
Significant Contributions from this Research Project	17
Reference Based SOFC Simulation System.....	18
Electrochemical Impedance Spectroscopy Method.....	18
Fuel Cell Performance and Degradation Mitigation Control.....	19
Copyright Acknowledgements.....	20
Organization of Dissertation	20
2. SOLID OXIDE FUEL CELLS	22
Electric Terminal Performance	24
HC Starck Anode Supported Fuel Cells	26
Fuel Cell Experiment Set Up	28
Fuel Cell Test Stands.....	29
Gas Flow and Temperature Control.....	31
Fuel Cell Start Up and Shut Down Protocol.....	33
Post-test Cell Analysis: Scanning Electron Microscopy	34
3. SIMULATION OF SOFC STACK ELECTRIC TERMINALS.....	38
Reference Simulator Topology and Operation	38
Experiment Procedure.....	43
Reference Simulator Performance	44
Discussion	48
Chapter Summary.....	50
4. TIME-DOMAIN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY	52
Ordinary Least-Squares Analysis.....	53

TABLE OF CONTENTS – CONTINUED

Measurement Uncertainty	57
Variance in Parameter Estimations	58
Non-Linear Distortion Upper Bound on Signal Amplitude	61
Experimental Procedure	61
Data Uncertainty Analysis	64
Electrochemical Impedance Spectroscopy Results	65
Discussion	69
Chapter Summary	73
 5. CASE STUDY: PERFORMANCE TESTING A HYBRID SOURCE POWER MANAGER	 74
Hybrid Source Power Manager Operation	74
Experimental Setup	77
Anti-Aliasing Filters	79
UAV Flight Profiles	81
Reference Cell Degradation and Recovery	82
HSPM Experimental Results	83
Discussion	88
Chapter Summary	91
 6. LOAD-INDUCED DEGRADATION AND RECOVERY IN SOLID OXIDE FUEL CELLS	 93
Anode Oxidation and Reduction	93
Electric Terminal Induced Degradation and Recoverability	95
Effects of Degradation and Recovery on DC Electrical Performance	97
Effects of Degradation and Recovery on AC Electrical Performance	100
Linear Interpolation Analyses of Electric Terminal Measurements	107
Application to Polarization Curve Data	110
Application to EIS Profiles	114
Single-Frequency Interpolation Analyses	119
Chapter Summary	126
 7. PULSE WIDTH MODULATED DEGRADATION CONTROL	 130
Pulse Width Modulation Control Strategy	131
Simulation Model	132
Degradation Model Dynamics	134
Simulation Results	136

TABLE OF CONTENTS – CONTINUED

Experimental Setup.....	138
Experimental Procedure	138
Experimental Results	141
Analysis and Discussion.....	151
Chapter Summary.....	155
8. CONTINUOUS CURRENT CONTROL OF DEGRADATION.....	157
Continuous Current Control of Degradation Strategy	158
Simulation Model.....	160
Degradation Model.....	161
Cell Voltage Model.....	164
Degradation Detection Model.....	166
Compensator Model	167
Simulation Results	168
Experimental Setup.....	176
Experimental Procedure	180
Experimental Results	182
Analysis and Discussion.....	195
Chapter Summary.....	202
9. CONCLUSION	204
REFERENCES CITED.....	210
APPENDICES	221
APPENDIX A: Linear Interpolation Analysis of Polarization Curves Measured During Degradation and Recovery Testing	222
APPENDIX B: Linear Interpolations of Degradation and Recovery Testing EIS Profiles	259
APPENDIX C: Single Frequency-Based Linear Interpolations of Degradation and Recovery Testing EIS Profiles	266
APPENDIX D: Linear Interpolations of PWM Control EIS Profiles	273
APPENDIX E: SEM Images from PWM Control Test	279
APPENDIX F: SEM Images from Continuous Current Control Test	291

LIST OF TABLES

Table	Page
1.1 Comparison of Fuel Cell and Conventional Electricity Generators	3
2.1 SEM Sample Polishing Protocol	36
6.1 Parameter Values For One-Dimensional and Two-Dimensional Linear Interpolations	119
6.2 Parameter Values For Single Frequency Interpolation Models	127
7.1 Degradation and Recovery Time Constants	135
7.2 Parameter Values Used in PWM Control Experiment	140
7.3 Parameter Values for One-Dimensional and Single-Frequency Impedance Magnitude Linear Interpolations	148
8.1 Parameter Values Used for Simulation	169
8.2 Passive Component Values for Control Circuit	178
8.3 Equivalent Parameter and Gain Values for Experiment	182
A.1 Full Results of Polarization Curve Linear Interpolation Analysis	258

LIST OF FIGURES

Figure	Page
2.1 Solid Oxide Fuel Cell Operation	22
2.2 Solid Oxide Fuel Cell Polarization Curve	24
2.3 Anode Supported Solid Oxide Fuel Cell Cross-Section	27
2.4 Solid Oxide Fuel Cell Test Stand A	29
2.5 Solid Oxide Fuel Cell Test Stand B	30
2.6 Gas Flow and Temperature Control Systems.....	32
2.7 Scanning Electron Microscopy Epoxy Mold A	35
2.8 Scanning Electron Microscopy Epoxy Mold B	35
2.9 Quartered Fuel Cell Diagram	37
3.1 Reference Based Simulator Schematic	38
3.2 Reference Based Fuel Cell Stack Simulator Dynamics	39
3.3 Reference Based Simulator Circuit Board.....	42
3.4 Simulated Polarization Performance	45
3.5 Simulator Performance with BLDC Motor	46
3.6 Simulator Performance with DC-DC Converter and Bulb.....	47
3.7 Simulator Electrochemical Impedance Spectroscopy	48
4.1 Electrochemical Impedance Spectroscopy Small-Signal Diagram	53
4.2 Conceptual Diagram of the Experiment and Measurement Set-up	62
4.3 EIS Measurements of Known RC Circuit	66
4.4 EIS Measurements of SOFC.....	67
4.5 Time-Domain Fitting of Measured Waveforms.....	69
4.6 Time-Domain Difference Signals of Measured Waveforms	70
5.1 Hybrid Source Power Manager Conceptual Diagram	75

LIST OF FIGURES – CONTINUED

Figure	Page
5.2 Hybrid Source Power Manager Image	76
5.3 Hybrid Source Power Manager Experiment Setup.....	78
5.4 Anti-Aliasing Filter Bank.....	79
5.5 Anti-Aliasing Filter Topologies.....	80
5.6 UAV Flight Profile	82
5.7 Time-Domain Waveforms.....	84
5.8 Time-Domain Waveforms with EIS Perturbation.....	85
5.9 Measured Cell and Simulated Stack Impedance - First Sweep.....	86
5.10 Measured Cell and Simulated Stack Impedance - Second Sweep.....	86
5.11 Measured Simulated Stack Impedance Comparison.....	87
5.12 Measured Degraded and Recovered Impedance Profiles.....	88
6.1 SEM Images showing Irreversible Degradation.....	96
6.2 SOFC Degradation and Recovery	99
6.3 SEM Images of Xuelei's Test Cell	101
6.4 EIS Progression for $V_{DC} = 670$ mV	103
6.5 EIS Progression for $V_{DC} = 430$ mV	104
6.6 EIS Progression for $V_{DC} = 200$ mV	105
6.7 SEM Image of Cell Used in EIS Tests.....	107
6.8 Conceptual Two-Dimensional and One-Dimensional Linear Interpolation Progressions	111
6.9 Normalized Sum of Squared Error for Polarization Curve Predictors	112
6.10 Linear Interpolation of Polarization Curve at 43 Hours.....	112

LIST OF FIGURES – CONTINUED

Figure	Page
6.11 EIS Linear Interpolations at $V_{DC} = 430$ mV After 4 Hours	116
6.12 EIS Linear Interpolations at $V_{DC} = 430$ mV After 8 Hours	116
6.13 EIS Linear Interpolations at $V_{DC} = 430$ mV After 12 Hours.....	117
6.14 EIS Linear Interpolations at $V_{DC} = 430$ mV After 20 Hours.....	117
6.15 EIS Linear Interpolations at $V_{DC} = 430$ mV After Recovery	118
6.16 Single Frequency Parameterization Sum of Squared Errors.....	120
6.17 Single Frequency Impedance Progression.....	122
6.18 EIS Single Frequency Interpolations at $V_{DC} = 430$ mV After 4 Hours.....	124
6.19 EIS Single Frequency Interpolations at $V_{DC} = 430$ mV After 8 Hours.....	124
6.20 EIS Single Frequency Interpolations at $V_{DC} = 430$ mV After 12 Hours	125
6.21 EIS Single Frequency Interpolations at $V_{DC} = 430$ mV After 20 Hours	125
6.22 EIS Single Frequency Interpolations at $V_{DC} = 430$ mV After Recovery	126
7.1 PWM Degradation Control Diagram	131
7.2 PWM Control Simulation Program Degradation Model	134
7.3 Exponential Fits of Resistance Progression.....	135
7.4 PWM Control Simulation Results.....	137
7.5 Conceptual Diagram of Experiment and Measurement Set-up	139
7.6 PWM Time-Domain Test Results.....	142
7.7 First Hour and Last Hour of Experiment	143

LIST OF FIGURES – CONTINUED

Figure	Page
7.8 Polarization Curve and Current-Power Relationship Progression	145
7.9 EIS Measurement Progressions	146
7.10 Linear Interpolation Analysis of EIS Measurements	148
7.11 SEM Images Showing Voids in Cathode	149
7.12 SEM Images Showing Crack in Cathode	150
8.1 Continuous Current Control Diagram	159
8.2 Continuous Current Control Simulation Control Loop	161
8.3 Degradation Model for Continuous Current Control Simulation Program	162
8.4 Degradation Rate Model with Dead-band	164
8.5 Simulated Degradation Progression	171
8.6 Simulated Degradation Estimate Signal Progression	171
8.7 Simulated Current and Voltage Progressions	173
8.8 Simulated Degradation Estimate Signal at 300 Seconds	173
8.9 Simulated Fuel Cell Current and Voltage Waveforms	175
8.10 Impedance Detection and Control Circuit Topology	177
8.11 Measured Impedance Magnitude and Phase	184
8.12 Op-amp OP4 Voltage Output Profile	184
8.13 DC Voltage and Current of Cell	185
8.14 Op-Amp Output Voltages	185
8.15 Fuel Cell Current and Voltage Waveforms	187
8.16 Polarization Curve and Current-Power Relationship	188
8.17 EIS Profiles at 1.5 A	190

LIST OF FIGURES – CONTINUED

Figure	Page
8.18 EIS Profiles at 4 A	190
8.19 EIS Profiles at 7 A	191
8.20 EIS Profiles at 10 A.....	191
8.21 EIS Profiles at 15 A.....	192
8.22 Degradation Model Fitting.....	193
8.23 Measured Data Compared to Updated Simulation Predictions.....	194
8.24 SEM Images Showing Large Void in Cathode.....	196
8.25 SEM Images Showing Small Crack in Cathode	197
8.26 SEM Images Showing Large Crack in Cathode	198
A.1 Linear Interpolations of the -4 - 1.33 Hour Polarization Curves.....	224
A.2 Linear Interpolations of the 1.67 - 3.33 Hour Polarization Curves.....	225
A.3 Linear Interpolations of the 3.67 - 5.33 Hour Polarization Curves.....	226
A.4 Linear Interpolations of the 5.67 - 7.33 Hour Polarization Curves.....	227
A.5 Linear Interpolations of the 7.67 - 9.33 Hour Polarization Curves.....	228
A.6 Linear Interpolations of the 9.67 - 11.33 Hour Polarization Curves.....	229
A.7 Linear Interpolations of the 11.67 - 13.33 Hour Polarization Curves	230
A.8 Linear Interpolations of the 13.67 - 15.33 Hour Polarization Curves	231

LIST OF FIGURES – CONTINUED

Figure	Page
A.9 Linear Interpolations of the 15.67 - 17.33 Hour Polarization Curves	232
A.10 Linear Interpolations of the 17.67 - 19.33 Hour Polarization Curves	233
A.11 Linear Interpolations of the 19.67 - 21.33 Hour Polarization Curves	234
A.12 Linear Interpolations of the 21.67 - 23.33 Hour Polarization Curves	235
A.13 Linear Interpolations of the 23.67 - 25.33 Hour Polarization Curves	236
A.14 Linear Interpolations of the 25.67 - 27.33 Hour Polarization Curves	237
A.15 Linear Interpolations of the 27.67 - 29.33 Hour Polarization Curves	238
A.16 Linear Interpolations of the 29.67 - 31.33 Hour Polarization Curves	239
A.17 Linear Interpolations of the 31.67 - 33.33 Hour Polarization Curves	240
A.18 Linear Interpolations of the 33.67 - 35.33 Hour Polarization Curves	241
A.19 Linear Interpolations of the 35.67 - 37.33 Hour Polarization Curves	242
A.20 Linear Interpolations of the 37.67 - 39.33 Hour Polarization Curves	243
A.21 Linear Interpolations of the 39.67 - 41.33 Hour Polarization Curves	244
A.22 Linear Interpolations of the 41.67 - 43.33 Hour Polarization Curves	245

LIST OF FIGURES – CONTINUED

Figure	Page
A.23 Linear Interpolations of the 43.67 - 45.33 Hour Polarization Curves	246
A.24 Linear Interpolations of the 45.67 - 47.33 Hour Polarization Curves	247
A.25 Linear Interpolations of the 47.67 - 49.33 Hour Polarization Curves	248
A.26 Linear Interpolations of the 49.67 - 51.33 Hour Polarization Curves	249
A.27 Linear Interpolations of the 51.67 - 53.33 Hour Polarization Curves	250
A.28 Linear Interpolations of the 53.67 - 55.33 Hour Polarization Curves	251
A.29 Linear Interpolations of the 55.67 - 57.33 Hour Polarization Curves	252
A.30 Linear Interpolations of the 57.67 - 58.33 Hour Polarization Curves	253
B.1 EIS Linear Interpolations at $V_{DC} = 670$ mV After 4 Hours	261
B.2 EIS Linear Interpolations at $V_{DC} = 670$ mV After 8 Hours	261
B.3 EIS Linear Interpolations at $V_{DC} = 670$ mV After 12 Hours	262
B.4 EIS Linear Interpolations at $V_{DC} = 670$ mV After 20 Hours	262
B.5 EIS Linear Interpolations at $V_{DC} = 670$ mV After Recovery	263
B.6 EIS Linear Interpolations at $V_{DC} = 200$ mV After 4 Hours	263

LIST OF FIGURES – CONTINUED

Figure	Page
B.7 EIS Linear Interpolations at $V_{DC} = 200$ mV After 8 Hours	264
B.8 EIS Linear Interpolations at $V_{DC} = 200$ mV After 12 Hours	264
B.9 EIS Linear Interpolations at $V_{DC} = 200$ mV After 20 Hours	265
B.10 EIS Linear Interpolations at $V_{DC} = 200$ mV After Recovery	265
C.1 EIS Single Frequency Interpolations at $V_{DC} = 670$ mV After 4 Hours	268
C.2 EIS Single Frequency Interpolations at $V_{DC} = 670$ mV After 8 Hours	268
C.3 EIS Single Frequency Interpolations at $V_{DC} = 670$ mV After 12 Hours	269
C.4 EIS Single Frequency Interpolations at $V_{DC} = 670$ mV After 20 Hours	269
C.5 EIS Single Frequency Interpolations at $V_{DC} = 670$ mV After Recovery	270
C.6 EIS Single Frequency Interpolations at $V_{DC} = 200$ mV After 4 Hours	270
C.7 EIS Single Frequency Interpolations at $V_{DC} = 200$ mV After 8 Hours	271
C.8 EIS Single Frequency Interpolations at $V_{DC} = 200$ mV After 12 Hours	271
C.9 EIS Single Frequency Interpolations at $V_{DC} = 200$ mV After 20 Hours	272
C.10 EIS Single Frequency Interpolations at $V_{DC} = 200$ mV After Recovery	272

LIST OF FIGURES – CONTINUED

Figure	Page
D.1 Linear Interpolations of PWM Control EIS Profiles After 20 Hours	275
D.2 Linear Interpolations of PWM Control EIS Profiles After 30 Hours	275
D.3 Linear Interpolations of PWM Control EIS Profiles After 40 Hours	276
D.4 Linear Interpolations of PWM Control EIS Profiles After 50 Hours	276
D.5 Linear Interpolations of PWM Control EIS Profiles After 60 Hours	277
D.6 Linear Interpolations of PWM Control EIS Profiles After 80 Hours	277
D.7 Linear Interpolations of PWM Control EIS Profiles After 90 Hours	278
E.1 Cathode Void Image 1	281
E.2 Cathode Void Image 2	282
E.3 Cathode Void Image 3	283
E.4 Cathode Void Image 4	284
E.5 Cathode Void Image 5	284
E.6 Cathode Void Image 6	285
E.7 Cathode Void Image 7	285
E.8 Cathode Void Image 8	286
E.9 Cathode Void Image 9	286
E.10 Cathode Crack Image 1	287
E.11 Cathode Crack Image 2	288
E.12 Cathode Crack Image 3	289

LIST OF FIGURES – CONTINUED

Figure	Page
E.13 Cathode Crack Image 4	289
E.14 Cathode Crack Image 5	290
E.15 Cathode Crack Image 6	290
F.1 Cathode Void Image 1	293
F.2 Cathode Void Image 2	293
F.3 Cathode Void Image 3	294
F.4 Cathode Void Image 4	294
F.5 Cathode Crack Image 1	295
F.6 Cathode Crack Image 2	296
F.7 Cathode Crack Image 3	297
F.8 Cathode Crack Image 4	298
F.9 Cathode Crack Image 5	299

GLOSSARY OF ACRONYMS

Acronym	Description
ASME	American Society of Mechanical Engineers
ASR	Area Sensitive Resistance
BLDC Motor	Brushless DC Motor
BOP	Balance of Plant
CHP	Combined Heat and Power
CRB	Cramér-Rao Bound
DAQ	Data Acquisition
DHiL	Device and Hardware-in-the-Loop
DMFC	Direct Methanol Fuel Cell
EDX	Energy-Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FFT	Fast Fourier Transform
FRA	Frequency Response Analysis
HPT	Pressurized-Hydrogen Tank
HiL	Hardware-in-the-Loop
HSPM	Hybrid Source Power Management
IEEE	Institute of Electrical and Electronics Engineers
LIA	Linear Interpolation Analysis
LSM	Lanthanum Strontium Manganese
MIT	Massachusetts Institute of Technology
NLLS	Nonlinear Least Squares
ODE	Ordinary Differential Equation
OLS	Ordinary Least Squares
PCU	Power Conditioning Unit
PEMFC	Proton Exchange Membrane Fuel Cell
PSD	Phase-Sensitive Detection
PWM	Pulse-width Modulation
SEM	Scanning Electron Microscopy (or Microscope)
SNR	Signal-to-Noise Ratio
SOFC	Solid Oxide Fuel Cell
UAV	Unmanned Aerial Vehicle
XPS	X-ray Photoelectron Spectroscopy
YSZ	Yttria Stabilized Zirconia

ABSTRACT

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices which can effect efficient, clean, and quiet conversion of chemical to electrical energy. In contrast to conventional electricity generation systems which feature multiple discrete energy conversion processes, SOFCs are direct energy conversion devices. That is, they feature a fully integrated chemical to electrical energy conversion process where the electric load demanded of the cell intrinsically drives the electrochemical reactions and associated processes internal to the cell. As a result, the cell's electric terminals provide a path for interaction between load side electric demand and the conversion side processes. The implication of this is twofold. First, the magnitude and dynamic characteristics of the electric load demanded of the cell can directly impact the long-term efficacy of the cell's chemical to electrical energy conversion. Second, the electric terminal response to dynamic loads can be exploited for monitoring the cell's conversion side processes and used in diagnostic analysis and degradation-mitigating control schemes.

This dissertation presents a multi-tier investigation into this electric terminal based performance characterization of SOFCs through the development of novel test systems, analysis techniques and control schemes. First, a reference-based simulation system is introduced. This system scales up the electric terminal performance of a prototype SOFC system, e.g. a single fuel cell, to that of a full power-level stack. This allows realistic stack/load interaction studies while maintaining explicit ability for post-test analysis of the prototype system. Next, a time-domain least squares fitting method for electrochemical impedance spectroscopy (EIS) is developed for reduced-time monitoring of the electrochemical and physicochemical mechanics of the fuel cell through its electric terminals. The utility of the reference-based simulator and the EIS technique are demonstrated through their combined use in the performance testing of a hybrid-source power management (HSPM) system designed to allow in-situ EIS monitoring of a stack under dynamic loading conditions. The results from the latter study suggest that an HSPM controller allows an opportunity for in-situ electric terminal monitoring and control-based mitigation of SOFC degradation. As such, an exploration of control-based SOFC degradation mitigation is presented and ideas for further work are suggested.

INTRODUCTION

Fuel cells are electrochemical devices which can effect efficient, clean, and quiet conversion of chemical to electrical energy. By essentially partitioning the chemical reaction involved in oxidation with a circuit, fuel cells derive usable electricity directly from the oxidation of a fuel source. The result is the highly efficient generation of electricity, and assuming hydrogen is used as the fuel source, the only byproducts created are heat and water. Further, fuel cells are free of moving mechanical parts and thus exhibit very little noise and vibration during operation. Due to these qualities, they are receiving much interest for a variety of applications including distributed electricity generation [1–3], backup and auxiliary power [4, 5] and transportation and vehicular power [6, 7].

Fuel Cell Technologies

Several different types of fuel cells exist. These different technologies are most often categorized by the material used in their electrolyte and the type of ionic conduction the material facilitates. For example, the proton exchange membrane fuel cell (PEMFC) uses a proton-conducting polymer membrane for an electrolyte, while the solid oxide fuel cell (SOFC) features a solid ceramic oxygen ion conducting electrolyte. Additionally, fuel cells can be categorized by their operating temperatures into high temperature fuel cells, e.g. SOFCs (600°C - 1000°C), and low temperature fuel cells, e.g. PEMFCs (<80°C). While these different types of cells employ very different materials and operate at widely different temperatures, they all feature a direct energy conversion process, which provides both advantages and disadvantages when compared to conventional electricity generation.

Fuel Cell Advantages

Conventional electricity generation systems generally rely on heat engine technologies featuring a multiple-step energy-conversion process. For example, in a steam turbine, chemical energy typically in the form of a fossil fuel [8], e.g. coal or natural gas, is burned to generate thermal energy. This energy heats the water in a boiler producing pressurized steam. The steam is then used to generate mechanical energy by turning a turbine connected to the rotor of a generator, which converts the mechanical energy into electricity, thus completing the full energy conversion process. While this form of electricity generation has proven reliable, it also has several less desirable traits.

First, the production and use of fossil fuels as the energy source in conventional electricity generation results in toxic emissions, e.g. sulfur dioxide and various nitrogen oxides, and greenhouse gas emissions such as carbon dioxide and methane. The latter of these emission types is of particular concern as greenhouse gas emissions from electricity generation systems are among the leading sources of anthropogenic climate change [9], and efforts to capture and store the greenhouse gas emissions are expensive, problematic, and result in a reduction in overall electricity generation efficiency [10,11].

Fuel cells on the other hand can use hydrogen derived from renewable energy systems, e.g. photovoltaic or wind powered electrolysis, as a fuel source with the salient byproducts being heat and water. In fact some fuel cells have the potential to also operate in reverse, performing electrolysis when provided with water and electric current [12,13]. Thus, fuel cell systems can operate as zero-emission electricity generators, and can be used to complement renewable energy systems by providing energy storage and power smoothing capabilities.

Device	Typical System Capacity Range	Operating Efficiency (%)	Cell Operating Voltage
<i>Conventional</i>			
Internal Combustion Engine	50 kW - 5MW	25-40	-
Gas Powered Turbine	1 MW - 100 MW	30-40	-
Steam Turbine	> 1 MW	34 avg.	-
<i>Fuel Cells</i>			
Proton Exchange Membrane FC	500 W - 1 MW	35-40	0.4-1.2 V/cell
Molton Carbonate FC	5 kW - 3 MW	50 avg.	0.4-1.0 V/cell
Solid Oxide FC	5 kW - 2 MW	45-65	0.4-1.0 V/cell
Solid Oxide FC with CHP*	5 kW - 2 MW	up to 80	0.4-1.0 V/cell

*CHP - combined heat and power

Table 1.1: Typical electrical generation capacity and operating efficiencies of various fuel cell electricity generators as compared to conventional technologies working [1,14].

Second, the overall energy conversion efficiency of conventional electricity generators is fundamentally limited by the heat engine. Each additional energy conversion step compounds the inefficiency due to additional losses, e.g. windage and friction losses in the generator. Further, conventional electricity generation systems are generally large capacity power plants and require an extensive network of transformer substations and high-voltage transmission lines to deliver electricity to loads. This electricity transmission results in even further losses in the overall energy conversion efficiency and delivery to point of use.

Conversely, fuel cells operate isothermally and are not restricted by the efficiency implications of a heat engine, and as they feature a single step energy conversion process, no intermediate conversion step losses exist to reduce efficiency. As shown in Table 1.1, this results in fuel cells offering chemical to electrical energy conversion efficiencies equal to or greater than those of conventional systems. Additionally, unlike

conventional generation systems which require large capacity systems for optimizing efficiency, fuel cell systems scale well in size without a significant impact on overall system efficiency [15]. Thus, fuel cells can be placed near loads and sized accordingly so that the additional efficiency losses due to electricity transmission are bypassed entirely.

Fuel Cell Disadvantages

Unfortunately, the same direct energy conversion processes that provides fuel cells with many advantages, also result in several important disadvantages. The far right column of Table 1.1 shows the low operating voltages for single fuel cells. These voltage potentials are governed by the electrochemical reactions occurring in the devices, and are too low for use with most practical loads. Thus, multiple fuel cells are typically stacked in series to boost the overall voltage to a useful level. This multi-cell system is referred to as a fuel cell stack. The stacking of cells presents a difficult system integration problem as generally each cell requires similar operating conditions, e.g. temperature and reactant flow rates, as the other cells in the stack for efficient and effective stack operation.

Second, while the direct energy conversion processes of fuel cells account for their high efficiencies, they also allow for potentially detrimental interactions between the fuel cell and the load. Whereas the multiple steps of the energy conversion process in conventional electricity generation act as buffers to isolate the dynamic load demands from the chemical energy conversion, in fuel cell devices the chemical to electrical energy conversion is a fully integrated process. Therefore, the magnitude and dynamic characteristics demanded by the electric load are fed back to the internal electrochemical and physicochemical processes within the cell via the cell's electric terminals. While the full effects of this interaction are still not well understood,

initial investigations suggest that it can lead to degradation of the fuel cell system and ultimately inefficient chemical to electrical energy conversion [16, 17].

Scope of this Research Project

As mentioned above, the electric terminals provide a path for interaction between load side electric demand and the fuel cell's energy conversion side processes. While this can potentially lead to cell degradation, it also presents an opportunity for monitoring the cell's electrochemical and physicochemical processes, which are otherwise not directly observable. Most importantly, this monitoring can be done in-situ, while the fuel cell is powering its load. In principle, the electric terminals of a fuel cell system can be monitored for characterizing fuel cell / load interactions, performing prognostic and diagnostic analysis, and even mitigating degradation if used as a feedback signal in a load demand control loop.

This research project aims to investigate this electric terminal based performance characterization of fuel cells. For this project, the specific fuel cell technology investigated are SOFCs. However, the testing systems, analysis techniques, and control schemes presented are applicable to other types of fuel cells, electrochemical technologies, e.g. batteries, and direct energy conversion devices such as photovoltaics and thermoelectrics.

First, a unique hardware-in-the-loop (HiL) simulation system is introduced for testing dynamic interactions between an SOFC stack and power electronic loads, power conditioning units (PCUs) and hybrid source power managers (HSPM). This system uses the current and voltage measurements available at the electric terminals of a prototype SOFC device, e.g. a single cell or small scale stack, as a reference for reproducing the electrical terminals of a full power-level stack. This amplification

method of simulation is advantageous in stack / load studies as it provides a low-cost alternative to full power-level fuel cell stacks while maintaining the explicit ability for post-test analysis, e.g. scanning electron microscopy (SEM), of the prototype system. This sort of post-test analysis is non-existent in model-based stack simulators and often problematic in commercially available fuel cell stacks which lack a nondestructive disassembly technique.

Next, a diagnostic technique for determining possible SOFC degradation is proposed. This technique uses a time domain ordinary least squares (OLS) approach to electrochemical impedance spectroscopy (EIS) developed for reduced-time monitoring of the fuel cell system through its electric terminals. The relative progression in impedance measurements during fuel cell operation provides insight into levels of degradation within the cell that hinder electrochemical reactions.

Following this, electric terminal measurements from operating fuel cells are presented which show that the degradation that occurs during heavy current-loading conditions is recoverable if the cell is allowed to operate at open circuit. This data is further analyzed to show that impedance measurements available at the fuel cell's electric terminals follows a predominantly linear progression with cell degradation.

Finally, an investigation into opportunities for control system integration aimed at mitigating SOFC cell degradation is presented. This investigation makes use of the results of the electric terminal measurements and the subsequent linear progression performed on the SOFCs undergoing degradation by heavy current loading to develop two different load-demand control systems. These systems, which utilize impedance measurements for degradation level feedback, are designed, built and tested for their ability to affect cell degradation.

Previous Contributions from the Scientific Community

Collectively, the intermediate objectives for this research project outlined above represent an entirely novel approach to fuel cell system performance characterization and control. However, significant contributions from the scientific community involving fuel cell modeling and emulation, diagnostic testing, and degradation mitigation have previously been reported. This section documents the relevant previous contributions to this research project in order to better contextualize its contributions which are listed in the next section. While the technology focus of this research project is SOFCs, many of the research studies described below feature other fuel cell or electrochemical device technologies. They are included because the methods and systems developed in those studies are easily applied to SOFC systems.

Fuel Cell Stack Simulation and Hardware-in-the-Loop Testing

The use of HiL testing strategies for investigating the integration of fuel cell stacks and electronic loads, PCUs and HSPMs represent a middle-ground solution between tests involving real systems and tests that are entirely simulated. While ideally the testing of various fuel cell system topologies with their intended loads would be completed with real fuel cell stacks, power electronic systems, and loads, doing so is usually impractical due to fuel cell stack costs, the extensive balance of plant (BOP) and auxiliary system requirements, and the lack of flexibility in terms of in-situ stack monitoring and modularity for post-test analysis. Purely simulated tests on the other hand are very cost-effective and only require adequate simulation software and computing power. However, they often lack the accuracy of real system tests as their simulation systems are only as accurate as the individual component

models. Additionally, as no real fuel cell system is used, in-situ monitoring and post-test analysis methods are unavailable.

In HiL testing, some system components are real, while others are emulated. For fuel cell system integration tests, typically the comparatively low cost and modular loads, PCUs and/or HSPMs are real electric systems, while the more complicated and integrated fuel cell stack systems are emulated based on models. These fuel cell stack simulation systems allow real-time analysis of stack-load interactions and PCU and HSPM performance.

To date, a great number of fuel cell stack emulation systems have been developed for HiL tests of dynamic loads powered by a fuel cell stack [18–30] and hybrid fuel cell power system topologies [31]. The majority of these stack emulators can be grouped into those based primarily on physical models [18–25,31] and those based exclusively on empirical data [26–28].

Physical model based emulators have the advantage of internal parameterization of the simulated electrochemical and physicochemical performance of a fuel cell stack in response to real dynamic loads. In terms of relating these interactions to mechanisms for degradation, the combined effects of the load characteristics and the emulated operating conditions on the emulator’s internal model variables, e.g. reactant temperatures and partial pressures, are fully observable. Observations of these variables during load testing can then be correlated to results from cell material tests involving these variables for predicting the effects of the load characteristics on fuel cell stack degradation. In [25], the authors provide an example of this by explicitly tracking the oxygen excess ratio of the simulated stack to determine loading conditions that might lead to oxygen starvation induced degradation in a real PEMFC stack.

However, these physically based emulators have key disadvantages. First, almost all of them utilize a switching power electronic output stage, which necessarily im-

parts a high frequency ripple on the simulated stack voltage. This ripple would not be present in a real fuel cell stack system and is only effectively mitigated through an output filter at the expense of system bandwidth. Second, a fundamental trade-off exists between simulator accuracy and computational speed. This results in emulators incorporating only specific component models. In fact, while collectively the physically based simulators listed above account for a stack's steady-state electrochemical performance along with dynamic effects due to the double-layer capacitance [18, 20, 22, 23], gas and fluid flow [19, 21, 23], thermal energy conservation [19, 23, 24], and balance of plant systems [21, 23], only [23] combine all the model types into one emulator. Even so, the models utilized are simplified and errors in the simulated stack electric terminal operation still exist, especially during emulation of the fuel cell stack's dynamic behavior under transient load conditions.

The fuel cell stack simulators based on empirical models result in less computational complexity because reduced parameter models are fit to the measured fuel cell performance. In [26] a 3rd order polynomial model is fit to the measured polarization curve of an SOFC stack under various hydrogen flow rates. Transient effects are added to the simulator by slew rate limiting the simulated stack output power. Lee et al. [27] use a linear approximation of a PEMFC stack ohmic region combined with an RC equivalent circuit for a delay effect, and in [28], a Direct Methanol Fuel Cell (DMFC) simulator is presented using a four parameter model consisting of open circuit voltage, nonlinear activation resistance, activation capacitance and ohmic resistance. While these emulators have good bandwidth performance, they are not useful for degradation studies as no parametric analysis is available, and the empirical data used for simulation models generally does not include degradation data.

A third class of fuel cell stack emulators allowing both Device and Hardware-in-the-Loop (DHiL) testing was first demonstrated in [29] by replacing the fuel cell

stack model of [28] with an operating single fuel cell for generating voltage and current command signals. In this novel approach, the electrical terminal characteristics, i.e. voltage and current, of the prototype cell are measured, scaled up, and reproduced at the simulator output terminals. Simulated stack operation close to that of a multi-cell stack is achieved while still significantly reducing system size and cost. However, despite improved accuracy and dynamic performance over model based simulators, the system is still limited to dynamics below 500 Hz. This significantly limits the range of load / stack interactions able to be studied. Further, as mentioned earlier, the output stage of the simulator is a switching-mode power supply that imposes a voltage ripple on the applied load voltage which is not present in the generated fuel cell voltage.

Electrochemical Impedance Spectroscopy Based Diagnostics

In EIS, a device is perturbed from steady-state operation by a potentiostatic or galvanostatic excitation signal over a desired frequency range. The resulting current and voltage response is then analyzed with the two signals' interrelated magnitude, phase and frequency content determining the localized impedance of the device as a function of frequency. The attraction of EIS lies in the direct correlation between the observable electric terminal performance of an electrochemical device and its non-observable electrochemical and physicochemical processes. Thus, EIS allows bulk monitoring of the internal processes of an electrochemical device with the results indicative of the device's dynamic performance and overall health.

The choice of the excitation signal has been the subject of much research regarding the tradeoffs between excitation signal classes and their optimizations [32–35]. Under non-stationary loading conditions, e.g. electric motor acceleration and deceleration

in electric vehicles, measurement time is limited. Therefore, multi-frequency harmonic [36, 37] or non-harmonic [38–40] sinusoidal perturbations are often used as they *parallel* the frequency components in time as opposed to the *sequential* stepping or sweeping of frequency components. However, a drawback to these methods is that even under optimal phasing conditions, the nonlinearity of the fuel cell system limits the individual sinusoidal component amplitudes when compared to single-frequency sinusoidal perturbation. Thus, the signal-noise ratio and accuracy of the impedance measurements are reduced for each frequency component.

Several standard signal processing techniques including Phase-Sensitive Detection (PSD), Frequency Response Analysis (FRA), and the Fast Fourier Transform (FFT) [41–44] have been used for impedance analysis. For all of these techniques, the fundamentals of the impedance extraction processes are quite similar. First, the measured current and voltage waveforms are multiplied by a reference waveform of a particular frequency. This results in product waveforms with phase and amplitude information in their DC-components. The product waveforms are then lowpass filtered to extract the phase and amplitude information of the current and voltage waveforms at the reference frequency. An impedance profile, i.e. a set of impedance measurements at select frequencies, is found by stepping through this process at frequencies of interest. In the case of the FFT, multiple frequencies are analyzed simultaneously, which most usefully applies to perturbation signals containing multi-frequency components.

As alternatives to PSD, FRA and FFT, least squares fit techniques have been applied to EIS. The major advantage of least squares over other analysis methods is that least squares can provide accurate parameter estimates even when the data signals contain a non-integer number of signal periods or even just a fraction of a period. This can lead to reduced time impedance measurements. In recent years, the

use of nonlinear least squares (NLLS) for impedance measurements was demonstrated for embedded system and portable instrument applications by Ramos et. al. [45, 46]. However, these methods were limited to static, single frequency (narrowband) sinusoid perturbation signals.

Several research groups have demonstrated the application of EIS in on-line in-situ monitoring of fuel cell systems using instrumentation hardware with varying degrees of complexity. In [47], Seger presented a minimal instrumentation monitoring technique that performed parametric impedance analysis of a grid-tied SOFC stack by monitoring the voltage and current ripple imposed by the power electronic switching of the PCU. While this method was limited to excitation frequencies corresponding to the switching frequency and harmonics of the PCU power-electronics, it did prove useful in showing evidence of stack degradation as a function of time.

In [48], an exogenous embedded frequency response analyzer was presented. This small device is placed in parallel with a fuel cell stack and can be used to draw a perturbation signal from the fuel cell stack while the stack powers a load. While more complex than the system in [47], this device has the advantage of providing an external perturbation signal that can be stepped through several frequencies for a more complete impedance profile.

In [49, 50], on-line in-situ electric terminal monitoring capabilities are added to an HSPM system. This system is designed to protect a fuel cell stack from harmful dynamic load conditions by paralleling an auxiliary battery device with the fuel cell stack, and diverting load transients to the battery. This additional power source increases the degree of freedom within the system allowing the fuel cell stack to operate at a set nominal DC operating point. Because the current-voltage relationship of a fuel cell is nonlinear, the appropriate application of EIS to fuel cell systems requires the DC operating point of the device to remain constant throughout the

measurement process. Thus, this HSPM system allows for effective EIS monitoring of the stack while still powering a dynamic load.

Fuel Cell Degradation Mechanisms and Performance

One of the major issues preventing wide-ranging fuel cell system implementation is that their electrical performance tends to degrade over time and with use. In regards to SOFCs, several mechanisms for degradation have been identified. In both the cathode and the anode of SOFCs, catalytic sites promoting the electrochemical reaction required for generating electricity can become occupied through the deposition of foreign phases. For example, in the cathode, volatile chromium present in the metallic fuel cell stack assembly components can result in the deposition of Cr_2O_3 on the cathode / electrolyte interface resulting in an increased cell resistance [51, 52]. In the anode, carbon in the form of graphite [53, 54] as well as contaminants in hydrocarbon fuels such as the sulfur in hydrogen sulfide [55–57] can attach to nickel in the anode blocking activation sites important for fuel oxidation.

It is important to note however that both carbon and sulfur deposition can be at least partially reversed by altering the operating conditions of the SOFC system. In [54], the authors show that the deposited carbon can be removed through oxidation in the form of CO and CO_2 through forced polarization of the cell while sequestering additional fuel from the anode. In [55], sulfur is shown to be effectively removed from the anode by introducing N_2 or air to the anode, while in [56], the deposited sulfur undergoes desorption potentially as SO_2 when the hydrogen sulfide is removed from the fuel stream. In all cases, the removal of the contaminants results in a large though only partial recovery of the cell’s electrical performance.

Independent of contaminant issues, the operational conditions of an SOFC system can also have grave consequences on the system’s efficiency and long-term health.

In particular, as mentioned above, excessive or dynamic loading of SOFC systems can lead to degradation in the systems electrical performance due to a variety of electrochemical, thermal and resulting-secondary microstructural effects. In the case of excessive loading, the corresponding ionic current (oxygen ions diffusing through the electrolyte from the cathode to the anode) results in oxidation of the anode nickel and a resulting decrease in catalytic activity, loss of electronic conductivity, and volumetric expansion which can cause microstructural failures such as delamination of the anode from the electrolyte [58].

While multiple studies have examined the effects of anode oxidation in air [58–60], few studies have investigated the ionic oxidation effects due to excessive load currents. In [61], the influence of electrochemically induced oxidation on anode nickel morphology and resulting anode expansion is studied through SEM imaging and residual stress measurements of the electrolyte, respectively. Similarly, Sarantaridis et. al. [62] measured the accumulated oxidation charge required for catastrophic SOFC failure finding that 5% Ni-oxidation lead to fractures in the cell electrolyte. In [63], the authors studied the electrochemically induced redox cycling effects on SOFC stability finding that repeated redox cycling lead to delamination between the active anode and bulk anode layers. In all three of these studies, the periods of oxidation occurred during fuel “starvation” operation, i.e. the absence of hydrogen gas. Of the studies, only [63] presented impedance data useful in correlating electric terminal measurements to mechanisms for degradation. It is interesting to note though that in the conclusion of [62], the author’s claim that the electrochemical performance is recoverable through reduction of the anode for total nickel oxidation levels less than 5%.

Dynamic current loading of an SOFC system is also proposed as a mechanism for significant degradation. Mazumder et. al. of the Laboratory for Energy and

Switching-Electronics at the University of Illinois at Chicago have produced the majority of the studies, e.g. [17, 64–66] attempting to characterize this mechanism. In the first three of those listed, the effects on tubular-design SOFC temperature and fuel utilization as functions of both inverter ripple current and transient current-steps are considered. For these studies, a temporally and spatially resolved dynamic SOFC system model is combined with dynamic models for the balance of plant, the application load, and the interconnecting power conditioning unit. These models predict large thermal and fuel utilization variations for large magnitude inverter ripple currents at low frequencies, and nonuniform thermal distributions during load transients. Because these parametric variations and distributions are associated with degradation due to heightened anodic exposure and microstructural damage due to thermal cycling, the author’s argue that these dynamic loading characteristics can lead to degradation [67].

More recently, the same group confirmed the degrading nature of repeated load transients and large-magnitude low-frequency current ripple dynamics through 900-hour tests of 25-cell and 5-cell planar SOFC stacks. The area sensitive resistance (ASR) of stacks undergoing repeated dynamic step changes in current demand or continuous large signal ripple current at 60 Hz increased by 25% and 15% respectively compared to just 10% for a similar SOFC stack operated under constant current [66]. However, no post-test material analysis for confirming mechanisms of degradation was presented.

Fuel Cell Degradation Mitigation

From the system integration perspective, approaches investigated for mitigation of fuel cell system degradation has almost exclusively focused on buffering techniques to protect the fuel cell system from excessive and dynamic loading. In these approaches,

the fuel cell system is coupled with auxiliary energy sources, e.g. battery or super-capacitor. The auxiliary source is then controlled to supply the additional power required during times of excessive or dynamic demand. This allows the fuel cell system to continue operation at or near a nominal, non-degrading operating point.

In addition to modeling and investigating load-induced mechanisms for SOFC degradation, Mazumder et. al of the Laboratory of Energy and Switching-Electronics System group at the University of Illinois at Chicago have also quantified the benefits of buffering techniques as well as proposed novel topologies and control methods for coupling energy storage devices to SOFC systems and loads. In [68–70] the benefits of coupling a battery or pressurized hydrogen tank (HPT) with an SOFC system for dynamic load buffering were presented through the comparison of system operation with and without the energy storage devices. These studies showed that through effective battery or HPT operation, spatial and temporal variations in current densities, temperature, and fuel utilization that would normally occur in an SOFC as a result of a large step-change in current load are largely mitigated.

In [71], Mazumder and Pradhan present a novel topology for a hybrid-source fuel cell stack and battery system. This hybrid-source power management (HSPM) system consists of multiple bidirectional DC-DC boost converter modules, with one converter dedicated to the fuel cell stack, one to the battery and the remaining able to be connected to either. A dynamic power manager controls the input connections of each module as well as their set currents so that under steady-state loading, maximum overall system efficiency is achieved. However, when a load transient occurs, any non-connected modules are connected to the battery for supplying the increase in current demanded by the load until a new steady-state load operation is reached. This topology and control method allow increased system efficiency while also providing

stack protection from degrading load transients, though these benefits are at the expense of increased system complexity and up-front component costs.

Numerous other topologies for hybrid systems have been proposed, the most simple of which provide stack load buffering capabilities by connecting an energy storage device directly to the output bus of a fuel cell system [72–74]. In the case of [72] and [73], the storage device used is a battery while in [74] the storage device is a super-capacitor. In all three systems, the fuel cell stack is connected to the output bus via a DC/DC converter. Additional topologies include dual bi-directional converters for fuel cell / battery hybrid systems [49,50,75], dual bi-directional converters for fuel cell / super-capacitor hybrid systems [76,77], and Z-source inverters for fuel cell / battery hybrid systems [78]. While these topologies and their respective power management control schemes vary significantly between designs, fundamentally they all aim to mitigate fuel cell system degradation by actively diverting excessive and dynamic load profiles from the fuel cell system and instead applying them to an auxiliary energy storage device. However, none of these control systems utilize fuel cell system measurements as inputs to the control system which dictates fuel cell performance.

Significant Contributions from this Research Project

This research projects presents several new contributions towards the study and understanding of SOFC operation, monitoring and interactions with electric loads. These significant contributions are described below in relation to the aforementioned contributions from the scientific community at large. Additionally, the portions of this dissertation which have received publication in conference proceedings or scientific journals are acknowledged.

Reference Based SOFC Simulation System

The reference based SOFC simulated stack system provides many significant contributions in DHiL testing by improving upon the original reference-based stack simulator design of [29], and demonstrating additional capabilities. First, by replacing the switching power electronic output stage with a linear-amplifier output stage, the imparted output voltage ripple is eliminated. Second, the use of continuous gain control using the inherent high gain-bandwidth product of the amplifier increases the simulator's bandwidth by almost two decades from 500 Hz to ~ 30 kHz. Third, the improved bandwidth allows accurate DHiL testing involving real power-electronic loads, HSPM systems, and in-situ EIS stack monitoring techniques, all of which are demonstrated within the DHiL environment. Finally, though not explicitly exploited in this dissertation, the linear amplifier output stage is bi-directional and affords capabilities for testing reversible fuel cell stack systems.

Electrochemical Impedance Spectroscopy Method

This dissertation presents a new method for EIS analysis using OLS with the novelty lying in the application of OLS for multi-decade EIS analysis. The perturbation signal used for this method is a logarithmically frequency-swept sinusoid current, which allows large-amplitude, frequency-continuous, short-time excitation that spans a broad range of frequencies (> 4 decades). Log-swept sinusoidal models are then fit to the measured current and voltage waveforms, revealing the requisite information for determining electrochemical impedance as a function of frequency. This method is unique from the least squares methods of [45, 46] as it features a non-static sinusoidal perturbation, and the use of ordinary least squares which allows standard non-iterative linear algebra solutions for non-parametric fuel cell stack impedance profiles. Additionally, the application of this method for on-line, in-situ, electric ter-

terminal monitoring of a solid oxide fuel cell stack is demonstrated through the HSPM system of [49].

Fuel Cell Performance and Degradation Mitigation Control

This dissertation presents an entirely novel approach to mitigating load-induced fuel cell degradation. Electric terminal measurements taken during fuel cell operation show that electric performance degradation caused by heavy current-loading and the presumed oxidation of anode-side nickel is recoverable when the cell is allowed to operate at open circuit. To the author's knowledge, this specific observation has not been previously published in literature. From this data, empirically-based linear interpolation models for the fuel cell's electric terminal performance as a function of load-induced degradation are created to describe both large-signal DC cell operation, and small-signal AC impedance. This also represents a novel approach to fuel cell modeling.

These models are then used to design two different and novel approaches to mitigating load-induced fuel cell degradation through impedance-feedback based control schemes. The first is a PWM method of control which uses the impedance measurement to vary the duty cycle of a cell alternating in operation between near-maximum power loading and open-circuit. The second is a continuous current control method which monitors the fuel cell's low-frequency impedance and alters the DC-operating point of the cell accordingly. In both of these control schemes, the intended operation is to affect the rate of the load-induced degradation by reducing the average load demanded of the cell as an increase in degradation is detected, and vice versa. To the author's knowledge, these represent the first attempts at active control of cell degradation strictly based on electric terminal measurements, whereas the previous solutions

involving hybrid power source systems only passively controlled cell degradation by buffering excessive or dynamic load-currents.

Copyright Acknowledgements

Portions of this dissertation have previously been published in scientific journals and conference proceedings. Specifically, a paper detailing an earlier incarnation of the reference based fuel cell stack simulation system (Chapter 3) was published in the proceedings from the American Society of Mechanical Engineers (ASME) 2010 8th International Conference on Fuel Cell Science, Engineering and Technology under the title, “Reference Based Fuel Cell Stack Simulator”, ©2010, ASME [30]. The time-domain based methodology for electrochemical impedance spectroscopy (Chapter 4) was published in the Institute of Electrical and Electronics Engineers (IEEE) Transactions on Instrumentation and Measurement under the title, “A Time-Domain Least Squares Approach to Electrochemical Impedance Spectroscopy”, ©2012, IEEE [79]. Finally, portions of Chapter 5 detailing the performance testing of the hybrid system power manager for a fuel cell and battery was included in a recently submitted article for publication in the IEEE Transactions on Power Electronics by lead author, John Cooley, under the title, “Multi-converter System Design for Fuel Cell Buffering and Diagnostics under UAV Load Profiles” [50].

Organization of Dissertation

The remainder of this dissertation is organized as follows. First, in Chapter 2 the general operation of an SOFC system is described. Additionally, details on the specific SOFC technology along with the test systems and experimental procedures used in this research project are given. Next, Chapters 3 and 4 detail the SOFC stack electric terminal simulation system and EIS electric terminal monitoring techniques,

respectively. In both chapters, extensive experimental results confirming the accuracy of the simulation system and EIS technique are also given. In Chapter 5, the combined usefulness of the two preceding techniques are shown through a collaborative effort between ourselves and a research team from MIT. This project used the SOFC stack simulator and EIS monitoring scheme to demonstrate the in-situ fuel cell stack protection and monitoring capabilities of an SOFC and battery hybrid source power management (HSPM) system designed by the MIT team. In Chapter 6, several experimental results showcasing fuel cell degradation due to current loading are extensively detailed. Additionally, in this chapter it is shown that by decreasing the load current, the fuel cell shows a propensity to recover in terms of its electrical performance. From these results, models for fuel cell degradation and recovery are suggested with an aim towards developing degradation mitigation control techniques. Chapters 7 and 8 feature explorations into two methods for regulating the degradation of an SOFC through load-end control. Finally, Chapter 9 concludes the dissertation with a summary of the main research projects contributions and findings, and suggestions for future work.

SOLID OXIDE FUEL CELLS

Figure 2.1 shows a conceptual diagram of a solid oxide fuel cell (SOFC). The cell is a layered structure consisting of porous anode and cathode layers separated by a dense electrolyte. Fuel is supplied to the cell's anode layer, while an oxidant is supplied to the cathode. The porous anode and cathode allow fuel and oxidant constituents to diffuse readily to the electrolyte / electrode boundary reaction sites. An electric load is interfaced with the cell such that as the load demands current, electrons pass from the anode to the cathode via the load. Once at the cathode, these electrons combine with oxygen gas at the electrolyte / cathode boundary, reducing the oxygen. The resulting oxygen ions diffuse through the ionically conductive electrolyte to the anode boundary where they oxidize the fuel constituents. This oxidation frees

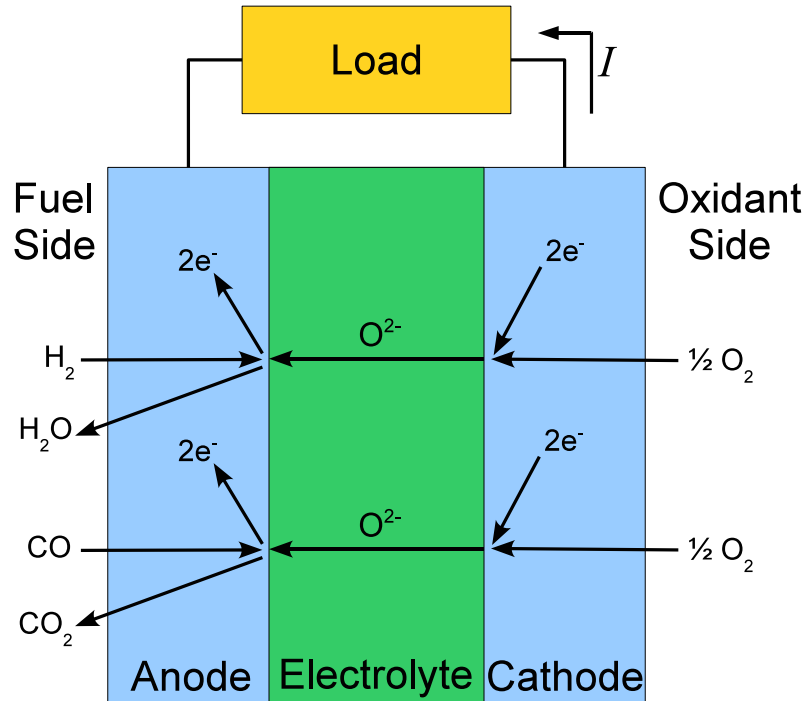


Figure 2.1: Conceptual cross-sectional diagram and operation of a solid oxide fuel cell (SOFC) operating on hydrogen and carbon monoxide fuel.

more electrons for availability to the external load, thus completing the circuit. The result of the full process is the direct conversion of fuel into delivered electricity with the electrochemical half cell reactions,



and



at the anode and cathode, respectively. The rates of these reactions are directly proportional to the current demanded by the load.

Unique to solid oxide fuel cells is the oxygen ion conducting electrolyte, which transports the oxygen from the cathode to the anode for oxidation of fuel. As indicated in Figure 2.1, with oxygen available at the anode, impurities in the hydrogen flow-stream to the fuel cell, e.g. carbon monoxide (CO), an often present byproduct of hydrocarbon fuels, also oxidize and thus actually operate as a fuel. This is in contrast with other fuel cell types such as the proton exchange membrane fuel cell (PEMFC) where CO in the fuel stream acts as a poison and reduces the cell's effectiveness by blocking active catalyst sites in the anode [4]. Additionally, the high temperature operation of the SOFC helps to facilitate internal reformation of more complex hydrocarbon fuels, e.g. natural gas or diesel fuel, into the simpler constituents shown in Figure 2.1. Combined with their high operating efficiencies, these two features of SOFCs make them highly attractive for use with traditional hydrocarbon energy sources.

Electric Terminal Performance

Figure 2.2 shows measured data representing the voltage available at an SOFC's electric terminals as a function of current density through the cell. While this data is specific to the fuel cell technology and operating conditions used in this study, the general characteristics of the current-voltage relationship shown are typical of most solid oxide fuel cells and even other fuel cell types operating under normal conditions.

A single SOFC's output voltage can be described as,

$$V_{fc} = E_{fc} - V_{fc,act} - V_{fc,ohm} - V_{fc,con}. \quad (2.4)$$

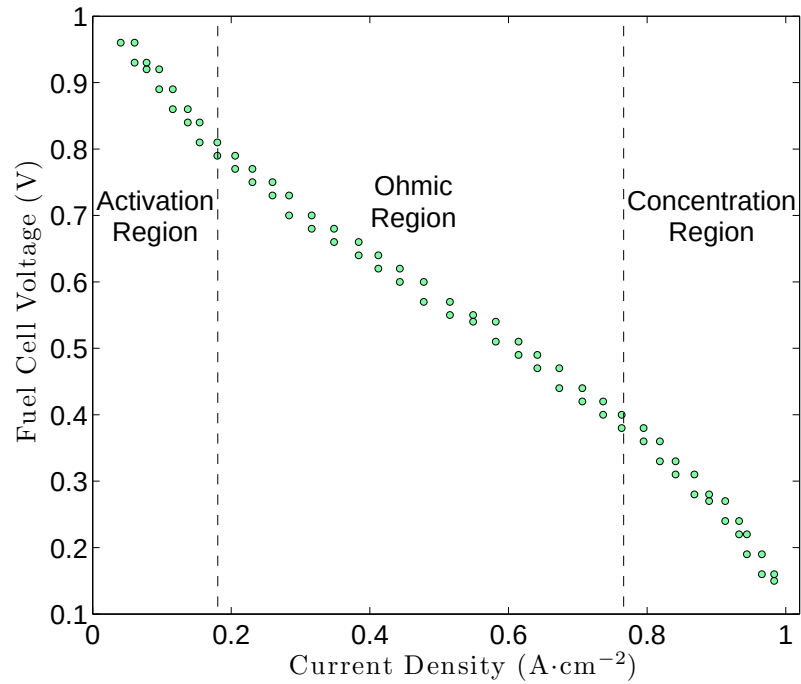


Figure 2.2: Measured steady-state current-voltage relationship of a single solid oxide fuel cell.

E_{fc} , represents the ideal performance of the fuel cell and is dependent on the operating conditions of the cell, i.e. temperature and pressure, the reactants involved,

nominally hydrogen and oxygen, and the reactants' concentration levels in the fuel and oxidant streams. However, as current through the cell is increased due to load demand, overpotential losses reduce the effective voltage applied to the load through the cell's electric terminals. These losses, represented in (2.4) as $V_{fc,act}$, $V_{fc,ohm}$, and $V_{fc,con}$, are overpotential losses due to the electrochemical activation processes, ohmic resistances in the cell components, and mass transport rates, respectively [4, 15, 80]. In (2.4), contributions of the anode and cathode are lumped.

Individual cells are typically “stacked,” i.e. electrically series connected, to form a power source with convenient output voltages. If these cells are identical and operating conditions including fuel and oxidant flow rates, reactant partial pressures, and cell temperatures are consistent across all cells in the stack, the fuel cell stack operation is derived from the individual cell operation by

$$V_s = nV_{fc}, \quad (2.5)$$

where n is the number of series connected cells [30, 73].

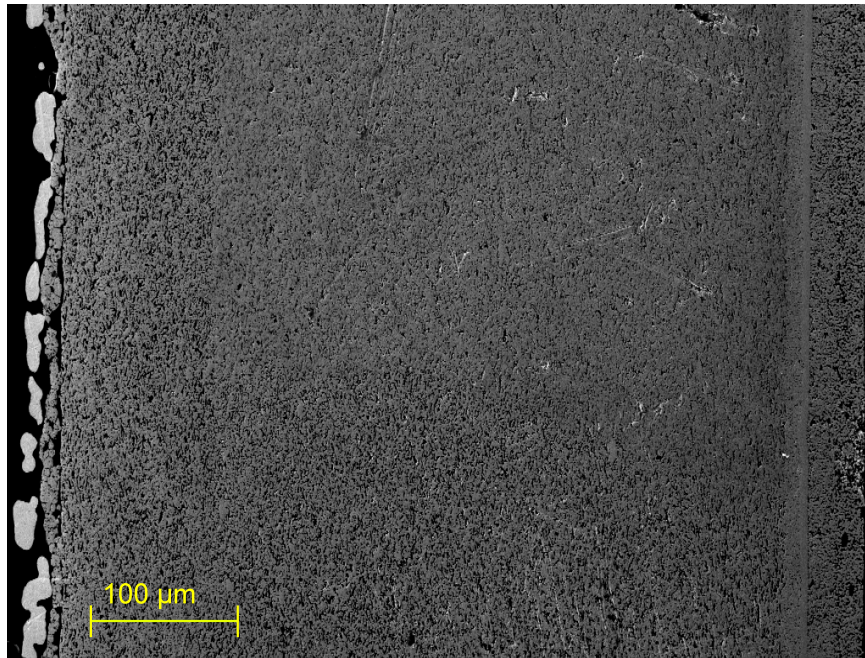
Each of the losses affecting cell and stack electric terminal performance as described in (2.4) and (2.5) has a unique relationship with load current demand that affects different regions of the polarization curve (Figure 2.2). $V_{fc,act}$ is related to the rate of the electrochemical reactions (2.2) and (2.3), which in turn is driven by the load demand. This relationship between voltage and current is logarithmic and so activation losses are most affecting in the low current demand region of the polarization curve. Ohmic losses within the cell due to O^{2-} transport through the electrolyte and electron transport through electrodes are directly proportional to current demand. As such, $V_{fc,ohm}$ is linear with current and dominates the medium current demand portion of Figure 2.2. Finally, $V_{fc,con}$, which affects the far right high current region

of the figure, is caused by mass-transport rate limits in reactant and product diffusion to and from the electrode / electrolyte boundaries, respectively. As current demand increases near these rates, the concentration of reactants available for the electrochemical reactions decreases, which in turn significantly increases overpotential.

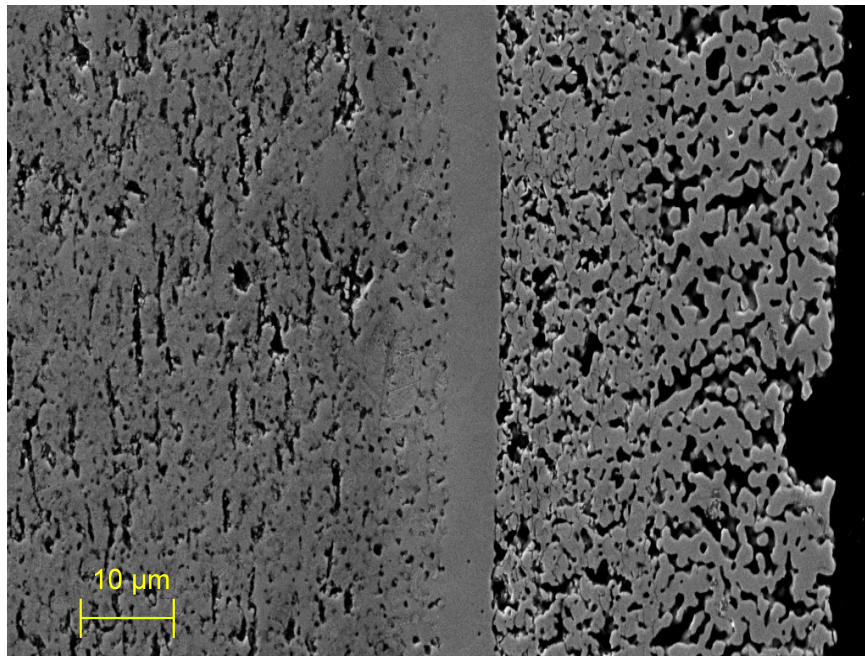
In addition to affecting the electric terminal performance of an SOFC system through the relationship between electrochemical overpotentials and load demand as described above, excessive or highly dynamic load demand can alter the efficacy of the electrochemical and physicochemical reactions. For example, high current demand can lead to oxidation of Ni-particles in an SOFC anode due to an excessive concentration of oxygen ions at the anode / electrolyte boundary [61,62]. This results in a loss of catalytic activity, loss of conductivity, and a volumetric expansion, which can lead to irreversible micro-structural damage such as cracking in the anode. These changes affect the electric terminal performance of the SOFC by increasing the activation barriers that oppose electrochemical reactions and decreasing surface area and increasing resistance, thus increasing overpotentials $V_{fc,act}$ and $V_{fc,ohm}$, respectively. This leads to a decrease in the efficiency of the chemical to electrical energy conversion process. More on this type of degradation is discussed in Chapter 6.

HC Starck Anode Supported Fuel Cells

The fuel cell technology used in all experiments related to this research project was the HC Starck ASC3 planar SOFC button cell. This cell uses materials standard in current SOFC cell and stack design. The anode is a porous double layer NiO / YSZ (Nickel-Oxide / Yttria Stabilized Zirconia) cermet with the bulk layer between 465 and 555 μm in thickness and the active layer between 5 and 10 μm in thickness. The bulk layer is optimized to achieve the required structural support for the cell



(a) Full Width of Cell



(b) Close-Up of Electrolyte

Figure 2.3: Cross-sectional images of an HC Starck ASC3 anode supported fuel cell. (a) shows a cross-sectional image of the entire cell thickness while (b) shows a close-up image of the cross-sectional area surrounding the solid electrolyte.

while maintaining high porosity for fuel and product gas diffusion, while the thin active layer is optimized to improve activation polarization by reducing porosity but increasing the number of anode / electrolyte interaction sites.

The electrolyte is a dense YSZ layer only 5 to 10 μm thick due to the high ionic resistivity of the electrolyte even at fuel cell operating temperatures, while the cathode is a porous, double layer structure of YSZ / LSM (YSZ / Lanthanum Strontium Manganese) and LSM with a total thickness between 30 and 60 μm . The diameter of the anode is 52 mm while the diameter of the electrolyte and cathode layers are 48 mm. Figure 2.3 shows cross-sectional images of an HC Starck ASC3 cell achieved using a field-emission scanning electron microscope (SEM). In, Figure 2.3a, the thin, lightly-colored strip towards the right edge of the image is the electrolyte which separates the cathode on the right from the anode on the left. Figure 2.3b shows a close-up image of the cross-sectional area around the electrolyte. In this image, the active anode region is observed as the slightly lighter colored region between the darker colored bulk anode on the left, and the dense electrolyte. Additionally, the double-layer cathode is observable by the slight change in porosity between the YSZ / LSM layer just to the right of the electrolyte and the LSM layer forming the edge of the cell.

Fuel Cell Experiment Set Up

The systems utilized throughout this research project for operating the SOFCs studied are described below along with the general protocol for fuel cell start up used for all tests.

Fuel Cell Test Stands

During testing, the cell is installed between two Inconel 600 platens as shown in Figures 2.4. These platens are multi-purposeful. The platen structures provide the support for installing the cell in an oven as shown in Figure 2.4b. The platen surfaces along with the silver mesh on the cathode side and the nickel foam on the anode side combine for current collection and distribution of reactant gasses across the cell's electrode surfaces. At each interface, i.e. Inconel / silver mesh, silver mesh / cathode, anode / Ni foam, and Ni foam / Inconel, a silver oxide paint (silver oxide in Xylene) is used to ensure good electrical contact and to protect against oxide layer formations during high temperature operation. At the interfaces involving cell electrodes, the silver oxide paint also includes an organic pore former to ensure porosity in the silver layer so that reactant gasses have adequate access to the electrode surface.

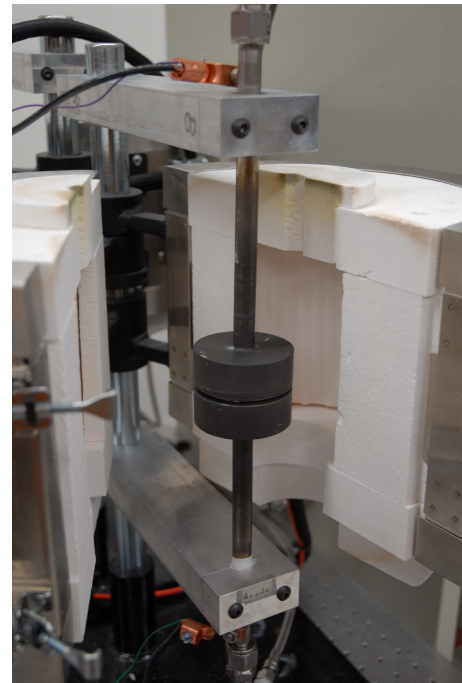
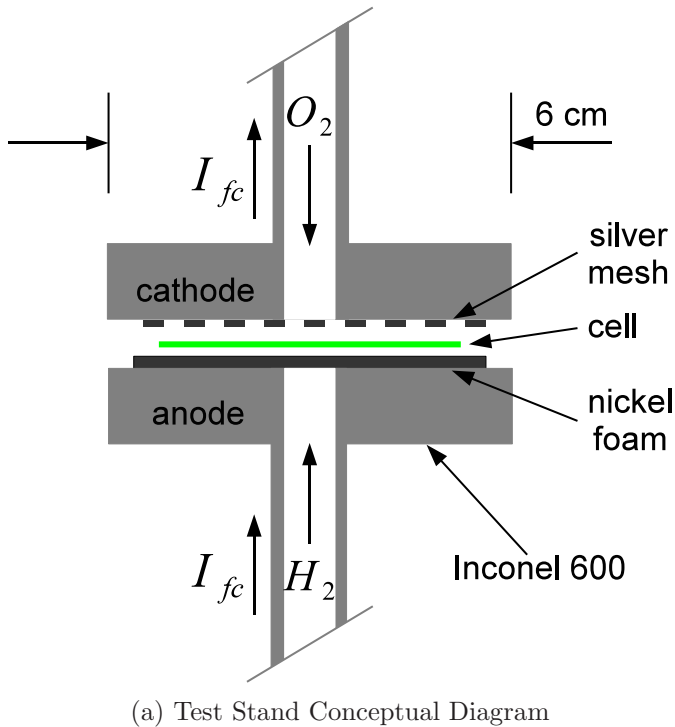
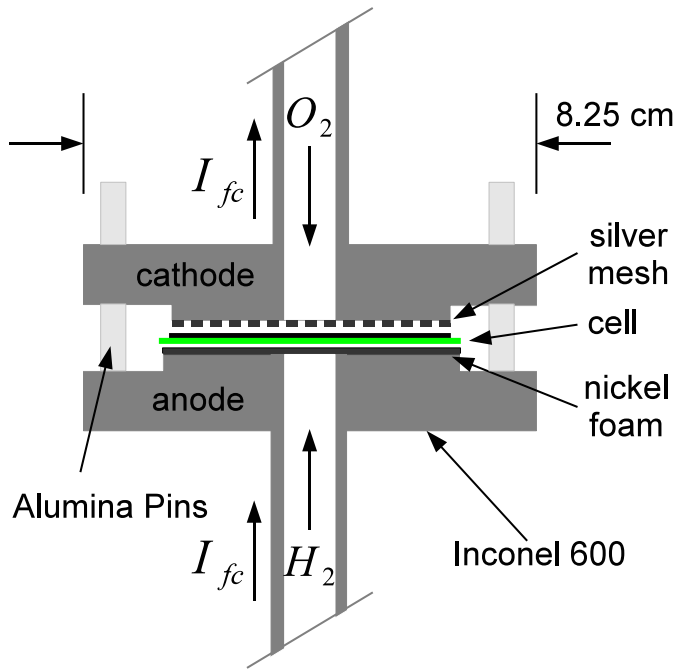
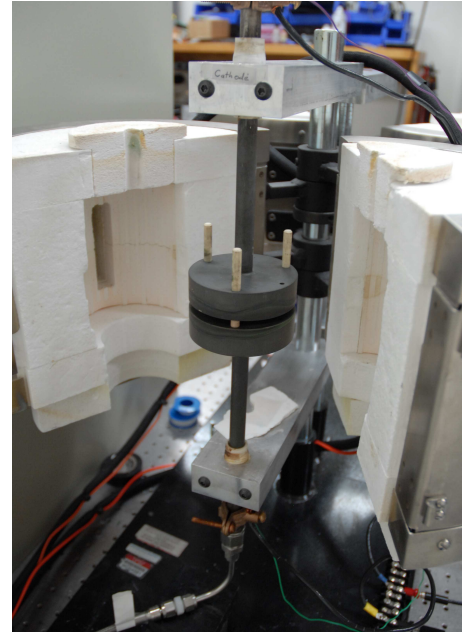


Figure 2.4: Fuel cell Test Stand A. (a) shows a conceptual diagram of the test fixture, while (b) shows the test fixture installed inside a clam-shell style oven.

The Inconel tubes welded to the platens serve as the gas flow conduits to the cell electrodes as well as the circuit path for the current drawn through the cell. External to the oven, Swagelok stainless steel braided hoses with electrically isolated fittings deliver gasses from the gas control manifold to the Inconel tubes. Also external to the oven, welded screw terminals at the ends of the Inconel tubes provide termination points for connecting other test circuit elements, e.g. power supplies and loads.



(a) Test Stand Conceptual Diagram



(b) Test Stand Image

Figure 2.5: Fuel cell Test Stand B. (a) shows a conceptual diagram of the test fixture, while (b) shows the test fixture installed inside a clam-shell style oven.

Prior to fuel cell degradation control testing (Chapter 7) an improved set of testing platens (Test Stand B, Figure 2.5) were manufactured and used for all subsequent fuel cell tests. Functionally, these platens are identical to those of the Test Stand A (Figure 2.4) design. However, Test Stand B features important manufacturing differences aimed at reducing the number of short circuit testing failures and improving the

uniformity between tests. Namely, Test Stand B features raised surface contact plates for cell placement and alumina pins for improved platen alignment.

The raised surface contact plates are machined to match the diameter of the cell electrodes which facilitates precise application of silver oxide paint and placement of the cell between the platens. This reduces the risk of misplaced or excess silver oxide paint creating a short between cell electrodes. The alignment holes and alumina pins ensure that once the cell is loaded between the Inconel platens, the platens do not shift when the oven is closed around the test stand. This also reduces the risk of cell shorting as well as ensuring good cell contact with platen surfaces. The only other difference between the two test stand systems are Test Stand B utilizes copper pipe grounding clamps for connecting external circuitry as opposed to the welded screw terminals of Test Stand A.

Gas Flow and Temperature Control

The test stand fixture and cell are housed inside an Applied Test Systems 3210 clam-shell type furnace. In conjunction with the Applied Test Systems Barber Colman Series temperature controller, the temperature of the fuel cell environment can be controlled up to 1200°C and preprogrammed for temperature ramping at a controlled rate during startup and shutdown. This oven features an N-type thermocouple mounted in the oven lining for feedback of temperature measurements to the controller. To minimize any error in cell temperature due to any thermal gradients present in the oven, the fuel cell test stand is mounted so that the height of the cell is in line with this thermocouple.

The gas flow manifold used to regulate cell reactants applied to the fuel cell consists of H₂, O₂ and N₂ supply tanks with flow rates controlled by MKS Mass-Flow Controllers. These controllers can effectively regulate the flow of each gas between 20

sccm (standard cubic centimeters per minute) and 2000 sccm to within 1% accuracy of full-scale. Figure 2.6 shows an image of the fuel cell gas flow and temperature control systems. Two clam-shell ovens are shown on the left and the gas tanks are on the far right. In the panel assembly shown in the middle, the gas flow control system is shown on top, while the two oven temperature controllers are shown on the bottom.



Figure 2.6: Gas delivery system and temperature control system for solid oxide fuel cell testing.

Fuel Cell Start Up and Shut Down Protocol

For fuel cell start up, the Inconel platens are first remachined using a lathe, removing around 0.5 mm off their cell interfaces. This is done to remove any oxidation and to ensure a high quality electrical connection with the cell assembly. The platens are then cleaned in an ultrasonic bath dried with Kimwipes and then cleaned further using an acetone soaked Kimwipe. This is done to remove any excess cutting oil and metal shavings which otherwise might damage the cell.

The cell is then mounted on the Inconel platens as shown in Figures 2.4 and 2.5, and the oven is latched closed. The oven is then programmed to climb to a temperature of 750°C at a rate of 3°C·min⁻¹. Upon reaching 500°C, nitrogen is introduced to the anode at a rate of 100 standard cm³·min⁻¹ and oxygen to the cathode at a rate of 30 standard cm³·min⁻¹. Once the operating temperature is reached, the nitrogen flow is slowly reduced to zero over the course of 10 minutes. In the nitrogen's place, hydrogen is introduced to the anode and ramped from zero to a rate of 260 standard cm³·min⁻¹ over the same period of time. The oxygen flow is simultaneously increased to 100 standard cm³·min⁻¹. The fuel cell is allowed to reach a steady state for at least four hours before testing begins so that the anode can reduce.

For fuel cell shut down, the oxygen and hydrogen flows to the cathode and anode, respectively, are slowly diminished over a 10 minute period while each being replaced by nitrogen ramped from zero to 100 standard cm³·min⁻¹ over the same period of time. Following this, the temperature controller is reprogrammed to ramp the temperature down from 750°C to room temperature at a rate of -2°C·min⁻¹. The oven however can only passively cool and so for oven temperatures below around 300°C, this rate of cooling is reduced even further. Once at room temperature, the cell is safe for removal from the oven.

Post-test Cell Analysis: Scanning Electron Microscopy

For all fuel cell degradation tests, a field-emission scanning electron microscope (SEM) was used to capture cross-sectional images of the fuel cell like the ones in Figure 2.3. These images allow the correlation of microstructural damage within the fuel cell to electric performance characteristics observable through the cell's electron terminals. To prepare a cell for SEM analysis, the cell is first carefully removed from the oven. In most instances, the cell is easily separated from the silver mesh and nickel foam as those two pieces are generally well bonded to the Inconel platen surfaces through the silver paint. In the few instances when the cell is not easily separated, a clean razor blade is used to carefully separate the cell from the silver mesh or nickel foam.

Once the cell is free, it is cast in an SEM specific epoxy in a specially designed mold. Prior to fuel cell degradation control testing (Chapter 7), the mold used, SEM Mold A, was the two piece aluminum mold shown in Figure 2.7. This mold worked well for the first several cell castings. However, following those several mold castings, residual hardened epoxy stuck to the aluminum pieces and created bonding points for new epoxy used in casting cells. This made it difficult to safely remove newly epoxy casted cells without risking damage to the cell. To overcome this issue, rather than machining a new aluminum mold, an aluminum negative mold was machined for casting a silicone based mold made from Momentive RTV 664. This mold, SEM Mold B, is shown in Figure 2.8.

Both epoxy molds feature ridge lines for creating stress-concentrating break-planes along the major axes of the fuel cell. These break-planes allow precise cross-sectioning of the fuel cell without the need for a diamond saw to cut through the ceramic material. The silicone based mold, SEM Mold B, however holds several advantages

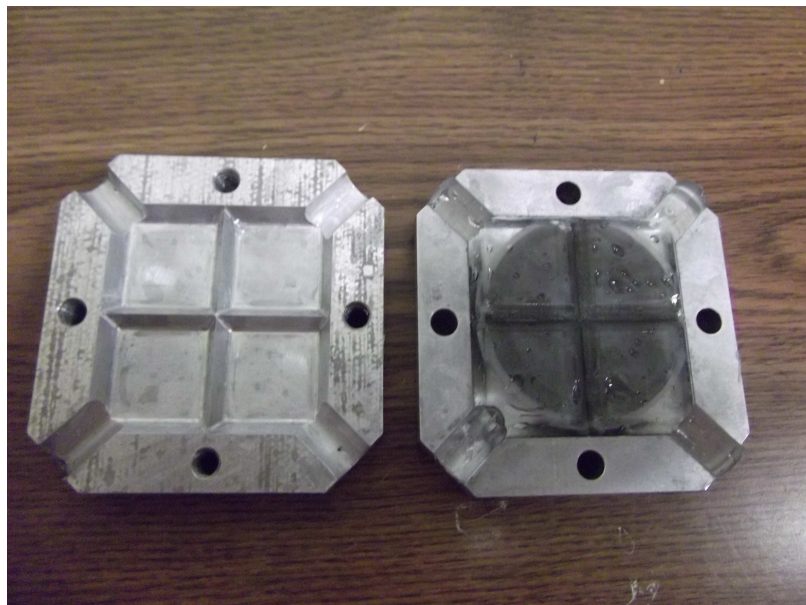


Figure 2.7: Image of the scanning electron microscopy epoxy mold A used to cast a fuel cell in epoxy in preparation for cell cross-sectioning and imaging under the scanning electron microscope.

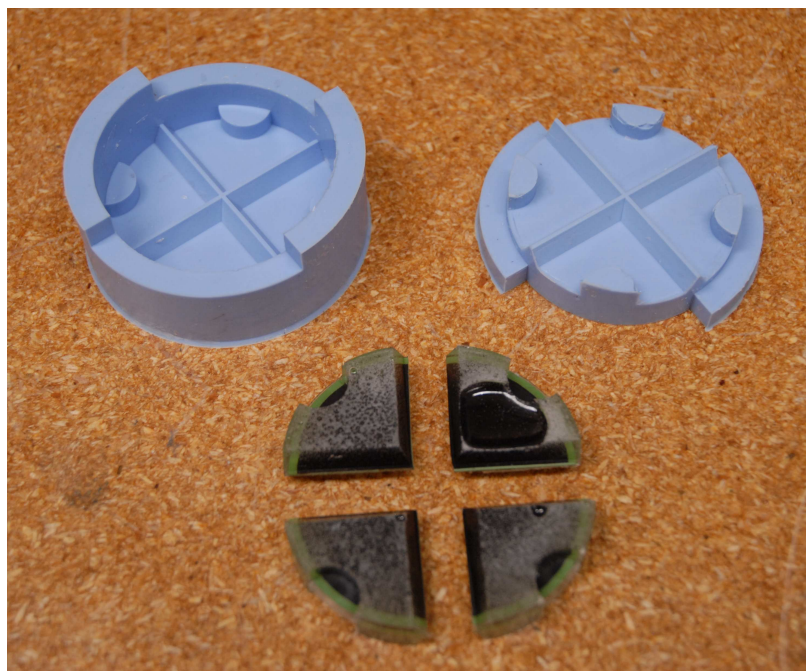


Figure 2.8: Image of the scanning electron microscopy epoxy mold B used to cast a fuel cell in epoxy in preparation for cell cross-sectioning and imaging under the scanning electron microscope.

over the aluminum mold. As mentioned above, newly epoxied cells became difficult to remove from the aluminum molds after several cell moldings. The silicone mold on the other hand is far less conducive to bonding with the epoxy, and due to the elasticity of the material, the mold can be flexed for safely freeing the epoxied cell. Additionally, the silicone mold features tabs for holding the cell in place and horizontal during the curing process.

Once the cell is cured, it is quartered by breaking the cell along its break planes. The quartered cell sample pieces are then labeled according to the diagram shown in Figure 2.9, and the edge of each sample that has the least amount of air bubbles present near the edge surface is chosen for polishing. Table 2.1 outlines this polishing procedure which results in a flat and well defined cross-sectional surface for easy distinguishing of the various layers within the fuel cell through SEM imaging. A copy of the diagram in Figure 2.9 accompanies each of the SEM images in Chapters 7 and 8, and in Appendices E and F, with the red arrow in those diagrams indicating the quartered sample imaged and location of the image along the sample's break plane. For SEM images prior to Chapter 7, no accompanying diagram is given as image locations were not recorded during SEM analysis.

Step	Medium	Grit	Average Grain Size	Time
1	Wet Silica Carbide Paper	240	52 μm	20 min.
2	Wet Silica Carbide Paper	400	30 μm	20 min.
3	Wet Silica Carbide Paper	600	15 μm	20 min.
4	Wet Silica Carbide Paper	800	10 μm	20 min.
5	Wet Silica Carbide Paper	1000	7 μm	20 min.
6	Wet Silica Carbide Paper	1200	5 μm	20 min.
7	Alumina Oxide Slurry	-	5 μm	20 min.
8	Alumina Oxide Slurry	-	0.3 μm	20 min.
9	Alumina Oxide Slurry	-	0.05 μm	20 min.

Table 2.1: SEM Sample Polishing Protocol

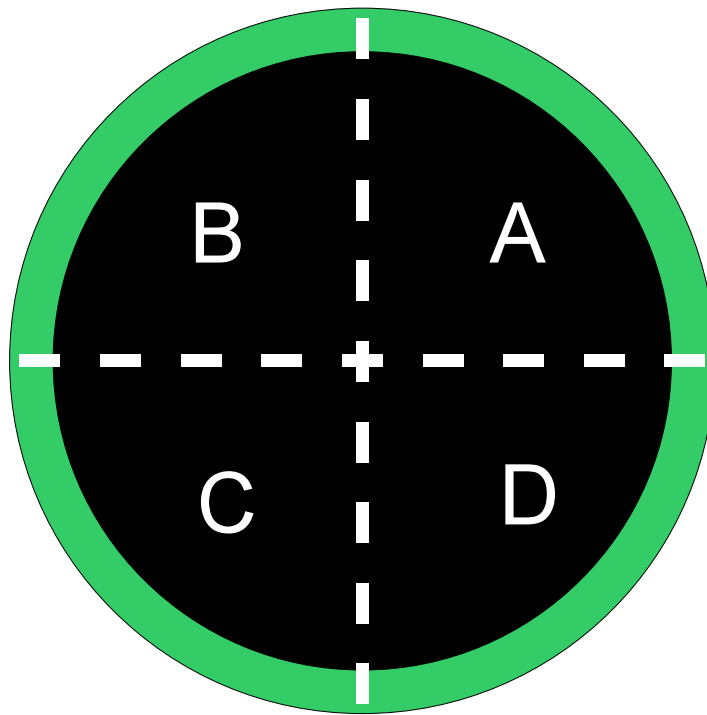


Figure 2.9: Diagram showing the labeling of the quartered fuel cell pieces.

SIMULATION OF SOFC STACK ELECTRIC TERMINALS

The first task of this research project was to build a test system which simulates the electrical terminal output of a power-level fuel cell stack based on the electric terminal performance of a prototype, single cell or small-scale stack. That is, the test system measures the voltage of the reference device and amplifies it to a level that would be generated by the full scale stack consisting of multiple series-connected cells. These voltage scaled electric terminals can be connected to a realistic load for studying stack / load interactions.

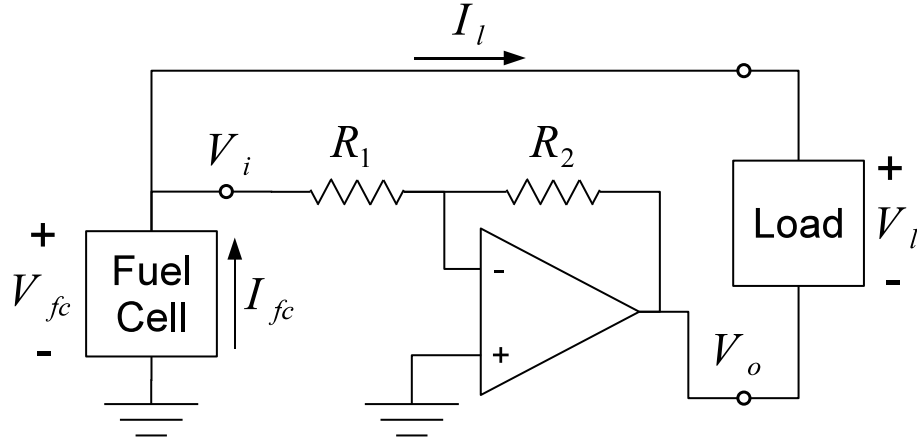
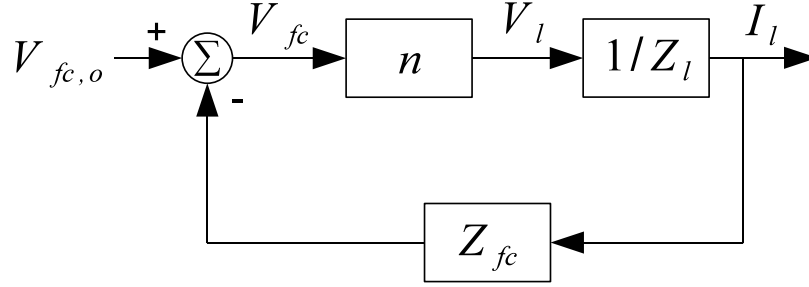


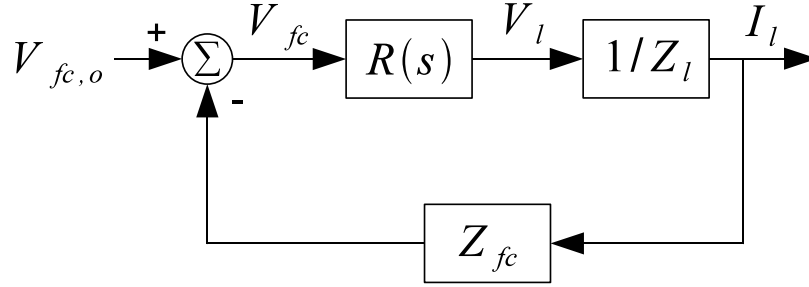
Figure 3.1: A simplified schematic for the reference based stack simulator.

Reference Simulator Topology and Operation

Figure 3.1 shows a simplified schematic of the proposed cell-reference stack simulator. The voltage on the reference fuel cell is amplified by an operational amplifier, represented in Figure 3.1 in a simplified fashion, so that the simulated stack voltage applied to a load is an amplified copy of the cell reference voltage. Furthermore, since the amplifier input has a high impedance, the reference fuel cell current is essentially



(a) n-cell fuel cell stack



(b) simulated fuel cell stack

Figure 3.2: Block diagrams showing the dynamic operation of a fuel cell stack made of n identical cells (a) and that of the simulated fuel cell stack (b).

identical to the current drawn by the load, i.e.,

$$I_l = I_{fc}. \quad (3.1)$$

If the operational amplifier works well, this circuit ensures that there is a scaling relationship between the reference fuel cell voltage and the simulated stack voltage, while the current in the reference fuel cell and the output is identical.

The extent to which the circuit in Figure 3.1 reveals the interactions that would occur in a stack of n series connected cells and a load can be understood by comparing the block diagrams of Figure 3.2. These block diagrams show the transfer function $\frac{I_l}{V_{fc,o}}$ for an n -cell stack (Figure 3.2a) and for the simulated stack produced by the reference simulator (Figure 3.2b). Here, the load is modeled as a complex impedance

Z_l , and the fuel cell is modeled by its Thevenin equivalent,

$$V_{fc} = V_{fc,o} - I_l Z_{fc}, \quad (3.2)$$

where $V_{fc,o}$ is the equivalent open circuit voltage of a cell producing voltage V_{fc} at current I_l with a localized complex impedance of Z_{fc} . From these diagrams, it is clear that the salient change in dynamics and gain from the n -cell stack to the simulated stack lies in the simulator's V_{fc} to V_l amplification, represented by the $R(s)$ block. The gain and dynamic contribution of $R(s)$ is found by analyzing the relationship between the fuel cell voltage V_{fc} , the simulated stack voltage V_l , and the load current I_l .

If the op-amp open-loop gain is $A(s)$ and the op-amp's input and output voltages with respect to ground are V_i and V_o , respectively and as shown in Figure 3.1, the following equations apply,

$$V_l = V_{fc} - V_o, \quad (3.3)$$

$$V_o = -A(s) \left[\frac{R_2}{R_1 + R_2} V_i + \frac{R_1}{R_1 + R_2} V_o \right], \quad (3.4)$$

$$V_i = V_{fc}. \quad (3.5)$$

Eliminating V_i and V_o leads to the transfer function

$$R(s) = \frac{V_l}{V_{fc}} = \frac{1 + A(s)}{1 + A(s) \frac{R_1}{R_1 + R_2}}. \quad (3.6)$$

If it is further assumed that the op-amp is dominant-pole compensated, so that $A(s)$ is well approximated by

$$A(s) = \frac{A_0}{\tau s + 1}, \quad (3.7)$$

where A_0 and τ are the op-amp's open loop gain and dominant pole time constant, then the dynamic contribution of the reference simulator is

$$R(s) = \left[\frac{A_0 + 1}{A_0 \frac{R_1}{R_1 + R_2} + 1} \right] \frac{\tau_1 s + 1}{\tau_2 s + 1}. \quad (3.8)$$

The first term in this expression reveals the DC accuracy of the simulator, which, in the limit of high A_0 has a gain of $\frac{R_1 + R_2}{R_1}$. This resistor ratio should be selected to match the number of cells n desired in the simulated stack. The dynamic effect of the simulator is in the second term above. In particular,

$$\tau_1 = \frac{\tau}{A_0} \quad (3.9)$$

and

$$\tau_2 = n\tau_1. \quad (3.10)$$

Thus, the simulator introduces a *lag*, where the zero location is a function of the performance of the amplifier selected, and the pole location depends on the amplifier and number of cells in the simulated stack. In general, under the assumption that an accumulation of phase jeopardizes the stability of the actual connection of stack to load, and without further compensation, the reference simulated stack will tend to be *less stable* than the actual connection of stack to load. This phenomenon gets worse as the number of cells to be simulated increases, but can potentially be corrected by appropriate compensation. This analysis neglects the effect of loading on the op-amp output stage, which may introduce further dynamics, and also amplifier nonlinearities. These also tend to reduce the stability of the reference simulated system compared to the real system.

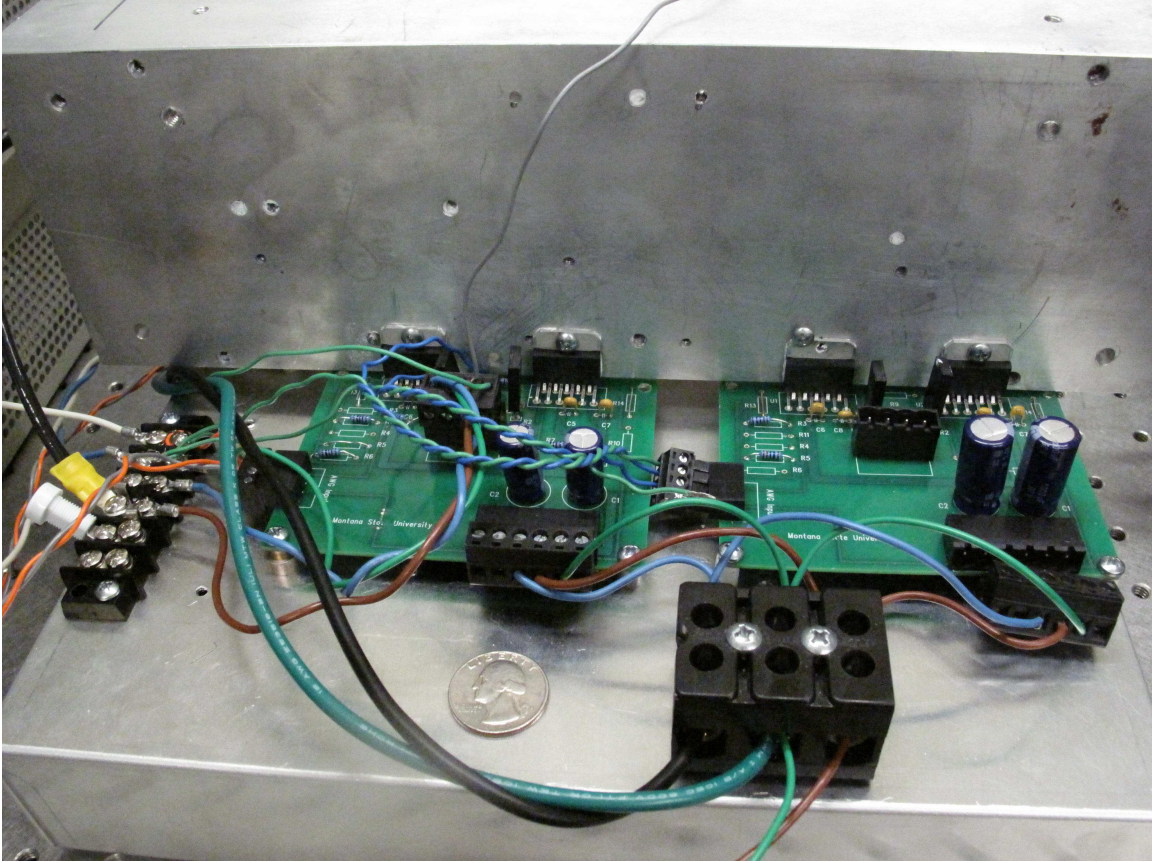


Figure 3.3: The actual amplifier used consisted of four OPA549 power-op amps operating in a master-slave configuration. The simulator effectively amplifies the voltage of a prototype fuel cell device and applies it to a load that is series connected to the prototype cell.

Since the combined dynamics of the fuel cell and load are unknown, it is difficult to ensure stability or other performance measures. However, the reference simulated system can be measured during an experiment. If the simulator performs accurately, and measurements show that it does not introduce significant errors under test conditions, then the interactions observed are those of a scaled stack.

The reference simulator circuit (Figure 3.1) was implemented using four Burr Brown OPA-549 power op amps in a master-slave configuration. Resistors R_2 and R_1 were chosen to be 19 k Ω and 1 k Ω , respectively, so that the DC gain of the system

corresponded to a 20 cell stack. A Xantrex XHR series power supply was used to supply the positive rail, while an HP6012B power supply was used on the negative rail. To reduce power dissipation in the op-amp, the negative rail was made compliant.

Experiment Procedure

To conduct experiments on the reference based SOFC stack simulator, the cell was first mounted on the Inconel 600 platens inside the clam-shell ovens, and brought to test conditions as described in Chapter 2. Multiple tests were performed using the fuel cell stack reference simulator. These included slow current ramp tests for comparing polarization curves of the cell and simulated stack, electrochemical impedance spectroscopy (EIS) tests, and using realistic power electronic loads such as a DC/DC converter powering an automotive bulb and a brushless DC (BLDC) motor turning a propeller. The current ramp tests and the EIS tests both used an Agilent N3305A programmable load in controlled current mode to vary the load current. The DC/DC converter used was a SynQor NQ60 set to provide a 12 V rail for lighting a Sylvania H6024 incandescent automotive bulb. The BLDC motor tests featured an AXI 5130 motor with an APC 14 x 10 propeller as the mechanical load. The motor controller used was a JETI Spin44 Opto controller. This BLDC motor system is similar to those which might be used in small fuel cell powered unmanned aerial vehicles (UAVs), e.g., [7, 81].

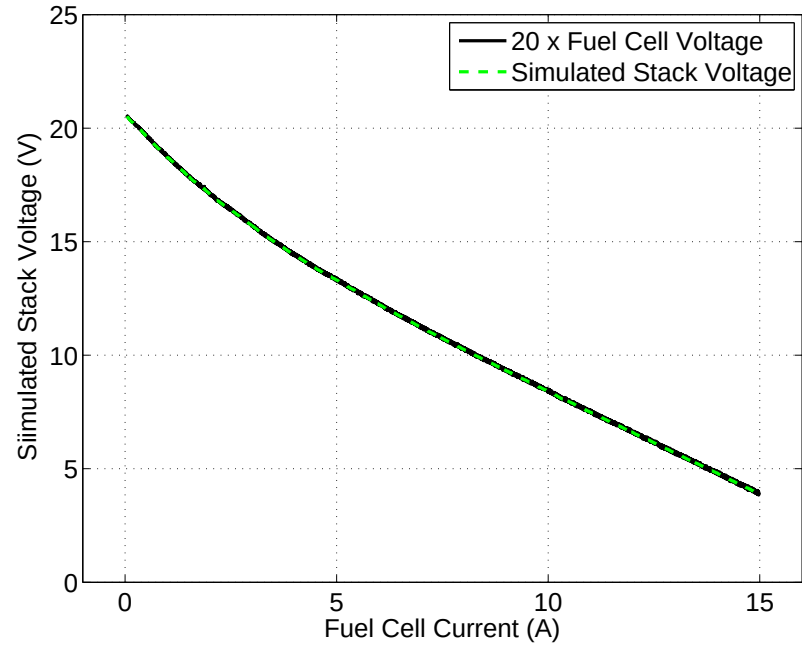
For each different load, the fuel cell remained connected to the reference simulator. The load was then connected, and the reference simulator power supplies were turned on. Measurements of the fuel cell voltage V_{fc} , simulated stack voltage V_l , and current I_l , were collected using a National Instruments 9206 16-bit 250 kHz data acquisition

module. During the BLDC motor test, the propeller speed was measured using a Check-line DT-205LR optical tachometer.

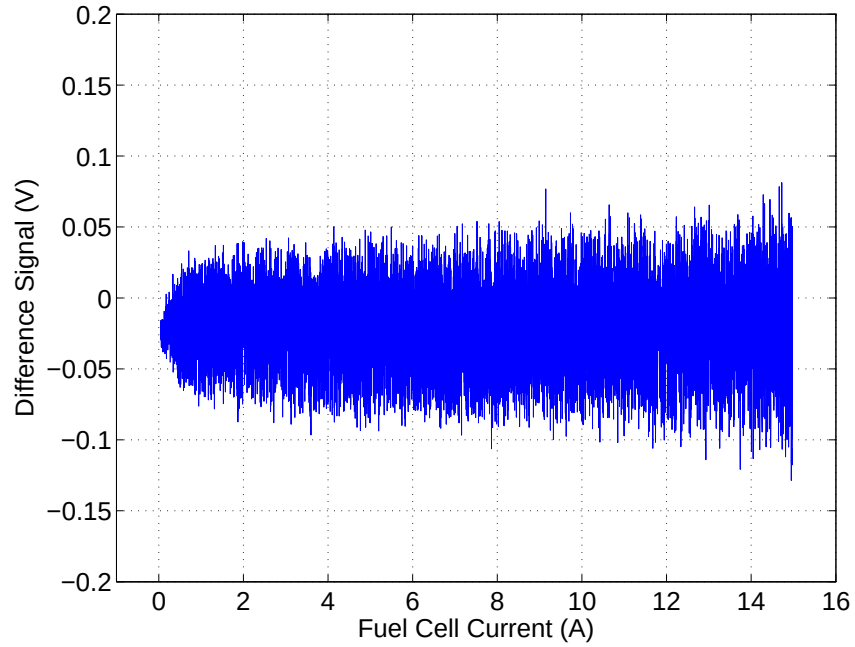
Reference Simulator Performance

Figure 3.4 shows a comparison of the measured polarization curves of the single InDEC SOFC cell and the simulated fuel cell stack. In Figure 3.4a, the measured fuel cell voltage is multiplied by the set n value of 20 for direct comparison to performance of the simulated stack. These stack output voltages are sufficient to test realistic and efficient power electronic topologies and their associate controls. In Figure 3.4b, the difference signal between the measured simulated stack polarization curve and that of the ideally scaled cell is given and shows a consistently small bias of only -20 mV between curves across the measured polarization relationships. For this test, the current drawn by the electronic load was increased from 0 to 15 A at a rate of $0.15 \text{ A}\cdot\text{s}^{-1}$, and voltage and current data were collected with a sample rate of 100 Hz.

As examples of the reference simulator's performance under dynamic loading, Figure 3.5 and Figure 3.6 compare the electric terminal performance of the simulated stack to the single reference fuel cell when under load by a brushless DC (BLDC) motor and propeller, and DC/DC converter powering an incandescent automotive bulb, respectively. In Figure 3.5, the load is an AXI 5330 brushless DC motor and APC 14 x 10 propeller load turning at a rate of $348 \text{ rad}\cdot\text{s}^{-1}$ (3320 revolutions per minute). The JETI Spin 44-opto motor controller used to commutate the motor windings also allows control of the motor speed by pulse-width modulating (PWM) the voltage applied to the motor terminals at a frequency of 8 kHz. As seen on the lower plot, this operation superimposes a small magnitude ripple at the PWM frequency on top the DC current drawn from the stack. The larger fluctuations in



(a) Polarization Curves



(b) Error Between Curves

Figure 3.4: Measured polarization performance of the reference-based stack simulator. (a) shows the measured polarization curve of the simulated stack compared to the measured polarization curve of the reference fuel cell multiplied by the ideal stack height, while (b) shows the difference signal between the two curves.

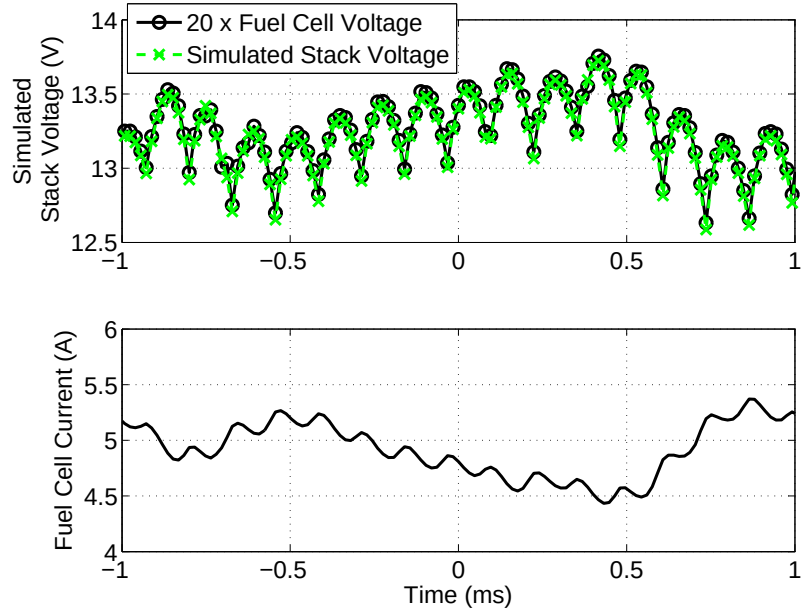


Figure 3.5: Current ripple and associated voltage transients of the reference fuel cell and simulated stack under load from an AXI 5330 BLDC motor with a JETI Spin 44-opto motor controller and APC 14 x 10 propeller.

current are induced by the powerful magnets rotating with the spinning rotor. The top plot shows the measured cell voltage and simulated stack voltage response to the current profile. Here, the fuel cell voltage data points are scaled by the set n value of 20. Data was collected at a sample rate of 62.5 kHz.

The test results of Figure 3.6 shows an example of a load and stack connection that produces a surprising interaction. In this case, the reference simulator load consists of a SynQor DC/DC converter, which is in turn connected to an incandescent light bulb. The plots show cell and simulator voltage and current to the power electronics for a bulb turn on transient. Ordinarily, an incandescent bulb connected to a voltage source draws a current spike as the filament heats up to steady state. In this case, the reference simulator reveals an unstable limit-cycle type nonlinear interaction. In particular, the in-rush current to the bulb filament causes the voltage on the cell to collapse and the power electronics to under-voltage at roughly nine volts. This

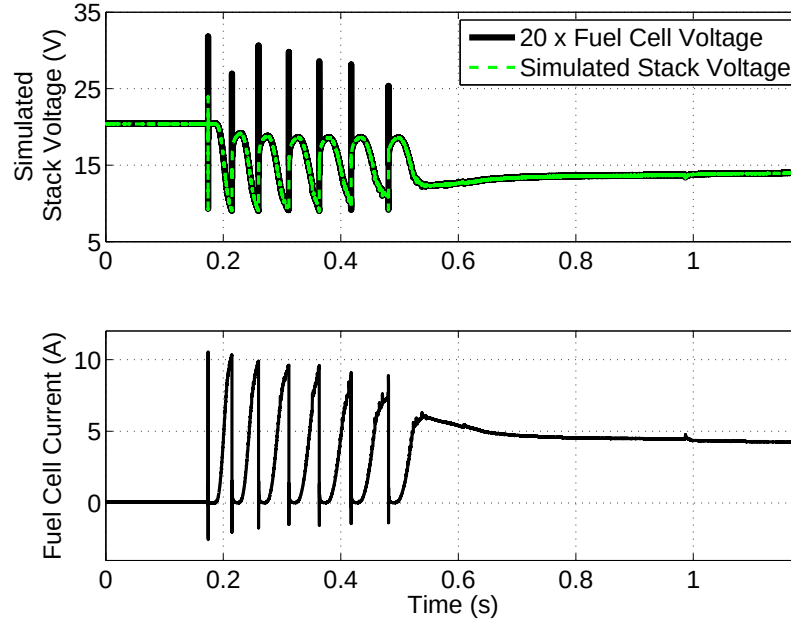


Figure 3.6: Turn on transient of the reference fuel cell and simulated stack under load of a SynCor DC/DC converter and automotive light bulb.

process continues for several cycles until the filament is sufficiently hot, after which the bulb functions normally.

Finally, Figure 3.7 shows a complex-plane plot comparing the impedance spectroscopy measurements of the reference fuel cell and that of the simulated stack. Here, the magnitude of the impedance measurements are multiplied by the gain factor, $n = 20$, for easy comparison with the simulated stack impedance. These results are suggestive of the reference simulator's ability to facilitate experiments to help link stack electrical output measurements and the inner operating mechanics of the stack. For this test, a logarithmically swept 600 mA peak-peak sinusoid ranging in frequency from 100 mHz to 1kHz over a period of 175 seconds was imposed on a DC current of 7 A. The resulting measured current and voltage waveforms were analyzed in MATLAB with their interrelated amplitude and phase determining the small signal impedance of the cell and simulated stack as functions of frequency. More information

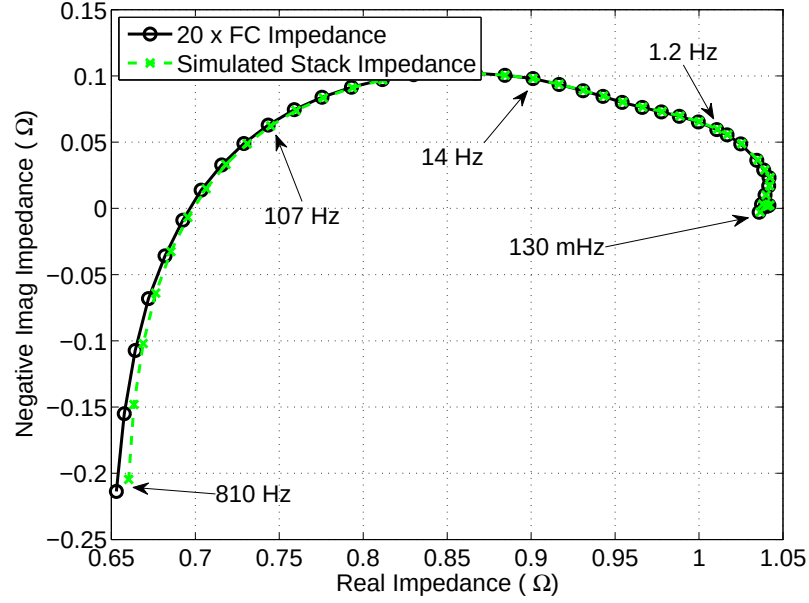


Figure 3.7: Electrochemical Impedance Spectroscopy (EIS) performed on the reference fuel cell stack simulator.

on the method used to extract the impedance profiles of Figure 3.7 from the measured time-domain current and voltage waveform signals is detailed in Chapter 4.

Discussion

Figures 3.4-3.7 reveal very good performance of the reference simulator in the steady-state and under dynamic loading. The polarization curves of Figure 3.4a and difference signal between these curves of Figure 3.4b shows the simulator's near-identical matching of the reference fuel cell's steady-state performance characteristics across a broad range of load currents. A maximum load current of 15 A was set as the upper bound because beyond this value the op amps of the reference simulator went into thermal shutdown due to ineffective heat dissipation by the heat sink. This performance could be improved through an active cooling system, e.g. fan mounted or water cooled heat sink, so that full quadrant I operation is achieved. Nevertheless,

the current system allows operation well beyond the simulated stack maximum power point (around 85 W at 9.6 A).

Figures 3.5 and 3.6 show two examples of the reference simulator’s utility in studying electrical interactions between a fuel cell stack and real dynamic loads. These types of tests are important as previous studies of various fuel cell technologies suggest that load / stack interactions are potential sources of degradation in fuel cell stacks [16, 17, 47]. In the case of the BLDC motor and propeller load (Figure 3.5), the fluctuations in the current due to the controller’s PWM switching and induction from the motor’s rotating magnets result in corresponding fluctuations in the generated voltages of the prototype cell and simulated stack. Because the current fluctuations have a relatively small magnitude and consist of high frequency components, the relationship between the current / voltage interaction is dominated by the ionic resistivity of the cell’s electrolyte, and the electronic resistivity and inductance of the Inconel platens and connecting cables.

Conversely, in the case of the turn on transient of the incandescent bulb powered through the DC/DC converter (Figure 3.6), the magnitude of the current draw and subsequent voltage response is much larger and at a much slower frequency. This leads to a more pronounced, highly non-linear fluctuation in voltage which is affected by the kinetics of the electrochemical reactions and diffusion rate limitations of the chemical species as well as the ohmic resistances of the cell and platens.

The effects of such interactions can be diagnosed in situ through EIS analyses like that in Figure 3.7. As degradation occurs, the characteristic shape of the complex-plane impedance plot will change as the cell’s reaction mechanisms and kinetics are directly related to its impedance dynamics. The result indicates the ability of the reference simulator system to match the scaled impedance of the reference fuel cell, and thus the simulator’s effectiveness in testing in situ impedance methods and an-

alyzers, e.g. [48, 49]. Several frequency markers are given to indicate the progression of impedance as a function of frequency. The quality of matching between the two sets of impedance measurements is an indication of the “flatness” of the simulators frequency response across the frequencies of excitation.

Chapter Summary

This chapter presents a fuel cell stack simulator that uses a single cell as a reference to provide electrical terminals equivalent to a stack of similar cells. The utility of this system is demonstrated by comparing the electric terminal performance of the simulated stack to that of the reference fuel cell. The polarization curve of Figure 3.4a demonstrates the wide-ranging quadrant I, power delivery capabilities of the simulator system. The experiments involving the connection of power electronics to the reference simulator (Figures 3.5 and 3.6) provide results that could not be obtained previously without building a stack. Moreover, these preliminary results demonstrate the possibility of complex nonlinear interactions between fuel cells and their loads. Additionally, the impedance spectroscopy experiments give results demonstrating the reference simulator’s usefulness in developing stack diagnostic tests and degradation mitigation control schemes.

The reference simulator concept can be extended in a number of useful ways. For example, a single degraded cell can be added in series with the load to study the impedance signature of single-cell degradation in stacks. Or, additional cells can be added to the reference simulated stack to represent thermal end-effects. There is also no need to restrict the reference fuel cell to be a single cell as a short stack could also be used. Importantly, the reference simulator allows a fuel cell system development to be a *parallel* as opposed to *sequential* process. In particular, the complexities of a

stack load interactions, as seen in the DC/DC converter result, can be studied and mitigated through power electronic control before or during the development of a stack system. Thus, the simulator system can be used to study system integration and control system interaction. Furthermore, the simulator's use can be extended to a range of direct energy conversion technologies that have inconveniently small potentials, such as biological fuel cells, photo and thermo-voltaics, and novel battery technologies.

TIME-DOMAIN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The development of in situ fuel cell monitoring techniques and associated monitoring devices is required for effective prognostic or diagnostic analysis of deployed fuel cell stacks. Due to the direct interaction of a fuel cell’s electric load and its internal electrochemical processes, the monitoring of a fuel cell device’s electric terminal response to a dynamic load has been proposed as a means for ascertaining information about the internal operation of the cell or stack. This type of monitoring is attractive due to its low complexity and cost, and several monitoring devices and schemes have been proposed [47–49, 82].

Electrochemical Impedance Spectroscopy (EIS) is the most common technique for gaining electrochemical performance information through electric terminal monitoring. In EIS, a device is perturbed from steady-state operation by a potentiostatic or galvanostatic excitation signal over a desired frequency range, as shown in Figure 4.1. This perturbation must be limited in magnitude due to the non-linear large signal polarization relationship of fuel cell devices. The resulting current $i_{eis}(t)$ and voltage $v_{eis}(t)$ response is then analyzed with the two signals’ interrelated magnitude, phase and frequency content determining the small-signal impedance of the device as a function of frequency. The characteristics of the impedance profile are directly influenced by the electrochemical processes internal to the device. Thus, EIS allows “bulk” monitoring of these processes with the results indicative of the device’s dynamic performance and overall health.

For this research project, a new method for EIS analysis in the time-domain using ordinarily least squares (OLS) is developed. The major advantage of OLS over other analysis methods is that OLS provides parameter estimates even when the data signals contain a non-integer number of signal periods or just a fraction of a period.

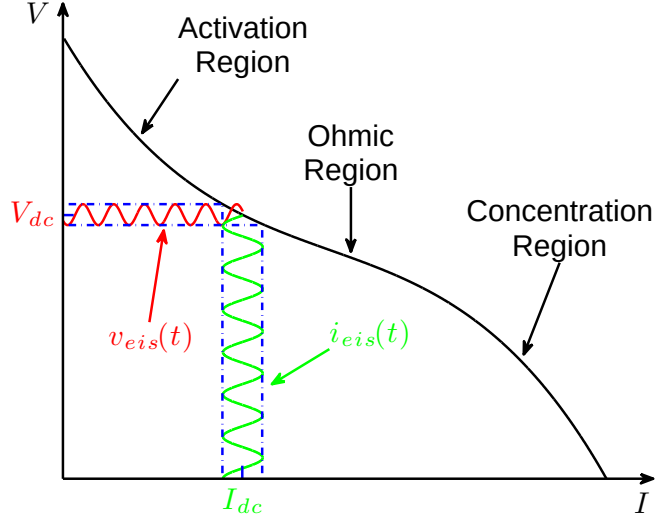


Figure 4.1: Conceptual polarization curve of a typical fuel cell device showing the non-linear characteristics of a cell's current-voltage relationship. Under small-signal perturbation, shown by the $v_{eis}(t)$ and $i_{eis}(t)$ signals, the cell can be approximated as linear.

This allows for a reduction in required measurement time. To complement this, the perturbation signal used for this method is a single sinusoidal current perturbation with the frequency logarithmically swept in time. This sort of perturbation allows a large-amplitude, frequency-continuous, short-time excitation signal that spans a broad range of frequencies.

Ordinary Least-Squares Analysis

For galvanostatic EIS using an ac-current excitation that is non-static in frequency, the current drawn through an electrochemical device can be described as,

$$I_{fc}(t) = I_{dc} + i_{eis}(t). \quad (4.1)$$

Here, I_{dc} represents the steady-state DC-current, while the sinusoidal term represents the ac-current excitation about I_{dc} . This perturbation elicits a response in the device's

generated voltage with similar terms such that,

$$V_{fc}(t) = V_{dc} + v_{eis}(t). \quad (4.2)$$

For the case where the perturbation current contains only a single instantaneous excitation frequency, $\omega(t)$, $i_{eis}(t)$ and $v_{eis}(t)$ take the form,

$$i_{eis}(t) = A_i(t) \cos(\phi(t) + \theta_i(t)), \quad (4.3)$$

and

$$v_{eis}(t) = A_v(t) \cos(\phi(t) + \theta_v(t)), \quad (4.4)$$

respectively.

In these equations, $\phi(t)$ is an absolute phase term and is the time-integral of the instantaneous excitation frequency [83], i.e.

$$\phi(t) = \int_0^t \omega(\tau) d\tau. \quad (4.5)$$

The amplitude terms $A_i(t)$, $A_v(t)$ and relative phase terms $\theta_i(t)$, $\theta_v(t)$ are described as time-varying. $A_i(t)$ and $\theta_i(t)$ may vary due to a non-ideal signal-to-current frequency response in the galvanostatic source controller (controlled current source), which sets the DC-operating point and ac-current excitation of the cell. $A_v(t)$ and $\theta_v(t)$ will vary with $\omega(t)$ if the device tested is not purely resistive. These variations are logarithmically frequency dependent. Therefore, a natural choice for excitation is a logarithmically swept sinusoid where the time allotted for a decade of frequency shift is constant through the whole sweep. Then, the time-relationship for instantaneous

frequency is given by,

$$\omega(t) = \omega_0 \beta^t. \quad (4.6)$$

In (4.6), ω_0 is the initial frequency of the sweep and β is a rate of frequency growth ($\beta > 1$) or decay ($\beta < 1$), and is related to initial frequency ω_0 , ending frequency ω_L , and time-length of the sweep L by,

$$\beta = (\omega_L/\omega_0)^{(1/L)}. \quad (4.7)$$

This β term directly impacts the rate at which the current and voltage magnitudes, $A_i(t)$ and $A_v(t)$, and relative phase terms, $\theta_i(t)$ and $\theta_v(t)$, change. If β is set such that $|\beta - 1|$ is sufficiently small, then for short segments of the swept excitation, the amount of frequency shift will be small, and $I_{fc}(t)$ and $V_{fc}(t)$ can be well approximated with constant amplitude and phase terms, i.e.

$$I_x(t_x) = I_{dc,x} + A_{i,x} \cos(\phi(t_x) + \theta_{i,x}), \quad (4.8)$$

and

$$V_x(t_x) = V_{dc,x} + A_{v,x} \cos(\phi(t_x) + \theta_{v,x}), \quad (4.9)$$

respectively.

The x index corresponds to a particular segment of the total sweep, which for simplicity and without a loss of generality to the method and results, is split into l sections of equal length, m , where lm is the sample-length of the full sweep. t_x is the portion of the time vector t corresponding to the x th segment.

The ac-excitation portions of (4.8) and (4.9) can be mapped to a phasor-domain rotating with $\phi(t_x)$ such that $\vec{I}_x = A_{i,x} e^{j\theta_{i,x}}$ and $\vec{V}_x = A_{v,x} e^{j\theta_{v,x}}$. The real and

imaginary components of these phasor representations are abstracted by applying a trigonometric angle sum identity to (4.8) and (4.9), so that $I_x(t_x)$ and $V_x(t_x)$ become

$$I_x(t_x) = I_{dc,x} + Re\{\vec{I}_x\} \cos(\phi(t_x)) - Im\{\vec{I}_x\} \sin(\phi(t_x)), \quad (4.10)$$

and

$$V_x(t_x) = V_{dc,x} + Re\{\vec{V}_x\} \cos(\phi(t_x)) - Im\{\vec{V}_x\} \sin(\phi(t_x)). \quad (4.11)$$

Because $\phi(t)$ is required knowledge for controlling $I(t)$, the $\cos(\phi(t_x))$ and $\sin(\phi(t_x))$ terms are known for the entire sweep. Thus, the parameters $I_{dc,x}$, $Re\{\vec{I}_x\}$, $Im\{\vec{I}_x\}$, $V_{dc,x}$, $Re\{\vec{V}_x\}$, and $Im\{\vec{V}_x\}$ can be found for each segment of the swept sinusoids by fitting the swept sinusoid models of (4.10) and (4.11) using OLS to collected voltage and current data. That is, for (4.10) and (4.11) rewritten in matrix form,

$$I_x(t_x) = \mathbf{A}_x \mathbf{p}_{I,x}, \quad (4.12)$$

and

$$V_x(t_x) = \mathbf{A}_x \mathbf{p}_{V,x}, \quad (4.13)$$

$\mathbf{p}_{I,x}$ and $\mathbf{p}_{V,x}$ are set to minimize the Euclidean-norms $\|\mathbf{A}_x \mathbf{p}_{I,x} - I_x(t_x)\|_2$ and $\|\mathbf{A}_x \mathbf{p}_{V,x} - V_x(t_x)\|_2$, respectively. Here, the $m \times 1$ column vectors $I_x(t_x)$ and $V_x(t_x)$ are the x th segments of the measured current and voltage data. $\mathbf{A}_x$ is the $m \times 3$ matrix $[\mathbf{1} \quad \cos(\phi(t_x)) \quad -\sin(\phi(t_x))]$ where $\mathbf{1}$ represents an $m \times 1$ column vector with every entry being 1, while $\mathbf{p}_{I,x}$ and $\mathbf{p}_{V,x}$ are the 3×1 parameter column vectors, $[I_{dc,x} \quad Re\{\vec{I}_x\} \quad Im\{\vec{I}_x\}]^T$ and $[V_{dc,x} \quad Re\{\vec{V}_x\} \quad Im\{\vec{V}_x\}]^T$, respectively.

From the parameter vectors, $\mathbf{p}_{I,x}$ and $\mathbf{p}_{V,x}$, the phasor representations of (4.8) and (4.9) are known, and the time averaged impedance for the swept segment x is given

by,

$$Z_x = \vec{V}_x / \vec{I}_x. \quad (4.14)$$

Similarly, with instantaneous frequency $\omega(t)$ known at each data collection instance, the time averaged frequency for the swept segment x can be calculated as

$$\omega_x = \frac{\sum_{t=t_{x,1}}^{t_{x,m}} \omega(t)}{t_{x,m} - t_{x,1}}, \quad (4.15)$$

where $t_{x,1}$ and $t_{x,m}$ are the time vector value extremes for time segment t_x .

Thus, for each segment of the sweep, an approximation of the device's small signal impedance as a function of frequency, is given by

$$Z(\omega_x) = Z_x. \quad (4.16)$$

This process can be repeated for all l segments of the measured current and voltage waveforms to obtain an l -number discrete representation of the cell's small signal impedance for the frequency range of excitation.

Measurement Uncertainty

Noise in the measured voltage and current signals results in variability in the impedance estimates. Thus, a large signal-to-noise ratio (SNR) is desired to ensure high precision estimates. However, electrochemical devices often exhibit a non-linear relationship between current and voltage. This violates the linearity assumption of EIS and results in harmonic distortion in the electrochemical device's voltage response to large ac-current excitation. Therefore, there is a tradeoff in increasing excitation

amplitude to increase SNR as resulting distortions in the voltage waveform can introduce a bias in impedance estimates, thus decreasing their accuracy.

Variance in Parameter Estimations

For excitation signals with β [see (4.7)] close to 1, any bias in the OLS impedance analysis technique is minimal, and the Cramér-Rao Bound (CRB) provides a reasonable estimate of the lower bound on the variance in the parameter estimates. The CRB is defined as the inverse of the Fisher Information Matrix, i.e. $\mathbf{CRB}(\mathbf{p}) = \mathbf{J}^{-1}(\mathbf{p})$. If any noise corrupting the current and voltage measurements of (4.1) and (4.2) is well modeled as additive white Gaussian noise with variances σ_i^2 and σ_v^2 , respectively, then the Fisher Information Matrices for the parameter estimates of equations (4.10) and (4.11) are given by $\mathbf{J}(\mathbf{p}_{I,x}) = \frac{1}{\sigma_i^2} \mathbf{A}_x^T \mathbf{A}_x$, and $\mathbf{J}(\mathbf{p}_{V,x}) = \frac{1}{\sigma_v^2} \mathbf{A}_x^T \mathbf{A}_x$ [84, 85]. The resulting CRBs then are

$$\mathbf{CRB}(\mathbf{p}_{I,x}) = \sigma_i^2 (\mathbf{A}_x^T \mathbf{A}_x)^{-1}, \quad (4.17)$$

and

$$\mathbf{CRB}(\mathbf{p}_{V,x}) = \sigma_v^2 (\mathbf{A}_x^T \mathbf{A}_x)^{-1}. \quad (4.18)$$

The diagonal elements of these matrices reveal the lower bound on the variances of the individual parameters of $\mathbf{p}_{I,x}$ and $\mathbf{p}_{V,x}$ while the off-diagonal elements give those for the parameter covariances. For added insight, consider the 3×3 matrix $\mathbf{A}_x^T \mathbf{A}_x$ of (4.17) and (4.18). This matrix has the form,

$$\mathbf{A}_x^T \mathbf{A}_x = \sum_{t_x} \begin{bmatrix} 1 & \cos(\phi(t_x)) & -\sin(\phi(t_x)) \\ \cos(\phi(t_x)) & \cos^2(\phi(t_x)) & \cos(\phi(t_x)) \sin(\phi(t_x)) \\ -\sin(\phi(t_x)) & \cos(\phi(t_x)) \sin(\phi(t_x)) & \sin^2(\phi(t_x)) \end{bmatrix} \quad (4.19)$$

The terms along the principal diagonal are summations of terms containing an offset bias, while those off diagonal are summations of terms oscillating about zero. Therefore, assuming a large number of data points m is used for parameter estimation, as the total phase encompassed by $\phi(t_x)$ increases, the diagonal terms become significantly larger than the off diagonal terms. This results in CRBs with negligible off diagonal covariance terms and relevant diagonal terms given by,

$$\text{Var}(\text{Re}\{\vec{I}_x\}) \geq [\mathbf{CRB}(\mathbf{p}_{I,x})]_{(2,2)} \approx \frac{2\sigma_i^2}{m}, \quad (4.20)$$

$$\text{Var}(\text{Im}\{\vec{I}_x\}) \geq [\mathbf{CRB}(\mathbf{p}_{I,x})]_{(3,3)} \approx \frac{2\sigma_i^2}{m}, \quad (4.21)$$

$$\text{Var}(\text{Re}\{\vec{V}_x\}) \geq [\mathbf{CRB}(\mathbf{p}_{V,x})]_{(2,2)} \approx \frac{2\sigma_v^2}{m}, \quad (4.22)$$

$$\text{Var}(\text{Im}\{\vec{V}_x\}) \geq [\mathbf{CRB}(\mathbf{p}_{V,x})]_{(3,3)} \approx \frac{2\sigma_v^2}{m}. \quad (4.23)$$

Here, $[\cdot]_{(j,k)}$ indicates the j , k th element of the matrix within the brackets. These CRB terms can be re-parameterized in terms of signal amplitude and phase (4.8) and (4.9) such that,

$$\mathbf{CRB}(\mathbf{q}_{I,x}) = \left[\frac{\partial \mathbf{q}_{I,x}}{\partial \mathbf{p}_{I,x}} \right] \mathbf{CRB}(\mathbf{p}_{I,x}) \left[\frac{\partial \mathbf{q}_{I,x}}{\partial \mathbf{p}_{I,x}} \right]^T, \quad (4.24)$$

and

$$\mathbf{CRB}(\mathbf{q}_{V,x}) = \left[\frac{\partial \mathbf{q}_{V,x}}{\partial \mathbf{p}_{V,x}} \right] \mathbf{CRB}(\mathbf{p}_{V,x}) \left[\frac{\partial \mathbf{q}_{V,x}}{\partial \mathbf{p}_{V,x}} \right]^T, \quad (4.25)$$

where $\mathbf{q}_{I,x}$ and $\mathbf{q}_{V,x}$ are the 3 x 1 parameter column vectors, $[I_{dc,x} \ A_{i,x} \ \theta_{i,x}]^T$ and $[V_{dc,x} \ A_{v,x} \ \theta_{v,x}]^T$, respectively. Following this transformation, lower bounds on

the variance in signal amplitude and phase are given by [85],

$$\text{Var}(A_{i,x}) \geq [\mathbf{CRB}(\mathbf{q}_{I,x})]_{(2,2)} \approx \frac{2\sigma_i^2}{m}, \quad (4.26)$$

$$\text{Var}(\theta_{i,x}) \geq [\mathbf{CRB}(\mathbf{q}_{I,x})]_{(3,3)} \approx \frac{2\sigma_i^2}{mA_{i,x}^2}, \quad (4.27)$$

$$\text{Var}(A_{v,x}) \geq [\mathbf{CRB}(\mathbf{q}_{V,x})]_{(2,2)} \approx \frac{2\sigma_v^2}{m} \quad (4.28)$$

$$\text{Var}(\theta_{v,x}) \geq [\mathbf{CRB}(\mathbf{q}_{V,x})]_{(3,3)} \approx \frac{2\sigma_v^2}{mA_{v,x}^2}. \quad (4.29)$$

Equations (4.26) - (4.29) reveal a relationship between signal parameter estimates and noise where the variance in signal amplitude is inversely proportional to only the number of data points used in the estimation, while variance in the signal phase is inversely proportional to the SNR (defined as $A^2/2\sigma^2$) while also inversely proportional to the number of data points. Finally, these parameter variances propagate through the impedance calculation of (4.14), such that the variances in impedance magnitude and phase estimates are given by,

$$\text{Var}(|Z_x|) \geq \frac{A_{v,x}^2}{mA_{i,x}^2} \left(\frac{1}{\text{SNR}_{v,x}} + \frac{1}{\text{SNR}_{i,x}} \right), \quad (4.30)$$

and

$$\text{Var}(\theta_{z,x}) \geq \frac{1}{m} \left(\frac{1}{\text{SNR}_{v,x}} + \frac{1}{\text{SNR}_{i,x}} \right). \quad (4.31)$$

Here, $\text{SNR}_{r,x}$ is the signal-to-noise ratio for segment x of signal r . (4.30) and (4.31) show an inversely proportional relationship between impedance estimate variance and signal SNR. Since the SNR of the two signals combine reciprocally, the smaller of the two ratio's dominates the contribution to estimate imprecision.

Non-Linear Distortion Upper Bound on Signal Amplitude

To ensure the accuracy of impedance estimates, Barsoukov and MacDonald [41] suggest as a general rule that an upper bound on ac-current excitation be based on the magnitude of resulting ac-voltage response. That is, as long as the resulting voltage response has an amplitude smaller than the electrochemical device's operating thermal voltage, $V_T = kT/q$ where k is the Boltzmann constant, T is the absolute temperature, and q is the electrical charge of an electron, a predominantly linear relationship between current and voltage exists, and the harmonic distortion present in $v_{eis}(t)$ can be ignored. For the case of a solid oxide fuel cell (SOFC) operating at 750°C, this restriction requires $|A_v(t)| < 88$ mV.

Typically, fuel cells exhibit strong non-linear current-voltage relationships in their low current and high current operation regions due to electrochemical activation processes and reactant mass transport limits, respectively [4, 86]. Empirically, we have found this definition of an upper bound to be optimistic, particularly in these low and high current operation regions, and as such roughly limit $|A_v(t)| < 30$ mV.

Experimental Procedure

Figure 4.2 shows a conceptual diagram of the experiment and measurement set-up used for demonstrating the EIS analysis methods. The experiment circuit consists of an HP 6012B bench-top power supply connected in series with a solid oxide fuel cell (SOFC) and an Agilent N3305A programmable electronic load. The programmable load serves as the controlled current source used to set the cell's DC operating point. Through the load's external analog controller ports (C_+ and C_-) the ac-current excitation signal, $s_{eis}(t)$ supplied from an Agilent 33220A Function Generator, imparts the ac-perturbation current, $i_{eis}(t)$ on top of the DC current setting. The power

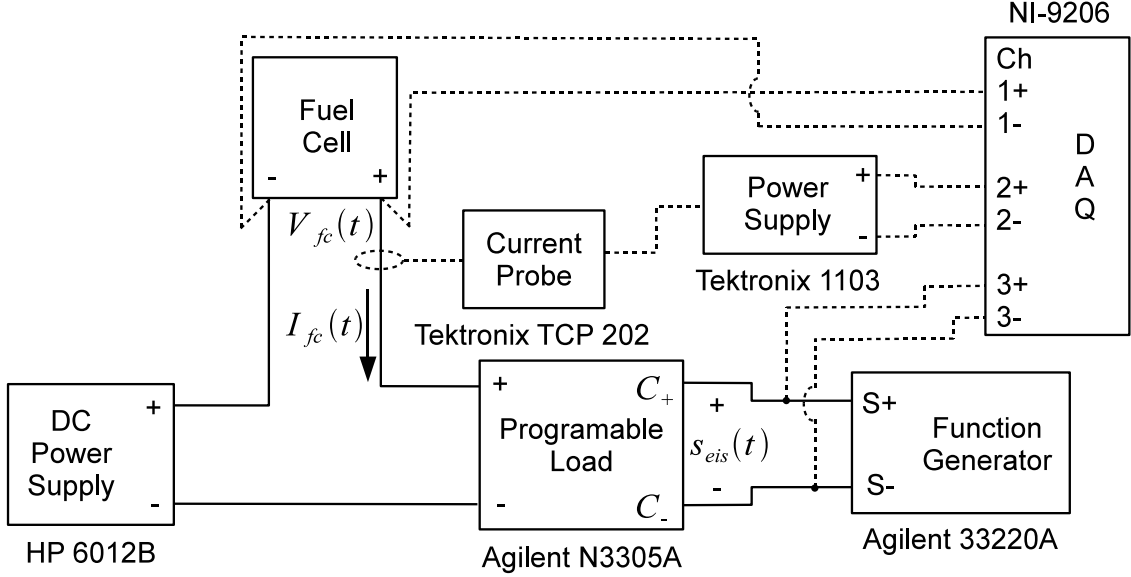


Figure 4.2: Conceptual diagram of the experiment and measurement set-up.

supply is required to increase the DC bias voltage applied across the electronic load, which when operating in controlled current mode requires a minimum voltage across its terminals of 1.4V. The fuel cell itself typically supplies a potential less than 1V.

The fuel cell used for demonstrating the EIS method capabilities was the anode supported ASC3 cell operating under the fuel and temperature conditions as described in Chapter 2. Measurements of the fuel cell voltage $V_{fc}(t)$, fuel cell current $I_{fc}(t)$, and function generator signal $s_{eis}(t)$ were taken using a National Instruments 9206 16-bit 250 kHz data acquisition (DAQ) module. For the voltage measurements, an unshielded, 22 AWG twisted-pair of aluminum wires was connected to the Inconel platens on the exterior of the oven through a welded screw terminal on each platen. These leads were then directly terminated across Channel 1 of the DAQ module. In this configuration, the measured voltage includes the voltage of the fuel cell as well as the voltage drop through the Inconel platens.

Current measurement was achieved using a Tektronix TCP202 current probe and 1103 power supply with the output fed through a 50Ω coax cable to Channel 2 of the

DAQ module in parallel with a 50Ω 1% resistor. The function generator signal, $s_{eis}(t)$ in Figure 4.2, is also measured at the input to the electronic load using unshielded, 22 AWG twisted-pair aluminum wires and terminated in channel 3 of the DAQ unit. The DAQ common was connected to the negative rail of the HP 6012B DC power supply. The experiment and measurement test system of Figure 4.2 was allowed to float; unconnected from earth ground.

To conduct the experiment, first the fuel cell was brought to the operating conditions, i.e. temperature and gas flow rates, described above. The cell was then allowed to activate and reach steady state during a four hour rest period before testing began. With cell activation reached, the desired DC-bias current was set by varying the DC-offset of the Agilent 33220A Function Generator output. Any slow-changing transients in the fuel cell voltage were allowed to settle. The amplitude of the AC signal output from the function generator was then increased until the maximum corresponding voltage response was around to 50 mV p-p. This excitation level provided a good signal to noise ratio in the measurements without violating the linearity assumption as outlined earlier. The DAQ module was then set to record using Labview SignalExpress installed on a Lenovo T-60 laptop computer with USB interface, and allowed to record a full sinusoidal sweep. For all fuel cell experiments, the small-signal ac-current excitation was one of a sinusoid swept in frequency from 100 mHz to 5 kHz over a period of 175 seconds. From (4.7), this gives a β value of 1.064. Data was measured at a sample rate of 50 kHz/channel.

In addition to the fuel cell experiments, a resistive-capacitive circuit was tested in place of the fuel cell to validate the EIS method with a known impedance. This circuit consisted of a 1.5Ω resistor in series with the parallel combination of a 2Ω resistor and a $470\mu\text{F}$ capacitor. Both resistors were Dale RH-50 wirewound resistors, and the capacitor was a Rubycon ZL series cap. Voltage and current measurements

of the circuit were made in accordance with the fuel cell set-up described above with the salient exception being ac voltage values were not amplitude restricted since the resistors and capacitors are nominally linear devices.

All data was analyzed in MATLAB with the OLS fits of the current and voltage data segments performed using the `mldivide()` function. This function solves (4.12) and (4.13) in the least squares sense through QR decomposition of the $\mathbf{A}_x$ matrices using Householder Reflections [87].

Data Uncertainty Analysis

An estimate of the precision in the subsequent impedance estimates (4.14) was achieved through a bootstrap analysis [88] of 10,000 iterations. Here, for each bootstrap iteration, the time index vector t_x of each data segment x , was randomly resampled with replacement under a discrete uniform probability distribution. New current and voltage data vectors, and model matrix A_x , were generated using the resampled time index vector and used to solve (4.12) and (4.13). The resulting parameters were then used to solve (4.14). From these 10,000 bootstrapped impedance estimates, the standard deviations in both the real and imaginary components were calculated and used as an estimate of the standard deviations $\sigma_{x,real}$ and $\sigma_{x,imag}$, of the original impedance estimate Z_x .

Additionally, the accuracy of the EIS sweep measurements was demonstrated by comparing the impedance measurements of the resistive-capacitive circuit with measurements gained using an Agilent E4980A Precision LCR Meter with a 16089B Kelvin Clip lead interface at all frequencies $\omega_x > 20$ Hz (the lower limit of the LCR meter's frequency range). For these measurements, the biasing and excitation conditions, i.e. the DC-current and ac-current amplitude, were kept similar to those of

the EIS sweeps. These conditions corresponded to an absolute LCR meter accuracy of around 0.6%.

The accuracy of the EIS sweep measurements depends primarily on the accuracy specifications of the instruments, i.e. the current probe, 50 Ω resistor and DAQ. Of these, the gain inaccuracies of the DAQ are negligible when compared to those of the current probe (3%) and resistor (1%). Since the resistor is used to multiply the current probe signal output, the combined accuracy rating is 3.2%. These two sets of measurements and their respective accuracies allow a direct comparison of the impedance values found using the EIS method described in this chapter to ones gained using a commercially available system. Typical instrumentation, e.g. an LCR meter, cannot be used directly with fuel cells as it lacks the ability to put the cell under load.

Electrochemical Impedance Spectroscopy Results

Figure 4.3 shows a complex plane plot representation of the measured impedance values for the resistive-capacitive circuit. Here, EIS measurements using the OLS method are shown by black circles and are compared against those found using the Agilent E4980A Precision LCR Meter, shown with green x markers. In the plot, the real component of the measured impedance is plotted against the horizontal axis while the imaginary impedance is plotted against the vertical axis. Several of the OLS method and LCR meter impedance marker pairs are labeled with the frequency corresponding to those impedance values. The maximum percentage offset between the two sets of measurements is 1.5% and well within the accuracy specifications dictated by the instruments used. The standard deviation in the measurements, $\sigma_{x,real}$ and $\sigma_{x,imag}$, averaged 0.38 m Ω and 0.37 m Ω , respectively. Measurements at low

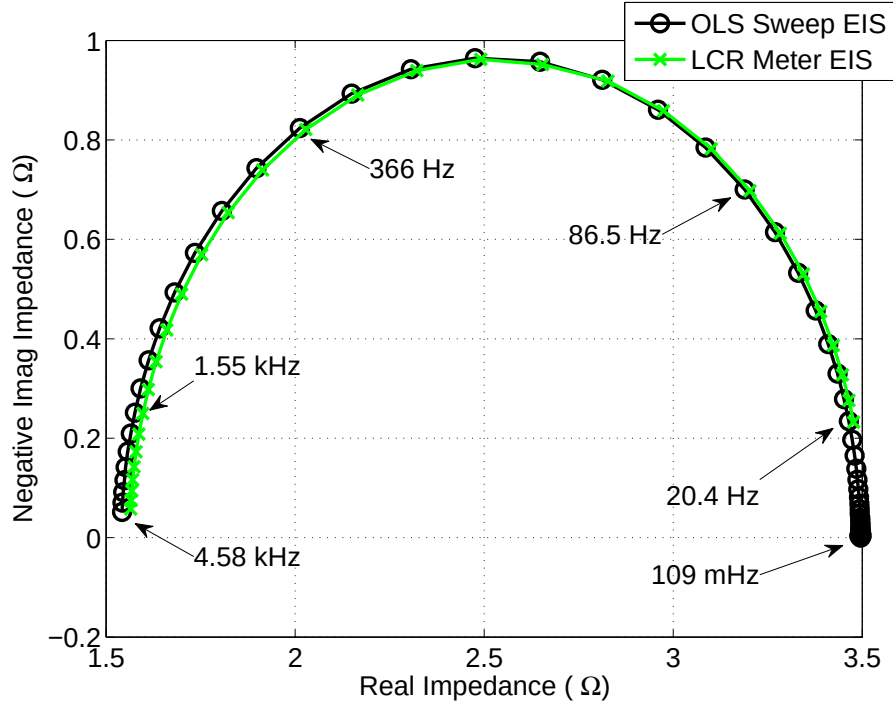
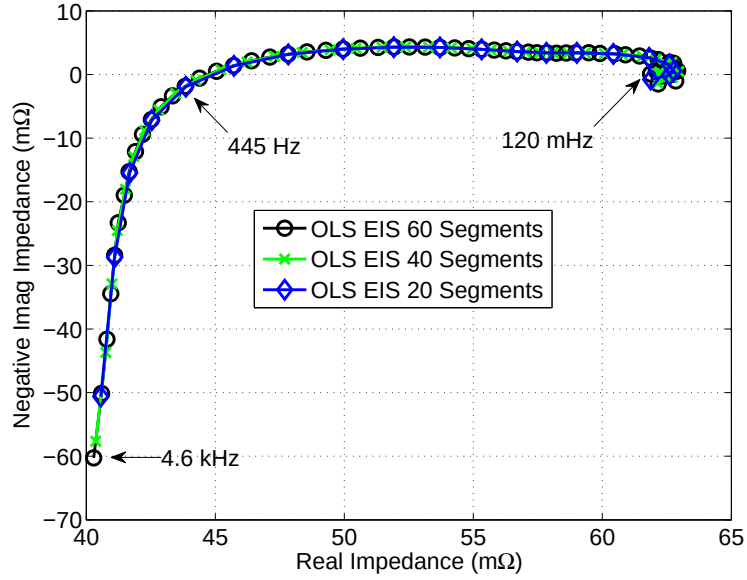


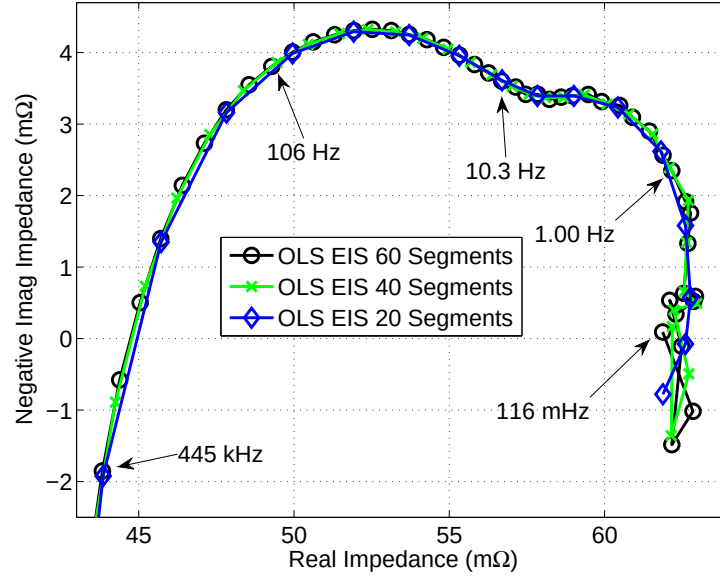
Figure 4.3: Complex plane plot comparison of EIS measurements of the resistive-capacitive circuit performed using the OLS method presented in this chapter and measurements taken using an Agilent Precision LCR meter. For both tests, the DC-bias was set to 50 mA and the AC perturbation to 30 mA p-p.

frequencies had the highest variability, with $\max(\sigma_{x,real}) = 1.3 \text{ m}\Omega$ and $\max(\sigma_{x,imag}) = 1.9 \text{ m}\Omega$. In general, this measure of precision improved with frequency.

Figure 4.4a shows several measured impedance curves of the SOFC using the OLS sweep method. Each curve was found using the same current and voltage data, with the salient difference in their analyses being the number of segments used in fitting the swept waveform to the data. The black curve with the circle markers shows the impedance measurements found by fitting 60 segments, the green curve with the x markers corresponds to 40 segments, and the blue curve with diamond markers corresponds to 20 segments. For all analyses, the total sweep was split into



(a) Cell Impedance (100 mHz to 5 kHz)



(b) Cell Impedance (100 mHz to 5 kHz)

Figure 4.4: Complex plane plot representation of the SOFC EIS measurements. The fuel cell was DC-biased around 7 A and perturbed such that the low frequency peak-peak fuel cell voltage was around 50 mV. (a) shows the impedance measurements for the full frequency range of excitation (100 mHz to 5 kHz), while (b) shows a close-up of the measurements for the frequency range 100 mHz to 5 kHz.

equal length, non-overlapping segments. Frequency values corresponding to various impedance measurements are labeled as in Figure 4.3.

Because voltage measurements were taken from the screw terminals of the Inconel platens, the measured SOFC impedance of Figure 4.4a includes the inductive effect of the platens. This causes the high frequency impedance measurements to increase in magnitude as the phase asymptotically approaches -90° . Figure 4.4b shows a magnified view of the impedance measurements within the frequency range of 100 mHz and 500 Hz and gives a better indication of the OLS sweep method's ability to depict the SOFC's electrochemical dynamics. The average standard deviation for the three sets of impedance measurements were $\sigma_{x,real} = 4.5\mu\Omega$ and $\sigma_{x,imag} = 4.6\mu\Omega$, $\sigma_{x,real} = 3.6\mu\Omega$ and $\sigma_{x,imag} = 4.\mu\Omega$, and $\sigma_{x,real} = 3.0\mu\Omega$ and $\sigma_{x,imag} = 3.7\mu\Omega$, for the 60, 40 and 20 segmented sweeps, respectively. All estimates of real and imaginary component standard deviation for all data points in Figure 4.4 were less than $17\mu\Omega$.

Figure 4.5 shows the first 5 time-domain fits for the 40-segmented sweep. These are represented by the green dashed curve while the original measured data is shown in black. The top plot displays the current fits, and the bottom plot displays the voltage fits, with blue vertical lines showing the separation of the five data segments and fit curves. The quality of the model's fit is shown by the extent to which the two waveforms overlap. Figure 4.6 further shows the effectiveness of the fit by plotting the difference between the measured data and the fit waveform for all 40 segments of the swept excitation. Here, the current difference signal is shown on the top plot, while the voltage difference signal is shown on the bottom. These signals contain elements of system and measurement noise as well as any biasing imposed by the OLS fit routine.

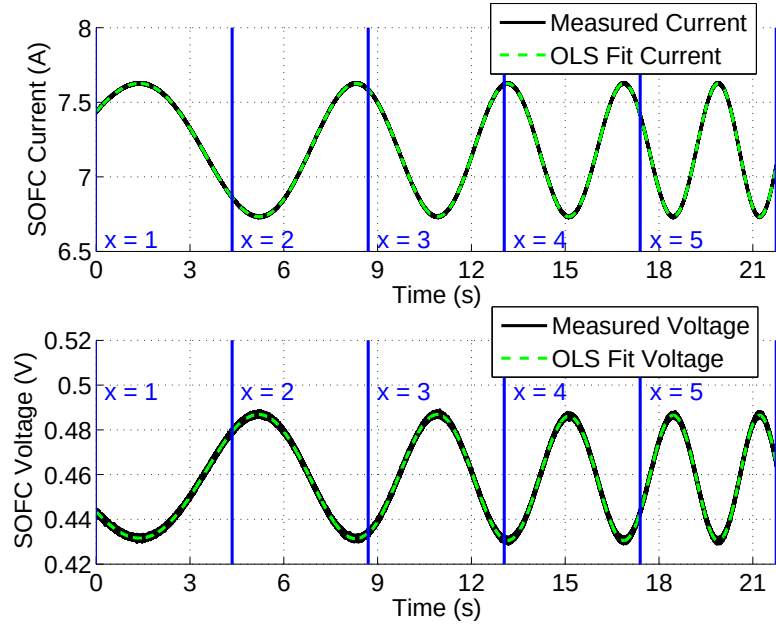


Figure 4.5: Time-domain fitting of the measured current and voltage waveforms. The fits shown by the green dashed curve here are for the 1st 5 segments of a 40 segmented sweep fit with the original measured data shown in black.

Discussion

From Figure 4.3 and the accuracy analysis explained above, it is evident that the EIS measurements achieved using the OLS method outlined in this chapter are consistent with measurements acquired using the commercially available LCR meter. Combined with high precision in the measurements found through the bootstrap analysis, it can be reasoned that the limiting factor in comparing the two measurements is the accuracy of the instrumentation and not the methodology. Additionally, another potential source of differences between measurements is inconsistent placement of the voltage measurement leads between the two tests. This would have the effect of a small shift in real impedance between the two sets of measurements, as seen in the figure.

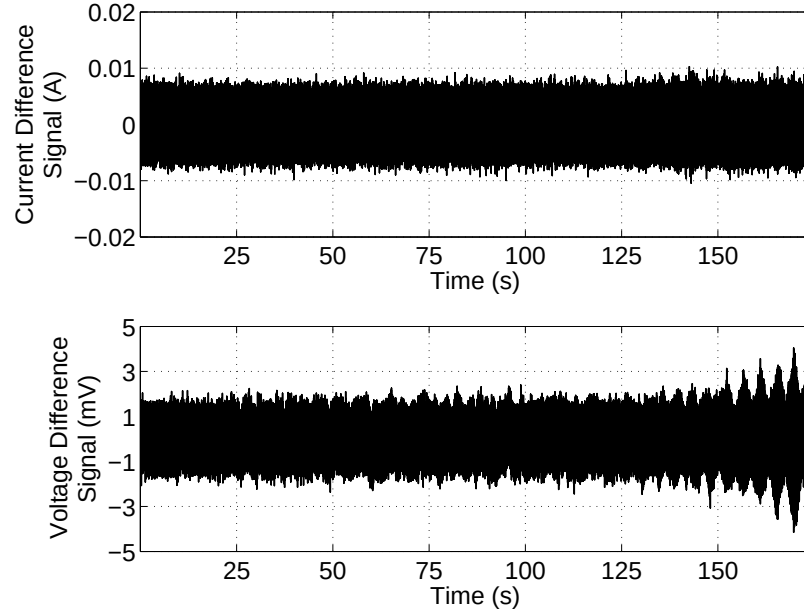


Figure 4.6: Difference signals for the voltage and current waveforms. These signals are the measured waveforms minus the fit waveforms and contain elements of system noise, measurement noise, and OLS fit errors.

The high precision exhibited in the bootstrap analysis of the fuel cell impedance measurements indicates that the structure of the measured voltage and current data is consistent with the swept waveform models used in the OLS fit. This is mirrored by the lack of a discernible structure in Figure 4.6 for most of either waveform. It is only near the high frequency end of the voltage waveform, when the parasitic inductance in the Inconel platens begins to dominate that a triangular envelope in the difference signal is revealed. The inductive impedance of the platens causes the measured voltage amplitude to change more quickly with time, which violates the assumptions of (4.8) and (4.9) that amplitude and phase change slowly. Thus, there is a small difference in the fit amplitude from that of the measured voltage at the beginning and ending of the sweep segments. This causes an increase in the estimated standard deviations for the high frequency segments, though as mentioned in the previous section, these estimates remain very small. And, because the OLS routine has the effect of averaging

the intrinsic amplitude and relative phase of each data point across each segment, the resulting impedance measurement still corresponds well to the average frequency for that segment.

An additional effect of measuring voltage through the Inconel platens is that the calculated impedance contains the bulk impedance information of the SOFC as well as the platens. This increases the real component of the impedance as well as adding a high frequency inductance effect as mentioned above. In previous studies [13], platinum wires woven through the silver mesh and depressed into the nickel foam were used to measure voltage directly from the cell’s electrodes. However, these wires had a tendency to short in the setup process, cause localized mechanical stress on the cell, and reduce contact area on the cell’s electrodes which could result in conduction “hotspots” through the cell. Thus, voltage was measured through the Inconel, though subsequent analysis of the impedance information gained requires accounting for the Inconel impedance, i.e. subtracting out the measured or estimated short-circuit impedance. This is similar to accounting for interconnects between cells when analyzing EIS measurements of fuel cell stacks.

The complex plane plots of the measured SOFC impedance shown in Figure 4.4 depict an important tradeoff concerning segment sizing in the OLS analysis. Comparing the low frequency impedance measurements for the three analysis iterations, it is evident that the accuracy in the measurements at these low frequencies decreases as the swept data is divided into increased segments. While this is in part due to a reduced number of data points used in segment estimates, it is also due to a reduction in distinguishable features of the sinusoid available for fitting. That is, as the total phase encompassed in $\phi(t_x)$ is decreased, less of the sinusoid is present. Then, from the Cramér-Rao Bound discussion, (4.20) - (4.23) no longer hold, and the off diagonal covariance terms in the CRB matrices are no longer negligible. Combined, this leads

to an increase in impedance estimate variance. Still, that there is little variability in the low frequency measurements of Figure 4.3 indicates that the variability seen in Figure 4.4 is possibly exacerbated by a non-linear operation of the fuel cell at low frequencies, e.g. low-frequency hysteresis. The lack of a full-period cycle is shown in Figure 4.5 where the first segment ($x = 1$) has about a half period of swept-sinusoid excitation compared to the fifth segment ($x = 5$) which has about one and a half periods.

It should also be noted that segment lengths do not need to remain uniform across all segments, and if measurement time is not restricted, low frequency impedance measurements increase in accuracy when a larger segment of the sinusoid is used for fitting. Also, segment lengths can be increased without reducing the number of segments l by overlapping the segments across the swept data. This however represents another tradeoff as overlapping increases the required computation time. For direct methods of OLS such as the QR factorization algorithm employed, the computational work is roughly proportional to the number of data points used in the least squares fit [87]. By overlapping the segments, some of the data points are included in both fit routines of two adjacent segments. Thus, while changing the number of segments used in the described algorithm has little effect on computation time, overlapping the segments increases the computation time proportional to the amount of overlap.

Lastly, as mentioned in the introduction, the OLS methodology easily extends to other perturbation signal classes including multi-frequency component perturbation signals. Here, each additional frequency component would add two quadrature related columns to the A_x matrix as each component needs inclusion in the model class. This would allow the use of the OLS methodology with reduced time perturbation signals

though assuming use of QR factorization for solving the least squares equations, the computational complexity increases with the number of columns squared [87].

Chapter Summary

This chapter presents a time-domain method for electrochemical impedance spectroscopy analysis using ordinary least squares. The validity of the method is demonstrated on a known resistive-capacitive impedance with the results comparing favorably against measurements performed using the commercially available Agilent E4980A Precision LCR Meter (Figure 4.3). Further, the method's utility is illustrated through its application to a solid oxide fuel cell (Figure 4.4), and the effectiveness of its operation depicted by comparing the OLS fit swept-sinusoid model to the original time-domain current and voltage data in Figure 4.5 and Figure 4.6. The novelty of this method lies in the application of OLS for time-limited EIS measurement across a broad frequency range, which would be beneficial for embedded impedance sensors for electrochemical devices. The use of OLS allows an unbiased estimate of impedance for measurements containing a non-integer number of signal periods or containing less than a full period. This leads to increased flexibility in EIS analysis and can decrease measurement time by achieving impedance estimates from fractions of full sinusoidal periods. Future applications of this method could be extended to multi-frequency component perturbation signals for further reducing the time required for EIS measurements.

CASE STUDY: PERFORMANCE TESTING A HYBRID SOURCE POWER MANAGER

Hybrid power source managers (HSPM), e.g. [49, 50, 74, 89–91], allow an increased degree of freedom in optimizing the use of fuel cell stacks as the primary energy source under dynamic load applications such as in electric vehicles [90, 91]. These systems employ energy storage devices such as batteries and ultra-capacitors along with bi-directional power electronics to allow fixed-point operation of the fuel cell stack while simultaneously improving load following capabilities and decreasing detrimental load / stack interactions. Additionally, as shown in this study, a properly designed HSPM can also deliver perturbation signals to the fuel cell stack electrical terminals for in-situ EIS monitoring.

In this chapter, the performance testing of an HSPM system [49] designed for use with a solid oxide fuel cell stack and auxiliary battery power source is described. The reference simulator system and EIS methodology of Chapters 3 and 4, respectively, provided the environment for these tests which aim to show the HSPM’s fuel cell stack protection and monitoring capabilities under realistic load and fuel cell stack operation.

Hybrid Source Power Manager Operation

Through a collaborative effort with a research group at the Massachusetts Institute of Technology, a prototype HSPM [49] with the general topology of Figure 5.1 was tested using the reference-based SOFC stack simulator outlined in Chapter 3. The HSPM, which was developed independently at the Massachusetts Institute of Technology (MIT), consists of two bi-directional DC/DC converters for interfacing a fuel cell stack and external battery with a load. The DC/DC converters of the

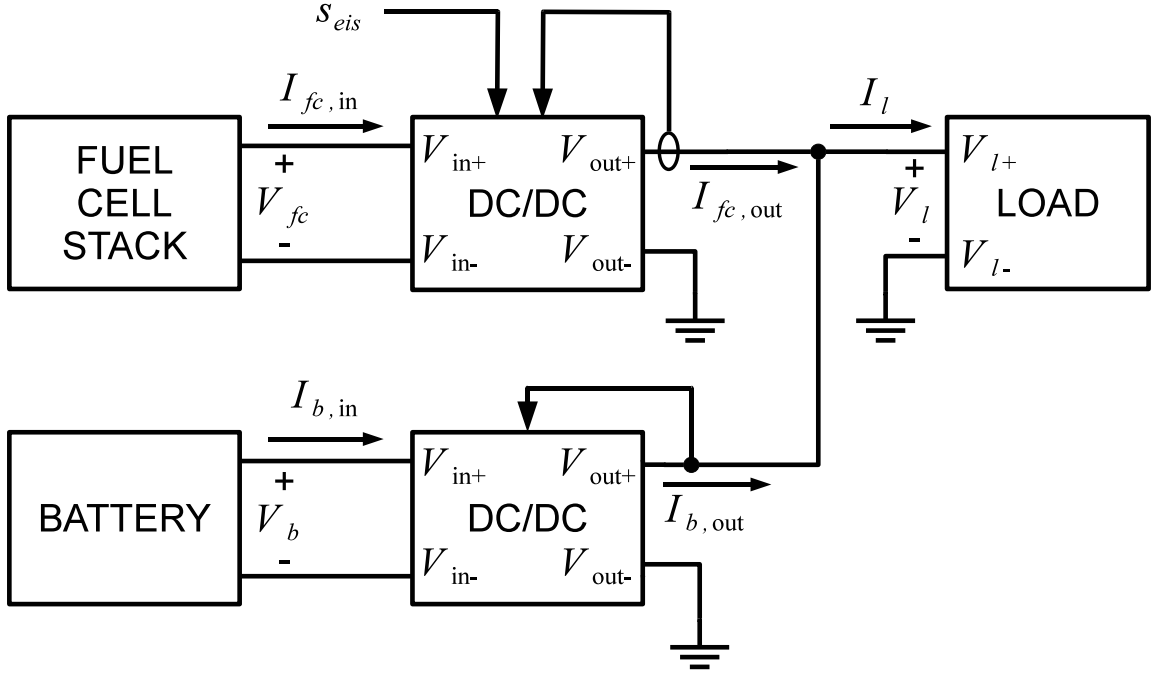


Figure 5.1: Conceptual diagram of power electronic control system used for stabilizing electric load demand from the fuel cell stack and performing in situ EIS monitoring.

two sources are controlled in a master-slave current-voltage regulated configuration so as to allow fixed-point operation of the fuel cell current and load voltage while still following the demanded load current.

The fuel cell side converter operates in a controlled current fashion and regulates the fuel cell stack operating current to a steady value regardless of any variations in the demanded load current. The battery side converter is voltage controlled and constrains the voltage applied to the load while simultaneously providing for excess and dynamic variations in the load current. The result is the ability to efficiently follow variations in load demand, while maintaining the fuel cell stack's DC operation at a nominal set point. It is important to note that when the load current, I_l , falls below the set fuel cell converter output current, $I_{fc, out}$, the excess current is driven from the fuel cell stack to the battery, thus automatically recharging the battery.

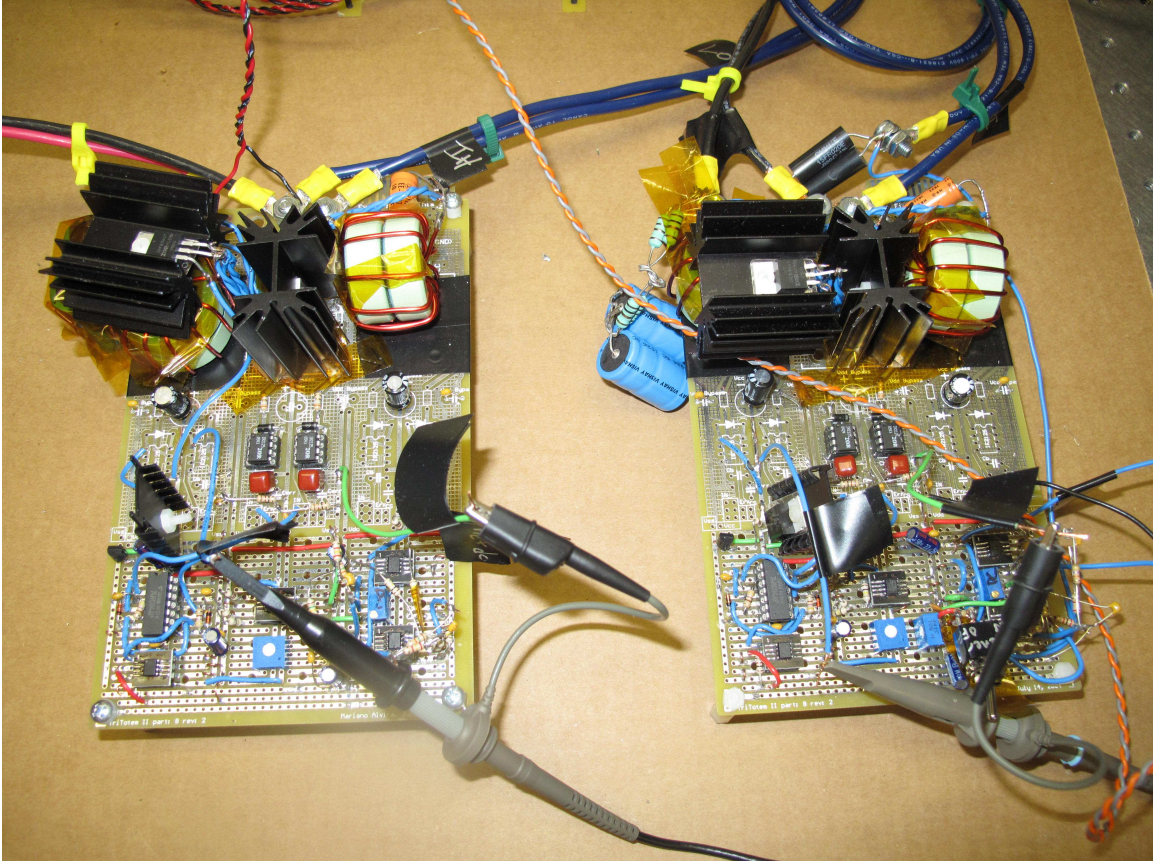


Figure 5.2: Image of the Hybrid Source Power Manager developed at MIT.

Additionally, the HSPM allows the injection of a small signal EIS current perturbation sourced from the battery and applied back to the stack terminals. This is accomplished through the external signal, s_{eis} , which varies the fuel cell current set point in accordance with the desired perturbation profile. The bandwidth of the HSPM system tested was sufficient for EIS measurements up to 1 kHz. Figure 5.2 shows an image of the HSPM electronic boards with the fuel cell stack designated DC/DC converter board on the left, and the battery DC/DC converter board on the right.

Experimental Setup

The experimental setup for testing the HSPM system consisted of the two bi-directional DC/DC converters, the reference based fuel cell stack simulation system described in Chapter 3, a bi-directional power source, an electronic load with signal generator for programming load current profiles, a second signal generator for providing the EIS perturbation signal, and a data acquisition system. The reference based fuel cell stack simulation system took the place of the fuel cell stack block in Figure 5.1, and used an InDEC ASC3 SOFC cell set-up and operated as described in Chapter 2 for a reference. As with the reference simulation testing of Chapter 3, the simulator's gain was set so that the total number of cells in the simulated stack was 20. For the battery system block, either a 12-volt lead-acid battery or a AE Techon 7224 bipolar linear power amplifier with an output voltage of 12 volts was used depending on the particular test being performed.

For all tests of the HSPM system, the load employed was an Agilent N3305A programmable electronic load, and for tests that required dynamic loading, a pre-programmed Agilent 33220A Function Generator was used to set the dynamic current demand through the analog control ports of the programmable load. A second Agilent 33220A Function Generator was used to supply the s_{eis} signal to the fuel cell side DC/DC converter for EIS analysis of the simulated fuel cell stack. All relevant current, voltage and control signal measurements were recorded using a National Instruments 9206 16-bit 250 kHz data acquisition (DAQ) module, which was controlled using LabView's Signal Express program installed on a Lenevo T-60 laptop computer. All current measurements were achieved using LEM LA55-P Hall-effect current transducers.

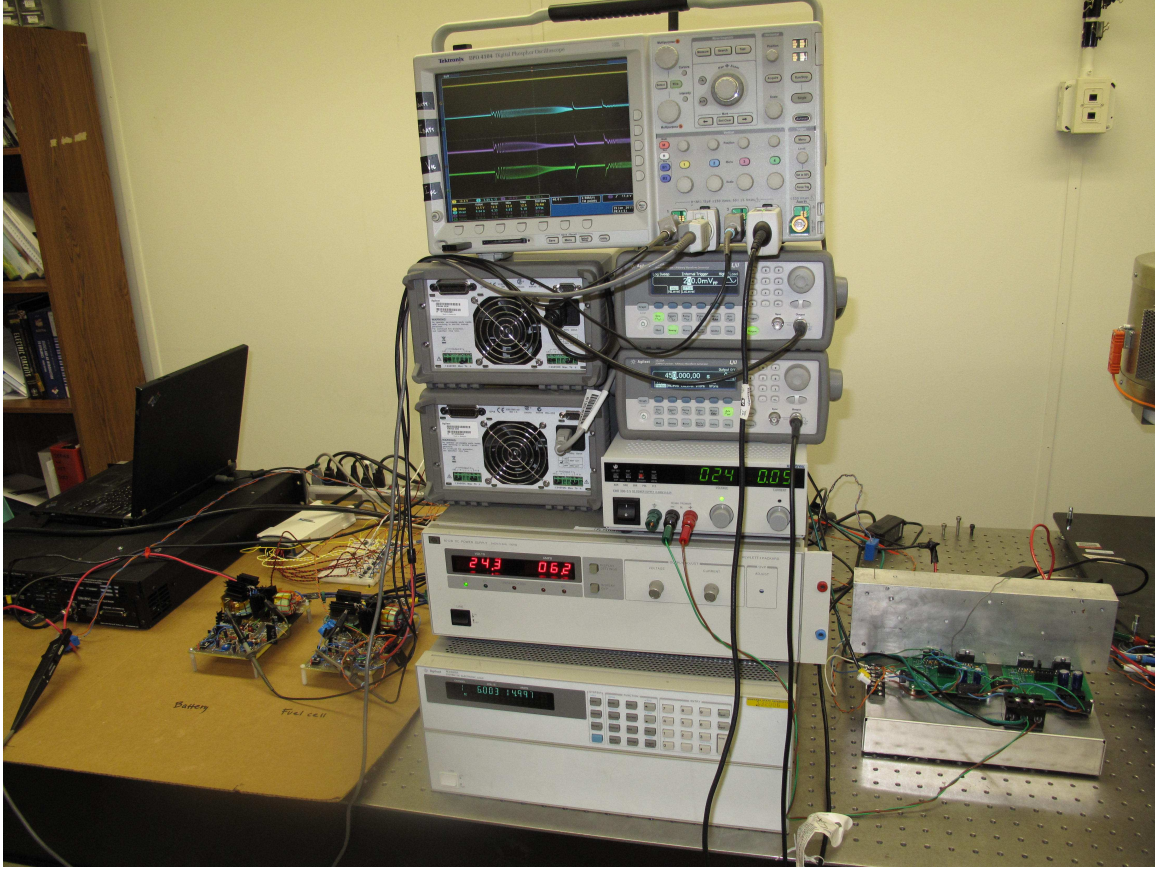


Figure 5.3: Image showing the experimental setup for testing the HSPM.

Figure 5.3 provides an image of the experiment setup. On the very far left of the image is the bipolar power amplifier used to simulate the battery, with the laptop computer and DAQ sitting on top, and next to the amplifier, respectively. To the right of the amplifier are the two DC/DC converter boards. The stack of instruments in the center of the image contains from bottom to top, the electric load, the two power supplies required for operating the reference simulator (see Chapter 3 for details), two Agilent E3649A dual power supplies for powering the current transducers and an active anti-aliasing filter bank shown in Figure 5.4, and the two Agilent 33220A function generators. On top of the stack is a Tektronix DPO4104 Oscilloscope used for real-time monitoring of the experiments. Finally, to the right of the instrument

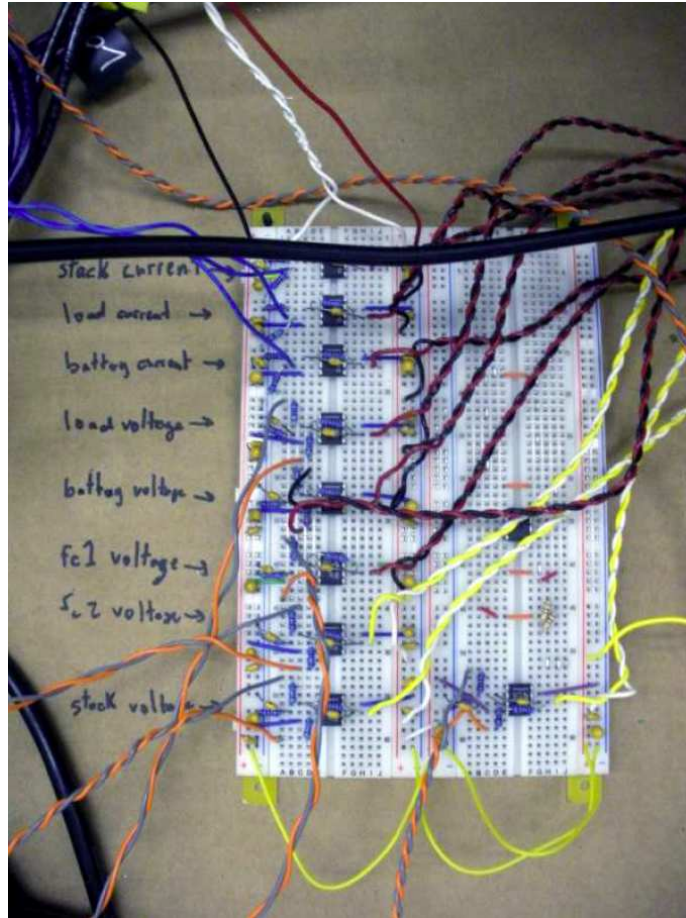
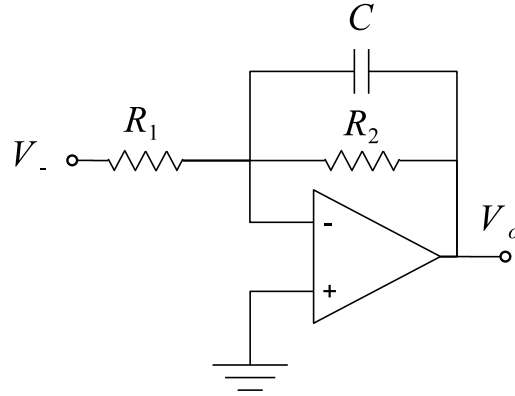


Figure 5.4: Image of the antialiasing filter bank used in measuring currents and voltages during HSPM testing.

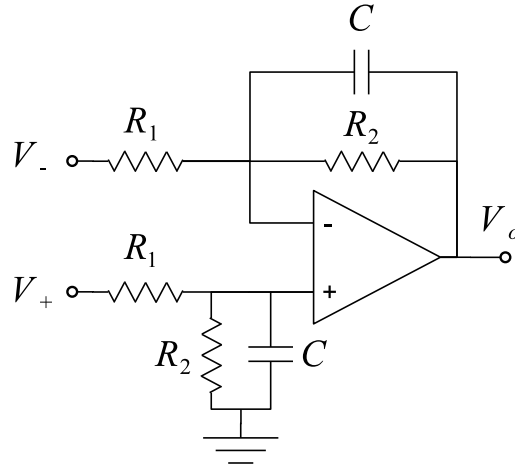
stack is the reference simulator circuitry. The fuel cell setup is not shown in this image.

Anti-Aliasing Filters

The anti-aliasing filters of Figure 5.4 were required due to the noise imparted on the HSPM system by the DC/DC converters, which feature a switching frequency of 400 kHz. With up to 10 channels of the DAQ in operation during testing, the maximum DAQ sample rate achievable was 25 kHz. Therefore, to remove higher frequency components from the measurements, single-pole low-pass op-amp filters with



(a) Current Measurement Filter Topology



(b) Voltage Measurement Filter Topology

Figure 5.5: General topologies for the current and voltage anti-aliasing filters used in data acquisition during HSPM testing.

inverting configurations for current transducer signals, and differential configurations for voltage measurements, were used to filter measured signal frequency components above the Nyquist rate of 12.5 kHz. Figures 5.5a and 5.5b show circuit diagrams for these two filter types with transfer functions,

$$\frac{V_o}{V_i} = -\frac{R_2}{R_1} \frac{1}{sR_2C + 1}, \quad (5.1)$$

and

$$\frac{V_o}{V_+ - V_-} = \frac{R_2}{R_1} \frac{1}{sR_2C + 1}, \quad (5.2)$$

respectively. All filters featured cut-off frequencies of 1 kHz and gains appropriate for maximizing the bit-resolution of the DAQ channels.

It should also be noted that because these filter poles are located at 1 kHz, these filters caused roll off in measured current and voltage magnitudes as well as phase shifts in the measured current and voltage signals during the higher frequency end of the EIS excitation. However, because the pole locations for all filters were set equal, the phase and amplitude shifts of both voltage and current measurements coincided and cancelled out during EIS analysis.

UAV Flight Profiles

UAV flight data available through a collaboration with the US Air Force were used for testing the performance of the HSPM system performance under dynamic loading conditions. Data from one of the flight profiles showing the total current draw and flight velocity of a UAV during taxiing, takeoff and flight is shown in Figure 5.6. In this plot, the first 4 minutes of data corresponds to UAV taxiing, followed by take off around the 4.5 minute mark. For the first 2 minutes of flight, the velocity and subsequent current drawn by the UAV's electric motor vary rather significantly. Following this period, the UAV enters steady flight with the velocity and current demand remaining relatively constant until the last minute of flight. This particular flight plan proved to be the most useful of the ones available due to the two different flight regions as the performance of the HSPM under highly dynamic loading could be compared to its performance under relatively constant loading conditions.

Because the flight data shown here was measured on a UAV utilizing a higher powered battery and electric motor system, the magnitude of the current demanded was too large for the test systems employed in this experiment. Thus, the magnitude of the current profile shown in Figure 5.6 was normalized and rescaled to a more appropriate power level for the systems of this test. However, the relative magnitude of the featured dynamics in comparison to the full scale current were maintained.

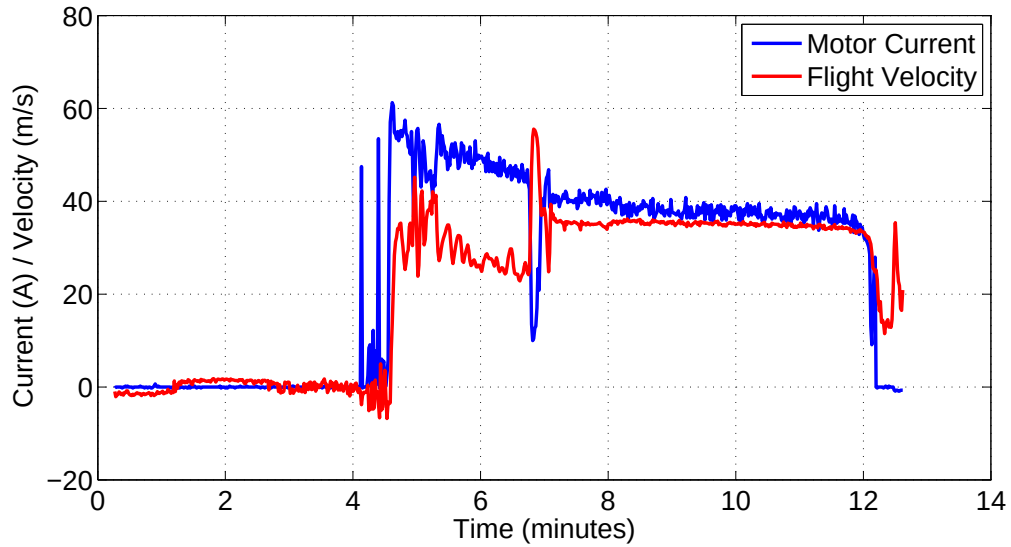


Figure 5.6: Measured unmanned aerial vehicle profile used as the basis for dynamic load testing of the HSPM system.

Reference Cell Degradation and Recovery

For some tests, the reference cell was electrically degraded prior to HSPM system testing in order to demonstrate the degradation detection capabilities of the EIS method when employed in a realistic application. To induce degradation, the reference fuel cell was disconnected from the reference simulator system and connected in series with the HP 6012B power supply and the electric load. The electric load was then set to voltage controlled mode and used to hold the operating voltage of the fuel cell between 30 mV and 50 mV for 11 hours. The accumulated effect of

the excessive current loading caused significant, though reversible, degradation to the cell. Once the cell was degraded, it was reconnected to the reference simulator circuit and the entire testing circuit was once again configured in accordance with Figure 5.1. Following subsequent testing of the HSPM system with the now degraded simulated fuel cell stack, the reference cell was allowed to “rest” at open circuit for 18 hours with oven temperature and reactant gas flow held at the normal operating values. These conditions allowed the cell to recover from the effects of the heavy current loading. Following this resting period, the cell was once again used as the reference for the simulated stack and the HSPM system was tested again. A more in-depth explanation of this type of electrically induced cell degradation is discussed in Chapter 6.

HSPM Experimental Results

As described above, the HSPM system serves two functions. First, the system diverts excess and dynamic current demand away from the fuel cell stack and towards the battery leaving the stack to operate at a nominal DC operating point. Second, the HSPM system provides the ability to perform diagnostic testing of the fuel cell stack during dynamic load operation through an external perturbation signal. This signal is imparted on the current drawn from the stack and supplied by the battery power source.

The ability of the HSPM system to perform these two functions is demonstrated in Figures 5.7 and 5.8. In both figures, the regulated load voltage (left) and demanded load current (right) are shown in the top row, the battery voltage (left) and battery current draw (right) are shown in the middle row, and the regulated fuel cell stack voltage (left) and current (right) are shown on the bottom plot. For both tests, the

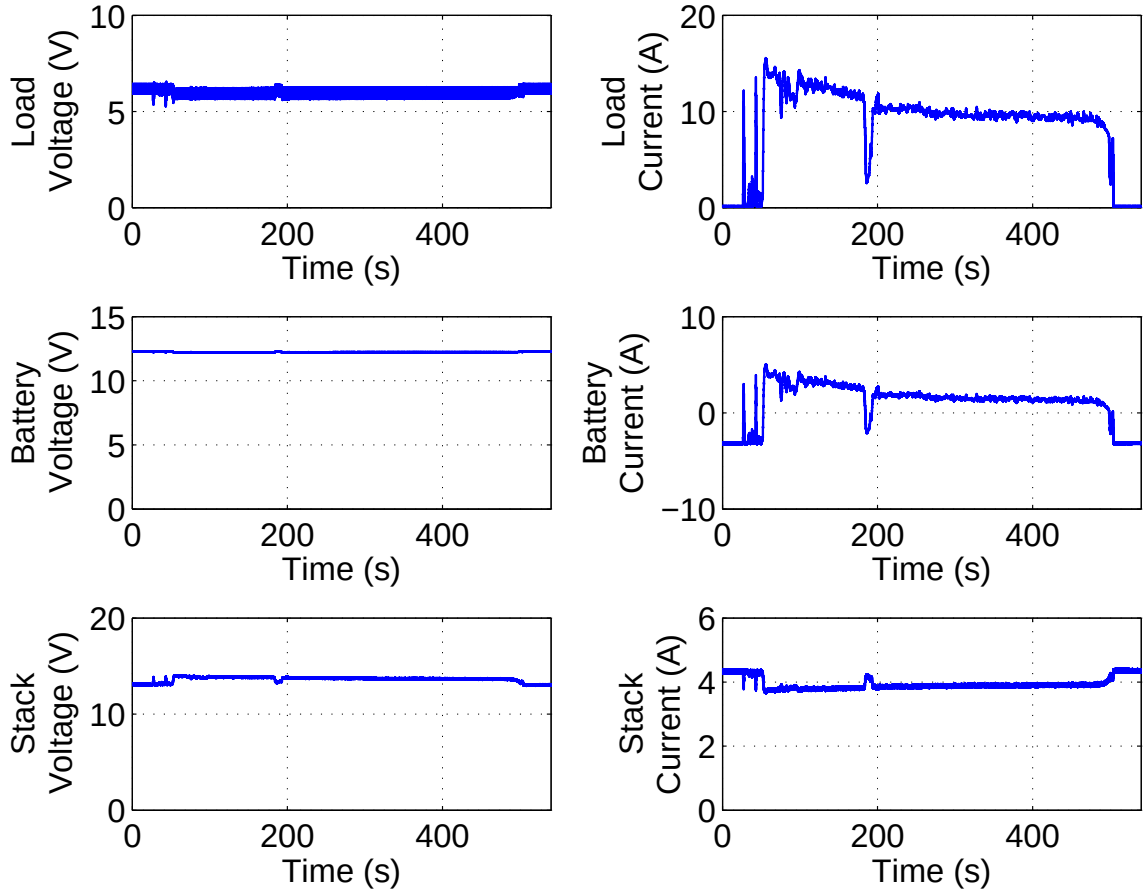


Figure 5.7: Time-domain load, battery, and simulated stack voltage and current waveforms measured during testing of the HSPM under the simulated UAV motor loading conditions. The highly dynamic load current demand (top right) are largely supplied by the battery (middle right) allowing the simulated fuel cell stack to operate near the desired set point around 4 A (bottom right).

demanded load current was generated in accordance with the measured UAV flight data of Figure 5.6, but scaled down by a factor of about 4 to match the power levels of the simulated fuel cell stack and HSMP system. For the first of these tests, no EIS perturbation signal was added the fuel cell stack current. In the second test, two logarithmically-swept sinusoidal EIS perturbation signals were added and are easily seen on the measured fuel cell stack voltage and current traces of Figure 5.8. The first sweep begins around the 60 second mark and lasts for 175 seconds after which

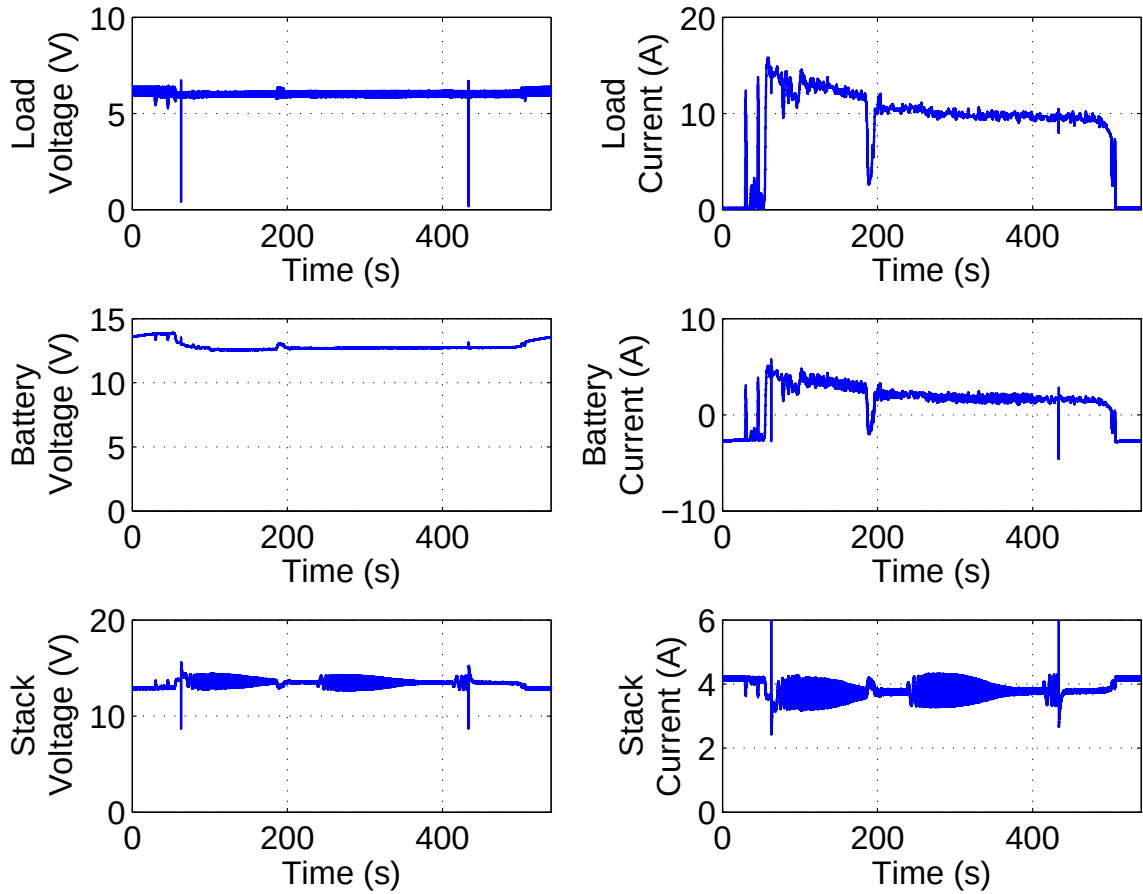


Figure 5.8: Time-domain load, battery, and simulated stack voltage and current waveforms measured during testing of the HSPM's in-situ EIS capabilities. Under the same loading profile of Figure 5.7 the HSPM is shown to impart a perturbation signal on the simulated fuel cell stack current (bottom right), while allowing the load to operate undisturbed (top right).

the second sweep immediately begins and ends around the 410 second mark. Both EIS perturbation sweeps spanned a frequency range of 100 mHz to 1 kHz.

Figures 5.9 - 5.11 show the resulting impedance measurements achieved during the flight simulation and EIS measurement test of Figure 5.8. The first two figures show comparisons of the reference fuel cell impedance profile (black circles) and the simulated stack impedance profile (green x's) resulting from the first EIS perturbation sweep (Figure 5.9) and the second EIS perturbation sweep (Figure 5.10). In both

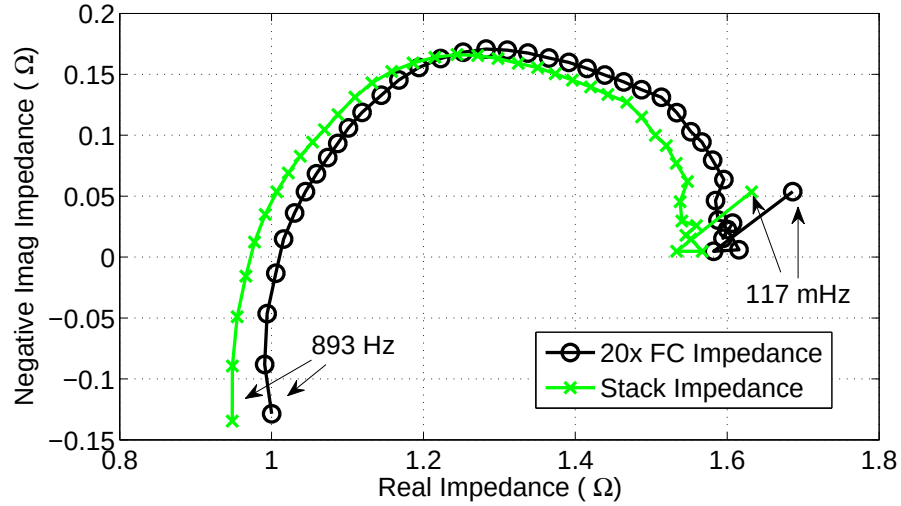


Figure 5.9: Impedance profiles of the simulated stack and the reference cell found using the current and voltage measurements during the first of the two frequency-swept perturbation signals seen in Figure 5.8. The reference cell impedance is scaled by the simulated number of cells, 20, for direct comparison with the measured stack impedance.

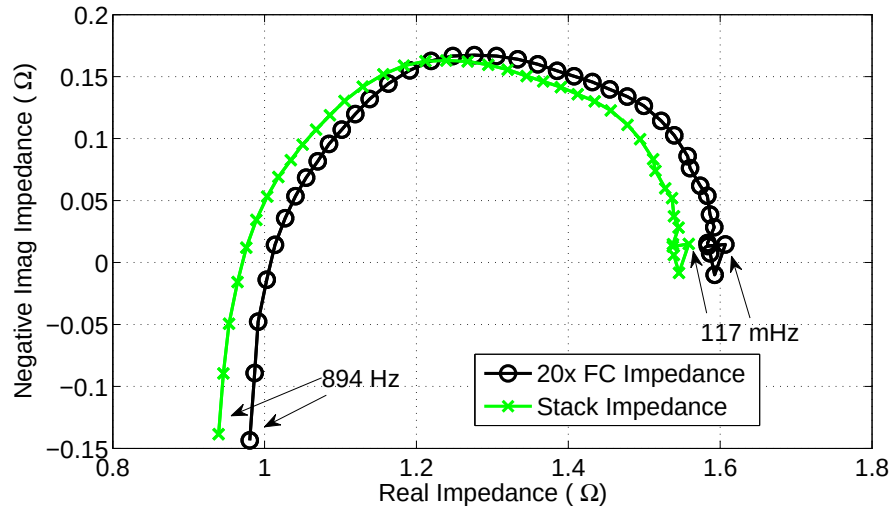


Figure 5.10: Impedance profiles of the simulated stack and the reference cell found using the current and voltage measurements during the second of the two frequency-swept perturbation signals seen in Figure 5.8. The reference cell impedance is scaled by the simulated number of cells, 20, for direct comparison with the measured stack impedance.

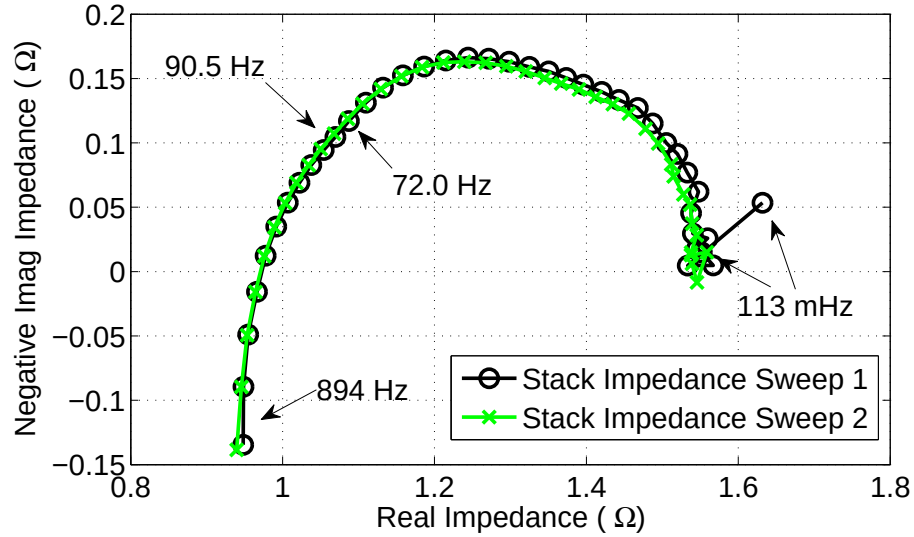


Figure 5.11: A comparison of the measured simulated stack impedance profiles found during the first and second swept perturbations.

figures, the cell impedance is multiplied by the number of series connected cells in the simulated stack, 20, for easy comparison with the simulated stack impedance profile. The extent to which the two impedance profiles overlap gives an indication of the reference simulator's effectiveness in EIS-based diagnostic testing under dynamic loading conditions.

These two sets of EIS measurements were performed under very different loading conditions. As can be seen in Figure 5.8, during the first sweep, a large dip in load current demand occurs about three-quarters of the way through the first EIS sweep. During the second EIS sweep, the demanded load current remains relatively constant throughout the flight profile. Figure 5.11 displays the two simulated stack impedance profiles achieved during these sweeps for comparison. Here, the measured impedance from the first sweep is shown with black circles and that of the second sweep is shown with green x's.

Finally, Figure 5.12 displays the measured impedance profiles for a second reference fuel cell that had been electrically degraded (black circles) and then allowed to recover (green x's). Both impedance measurements were made using the EIS capabilities of the HSPM system while under the current loading of the UAV flight profile described above and during the time segment of the first EIS sweep in Figure 5.8.

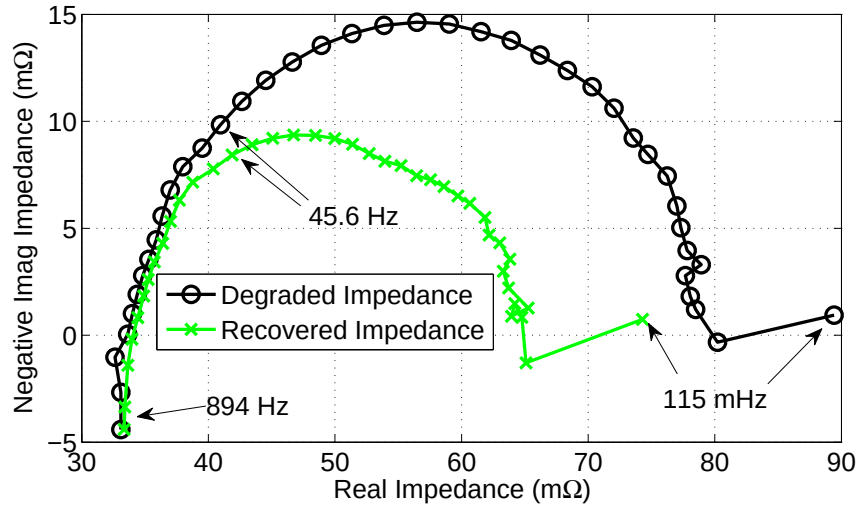


Figure 5.12: A comparison of the measured simulated stack impedance profiles found following a significant period of degradation and a period of recovery.

Discussion

The time-domain data of Figure 5.7 proves the effectiveness of the HSPM system in protecting a fuel cell stack from dynamic and excessive current loading by diverting this current away from the fuel cell stack while maintaining a steady load voltage and good load demand following. For this test, the fixed point operation of the fuel cell stack was set through the fuel cell side DC/DC converter to maintain a current level of 4 A. The demanded current during UAV flight (shown in the top right plot) ranges in amplitude from 0 A to 15 A. However, from the bottom right plot of this figure, it is seen that the fuel cell stack current only ranges from around 3.8 A to 4.3 A.

This represents a large signal attenuation of about 30 dB and results in limiting the simulated fuel cell stack voltage to a total dynamic voltage range of about 0.9 V. The excess current demand required for load following is supplied by the battery. The battery's measured current profile is shown in the middle right plot. Simultaneously, the load voltage (top left plot) is maintained by the battery side DC/DC converter at 6 V plus or minus 0.2 V throughout the test.

Maintaining the fuel cell stack at a localized DC operating point allows meaningful wide-band EIS measurements to be made. Figure 5.8 shows the ability of the HSPM system to impart an EIS perturbation signal on the fuel cell current draw while simultaneously diverting dynamic load current to the battery power source. This is a very important result as EIS analysis is dependent on the fuel cell stack operating in a predominantly linear manor for the duration of the EIS excitation. If the dynamic load current causes large swings in fuel cell current or causes the DC operating point of the fuel cell to shift significantly, then the linearity assumptions required are violated. From the fuel cell voltage and current plots of this figure, one can see that the DC operating point remains very constant throughout both EIS testing cycles. It should be noted that the large spikes seen in several of the plots prior to and following the two EIS sweeps were caused by the turning on of the signal generator output and is a product of the circuitry within the signal generator.

The impedance measurements of Figures 5.9 and 5.10 are those derived from the time-domain voltage and current data of Figure 5.8. These figures show reasonably good matching in the simulated stack impedance as compared to the reference cell impedance further solidifying the effectiveness of the reference simulator system of Chapter 3 in device and hardware-in-the-loop testing. Unlike the results figures from that chapter however, these figures do show a small DC resistance offset in the measured simulated stack impedance from that of the reference cell as indicated by the

simulated stack impedance profile being slightly shifted left along the real axis. This effect is present in both Figure 5.9 and 5.10, and is due to the measuring of the simulated stack voltage at the terminals of the FC-side DC/DC converter. Thus, there is a small voltage drop across the cables connecting the simulated stack to the DC/DC converter not included in the stack voltage measurement resulting in the slightly lower estimate of stack resistance.

Figure 5.11 compares the simulated stack impedance gained from the first sweep to that of the second, with the two impedance profiles showing a very close matching across the entire frequency range. As mentioned above, during the first sweep, a large load transient occurs just before the 200 second mark as seen in Figure 5.8. During this transient, the EIS perturbation signal is exciting the simulated stack over a frequency range of around 60 Hz to 110 Hz. The two most affected impedance points are labelled with their corresponding frequencies, 72.0 Hz and 90.5 Hz in Figure 5.11 and show no perceivable deviation from the general shape of the impedance profile. This suggests that the amount of transient load buffering provided by the HSPM system combined with the EIS methodology described in this dissertation are able to achieve accurate EIS measurements even during large load transients.

Finally, the usefulness of accurate, in-situ EIS capabilities is well intimated through the result of Figure 5.12, which compares the impedance profile of a reference fuel cell following electrically induced degradation to the profile measured following a period of no-load recovery. The degradation procedure described above caused a significant increase in the low frequency impedance magnitudes (< 45.6 Hz), while those at higher frequencies (> 45.6 Hz) remained relatively unchanged when compared to the recovered impedance profile. This increase in the internal impedance of the cell corresponds to a decrease in the electrical power available to the load from the simulated fuel cell stack. It is postulated, and further discussed in the next chapter,

that this increase in impedance coincides with nickel-oxidation within the fuel cell's anode layer. Thus, the impedance information that is afforded by the HSPM system and EIS methodology of this study, can be used for in-situ diagnostic assessment of a fuel cell stack even under dynamic loading.

Chapter Summary

This chapter presents a collaborative research case study testing the performance of a hybrid source power management (HSPM) system designed for operation with a solid oxide fuel cell stack and battery power source. For the testing of the HSPM system, the reference simulator system of Chapter 3 was used to simulate the primary power source fuel cell stack and the EIS methodology of Chapter 4 was used in extracting the simulated stack impedance profiles.

The results of the testing included in this chapter are important for several reasons. First, they demonstrate the capability of the HSPM system to buffer the fuel cell stack from dynamic and excessive current loading while simultaneously allowing for EIS diagnostic measurement of the fuel cell stack. Second, they further emphasize the utility of the reference simulator system for Device and Hardware-in-the-Loop (DHiL) testing of fuel cell stack power systems in combination with real loads and power management systems. Without the reference simulator system, realistic testing of the HSPM system would only have been achievable with a costly full-scale fuel cell stack. Third, the results showcasing the impedance measurement capabilities of the HSPM system in combination with the EIS methodology (Figures 5.12) indicate that fuel cell degradation can be detected in-situ.

It is this final result that suggests that the next logical extension of the HSPM system is its inclusion in a load-demand control scheme. In Figure 5.12, it is seen

that when allowed to rest at open circuit, the reference fuel cell had a propensity to recover from the electrically induced degradation. This, combined with the noticeable differences in the cell’s degraded-state low-frequency impedance from that of its recovered-state suggests that it may be possible to use the cell’s impedance information as a measure of degradation. This measure can then be fed back to an HSPM controller configured to vary the fuel cell’s DC load demand in order to control the degradation affecting the fuel cell stack. Further investigations into fuel cell degradation and recovery as well as initial studies on regulating fuel cell degradation through load control are presented in Chapters 6 and 7, respectively.

The HSPM system involved in this study was designed and built by a research team at MIT lead by Dr. John Cooley, PhD, and the results achieved through our collaborative effort became a major component in Dr. Cooley’s PhD dissertation [49]. Additionally, a paper further describing the design, building and testing of this HSPM system was recently submitted to the IEEE Transactions on Power Electronics for publication under the title “Multi-Converter System Design for Fuel Cell Buffering and Diagnostics Under UAV Load Profiles” [50].

LOAD-INDUCED DEGRADATION AND RECOVERY IN SOLID OXIDE FUEL CELLS

As shown in the previous chapter, a multi-source power system and appropriately designed power manager offers an additional degree of freedom for decoupling the power demanded of the fuel cell stack from the power required by the load. This is a powerful result as it allows protection of the fuel cell stack from potentially degrading dynamic or excessive electric loading as well an opportunity for stack monitoring schemes such as EIS. Moreover, in the event that any load-demand imparted degradation is recoverable by eliminating the degrading element of the load-demand, then the additional degree of freedom can be exploited within a load-end control scheme.

With that goal in mind, this chapter details load-induced degradation tests performed to correlate the electric terminal performance of SOFCs with mechanisms for degradation. Perhaps the most interesting observation from these tests is that some electric terminal performance degradation is reversible, and that under certain operating conditions the fuel cell under test is able to recover to partial or full pre-degradation levels in terms of its electrical performance. The results from these degradation and recovery tests are analyzed in depth to gain insight into the implications of electric loading on cell performance and to develop models of cell degradation useful for determining control schemes aimed at mitigating degradation during cell operation.

Anode Oxidation and Reduction

For solid oxide fuel cells employing a Ni-YSZ cermet as the anode material, the nickel serves two functions. First, the nickel improves the electronic conductivity of the anode which would otherwise be very low as YSZ is a poor electronic conductor.

This reduces the ohmic losses in the cell (V_{ohm} in (2.4)). Second, the nickel acts as an electrocatalyst in the oxidation of the hydrogen fuel. This reduces the cell's over potential losses associated with anode activation (V_{act} in (2.4)).

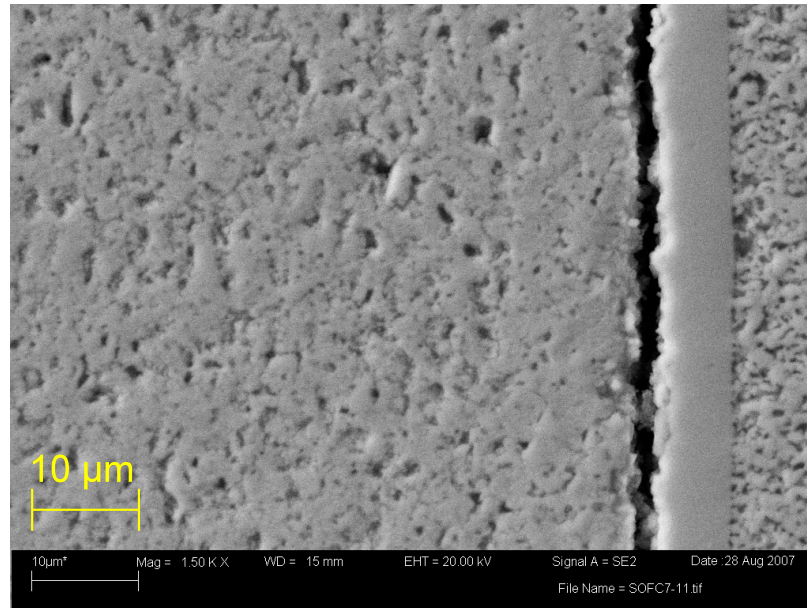
During cell manufacturing, typically the anode cermet is sintered in an oxidizing atmosphere so that the anode is comprised of NiO-YSZ [4]. Then, during cell startup, the anode is reduced to Ni-YSZ prior to operation by supplying hydrogen fuel to the cell. The hydrogen readily accepts the oxygen ions, generating water, and in turn reducing the nickel. This reduction is accompanied by a volumetric decrease in the nickel particles, which increases the porosity in the anode for facilitating adequate gas diffusivity to the anode / electrolyte boundary.

However, during cell operation, the current drawn by the load causes oxygen ions to diffuse through the electrolyte from the cathode to the anode, which can lead to reoxidation of the nickel if there is an insufficient amount of hydrogen fuel present at the anode / electrolyte interface. This reoxidation of nickel results in a decrease in the catalytic efficiency of the fuel oxidation as well as an increase in the resistivity of the cell. Additionally, the reoxidation results in a volumetric expansion in the nickel particles beyond the initial oxidized situation [92], which can cause stress to the cell. In the extreme case, e.g. when there is a disruption in the fuel supply or excessive current is demanded by the load, this stress can cause irreversible mechanical failures in the cell such as a delamination of the active anode layer from the electrolyte and fracturing of the electrolyte [62,63]. Even in the less extreme case where no irreversible damage to the cell occurs, the electric terminal performance of the cell decreases due to the higher losses associated with reduced anode activity and increased impedance.

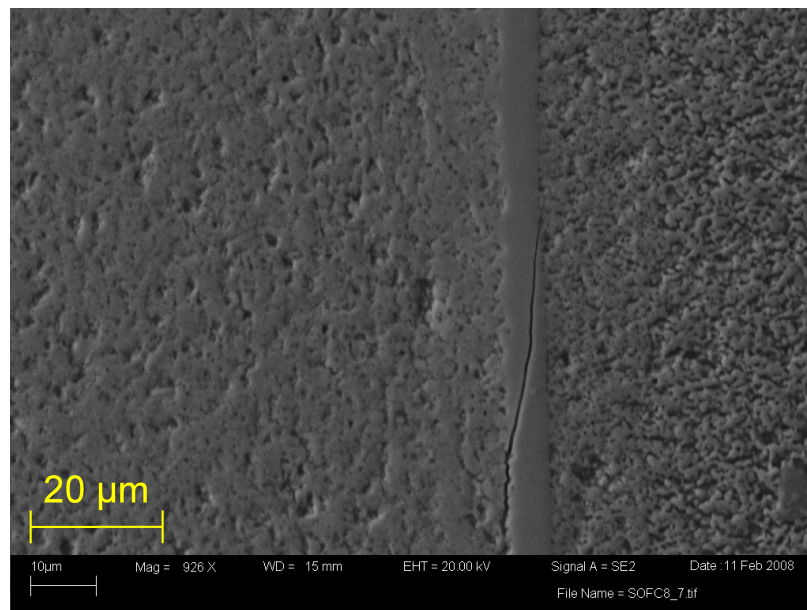
Electric Terminal Induced Degradation and Recoverability

In previous SOFC electric terminal characterization testing performed in Dr. Shaw's lab by former graduate student Xuelei Hu, the DC electrical conditions leading to fuel cell degradation were investigated. In these tests, InDec ASC3 SOFC cells, the same cell type used in this research project, were subjected to severe loading conditions enforced by clamping the cell's generated voltage to near-zero and in some cases sub-zero voltage levels. During the more severe tests, when the fuel cell's voltage was clamped to sub-zero voltage levels, the fuel cell experienced enough reoxidation of the nickel in the anode to cause irreversible degradation.

Figure 6.1 shows images of two representative examples of irreversible degradation often observed during post-test SEM analysis of these cells. In these images, the anode region is shown on the far left, the cathode on the far right, and the thin, dense electrolyte layer is shown in the middle. The scale bar on the bottom left of the images gives an indication of the image magnification. In the top photo, the active anode region is shown to have delaminated from the dense electrolyte, while in the bottom photo, this delamination is shown to have spread into the electrolyte causing a fracture through the entire electrolyte. Both examples of degradation are believed to have been induced by the anodic nickel expansion causing stress on the cell. In the case of the delamination, the electrochemical efficiency of the fuel cell is negatively affected due to the reduction in the effective active triple-phase interfacial area at the anode-electrolyte. In the case of the electrolyte fracturing, in a localized area, the effective partial pressures of the cell reactants on each side of the electrolyte are decreased as the crack in the electrolyte allows gasses to bleed through and combine without releasing electrons to the external circuit. In terms of the cell's electrical characteristics, these forms of irreversible degradation result in a permanent increase



(a) Anode Delamination from Electrolyte



(b) Fracture in Electrolyte

Figure 6.1: Examples of irreversible degradation to the fuel cell caused by high current loading. The anodic expansion due to nickel oxidation causes stress on the cell resulting in the (a) delamination of the anode from the electrolyte, and (b) fractures in the thin electrolyte.

in the internal impedance of the cell and thus a decrease in the converted power available for the load.

Effects of Degradation and Recovery on DC Electrical Performance

Even when the electrically induced reoxidation of the anode nickel does not result in mechanical failure in the cell, a degradation in the electrical performance of the cell does occur under sufficient loading due to the reduced catalytic activity and increased resistance of the reoxidized nickel. To monitor this sort of degradation, periodic voltammetry tests measuring the quadrant I polarization relationship of the cell were performed at 20 minute intervals throughout the degradation experiment.

During some cell tests, following periods of significant load-induced degradation, the cell was allowed to “rest” under open circuit conditions for several hours. During this time, fuel and oxygen were still supplied to the anode and cathode, respectively. However, in the absence of a current demand from the load, the ionic oxygen supply to the anode ceased allowing the anode nickel to re-reduce. This resulted in a recovery in the electrical performance, which was reflected by an improvement in the measured polarization curves.

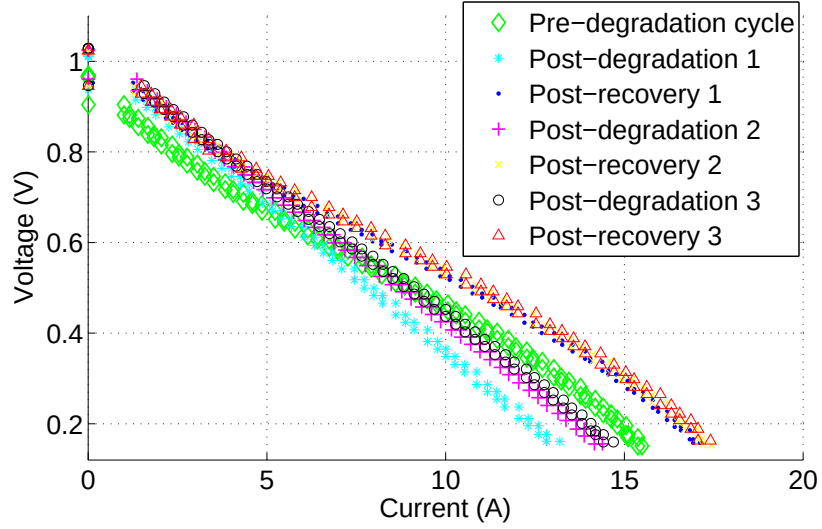
Figure 6.2 shows select measured polarization curves from one such test along with the profile of the large-signal cell resistance parameter, R_{th} , achieved by fitting a Thevenin equivalent model, i.e.

$$V_{fc} = V_0 - I_{fc}R_{th}, \quad (6.1)$$

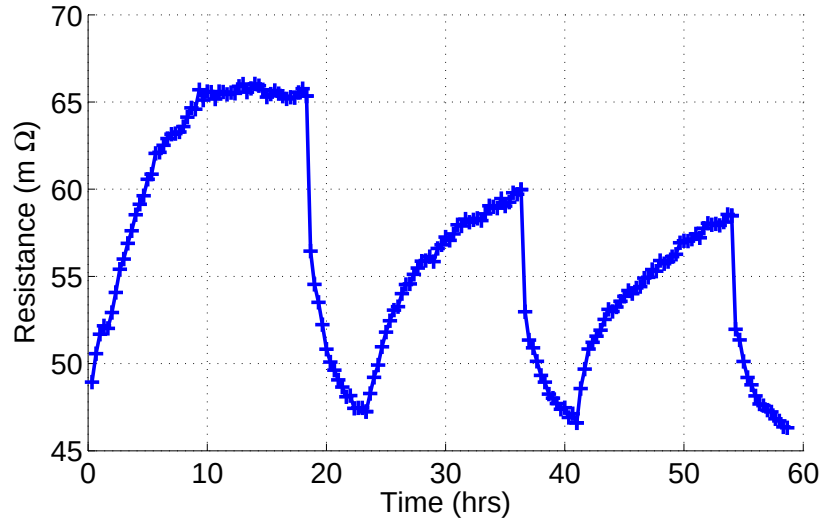
to each polarization curve measured during the test. In (6.1), V_{fc} and I_{fc} represent the measured fuel cell voltage and current, and V_0 and R_{th} represent the equivalent open circuit voltage and large signal DC resistance of the cell, respectively.

For this test, the cell underwent 3 cycles of heavy loading and open circuit operation. During the periods of heavy current loading, the fuel cell's generated voltage was clamped between 80 and 100 mV corresponding to a current draw initially around 16 A and decreasing to around 14 A as the cell degraded. These three periods of degradation lasted for 18.7 hours, 13 hours, and 13 hours, respectively. In between, the cell was allowed to recover under open circuit conditions for periods of 5 hours, 4.67 hours, and 4.67 hours, respectively.

The polarization curves shown in Figure 6.2a correspond to the curve measured just prior to the commencement of cell testing, those measured at the end of each degradation period, and those measured following each recovery period. From this plot it is easy to see that the electrical performance of the fuel cell decreases significantly during the periods of current loading. For a given operating voltage, the amount of current available to the load following the periods of heavy loading is significantly less than the amount of current available to the load following the periods of cell recovery. In terms of the cell's available maximum power, following periods of rest, the cell showed an average improvement of 24%. It should be noted that the initial polarization curve measured prior to cell testing shows an electrical performance closer to the degradation curves than the recovered curves. This is possibly due to the anode not having fully reduced during the initial four hour resting period following cell startup. Additionally, other researchers have reported observing a cathodic activation process associated with initial current loading [93]. However, this sort of prolonged activation was not always observed in our experiments, particularly when a cell's initial resting period was extended well past four hours.



(a) Polarization Curves



(b) Large Signal Resistance

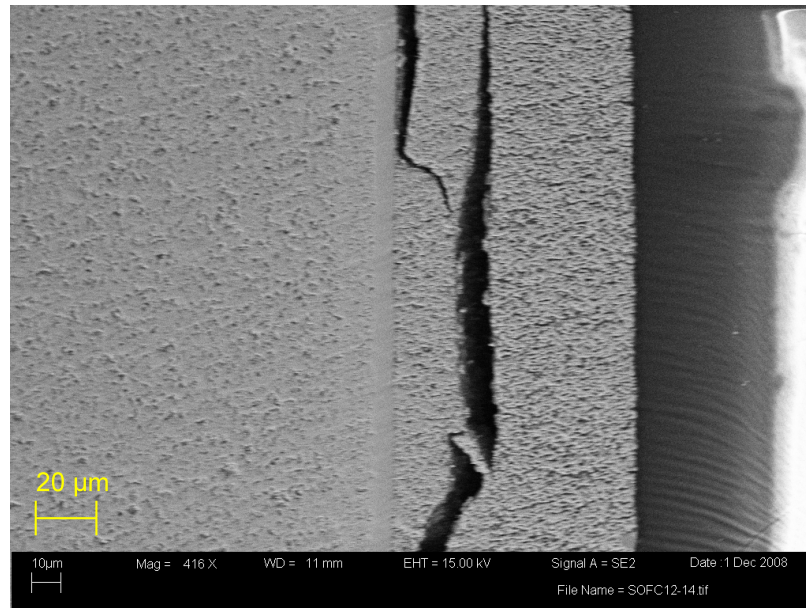
Figure 6.2: Voltammetry test results of the degradation and recovery cycling of the SOFC. On top, the measured polarization curves immediately preceding and immediately following alternating degradation and recovery cycles are shown. On the bottom, the Thevenin equivalent large-signal resistance fits of the polarization curves shows the impedance cycling of the cell.

Figure 6.2b shows the progression in the large signal resistance of the fuel cell during the periods of degradation and recovery. Found by fitting a Thevenin equivalent model to each of the polarization curves obtained during the cell's test, the resistance value of each data point indicates the slope of a linear fit of the corresponding polarization curve.

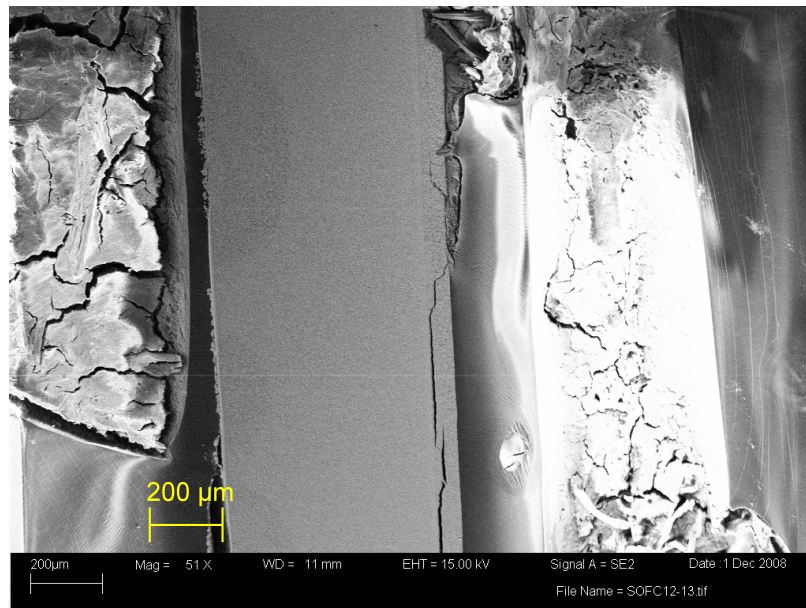
Finally, Figure 6.3 shows a low magnification and high magnification image of the cross-section of the cell used in Hu's degradation and recovery experiment [94]. While no significant anode irreversible damage was observed, massive cracks were observed in the cathode. However, Hu postulated in his report of this test that these cracks possibly developed post-test and not during the time the cell was under operation. According to his report, following the cool down procedure, the cell may have been damaged during removal from the oven, or during the SEM-prep polishing procedure as the cell sample was dropped. In this author's opinion, it is highly likely that this damage occurred post test because damage that severe should show more significant degradation in the fuel cell's electrical terminal performance.

Effects of Degradation and Recovery on AC Electrical Performance

The fuel cell tests performed by Xuelei Hu were the first in our lab to indicate that some amount of SOFC electrical performance degradation is reversible. However, during these tests, only voltammetry measurements were performed. As such, only an increased understanding of the degradation and recovery effects on a fuel cell's large-signal DC electrical operation was achieved. During the HSPM case study described in the previous chapter, initial observations of the effects of load-driven degradation and recovery on EIS measurements were made (Figure 5.12). An additional test, described here, was performed to expand on this initial observation with a goal of



(a) Cathode Cracking 416x Magnification



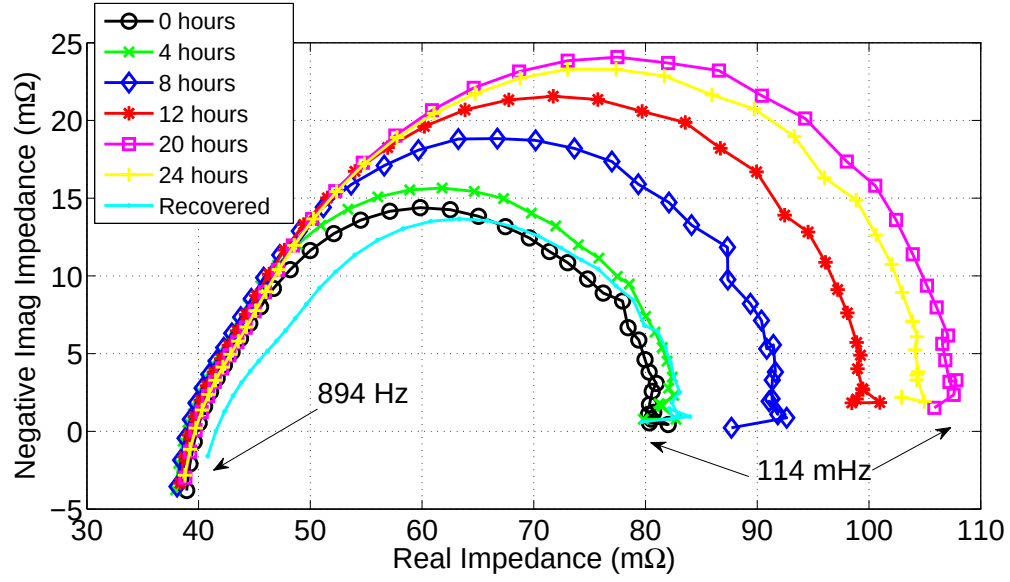
(b) Cathode Cracking 51x Magnification

Figure 6.3: SEM images showing a massive crack in the cathode following the fuel cell degradation and recovery test performed by Xuelel Hu. No anode degradation was observed. In his report on this test, Hu postulated that these cracks likely occurred post test due to difficult removal of the cell from the oven or the sample being dropped during the polishing procedure.

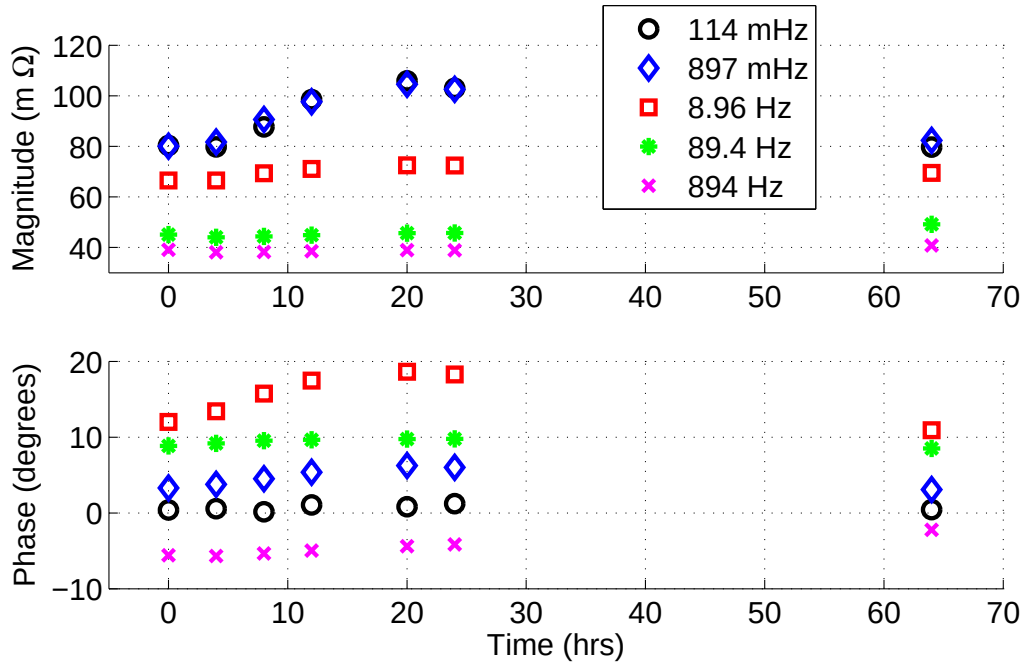
providing information on the progression in impedance measurements as the fuel cell degrades.

For this test, an SOFC fuel cell was used in conjunction with the reference simulator system of Chapter 3, with the simulated stack (set to a stack height of 20 cells) connected to a programmable electronic load. The load, operated in voltage control mode, was clamped at 4 V, or 200 mV / simulated cell. This corresponded to an initial current draw of 11 A, with the current decreasing to around 9 A as the fuel cell degraded. It should be noted that these current measurements were significantly lower than those observed during the fuel cell testing performed by Hu. This is due to a difference in the location of fuel cell voltage measurements between tests. Hu used thin platinum wires connected directly to the SOFC electrodes for measuring voltage, while voltage measurements for this test were made at the reference simulator's input terminals as that is the voltage referenced for stack simulation. Thus, the effective fuel cell resistance here was increased to include that of the Inconel platens, copper lugs and wires used to connect the cell to the reference simulator.

Figures 6.4 - 6.6 show the achieved impedance profile progressions at three different DC operating points: $V_{fc} = 670$ mV, $V_{fc} = 430$ mV and $V_{fc} = 200$ mV, respectively. Impedance measurements, performed using the EIS measurement method of Chapter 4, were performed at these three DC operating points several times over a 24 hour period as the fuel cell degraded and then again following a 40-hour period of open-circuit cell recovery. On the top plot of these figures, the full impedance profiles achieved at these time periods are shown on the complex plane, while on the bottom plots, the impedance magnitude and phase value progressions are shown for the excitation frequencies of 114 mHz, 897 mHz, 8.96 Hz, 89.4 Hz, and 894 Hz. The excitation signal used for all impedance measurements was a swept sinusoid ranging in frequency from 100 mHz to 1 kHz over 175 seconds.

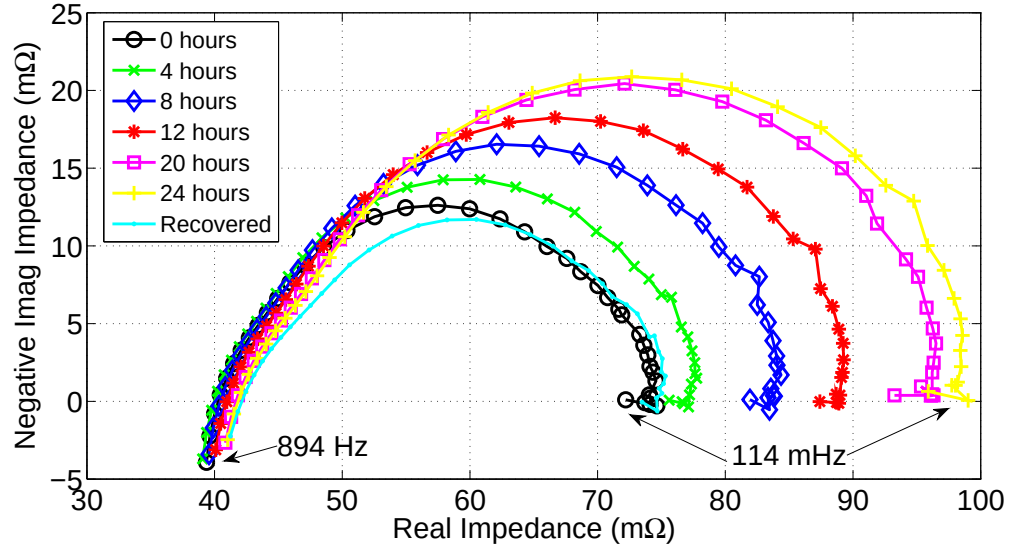


(a) Complex Plane Profile

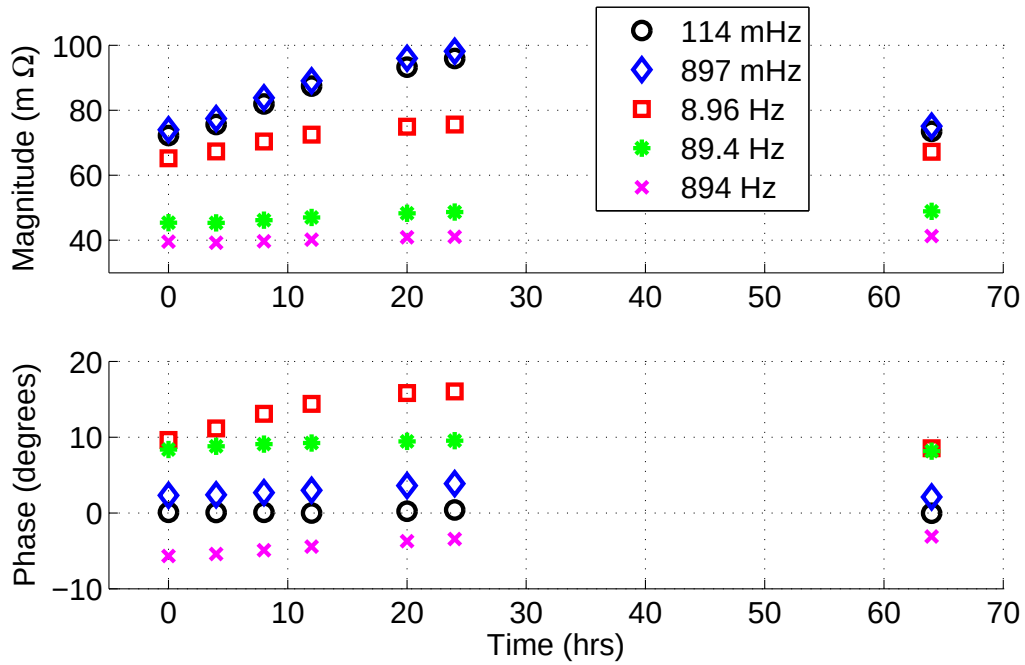


(b) Magnitude and Phase Profile

Figure 6.4: Progression in impedance profile measurements taken with the EIS bias voltage set to $V_{DC} = 670$ mV.

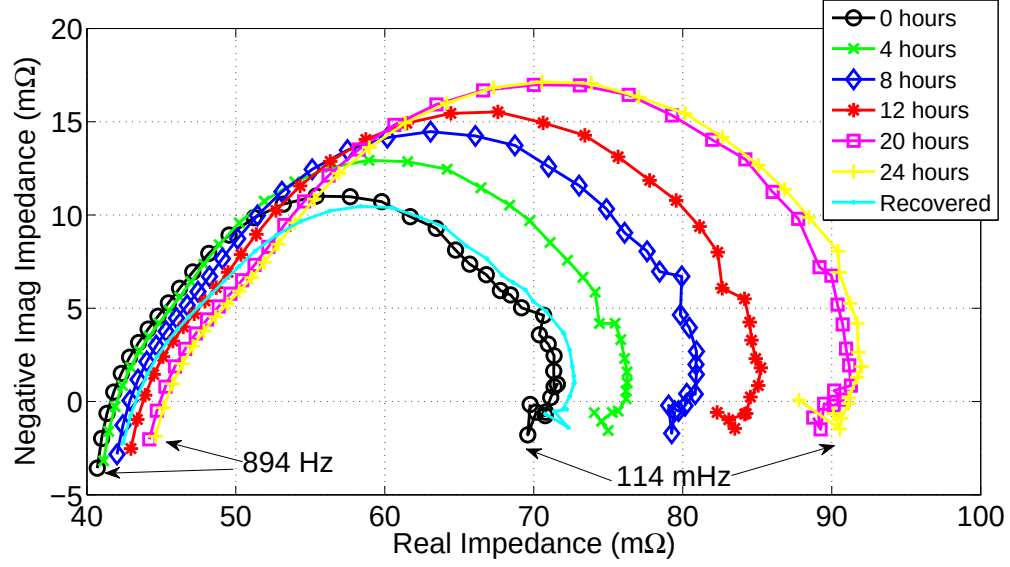


(a) Complex Plane Profile

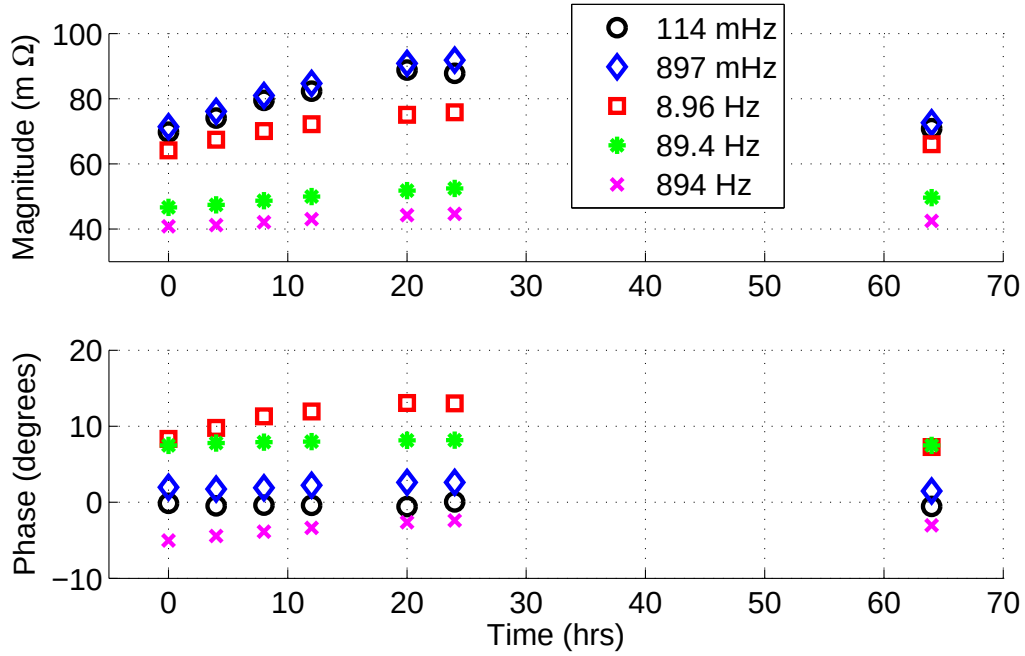


(b) Magnitude and Phase Profile

Figure 6.5: Progression in impedance profile measurements taken with the EIS bias voltage set to $V_{DC} = 4300$ mV.



(a) Complex Plane Profile



(b) Magnitude and Phase Profile

Figure 6.6: Progression in impedance profile measurements taken with the EIS bias voltage set to $V_{DC} = 200$ mV.

These impedance profile progressions confirm that the low frequency impedance measurements are most affected by excessive current-induced degradation, which was originally observed in comparing the degraded and recovered impedance profiles of Figure 5.12 measured during the HSPM case study of Chapter 5. At all three DC operating points here, $V_{fc} = 670$ mV, $V_{fc} = 430$ mV and $V_{fc} = 200$ mV, the lowest frequency (114 mHz) impedance measurements progressed along the real axis 22.6, 23.7 and 20.0 m Ω , respectively. This is a larger total magnitude shift than what was estimated by fitting a Thevenin equivalent to the polarization curves from Hu's experiment (Figure 6.2, Table 7.1). However, those polarization curve fits were performed across the entire curve including the low current regions where little change in the polarization curve occurs during degradation. Thus, the progression in large signal resistance estimates should not be expected to align well with the progression in low frequency impedance measurements of the EIS profiles.

It is also important to note that a simultaneous activation process was not observed during the degradation measured in this test unlike in Hu's experiment. This is likely due to an aborted degradation and recovery test that was performed using this particular fuel cell prior to the successful one reported here. During this aborted test, which was aborted due to incorrect operation of the DAQ, the cell was operated under the degrading conditions for several hours before being allowed to return to a recovered state through several hours of open circuit operation. Thus, any anode and cathode activation processes likely completed during this period.

Figure 6.7 shows an SEM image representative of those taken of the cell used in this degradation and recovery test involving EIS measurements. No significant damage to either the anode or cathode was observed.



Figure 6.7: SEM image showing the lack of any discernible irreversible degradation in the fuel cell used to achieve EIS measurements during load-driven degradation and recovery.

Linear Interpolation Analyses of Electric Terminal Measurements

Figures 6.2, 6.4 - 6.6 provide data useful in establishing empirically based relationships between SOFC degradation caused by excessive loading, and easily available electrical terminal measurements. By establishing these relationships, real-time electric terminal measurements can be used to estimate the degradation level of an SOFC cell or stack. Additionally, the data from these figures indicate that the electric terminal performance of the SOFC can be recovered by reducing the load-demand of the cell. Therefore, by establishing relationships between SOFC degradation levels and electric terminal measurements, these measurements can be used for real-time estimation of SOFC degradation and used as feedback in control systems aimed at controlling the amount of degradation occurring in the SOFC cell or stack.

In this section, a Linear Interpolation Analysis (LIA) is introduced and used to determine if the progression in the electrical terminal measurements of Figures 6.2, 6.4 - 6.6 follows a predominantly linear trend as related to cell degradation. If so, then these electric terminal measurements may be used for linear feedback within a control system for regulating the amount of degradation in the cell. Both polarization curve data and EIS data are analyzed with this method and both show predominantly linear relationships with cell degradation and recovery.

The purpose of the LIA is to determine how well measurements taken at an intermediate state of a system can be predicted as a linear combination of measurements taken at the extrema states of the system. That is, how well does the linear interpolator's predictor,

$$\hat{\mathbf{D}} = \mathbf{D}_i x_1 + \mathbf{D}_f x_2 \quad (6.2)$$

match the measured data, $\mathbf{D}$ corresponding to the intermediate state. In (6.2), $\mathbf{D}_i$ and $\mathbf{D}_f$ are data sets corresponding to the initial and final states of the system, respectively, and x_1 and x_2 are scalars defining the portion of the initial and final state data, respectively, used to estimate the intermediate state data $\mathbf{D}$. In this analysis, all data sets must have the same length, and indexed according to an independent variable common to all data sets, e.g. frequency for impedance measurements. For convenience, the initial state data is set to correspond to $x_1 = 1$ and $x_2 = 0$, and the final state data to $x_1 = 0$ and $x_2 = 1$.

The analysis works by solving for x_1 and x_2 in the linear least-squares sense, i.e.

$$\mathbf{x} = (\mathbf{A}_D^T \mathbf{A}_D)^{-1} \mathbf{A}_D^T \mathbf{D} \quad (6.3)$$

where $\mathbf{x} = [x_1, x_2]^T$ and $\mathbf{A}_D = [\mathbf{D}_i, \mathbf{D}_f]$. This achieves x_1 and x_2 which predict through equation (6.2), $\hat{\mathbf{D}}$ that minimizes the sum of the squared error,

$$SSE = (\mathbf{D} - \hat{\mathbf{D}})^2 \quad (6.4)$$

This sum of squared error can be normalized against an “absolute” sum of squared errors term for the defined system, i.e. the sum of squared errors between the extrema data sets, as

$$SSE_N = \frac{SSE}{SSE_{abs}}, \quad (6.5)$$

where SSE_{abs} is given by,

$$SSE_{abs} = (\mathbf{D}_i - \mathbf{D}_f)^2. \quad (6.6)$$

If this normalized error is small for all intermediate data, then the system is considered to progress predominantly linearly between the two extrema states.

For this study, the extrema states were defined as the least degraded state and most degraded state of the fuel cell, and both the polarization curve data and each of the impedance profile progressions were analyzed with this method. The intermediate levels of degradation can then be defined as a function of x_1 and x_2 , i.e.

$$\gamma = f(x_1, x_2). \quad (6.7)$$

One useful choice for this function is $\gamma = x_2$ with the added restriction that $x_1 + x_2 = 1$. This reduces the two-dimensional predictor of (6.2) to the single-dimensional one,

$$\hat{\mathbf{D}} = \mathbf{D}_i(1 - \gamma) + \mathbf{D}_f\gamma, \quad (6.8)$$

and the best fit prediction for this interpolator is found through the restricted least squares solution,

$$\gamma = ((\mathbf{D}_f - \mathbf{D}_i)^T (\mathbf{D}_f - \mathbf{D}_i))^{-1} (\mathbf{D}_f - \mathbf{D}_i)^T (\mathbf{D} - \mathbf{D}_i). \quad (6.9)$$

A graphical interpretation of the difference between these two predictors is shown Figure 6.8. This plot shows hypothetical one-dimensional and two-dimensional progressions in a fuel cell's impedance as the cell transitions from a non-degraded state (green circles) to a fully-degraded state (red pluses). The two-dimensional progression in impedance values, having less stringent restrictions, can follow any generalized contour from the non-degraded impedance values to the fully-degraded impedance values. The one-dimensional progressions on the other hand must follow a straight line from the non-degraded state to the fully-degraded state.

Application to Polarization Curve Data

As mentioned above in the description of the LIA, the data sets used must be of the equal length and indexed according to an independent variable. For the polarization curve data originally collected by Xuele Hu, the cell's potential was controlled and varied from open circuit to around 150 mV, with both current and voltage recorded for producing polarization curves. However, the step sizes in voltage were not consistent across all polarization curves resulting in data sets of different lengths and not uniformly indexed by voltage. Thus, performing the LIA on the raw data is impossible. Instead, each original polarization data set was fit with a 3rd-order polynomial function, which was then used to create a new pseudo-data set indexed by a uniform current vector ranging from 0 to 15 A in 0.1 A increments.

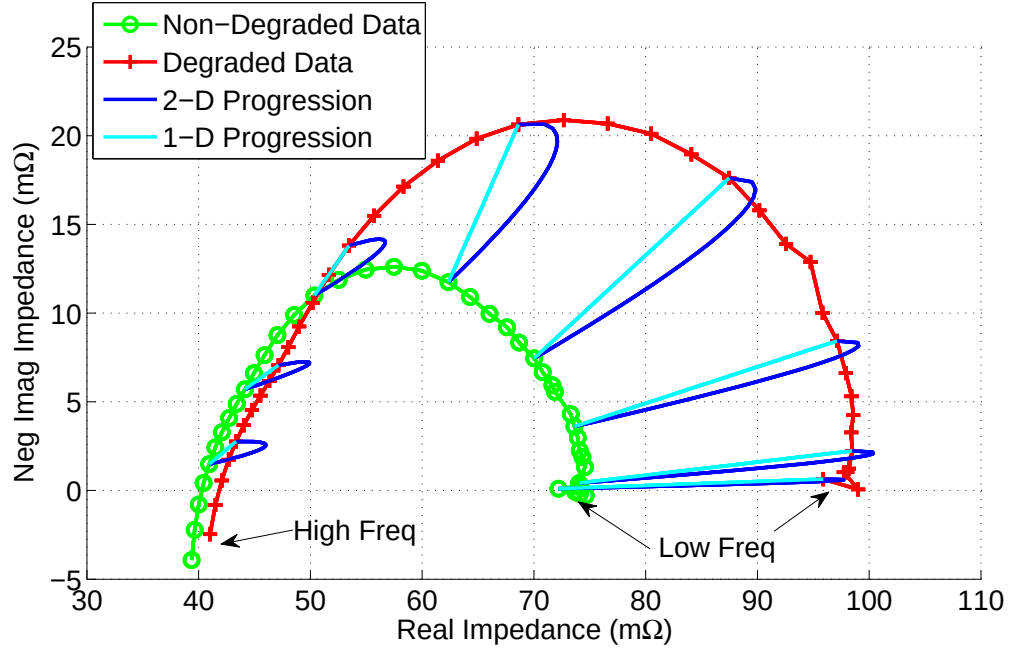


Figure 6.8: Conceptual two-dimensional and one-dimensional linear interpolation progressions. The two-dimensional progression can follow any general contour, while the one-dimensional progression is defined to follow a straight line progression.

For extrema data sets, the polynomial fits of the polarization curve following the first degradation cycle (light blue asterisks in Figure 6.2a) and the polarization curve following the final recovery cycle (red triangles) were chosen as they represented the most degraded and least degraded states of the cell. These data sets were collected at the 18 hour mark and the 58.33 hour mark, respectively. While an obvious choice for data representing the cell's least degraded state is the initial polarization curve prior to any degradation occurring, as mentioned earlier, there is one or more competing extended activation processes occurring during the first several hours of testing. Thus, the initial polarization data is not well representative of the least degraded state.

Using these extrema sets, all other measured polarization curve pseudo-data sets were analyzed using both the two-dimensional and one-dimensional analysis predictors. For SSE_N calculations, a subset of the originally measured current values

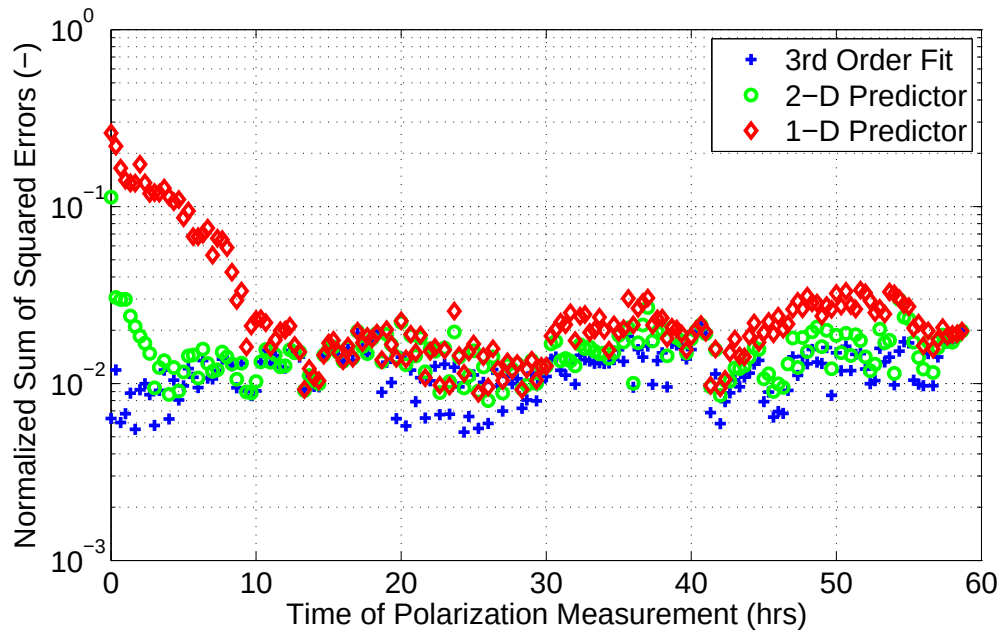


Figure 6.9: Comparison of the normalized sum of squared error values for the 3rd-order polynomial fits of the voltammetry test data with those for the two-parameter and one-parameter polarization curve predictions.

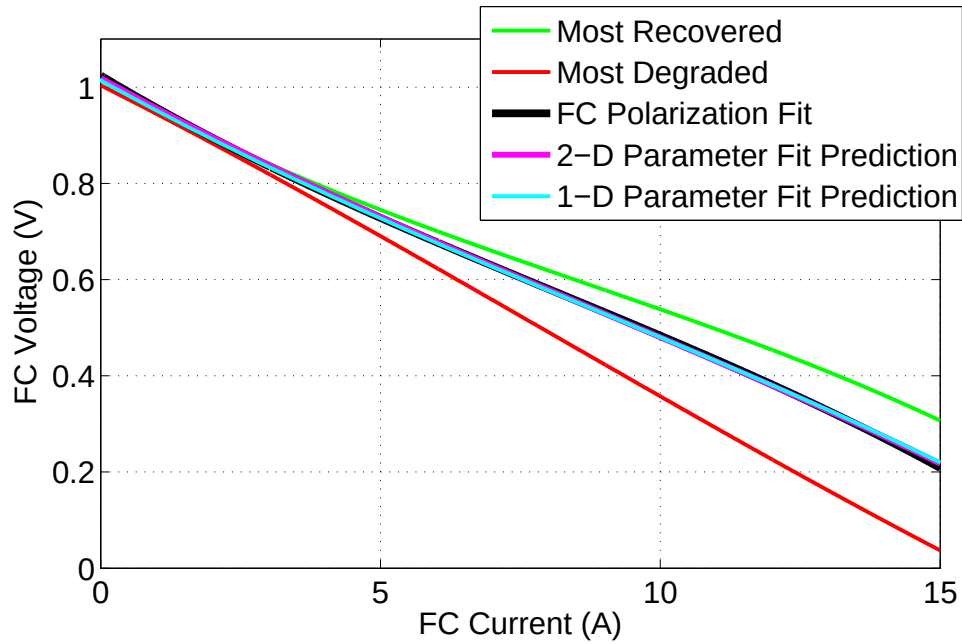


Figure 6.10: Comparison of the two-parameter and one-parameter polarization curve predictions with the 3rd-order polynomial fit of the measured polarization data collected at the 43rd hour mark of the degradation / recovery experiment.

corresponding to each data set was used with the interpolated 3rd order polynomial predictors to generate predicted voltages that are compared against originally measured voltage values. Because not all original data sets were of the same length, each SSE_N calculation was done with the number of data points in the smallest data set, with selected current values evenly distributed across the full range of original data current values. This allows meaningful relative SSE_N values between data sets.

Figure 6.9 shows plots of the calculated SSE_N for each polarization curve collected throughout the degradation and recovery test as well as the SSE_N for the 3rd order polynomial fit of each original polarization curve data set. For the polarization curves measured during the first 10 hours of the test, the one-dimensional predictions are very poor which leads to the large SSE_N values. However, after the 10 hour mark, these predictions are very accurate with SSE_N values similar to those of the polynomial fit. The fact that the one-dimensional interpolator performs poorly for data measured prior to the extrema datasets is not surprising as predicting these data sets actually represent an extrapolation rather than interpolation. Further, these initial SSE_N values are adversely affected by the activation processes that occur during the initial loading stages of the fuel cell, which compete with the degradation process in progressing the polarization data.

In contrast, aside from the first few polarization data predictions, the two-dimensional predictor does well in terms of matching a linear combination of the extrema polarization data to the initial polarization profiles as evident by the low SSE_N values. However, this is certainly a case of over fitting as the activation that is occurring during this time is not represented in the extrema polarization data.

The low SSE_N values measured following the most degraded extrema (18 hours) indicate that the polarization curve progressions as the cell degrades and recovers predominantly follows a linear trend that is well modeled by the one-dimensional

linear analysis predictor of (6.9). Figure 6.10 shows an example of the polarization curves predicted by the two-dimensional and one-dimensional analysis predictors compared to the pseudo-data generated from the polarization curve measurements. In this example, the 3rd order polynomial fit of the polarization data is shown in black, and the two-dimensional and one-dimensional predictions, shown in purple and light blue, respectively, show good matching to the fit data. This example is representative of the quality of the linear predictors for polarization measurements made following activation. A full portfolio of the predicted polarization curves for all data measurements are shown in Appendix A.

Application to EIS Profiles

Unlike with the polarization curve data collected by Hu, the impedance data of Figures 6.4 - 6.6 do not require preconditioning as each impedance profile is of the same length and indexed by the same excitation frequency values. However, in order to restrict the parameters such that $x_1, x_2, \gamma \in \mathbb{R}$, the impedance data was restructured into the vector form, $\mathbf{Z}_{\mathbf{fc}}' = [Re\{\mathbf{Z}_{\mathbf{fc}}\}^T, Im\{\mathbf{Z}_{\mathbf{fc}}\}^T]^T$, where $\mathbf{Z}_{\mathbf{fc}} = [z(\omega_1), z(\omega_2), \dots, z(\omega_N)]^T$, $z(\omega_k)$ is the complex impedance data point of profile $\mathbf{Z}_{\mathbf{fc}}$ corresponding to the k th excitation frequency, and N is the total number of impedance points in each profile. Each of the three DC operating point profile projections were analyzed independently using each 0 hour impedance data as representative of the least degraded state, and the 24 hour impedance data as representative of the most degraded state.

Figures 6.11 - 6.15 compare the predicted impedance profiles for the 4, 8, 12, and 20 hour measurements found through the one-dimensional and two-dimensional interpolation methods to the measured impedance profiles for the $V_{DC} = 430$ mV

DC operating point. Comparisons for the 0 and 24 hour measurements are not included as they are used to define the interpolators. Also shown in these figures are the extrema profiles for reference of the total full scale progression. For the four intermediate profile comparisons showing the progression in impedance as the cell degrades (Figures 6.11 - 6.14), the two-dimensional and the one-dimensional interpolator produce nearly identical predictions with both matching well to the measured impedance profile. This quality of matching is represented in the low SSE_N values for these predictors which are shown in Table 6.1 along with estimated values for parameters x_1 , x_2 , and γ . It is interesting to note that even though no restriction is placed on the relationship between x_1 and x_2 , the tendency of the best fit parameter values is for $x_1 + x_2 \approx 1$, with x_1 and x_2 values that are similar to the $1 - \gamma$ and γ values found in the one-dimensional predictions.

The one-dimensional and two-dimensional interpolator predictions for the recovered impedance data (Figure 6.15) are not as identical and do not match the measured impedance data as well as the intermediate data measurements of Figures 6.11 - 6.14. In comparing the measured recovered impedance data to the initial zero hour data, the low frequency impedance points match fairly well, while the high frequency impedance points tend to have a larger real component of impedance than the initial data. Thus, there is some hysteresis in the high frequency impedance measurements as the cell degrades and recovers, which results in increased error in the impedance profile predictions. Additionally, similar to the initial 20 hours of polarization data, this final impedance profile represents an extrapolation rather than an interpolation since the measurement was taken outside of the two extrema profile measurements.

Still, while the SSE_N numbers are not as low as those for the intermediate data measurements, these numbers are still relatively small and at least for low frequency impedance measurements, the two-dimensional and one-dimensional predictors do

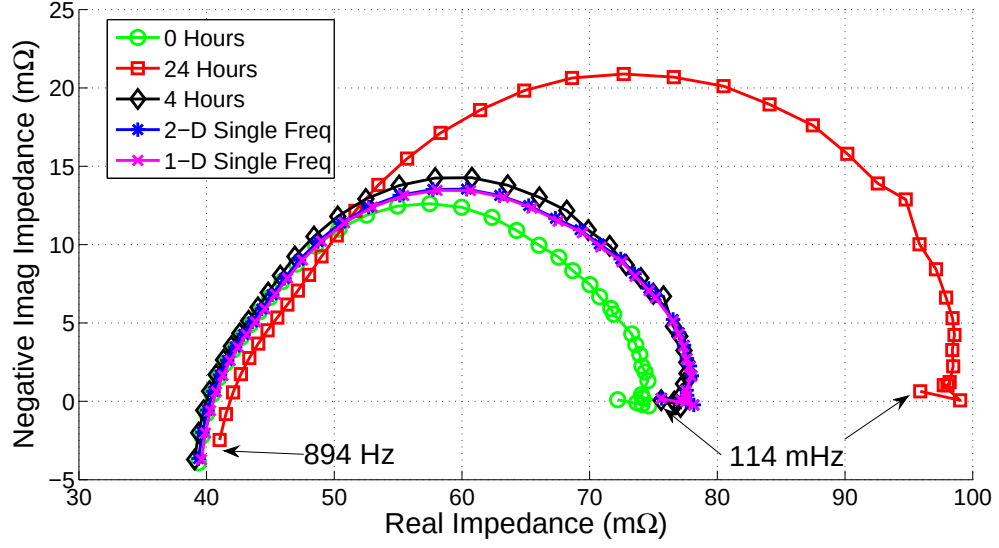


Figure 6.11: Comparison of the one-dimensional and two-dimensional linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 4 hours of degradation.

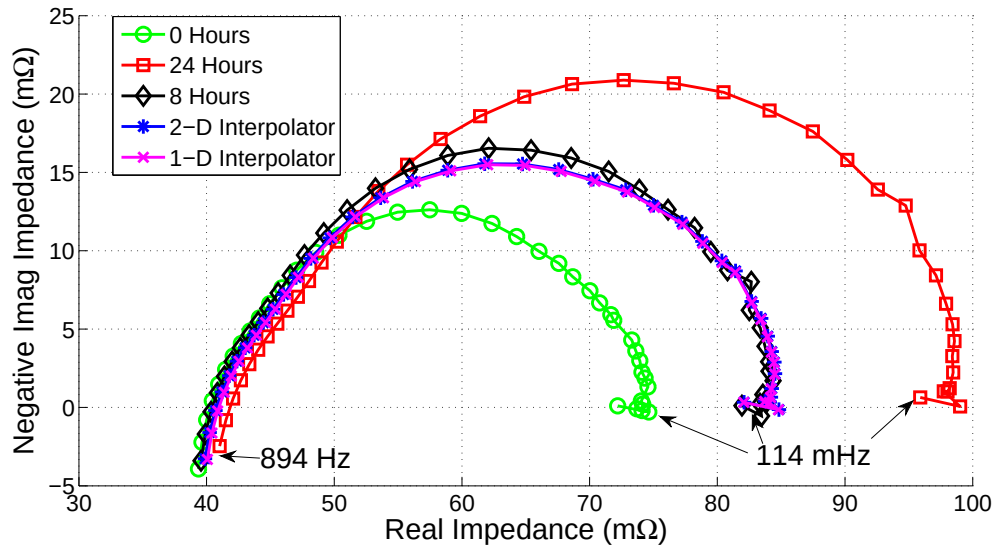


Figure 6.12: Comparison of the one-dimensional and two-dimensional linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 8 hours of degradation.

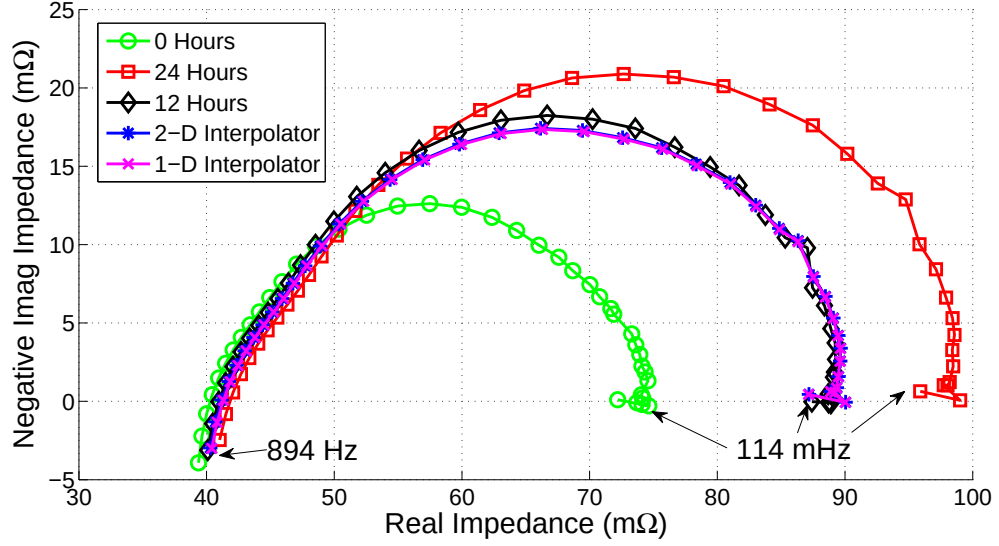


Figure 6.13: Comparison of the one-dimensional and two-dimensional linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 12 hours of degradation.

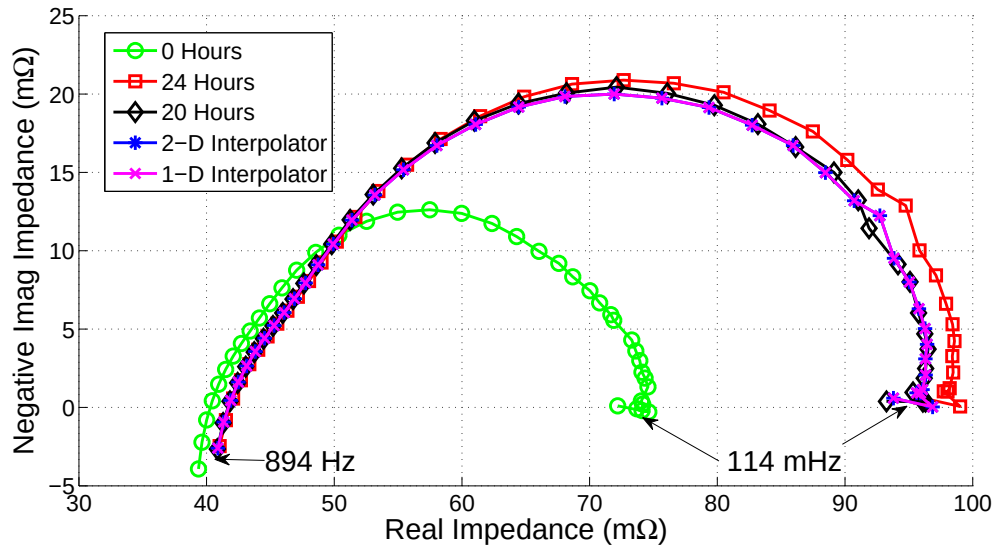


Figure 6.14: Comparison of the one-dimensional and two-dimensional linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 20 hours of degradation.

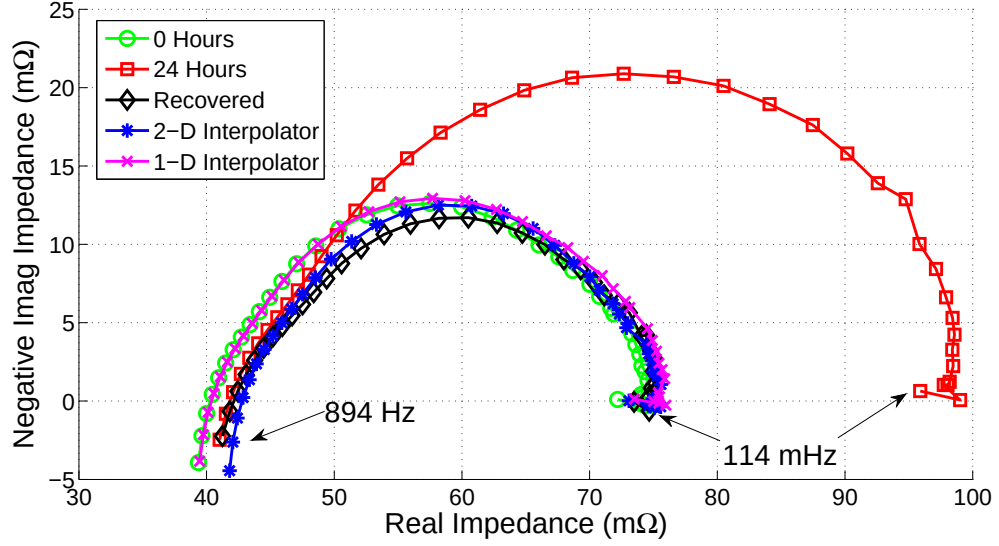


Figure 6.15: Comparison of the one-dimensional and two-dimensional linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after a 24 hours of degradation and 40 hours of degradation.

match the measured impedance fairly well. Similarly to the polarization predictions pre 20 hours, the fact that the two-dimensional predictor matches better than the one-dimensional predictor is a product of the extra parameter which allows over fitting of the data.

Finally, it is important to note that the best fit parameter values for both the two-dimensional (x_1 and x_2) and one-dimensional (γ) predictors, vary by up to about 20% full-scale between the three DC operating points. For example, at the 4 hour mark, the estimated γ values for the 670 mV operating point and the 200 mV operating point are 6.2% and 24%, respectively. This indicates that while the progression in impedance values follows a general linear trend, the rate of change in impedance values as a function of degradation might vary throughout the degradation process and between DC operating points. Still, this analysis shows that a reasonable approximation of the level of cell degradation is afforded through the measurement of the cell's impedance

		2-D Model			1-D Model		
Time	V_{DC}	x_1	x_2	SSE_N	$1 - \gamma$	γ	SSE_N
4 Hours	670 mV	0.84	0.14	0.0015	0.94	0.062	0.0046
	430 mV	0.83	0.17	0.0012	0.86	0.14	0.0014
	200 mV	0.70	0.29	0.0015	0.76	0.24	0.0018
8 Hours	670 mV	0.48	0.51	0.0036	0.54	0.46	0.0047
	430 mV	0.56	0.43	0.0022	0.58	0.42	0.0023
	200 mV	0.45	0.53	0.0015	0.53	0.47	0.0021
12 Hours	670 mV	0.16	0.83	0.0011	0.21	0.79	0.0018
	430 mV	0.35	0.64	0.0018	0.37	0.63	0.0018
	200 mV	0.26	0.72	0.0011	0.33	0.67	0.0016
20 Hours	670 mV	-0.12	1.1	0.0010	-0.098	1.1	0.0012
	430 mV	0.089	0.91	0.00057	0.089	0.91	0.00057
	200 mV	-0.021	1.0	0.0009	0.041	0.96	0.0013
Recovered	670 mV	1.2	-0.16	0.0065	0.92	0.08	0.039
	430 mV	1.2	-0.17	0.0036	0.95	0.055	0.021
	200 mV	1.2	-0.18	0.0032	0.90	0.10	0.0155

Table 6.1: Best-fit parameter values for the one-dimensional and two-dimensional linear interpolation models.

through the electric terminals. The linear interpolation predictions for the $V_{DC} = 670$ mV and $V_{DC} = 200$ mV operating points are available in Appendix B.

Single-Frequency Interpolation Analyses

For a final analysis involving the linear interpolation analysis, impedance measurements at individual frequencies were used in the prediction of the entire impedance profile. Here, D_i and D_f in (6.2) and (6.8) were set to the impedance values from the extrema profiles corresponding to an individual excitation frequency. Parameters x_1 , x_2 and γ were then found and used to predict the rest of the impedance values in an impedance profile. This process was performed at each frequency and across all three DC operating points, and the total sum of squared errors at each frequency was calculated. Additionally, a third model where D_i and D_f are set to the magni-

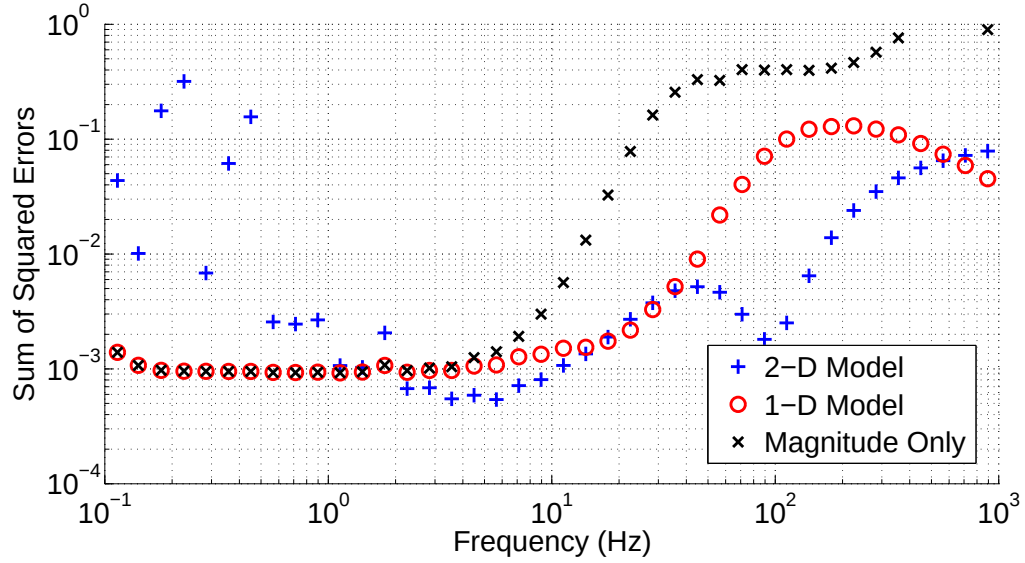


Figure 6.16: The sum of squared errors corresponding to parametric interpolation using individual-frequency impedance progressions.

tude of the individual impedance points was used to solve for γ , with the prediction and *SSE* calculation process also performed. γ for this model is found as the ratio of the difference in magnitude between the intermediate impedance point and the initial impedance point, and the difference in magnitude between the two extrema impedance points, i.e.

$$\gamma = \frac{|z(\omega)| - |z_i(\omega)|}{|z_f(\omega)| - |z_i(\omega)|}. \quad (6.10)$$

Figure 6.16 shows these *SSE* values at each frequency for all three models. Those found using the one-dimensional and the magnitude-based interpolation models show a clear trend with the quality of the impedance profile predictions based on low frequency impedance measurements being far superior to those determined by high frequency impedances. This is to be expected considering that the low frequency impedance measurements are far more affected by the load-induced degradation, and thus there is greater resolution in detecting degradation at these frequencies.

The trend is less clear though from the two-dimensional SSE values with those at low frequencies displaying high values and large variability. This can be explained by considering the implications of reducing the total information in the two-dimensional interpolation model. By substituting $|z_i(\omega)|$ and $|z_f(\omega)|$ for D_i and D_f in (6.2), respectively, the system is no longer overdetermined and exact solutions for x_1 and x_2 are found. With the impedance measurements exhibiting higher variability at low frequencies, x_1 and x_2 then can give a poor representation of the entire impedance profile resulting in large errors in the impedance predictions at other frequencies. As the frequency of excitation increases and the variability in the impedance measurements decreases, the calculated SSE values decrease and a minimum in the SSE values is seen at 5.65 Hz.

The one-dimensional and magnitude-based interpolators do not exhibit this poorly fit trend at low frequencies. For the one-dimensional case, the interpolator solves for γ the value that corresponds to the orthogonal projection of the measured impedance value at the excitation frequency onto a line that connects the two extrema impedance values. This is still an overdetermined system, and thus is not subject to as severe an over fitting. Additionally, any component of the variability in the low frequency impedance measurements that is parallel to the projection has no effect on the fit error. In the case of the magnitude-based interpolation, while the model is not overdetermined, the measured magnitude difference is transferred to the linear progression by the restriction of the one-dimensional parameterization, and similarly to the one-dimensional case, only the variability in impedance measurements that alters the measurement's distance from the initial impedance causes variability in the SSE_N values.

This single-frequency impedance interpolation analysis provides numerical insight into which frequencies of excitation are best observed for detecting degradation as

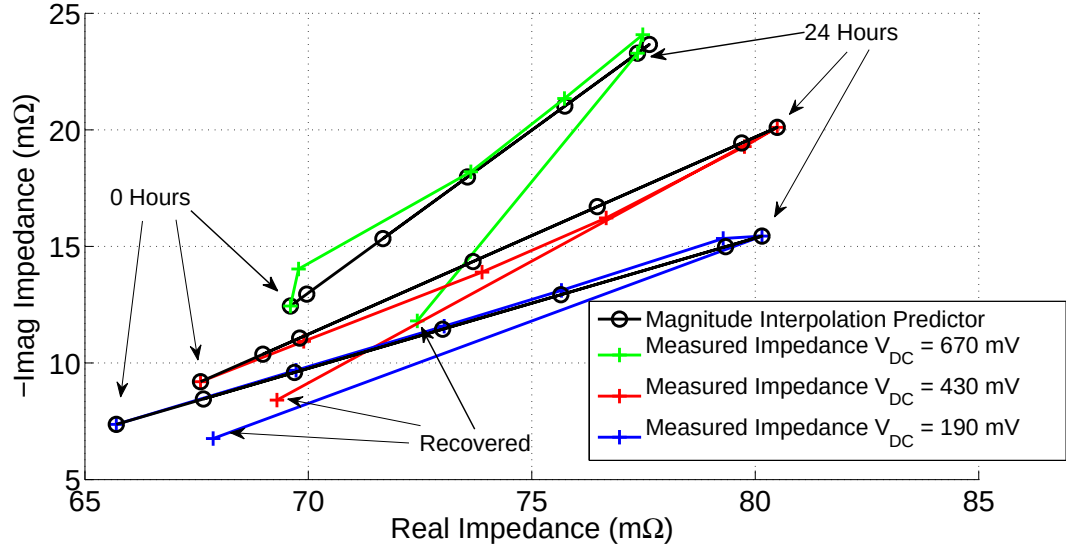


Figure 6.17: Comparison of the measured single frequency impedance progressions at 5.65 Hz to the impedance magnitude based interpolator.

well as how much impedance information is required. In regards to the load-induced degradation, Figure 6.16 suggests that measuring a change in the magnitude of the cell's impedance at a frequency within the range of DC to around 6 Hz provides roughly as accurate a measure of degradation as separately measuring the real and imaginary components of the impedance.

To illustrate the effectiveness of the magnitude-based interpolation, the impedance measurements at 5.65 Hz were used to determine x_1 , x_2 , and γ (for both the one-dimensional and magnitude-based interpolators). This frequency was used as it corresponds to the low point in the two-dimensional interpolator's *SSE* curve, as well as the “knee” point in the magnitude-based interpolator's *SSE* curve. As will be discussed in Chapter 7, there is a benefit to exciting the system with a frequency at the upper end of the accurate degradation detection region of the magnitude-based impedance measurements, and thus 5.65 Hz represents a good trade-off between detection accuracy and increased frequency of excitation.

Figure 6.17 shows the comparison of the measured single frequency impedance progressions at 5.65 Hz to the magnitude-based interpolator predictions for all three DC operating points. In this figure, the colored ‘+’ data points give the measured impedance data, while the black ‘o’ points show the corresponding interpolator predictions. These plots show that as the cell degrades, the impedance at this frequency does indeed follow the assumed linear trend. Following recovery however, the impedance measurements do tend to misalign with the assumed linear progression due to the hysteresis effect discussed earlier. This is most pronounced at the 670 mV DC operating point.

Figures 6.18 - 6.22 compare the full profile impedance predictions for the two-dimensional, one-dimensional, and magnitude-based single-frequency impedance interpolators for the $V_{DC} = 430$ mV operating point. In the figures containing the intermediate impedance measurements, the predictions based on the magnitude only measurement of impedance show profile matches the measured data similarly to those based on the full knowledge of the real and imaginary components of the impedance. Only in the case of the recovered impedance data does the magnitude based prediction deviate from the measured data due to the hysteresis, and even then this deviation is small compared to the full-scale progression in the impedance profile from zero-degradation to full-degradation.

Table 6.2 gives the found parameter values for the single-frequency impedance predictions along with the calculated normalized SSE_N for each impedance measurement time and across all DC operating points. As was the case with analysis using full EIS profile information, there sometimes is a large variance in parameter estimates between DC operating points. However, these differences are not significantly larger than those in the full profile analyses further indicating that the single frequency impedance measurement reveals significant information about the level of degrada-

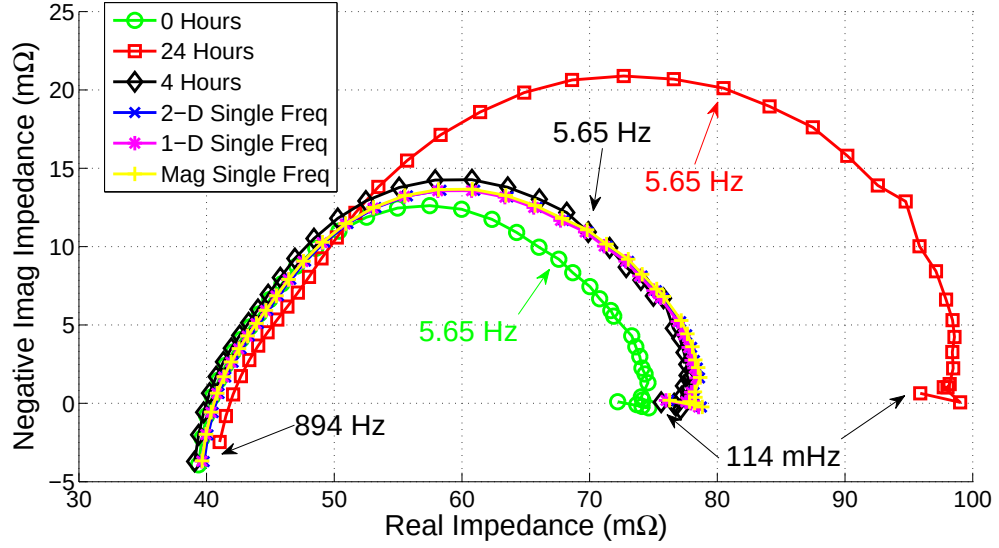


Figure 6.18: Comparison of the two-dimensional, one-dimensional and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 4 hours of degradation.

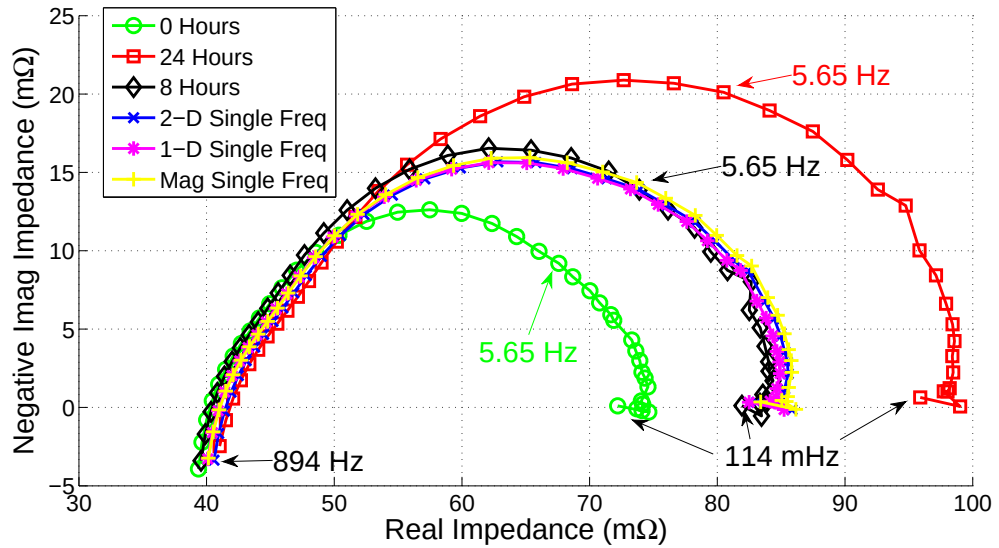


Figure 6.19: Comparison of the two-dimensional, one-dimensional and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 8 hours of degradation.

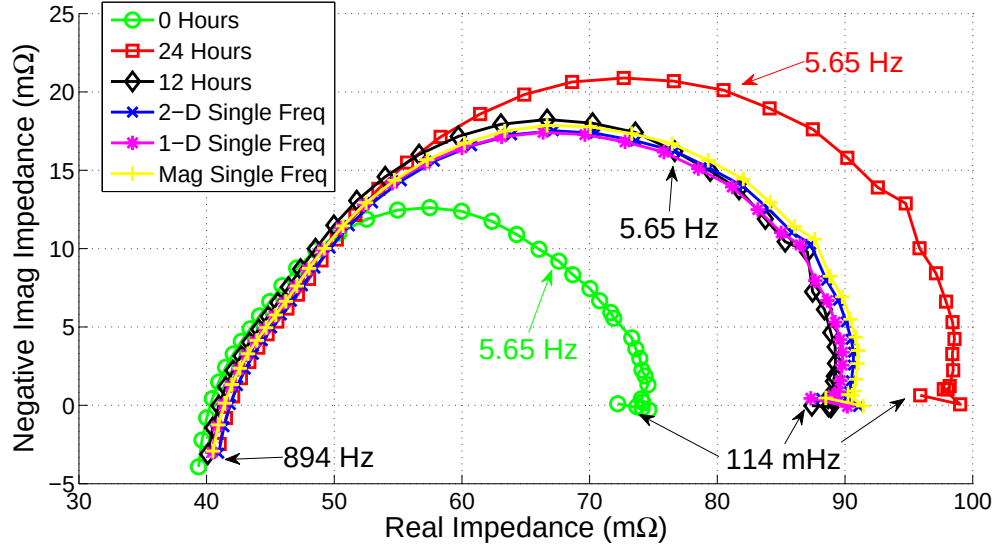


Figure 6.20: Comparison of the two-dimensional, one-dimensional and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 12 hours of degradation.

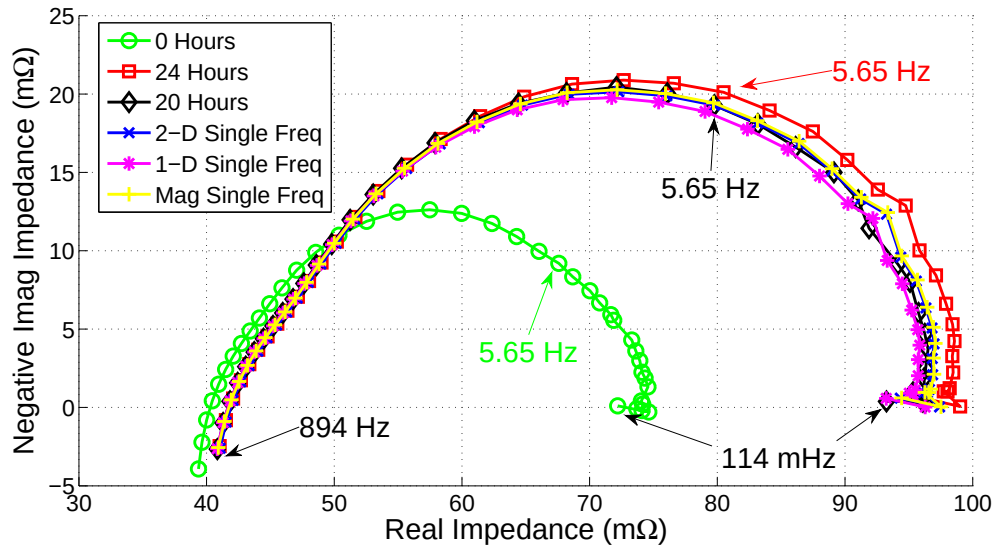


Figure 6.21: Comparison of the two-dimensional, one-dimensional and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 20 hours of degradation.

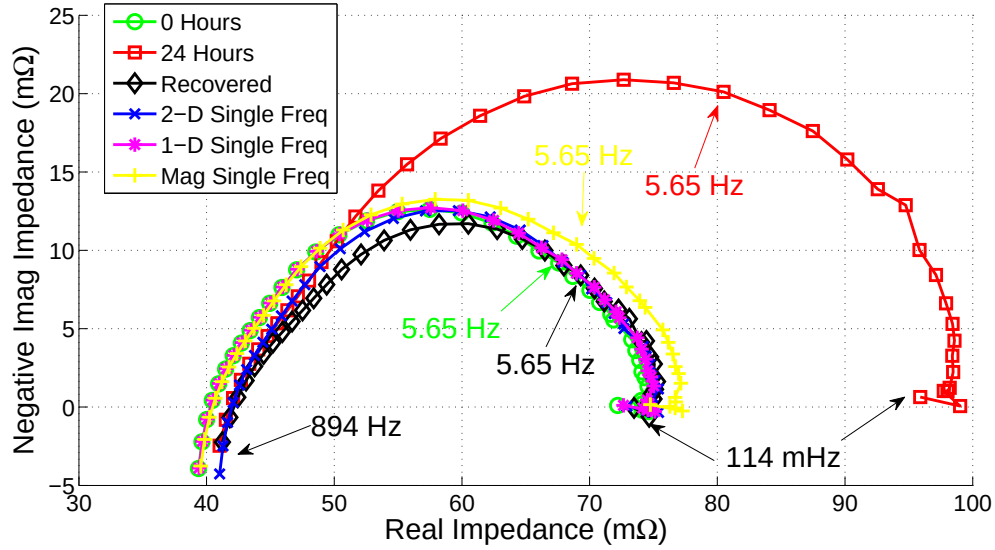


Figure 6.22: Comparison of the two-dimensional, one-dimensional and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 430$ mV after 24 hours of degradation and 40 hours of recovery.

tion in the cell. Figures showing the single-frequency linear interpolation predictions for the $V_{DC} = 670$ mV and $V_{DC} = 200$ mV operating points are available in Appendix C.

Chapter Summary

This chapter details the electric-load induced degradation of solid oxide fuel cells. This type of degradation is believed to be caused by the reoxidation of the anode-side nickel which leads to a decrease in the catalytic efficiency of the fuel oxidation as well as an increase in the resistivity of the cell. In turn, these effects result in a decrease in the cell's electric terminal performance. In the extreme case, as shown in Figure 6.1 the volumetric expansion that also accompanies the nickel oxidation results in an additional permanent degradation due to microstructural failure within the cell most often observed as a delamination of the anode from the electrolyte. However, in the

		Single Frequency 2-D Model			Single Frequency 1-D Model			Single Frequency Magnitude Model		
Time	V_{DC}	x_1	x_2	SSE_N	$1 - \gamma$	γ	SSE_N	$1 - \gamma$	γ	SSE_N
4 Hours	670 mV	0.82	0.16	0.0039	0.90	0.10	0.0064	0.95	0.047	0.0048
	430 mV	0.85	0.16	0.0025	0.84	0.16	0.0022	0.83	0.17	0.0022
	200 mV	0.71	0.29	0.0034	0.72	0.28	0.0036	0.72	0.28	0.0032
8 Hours	670 mV	0.47	0.53	0.0091	0.47	0.53	0.0092	0.49	0.51	0.0073
	430 mV	0.59	0.42	0.0056	0.57	0.43	0.0046	0.53	0.47	0.0055
	200 mV	0.47	0.53	0.0035	0.49	0.51	0.0039	0.49	0.51	0.0034
12 Hours	670 mV	0.17	0.81	0.0018	0.19	0.81	0.0021	0.21	0.79	0.0018
	430 mV	0.38	0.63	0.0050	0.36	0.64	0.0041	0.31	0.69	0.0051
	200 mV	0.28	0.72	0.0020	0.31	0.69	0.0024	0.31	0.69	0.0021
20 Hours	670 mV	-0.089	1.1	0.0029	-0.053	1.1	0.0032	-0.03	1.03	0.0053
	430 mV	0.084	0.92	0.0012	0.11	0.89	0.0011	0.06	0.94	0.0013
	200 mV	-0.012	1.0	0.0010	0.049	0.95	0.0013	0.056	0.94	0.0015
Recovered	670 mV	1.2	-0.12	0.0083	0.92	0.08	0.039	0.73	0.27	0.073
	430 mV	1.2	-0.11	0.0055	0.95	0.055	0.0207	0.89	0.11	0.024
	200 mV	1.2	-0.13	0.0035	0.98	0.019	0.016	0.87	0.13	0.017

Table 6.2: Best-fit parameter values for the single frequency two-dimensional, one-dimensional and magnitude-based linear interpolation models.

case that the current-loading is not so severe that the volumetric expansion results in microstructural failure, the tests detailed in this chapter show that the accompanying degradation in the cell's electric terminal performance is recoverable when the cell is allowed to "rest" at open-circuit. This recovery is attributed to the re-reduction of the anode-side nickel in the absence of ionic oxygen to the anode.

Tests involving both DC electric terminal measurements (Figure 6.2) and AC electric terminal measurements (Figure 6.4 - 6.6) were performed with the results here showing the associated effects of this degradation on the cell's electric terminal performance. Both sets of measurements were analyzed using a linear interpolation method to show that the progressions in these measurements predominantly followed a linear relationship with degradation. Further, the results of the linear interpolation analysis of single-frequency impedance measurements suggests that there is a range of frequencies between DC and 6 Hz where individual frequency impedance magnitude measurements provide a good measure of cell degradation levels.

That the degradation in an SOFC's electric terminal performance is recoverable by reducing the load-demand of the cell is a very important observation. If extrapolated to the performance of a full scale SOFC stack, the result adds an additional consideration for optimizing the stack's operation. That is, in addition to operating the stack based on considerations of load following, fuel utilization, and system efficiency, etc, the level of stack degradation can also be considered and potentially controlled, particularly if the stack is load connected as part of a hybrid-power source system. As discussed in Chapter 5, a hybrid-power source manager and system affords an extra degree of freedom which could be utilized for active control of the level of stack degradation through the buffering of the demanded load. For this, the results of the linear interpolation analyses are important as they suggest that electric terminal impedance measurements can be used for linear feedback within such a control system.

This latter result is explored in the next two chapters which detail two investigated methods of controlling an SOFC cell's level of degradation through the use of cell impedance measurements for feedback in the control of the cell's DC operation.

PULSE WIDTH MODULATED DEGRADATION CONTROL

The final aspect of this research project was to investigate opportunities and methods for using electrical terminal measurements for feedback within control schemes aimed at minimizing the amount of load-induced degradation occurring in a fuel cell system. Two types of control systems were proposed, designed, and tested, with the two systems based primarily on results and observations of Chapter 6. The first of these systems is a Pulse-Width Modulation (PWM) Control Strategy based on the degradation and recovery cycling observations of Figure 6.2. Under this strategy, the cell's operation is alternated between open-circuit and near-max power, and DC resistance measurements taken at the cell's electrical terminals are fed back to affect the timing of the alternation and to regulate the degradation and recovery cycling. The second of these systems is an Impedance Magnitude Based control strategy based on the linear impedance analysis of Chapter 6. This control strategy is discussed in Chapter 8.

The intent in experimenting with these control strategies is to explore the ability to affect the course of degradation in a cell through the monitoring of the cell's electrical characteristics and operational adjustments. Both of these control strategies require control over the cell's load, which is unrealistic in most real-world applications. However, the initial goal here is not to develop control schemes to be employed in the real world. Rather, the goal is to show the affecting of degradation through closed loop system operation. Ultimately, information gained here on the single cells can be applied in developing more realistic control schemes that can be developed for full scale stack and utilizing devices such as the HSPM system of Chapter 5 so that adequate power can continuously be delivered to a load while the stack is being monitored and controlled to avoid significant degradation.

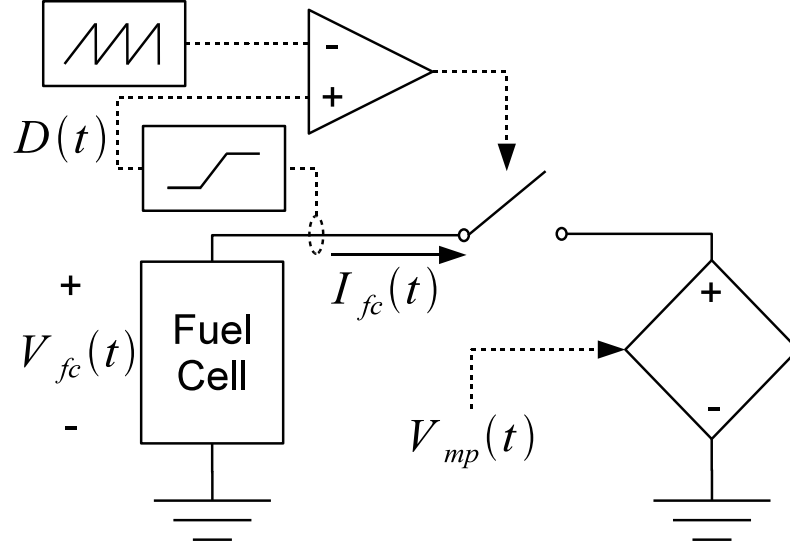


Figure 7.1: Conceptual diagram of the proposed duty-cycle control scheme aimed at limiting load-induced fuel cell degradation.

Pulse Width Modulation Control Strategy

The first investigation into degradation control of a single SOFC cell was designed to exploit the degradation and recovery cycling effects seen in Figure 6.2. In this scheme, a PWM based control system is implemented in an attempt to regulate the fuel cell's level of degradation. Under this type of control, the fuel cell repeatedly switches from operating under load near the cell's maximum power point and operating under no load. The cell's large-signal resistance is used as a measure of degradation, and the PWM duty cycle is determined through a negative-directly proportional relationship with this estimate of degradation. In this way, the portion of an operating period that the cell operates at open circuit increases as the amount of fuel cell degradation increases in order to facilitate a longer recovery. Alternatively, as the cell's impedance decreases indicating that the fuel cell's performance has recovered, the portion of time the cell is operated under load will increase in order to deliver more average power.

Figure 7.1 shows a conceptual layout of the duty cycle control scheme. The cell is connected to a controlled voltage source through a duty-cycle controlled relay. The controlled voltage source is set to hold the fuel cell near its maximum power point when the cell is operating under load. While the polarization relationship of a fuel cell is not strictly linear due to the activation and concentration electrochemical effects (as described in Chapter 2), these nonlinearities are relatively small and the cell's steady-state operation can be reasonably well modeled by a Thevenin equivalent circuit. With an open-circuit voltage of an SOFC under normal operating conditions around 1 V, the operating voltage at the cell's electric terminals corresponding to its maximum power point, V_{mp} , can be well approximated as 0.5 V.

Similarly, the cell's large-signal resistance estimate as defined by a Thevenin fit of the cell's polarization curve, is well correlated to the loading imposed on the cell when the electric terminal voltage is clamped at 0.5 V. Thus, a current measurement taken during the cell's closed circuit operation can be used directly in the feedback loop. This current measurement can then be transformed to a duty cycle set point, $D(t)$ through a linear transformation with maximum and minimum duty cycle constraints as shown in Figure 7.1. By comparing this duty cycle measurement to a sawtooth waveform, a digital signal is generated for controlling the relay.

Simulation Model

To illustrate the proposed operation of the duty cycle control system, a full-system simulation model was constructed in the MATLAB environment. This model consists of an empirically based solid-oxide fuel cell degradation model, a current to duty cycle set point transformer, a sawtooth waveform generator and comparator for implementing the control. The SOFC degradation model is a first-order linear model

that determines the polarization relationship of the SOFC at each time instance based on the results of the one-dimensional linear interpolation analysis of a cell's polarization curves described in Chapter 6. This model uses 3rd order polynomial fits of the most degraded and most recovered polarization curves of Figure 6.2 as representations of fully degraded and fully recovered fuel cells, respectively. Migration of the polarization relationship along the intermediate spectrum between these two extremes is interpolated according to a first-order linear relationship between current loading and degradation, with the dynamics of the model based on empirical measurements of degradation and recovery time constants. A more detailed explanation of the dynamic performance of this degradation model is given below.

The current to duty cycle set point transformer employs a negative-directly proportional relationship between fuel cell operating current under load and duty cycle, with the gain from DC-current to duty cycle set by the user. Hard limits can be placed on the control so that the duty cycle does not rise above or fall below user set values. At each time instance of the simulation, the cell's near-maximum operating point current is determined based on the current interpolated polarization relationship. If the simulated cell is under load, this current value is used to update the duty cycle signal, which is compared against the sawtooth waveform so that when the sawtooth rises above the duty cycle set point, the cell model is set to open-circuit operation, and when the sawtooth falls below the duty cycle set point, the cell model is loaded near its maximum power point. If the cell is at open-circuit, no adjustment in the duty cycle is made.

Regardless of cell operation, at each time instance the interpolated polarization curve is updated using the one-dimensional predictor of (6.8), with γ calculated according to the degradation model shown in Figure 7.2. Here, a steady-state degradation level is assumed to be directly proportional to the magnitude of DC current.

For this simulation, the gain K was calculated by setting the average DC current driven through the fuel cell during the degradation cycling portions of Figure 6.2 to correspond to $\gamma_{ss} = 1$. The simulated cell is considered to be degrading if $\gamma_{ss} > \gamma$ and recovering if $\gamma_{ss} < \gamma$, and τ is set to the corresponding degradation time constant, τ_d , or recovery time constant, τ_r , accordingly. In the simulation program, Euler's approximation for discretizing a continuous-time transfer function is used for applying this described current to degradation relationship [95].

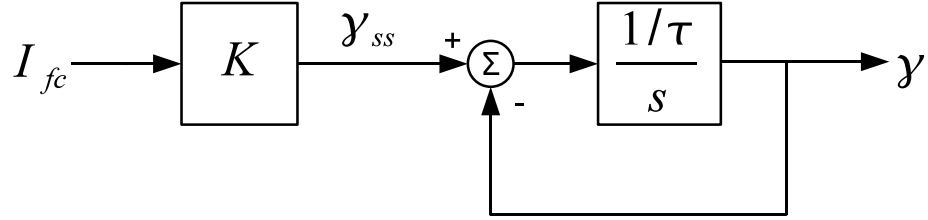


Figure 7.2: First order degradation model used in the PWM control simulation program. Depending on the sign of $\gamma_{ss} - \gamma$, the cell is either degrading or recovering, and τ is set to the corresponding time constant.

Degradation Model Dynamics

The dynamics of this model are also based on the results of Figure 6.2. During that experiment, it was observed that the resistance parameter fits of the measured polarization curves, shown in Figure 6.2b, follow a roughly 1st-order exponential progression in both degradation and recovery. Estimates for the time constants associated with these progressions in degradation and recovery then can be found by fitting the exponential relationships,

$$R_{th} = R_{deg} - (R_{deg} - R_{rec})e^{-(t-t_0)/\tau_{deg}}, \quad (7.1)$$

and

$$R_{th} = R_{rec} + (R_{deg} - R_{rec})e^{-(t-t_0)/\tau_{rec}}, \quad (7.2)$$

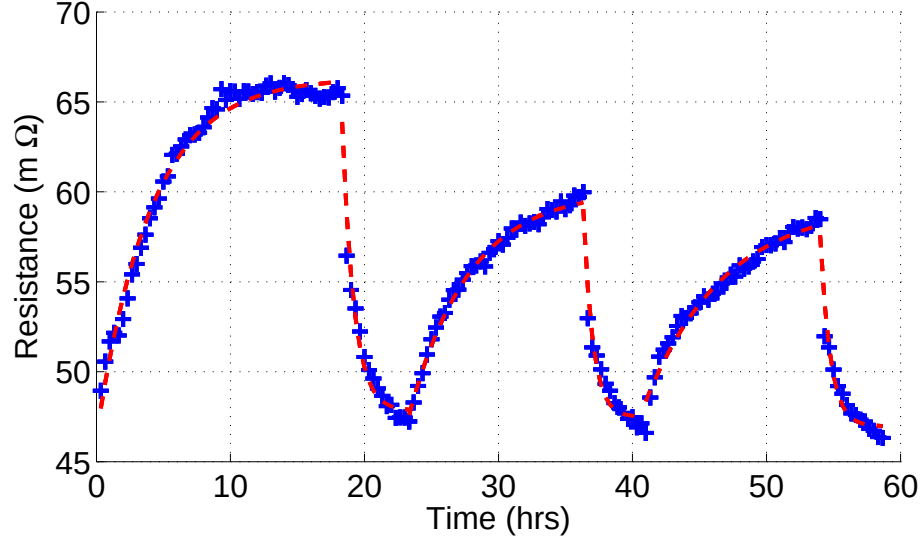


Figure 7.3: First order exponential fits of the progression in the estimated large signal resistance parameter associated with the polarization curves of Figure 6.2. In this figure, the blue pluses correspond to resistance parameter estimates of the Thevenin equivalent fit of the associated polarization curve, while the dashed red lines show the exponential fit for each degradation or recovery period.

Period	Data Time Range (h)	R_{deg} (m Ω)	R_{rec} (m Ω)	Time Constant (τ_{deg} or τ_{rec} , mins)
Degradation Period 1	0 - 18.7	66.4	48.0	244
Recovery Period 1	18.7 - 23.7	63.9	47.8	53
Degradation Period 2	23.7 - 36.7	60.1	47.6	270
Recovery Period 2	36.7 - 41.4	59.0	47.5	43
Degradation Period 3	41.4 - 54.4	59.4	48.4	357
Recovery Period 3	54.4 - 59.1	57.6	47.0	45

Table 7.1: Estimated exponential time constant values for the progression in the fuel cell's internal resistance value shown in Figure 6.2b.

to each period of degradation and recovery, respectively. Here, R_{deg} is the estimate of the cell's large signal resistance when fully degraded, R_{rec} is that when fully recovered, and τ_{deg} and τ_{rec} are the first-order time constants for the degradation and recovery processes, respectively.

Figure 7.3 shows the quality of the fits compared to the original data with the parameter estimates associated with each exponential fit given in Table 7.1. In this figure, the blue pluses correspond to resistance parameter estimates of the Thevenin equivalent fit of the associated polarization curve, while the dashed red lines show the exponential fit for each degradation or recovery period. For use in the simulation program, the three estimated degradation time constants are averaged to form modeled degradation time constant. Similarly, the three estimated recovery time constants are averaged for the modeled recovery time constant.

Simulation Results

Figure 7.4 shows the simulation results of a fuel cell operating under this PWM control scheme. For this simulation, the duty-cycle period was set to one hour for better illustration of the simulation's operation. In laboratory tests, this duty-cycle period was set much lower. The figure shows the duty cycle set point, resulting current and voltage loading profiles, simulated resistance, and the cell's available maximum power output for two cases. The first case, shown in red, depicts the expected cell behavior if constantly loaded near it's maximum power point. The second case, shown in blue, depicts the expected cell behavior when under control by the PWM scheme outlined above. A comparison of these sets of curves shows that without duty-cycle control, the simulation program predicts a higher internal cell impedance and a reduction in the ability of the cell to deliver power to a load.

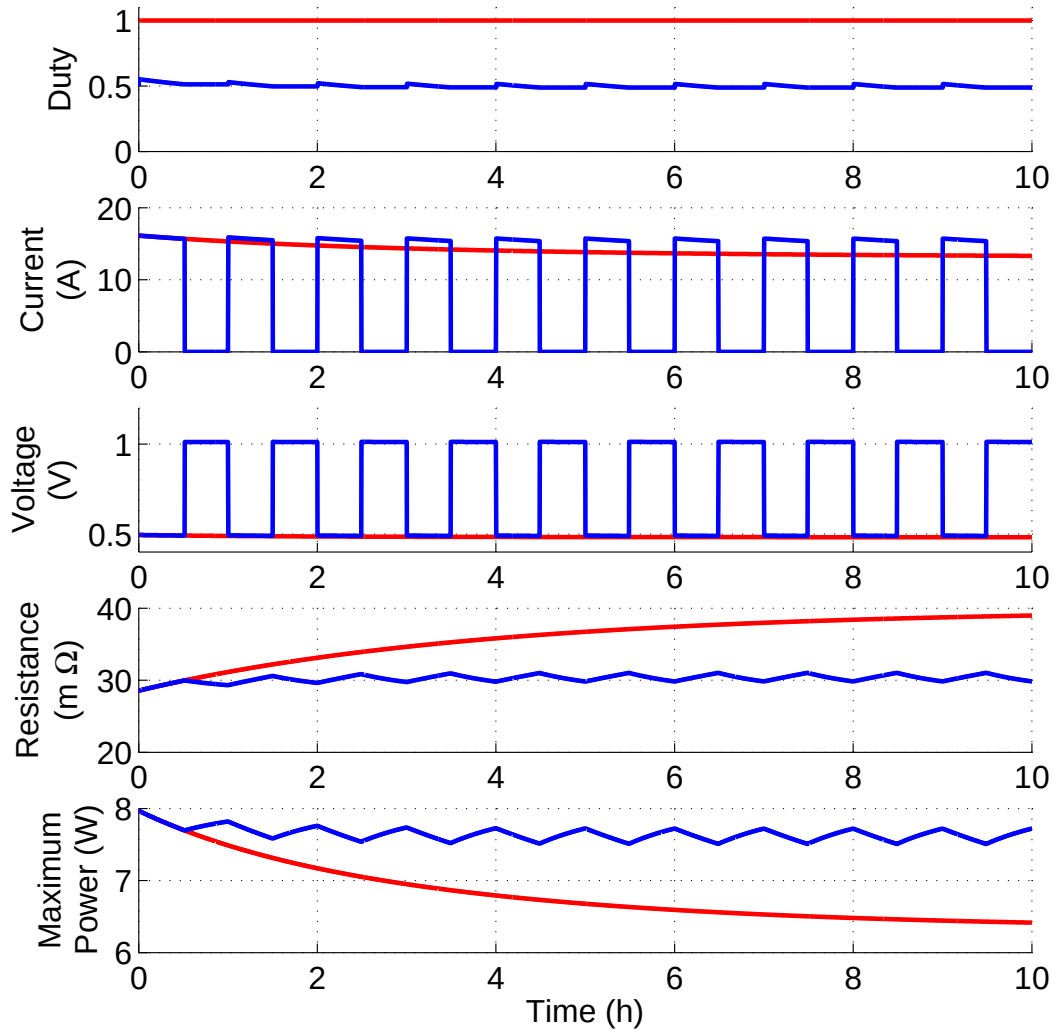


Figure 7.4: Simulation results of the fuel cell degradation mitigation through the PWM control scheme.

Experimental Setup

A conceptual diagram of test and measurement setup is shown in Figure 7.5. The experiment circuit consists of an HP 6012B bench-top power supply connected in series with the fuel cell and an Agilent N3305A programmable electronic load. The power supply is required to increase the DC bias voltage applied across the electronic load as the voltage required is larger than the operating fuel cell voltage. The remote voltage terminals of the load are connected to the fuel cell terminals so that load set points correspond to the fuel cell. During general PWM-control operation, the load operates in voltage control mode with the PC dictating the operating voltage of the cell through the load's GPIB port. Voltage and current measurements are made using the NI 9206 and LEM LA 55-P current transducer and communicated to the computer via an ethernet port.

A control system software program coded in the LabVIEW environment was used to control and communicate with the hardware systems detailed above as well as the current to duty cycle transformation. Periodically during the PWM-control testing, the LabVIEW program suspends the PWM-control in order to perform voltammetry and EIS measurements. When performing EIS measurements, the load operation is switched to current control mode and the AC portion of the current excitation is dictated by the Agilent 33220A function generator, which is also controlled by the computer via its GPIB port. Upon completion of the voltammetry and EIS measurements, the PWM-control resumes.

Experimental Procedure

First, an initial voltammetry analysis is performed on the cell to characterize the cell polarization profile. For this, the output voltage of the cell was stepped down

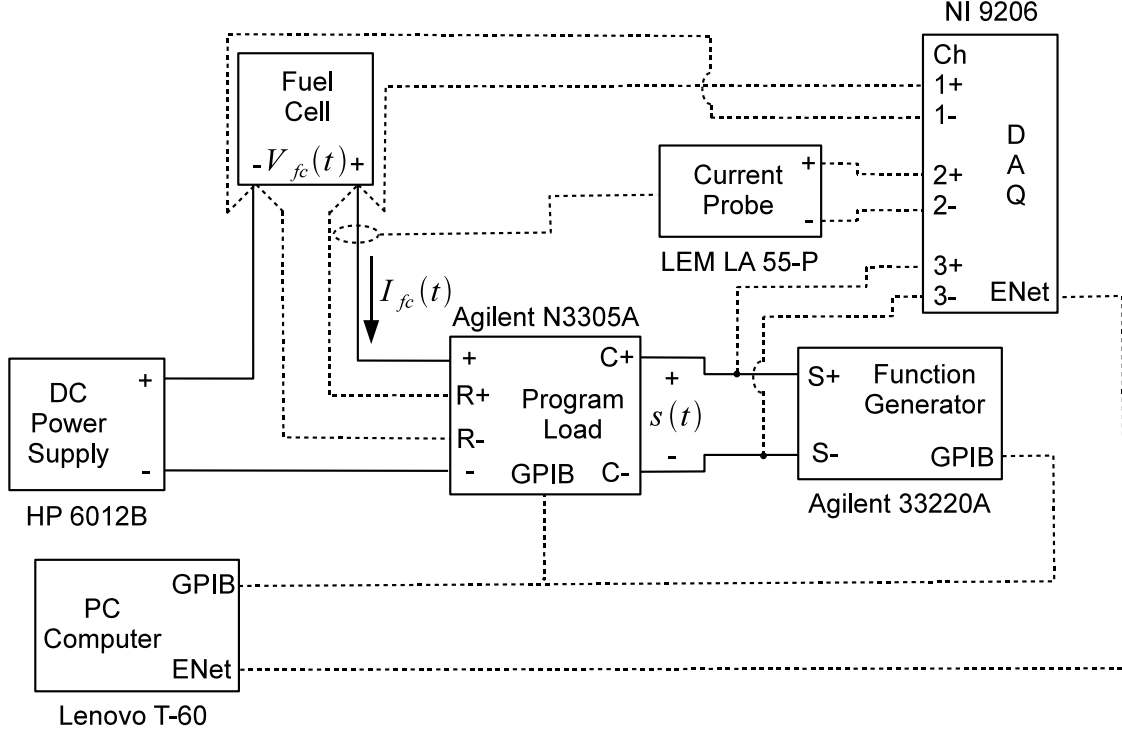


Figure 7.5: Conceptual diagram of the experiment and measurement set-up.

from open-circuit to 200 mV over 40 equidistant steps each lasting three seconds. From this data, a 5th order polynomial curve relating cell current to voltage was fit and used to set the various parameters for the duty cycle test. Namely, the on state voltage V_{on} was set to 0.5 V, the DC current level for EIS tests I_{EIS} was set to 80% of the current at the estimated maximum power point I_{max} , and the AC excitation for EIS i_{eis} was set with the intention of fixing the maximum ac-voltage amplitude during EIS v_{eis} to around 30 mV.

Additionally, the parameter values A and B for linearly transforming average on-state fuel cell current $\bar{I}_{on}$ to duty cycle D , i.e.

$$D = A\bar{I}_{on} + B, \quad (7.3)$$

were set based on this initial polarization curve as compared to the initial, least degraded, and most degraded polarization curves of Figure 6.2. It was assumed that the relative performance between the two initial polarization curves would hold for the maximum degraded polarization curves and maximum recovered polarization curves. More simply put, the ratio of the initial on-state current of this cell to the initial on-state current of the cell in Figure 6.2 was assumed the same as the ratio of on-state currents when the two cells are most degraded and most recovered.

The duty cycle corresponding to the most degraded performance was set to 20%, the duty cycle corresponding to the most recovered performance was set to 80%, and the initial duty cycle for the test was set to 44%. Table 7.2 below lists the values found for the parameters described above along with other relevant measurements.

Parameter	Value	Description
P_{max}	6.9 W	Estimated maximum power
V_{max}	0.44 V	Voltage at estimated maximum power
I_{max}	15.8 A	Current at estimated maximum power
V_{on}	0.5 V	On state voltage for duty cycle control test
I_{EIS}	8.6 A	DC current level for EIS testing
i_{EIS}	1.02 A	AC current level for EIS testing
A	0.1853	Slope parameter for calculating duty cycle
B	-1.98	Offset parameter for calculating duty cycle

Table 7.2: Control system parameter values used in performing the PWM control testing.

After the initial voltammetry test, an initial EIS test was performed. For this test, the DC current level was set to the I_{EIS} value dictated above and the cell was allowed to equilibrate for 5 minutes. Following that, an AC current signal with amplitude i_{EIS} was super imposed onto I_{EIS} and swept in frequency from 0.5 Hz to 5 kHz logarithmically over a 180 second period.

Following the initial voltammetry and EIS tests, the actual duty cycle control test was performed. For this test, the on-state voltage V_{on} , parameters A and B , and the

initial duty cycle were set as dictated above. Additionally, maximum and minimum duty cycle values were clamped to 20% and 80%, respectively. The off-state set point voltage was set to 1.2 V so that the off-state voltage of the cell would revert to its open circuit voltage. The duty cycle periods were 240 seconds. Every 10 hours, the program suspended the PWM control program and performed polarization and EIS measurements under the same parameter settings as the initial sweeps described above. Once these sweeps were performed and the collected data stored, the program then resumed the duty-cycle control loop.

After 100 hours of PWM control testing, a final round of voltammetry and EIS measurements were performed, and the cell was set to open circuit operation. The cell was then shut down, removed from the oven, and prepared for SEM imaging. Protocols for shut down and SEM image preparation were described in Chapter 2.

Experimental Results

Figure 7.6 shows the full 100 hour profiles of the time domain data collected during the PWM control testing including duty-cycle set point, measured cell current and voltage, the cell's large signal resistance estimate, and the cell's maximum power point. These last two signals are calculated from the periodic polarization curve measurements, with the measure of resistance taken from the R_{th} parameter of a Thevenin equivalent fit of the polarization data. The maximum power point is estimated by solving for the roots of the 6th order polynomial current-power curve generated using a 5th order polynomial fit of the polarization curve.

A detailed comparison of the cell's measured current, voltage and instantaneous power during the initial hour of PWM control operation and the final hour of PWM control operation is given in Figure 7.7. During the 1st hour of operation, the duty

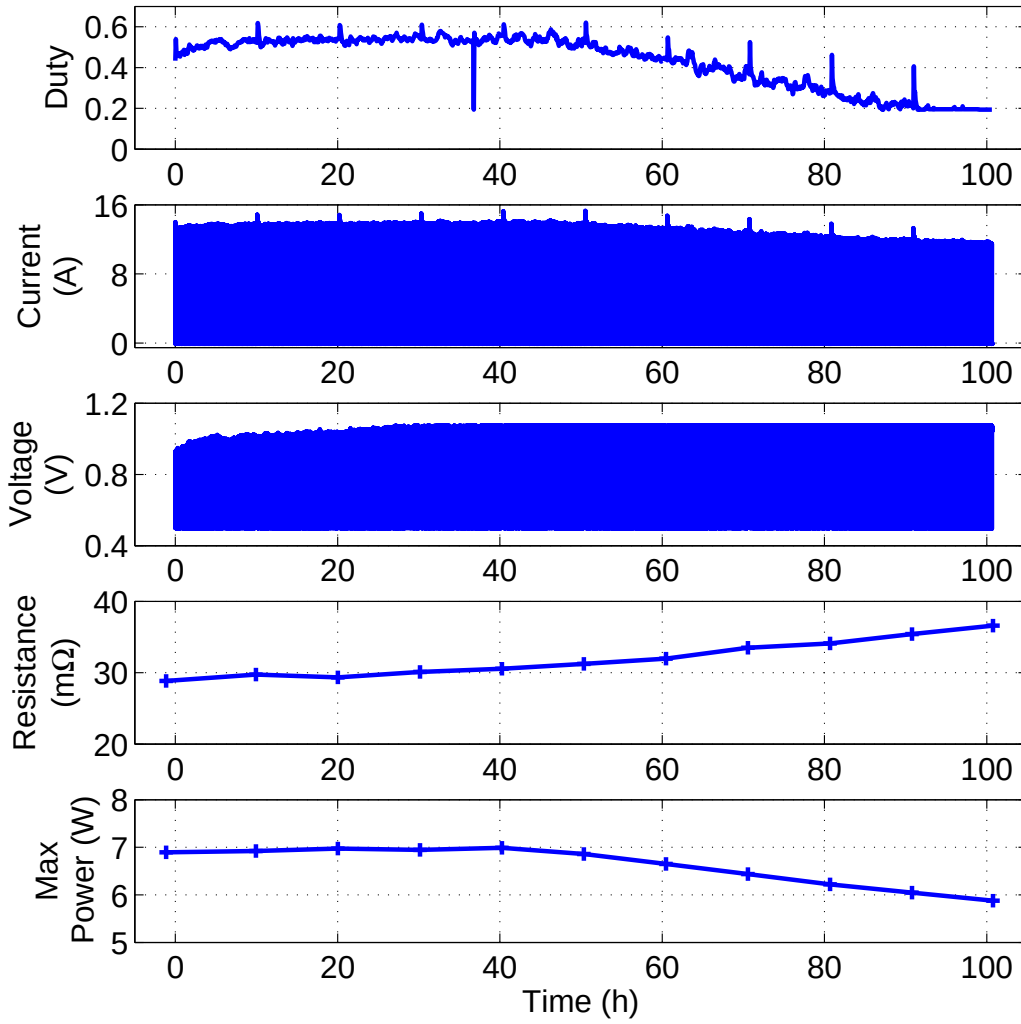
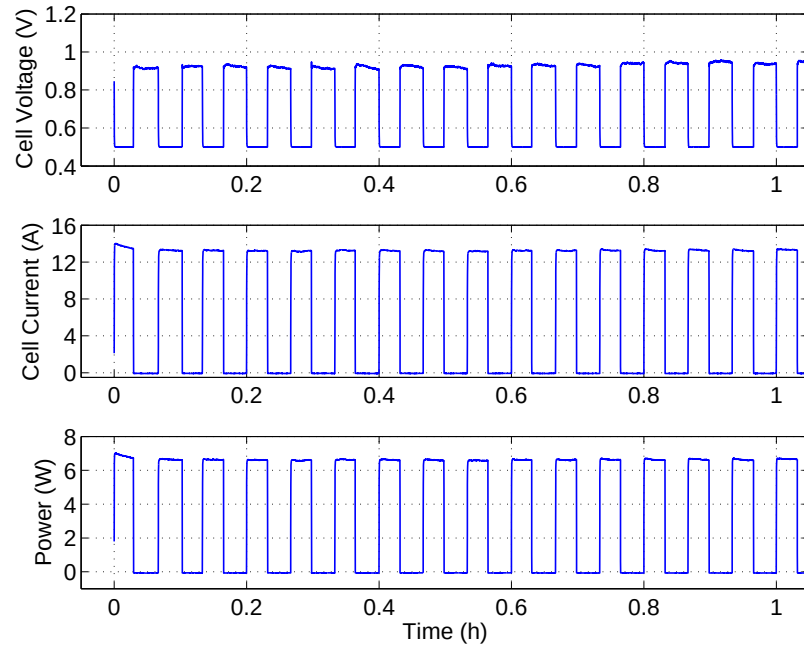
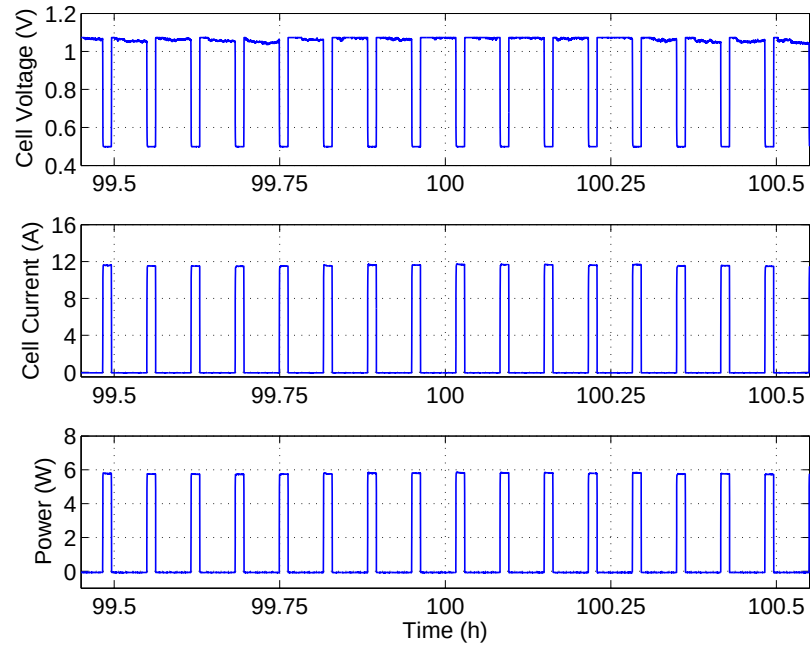


Figure 7.6: Full 100 hour test profiles of the time-domain signals collected during the PWM control test.



(a) 1st Hour



(b) Last Hour

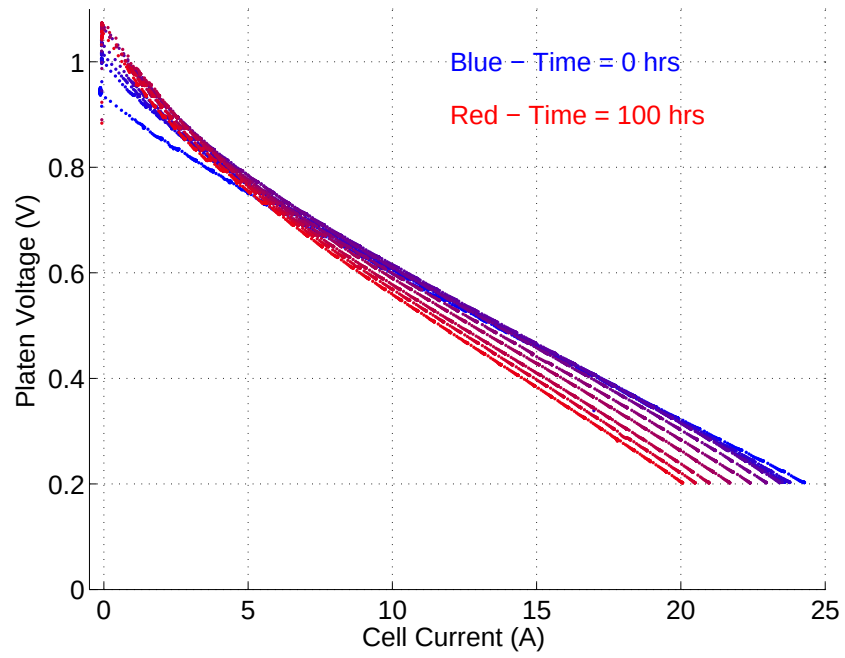
Figure 7.7: Time-domain plots of fuel cell voltage, current, and real-time power during the (a) first and (b) last hours of the PWM control experiment.

cycle set point was around 47% while during the final hour of operation, the duty cycle set point had fallen to around 20%. This is reflected in the width, i.e. time-length, of the measured on-state current pulses.

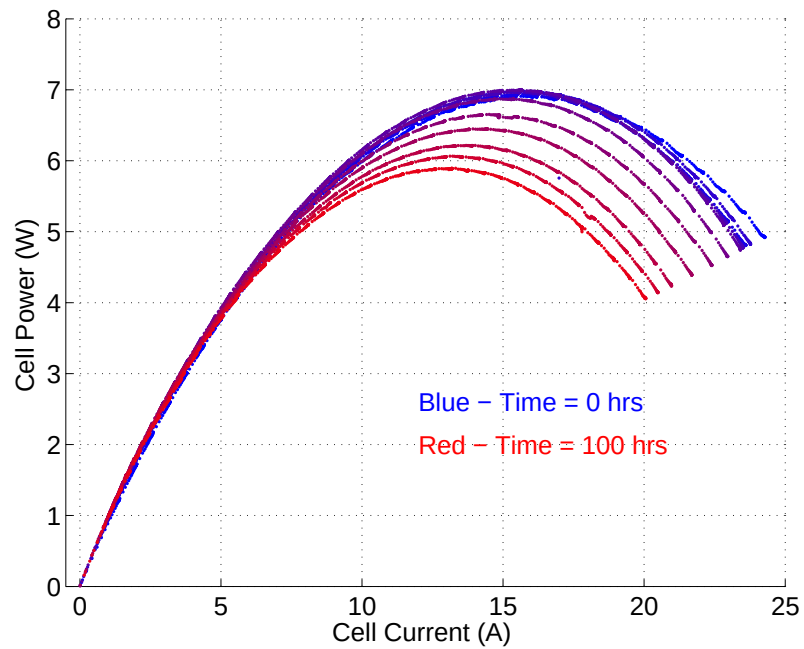
Figure 7.8 depicts the progression in the polarization curves and current-power curves measured before, during, and after the PWM control testing. In these two plots, the initial curves are depicted in pure blue and the final curves in pure red. The shade of the intermediate curves progresses from blue to red with the time of the curve's measurement.

Figure 7.9 shows the resulting impedance profiles achieved during the periodic EIS testing. The first of these plots, Figure 7.9a, gives the initial and post-PWM control test impedance profiles of the cell excited about $I_{EIS} = 8.6$ A, while the second of the plots, Figure 7.9b, depicts the impedance profiles of the cell achieved periodically during the PWM control testing. This second set of impedance profiles had a different excitation point of $I_{EIS} = 6$ A. The intent was to have these periodic impedance measurements performed at $I_{EIS} = 8.6$ A, however the current range setting of the electronic load was set to a maximum current draw of 6 A. Thus, this second set of impedance profiles are not directly comparable to those in Figure 7.9a and are shown in a separate plot.

Figure 7.10 gives a representative example of the predicted $I_{EIS} = 6$ A impedance profiles found through the one-dimensional interpolation analysis model (6.8) using γ estimated from the entire impedance profile (6.9) and γ estimated from the single-frequency impedance magnitude at 5.65 Hz (6.10). Because there is no zero hour impedance data at this operating point, the 10 hour data set was set to correspond to $\gamma = 0$, while the 100 hour data set was set to correspond to $\gamma = 1$. Measured parameter values along with the calculated normalized sum of squared errors for the

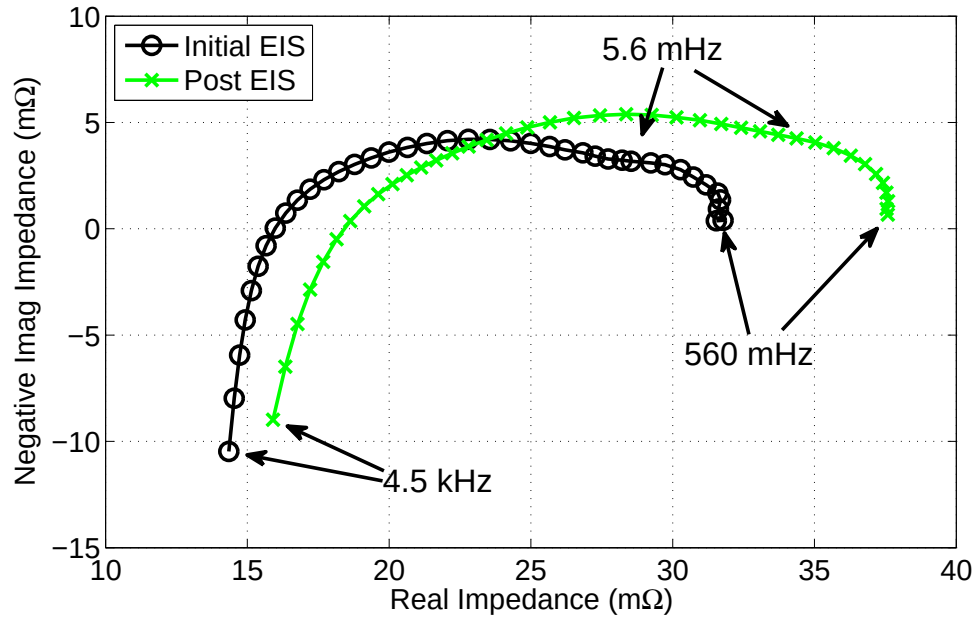


(a) Current-Voltage Progression

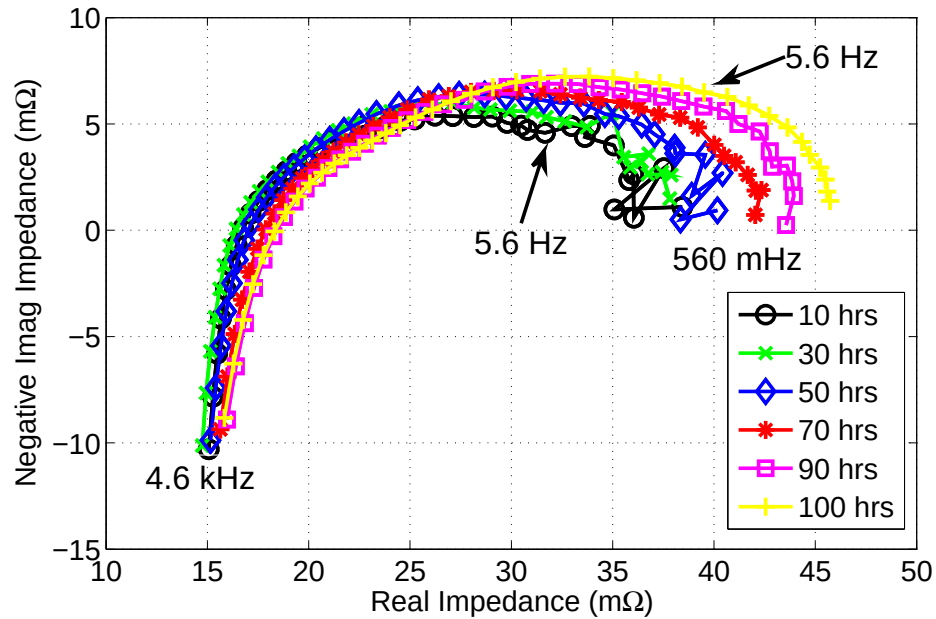


(b) Current-Power Progression

Figure 7.8: (a) Measured polarization curves taken every 10 hours during the PWM control test along with (b) the calculated current-power relationships.



(a) EIS Measurements at 8.6 A



(b) EIS Measurements at 6 A

Figure 7.9: EIS profile of the fuel cell taken (a) pre-PWM control testing and post-PWM control testing at 8.6 A and (b) during the PWM control testing at 6 A.

two prediction models are given in Table 7.3. The full set of these interpolation predictions is given in Appendix D.

Lastly, Figures 7.11 and 7.12 show cross-sectional images of the fuel cell achieved post-testing using a Field-Emission Scanning Electron Microscope (SEM). These images depict the two most commonly observed cell defects in the two cell sample quarters investigated. The red arrow in the SOFC diagram accompanying each image indicates the quartered sample imaged and location along the break plane corresponding to the image. Figure 7.11 depicts a full cross-sectioned view and a close-up view of an area of the cell where large voids are contained in the cathode. These voids were observed to be sparsely scattered throughout the cathode across the both cross-sectioned sample areas observed and ranged in size from around $1\text{ }\mu\text{m}$ to around $10\text{ }\mu\text{m}$ in diameter.

The second most commonly observed cell defect was cracking in the cathode between the cathode's bulk LSM layer and its active LSM / YSZ layer. Each of the cracks observed appeared at a well defined boundary at roughly the midpoint of the cathode where a more porous outer layer (the LSM layer) meets a slightly less porous inner layer (the LSM / YSZ layer). In the first sample, only slight evidence of cracks were found. However, the second sample had 3 well defined cracks with the most severe being several hundred μm in length and around $2\text{ }\mu\text{m}$ in width. This crack is shown in Figure 7.12. For both images, a diagram is included showing the approximate point in the fuel cell where the image was collected. Further example images showing both cathode voids and cathode cracking are given in Appendix E.

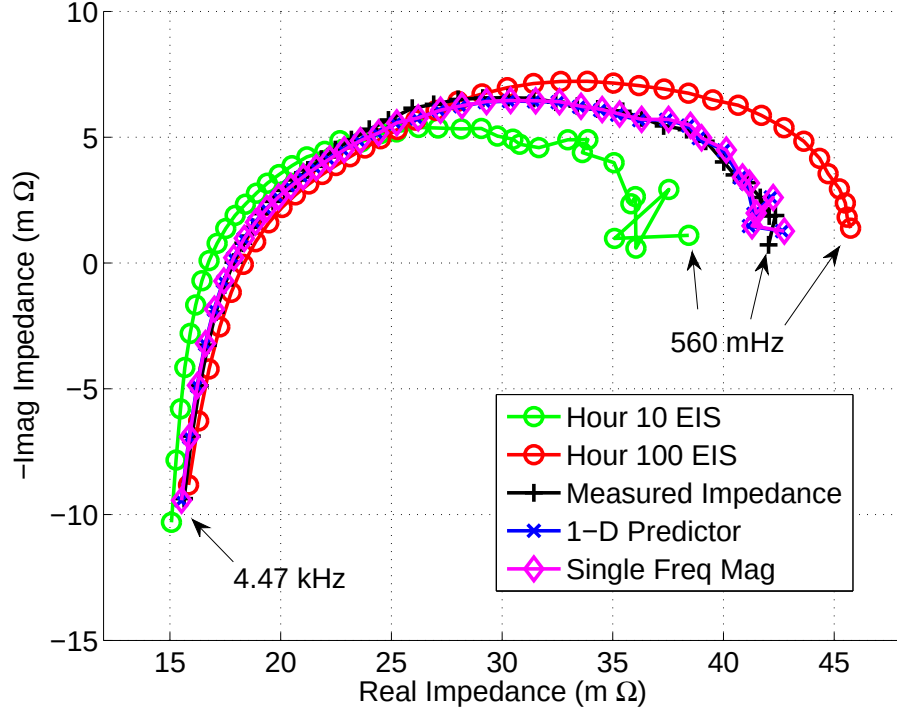
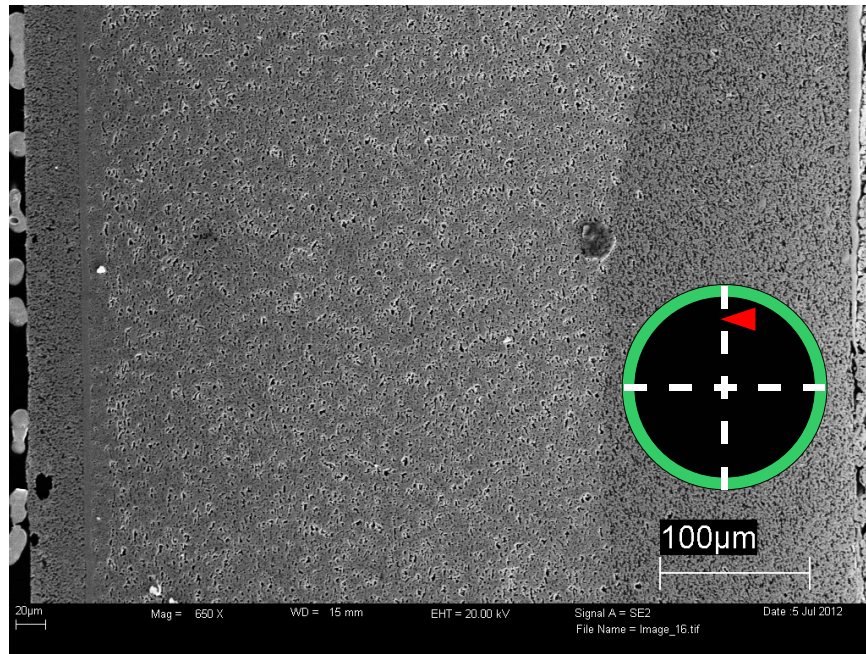


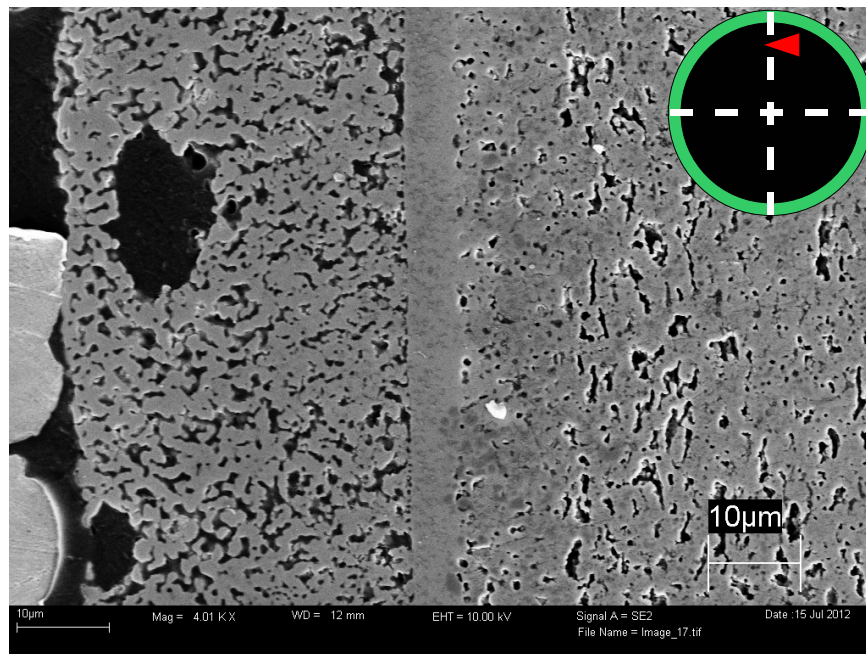
Figure 7.10: Comparison of the 1-D and single impedance magnitude-based linear interpolator predictions to the measured impedance at $I_{DC} = 6\text{A}$ after 70 hours of PWM control operation.

		1-D Model			Single Freq. Mag.		
Time	I_{DC}	$1 - \gamma$	γ	SSE_N	$1 - \gamma$	γ	SSE_N
20 Hours	6 A	1.07	-0.072	0.021	1.04	-0.040	0.024
30 Hours	6 A	0.94	0.064	0.038	0.87	0.13	0.056
40 Hours	6 A	0.86	0.14	0.033	0.78	0.22	0.0053
50 Hours	6 A	0.70	0.30	0.021	0.62	0.38	0.042
60 Hours	6 A	0.65	0.35	0.015	0.58	0.42	0.025
70 Hours	6 A	0.42	0.58	0.0057	0.41	0.59	0.0065
80 Hours	6 A	0.22	0.78	0.0038	0.22	0.78	0.0039
90 Hours	6 A	0.15	0.85	0.0055	0.15	0.85	0.0054

Table 7.3: Parameter values for the one-dimensional and single-frequency impedance magnitude linear interpolations.

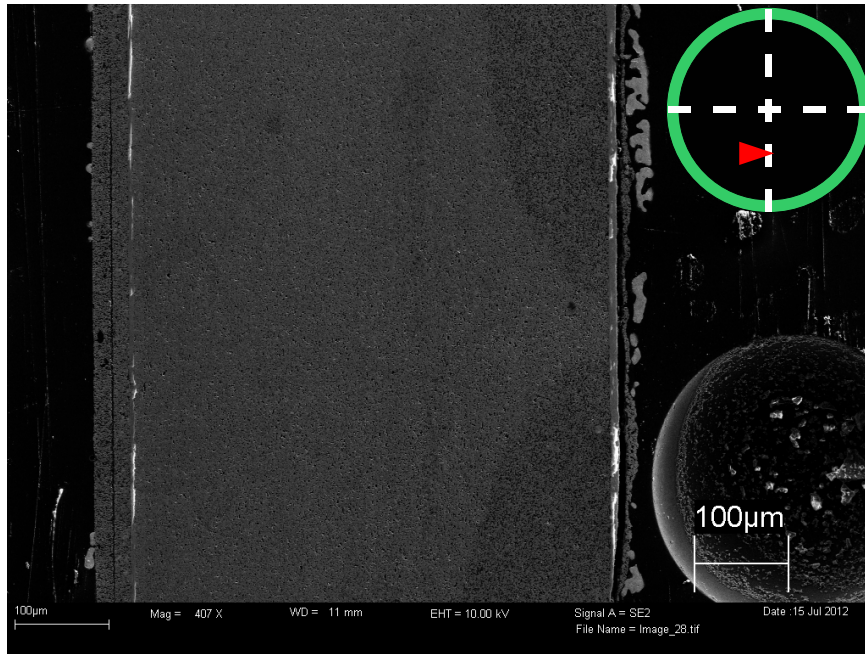


(a) Cathode Voids

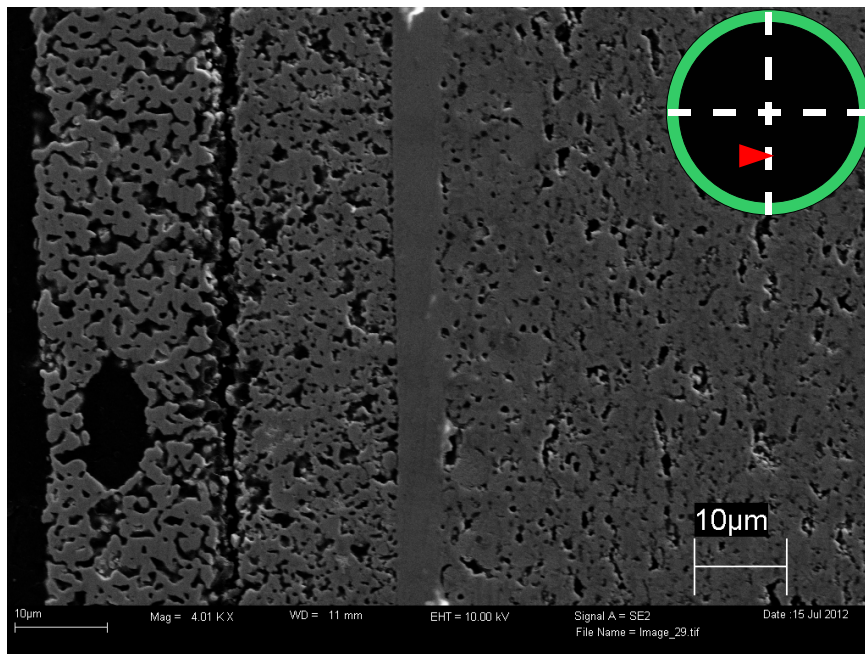


(b) Close Up of Cathode Voids

Figure 7.11: The most prominent type of mechanical defect observed during post-test SEM Imaging was voids in the cathode. It is believed that these voids are a manufacturing defect and not a result of cell testing.



(a) Full View of Cathode Crack



(b) Close Up View of Cathode Crack

Figure 7.12: The second most prominent type of mechanical defect observed during post-test SEM Imaging was a cracking in the cathode at the interface between the cathode's LSM layer and LSM / YSZ active layer. (a) Shows the full FEM imaging view of one such crack while (b) shows a close up of the same crack.

Analysis and Discussion

In terms of the overall electric terminal performance of the fuel cell under test, the results of this experiment indicate that the cell still underwent some degradation despite the PWM control. Over the course of the test, the measured polarization curves (Figure 7.8a), power curves (Figure 7.8b) and EIS impedance profiles (Figures 7.9) show that the low frequency impedance of the cell increased by 20% and the ability of the cell to deliver power decreased by 15%. In comparison, during the original 60-hour degradation and recovery testing performed by Xuelei Hu (Figure 6.2), the large signal resistance slightly decreased by about 5% from the initial value to that measured following the third recovery cycle.

However, the duty cycle control method did perform as intended. As shown in Figure 7.6, as the measured large-signal resistance of the cell increased, the applied PWM duty-cycle decreased. The effect of this duty cycle change on the on-state time lengths of the current signal is easily seen in comparing the 1st hour data plots to the final hour data plots in Figure 7.7.

As observed in the time-domain plots of Figure 7.6, the rate of increase in the cell's resistance is small over the first 50 hours when compared to the final 50 hours of the experiment. This is also reflected in the duty cycle set point which actually increases (from around 47% to around 54%) over the first 5 to 10 hours of testing before holding steady from the 10 to 50 hours marks, and the available maximum output power which hovers around 7 W until hour 50. This is likely due to one or both of the activation processes described in Chapter 6, which results in an initial process that improves the electrical performance of the cell competing with any degradation occurring within the cell. This activation would also account for the initial increases

in open-circuit voltage and on-state current seen over the first half of the duty cycle test.

Perhaps most interesting regarding the time-domain results is that following the roughly 10 minute periods where the duty cycle control loop is suspended for voltammetry and EIS testing, large spikes in the duty-cycle set-point are seen. This indicates that following the IV and EIS testing, the fuel cell showed significant improvement in available power if only for one cycle. This is mirrored when looking at the cell current and cell power plots of Figure 7.6, which show small spikes in current and power every 10 hours. This indicates that the cell would potentially benefit from longer periods so that the time-length of the off-state is increased.

The polarization and power curves of Figure 7.8 show that while the cell's open circuit voltage tended to increase throughout the test, the cell's ability to deliver power while under load decreased significantly. This increase in open circuit voltage is likely due to the activation processes mentioned above and would be responsible for the slight increase in P_{max} seen through the first 50 hours, while the decrease in available output power is due to the cell's degradation. The EIS curves of Figure 7.9 show a significant increase in cell impedance particularly under low-frequency excitation. This caused the general shape of the EIS curves to remain mostly semicircular, but with a shift along the real axis, particular at the 8.6 A operating point, and a significant increase in the width of the semicircle.

This general progression in the shape of the measured EIS profile matches well with progression in impedances observed in earlier load-induced degradation testing of SOFCs (Figures 6.4 - 6.6). Additionally, the results of the linear interpolation analysis using the one-dimensional interpolator and the single-frequency impedance magnitude-based interpolator (Figure 7.10 and Table 7.3) confirm that like the degradation observed in the earlier analysis where the cell was heavily loaded at a DC oper-

ating point, the degradation here when the cell's operation alternates between open-circuit and near-maximum power, also follows a predominantly linear trend. Further, as was the case with the earlier analysis, accurate interpolations of an impedance profile can be made using knowledge of the impedance magnitude at an excitation frequency of around 6 Hz.

The post-test SEM imaging analysis (Figures 7.11, 7.12 and those in Appendix E) revealed no delamination of the SOFC anode from the electrolyte, nor any cracking in the electrolyte. As described in Chapter 6, these two forms of irreversible degradation are indicative of excessive anode-side nickel oxidation. However, instances of cathode-side defects were observed. The most frequently observed defects were large voids in the cathode (Figure 7.11), though it is not believed that these voids are a product of the current-loading. Instead, it is believed that these pores are most likely due to a manufacturing issue rather than being a product of degradation. The several cracks found at the interface of the cathode LSM and LSM / YSZ layer, however, are believed to either be a product of the fuel cell's operation, the post-test processing of the cell in preparation for SEM imaging, or a combination of the two.

As represented in Figure 7.12, each of the cracks observed appeared at a well defined boundary at roughly the midpoint of the cathode where a more porous outer layer (the LSM layer) meets a slightly less porous inner layer (the LSM / YSZ layer). While the cracking was observed in both of the two quartered-cell samples imaged with the SEM, only one minute instance of cathode cracking was observed in the first sample, while three significant cracks were observed in the second sample. Additionally, massive cracks in the cathode were observed in earlier fuel cell SEM imaging (Figure 6.3) and in SEM imaging of the cell used in the impedance-magnitude control experiment discussed in Chapter 8 (Figure 8.26). Both of these samples however, experienced significant issues during preparation for the SEM. The cell of Figure 6.3

experienced a difficult removal from the oven and was dropped during polishing, while the cell of Figure 7.12 became dislodged from the sample mount during polishing. In both cases, these cells experienced excessive forces which likely caused or at least significantly exacerbated any cracking in the cell. Thus, while it is possible that the cracking observed in this test is the product of the cell's operation, it is also possible that the cell's preparation for SEM imaging lead to the cracking, just to a much lesser extent than the cells that showed significant cracking.

Combined, the time-domain, voltammetry, EIS, and SEM image results suggest that while degradation did occur, it is possible that this degradation can be attributed to a different mechanism other than the magnitude of electric loading applied to the cell. In comparing the operation of the fuel cell in this study to the one used when the degradation and recovery cycling was first observed, this cell experienced a larger percentage of operational time at open circuit and a lower percentage of time under load than the cell that showed recoverability. This suggests that the degradation seen here is non-recoverable, which coincides well with the SEM images showing evidence of irreversible degradation in the form of cracks in the cathode layer.

In the event that these cracks did occur during cell operation and not during SEM preparation, one possible explanation is that they may have occurred due to electrically-induced thermal variations within the cell caused by the electric cycling of the PWM control scheme. This sort thermal variations induced by low-frequency dynamic loading has been suggested to cause microstructural damage in SOFCs in previous studies [17]. However, because Ni-YSZ features a higher mismatch in thermal expansion coefficients ($12.5\text{-}13\cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ depending on nickel content [96]) to YSZ ($10.5\cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [97]) than LSM ($12.0\cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [97]), it would be reasonable to expect thermal variations in the cell to also affect the integrity of the electrolyte - anode boundary. No damage to this boundary was observed during SEM analysis.

Alternatively, and despite the fact that no anode delamination or electrolyte cracking was observed, it is still possible that anode-side degradation did occur in the form of nickel grain agglomeration. This has been shown to occur in Ni-YSZ cermets during reduction and oxidation cycling in air [58, 98, 99]. This agglomeration is suggested to lead to a reduction in active sites for hydrogen oxidation as well as a reduction in electronic conductivity through the anode due to decreased electronic contact between Ni-particles. It is possible then that the electrochemically induced oxidation and reduction caused by the switching operation of the controlled loading resulted in similar agglomeration. This could also explain the increase in cell impedance.

Chapter Summary

In this chapter, a PWM-based control strategy for affecting the type and total amount of degradation occurring in an operating solid oxide fuel cell is presented. This strategy is based on previous observations of SOFC operational behavior which showed that the electrical performance degradation of an SOFC when under load could be recovered when allowed to rest at open circuit. A simulation program including a proposed 1st-order model of degradation is presented along with results that illustrated the PWM control system operation. The results from a 100 hour test of single SOFC cell operating under this type of control are presented in the form of time domain data and periodic voltammetry and EIS measurements. This data is used to access the PWM control's operation and the cell's level of degradation. SEM images taken post-testing are used to correlate measured electric terminal cell behavior to possible internal mechanisms for degradation. The results of the test indicate that while degradation still occurred, it is possible that the degradation can be attributed

to the dynamic loading characteristics of the PWM control scheme rather than the magnitude of electric loading.

CONTINUOUS CURRENT CONTROL OF DEGRADATION

The second proposed method for degradation mitigation is the continuous current control method. This method was conceived with the desire to control the accumulated current loading of a fuel cell without the large dynamic loading characteristics of the PWM-based control method since it was postulated in the previous chapter that the low frequency switching of the load may have caused irreversible degradation to the fuel cell. Instead, the continuous current method varies the DC loading conditions of a fuel cell in a smooth and continuous manor based on fed back measurements of the cell's impedance magnitude, which is used as the measure of degradation. That is, if the the impedance magnitude of the fuel cell increases, then the DC operating point is decreased, and vice versa.

Here, the assumption is that degradation is a monotonically increasing though not necessarily linear function of DC current, and that decreasing the cell's DC operation can reduce, halt or even reverse the rate of degradation in a fuel cell. This assumption represents an interpolation as cell recoverability has only been observed at open-circuit, while load-induced cell degradation has only been observed at relatively high levels of current loading. Never-the-less, so long as a cell's degradation-recovery function of current is continuous, then there exists some range of positive current values which induce degradation recovery, and at least some current level or perhaps a range of current levels where no significant degradation or recovery occurs.

This chapter details the experimental investigation into this type of SOFC degradation control. First, the conceptual control strategy is detailed followed by the description of a full-system simulation model of a cell under this type of control. Results of this simulation are then shown to explain the expected operation of the fuel cell. Next, the experimental setup used for testing an SOFC is described including

the analog circuitry employed to implement the control strategy. Finally, the results of the experiment are then presented followed by a discussion of the results and a chapter summary.

Continuous Current Control of Degradation Strategy

The use of the cell's impedance magnitude as a measure of degradation is based on the results of the single frequency linear interpolation analysis of Chapter 6. This analysis showed that the total accumulated degradation in a fuel cell can be estimated with reasonable accuracy based on single frequency impedance magnitude measurements taken in the frequency range of DC to 6 Hz. These impedance measurements then can be used as feedback in a control scheme which aims to affect the rate of cell degradation by adjusting the DC load.

Figure 8.1 shows a conceptual layout of the continuous current control of degradation scheme. The cell is connected in series with a power supply and programmable electric load. Measurements of the fuel cell's current, $\hat{I}_{fc}$, and voltage, $\hat{V}_{fc}$ are made in real-time and fed to a control circuit. This control circuit takes as an input, an impedance level set point which can be separated into two terms. The first is the nominal, zero-degradation level of the cell's impedance magnitude $|Z|_o$, and the second, δ_{set} , is a set increase in cell impedance magnitude beyond the nominal value. The output of the control circuit is a current set point, I_c , with a DC component that is proportional to the difference between the input $|Z|_o + \delta_{set}$ and the measure of cell impedance $|Z|$ which is determined from the measured current and voltage waveforms.

This current set point is used to control the deviation of the fuel cell's loading from a nominal set point value of I_o . This I_o corresponds to the desired operating

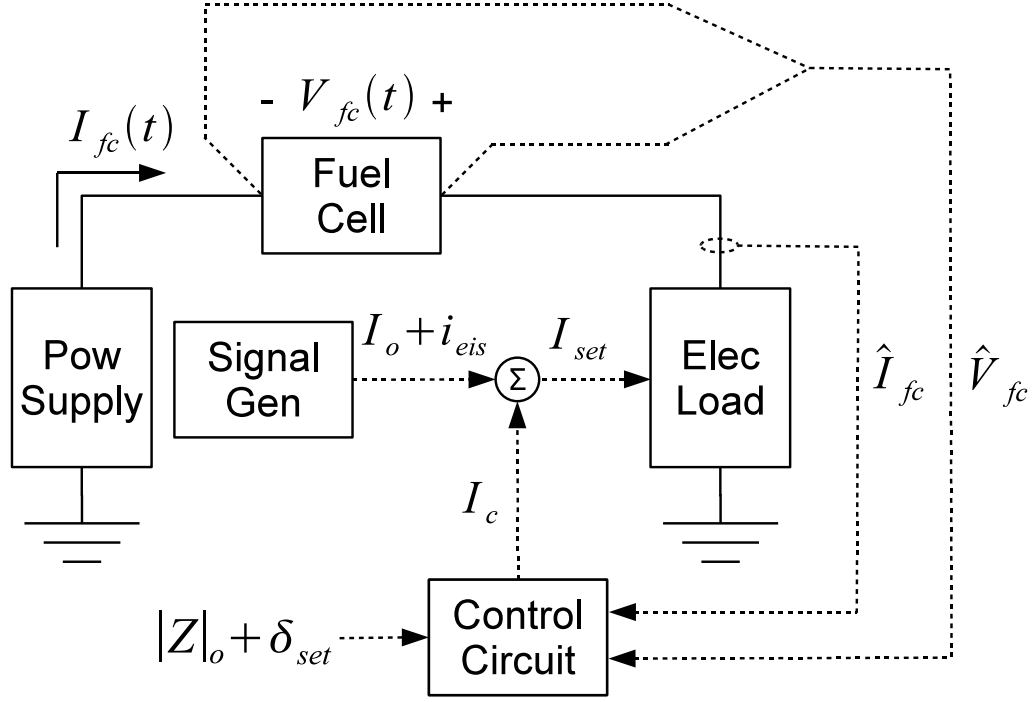


Figure 8.1: Conceptual diagram of the proposed continuous current control scheme using the small-signal impedance magnitude as a measure of degradation.

point of the fuel cell when no degradation of the fuel cell has occurred, i.e. $|Z| = |Z|_o$. In order to measure impedance, a perturbation signal, i_{eis} is added to the controlled current point of the fuel cell. The frequency of this perturbation signal should be one towards the higher end of the accurate degradation prediction range determined to be between DC and 6 Hz. Doing so affords accurate degradation measurements while simultaneously allowing easier compensator filtering of fundamental and harmonic frequency components unwanted in the compensator output current set point, I_c . That is, because the control circuit compensator features analog filtering, a higher perturbation frequency reduces the resistor and capacitor size requirements for adequate signal attenuation.

Simulation Model

Several nonlinearities exist in the closed loop system operation of Figure 8.1. These nonlinearities include the nonlinear polarization relationship of the fuel cell and the nonlinear method of impedance detection which will be described below. Additionally, while it is likely that the relationship between the rate of degradation in the cell and the fuel cell's current level is a monotonically increasing one, it is also likely that this relationship is nonlinear, in that the gain relating current to the rate of degradation is not constant across all current levels. In [93], degradation rates of similar SOFC technology fuel cells were studied as a function of current and temperature in 1500 hour tests. Following an initial activation process, these cells showed initial degradation rates positively correlated to load-current density with little or no degradation observed under low current loading, and significant degradation observed under high current loading. These results support the presumption that degradation rates follow a nonlinear but monotonically increasing relationship with current loading. Further, with little or no degradation observed under a reduced load, the results also suggest that this nonlinear relationship includes a dead-band region separating the regions of cell recovery and cell degradation where no degradation or recovery occurs.

These nonlinearities make analysis of the proposed control method very difficult. Thus, a full-system simulation program was developed for investigating the implications of the continuous current control of degradation scheme under various assumptions of degradation and various control parameter settings. This section describes this simulation program and the individual dynamic models of which it is comprised.

Figure 8.2 shows a block diagram describing the simulation program's operation. The program consists of a compensator model, shown in the figure by the $G_c(s)$ block, a nonlinear degradation model, a nonlinear fuel cell voltage model, and the impedance

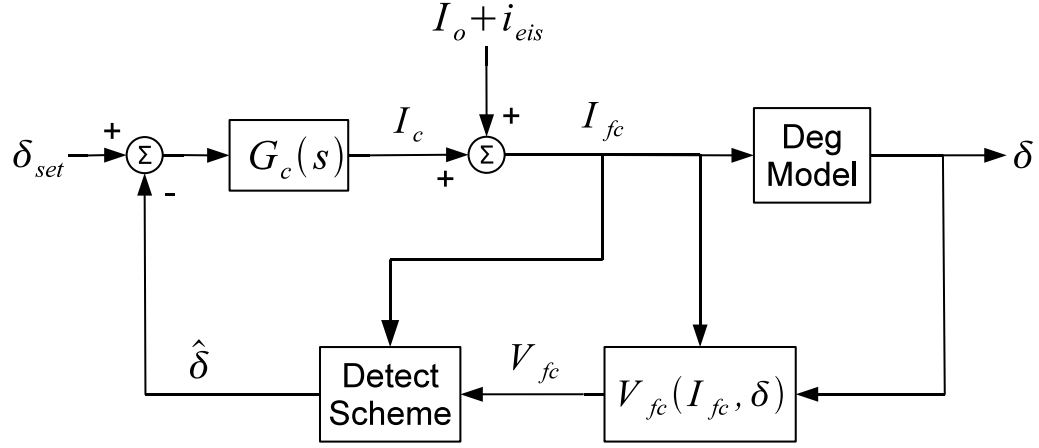


Figure 8.2: Large signal control loop used in the simulation program to predict the cell degradation behavior under the impedance magnitude based control.

magnitude detection scheme. These models, which are individually described below, are collectively programmed in the MATLAB environment as a system of nonlinear ordinary differential equations (ODE). The dynamics of the degradation model are significantly slower than the dynamics of the compensator and even slower than the excitation signal period ($T_{eis} = 1/f_{eis}$). Thus, this system of equations represents a stiff problem, and the built-in MATLAB ODE solver, `ode15s()`, designed to numerically solve stiff differential equation problems, is used with this simulation code.

Degradation Model

The model used in the simulation to describe the accumulated fuel cell degradation is shown in the block diagram of Figure 8.3. Here, a nonlinear function, $g()$ is employed to describe the resulting time rate of degradation or recovery that occurs due to the level of current loading, and an integrator block is used to describe the accumulation of this degradation within the fuel cell. The general functional shape

$g(I_{fc})$ is described through the piecewise equation,

$$\frac{d\delta}{dt} = g(I_{fc}) = \begin{cases} k_d(I_{fc} - \sigma_h) & \text{for } I_{fc} > \sigma_h \\ 0 & \text{for } \sigma_l \leq I_{fc} \leq \sigma_h \\ k_r(I_{fc} - \sigma_l) & \text{for } I_{fc} < \sigma_l. \end{cases} \quad (8.1)$$

This model assumes that there is a dead-band region in the relationship between degradation rate and fuel cell current within which no degradation or recovery occurs. The limits of this region are set by the σ_l and σ_h terms. Above this region, i.e. when $I_{fc} > \sigma_h$, the model describes the rate of degradation as being positive meaning that degradation is occurring. Below this region, i.e. when $I_{fc} < \sigma_l$, the model describes the rate of degradation as being negative meaning that recovery is occurring.

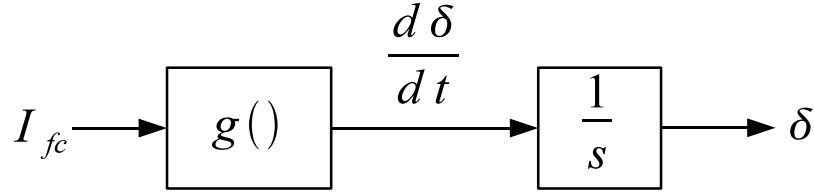


Figure 8.3: 1st order degradation model used in the impedance magnitude based degradation control simulation program. The rate of degradation is modeled as a nonlinear function of DC operating current and the total degradation is accumulated with time.

Aside from this nonlinear function $g()$, the primary difference between this model and the one used in the PWM control scheme (Figure 7.2) of the previous chapter lies in how the accumulated degradation is modeled. Here the accumulated degradation is modeled by a pure integrator with a pole at DC while the PWM control degradation model had accumulated degradation modeled as following a low-pass relationship with the pole at some slow time constant. The fundamental difference between these two is that the model of the PWM control scheme contains an inherent negative

feedback term from δ to $\frac{d\delta}{dt}$ that limits the total amount of degradation that can be accumulated or recovered. This model here then is limited to a range of accumulated degradation values as clearly the cell cannot recover beyond a level of no degradation, while an excess of degradation beyond some upper level will likely cause irreversible degradation effects such as anode delamination as described in Chapter 6.

The derivatives of the exponential fits, (7.1) and (7.2), of the large-signal resistance parameter progressions observed in the initial degradation and recovery cycling experiment (Figures 6.2 and 7.3) were used for estimating the gains, k_r and k_d , which describe the simulated rate of recovery or degradation, respectively. These derivatives are given by the equations,

$$\frac{dR_{th}}{dt} = \frac{(R_{deg} - R_{rec})}{\tau_{deg}} e^{-(t-t_0)/\tau_{deg}}, \quad (8.2)$$

and

$$\frac{dR_{th}}{dt} = -\frac{(R_{deg} - R_{rec})}{\tau_{rec}} e^{-(t-t_0)/\tau_{rec}}, \quad (8.3)$$

for the degradation and recovery fits, respectively. The corresponding rate of large signal resistance change without feedback is found through these derivatives at the time instance, $t = t_0$, i.e.,

$$\left. \frac{dR_{th}}{dt} \right|_{t=t_0} = \frac{(R_{deg} - R_{rec})}{\tau_{deg}}, \quad (8.4)$$

and

$$\left. \frac{dR_{th}}{dt} \right|_{t=t_0} = -\frac{(R_{deg} - R_{rec})}{\tau_{rec}}. \quad (8.5)$$

Further, assuming that these rates of degradation and recovery, respectively, will hold for $\frac{d\delta}{dt}$, the gains k_d and k_r can be estimated from the equations,

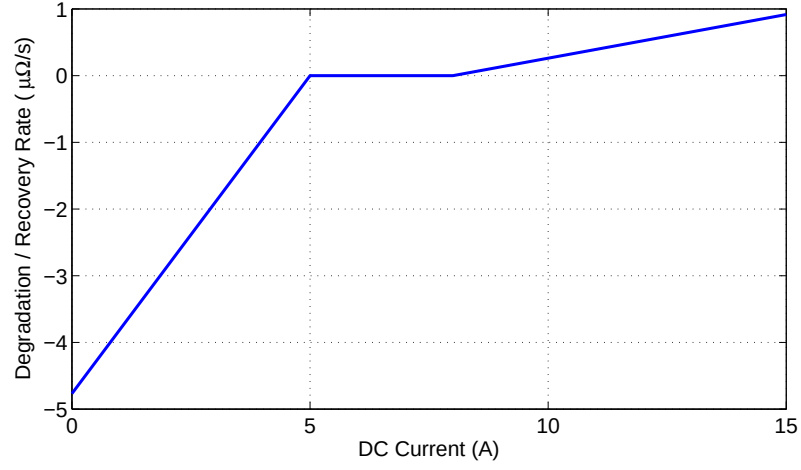


Figure 8.4: Graphical representation of the modeled time rate of degradation as a function of current loading. The range of currents between 5 A and 8 A correspond to a dead-band in the model where no degradation or recovery occurs.

$$k_d = \frac{(R_{deg} - R_{rec})}{\tau_{deg}(I_{fc} - \sigma_h)}, \quad (8.6)$$

and

$$k_r = \frac{(R_{deg} - R_{rec})}{\tau_{rec}(\sigma_l - I_{fc})}. \quad (8.7)$$

For the degradation and recovery cycling test of Figure 6.2, the average current magnitude that induced degradation was 14 A, while the current magnitude that induced recovery was 0 A. Using the average values of R_{deg} , R_{rec} , τ_{deg} , and τ_{rec} from Table 7.1, and setting the limits of the dead-band to $\sigma_l = 5$ A and $\sigma_h = 8$ A, k_d is found to be $0.13 \frac{\mu\Omega}{A \cdot s}$ and k_r is found to be $0.94 \frac{\mu\Omega}{A \cdot s}$. Figure 8.4 shows a plot of this function, $g(I_{fc})$.

Cell Voltage Model

In Chapter 6, a linear interpolation analysis was performed on the measured polarization curves obtained periodically during the degradation and recovery cycling

of an SOFC. This analysis showed that the one-dimensional interpolator performed well in predicting the polarization relationship of a fuel cell at an intermediate level of degradation from the polarization relationships of the fuel cell under full degradation and zero degradation. This simulation program then uses 3rd order polynomial fits of the least degraded and most degraded polarization curves of Figure 6.2, and the measure of degradation, δ , to determine a 3rd order voltage polynomial corresponding to that particular level of degradation. V_{fc} is then found by the equation,

$$V_{fc}(I_{fc}, \delta) = (a_{rec}(1 - \gamma) + a_{deg}\gamma)I_{fc}^3 + (b_{rec}(1 - \gamma) + b_{deg}\gamma)I_{fc}^2 + (c_{rec}(1 - \gamma) + c_{deg}\gamma)I_{fc} + (d_{rec}(1 - \gamma) + d_{deg}\gamma), \quad (8.8)$$

where the terms x_{rec} and x_{deg} are the x th-power coefficient for the most recovered and most degraded polynomial fits, respectively. In (8.8), γ is the normalized measure of degradation originally used in the linear interpolation analysis and is related to the ohmic measure of degradation, δ through the equation,

$$\gamma = \frac{\delta}{\delta_{fs}}. \quad (8.9)$$

Here, δ_{fs} is the full scale ohmic measure of degradation corresponding to $\gamma = 1$ for the nominal cell operating current, I_o .

It should be noted that this model for V_{fc} is derived from DC current and voltage measurements while δ corresponds to a change in the measured cell impedance magnitude, $|Z|$, at a the perturbation frequency, f_{eis} . The assumption taken by combining the two is that $|Z|$ is similar in magnitude to the cell's small signal DC resistance, R , and that the variation in $|Z|$ as a function of DC current will follow a similar trend to that of R .

Degradation Detection Model

To detect degradation through the small signal impedance. The fuel cell is continuously perturbed about a DC operating point by a sinusoidal signal, $i_{eis} = A \sin(\omega t)$, where $\omega = 2\pi f_{eis}$, so that the total current through the fuel cell is given by,

$$I_{fc} = I_o + I_c + i_{eis}. \quad (8.10)$$

The resulting fuel cell voltage can be written as,

$$V_{fc} = V_{DC} - v_{eis}, \quad (8.11)$$

where v_{eis} is the small signal response of the fuel cell to the input perturbation. For the simulation model, the assumption is made that the phase-shift imparted on this voltage response due to the non-real component of impedance is negligible so that,

$$v_{eis} = |Z|i_{eis}, \quad (8.12)$$

with the impedance magnitude given by,

$$|Z| = |Z|_o + \delta. \quad (8.13)$$

An estimate for this measure of degradation, δ , can be extracted from the voltage and current measurements. First, the measured large signal voltage and current waveforms have the nominal operating voltage and current values subtracted from them, and the two are combined to form the waveform,

$$\hat{V}_\delta = \hat{V}_{fc} - V_o + (\hat{I}_{fc} - I_o)|Z|_o. \quad (8.14)$$

Assuming the current and voltage measurements are true, i.e. $\hat{I}_{fc} = I_{fc}$ and $\hat{V}_{fc} = V_{fc}$, (8.10) - (8.14) can be combined, and V_δ can be rewritten as,

$$\hat{V}_\delta = V_{\delta,DC} - v_\delta, \quad (8.15)$$

where $V_{\delta,DC} = V_{DC} - V_o + I_c|Z|_o$, and $v_\delta = \delta \sin(\omega t)$. Thus, by full-wave rectifying the signal, V_δ , the resulting DC component is proportional to the change in impedance, δ , that has occurred in the cell. In the simulation, this is done by multiplying V_δ by a square wave in phase with the EIS voltage response, v_{eis} . This rectified signal,

$$\hat{\delta} = \frac{\pi}{2A} Sq(\omega t + \pi) V_\delta, \quad (8.16)$$

is fed back to the control system compensator as a measure of degradation in the fuel cell. In (8.16), the square wave amplitude term $\frac{\pi}{2A}$ is required so that the units of $\hat{\delta}$ are Ω . Additionally, it should be noted that the nominal DC voltage terms, V_o and $I_o|Z|_o$ are subtracted from the combined signal of (8.14), in order to limit the magnitude of the DC component. This is done because any DC component in V_δ translates into a square-wave component in $\hat{\delta}$ at the frequency of excitation, which would otherwise increase the filtering requirements of the controller compensator.

Compensator Model

The compensator type used for this control system is a dominant-pole compensator with the transfer function,

$$\frac{I_c}{e} = \frac{K_c}{\tau_c s + 1}, \quad (8.17)$$

where $e = \delta_{set} - \hat{\delta}$. The compensator gain, K_c , sets the steady-state relationship between this error and the deviation in the current driven through the fuel cell from

the nominal level of I_o . Thus, a higher gain means a larger change in current, which would potentially have a larger effect on cell degradation. However, this gain needs to be balanced by the compensator time constant, τ_c which is required to filter the non-DC components of $\hat{\delta}$, which are also multiplied by the gain K_c . This filtering is required as any non-DC component that passes through the compensator is imparted on the fuel cell's current, I_{fc} . If the magnitude of these non-DC components are too large, then the perturbation of the fuel cell will be driven outside the cell's pseudo-linear operation region. This negatively affects the accuracy of the impedance measurements and further could potentially cause unintended degradation to the cell through large, low-frequency, variations in the cell's operation.

Simulation Results

For testing of SOFCs under this type of control, it was decided to set the SOFC's DC operation point to a current loading level just outside the anticipated upper-limit of the degradation dead-band so that initially the cell is operating under degrading conditions. However, the degradation set point input to the control system, δ_{set} , is left at 0 m Ω so that as degradation occurs, the controller reduces the DC operating point of the cell into the dead-band region causing the accumulated degradation to level off. The operation of the continuous current control scheme and the resulting electric terminal behavior of the fuel cell is illustrated here through the results of the simulation program described in the previous section.

For this simulation, the nominal DC cell current, I_o , is set to 9.5 A, and the 3rd-order polarization curve polynomial corresponding to a fully recovered cell is used to calculate the $\delta = 0$ values for cell voltage V_o and cell impedance, $|Z|_o$. These values are 560 mV and 40 m Ω , respectively. The perturbation signal frequency selected is

Variable	Value	Description
<i>DC Setpoint</i>		
I_o	9.5 A	Nominal DC Current
V_o	560 mV	Nominal DC Voltage
$ Z _o$	40 m Ω	Zero-degradation Impedance Magnitude
<i>Perturbation Setpoint</i>		
A	0.5 A	Perturbation Amplitude
f_{eis}	5 Hz	Perturbation Frequency
<i>Degradation Model</i>		
k_d	0.13 $\mu\Omega/s$	Degradation Gain
k_r	0.94 $\mu\Omega/s$	Recovery Gain
σ_h	8 A	Dead-band Upper Limit
σ_l	5 A	Dead-band Lower Limit
<i>Cell Voltage Model</i>		
a_{rec}	$-1.22 \cdot 10^{-4}$	3rd Order Recovered Polynomial Parameters
b_{rec}	$-3.18 \cdot 10^{-3}$	
c_{rec}	$-6.76 \cdot 10^{-2}$	
d_{rec}	1.02	
a_{deg}	$-7.91 \cdot 10^{-5}$	3rd Order Degraded Polynomial Parameters
b_{deg}	$1.65 \cdot 10^{-3}$	
c_{deg}	$-6.50 \cdot 10^{-2}$	
d_{deg}	1.01	
δ_{fs}	15 m Ω	Full Scale Degradation
<i>Compensator Model</i>		
K_c	200 A/ Ω	Compensator Gain (as defined in (8.17))
τ_c	8.1 s	Compensator Time Constant
δ_{set}	0	Degradation Setpoint

Table 8.1: Parameter values used for the continuous current control simulation program.

5 Hz and the amplitude of the perturbation current is set to 0.5 A. This value is chosen so that the amplitude of the voltage response is around 50-60 mV peak-peak at full-scale degradation, i.e. $\delta_{fs} = 15 \text{ m}\Omega$. For control compensation, the DC gain is set to 200 A/ Ω , and the dominant pole time constant is set to 8.1 seconds, which corresponds to a total signal attenuation of around -50 dB at 5 Hz. Table 8.1 summarizes these parameter values along with the previously discussed parameter values for the degradation model. Also, the 3rd-order polynomial coefficients for the fully degraded and fully recovered polarization relationship models used in determining cell voltage are given.

Figures 8.5 - 8.9 show the results of a 100 hour simulation with Figures 8.5 - 8.7 depicting the cell and control circuit operation for the entire simulation, and Figures 8.8 and 8.9 depicting operation at specific time instances. Figure 8.5 shows the progression in the cell's degradation. Here, the red curve gives the accumulated degradation as would be measured at the nominal operating point of $I_o = 9.5 \text{ A}$, while the blue curve gives the true simulated measure of degradation as the DC operating point of the cell is reduced. These two curves differ because the local impedance of the cell changes with the DC operating point, and it is this local impedance value that is used for degradation level feedback.

Direct measurement of this true measure of degradation is not available to the controller and must be extracted from the voltage and current measurements as described in (8.14) - (8.16). The estimate signal, $\hat{\delta}$, for this measure of degradation is shown in Figure 8.6 for the entire 100 hour simulation. As seen here, the envelope of this signal grows significantly during the test. This is caused by the control system's shifting of the cell's DC operation away from the nominal operating point as the cell degrades. This results in a growth in the DC term of the combined waveform of (8.14) and (8.15), which when rectified to generate $\hat{\delta}$, translates into an increase in

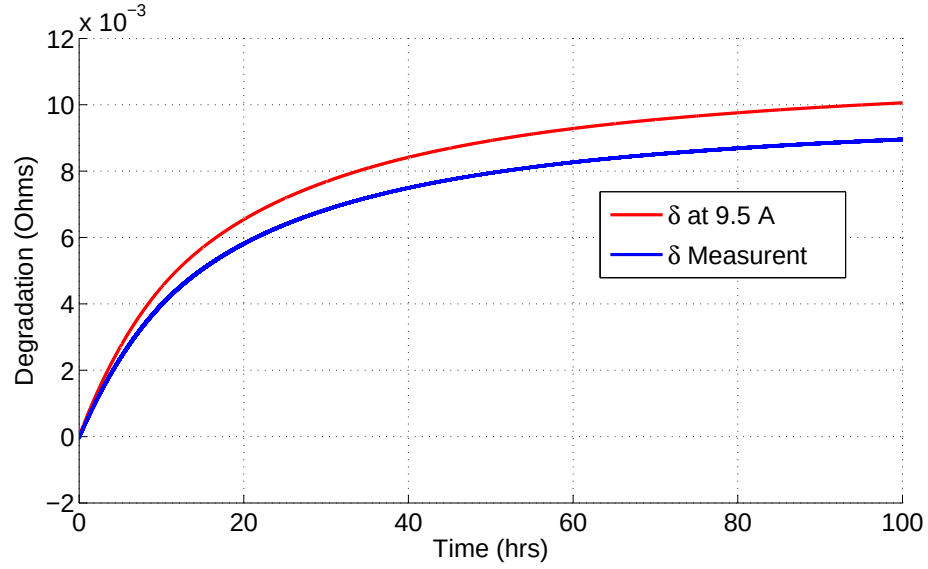


Figure 8.5: Progression in the simulated degradation. The red curve shows the effective degradation in terms of increased impedance magnitude at the nominal DC current operating point of $I_o = 9.5$ A, and the blue curve shows the ideal degradation measurement as the operating point moves along the cell's polarization curve.

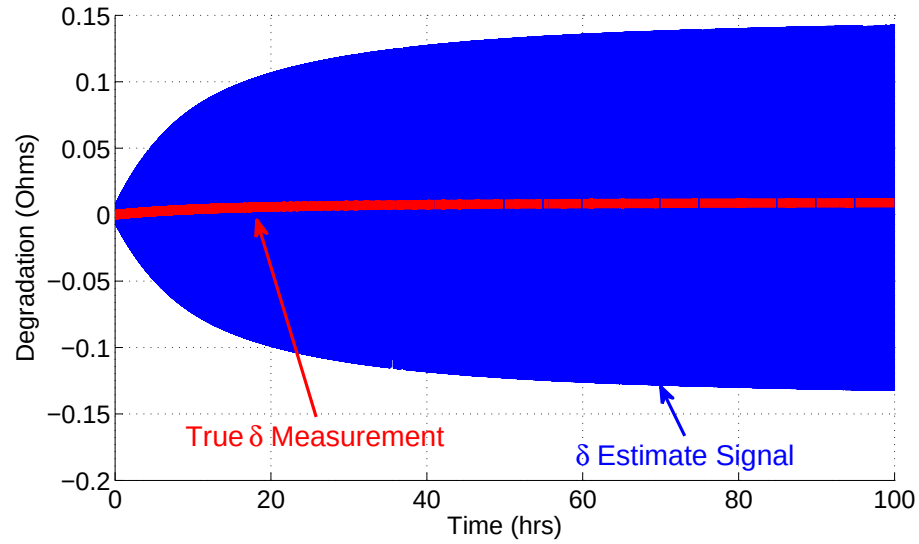


Figure 8.6: Simulated degradation estimate signal for the entire test. The true degradation measurement is shown in red.

the amplitude of this signal's AC component. This becomes important if the total amount of signal filtering provided by the control system compensator is inadequate for sufficiently attenuating this signal. In this plot, the true degradation measurement value is shown in red.

Figure 8.7 shows the resulting controlled DC current and voltage profiles for the cell over the 100 hour simulation. On the bottom plot, the DC current is given by the blue curve, and for comparison, the progression in the ideal degradation measurement is scaled by the compensator's DC gain and shown here by the dashed red curve. These two curves essentially align, which indicates that the simulated degradation estimate signal, $\hat{\delta}$ is accurate. The resulting progression in the cell's DC voltage is given on the top plot and shows that the cell's voltage actually increases slightly during the simulation.

Figure 8.8 illustrates the generation of the degradation estimate signal, $\hat{\delta}$ from the combined waveform signal, $\hat{V}_{\delta}$ over a single-second time interval at the 300 second mark. The combined waveform, shown in red, is full-wave rectified through multiplication with a square wave resulting in the the degradation estimate waveform shown in blue. The mean value of this estimate waveform is proportional to the AC-amplitude of the combined waveform, which as shown in (8.15) is the amount of degradation in the cell. The compensator filters the AC portion of this rectified signal. The compensator output is shown here in green and scaled by the inverse of the compensator gain for comparison with the $\hat{\delta}$ signal. It should be noted that the combined waveform is slightly distorted due to the cell's voltage being derived from the nonlinear 3rd-order polynomial models.

Figure 8.9 shows two sets of simulated current and voltage waveforms over one-second long intervals near the beginning of the simulation (250 seconds in, Figure 8.9a) and the end of the simulation (96 hours in, Figure 8.9b). In both sets of plots, the

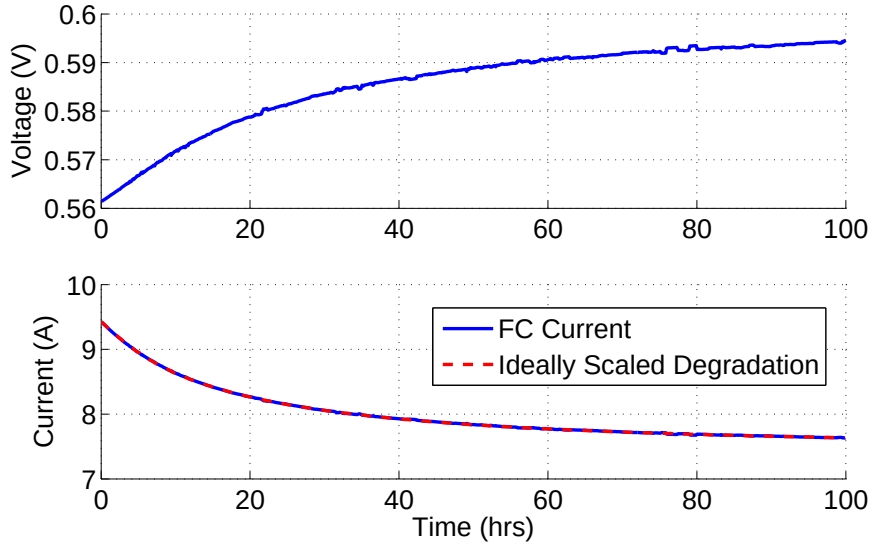


Figure 8.7: Simulated progressions in the cell's average voltage and current. On the current plot, the simulated current is shown in blue, while the dashed red curve gives the simulated degradation measurement scaled by the compensator's DC gain and offset by the nominal fuel cell current.

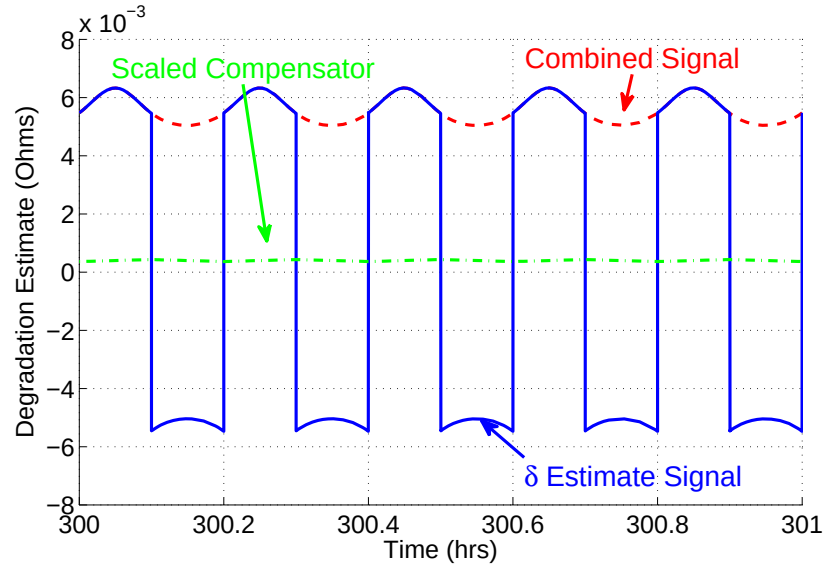
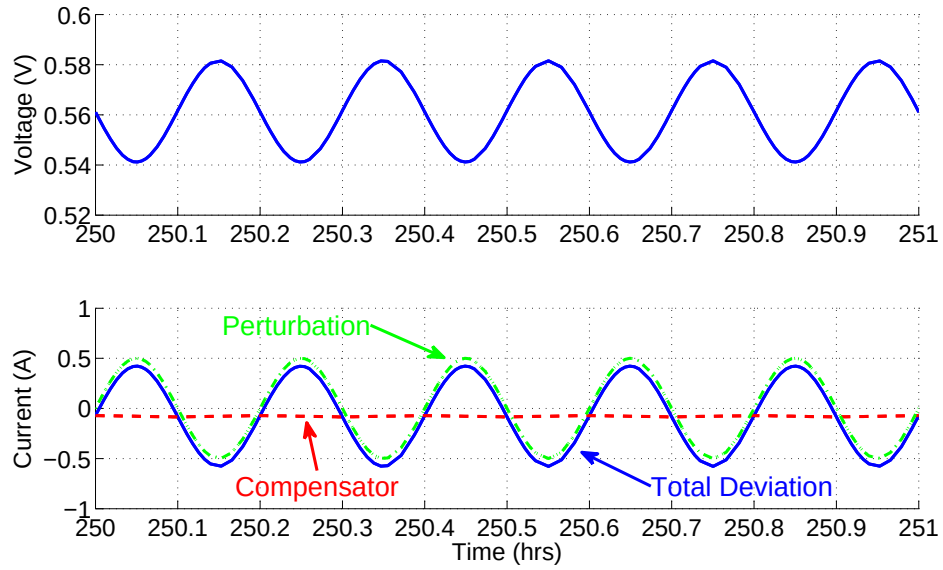


Figure 8.8: The simulated degradation estimate signal is the rectified version of the combined signal (8.14) given by the dashed red line. The compensator output signal scaled down by the DC gain is shown by the green dashed curve.

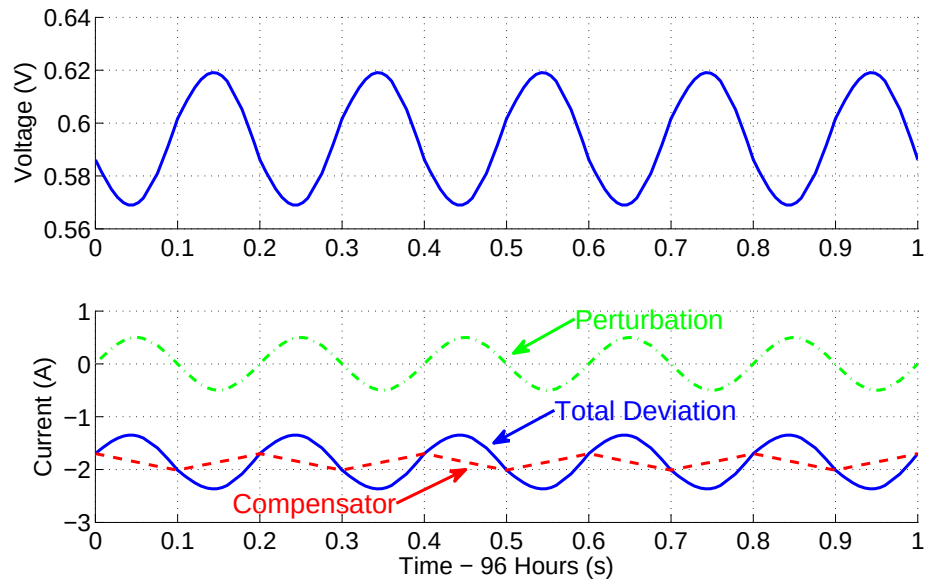
compensator's output current and added cell perturbation current are given by the dashed red and dashed green waveforms, respectively. The blue waveform represents the sum of these two and is the total deviation in cell current from the nominal value of $I_o = 9.5$. The resulting voltage response to this total deviation is given in the top plots.

After only 250 seconds, the amount of accumulated degradation in the cell is minimal, the responding compensator current is still near zero, and the DC operating point of the fuel cell is still near its nominal operating point. Therefore, the combined waveform of (8.14) and (8.15) has a relatively small DC component, $V_{\delta,DC}$. The compensator output current, which is the rectified, gained and filtered version of this waveform then has a relatively small AC component so that the shape of the total current deviation waveform is almost identical to that of the perturbation waveform.

At the 96 hour mark, however, the degradation in the cell is substantial and the DC operating point is shifted by about 30 mV and 1.7 A (Figure 8.7) due to the compensator's output. As described above, this shift results in a combined waveform of (8.15) with a large DC component, $V_{\delta,DC}$, which translates into a large AC component in the degradation estimate waveform (8.16). However, because there is adequate filtering in the compensator, this AC component is largely attenuated as shown here with AC component of the compensator current magnitude only one-third that of the perturbation current. While this magnitude is large enough to result in some noticeable distortion to the total deviation current waveform and the resulting voltage response, it is not so large that the magnitude of the voltage response is significantly affected. As stated earlier, this is important both in terms of maintaining a predominantly linear voltage response for accurate impedance detection and in preventing additional degradation caused by large swings in cell operation.



(a) 250 seconds



(b) 96th Hour

Figure 8.9: Simulated fuel cell current and voltage waveforms at the (a) 250 second mark of the experiment, and the (b) 96th hour of the experiment. In each, the top plot shows the cell's voltage response to the perturbation current. The bottom plot shows the total cell current deviation from the nominal current. This total deviation current is comprised of the compensator output (dashed red curve) and the perturbation current (dashed green curve).

Collectively, these figures illustrate the operation of the control system and give an indication of the anticipated cell and control system behavior over the course of a full 100 hour test. As degradation occurs and cell impedance increases, the control system reduces the DC-current loading of the fuel cell, which in turn reduces the time rate of degradation in accordance with the simulated degradation model. This results in a slowing of the accumulated degradation and impedance increase. Just after the 40 hour mark, the cell's impedance increases to a point where the resulting DC current enters the dead-band region which has an upper limit of 8 A. This is seen in Figure 8.7. However, while not shown in that plot, the fuel cell current also includes the perturbation component which causes the total cell current to periodically exceed the dead-band upper limit, thus continuing the simulated degradation. After 100 hours, the cell's measured impedance is increased by around 9 m Ω resulting in the controlled decrease in the cell's operating current of about 1.8 A.

Experimental Setup

The experimental setup for the continuous current control of degradation experiment consists of the experiment circuit, the control circuit, and the data acquisition system. The experiment circuit consists of an HP 6012B bench-top power supply connected in series with the fuel cell and an Agilent N3305A programmable electronic load. The power supply is required to increase the DC bias voltage applied across the electronic load as the voltage required is larger than the operating fuel cell voltage.

Figure 8.10 shows a schematic for the control circuit used in this experiment. Operational amplifiers, OP1 and OP2, are AD620 instrumentation amplifiers used to measure V_{fc} and $I_{fc}|Z|_o$, respectively as well as provide gain, k_1 , to these measurements. Because $|Z|_o$ is particular to the fuel cell under test, R_{Gi} which sets the gain

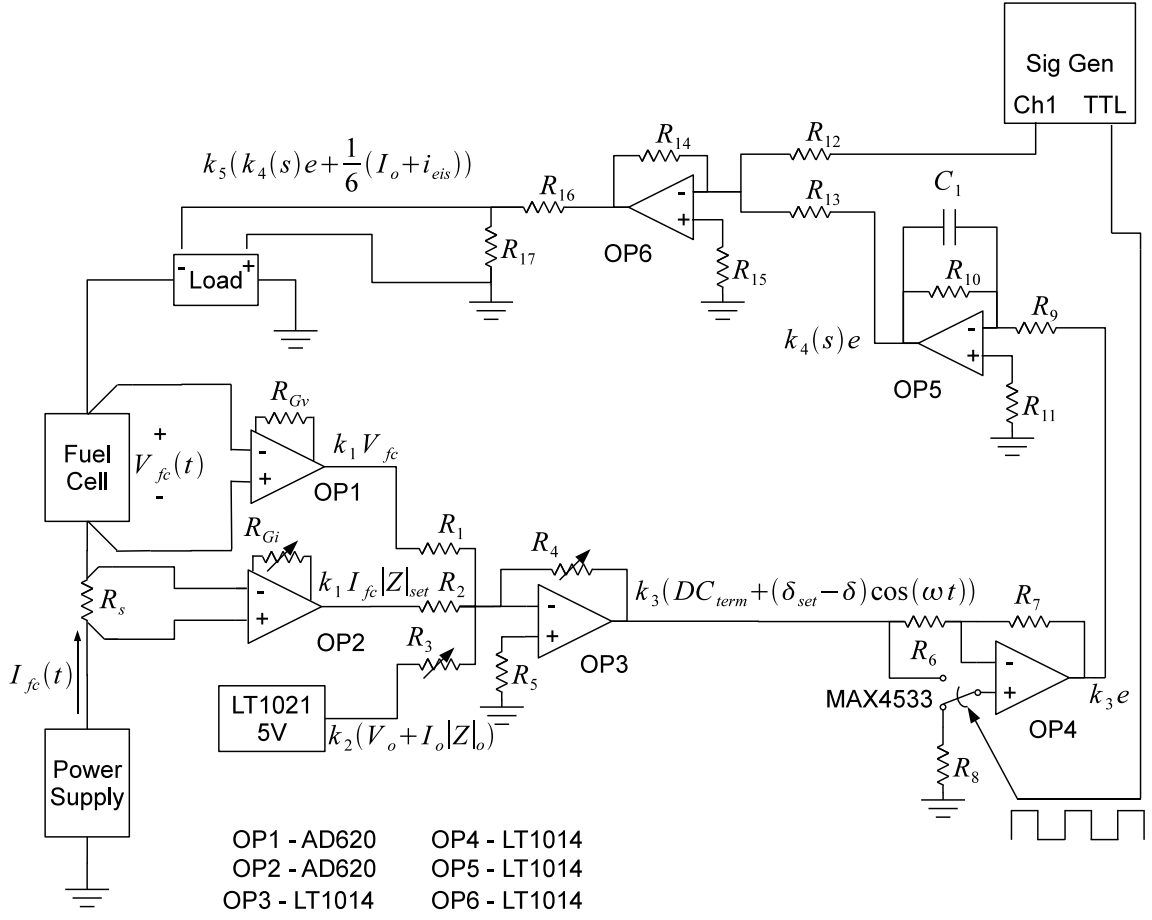


Figure 8.10: Simplified impedance magnitude detection and control circuitry utilized in the impedance magnitude based degradation control scheme.

of OP2, is variable and adjusted so that this op-amp gain is given by,

$$G_i = k_1 \frac{|Z|_{set}}{R_s}. \quad (8.18)$$

R_{Gi} then is also used to input the degradation set point, δ_{set} as $|Z|_{set} = |Z|_o + \delta_{set}$. An LT1021 precision reference chip with 5V output in combination with R_3 is used to provide the DC offset term subtracted from the combined voltage signal of equation

Component	Value	Tolerance / Resolution
R_s	0.1 Ω	1%
R_{G_V}	5.49 k Ω	1%
R_{G_I}	0 - 50 k Ω	25 Turns
R_1	9.09 k Ω	1%
R_2	9.09 k Ω	1%
R_3	0 - 10 k Ω	25 Turns
R_4	0 - 50 k Ω	25 Turns
R_5	2.74 k Ω	1%
R_6	10.5 k Ω	1%
R_7	10.5 k Ω	1%
R_8	5.23 k Ω	1%
R_9	267 k Ω	1%
R_{10}	2.7 M Ω	5%
R_{11}	243 k Ω	1%
R_{12}	10.5 k Ω	1%
R_{13}	10.5 k Ω	1%
R_{14}	10.5 k Ω	1%
R_{15}	3.48 k Ω	1%
R_{16}	4 k Ω	1%
R_{17}	2 k Ω	1%
C_1	3x 1 μ F	10%

Table 8.2: Component values for the impedance magnitude detection and current control schematic of Figure 8.10.

(8.14). The gain, k_2 is given by

$$k_2 = \frac{5V}{V_o + I_o|Z|_o}. \quad (8.19)$$

OP3 subtracts the DC offset from the sum of the OP1 and OP2 outputs, with the variable resistor R_3 set as,

$$R_3 = -\frac{k_2}{k_1}R_1, \quad (8.20)$$

in order to adjust the overall gain of the offset term to match that applied to the current and voltage measurements. Variable resistor R_4 is adjusted so that the gain

applied to the combined signal is,

$$k_3 = -k_1 \frac{\pi}{2A}, \quad (8.21)$$

so that k_3 has the units of $k_1\Omega$.

Operational amplifier, OP4, in combination with the MAX4533 analog switch, serves to full-wave rectify the output of OP3. This is done through an exogenous input signal, shown in Figure 8.10 as being provided by a Tektronix AFG 3022B signal generator's TTL logic output, which controls the switching of the MAX4533. This logic output signal should be in phase with the fuel cell's voltage response, v_{eis} . This way, when this voltage response is positive, the switch closes high so that the positive terminal of the OP4 is connected to the output of OP3, and OP4 effectively behaves as a voltage follower. When the voltage response is negative, the switch closes low, and OP4 is rendered to behave like an inverting op-amp with a gain of -1.

This rectified waveform, k_3e is then passed to OP5 which sets the compensator time constant of (8.17) as, $\tau_c = R_{10}C_1$, and an additional DC gain, $-R_{10}/R_9$ is applied to the signal so that,

$$k_4(s) = -k_3 \frac{R_{10}}{R_9} \frac{1}{\tau_c s + 1}. \quad (8.22)$$

This time constant needs to be set so that $\tau_c \gg 1/\omega_{eis}$ in order to provide adequate filtering of the non-DC components of e . Finally, the nominal current set point, I_o , and the EIS perturbation current set point, i_{eis} , are added to the filtered error signal through OP6, with $R_{12} - R_{14}$ set equal so that OP6 has an inverting gain of 1.

Following the voltage divider which provides adjustability to the full system gain, the combined signal is passed to the load's analog input terminals for translation to

the fuel cell's current, with

$$k_5 = -\frac{R_{17}}{R_{16} + R_{17}}k_4 \quad (8.23)$$

The $\frac{1}{6}$ terms shown here in Figure 8.10 are due to the electronic load imparting a gain of 6 in translating the signal at its analog input terminals to the demanded fuel cell current. Thus, the set point signal for I_o and i_{eis} coming from the signal generator need to be appropriately reduced in magnitude.

The primary function of the voltage divider is to provide attenuation, which allows larger gains in the earlier stages of the control circuit. This increases the signal magnitudes at these earlier stages which helps to counteract voltage offset issues that otherwise result in offset errors to the controlled current. The passive component values used in building the circuit of Figure 8.10 are given along with their tolerances in Table 8.2.

Experimental Procedure

Following fuel cell setup in accordance with the procedures outlined in Chapter 2, the fuel cell is allowed to activate over night as opposed to just 4 hours in order to avoid the delayed activation observed in some of the previous tests. Following this extended activation, initial polarization and EIS measurements of the cell are performed. For the polarization data measurements, cell current is ramped from 0 A to about 20 A at a constant rate of 0.11 A/s, and fuel cell voltage and current data are collected at a rate of 10 Hz by the NI9206 DAQ.

Five sets of EIS measurements are performed; one at each DC operating point of 1.5 A, 4 A, 7 A, 10 A and 15 A. For each set of EIS measurements, two rounds of EIS measurements are recorded. The first round features an EIS perturbation signal that sweeps in frequency logarithmically from 100 mHz to 1 kHz over 175 seconds, while

the second round features a single frequency EIS perturbation signal at 5 Hz for 20 seconds. This 5 Hz frequency is the frequency used for the continuous perturbation of the cell, and so the single frequency EIS measurements are used to calibrate the control system, i.e. set V_o , I_o , $|Z|_o$ and A . During EIS testing, the DAQ samples the voltage and current signals at a rate of 50 kHz.

Once this initial data collection is complete, the cell is connected to the experiment circuit and control circuit as shown in Figure 8.10, except that R_{13} is disconnected from the output of OP5 and grounded so that the system is initially operated open-loop. The gains of potentiometers R_{Gi} , R_3 , and R_4 , and the amplitude of the perturbation signal coming from the signal generator, are adjusted in accordance with the calibrated values of V_o , I_o , $|Z|_o$ and A , so that the output of OP3 is minimized about zero. Any desired δ_{set} value is then input to the system by adjusting the value of R_{Gi} and monitoring the amplitude of the output signal at OP3. The system is now ready for operation, and resistor R_{13} is reconnected to the output of OP5, thus closing the loop. Table 8.3 gives the measured values for I_o , V_o , and $|Z|_o$ for the fuel cell used in the experiment along with the amplitude A of the perturbation signal, the resulting variable resistor set points and gains $k_1 - k_5$ and overall compensation gain K_c for the experiment shown here.

During testing, DAQ channels are set up to record the fuel cell voltage, the fuel cell current, the output voltages of each op-amp, and the two inputs from the signal generator, i.e. the nominal and eis perturbation set point. All channels are recorded at a sample rate of 200 Hz. Following a 100 hour test period, the control circuit is disconnected from the cell and experimental circuit, and the same polarization and EIS measurements performed prior to cell testing are repeated. The cell is then disconnected from the experiment circuit and shut down, removed from the oven, and prepared for SEM imaging in accordance with the protocols described in Chapter 2.

Variable	Value	Description
<i>DC Setpoint</i>		
I_o	9.5 A	Nominal DC Current
V_o	640 mV	Nominal DC Voltage
$ Z _o$	27.6 m Ω	Zero-degradation Impedance Magnitude
<i>System Setting</i>		
A	0.5 A	Perturbation Amplitude
R_{Gi}	28.07 k Ω	OP2 Gain Resistor
R_3	5.04 k Ω	DC Offset Gain Resistor
R_4	28.6 k Ω	Combined Signal Gain Resistor
<i>Gains</i>		
Gv	10	OP1 Gain
Gi	2.76	OP2 Gain
k_1	-10	Voltage and Current Measurement Gain
k_2	5.54	Effective Offset Gain
k_3	31.4	Gain at OP3 Output
k_4	-317	DC Gain at OP5 Output
k_5	106	Gain at Load Input
K_c	202	Total System Gain (as defined in (8.17))

Table 8.3: Continuous current control experimental set point, parameter and gain values.

Experimental Results

Figure 8.11 shows the progression in the measured fuel cell impedance magnitude and phase over the course of the nearly 100 hour test. These measures of impedance were performed using 100-second sections of measured current and voltage data. Because only a single known frequency excitation signal was used for perturbation, rather than extract the impedance information using the least squares fit routine of Chapter 4, the simpler frequency response analysis (FRA) technique was used [43]. It should be noted that these measures of impedance were calculated post-testing in

software and are independent of the control system's internal measure of impedance magnitude.

Figure 8.12 shows the control circuit voltage measurement taken at the output pin of OP4. Because $\delta_{set} = 0$, this measured voltage should have a DC component that is proportional to the degradation, δ , with a scaling factor of k_1 . The top plot shows the full profile of this voltage measurement recorded throughout the cell test, while the bottom plot gives the output voltage averaged over 100 second segments. This output voltage is analogous to the degradation estimate signal (8.16) and features a similar envelope growth profile as that seen in the simulation (Figure 8.6). This again is due to the control system's shifting of the cell's DC operating point away from its nominal value as degradation is detected.

For comparison, the actual measured degradation in the cell defined as $\delta = |Z| - |Z|_o$ and calculated from the values shown in Figure 8.11, is shown on the bottom plot multiplied by the ideal scaling factor, k_1 . From this comparison, it is evident that the degradation estimate does not scale as intended, with the total change in estimated impedance from time $t = 0$ hours to $t = 96$ hours around half of the measured accumulated degradation.

The effect of this improperly scaled estimate of detection on the controlled current is shown in Figure 8.13. In this figure, the cell's DC voltage is shown on the top plot and the DC current is shown on the bottom. These DC measurements are estimated by averaging measured cell voltage and current over 100 second intervals. The bottom plot showing current also includes the measure of degradation, δ negatively scaled by the ideal compensator gain of K_c . This represents the expected DC fuel cell current profile. However, because the degradation estimate of Figure 8.12 is incorrectly scaled, the resulting measured DC current only decreases by about half this expected amount.

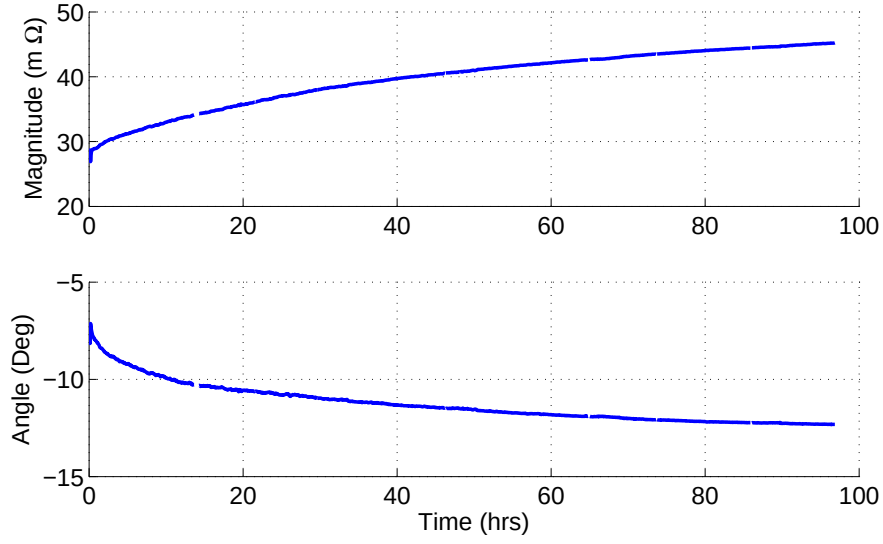


Figure 8.11: Cell impedance continuously measured throughout the 100 hour experiment. The top plot shows the cell's impedance magnitude while the bottom plot shows the cell's impedance phase.

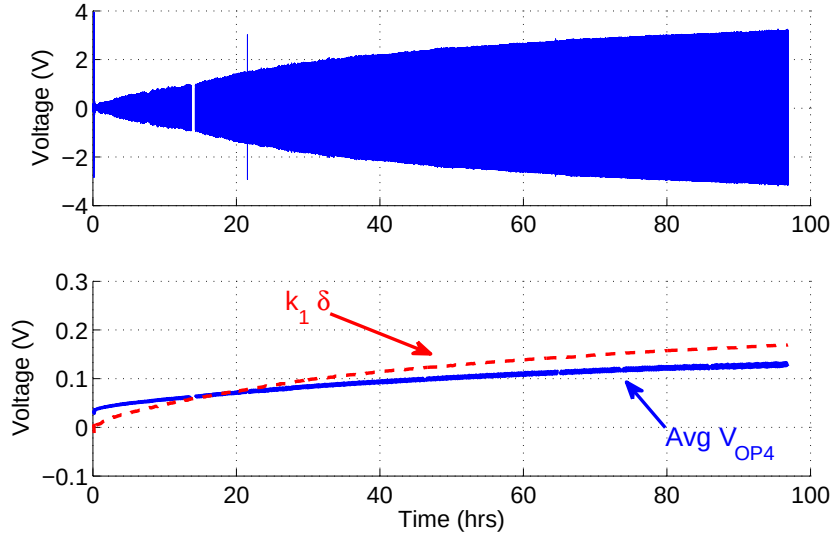


Figure 8.12: Output voltage of op-amp OP4. The top plot shows the full profile of this rectified signal while the bottom plot gives the output voltage averaged over 100 second segments. In this bottom plot, the cell's measure of degradation, δ , is plotted multiplied by the gain, k_1 , for direct comparison.

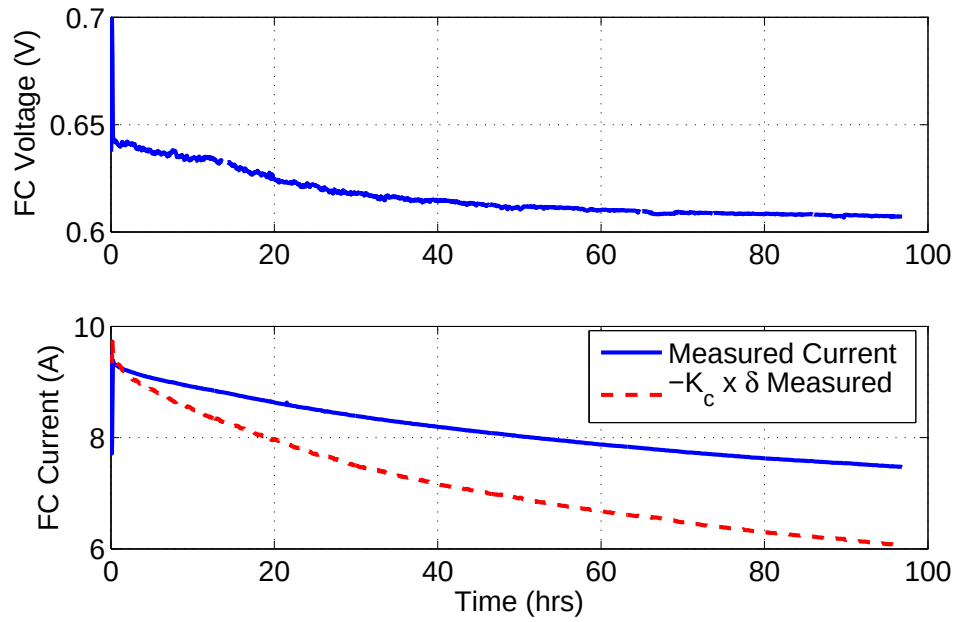


Figure 8.13: Fuel cell's (top) DC voltage and (bottom) current measured throughout the 100 hour experiment.

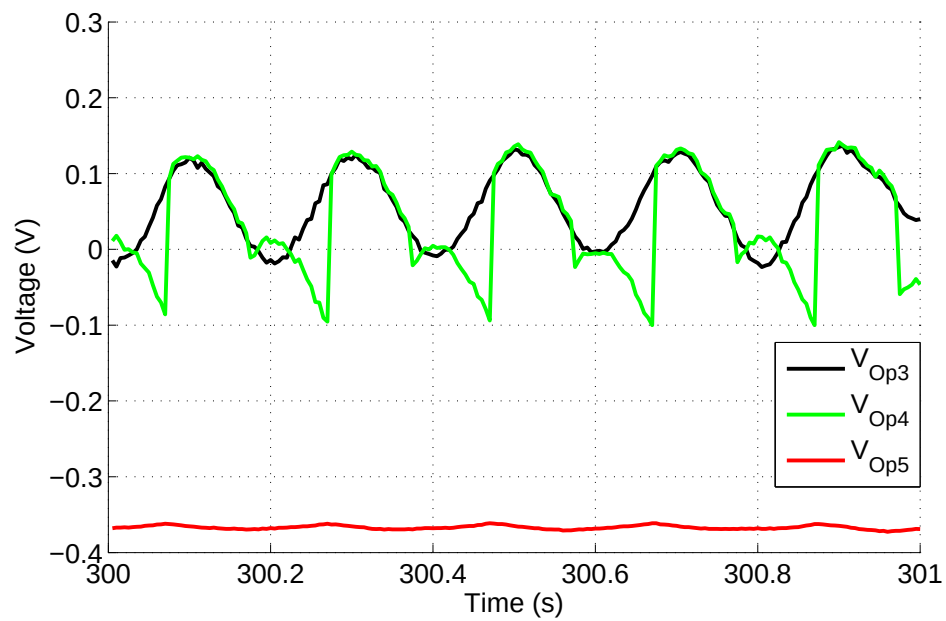


Figure 8.14: Output voltages for op-amps 3, 4, and 5 in Figure 8.10. In comparing.

The waveforms in Figure 8.14 are the voltage measurements taken at the output terminals of op-amps OP3, OP4 and OP5, over a one second time interval at the 300 second mark of testing. What is immediately evident from this figure is that the switching of the positive input terminal of OP4 is out of phase with the combined voltage output of OP3. This was caused by the TTL logic output port of the Tektronix AFG 3022B that provides the logic command to the MAX4533 switch incorrectly phase-shifted from the output channel used to provide the EIS perturbation signal. This offset in phase translates into a reduction in system gain as a portion of the signal is rectified to a negative value. This explains the reduced scaling of the degradation estimate in Figure 8.12 and the reduced deviation in the DC operating point of the fuel cell from its nominal operating as shown in Figure 8.13. V_{OP5} shows the measured signal resulting from the amplification and filtering of V_{OP4} provided by OP5. This output voltage corresponds well to the expected DC gain and filtering levels applied to V_{OP4} .

Figure 8.15 show measured current and voltage waveforms collected over one-second intervals near the beginning of testing (250 second mark, Figure 8.15a) and near the end of the test (96 hour mark, Figure 8.15b). The waveforms collected at $t=250$ seconds show very little distortion in their shape, while those at $t=96$ hours shows rather significant distortion. This increased distortion observed at the end of the test is due to the increase in the AC-component of the rectified output voltage at OP4 as the cell's DC operating point shifts. The magnitude in the resulting AC-component of cell voltage is around 70 mV peak-peak.

The measured polarization curves performed prior to testing and after testing are compared in Figure 8.16a, and the associated current-power curves found by multiplying the measured current and voltage signals together are compared in Figure 8.16b. These plots show the initial polarization and power curves in green and the final

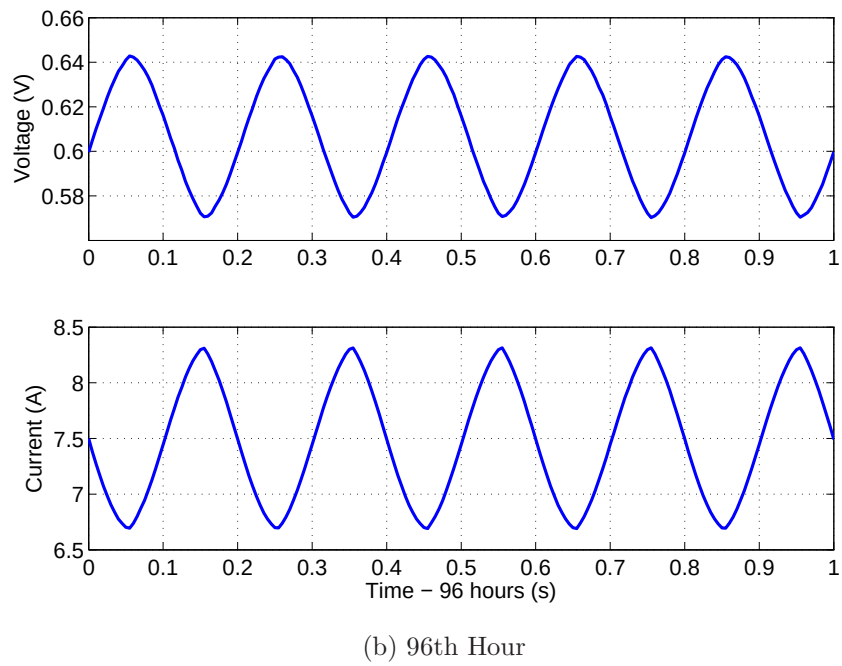
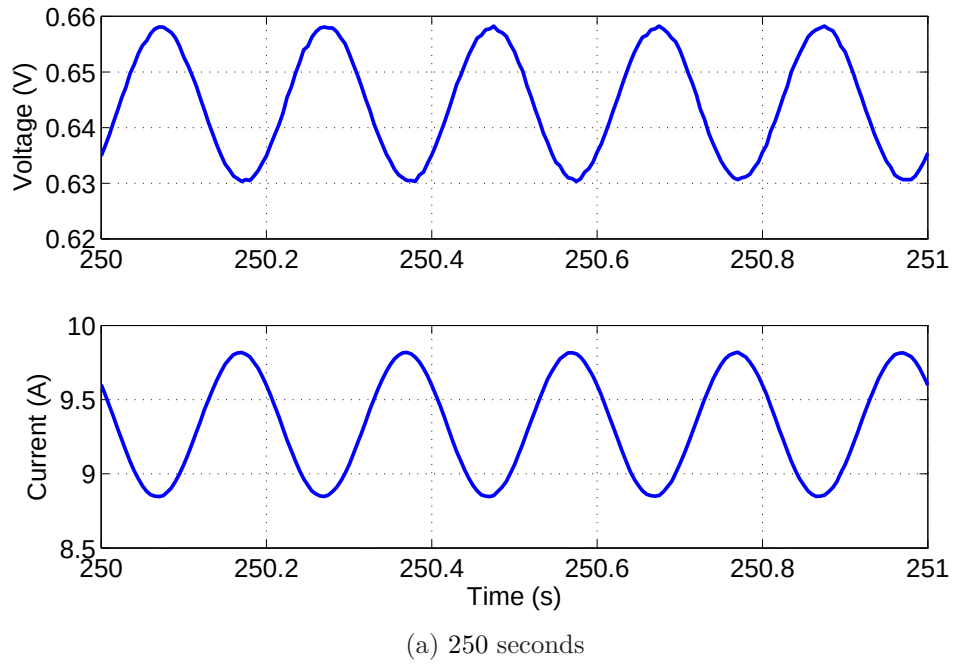
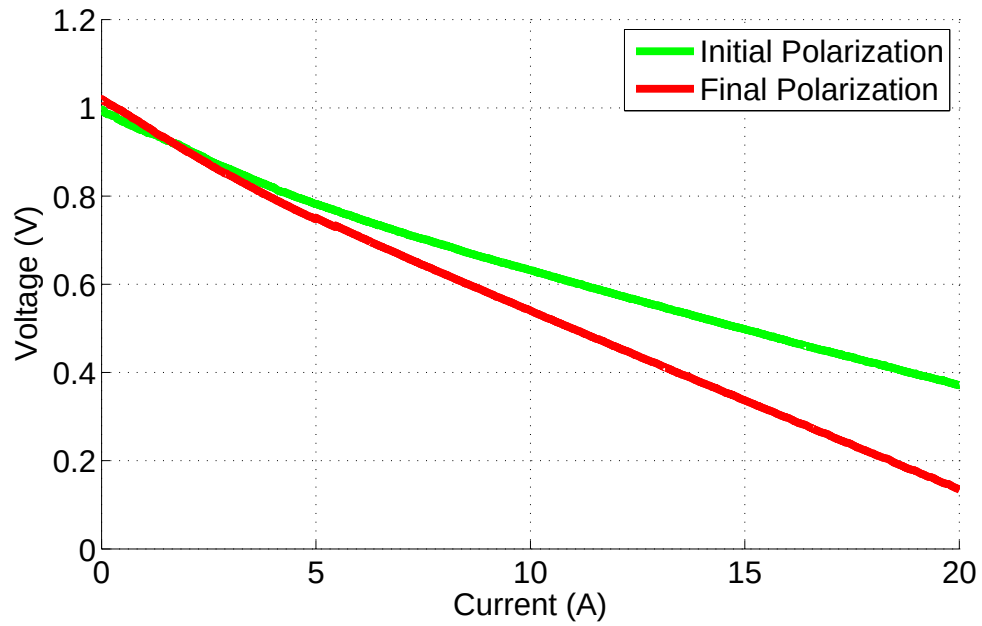
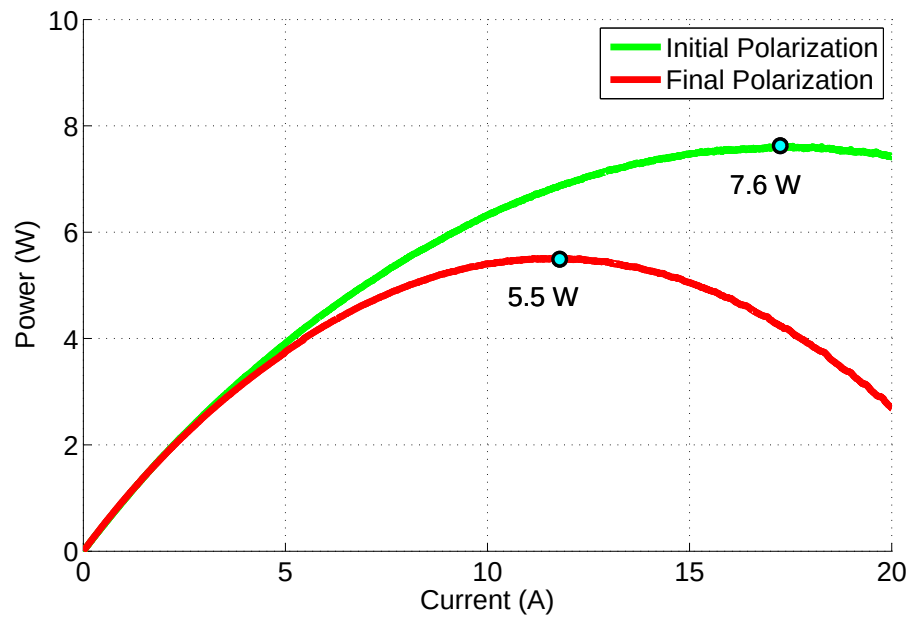


Figure 8.15: Measured fuel cell current and voltage waveforms at the (a) 250 second mark of the experiment, and the (b) 96th hour of the experiment.



(a) Current-Voltage Relationship



(b) Current-Power Power Relationship

Figure 8.16: (a) Measured polarization curves and (b) the current to power relationship for the fuel cell prior to and following testing. The light blue points on the power curves represent the maximum power points.

curves in red. In the current-power plot, the maximum power points for each curve is indicated by the blue dots and are labelled with the maximum available power value. From these values, it is seen that the maximum available output power of the fuel cell reduces by 28% over the course of the entire test.

The effects of this degradation on the electrochemical impedance of the cell at a range of operating points from 1.5 A to 15 A are shown in Figures 8.17 - 8.21. In each of these figures, the initial measured EIS profile is shown in black while the final profile is shown in green. For these measurements, the EIS perturbation signal was a swept sinusoid that ranged logarithmically in frequency from 100 mHz to 1 kHz. Additionally, the impedance at the excitation frequency used during the test, 5 Hz, was measured independent of the EIS sweep. These measurements are shown by the red dots.

Figure 8.22 shows the results of an analysis test performed to fit the observed cell degradation as a function of the observed current to the degradation model of Figure 8.3. Here, the top plot shows the calculated change in degradation over 100-second intervals found by subtracting the measured cell impedance magnitude value at the time instance $t - 100$ seconds from that at the time instance t . The current values of the x-axis correspond to the average of the measured current values (Figure 8.13) at time instances t and $t - 100$ seconds. The dashed red line represents the best fit line of this data, which is used to estimate a local model of degradation rate as a function of current loading. The total accumulated degradation using this model of degradation rate with the measured current profile as an input is shown by the red curve in Figure 8.22b, while the actual measured degradation is shown in blue.

Figure 8.23 shows follow-up results of a simulation run following an update of the simulation program based on the information gained from the measured data. Notably, this update removes the nonlinear model for fuel cell voltage and replaces

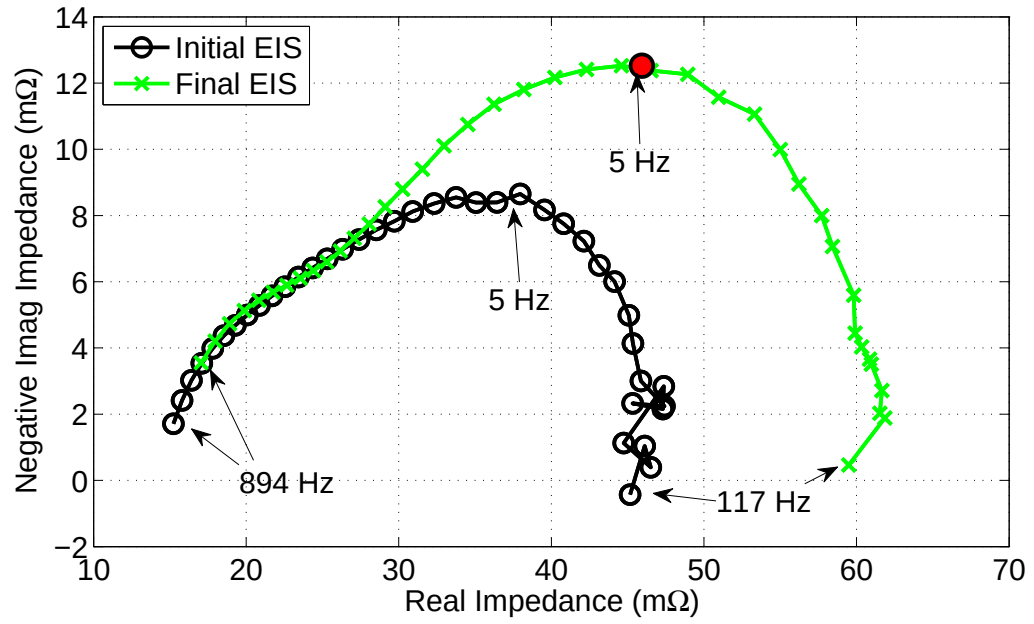


Figure 8.17: Measured EIS profiles before and after testing at a DC operating point of 1.5 A.

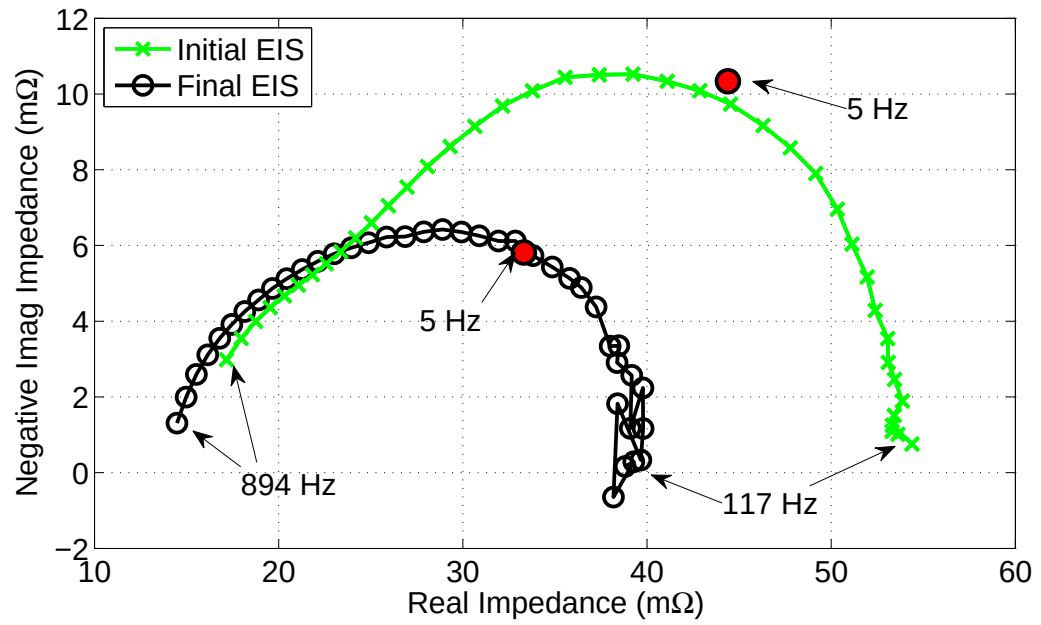


Figure 8.18: Measured EIS profiles before and after testing at a DC operating point of 4 A.

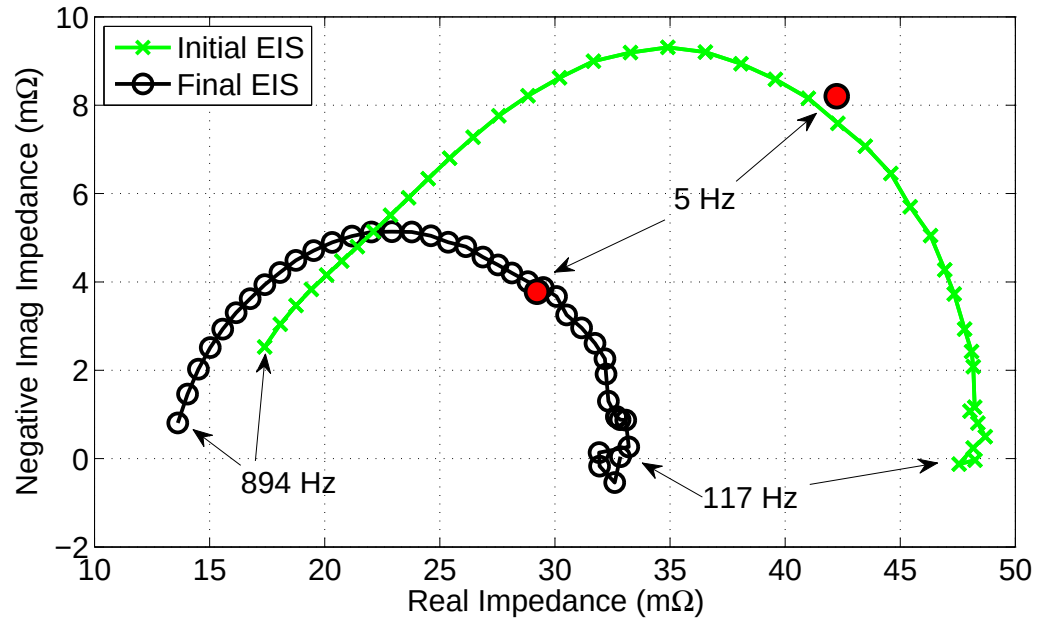


Figure 8.19: Measured EIS profiles before and after testing at a DC operating point of 7 A.

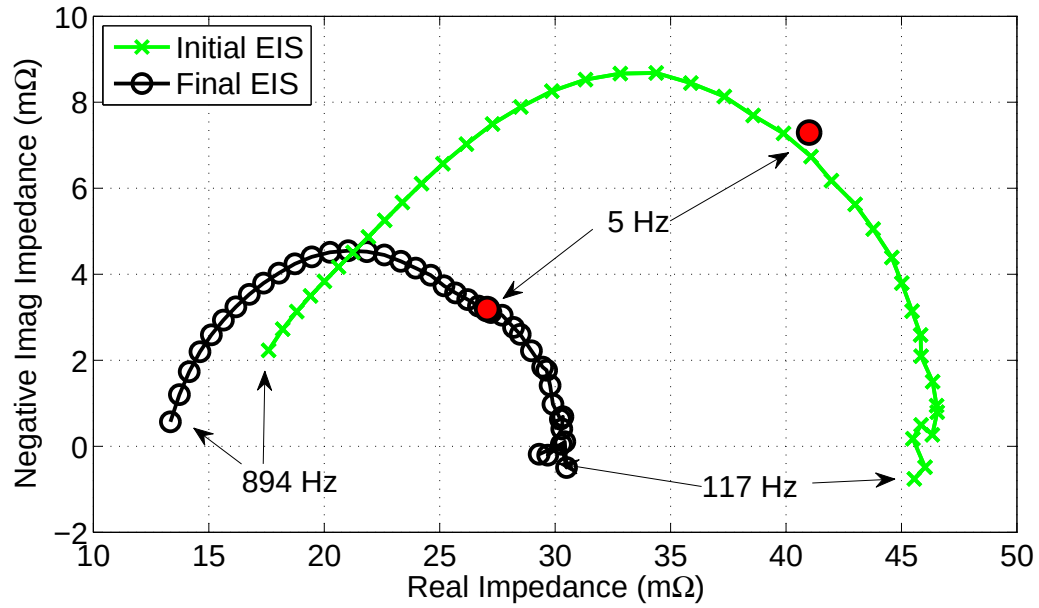


Figure 8.20: Measured EIS profiles before and after testing at a DC operating point of 10 A.

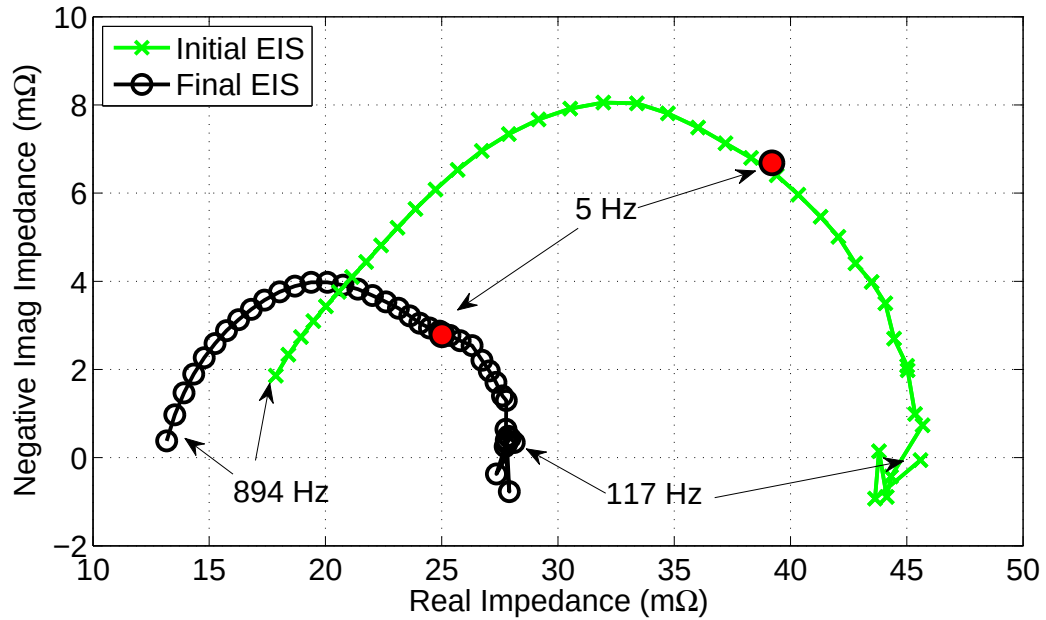
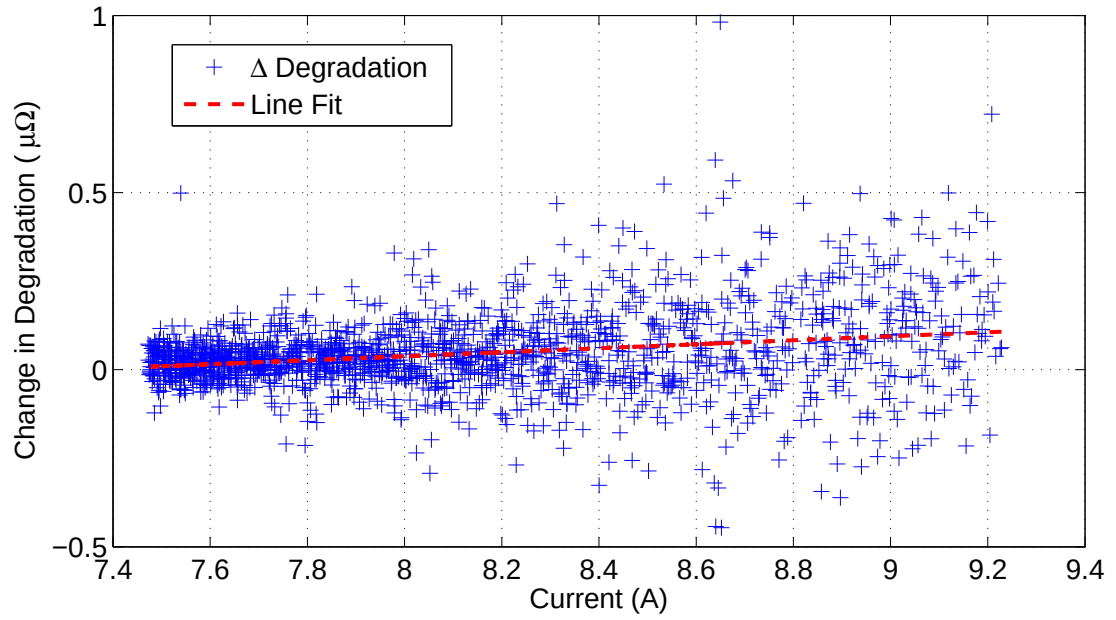


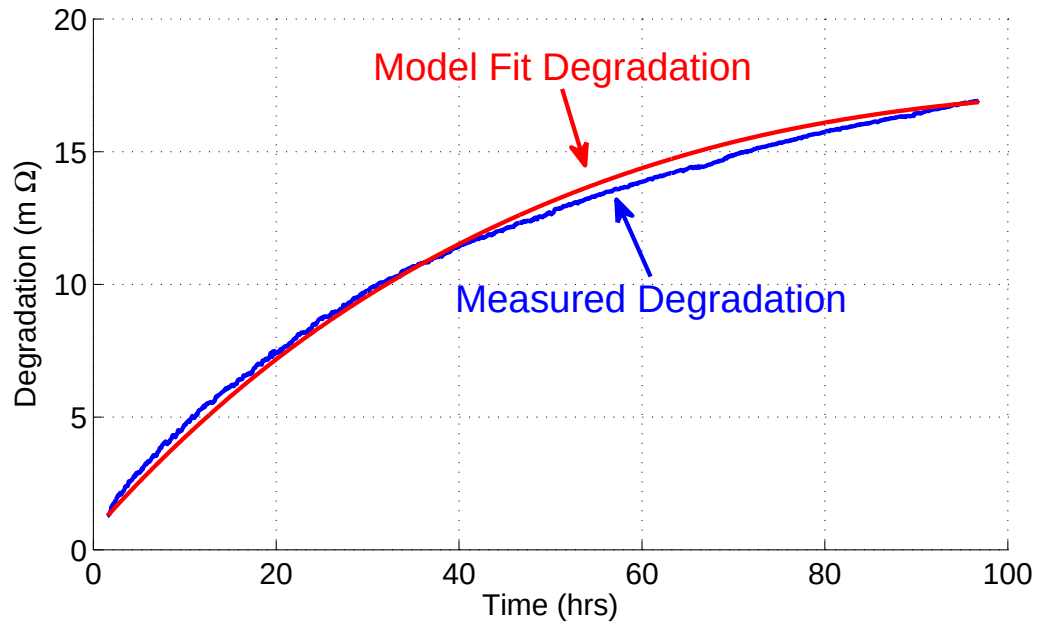
Figure 8.21: Measured EIS profiles before and after testing at a DC operating point of 15 A.

it with a linear model where the cell impedance is assumed constant across all DC current values. This is a reasonable update since the DC operating current during the test only varied by 1.8 A and so changes in the impedance due to the shifting operating point are minimal. Additionally, the fuel cell degradation model is updated based on the results of Figure 8.22 as well is the compensator model to reflect the effective gain during the test as opposed to the intended gain.

Figures 8.24 - 8.26 show SEM cross-sectional images of the fuel cell taken following control testing. The red arrow in the SOFC diagram accompanying each image indicates the quartered sample imaged and location along the break plane corresponding to the image. As was the case with the SOFC used for the PWM-control testing of Chapter 7, voids such as the one in Figure 8.24 were observed in the LSM layer of the cathode, though with a much lower frequency. As discussed in that chapter, these voids are not believed to be due to cell operation and instead are a product of cell

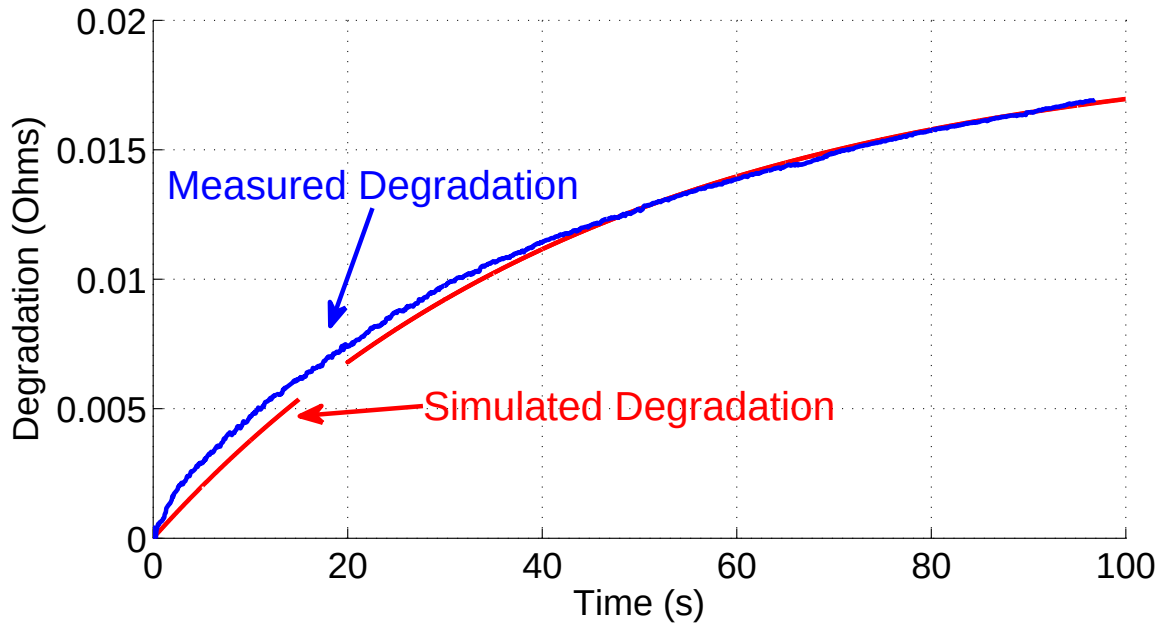


(a) Change in Estimated Degradation

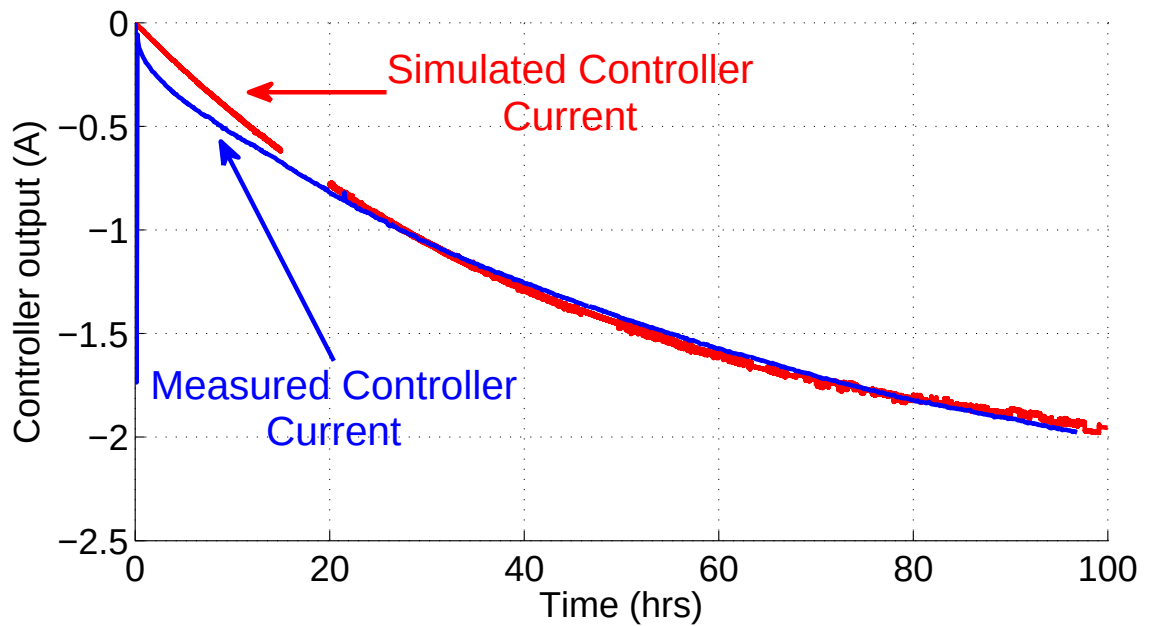


(b) Degradation Model Fit

Figure 8.22: Results of fitting measured current and degradation data to assumed degradation model with (a) showing the measured derivative relationship of degradation and current, and (b) showing the measured and predicted degradation using the model fit.



(a) Degradation



(b) Controller Current

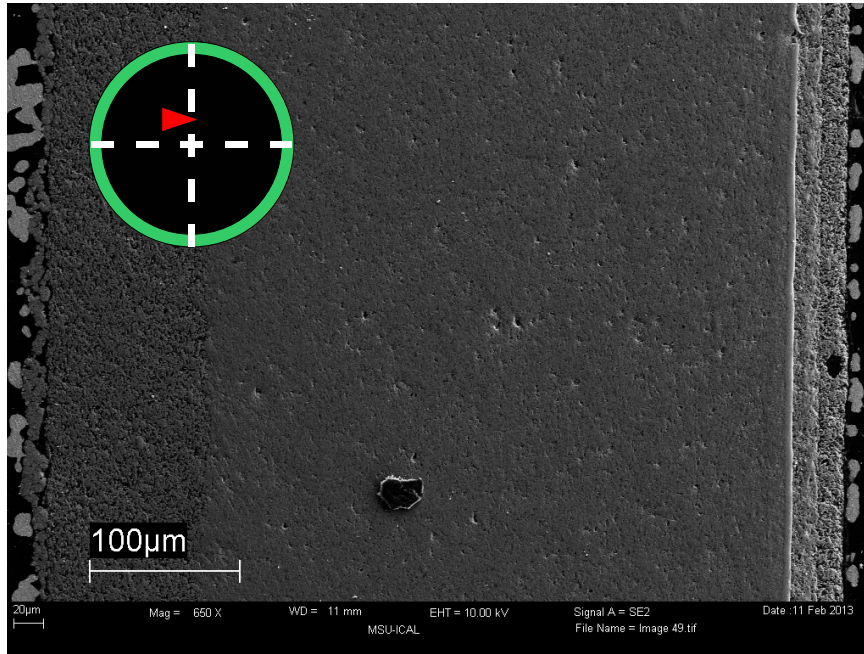
Figure 8.23: Comparison of the (a) measured degradation and (b) controlled current data with the results of the updated simulation.

manufacturing. The cell used in this test is from a different manufacturing batch of cells than the one used in the PWM-control test, and the fact that fewer voids are observed is most likely due to variability in the manufacturing process.

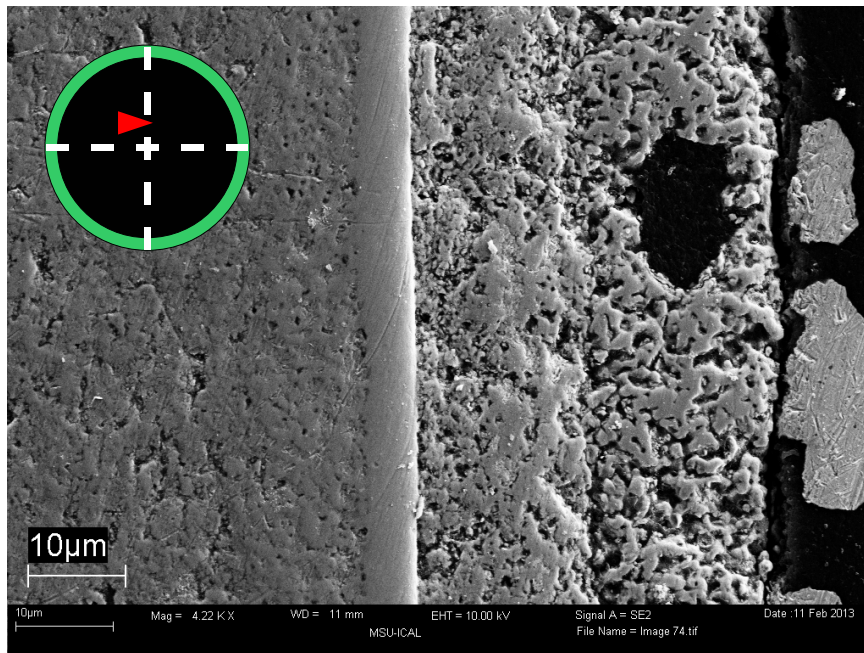
Figure 8.25 shows a small narrow crack in the cathode between the LSM layer and the LSM-YSZ layer. This crack is similar in size to those seen in the fuel cell following PWM testing. Figure 8.26 however shows a very large crack in the cathode similar in scale to that seen in the fuel cell used to test degradation and recovery cycling (Figure 6.3). During the SEM preparation processing of that cell, the sample was dropped during polishing which was thought to have caused the observed cracking. The sample shown in these figures also was potentially damaged during the polishing process as the sample came loose from the mount used for polishing with the silica carbide paper. Thus, the sample was allowed to rattle around for several minutes during polishing. In the close-up image of this crack shown in Figure 8.26b, roughly $5\text{ }\mu\text{m}$ -wide particles of alumina from the alumina polishing slurry are seen wedged within this crack.

Analysis and Discussion

Despite the issue of the offset in the TTL logic signal phase, the results of the previous section show that the continuous current control circuit performed as intended albeit with a smaller effective DC gain in the compensator. This essentially resulted in a less “aggressive” controlling of the cell current and subsequent accumulated degradation, which is easily seen in Figure 8.13 in the comparison of the measured fuel cell DC current to the ideally gain-scaled measured cell degradation. The effective average DC compensation gain for the system was determined to be around $120\text{ A}/\Omega$ through a least squares fit of the measured current as a linear function of measured

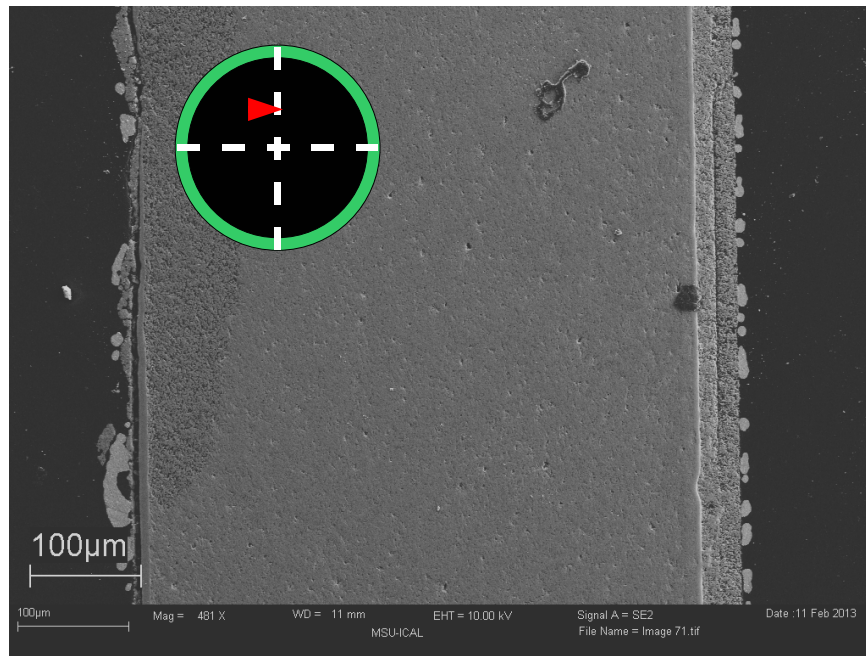


(a) Full View of Large Cathode Void

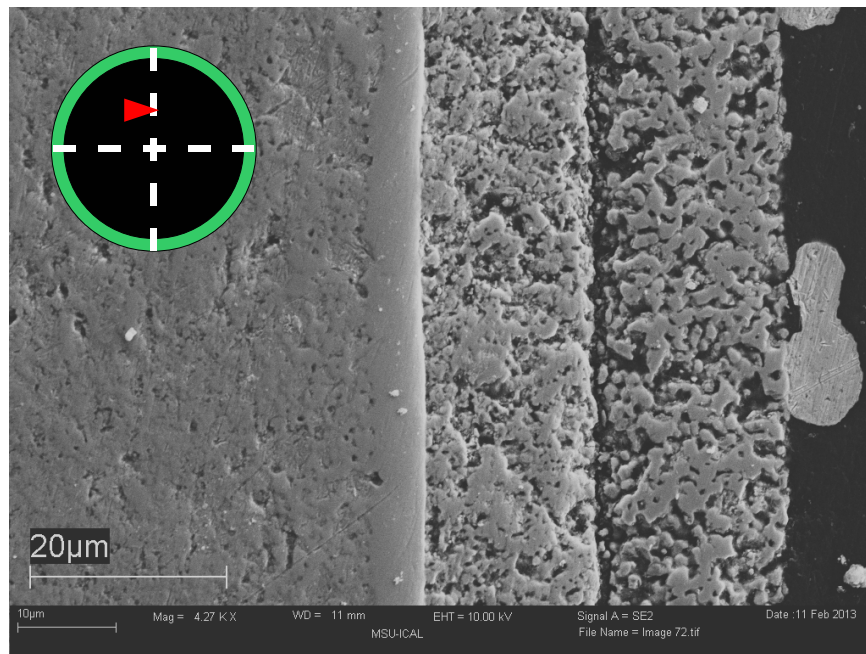


(b) Close Up View of Large Cathode Void

Figure 8.24: Large void in the LSM layer of the SOFC cathode. (a) Shows the full-cell width image while (b) shows a close up of the area around the void.

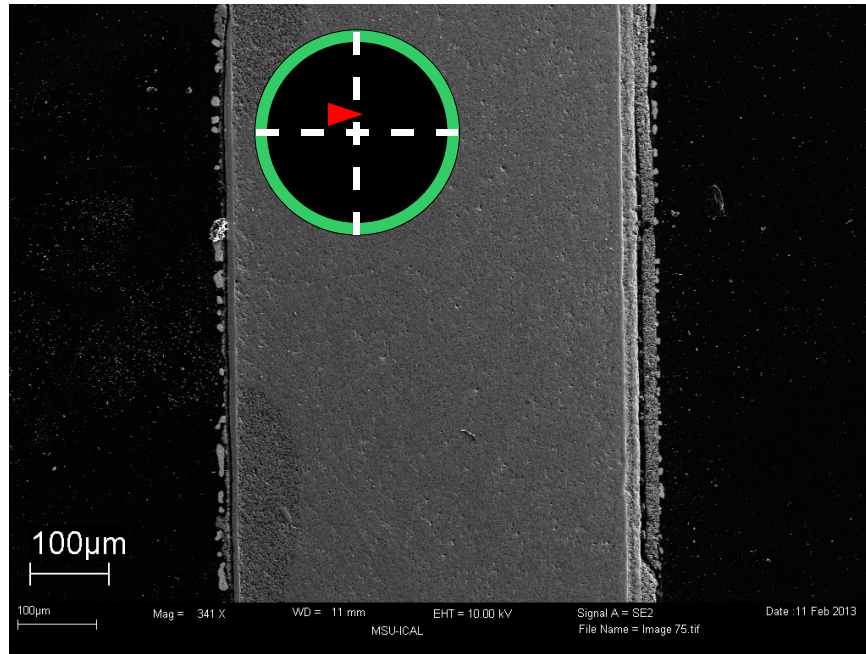


(a) Full View of Small Cathode Crack

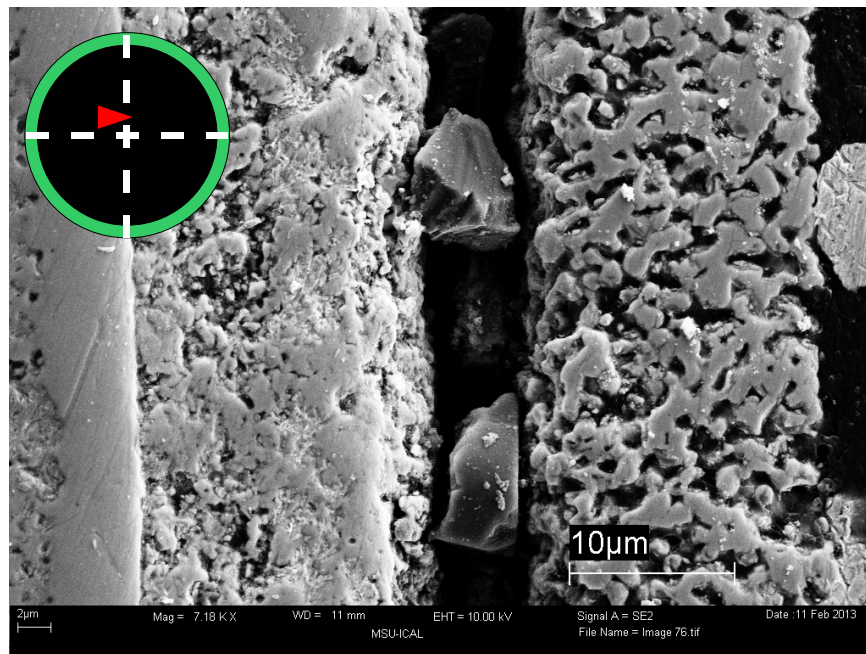


(b) Close Up View of Small Cathode Crack

Figure 8.25: Several cracks were observed in the cathode at the LSM layer's interface with the LSM / YSZ active layer. This one is similar in scale to those observed in Figure 7.12. (a) Shows the full SEM imaging view while (b) shows a close up.



(a) Full View of Large Cathode Crack



(b) Close Up View of Large Cathode Crack

Figure 8.26: Several cracks were observed in the cathode at the LSM layer's interface with the LSM / YSZ active layer. This one is large and similar in scale to that of Figure 6.3. (a) Shows the full SEM imaging view while (b) shows a close up.

degradation. However, this effective gain actually varied slightly through the test as the phase of the impedance decreased from -7.7° to -12.3° .

While not a perfect direct comparison because the parameter values for the cell and degradation models of the simulation are slightly off from those that best describe the cell used in this test, contrasting the measurement progressions of Figures 8.11 - 8.13 to the analogous figures of the simulation results (Figures 8.5 - 8.7) do give an indication of the effect this reduced gain has on the accumulated degradation. From Figure 8.5, the simulation program predicts a total accumulated degradation level of $9\text{ m}\Omega$ following the 100 hour test, while the measured increase in impedance, which is used as the measure of degradation for the experiment test, was found to be $17\text{ m}\Omega$. This larger value is primarily caused by the smaller decrease in cell current as degradation increases. Thus, the rate of cell degradation remains at a larger value for longer than what was simulated leading to a larger total accumulation of degradation over the 100 hour test.

Because it was desired to maintain a smooth and continuous progression in cell degradation and cell operation throughout the test, no intermediate polarization relationship nor multi-frequency EIS measurements were performed. Thus, no data is available to perform interpolation analyses. However, the polarization and EIS profiles collected prior to and subsequently after testing can be compared to the extrema profiles of previous test. Doing so, reveals similar overall progressions. In Figure 8.16, the polarization curve following testing shows that the fuel cell has a slightly higher open circuit voltage following degradation than it did prior to testing. Additionally, both the activation region and ohmic region have higher equivalent slope values with the ohmic region showing the most significant change following degradation. This is consistent with the polarization curves from the PWM control test (Figure 7.8) and those from the original degradation and recovery study (Figure 6.2).

Similarly, the EIS profiles of Figures 8.17 - 8.21 feature traits consistent with those from the degradation and recovery analysis (Figures 6.4 - 6.6), and the PWM control test (Figure 7.9). As was the case in the EIS progressions from those tests, the EIS profiles measured here show the largest shifts in impedance magnitudes at low frequencies. Additionally, as the DC operating point at which the EIS measurements are performed is increased, the shift in the real component of the high frequency impedance measurements as the cell degrades increases as well. This is easily seen in comparing the EIS profiles at 15 A (Figure 8.21) to those at 1.5 A (Figure 8.17). This too is consistent with the EIS profile progressions of the other tests.

The least-squares fit analysis of Figure 8.22 along with the subsequent results of the updated simulation program of Figure 8.23 provide a method for determining if the degradation progression observed for the fuel cell under the continuous current control can be described by the degradation model used in the simulation program. In this analysis, the best-fit line of the calculated change in degradation as a function of DC cell current is used to describe the portion of the degradation model (8.1) corresponding to $I_{fc} > \sigma_h$, with the line giving parameter values, $\sigma_h = 7.3$ A and $k_d = 0.056 \frac{\mu\Omega}{A \cdot s}$. As shown in Figure 8.22b, when using the measured current waveform for its input, this updated degradation model produces a total accumulated degradation profile very similar to the degradation profile measured. Further, when the simulation model is also updated to reflect the reduced effective gain of the compensator, the simulated accumulated degradation and simulated controller current also match reasonably well to the measured degradation and controller current as shown in Figure 8.23.

While these results indicate that the models comprising the simulation collectively can describe the observed circuit operation and cell degradation, this simply means that the model is consistent with the measured data. It is also possible that unmod-

eled effects contribute to the slow down in degradation. For example, because the amount of nickel in the anode at the triple phase boundary, i.e. where the anode, electrolyte and hydrogen meet, is limited, it is possible that for a given cell current, there is an upper limit to the amount of degradation that occurs. This can be modeled by a feedback term negatively relating the total accumulated degradation to the rate of degradation. Further, many other mechanisms for SOFCs have been proposed [include citations], and it's likely that at least a small amount of the degradation observed is unrelated to the loading profile.

It is also interesting to compare these parameter values to the corresponding values used in the original simulation model of 8 A and $0.13 \frac{\mu\Omega}{A.s}$, respectively. These values compare reasonably well particularly when considering the large variability in the calculated change in degradation values used to find these parameters. Additionally sources of mismatch in these parameter values likely come from the different methods used to calculate them as well as the different operating conditions of the two tests from which impedance data is collected. The original degradation model parameters were estimated using exponential waveform fits of the accumulated degradation (Figure 7.3 and Table 7.1) with the metric for degradation being large-signal resistance values, whereas here the parameter values were estimated based on changes in small-signal impedance measurements. Additionally, the degradation induced during the degradation and recovery testing occurred under substantially higher current-loading conditions (14-16 A) than those of this test (7.7-9.5 A).

The post-test SEM analysis of the fuel cell used in this test showed significant cracking (Figures 8.25 and 8.26) in the cathode between the LSM-YSZ layer and the LSM layer. As further seen in the additional SEM images of Appendix F, this cracking was wide-spread. However, as was the case with the cell used in the degradation and recovery study which also showed massive cracking in the cathode (Figure 6.3), it is

believed that the extent of this cracking is caused or at least exacerbated by damage incurred during the cell polishing process, as the epoxied sample broke loose of the sample mount during polishing with the 400 grit wet silica carbide paper. As also was the case with the previous cell SEM analyses, no detectable irreversible anode degradation was observed.

Chapter Summary

In this chapter, the continuous current control strategy for affecting load-induced SOFC degradation is presented. In contrast to the PWM-based control method of Chapter 8 which features large, low-frequency switching in the loading of the cell, this control method varies the DC loading conditions of a fuel cell in a smooth and continuous manner based on feedback measurements of the cell's impedance. This control strategy features a nonlinear impedance magnitude measurement technique based on the full-wave rectification of a combined voltage and current measurement signal along with a dominant-pole compensator for regulating cell current. The operation of the control circuit along with the effect of the control strategy on the level of cell degradation is illustrated through a nonlinear ordinary differential equation-based simulation program comprised of models for cell degradation, cell polarization, impedance detection, and control compensation.

An analog impedance detection and cell current control circuit is presented and used to regulate the degradation level of a single SOFC cell. The results of this test indicate that the rate of cell degradation decreased as the control circuit reduced the level of cell loading during the test. However, it is possible that this reduced rate of degradation is also partially due to a feedback effect inherent in the degradation process, which limits the total accumulated degradation that can occur in the cell.

This feedback effect is not modeled in the simulation program. Additional testing, with a particular emphasis on increasing the compensator gain, should be performed to determine if the cell accumulates a lower amount of degradation under more “aggressive” control operation.

CONCLUSION

This dissertation presents a multi-tier investigation into the performance characterization of SOFC systems from the electric terminal perspective. The novel test systems, analysis techniques and control schemes described provide unique capabilities for analyzing various implications of SOFC system operation stemming from their direct energy conversion process.

A reference-based fuel cell stack simulation system is introduced in Chapter 3. This simulator emulates the electric terminals of a full-scale stack by sensing and scaling-up the electric terminal performance of a reference prototype fuel cell system and applying it to a load. The results from tests of the stack simulator's performance presented in this section prove its ability to accurately simulate the full quadrant I steady-state and dynamic performance of a power-level full-scale stack when connected to real power-electronic loads. This powerful testing system allows the investigation into the implications of electric load / fuel cell stack interactions using real SOFC technologies without the need of a full-scale stack. Additionally, the system maintains explicit modularity for testing different SOFC prototype configurations and topologies, and offers the ability for post-test analysis, e.g. SEM imaging, for correlating the electric terminal performance of the SOFC stack to micro-structural changes within the cell. This type of interaction study is unavailable with model based SOFC stack emulators, and often difficult with non-modular full-scale stacks.

In Chapter 4 a time-domain technique for electrochemical impedance spectroscopy (EIS) using ordinary least squares (OLS) is detailed, and its validity demonstrated through the wideband impedance measurement of a known impedance. The method is shown to be effective in providing impedance profiles of SOFC systems including that of a reference simulated stack that can be used to track the evolution in stack

degradation. The novelty of this method lies in the use of OLS as it provides accurate estimates of impedance values even when current and voltage measurements contain a non-integer number of signal periods or less than a full period. Further, while this method is developed for an logarithmically swept single-frequency sinusoid perturbation signal, the method could easily be extended to other perturbation signal classes including multi-frequency component signals simply by increasing the number of terms in the sinusoidal model. This could be used to further reduce the time required for EIS measurements.

Combined, the reference simulator system and time-domain EIS method provide the framework for electric terminal monitoring for SOFC stack performance characterization during the testing of the hybrid source power management (HSPM) system detailed in Chapter 5. In this study, a simulated 20-cell SOFC stack is used for the performance testing of an HSPM system developed by a research team at MIT for interfacing an SOFC stack and auxiliary battery to a load. This system is designed to decouple undesirable loading profiles from the internal operation of a fuel cell stack, and to provide electric terminal monitoring capabilities. The time-domain data waveform plots in Figures 5.7 and 5.8 prove the HSPM's effectiveness in achieving these goals, and the subsequent impedance plot (Figure 5.9) giving the impedance profile for the simulated SOFC stack attained during dynamic loading operation indicates the relevance of the developed EIS method relevance in embedded systems.

In Chapter 6, electric terminal performance measurements of SOFCs during load-induced degradation tests are detailed. The results of these tests show that the load-induced degradation, which is believed to be caused by oxidation in the anode nickel, is reversible if the cell is operated at open-circuit. Polarization relationship measurements and electrochemical impedance spectroscopy (EIS) measurements achieved during degradation and recovery cell operation are analyzed using a linear

interpolation analysis to show that progressions in these measurements follow a predominantly linear trend. These analyses are used to determine best frequencies of impedance measurements for detecting this degradation.

Finally, Chapters 7 and 8 feature explorations into opportunities for degradation mitigation control schemes using electric terminal measurements for control feedback. The motivation for this exploration is born out of the results of the HSPM system tests of Chapter 5, which intimate the ability for degradation mitigation through load demand control, and the electric terminal characterization studies on SOFCs (Chapter 6) which show that some degradation mechanisms are reversible and controllable. As a precursor to degradation mitigation control using an HSPM system, two methods for regulating the load-induced degradation levels of an operating fuel cell are investigated. In Chapter 7, a PWM-based control scheme that regulates the average loading of a cell that alternates in operation between open-circuit and near-maximum power loading. The results from this test show that while no anode-side degradation is detected, cell performance still degrades possibly due to micro structural failures in the cathode. In Chapter 8 a continuous current control method is presented which uses low-frequency impedance measurements as feedback for regulating the DC operating point of the cell. The results of this test suggest that degradation rates are decreased due to the active control of the cell. As far as the author is aware, these two methods represent the first reported attempts at SOFC degradation mitigation control using electric terminal measurements for control system feedback.

The most interesting and logical extension of the work presented in this dissertation involves the further investigation of electric terminal measurement based degradation control. In particular, the continuous control method of Chapter 8 showed promising results though still underwent significant degradation despite the active control system. As recommended in the conclusion of that chapter, a more “aggres-

sive” control implementation where the system gain is increased is recommended for determining if cell degradation can be further mitigated.

It is also recommended that additional material analyses be performed on for any future degradation control testing. Under both types of load-based degradation control described in this dissertation (Chapters 7 and 8), the cells tested underwent degradation despite the active control systems. In the post-test SEM analyses, neither cell tested showed signs of anode delamination or electrolyte cracking which would signify excessive nickel oxidation in the anode. Instead, both cells exhibited cracking in the cathodes though it is unclear if this cracking occurred during cell operation or if it occurred during cell sample polishing in preparation for SEM analysis. The additional material analyses would help to correlate the electric terminal impedance measurements used in control feedback to direct measures of reaction mechanisms and ensure that the control methods are having the intended effect of limiting nickel oxidation.

In the studies presented in this dissertation, ex-situ post-test SEM analysis is used as the method for material investigation of degradation mechanisms. As seen in the various SEM figures of this dissertation, this technology allows for high quality topographical imaging of the tested cell’s cross section useful in observing mechanical failures in the cell. Additionally, the SEM machine in the Imaging and Chemistry Analysis Laboratory (ICAL) at Montana State University has energy-dispersive X-ray spectroscopy (EDX) capabilities for elemental analysis of the bulk material. However, while this technology can delineate the elements present and their atomic percentages within a bulk material, it cannot distinguish the empirical formulas of the bulk compounds. Thus, the oxygen that might have oxidized the nickel is not directly distinguishable from the oxygen in the yttria (Y_2O_3) stabilized zirconia (ZrO_2) ceramic.

Examples of more insightful analysis methods are X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy which can not only detect elemental composition, but also the empirical formulas of the bulk compounds. Several studies have used these techniques for ex-situ post-test analysis of SOFC anodes to quantify various degradation mechanisms including the deposition of fuel impurities [56, 100, 101] as well as the formation of nickel oxides [102]. Thus, incorporating these ex-situ analysis methods into the post-test analysis of SOFCs operated under degradation control would allow a direct measurement of the amount of nickel oxidation present in the anode at the end of the test.

Recently, specially designed SOFC testing apparatuses for incorporating in-situ Raman spectroscopy have been used for non-invasive direct monitoring of SOFC degradation mechanisms during cell operation [54, 58, 102, 103]. Specifically, in [58], the authors use in-situ Raman spectroscopy to monitor the oxidation and reduction kinetics of Ni-YSZ SOFC anodes in air with a time resolution of 10 seconds. This monitoring technique then could be applied to an SOFC operating under degradation control for correlating direct measures of nickel oxidation to electric terminal impedance measurements made during cell operation and not just those made at the end of the test. However, it is important to note that Raman spectroscopy provides predominantly surface monitoring capabilities only and thus is not suitable for observing nickel oxidation in the active anode region of an anode supported cell due to the thickness of the bulk anode layer. Thus, any future degradation control tests to incorporate in-situ Raman spectroscopy monitoring must use an electrolyte supported cell with a thin anode layer rather than the anode supported cell used in this study.

As a further extension of this research, degradation control using impedance measurements for feedback could also be applied to other forms of degradation. For example, as described in the Introduction, both the deposition of carbon and the

deposition of sulfur have been shown to be reversible. In the case of carbon removal, Kirtley et al. [54] showed the removal of carbon through oxidation by sequestering the methane fuel and polarizing the cell so that oxygen ions diffused through the electrolyte from the cathode to the anode. For sulfur removal, Xia et al. [55] were able to recover the cell by introducing nitrogen or air to the anode. In both studies, electrochemical impedance spectroscopy measurements were correlated to the increasing presence of the tests respective contaminants. Thus, impedance measurements could be used to detect anode contamination and the operation of the cell could be adjusted accordingly in order to recover electrical performance.

Finally, it is important to keep in mind that the ultimate end goal of this research is to develop control strategies for mitigating degradation in full scale stacks utilizing devices such as the hybrid system power manager of Chapter 5. The studies presented in this dissertation as well as those outlined here for future research are aimed to gain insight into degradation mitigation control through the monitoring of SOFC system performance through the electric terminals. The information gained through these studies still require adaption for realistic application in fuel cell stack power systems. Nevertheless, the observations, results, analysis and future research goals discussed in this dissertation provide the foundation for realistic mitigation control methods which hold significant promise in making the widespread deployment of fuel cell systems a reality.

REFERENCES CITED

- [1] M. Hashem Nehrir, Caisheng Wang. *Modeling and Control of Fuel Cells*. John Wiley & Sons, Inc., 2009.
- [2] M.C Williams, J.P Strakey, Subhash C Singhal. U.s. distributed generation fuel cell program. *Journal of Power Sources*, 131(1–2):79 – 85, 2004. doi:10.1016/j.jpowsour.2004.01.021.
- [3] Natural gas-fueled distributed generation solid oxide fuel cell systems. Technical Report, J. Thijssen, LLC prepared for the US Department of Energy, 2009.
- [4] EG & G Technical Services Inc. *Fuel Cell Handbook*. U.S.Department of Energy, edition 7, 2004.
- [5] S.C Singhal. Solid oxide fuel cells for stationary, mobile, and military applications. *Solid State Ionics*, 152–153(0):405 – 410, 2002. doi:10.1016/S0167-2738(02)00349-1.
- [6] T. Gilchrist. Fuel cells to the fore [electric vehicles]. *Spectrum, IEEE*, 35(11):35–40, nov 1998. doi:10.1109/6.730518.
- [7] Peter Lindahl, Eric Moog, Steven R. Shaw. Simulation, design, and validation of an uav sofc propulsion system. *Aerospace and Electronic Systems, IEEE Transactions on*, 48(3):2582 –2593, july 2012. doi:10.1109/TAES.2012.6237610.
- [8] Annual energy outlook 2012. Technical Report, U.S. Energy Information Administration, 2012.
- [9] Contribution of working groups i, ii and iii to the fourth assessment report of the intergovernmental panel on climate change. Technical Report, Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, NY, USA, 2007.
- [10] Cost and performance baseline for fossil energy plants, volume 1: Bituminous coal and natural gas to electricity. Technical Report, National Energy Technology Laboratory, 2010.
- [11] Matthias Finkenrath. Cost and performance of carbon dioxide capture from power generation. Technical Report, International Energy Agency, 2011.
- [12] Thomas L. Cable, John A. Setlock, Serene C. Farmer, Andrew J. Eckel. Regenerative performance of the nasa symmetrical solid oxide fuel cell design. *International Journal of Applied Ceramic Technology*, 8(1):1–12, 2011. doi:10.1111/j.1744-7402.2009.02477.x.
- [13] Matthew Cornachione. Reversible fuel cell performance and degradation. Master’s Thesis, Montana State University, 2011.

- [14] Electric power annual 2010. Technical Report, U.S. Energy Information Administration, 2011.
- [15] Xianguo Li. *Principles of Fuel Cells*. Taylor & Francis, 2006.
- [16] Randall S. Gemmen. Analysis for the effect of inverter ripple current on fuel cell operating condition. *Journal of Fluids Engineering*, 125(3):576–585, 2003. doi:10.1115/1.1567307.
- [17] S.K. Mazumder, K. Acharya, C.L. Haynes, Jr. Williams, R., M.R. von Spakovsky, D.J. Nelson, D.F. Rancruel, J. Hartvigsen, R.S. Gemmen. Solid-oxide-fuel-cell performance and durability: resolution of the effects of power-conditioning systems and application loads. *Power Electronics, IEEE Transactions on*, 19(5):1263 – 1278, Sept 2004. doi:10.1109/TPEL.2004.833992.
- [18] J.M. Correa, F.A. Farret, J.R. Gomes, M.G. Simoes. Simulation of fuel-cell stacks using a computer-controlled power rectifier with the purpose of actual high-power injection applications. *IEEE Transactions on Industry Applications*, 39(4):1126–1142, 2003. doi:10.1109/TIA.2003.814548.
- [19] Abraham Gebregergis, Pragasen Pillay. Implementation of fuel cell emulation on dsp and dspace controllers in the design of power electronic converters. *Industry Applications, IEEE Transactions on*, 46(1):285–294, Jan-Feb 2010. doi:10.1109/TIA.2009.2036676.
- [20] M. Cirrincione, M. C. Di Piazza, G. Marsala, M. Pucci, G. Vitale. Real time simulation of renewable sources by model-based control of dc/dc converters. *Proceedings International Symposium on Industrial Electronics, IEEE ISIE 2008*, Cambridge, United Kingdom, June-July 2008. The Institute of Electrical and Electronics Engineers. doi:10.1109/ISIE.2008.4676960.
- [21] Giuseppe Marsala, Marcello Pucci, Gianpaolo Vitale, Maurizio Cirrincione, Abdellatif Miraoui. A prototype of a fuel cell pem emulator based on a buck converter. *Applied Energy*, 86(10):2192 – 2203, 2009. doi:10.1016/j.apenergy.2008.12.028.
- [22] C.A. Ramos-Paja, A. Romero, R. Giral, E. Vidal-Idiarte, L. Martinez-Salamero. Fuzzy-based modelling technique for pemfc electrical power generation systems emulation. *Power Electronics, IET*, 2(3):241–255, May 2009. doi:10.1049/iet-pel.2008.0008.
- [23] Fei Gao, Benjamin Blunier, Marcelo Godoy Simoes, Abdellatif Miraoui. Pem fuel cell stack modeling for real-time emulation in hardware-in-the-loop applications. *Energy Conversion, IEEE Transactions on*, 26(1):184 –194, march 2011. doi:10.1109/TEC.2010.2053543.

- [24] Fei Gao, B. Blunier, D. Chrenko, D. Bouquain, A. Miraoui. Multirate fuel cell emulation with spatial reduced real-time fuel cell modeling. *Industry Applications, IEEE Transactions on*, 48(4):1127 –1135, july-aug. 2012. doi:10.1109/TIA.2012.2198909.
- [25] C. Restrepo, C.A. Ramos-Paja, R. Giral, J. Calvente, A. Romero. Fuel cell emulator for oxygen excess ratio estimation on power electronics applications. *Computers & Electrical Engineering*, 38(4):926 – 937, 2012. doi:10.1016/j.compeleceng.2012.02.012.
- [26] P. Acharya, P. Enjeti, I.J. Pitel. An advanced fuel cell simulator. *Proceedings Applied Power Electronics Conference and Exposition 2004, IEEE APEC '04*, Anaheim, California, February 2004. The Institute of Electrical and Electronics Engineers. doi:10.1109/APEC.2004.1296071.
- [27] Tae-Won Lee, Byoung-Kuk Lee, Su-Jin Jang, Sung-Ho Kim, Chung-Yuen Won. Development of a 3 kw fuel cell generation system with an active fuel cell simulator: topology, control, and design. *Power Electronics Specialists Conference, 2004. PESC 04. 2004 IEEE 35th Annual*, Volume 6, pages 4743–4748, 2004. doi:10.1109/PESC.2004.1354837.
- [28] M. Ordonez, M. T. Iqbal, J. E. Quaicoe. Development of a fuel cell simulator based on an experimentally derived model. *Proceedings Canadian Conference on Electrical and Computer Engineering*, Saskatoon, Saskatchewan, 2005. The Institute of Electrical and Electronics Engineers. doi:10.1109/CCECE.2005.1557252.
- [29] M. Ordonez, M. T. Iqbal, J. E. Quaicoe. A novel fuel cell simulator. *Proceedings Power Electronics Specialists Conference*, pages 178 – 184. The Institute of Electrical and Electronics Engineers, June 2005. doi:10.1109/APEC.2004.1296071.
- [30] Peter A. Lindahl, Steven R. Shaw. Reference based fuel cell stack simulator. *Preceedings from the ASME Fuel Cell Science, Engineering and Technology Conference*, pages 249–255, 2010. doi:10.1115/FuelCell2010-33315.
- [31] Lucia Gauchia, Javier Sanz. A per-unit hardware-in-the-loop simulation of a fuel cell/battery hybrid energy system. *IEEE Transactions on Industrial Electronics*, 57(4), 2010. doi:10.1109/TIE.2009.2036641.
- [32] J. Schoukens, R. Pintelon, E. van der Ouderaa, J. Renneboog. Survey of excitation signals for fft based signal analyzers. *Instrumentation and Measurement, IEEE Transactions on*, 37(3):342 –352, sep 1988. doi:10.1109/19.7453.

- [33] D.C. Evans, D. Rees, D.L. Jones. Design of test signals for identification of linear systems with nonlinear distortions. *Instrumentation and Measurement, IEEE Transactions on*, 41(6):768–774, dec 1992. doi:10.1109/19.199395.
- [34] G. S. Popkirov, R. N. Schindler. Optimization of the perturbation signal for electrochemical impedance spectroscopy in the time domain. *Review of Scientific Instruments*, 64(11):3111–3115, 1993. doi:10.1063/1.1144316.
- [35] Gerald Wiegand, Klaus R. Neumaier, Erich Sackmann. Fast impedance spectroscopy: General aspects and performance study for single ion channel measurements. *Review of Scientific Instruments*, 71(6):2309–2320, 2000. doi:10.1063/1.1150447.
- [36] Jenő Hazi, Darrell M. Elton, W. Alexander Czerwinski, Jörg Schiewe, Victoria A. Vicente-Beckett, Alan M. Bond. Microcomputer-based instrumentation for multi-frequency fourier transform alternating current (admittance and impedance) voltammetry. *Journal of Electroanalytical Chemistry*, 437(1-2):1–15, 1997. doi:10.1016/S0022-0728(96)05038-3.
- [37] J.L. Morrison, B. Smyth, J. Wold, D.K. Butherus, W.H. Morrison, J.P. Christopher, C.G. Motloch. Fast summation transformation for battery impedance identification. *Aerospace conference, 2009 IEEE*, pages 1–9, march 2009. doi:10.1109/AERO.2009.4839680.
- [38] G. S. Popkirov, R. N. Schindler. A new impedance spectrometer for the investigation of electrochemical systems. *Review of Scientific Instruments*, 63(11):5366–5372, nov 1992. doi:10.1063/1.1143404.
- [39] G. S. Popkirov. Fast time-resolved electrochemical impedance spectroscopy for investigations under nonstationary conditions. *Electrochimica Acta*, 41(7-8):1023 – 1027, 1996. Electrochemical Impedance Spectroscopy. doi:10.1016/0013-4686(95)00434-3.
- [40] J.L. Morrison, W.H. Morrison. Real time estimation of battery impedance. *Aerospace Conference, 2006 IEEE*, page 13 pp., 0-0 2006. doi:10.1109/AERO.2006.1656090.
- [41] Evgenij Barsoukov, J. Ross Macdonald, editors. *Impedance Spectroscopy: Theory, Experiment, and Applications*. Wiley-Interscience, edition 2nd, 2005.
- [42] Mark E. Orazem, Bernard Tribollet. *Electrochemical Impedance Spectroscopy*. Wiley, 2008.
- [43] Andrzej Lasia. Electrochemical impedance spectroscopy and its applications. B. E. Conway, J. O’M. Bockris, Ralph E. White, editors, *Modern Aspects of*

- Electrochemistry*, Volume 32 series *Modern Aspects of Electrochemistry*, pages 143–248. Springer US, 2002. doi:10.1007/0-306-46916-2_2.
- [44] Peter E. Wellstead. Frequency response analysis: Technical report 10. Technical Report, Solartron Instruments, 2003.
 - [45] P.M. Ramos, M. Fonseca da Silva, A. Cruz Serra. Low frequency impedance measurement using sine-fitting. *Measurement*, 35(1):89 – 96, 2004. doi:10.1016/j.measurement.2003.08.008.
 - [46] T. Radil, P.M. Ramos, A.C. Serra. Impedance measurement with sine-fitting algorithms implemented in a dsp portable device. *Instrumentation and Measurement, IEEE Transactions on*, 57(1):197 –204, jan. 2008. doi:10.1109/TIM.2007.908276.
 - [47] Eric Matthew Seger. In-situ electrical terminal characterization of fuel cell stacks. Master’s Thesis, Montana State University, 2010.
 - [48] M. Ordonez, M. O. Sonnaillon, J. E. Quaiocoe, M. T. Iqbal. An embedded frequency response analyzer for fuel cells monitoring and characterization. *Industrial Electronics, IEEE Transactions on*, 57(6):1925–1934, June 2010. doi:10.1109/TIE.2009.2028295.
 - [49] J. J. Cooley. *Analysis, Modeling and Design of Energy Management and Multi-source Power Systems*. Doctoral Dissertation, Massachusetts Institute of Technology, 2011. doi:1721.1/65966.
 - [50] John J. Cooley, Peter Lindahl, Grant Jordan, Matthew Cornachione, Clarissa Z. Cooley, Steven R. Shaw, Steven B. Leeb. Multi-converter system design for fuel cell buffering and diagnostics under uav load profiles. *Submitted for Publication*, 2013.
 - [51] Yoshio Matsuzaki, Isamu Yasuda. Electrochemical properties of a sofc cathode in contact with a chromium-containing alloy separator. *Solid State Ionics*, 132(3–4):271–278, 7 2000. doi:http://dx.doi.org/10.1016/S0167-2738(00)00654-8.
 - [52] Yoshio Matsuzaki, Isamu Yasuda. Dependence of sofc cathode degradation by chromium-containing alloy on compositions of electrodes and electrolytes. *Journal of The Electrochemical Society*, 148(2):A126–A131, 01 2001.
 - [53] Bryan C. Eigenbrodt, Michael B. Pomfret, Daniel A. Steinhurst, Jeffrey C. Owrutsky, Robert A. Walker. Direct, in situ optical studies of niysz anodes in solid oxide fuel cells operating with methanol and methane. *The Journal of Physical Chemistry C*, 115(6):2895–2903, 2013/03/19 2010. doi:10.1021/jp109292r.

- [54] John D. Kirtley, David M. Halat, Melissa D. McIntyre, Bryan C. Eigenbrodt, Robert A. Walker. High-temperature “spectrochronopotentiometry”: Correlating electrochemical performance with in situ raman spectroscopy in solid oxide fuel cells. *Analytical Chemistry*, 84(22):9745–9753, 2012. arXiv:<http://pubs.acs.org/doi/pdf/10.1021/ac301504g>, doi:10.1021/ac301504g.
- [55] Shenjiang Xia, V. Birss. Deactivation and recovery of ni-ysz anode in h₂ fuel containing h₂s. *Meeting Abstracts*, MA2005-01(30):1057, 2006. arXiv:<http://ma.ecsdl.org/content/MA2005-01/30/1057.full.pdf+html>.
- [56] A. Lussier, S. Sofie, J. Dvorak, Y. U. Idzerda. Mechanism for sofc anode degradation from hydrogen sulfide exposure. *International Journal of Hydrogen Energy*, 33(14):3945–3951, 7 2008. doi:<http://dx.doi.org/10.1016/j.ijhydene.2007.11.033>.
- [57] Viola I. Birss, Lisa Deleebeeck, Scott Paulson, Tyler Smith. Understanding performance losses at ni-based anodes due to sulphur exposure. *ECS Transactions*, 35(1):1445–1454, 2011. arXiv:<http://ecst.ecsdl.org/content/35/1/1445.full.pdf+html>, doi:10.1149/1.3570130.
- [58] John Kirtley, Bryan Eigenbrodt, Robert Walker. In situ optical studies of oxidation kinetics of ni/ysz cermet anodes. *ECS Transactions*, 33(40):25–37, 2011. doi:10.1149/1.3589182.
- [59] D. Sarantaridis, A. Atkinson. Redox cycling of ni-based solid oxide fuel cell anodes: A review. *Fuel Cells*, 7(3):246–258, 2007. doi:10.1002/fuce.200600028.
- [60] Antonin Faes, Aïcha Hessler-Wyser, Amédée Zryd, Jan Van herle. A review of redox cycling of solid oxide fuel cells anode. *Membranes*, 2(3):585–664, 2012. doi:10.3390/membranes2030585.
- [61] Toru Hatae, Yoshio Matsuzaki, Yohtaro Yamazaki. Study on electrochemical re-oxidation of anode-supported solid oxide fuel cells using oxide ion current. *Solid State Ionics*, 179:274 – 281, 2008. doi:10.1016/j.ssi.2008.01.018.
- [62] D. Sarantaridis, R.A. Rudkin, A. Atkinson. Oxidation failure modes of anode-supported solid oxide fuel cells. *Journal of Power Sources*, 180(2):704 – 710, 2008. doi:10.1016/j.jpowsour.2008.03.011.
- [63] J. Laurencin, G. Delette, B. Morel, F. Lefebvre-Joud, M. Dupeux. Solid oxide fuel cells damage mechanisms due to ni-ysz re-oxidation: Case of the anode supported cell. *Journal of Power Sources*, 192(2):344 – 352, 2009. doi:10.1016/j.jpowsour.2009.02.089.

- [64] K. Acharya, S.K. Mazumder, R.K. Burra, R. Williams, C. Haynes. System-interaction analyses of solid-oxide fuel cell (sofc) power-conditioning system. *Industry Applications Conference, 2003. 38th IAS Annual Meeting. Conference Record of the*, Volume 3, pages 2026 – 2032, 2003.
- [65] K. Acharya, S.K. Mazumder, R.K. Burra. Impact of power-electronics systems on the performance and durability of tubular solid-oxide fuel cell. *Applied Power Electronics Conference and Exposition, 2004. APEC '04. Nineteenth Annual IEEE*, Volume 3, pages 1515–1520 Vol.3, 2004. doi:10.1109/APEC.2004.1296065.
- [66] Sanjaya K. Pradhan, Sudip K. Mazumder, Joseph Hartvigsen, Michele Hollist. Effects of electrical feedbacks on planar solid oxide fuel cell. *Journal of Fuel Cell Science and Technology*, 4, 2007.
- [67] S. K. Mazumder, M. R. von Spakovsky, C. Haynes, K. Acharya, R. Burra, D. Rancruel, R. Williams, D. Nelson. An investigation to resolve the interaction between fuel cell, power conditioning system and application loads. Technical Report, Phase-I Topical Rep., U.S. DoE, Cooperative Agreement DE-FC26-02NT41574, 2002.
- [68] S.K. Mazumder, S.K. Pradhan, K. Acharya, J. Hartvigsen, M.R. Von Spakovsky, C. Haynes. Load-transient mitigation techniques for solid-oxide fuel cell (sofc) power-conditioning system. *Telecommunications Energy Conference, 2004. INTELEC 2004. 26th Annual International*, pages 174–181, Sept. 2004. doi:10.1109/INTLEC.2004.1401463.
- [69] S.K. Mazumder, K. Acharya, S.K. Pradhan, J. Hartvigsen, M.R. Von Spakovsky, C. Haynes. Energy buffering techniques for load transient mitigation of solid-oxide fuel cell (sofc) power conditioning system (pcs). *Power Electronics Specialists Conference, 2004. PESC 04. 2004 IEEE 35th Annual*, Volume 6, pages 4749–4754 Vol.6, June 2004. doi:10.1109/PESC.2004.1354838.
- [70] S.K. Mazumder, S.K. Pradhan, J. Hartvigsen, M.R. Von Spakovsky, D.F. Rancruel. Effects of battery buffering on the post-load-transient performance of a psofc. *Energy Conversion, IEEE Transactions on*, 22(2):457–466, June 2007. doi:10.1109/TEC.2006.876420.
- [71] Sudip K. Mazumder, Sanjay Pradhan. Efficient and robust power management of reduced cost distributed power electronics for fuel-cell power system. *Journal of Fuel Cell Science and Technology*, 7, 2010.
- [72] Andreas Jossen, Juergen Garche, Harry Doering, Markus Goetz, Werner Knaupp, Ludwig Joerissen. Hybrid systems with lead-acid battery and proton-exchange membrane fuel cell. *Journal of Power Sources*, 144(2):395

- 401, 2005. `Selected papers from the Ninth European Lead Battery Conference`. Ninth European Lead Battery Conference. doi:10.1016/j.jpowsour.2004.11.010.
- [73] C. Wang, M. H. Nehrir. A physically based dynamic model for solid oxide fuel cells. *IEEE Transactions on Energy Conversion*, 22:887 – 897, December 2007. doi:10.1109/TEC.2007.895468.
- [74] A. Vahidi, A. Stefanopoulou, Huei Peng. Current management in a hybrid fuel cell power system: A model-predictive control approach. *Control Systems Technology, IEEE Transactions on*, 14(6):1047 –1057, Nov 2006. doi:10.1109/TCST.2006.880199.
- [75] Su-Jin Jang, Tae-Won Lee, Won-Chul Lee, Chung-Yuen Won. Bi-directional dc-dc converter for fuel cell generation system. *Power Electronics Specialists Conference, 2004. PESC 04. 2004 IEEE 35th Annual*, Volume 6, pages 4722–4728 Vol.6, June 2004. doi:10.1109/PESC.2004.1354834.
- [76] Phatiphat Thounthong, Stéphane Raïl, Bernard Davat. Control strategy of fuel cell/supercapacitors hybrid power sources for electric vehicle. *Journal of Power Sources*, 158(1):806 – 814, 2006. doi:10.1016/j.jpowsour.2005.09.014.
- [77] T. Allag, T. Das. Robust control of solid oxide fuel cell ultracapacitor hybrid system. *Control Systems Technology, IEEE Transactions on*, 20(1):1–10, Jan. 2012. doi:10.1109/TCST.2010.2098478.
- [78] Fang Zheng Peng, Miaosen Shen, K. Holland. Application of z-source inverter for traction drive of fuel cell and battery hybrid electric vehicles. *Power Electronics, IEEE Transactions on*, 22(3):1054–1061, May 2007. doi:10.1109/TPEL.2007.897123.
- [79] P.A. Lindahl, M.A. Cornachione, S.R. Shaw. A time-domain least squares approach to electrochemical impedance spectroscopy. *Instrumentation and Measurement, IEEE Transactions on*, 61(12):3303–3311, Dec. 2012. doi:10.1109/TIM.2012.2210457.
- [80] Ryan P O’Hayre, Suk-Won Cha, Whitney Colella, Fritz B. Prinz. *Fuel Cell Fundamentals*. John Wiley & Sons, Inc., 2006.
- [81] Thomas H. Bradley, Blake A. Moffitt, Dimitri N. Mavris, David E. Parekh. Development and experimental characterization of a fuel cell powered aircraft. *Journal of Power Sources*, 171(2):793 – 801, 2007.

- [82] J. J. Cooley, E. Seger, S. Leeb, S. R. Shaw. Characterization of a 5 kw solid oxide fuel cell stack using power electronic excitation. *Applied Power Electronics Conference and Exposition (APEC), 2010 Twenty-Fifth Annual IEEE*, page 2264. IEEE, 2010. doi:10.1109/APEC.2010.5433552.
- [83] B. Boashash. Estimating and interpreting the instantaneous frequency of a signal. i. fundamentals. *Proceedings of the IEEE*, 80(4):520 –538, apr 1992. doi:10.1109/5.135376.
- [84] P. Handel. Properties of the ieee-std-1057 four-parameter sine wave fit algorithm. *Instrumentation and Measurement, IEEE Transactions on*, 49(6):1189 –1193, dec 2000. doi:10.1109/19.893254.
- [85] T. Andersson, P. Handel. Ieee standard 1057, cramer-rao bound and the parsimony principle. *Instrumentation and Measurement, IEEE Transactions on*, 55(1):44 – 53, feb. 2006. doi:10.1109/TIM.2005.861497.
- [86] S. Pasricha, M. Keppler, S. R. Shaw, M. H. Nehrir. Comparison and identification of static electrical terminal fuel cell models. *IEEE Transactions on Energy Conversion*, 22:746 – 754, September 2007.
- [87] Lloyd N. Trefethen, David Bau III. *Numerical Linear Algebra*. Society for Industrial and Applied Mathematics, 1997.
- [88] Abdelhak M. Zoubir, D. Robert Iskander. *Bootstrap Techniques for Signal Processing*. Cambridge University Press, 2004.
- [89] J.L. Duarte, M. Hendrix, M.G. Simoes. Three-port bidirectional converter for hybrid fuel cell systems. *Power Electronics, IEEE Transactions on*, 22(2):480 –487, March 2007. doi:10.1109/TPEL.2006.889928.
- [90] Fang Zheng Peng, Miaosen Shen, K. Holland. Application of z-source inverter for traction drive of fuel cell / battery hybrid electric vehicles. *Power Electronics, IEEE Transactions on*, 22(3):1054 –1061, May 2007. doi:10.1109/TPEL.2007.897123.
- [91] J. Bauman, M. Kazerani. A comparative study of fuel-cell-battery, fuel-cell-ultracapacitor, and fuel-cell-battery-ultracapacitor vehicles. *Vehicular Technology, IEEE Transactions on*, 57(2):760 –769, March 2008. doi:10.1109/TVT.2007.906379.
- [92] Jürgen Malzbender, Egbert Wessel, Rolf W. Steinbrech. Reduction and re-oxidation of anodes for solid oxide fuel cells. *Solid State Ionics*, 176(29-30):2201 – 2203, 2005. doi:10.1016/j.ssi.2005.06.014.

- [93] Anke Hagen, Rasmus Barfod, Peter Vang Hendriksen, Yi-Lin Liu, Severine Ramousse. Degradation of anode supported sofc as a function of temperature and current load. *Journal of Electrochemical Society*, 2006.
- [94] Xuelei Hu. Report sofc experiment - 12. SOFC Degradation Experiments, Montana State University, 2008.
- [95] Lennart Ljung. *System Identification: Theory for the User*. Prentice Hall PTR, 1999.
- [96] Masashi Mori, Tohru Yamamoto, Hibiki Itoh, Hideaki Inaba, Hiroaki Tagawa. Thermal expansion of nickel/zirconia anodes in solid oxide fuel cells during fabrication and operation. *Journal of The Electrochemical Society*, 145(4):1374–1381, 1998. arXiv:<http://jes.ecsdl.org/content/145/4/1374.full.pdf+html>, doi:10.1149/1.1838468.
- [97] F. Tietz. Thermal expansion of sofc materials. *Ionics*, 5(1-2):129–139, 1999. doi:10.1007/BF02375916.
- [98] J. Laurencin, G. Delette, O. Sicardy, S. Rosini, F. Lefebvre-Joud. Impact of redox cycles on performances of solid oxide fuel cells: Case of the electrolyte supported cells. *Journal of Power Sources*, 195(9):2747 – 2753, 2010. doi:10.1016/j.jpowsour.2009.10.099.
- [99] M. Ettler, H. Timmermann, J. Malzbender, A. Weber, N.H. Menzler. Durability of ni anodes during reoxidation cycles. *Journal of Power Sources*, 195(17):5452 – 5467, 2010. doi:10.1016/j.jpowsour.2010.03.049.
- [100] Chunchuan Xu, John W. Zondlo, Harry O. Finklea, Oktay Demircan, Mingyang Gong, XingBo Liu. The effect of phosphine in syngas on ni-ysz anode-supported solid oxide fuel cells. *Journal of Power Sources*, 193(2):739–746, 9 2009. doi:<http://dx.doi.org/10.1016/j.jpowsour.2009.04.044>.
- [101] Julie Mougin, Serge Ravel, Eric de Vito, Marie Petijean. Influence of fuel contaminants on sofc operation: Effect on performance and degradation mechanisms. *ECS Transactions*, 7(1):459–468, 2007. arXiv:<http://ecst.ecsdl.org/content/7/1/459.full.pdf+html>, doi:10.1149/1.2729124.
- [102] Michael Pomfret. *An Investigation of Solid Oxide Fuel Cell Chemistry: A Spectroscopic Approach*. Doctoral Dissertation, University of Maryland, 2007.
- [103] Michael B. Pomfret, Jeffrey C. Owrutsky, Robert A. Walker. In situ optical studies of solid-oxide fuel cells. *Annual Review of Analytical Chemistry*, 3(1):151–174, 2010. doi:10.1146/annurev.anchem.111808.073641.

APPENDICES

APPENDIX A

LINEAR INTERPOLATION ANALYSIS OF POLARIZATION CURVES
MEASURED DURING DEGRADATION AND RECOVERY TESTING

In Chapter 6 the application of the linear interpolation analysis method was used to show that the progression in a fuel cell's measured polarization curve follows a linear trend with degradation and recovery. Figure 6.10 gave a representative example of the quality of the linear interpolation's matching of the measured data. This appendix contains the full results of that analysis including all figures comparing the best fit interpolation predictors to the measured data for all measured polarization curves taken during cell testing. The first set of polarization curves and predictors shown here is for the initial measurement prior to the 4 hour activation process. This is labelled to correspond to a time of -4 hours. The time of 0 hours corresponds to the polarization curve measurement immediately preceding degradation and recovery commencement. The table at the end of this appendix gives the best-fit parameter values for each predictor along with calculated values of the normalized sum of squared errors (SSE_N). These SSE_N values are those which are plotted in Figure 6.9.

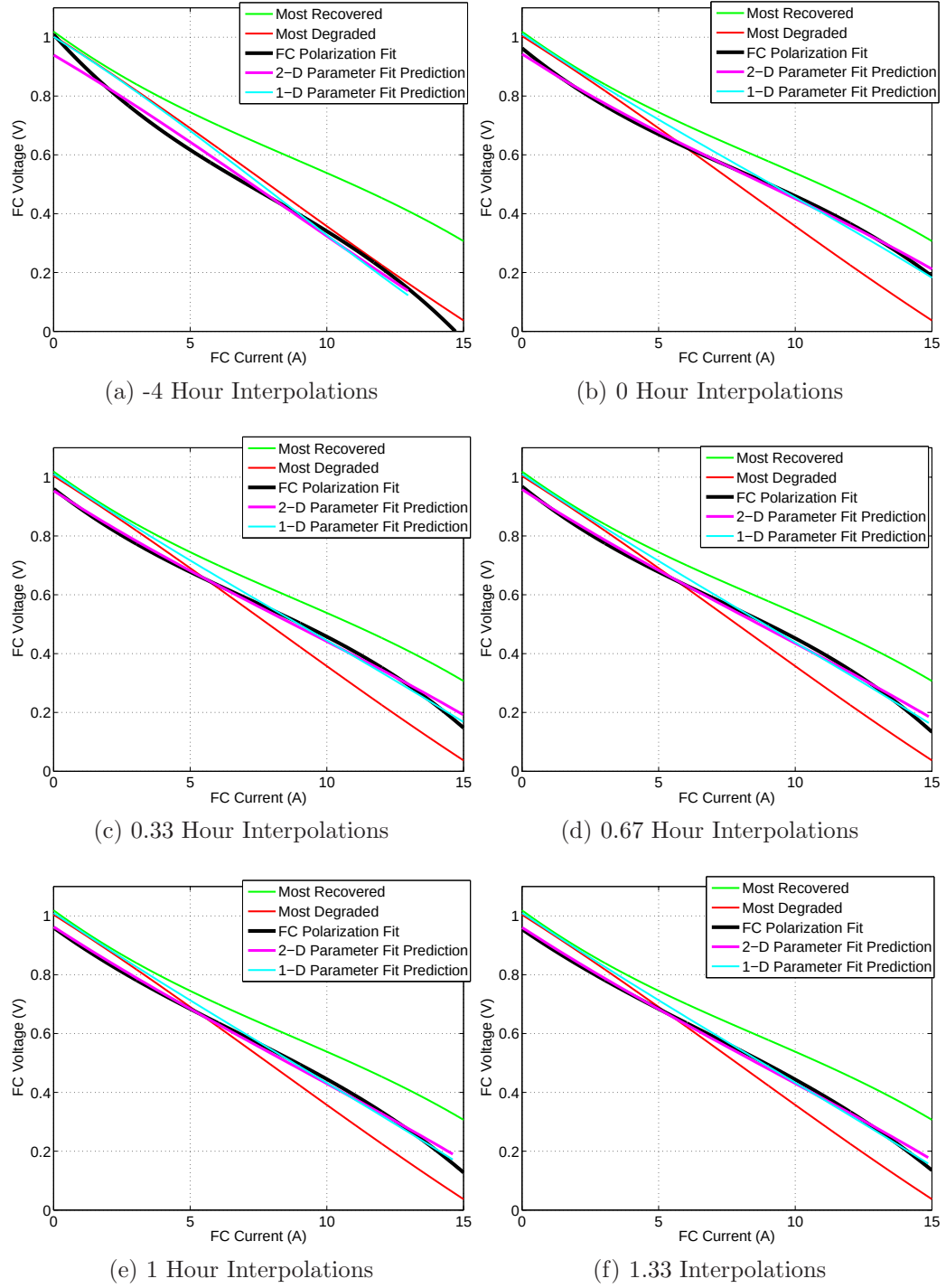


Figure A.1: Linear Interpolations of the -4 - 1.33 Hour Polarization Curves

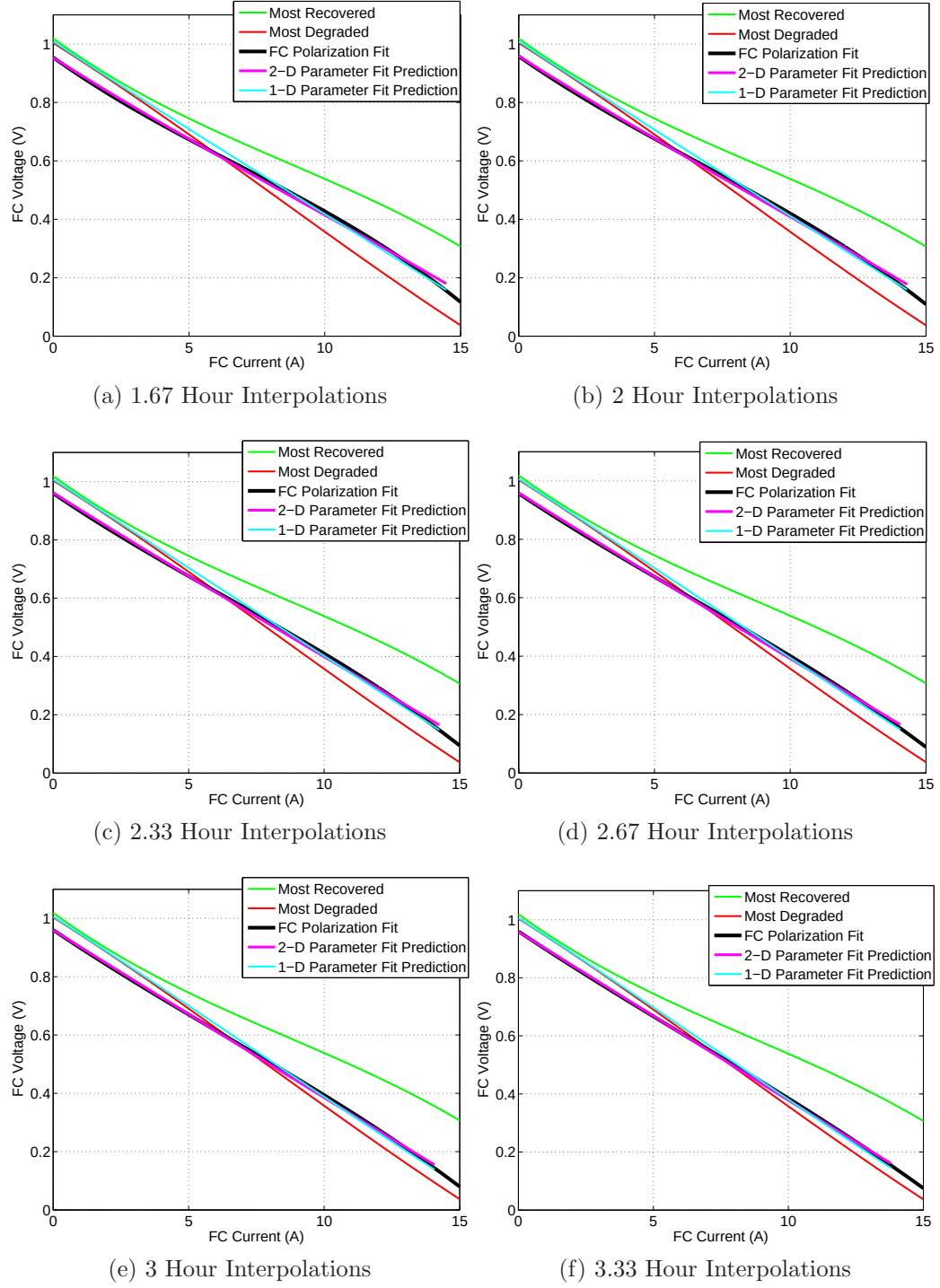


Figure A.2: Linear Interpolations of the 1.67 - 3.33 Hour Polarization Curves

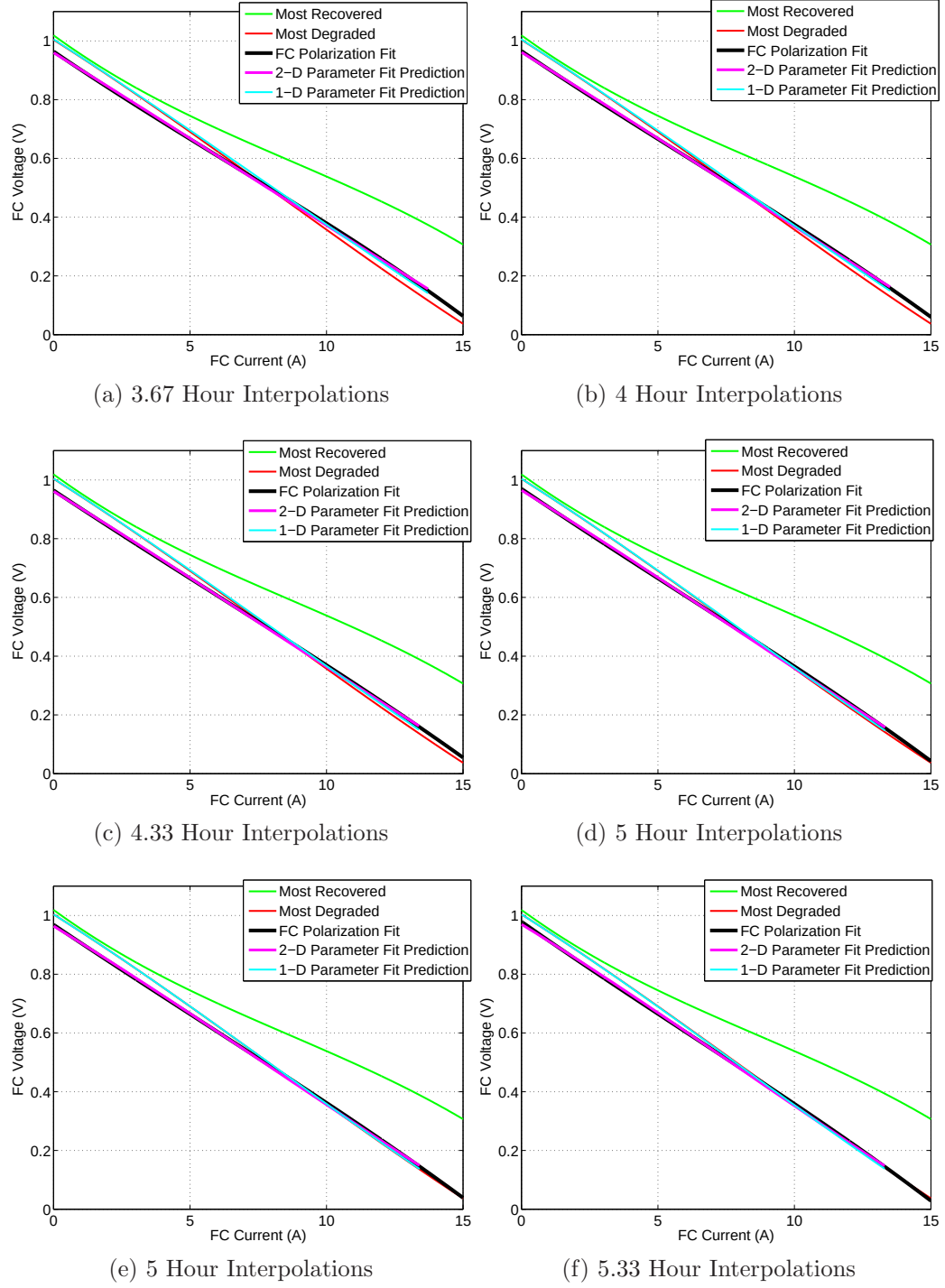


Figure A.3: Linear Interpolations of the 3.67 - 5.33 Hour Polarization Curves

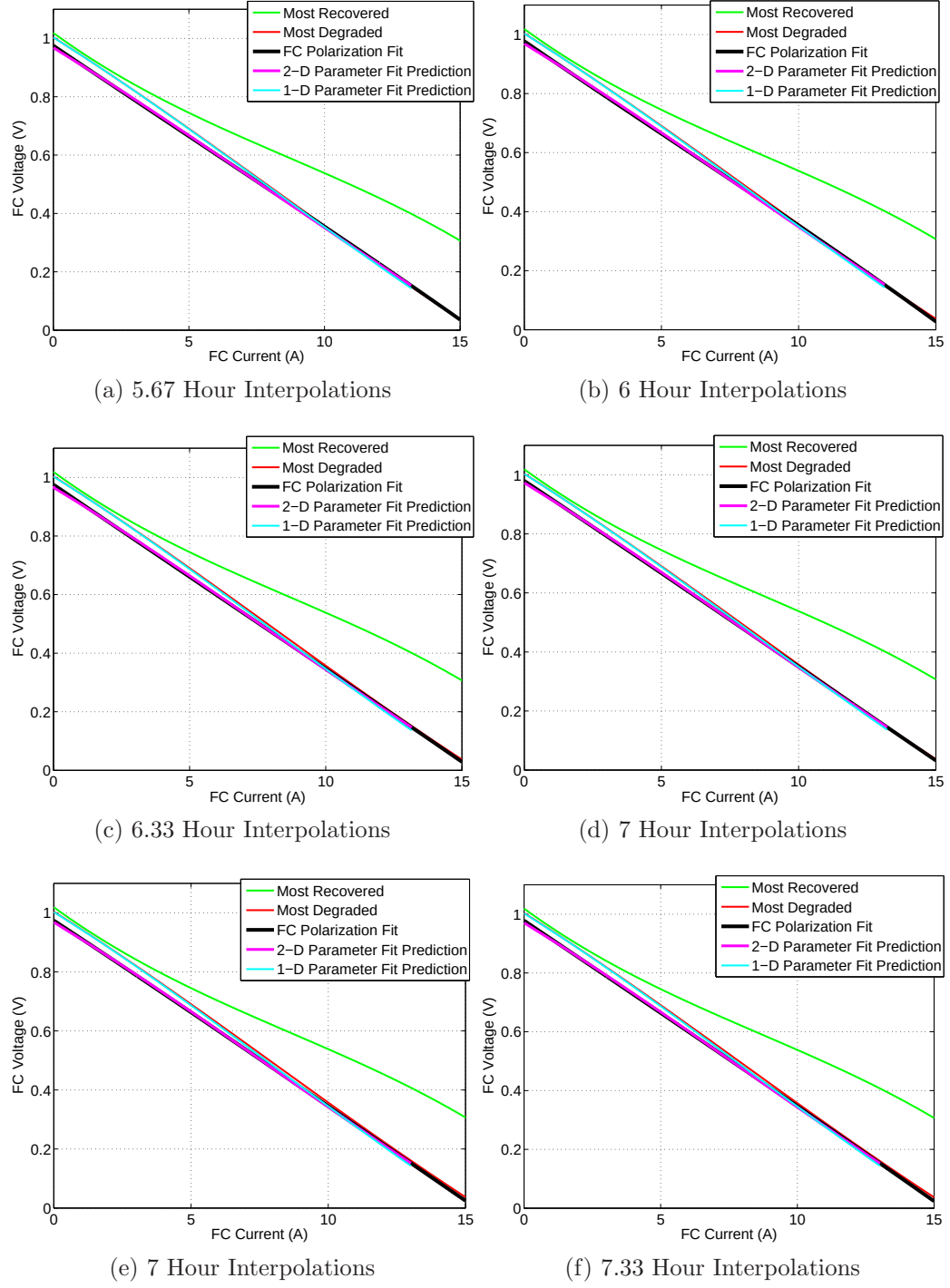


Figure A.4: Linear Interpolations of the 5.67 - 7.33 Hour Polarization Curves

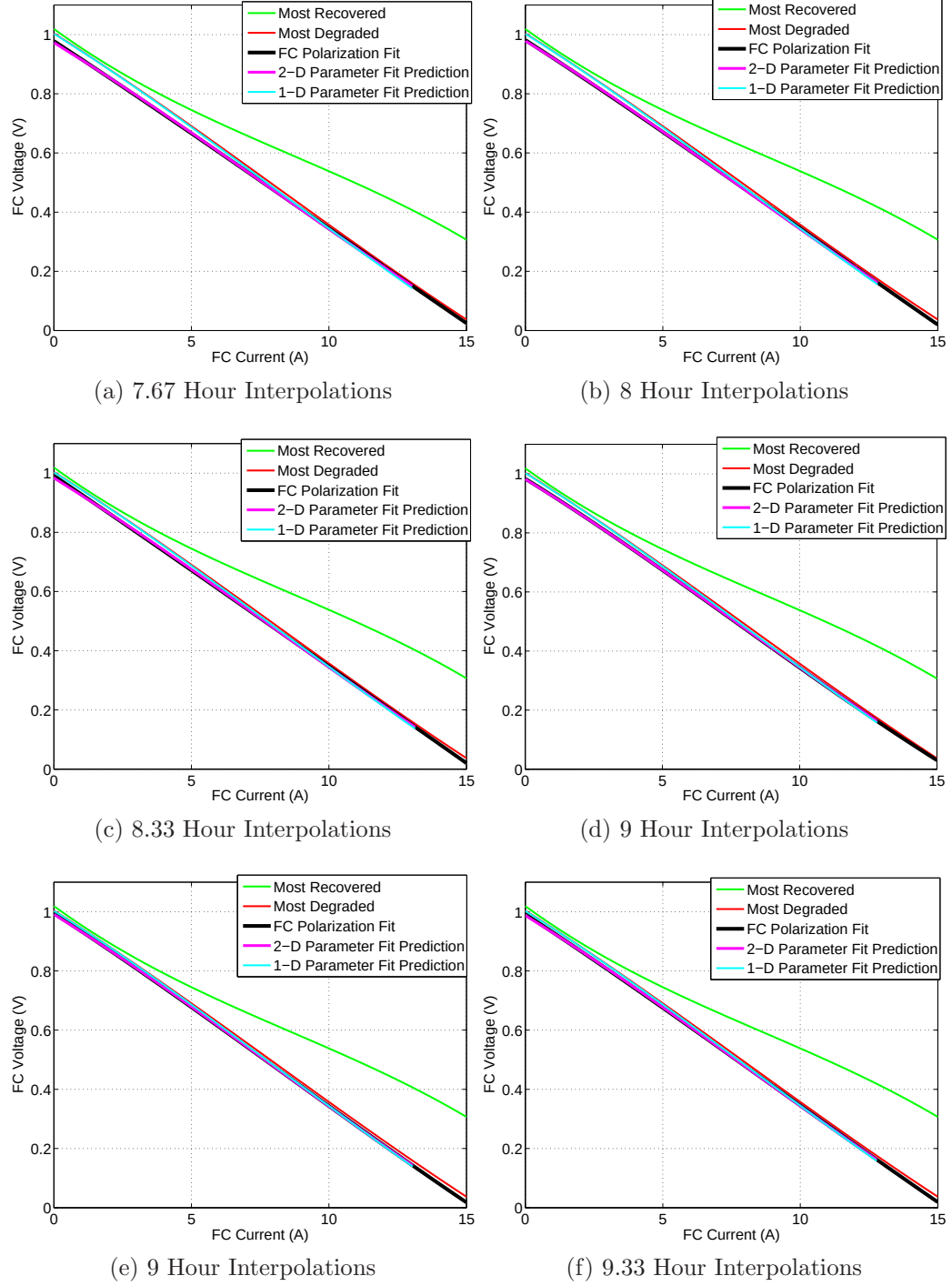


Figure A.5: Linear Interpolations of the 7.67 - 9.33 Hour Polarization Curves

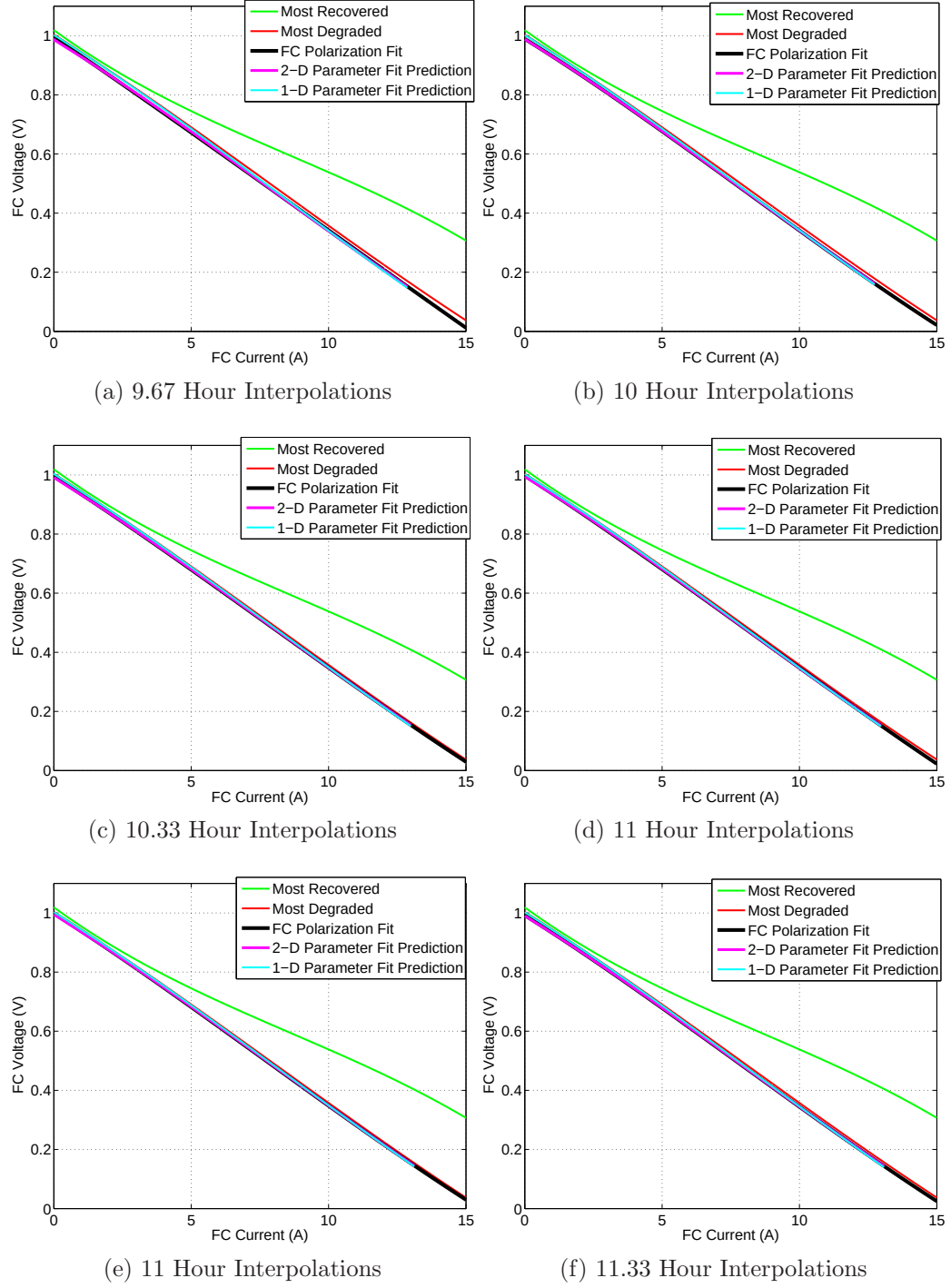


Figure A.6: Linear Interpolations of the 9.67 - 11.33 Hour Polarization Curves

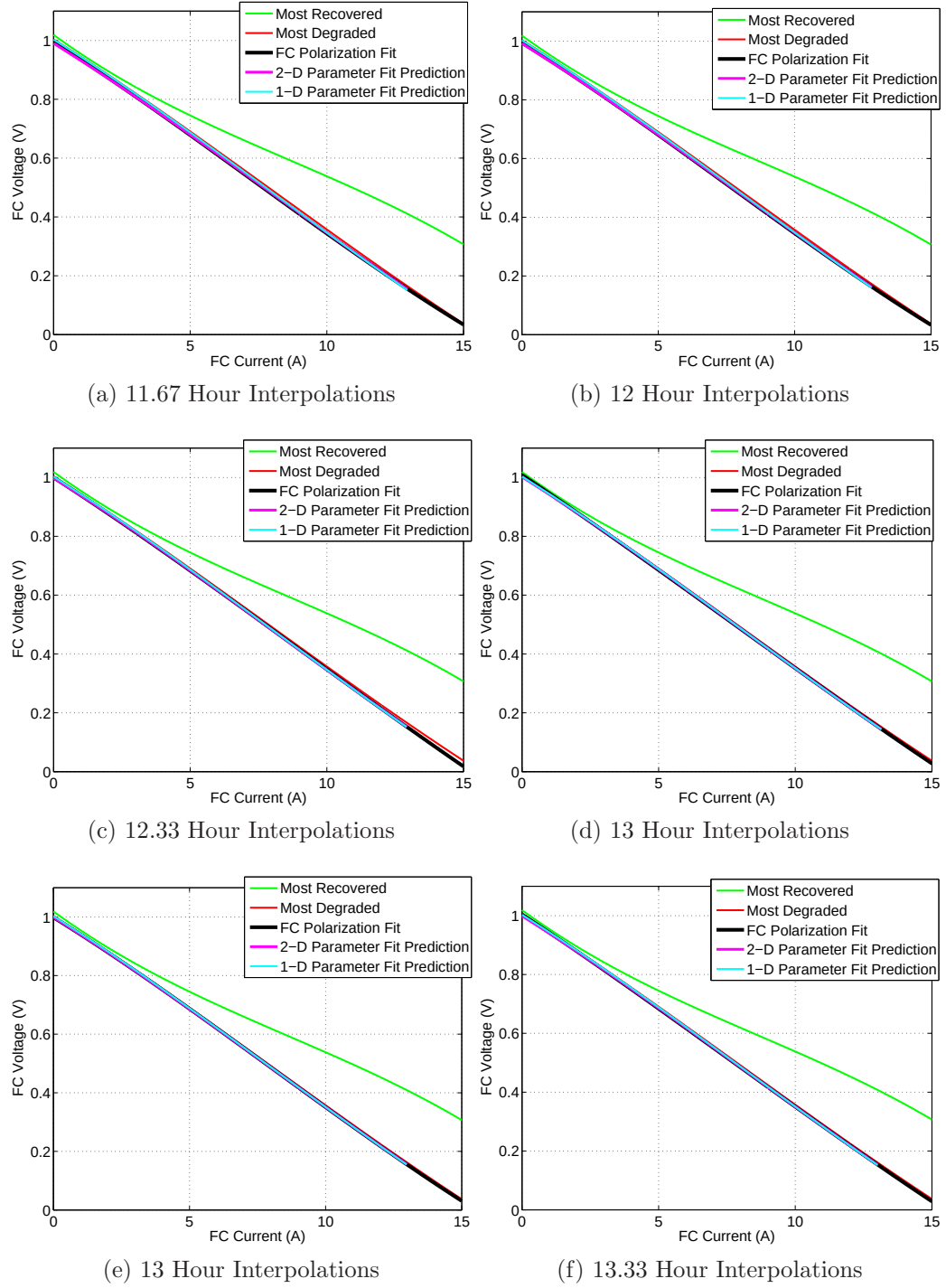


Figure A.7: Linear Interpolations of the 11.67 - 13.33 Hour Polarization Curves

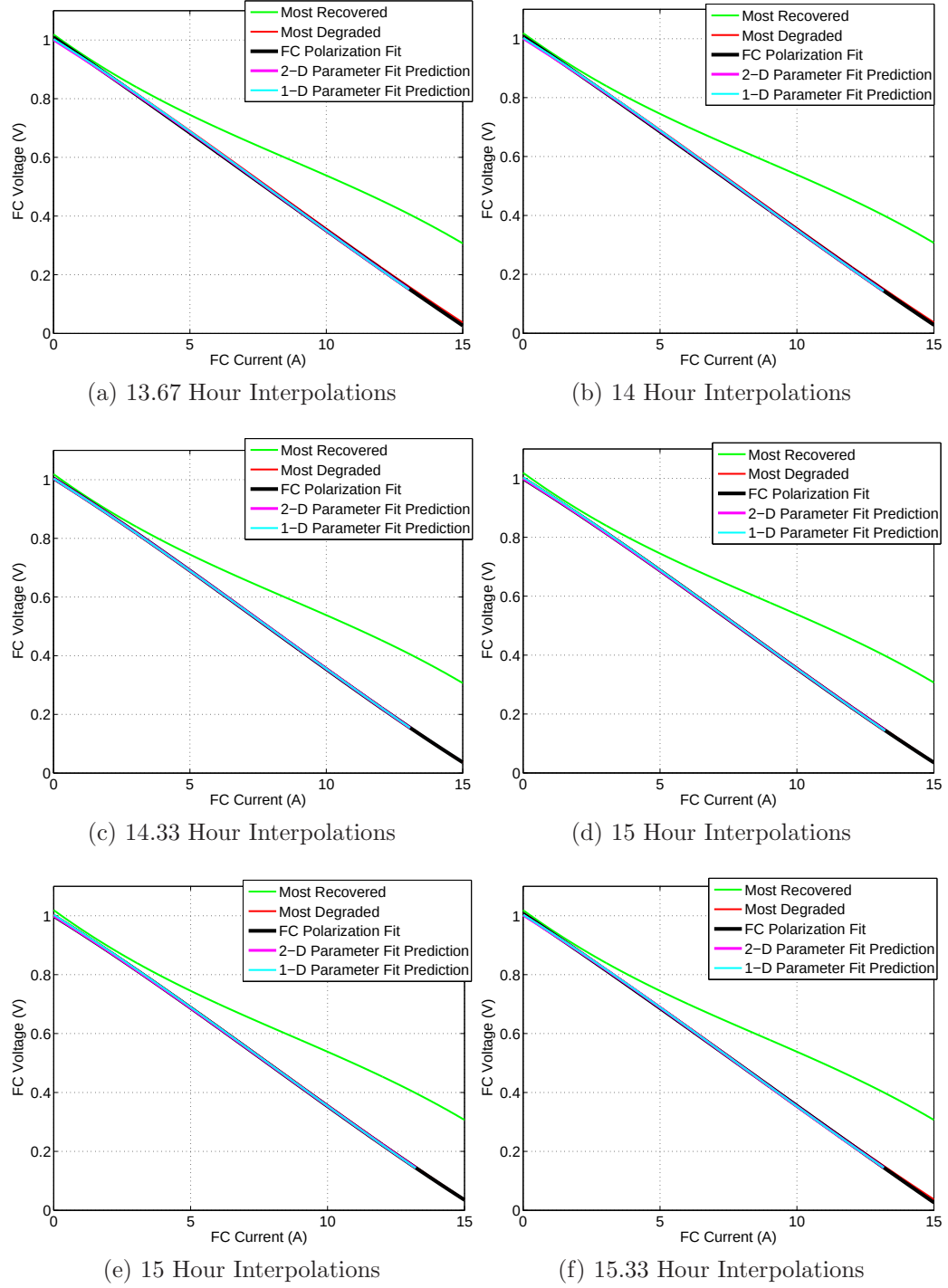


Figure A.8: Linear Interpolations of the 13.67 - 15.33 Hour Polarization Curves

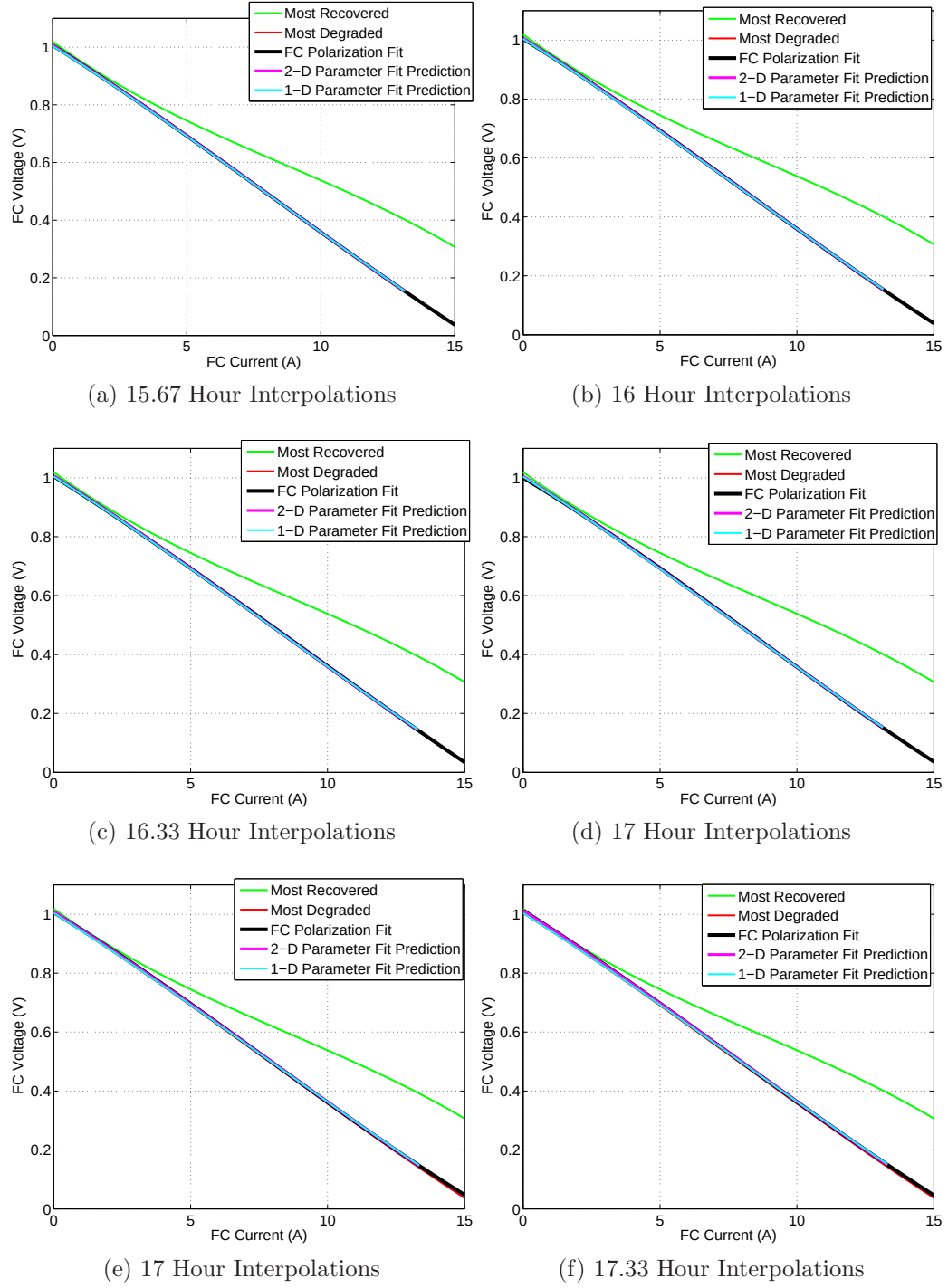


Figure A.9: Linear Interpolations of the 15.67 - 17.33 Hour Polarization Curves

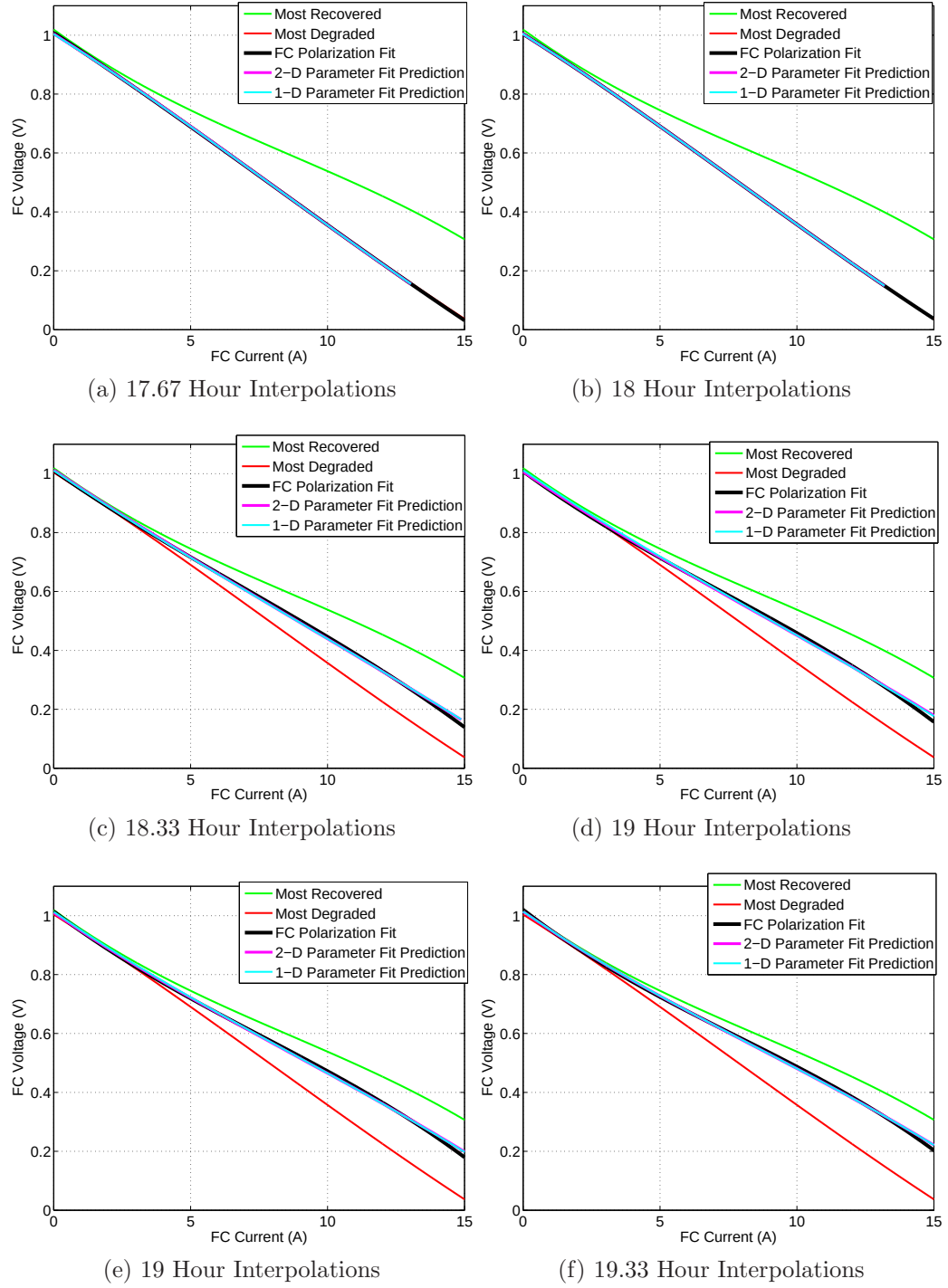


Figure A.10: Linear Interpolations of the 17.67 - 19.33 Hour Polarization Curves

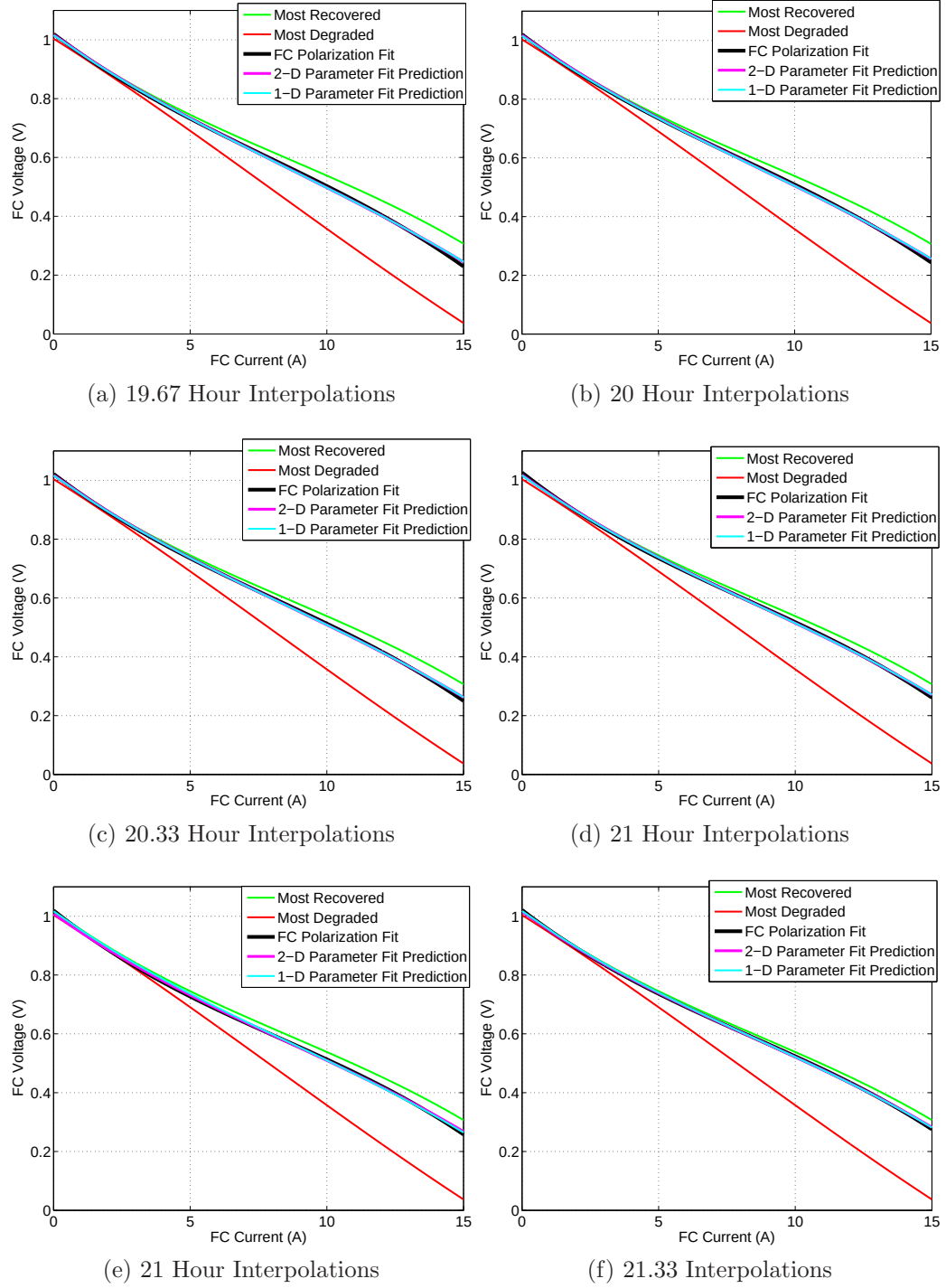


Figure A.11: Linear Interpolations of the 19.67 - 21.33 Hour Polarization Curves

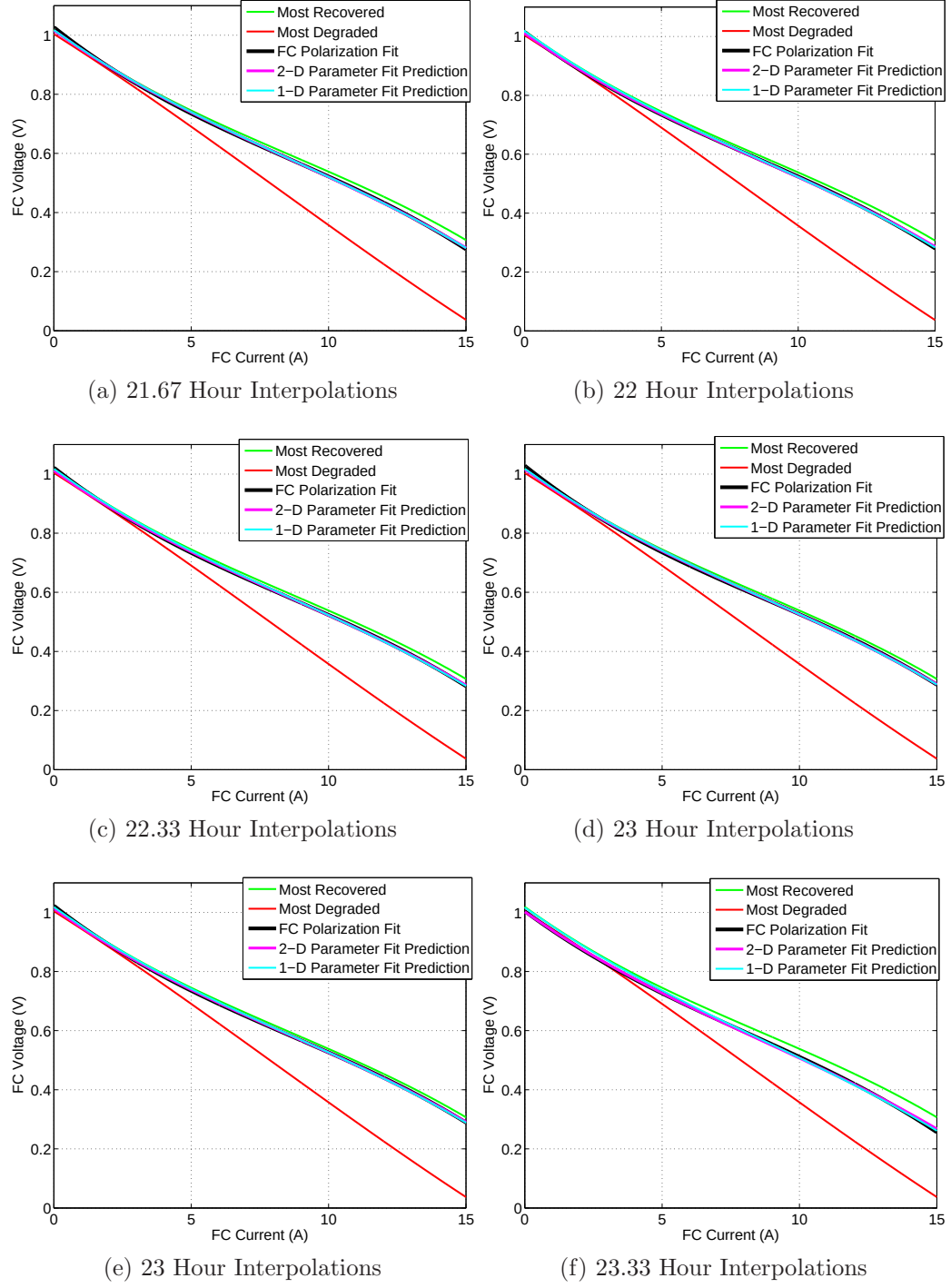


Figure A.12: Linear Interpolations of the 21.67 - 23.33 Hour Polarization Curves

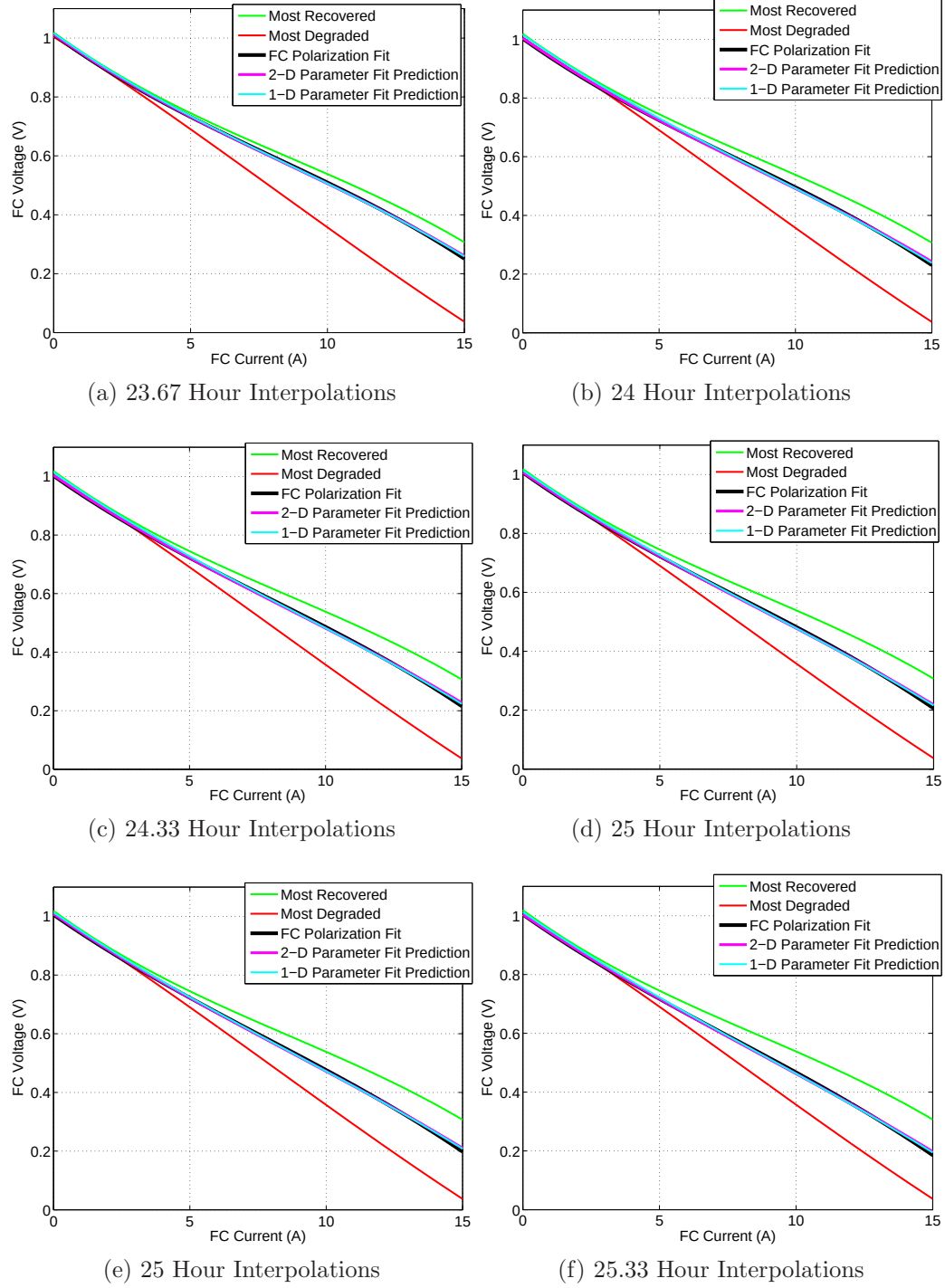


Figure A.13: Linear Interpolations of the 23.67 - 25.33 Hour Polarization Curves

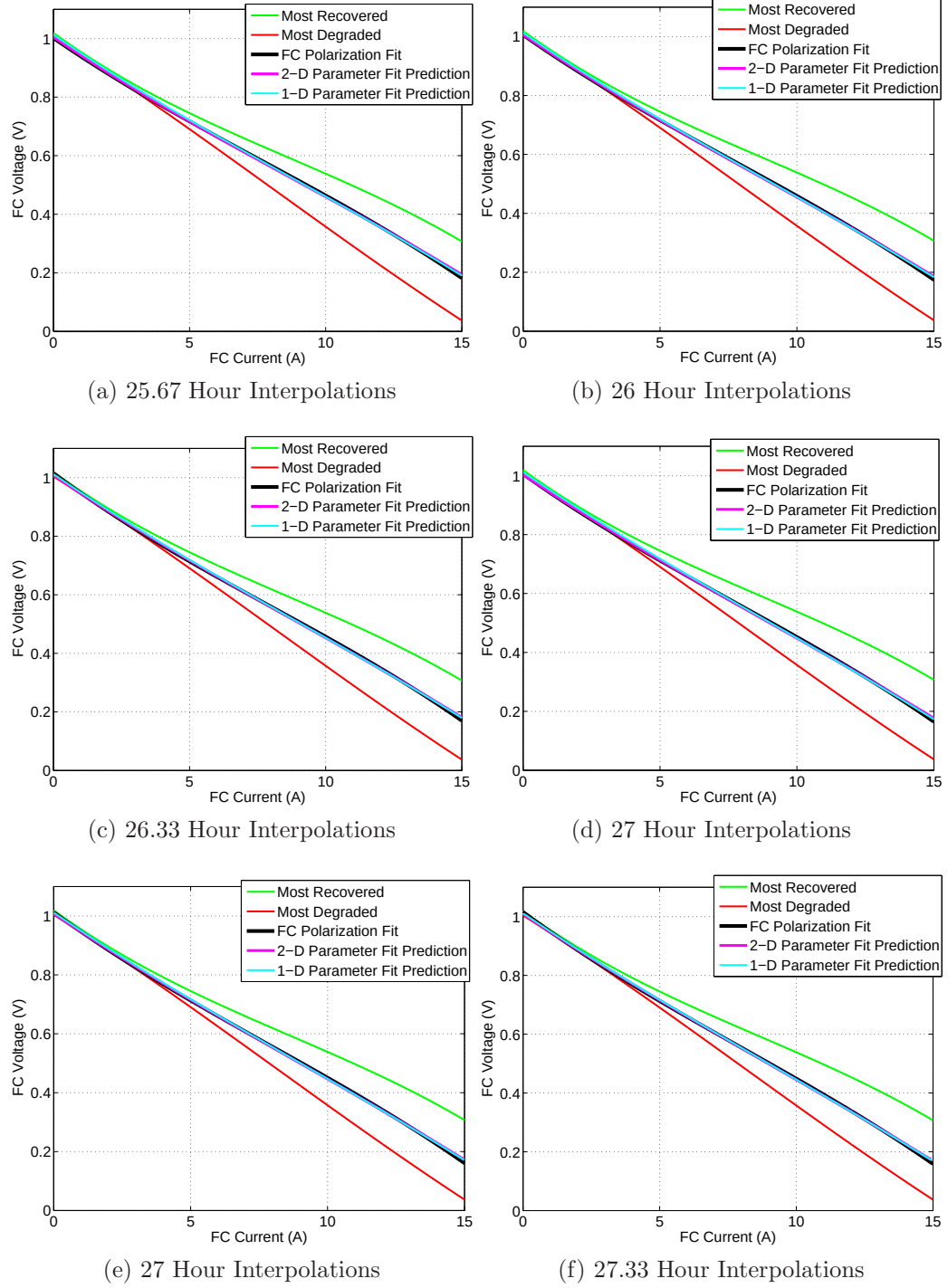


Figure A.14: Linear Interpolations of the 25.67 - 27.33 Hour Polarization Curves

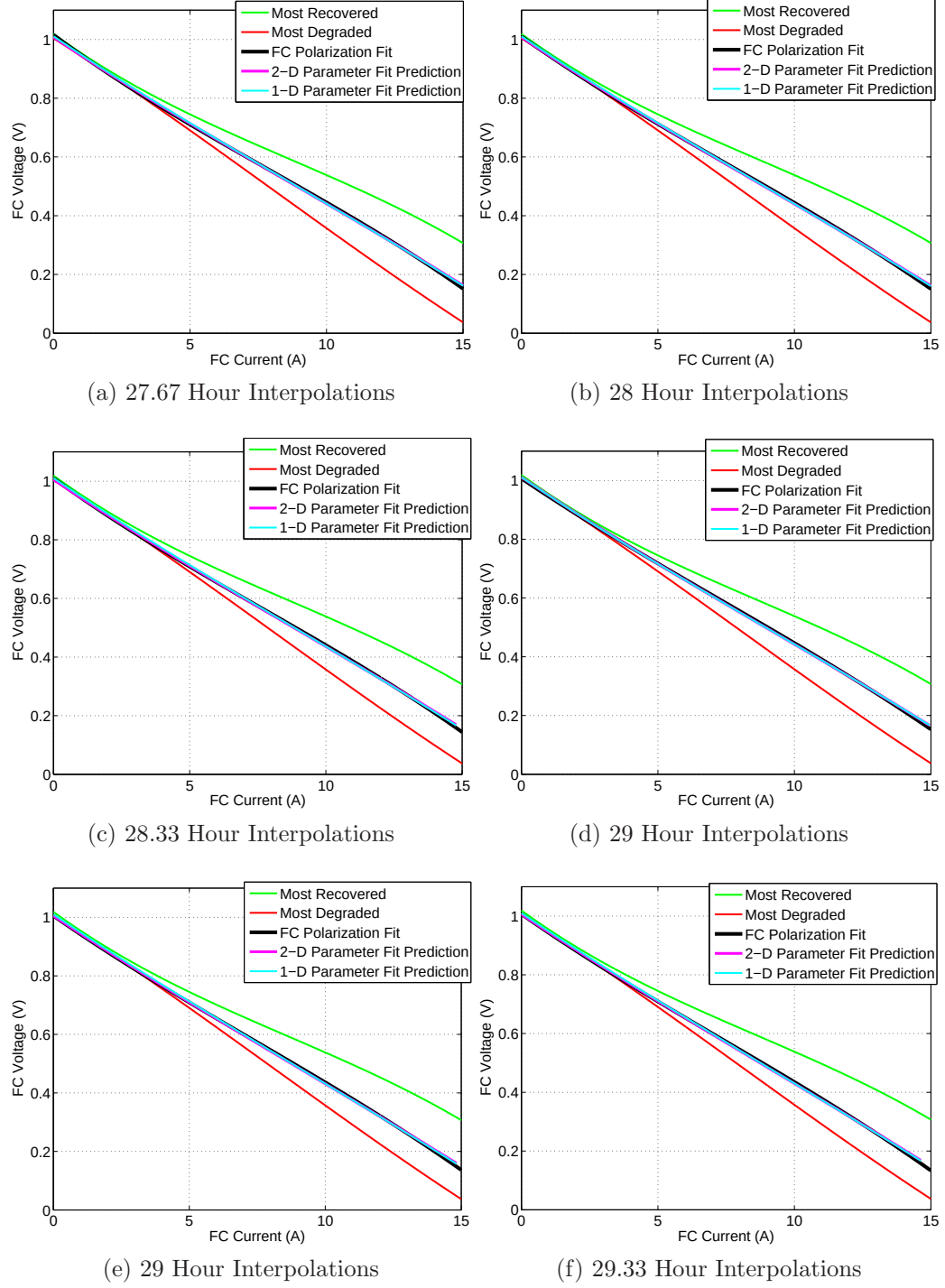


Figure A.15: Linear Interpolations of the 27.67 - 29.33 Hour Polarization Curves

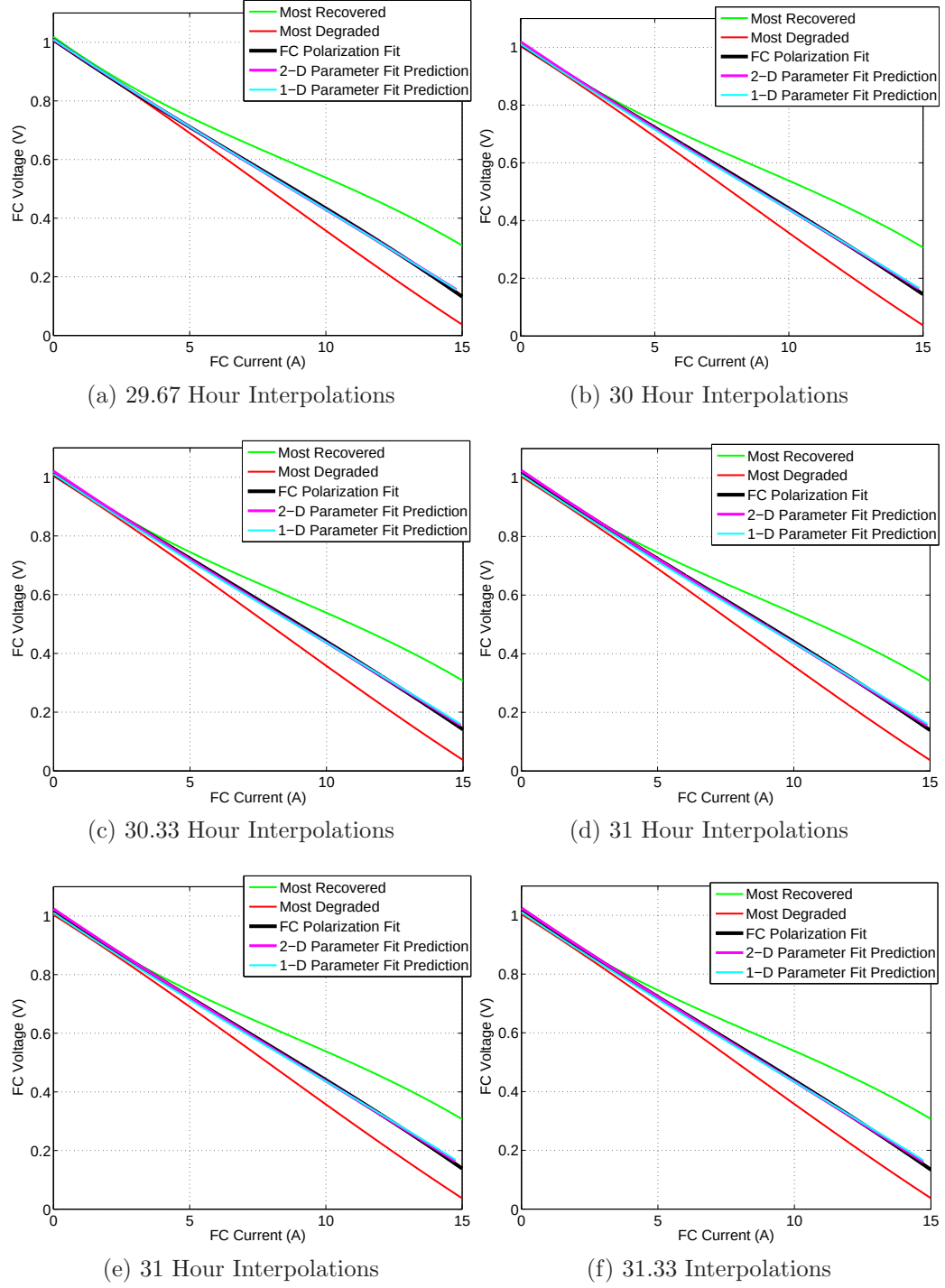


Figure A.16: Linear Interpolations of the 29.67 - 31.33 Hour Polarization Curves

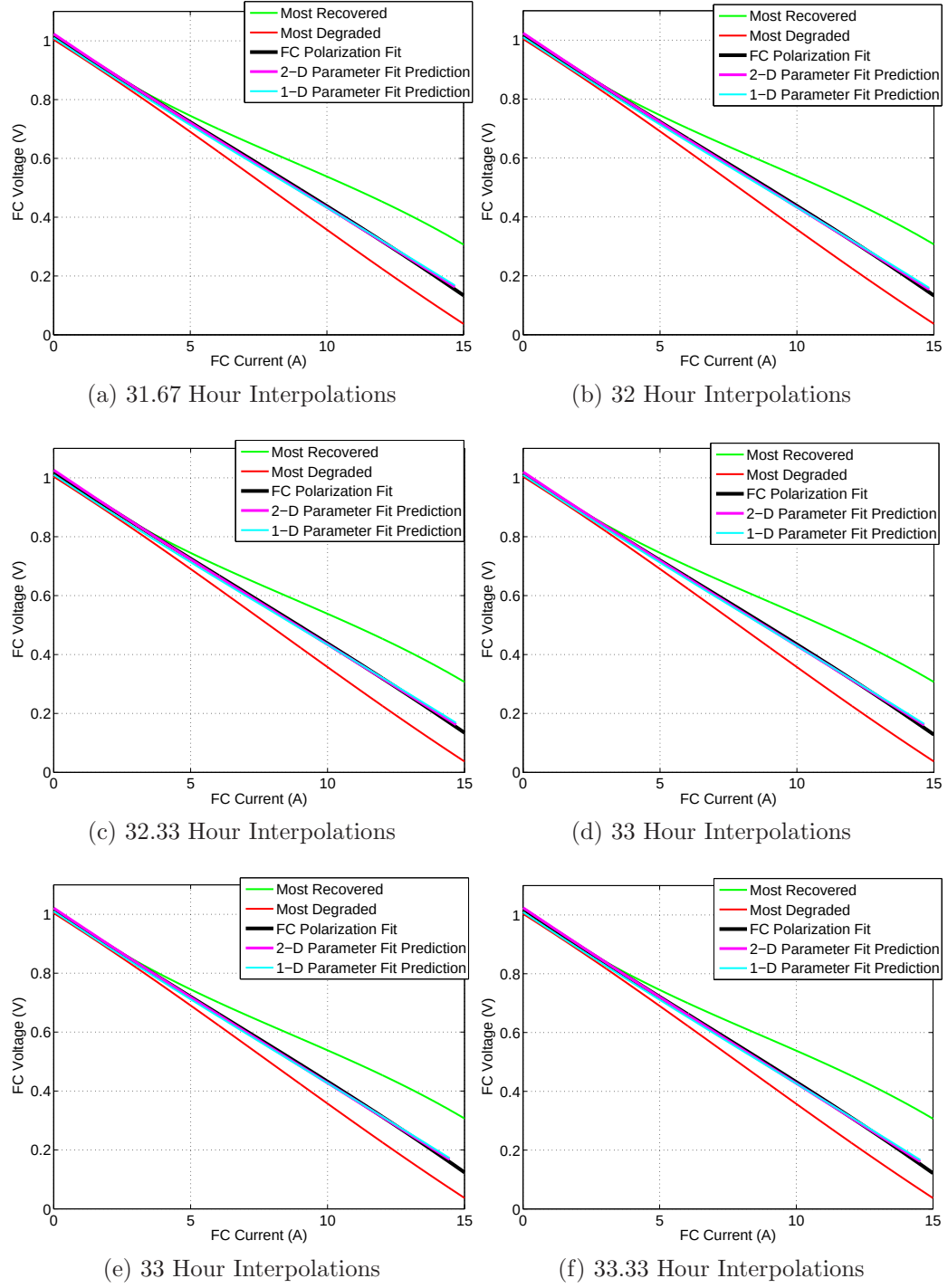


Figure A.17: Linear Interpolations of the 31.67 - 33.33 Hour Polarization Curves

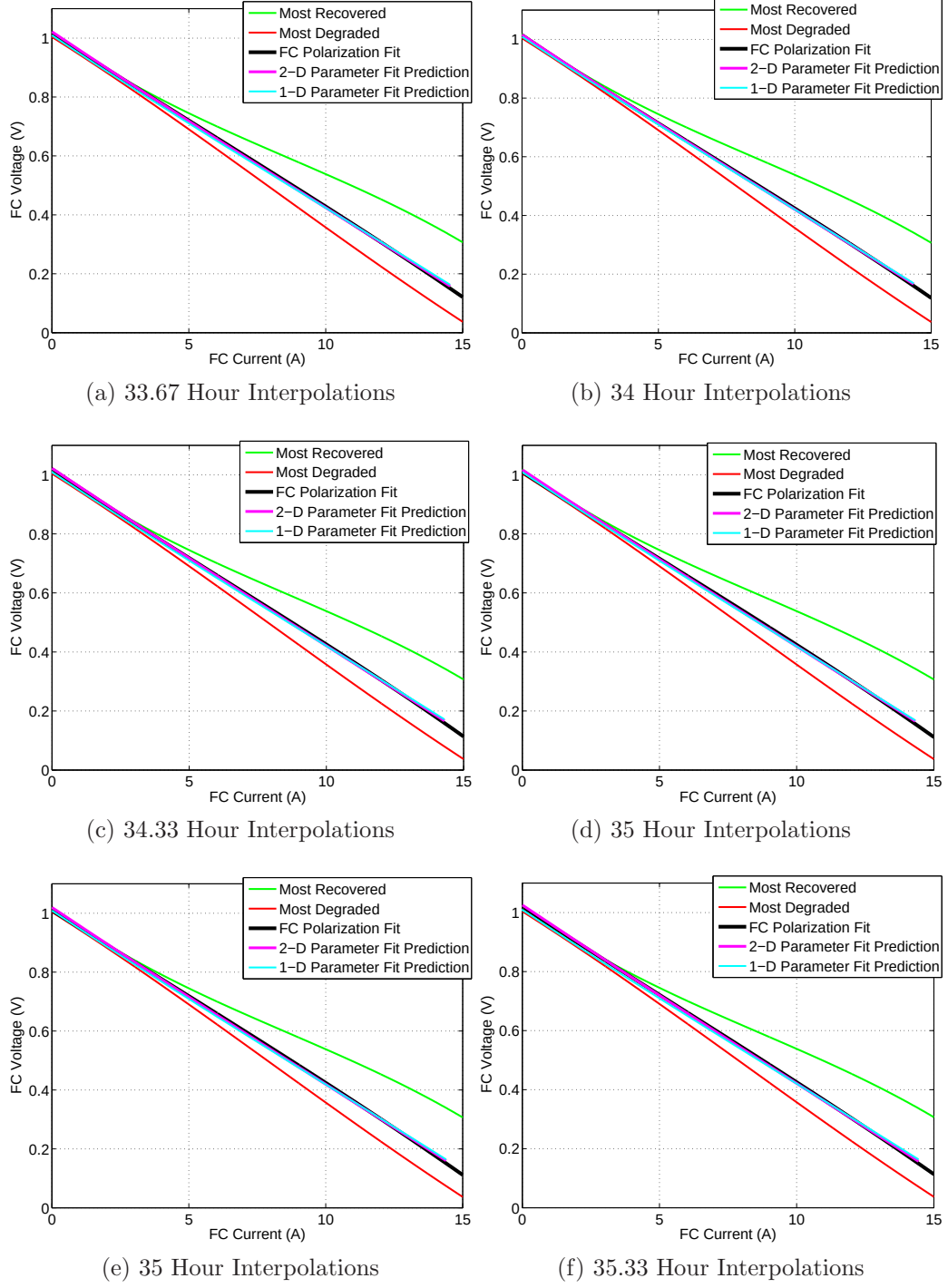


Figure A.18: Linear Interpolations of the 33.67 - 35.33 Hour Polarization Curves

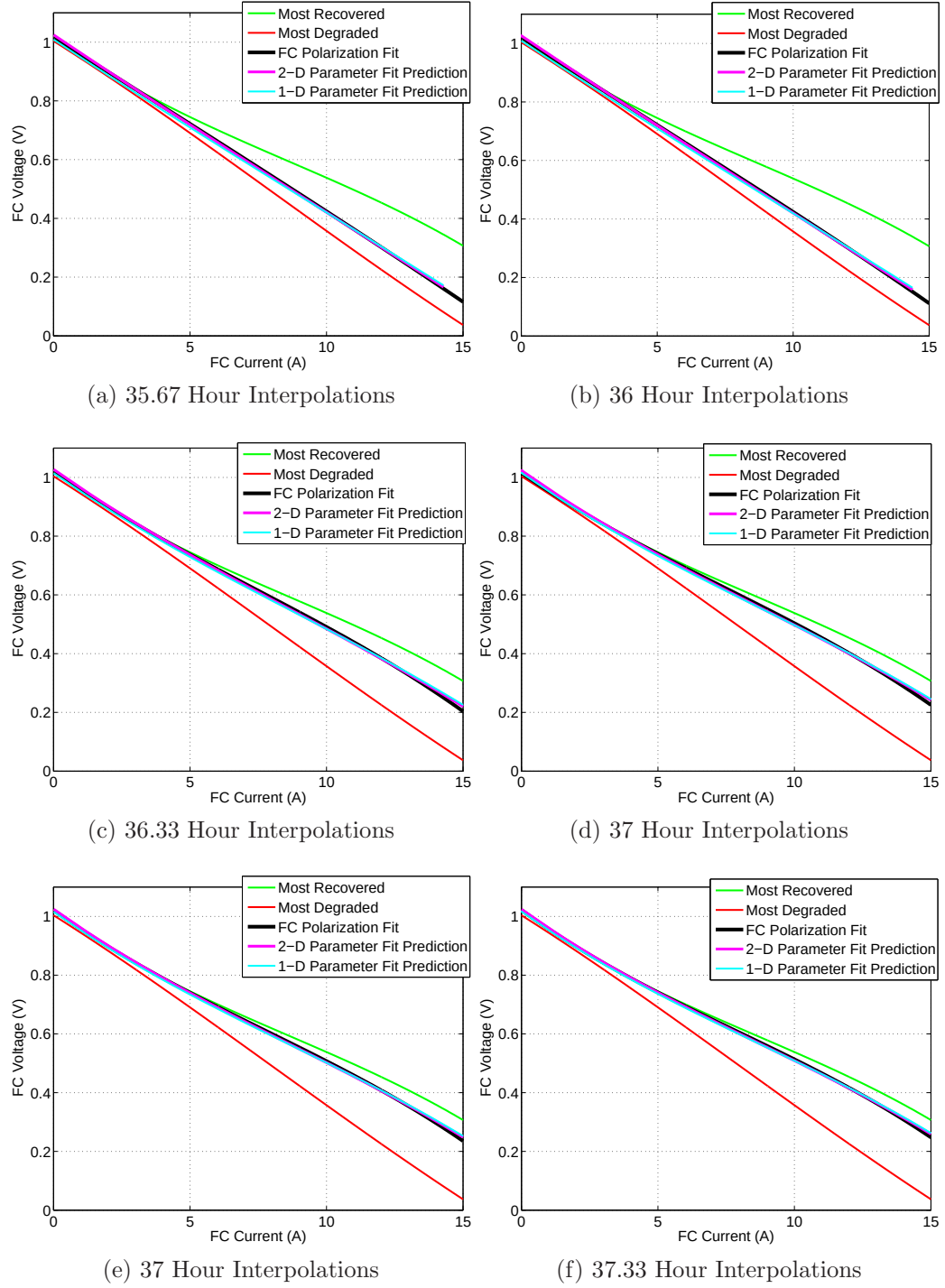


Figure A.19: Linear Interpolations of the 35.67 - 37.33 Hour Polarization Curves

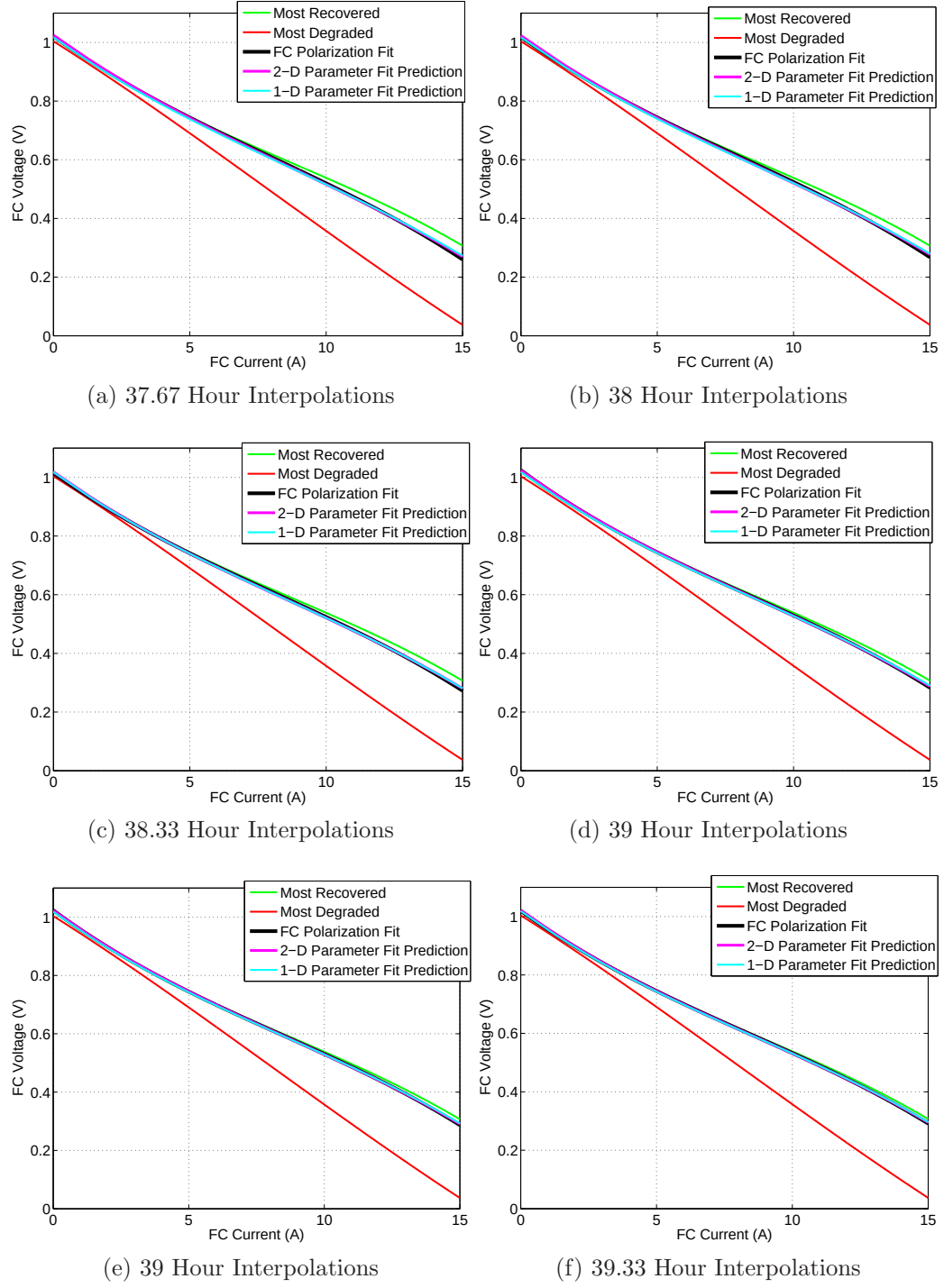


Figure A.20: Linear Interpolations of the 37.67 - 39.33 Hour Polarization Curves

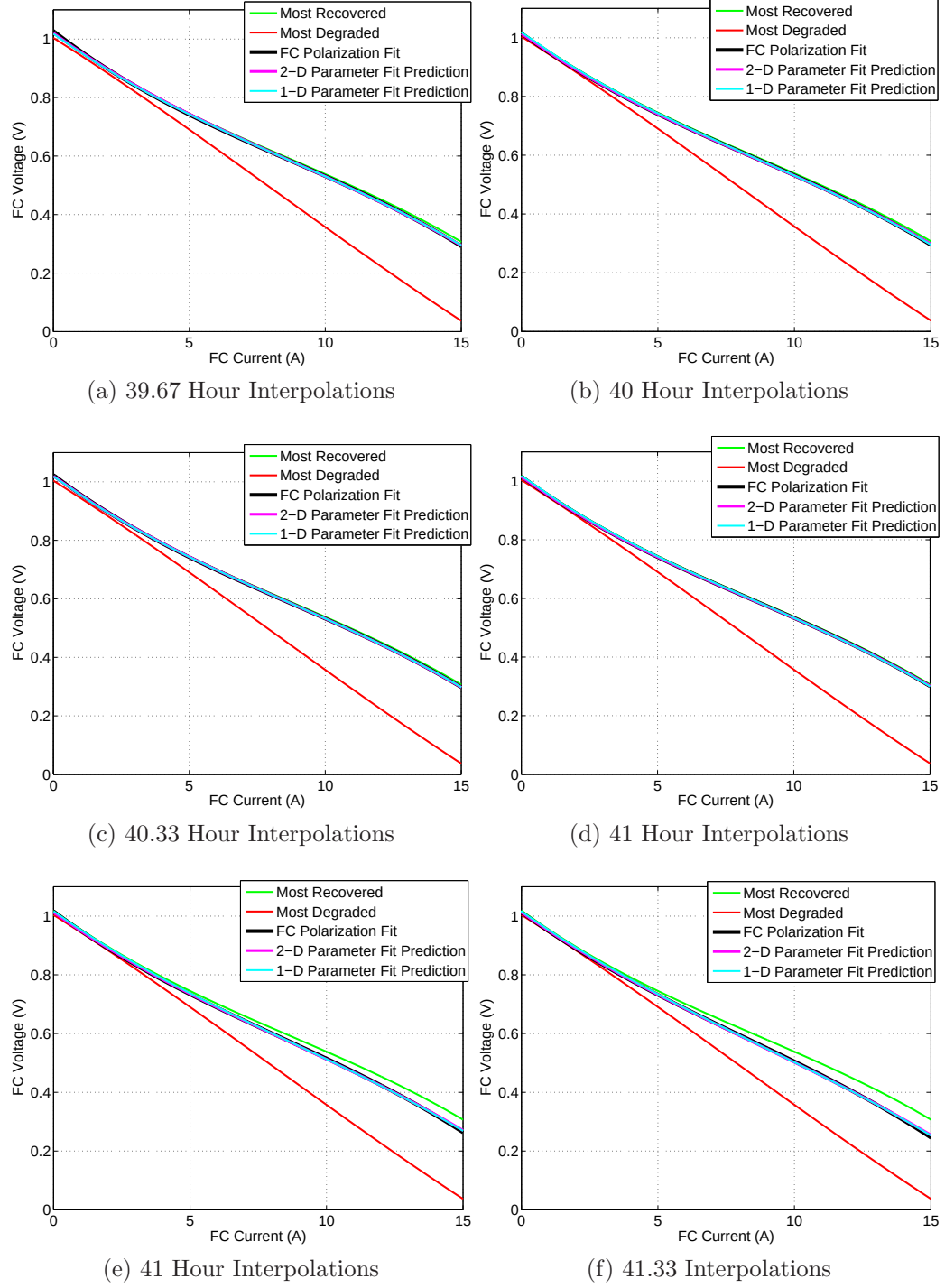


Figure A.21: Linear Interpolations of the 39.67 - 41.33 Hour Polarization Curves

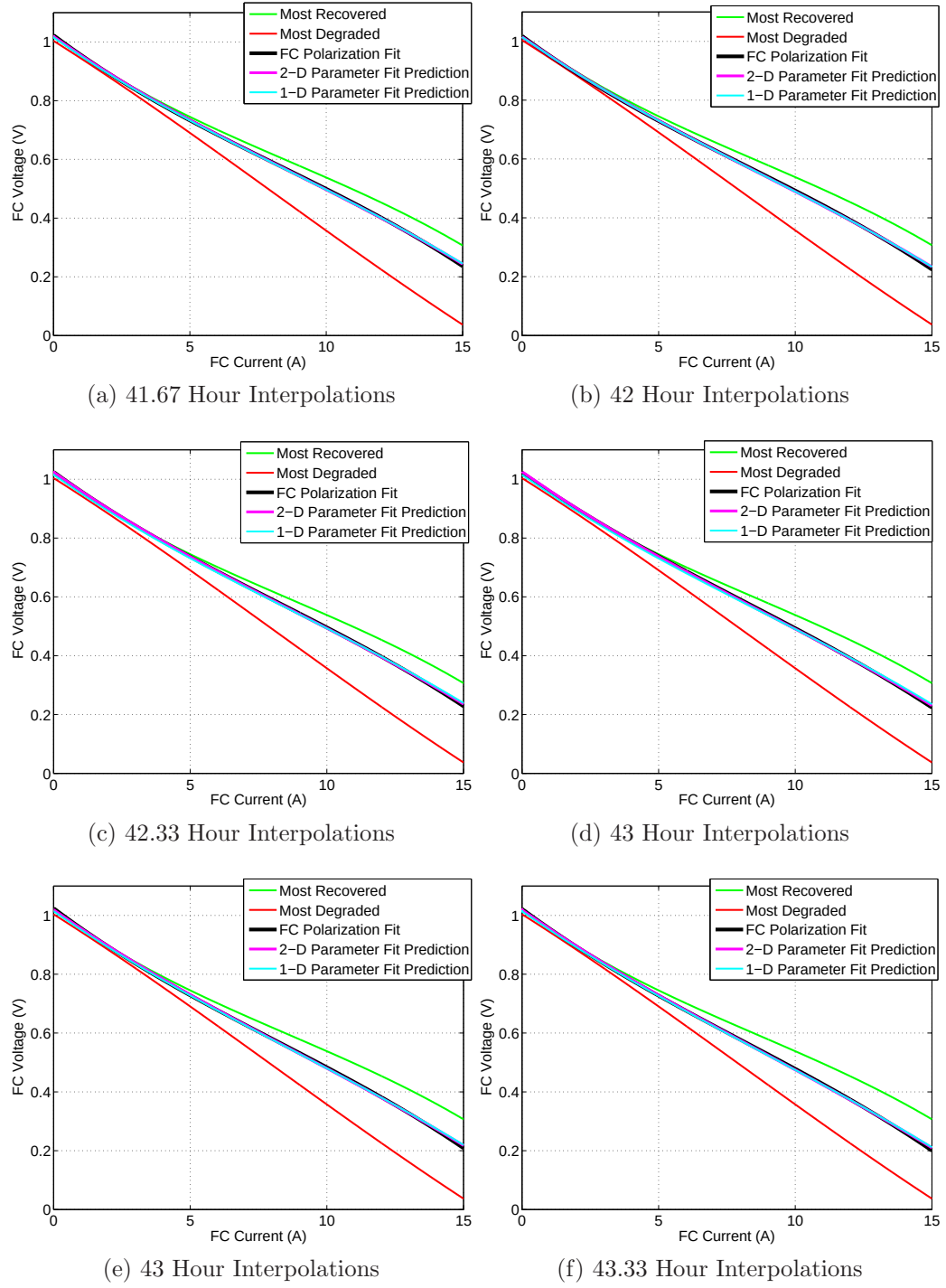


Figure A.22: Linear Interpolations of the 41.67 - 43.33 Hour Polarization Curves

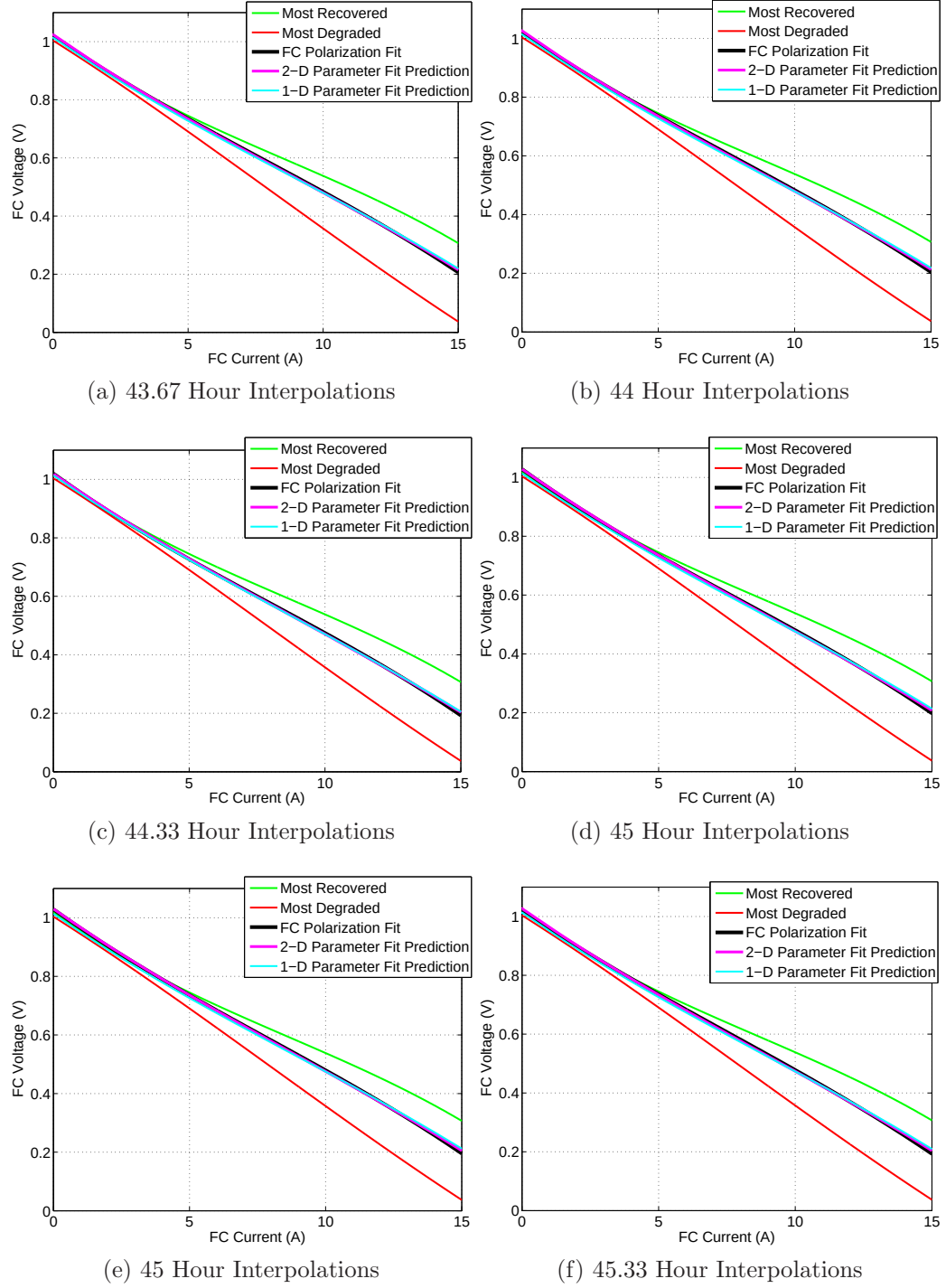


Figure A.23: Linear Interpolations of the 43.67 - 45.33 Hour Polarization Curves

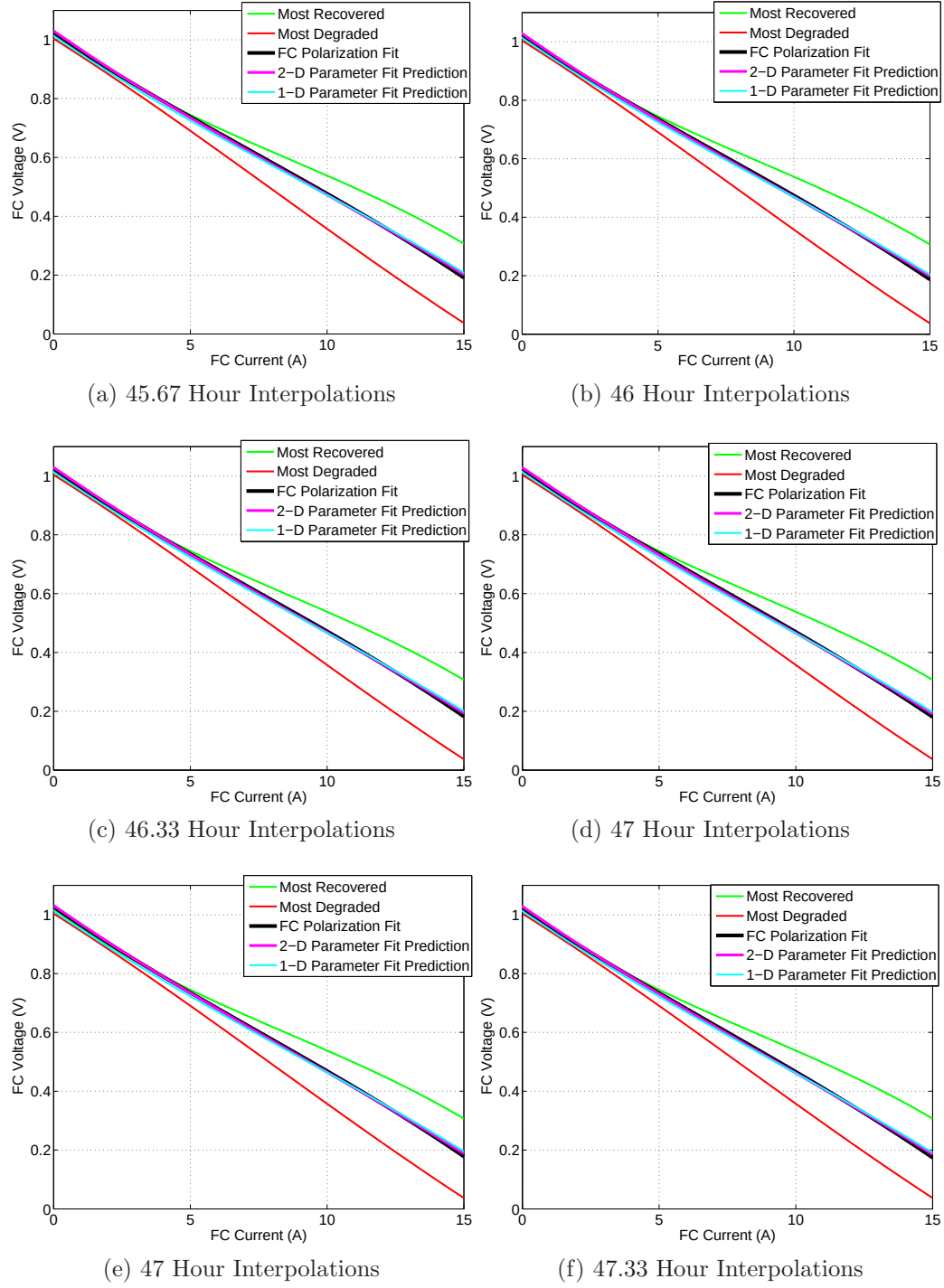


Figure A.24: Linear Interpolations of the 45.67 - 47.33 Hour Polarization Curves

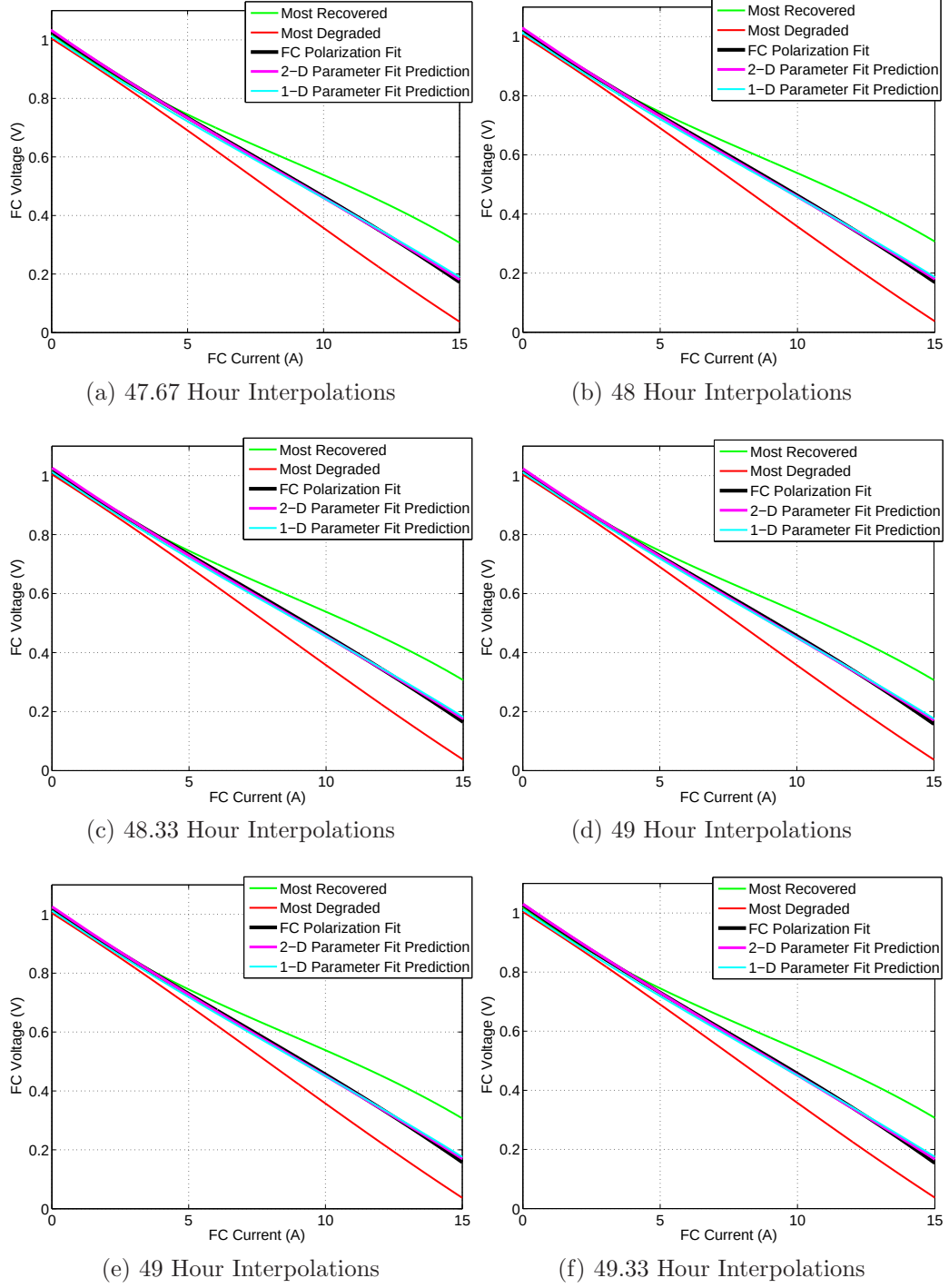


Figure A.25: Linear Interpolations of the 47.67 - 49.33 Hour Polarization Curves

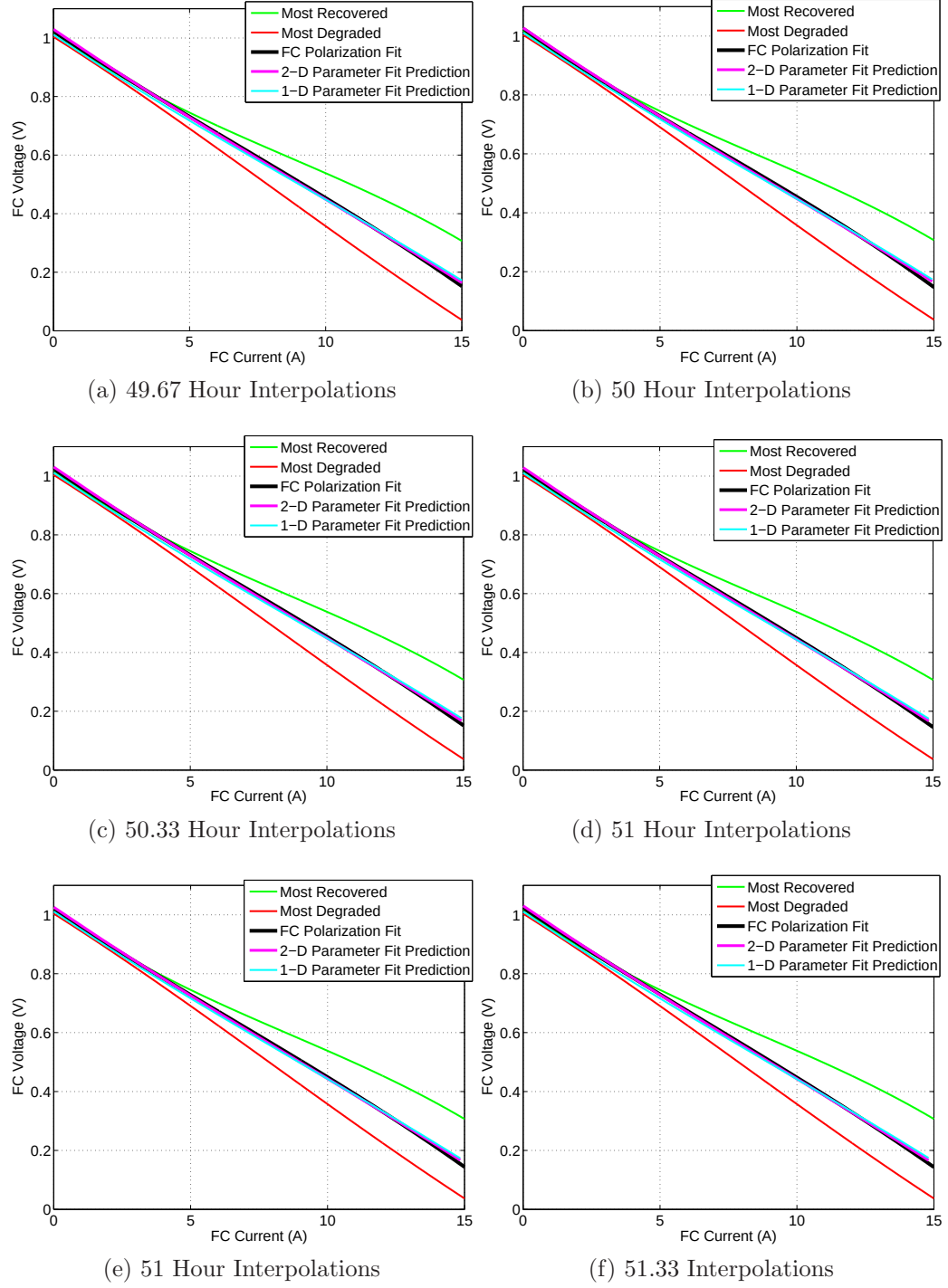


Figure A.26: Linear Interpolations of the 49.67 - 51.33 Hour Polarization Curves

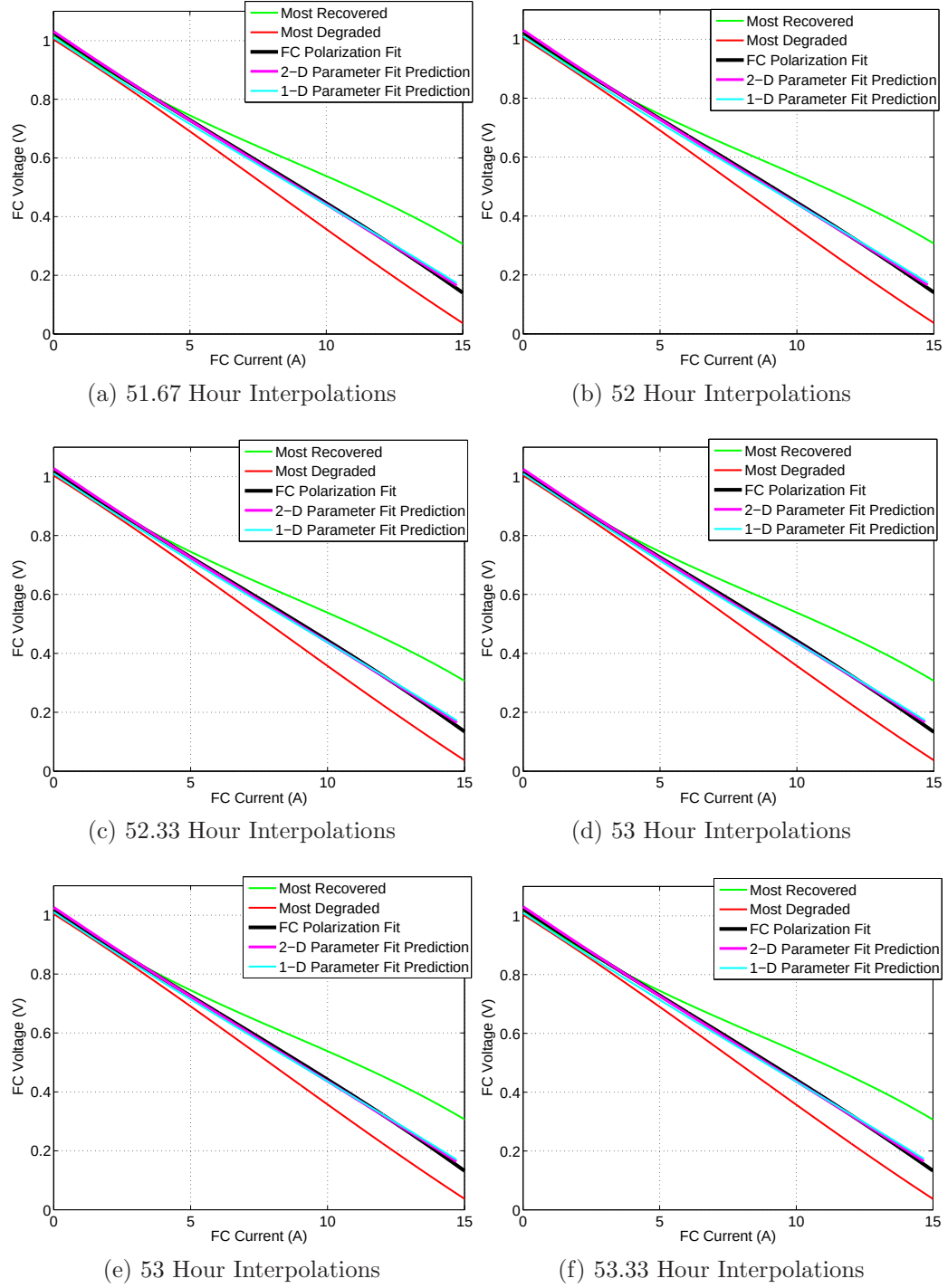


Figure A.27: Linear Interpolations of the 51.67 - 53.33 Hour Polarization Curves

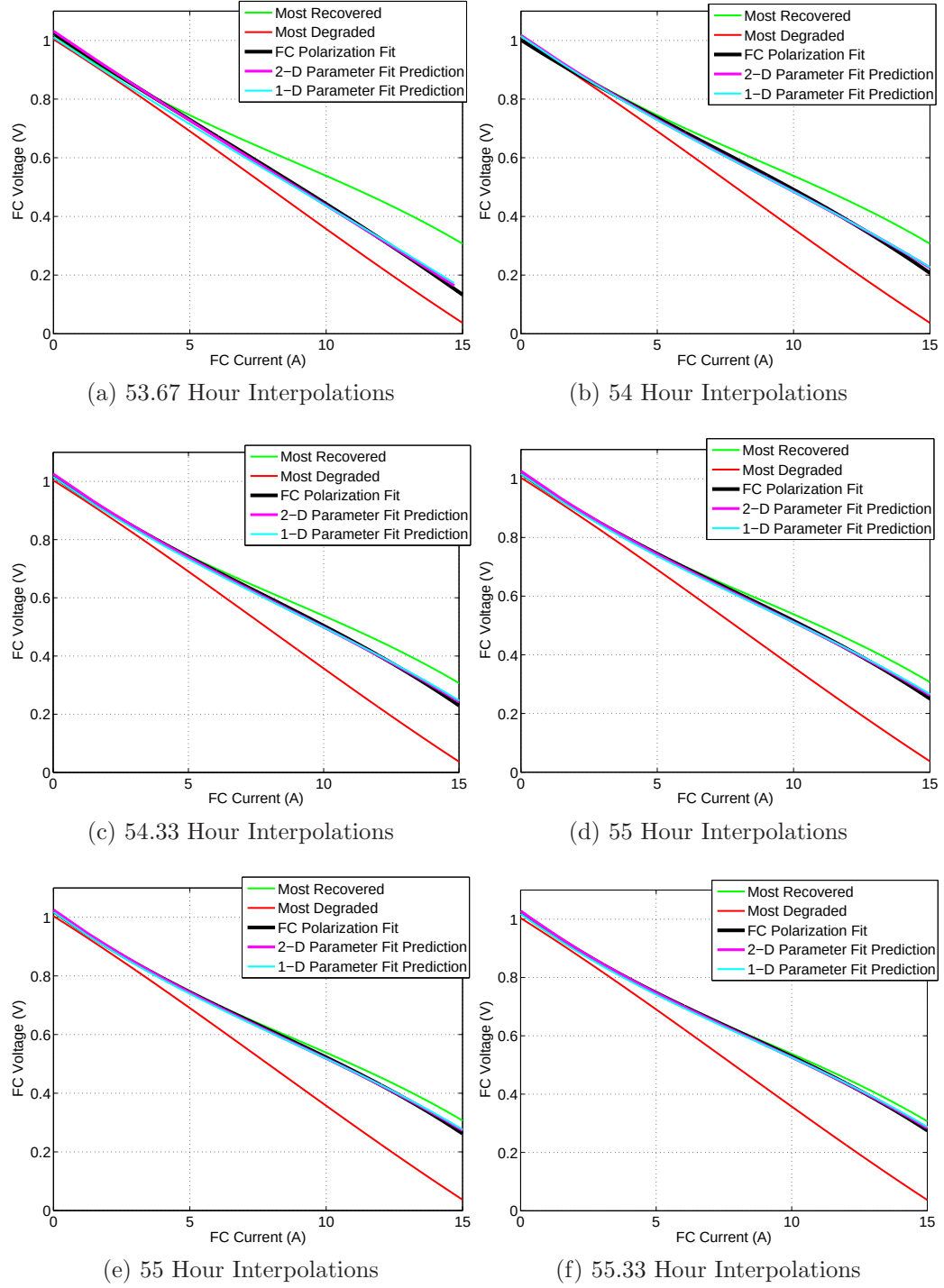


Figure A.28: Linear Interpolations of the 53.67 - 55.33 Hour Polarization Curves

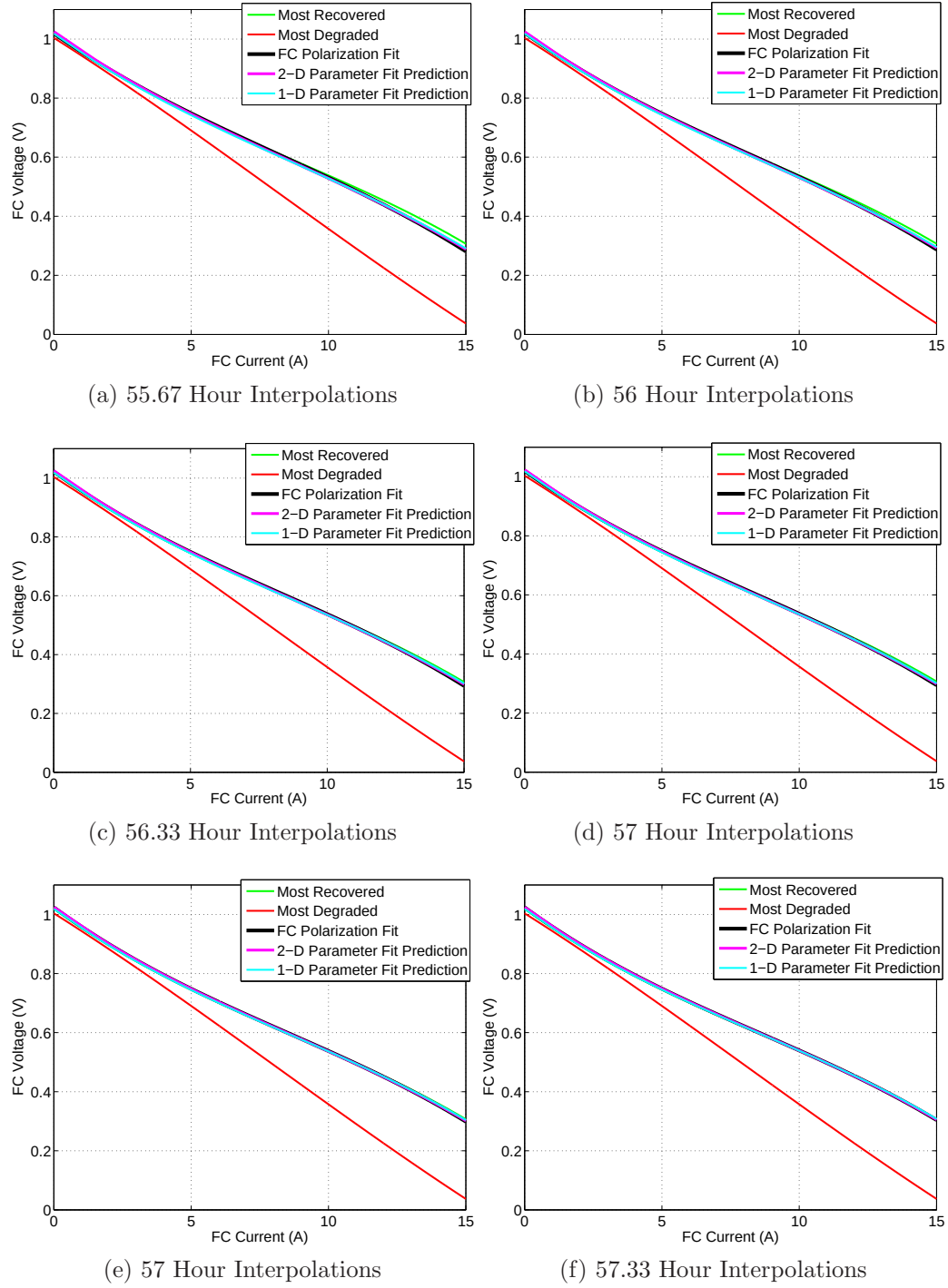


Figure A.29: Linear Interpolations of the 55.67 - 57.33 Hour Polarization Curves

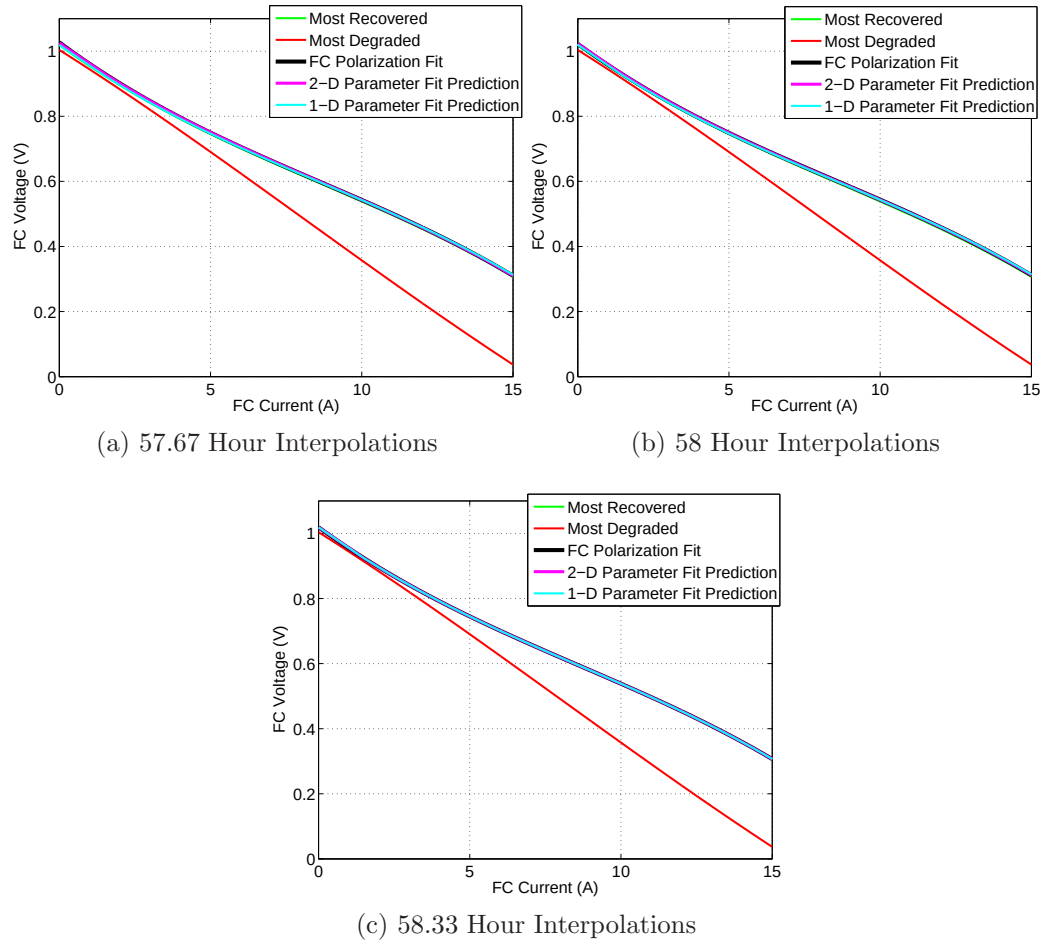


Figure A.30: Linear Interpolations of the 57.67 - 58.33 Hour Polarization Curves

	2-D Model			1-D Model		
Time (hrs)	x_1	x_2	SSE_N	$1 - \gamma$	γ	SSE_N
-4.00	-0.061	0.998	0.113	-0.166	1.166	0.260
0.00	0.658	0.272	0.031	0.540	0.460	0.219
0.33	0.580	0.361	0.030	0.482	0.518	0.165
0.67	0.536	0.411	0.030	0.447	0.553	0.141
1.00	0.496	0.456	0.024	0.415	0.585	0.136
1.33	0.504	0.445	0.021	0.419	0.581	0.135
1.67	0.430	0.514	0.019	0.335	0.665	0.173
2.00	0.384	0.565	0.017	0.300	0.700	0.136
2.33	0.325	0.628	0.015	0.246	0.754	0.118
2.67	0.287	0.664	0.009	0.205	0.795	0.120
3.00	0.249	0.703	0.012	0.170	0.830	0.119
3.33	0.213	0.739	0.013	0.131	0.869	0.127
3.67	0.174	0.780	0.009	0.097	0.903	0.114
4.00	0.151	0.805	0.012	0.077	0.923	0.106
4.33	0.125	0.830	0.009	0.051	0.949	0.110
4.67	0.089	0.870	0.012	0.022	0.978	0.086
5.00	0.074	0.886	0.014	0.006	0.994	0.094
5.33	0.040	0.926	0.014	-0.018	1.018	0.068
5.67	0.038	0.926	0.011	-0.022	1.022	0.068
6.00	0.019	0.946	0.016	-0.039	1.039	0.070
6.33	0.002	0.960	0.013	-0.061	1.061	0.075
6.67	0.009	0.960	0.012	-0.042	1.042	0.053
7.00	-0.013	0.978	0.012	-0.072	1.072	0.066
7.33	-0.010	0.977	0.015	-0.066	1.066	0.065
7.67	-0.017	0.987	0.014	-0.069	1.069	0.059
8.00	-0.033	1.009	0.013	-0.074	1.074	0.043
8.33	-0.032	1.012	0.011	-0.065	1.065	0.029
8.67	-0.029	1.008	0.013	-0.065	1.065	0.033
9.00	-0.058	1.046	0.009	-0.079	1.079	0.016
9.33	-0.045	1.029	0.009	-0.071	1.071	0.021
9.67	-0.067	1.050	0.010	-0.094	1.094	0.023
10.00	-0.060	1.045	0.013	-0.084	1.084	0.023
10.33	-0.027	1.015	0.016	-0.047	1.047	0.022
10.67	-0.042	1.034	0.013	-0.056	1.056	0.016
11.00	-0.032	1.023	0.015	-0.046	1.046	0.018
11.33	-0.045	1.033	0.012	-0.067	1.067	0.020
11.67	-0.035	1.022	0.013	-0.057	1.057	0.020
12.00	-0.033	1.022	0.016	-0.052	1.052	0.021
12.33	-0.053	1.048	0.015	-0.061	1.061	0.016

Table A.1 – *Continued on next page*

	2-D Model			1-D Model		
Time (hrs)	x_1	x_2	SSE_N	$1 - \gamma$	γ	SSE_N
12.67	-0.030	1.029	0.015	-0.033	1.033	0.015
13.00	-0.026	1.022	0.009	-0.032	1.032	0.009
13.33	-0.029	1.025	0.011	-0.036	1.036	0.012
13.67	-0.033	1.030	0.010	-0.038	1.038	0.011
14.00	-0.029	1.026	0.010	-0.033	1.033	0.010
14.33	-0.012	1.012	0.014	-0.011	1.011	0.014
14.67	-0.011	1.007	0.016	-0.017	1.017	0.017
15.00	-0.010	1.005	0.016	-0.020	1.020	0.018
15.33	-0.021	1.020	0.015	-0.024	1.024	0.015
15.67	0.000	1.002	0.013	0.005	0.995	0.013
16.00	0.005	0.998	0.016	0.010	0.990	0.016
16.33	0.005	0.997	0.014	0.010	0.990	0.014
16.67	-0.003	1.004	0.020	0.000	1.000	0.020
17.00	0.024	0.981	0.016	0.032	0.968	0.017
17.33	0.023	0.985	0.015	0.037	0.963	0.018
17.67	-0.014	1.015	0.018	-0.013	1.013	0.018
18.00	0	1	0.019	0	1	0.019
18.33	0.448	0.554	0.013	0.452	0.548	0.014
18.67	0.527	0.467	0.019	0.518	0.482	0.020
19.00	0.601	0.396	0.017	0.596	0.404	0.017
19.33	0.683	0.316	0.014	0.682	0.318	0.014
19.67	0.770	0.232	0.022	0.772	0.228	0.023
20.00	0.811	0.191	0.013	0.814	0.186	0.014
20.33	0.833	0.167	0.019	0.835	0.165	0.019
20.67	0.866	0.136	0.014	0.868	0.132	0.015
21.00	0.858	0.134	0.018	0.843	0.157	0.019
21.33	0.910	0.087	0.012	0.906	0.094	0.011
21.67	0.904	0.095	0.016	0.901	0.099	0.015
22.00	0.925	0.068	0.015	0.913	0.087	0.016
22.33	0.923	0.071	0.009	0.913	0.087	0.010
22.67	0.934	0.064	0.016	0.930	0.070	0.015
23.00	0.941	0.053	0.010	0.933	0.067	0.010
23.33	0.856	0.129	0.020	0.832	0.168	0.026
23.67	0.829	0.166	0.014	0.822	0.178	0.014
24.00	0.763	0.226	0.009	0.744	0.256	0.011
24.33	0.708	0.282	0.011	0.691	0.309	0.015
24.67	0.675	0.319	0.015	0.664	0.336	0.017
25.00	0.642	0.352	0.009	0.634	0.366	0.009
25.33	0.597	0.394	0.012	0.584	0.416	0.014

Table A.1 – *Continued on next page*

	2-D Model			1-D Model		
Time (hrs)	x_1	x_2	SSE_N	$1 - \gamma$	γ	SSE_N
25.67	0.582	0.410	0.008	0.568	0.432	0.010
26.00	0.551	0.443	0.014	0.541	0.459	0.016
26.33	0.535	0.461	0.012	0.529	0.471	0.012
26.67	0.517	0.474	0.009	0.504	0.496	0.010
27.00	0.501	0.495	0.013	0.495	0.505	0.013
27.33	0.490	0.508	0.012	0.486	0.514	0.012
27.67	0.468	0.529	0.013	0.462	0.538	0.013
28.00	0.463	0.534	0.009	0.458	0.542	0.009
28.33	0.444	0.550	0.010	0.435	0.565	0.012
28.67	0.470	0.531	0.014	0.470	0.530	0.014
29.00	0.418	0.577	0.010	0.410	0.590	0.010
29.33	0.409	0.587	0.012	0.402	0.598	0.013
29.67	0.397	0.602	0.013	0.396	0.604	0.013
30.00	0.431	0.577	0.017	0.446	0.554	0.019
30.33	0.418	0.592	0.017	0.435	0.565	0.020
30.67	0.412	0.603	0.013	0.437	0.563	0.022
31.00	0.411	0.603	0.014	0.435	0.565	0.022
31.33	0.394	0.621	0.013	0.419	0.581	0.025
31.67	0.395	0.619	0.013	0.417	0.583	0.017
32.00	0.392	0.622	0.017	0.416	0.584	0.024
32.33	0.393	0.624	0.016	0.420	0.580	0.025
32.67	0.380	0.631	0.016	0.397	0.603	0.019
33.00	0.364	0.648	0.015	0.384	0.616	0.020
33.33	0.355	0.661	0.015	0.381	0.619	0.024
33.67	0.346	0.667	0.015	0.367	0.633	0.020
34.00	0.336	0.671	0.014	0.348	0.652	0.015
34.33	0.326	0.688	0.015	0.348	0.652	0.021
34.67	0.325	0.683	0.019	0.339	0.661	0.020
35.00	0.322	0.689	0.017	0.340	0.660	0.020
35.33	0.320	0.697	0.021	0.348	0.652	0.030
35.67	0.319	0.697	0.010	0.346	0.654	0.021
36.00	0.313	0.705	0.017	0.342	0.658	0.027
36.33	0.677	0.336	0.021	0.699	0.301	0.029
36.67	0.758	0.251	0.027	0.772	0.228	0.030
37.00	0.784	0.225	0.017	0.799	0.201	0.021
37.33	0.823	0.185	0.020	0.836	0.164	0.023
37.67	0.862	0.146	0.020	0.874	0.126	0.023
38.00	0.889	0.117	0.014	0.899	0.101	0.018
38.33	0.903	0.098	0.021	0.904	0.096	0.021

Table A.1 – *Continued on next page*

	2-D Model			1-D Model		
Time (hrs)	x_1	x_2	SSE_N	$1 - \gamma$	γ	SSE_N
38.67	0.929	0.077	0.018	0.938	0.062	0.020
39.00	0.940	0.065	0.017	0.948	0.052	0.019
39.33	0.956	0.047	0.015	0.960	0.040	0.016
39.67	0.953	0.049	0.018	0.956	0.044	0.018
40.00	0.965	0.031	0.020	0.958	0.042	0.020
40.33	0.966	0.035	0.021	0.967	0.033	0.022
40.67	0.980	0.016	0.019	0.974	0.026	0.019
41.00	0.865	0.131	0.010	0.859	0.141	0.010
41.33	0.806	0.191	0.016	0.800	0.200	0.016
41.67	0.765	0.239	0.009	0.770	0.230	0.009
42.00	0.727	0.273	0.010	0.728	0.272	0.011
42.33	0.734	0.275	0.010	0.749	0.251	0.015
42.67	0.716	0.295	0.012	0.735	0.265	0.018
43.00	0.669	0.336	0.012	0.678	0.322	0.014
43.33	0.640	0.365	0.013	0.648	0.352	0.014
43.67	0.659	0.352	0.014	0.677	0.323	0.018
44.00	0.652	0.361	0.016	0.672	0.328	0.022
44.33	0.615	0.391	0.016	0.625	0.375	0.017
44.67	0.631	0.383	0.011	0.656	0.344	0.019
45.00	0.621	0.396	0.011	0.649	0.351	0.022
45.33	0.617	0.397	0.009	0.640	0.360	0.019
45.67	0.606	0.411	0.010	0.634	0.366	0.024
46.00	0.593	0.421	0.010	0.618	0.382	0.020
46.33	0.578	0.439	0.013	0.605	0.395	0.022
46.67	0.568	0.448	0.018	0.595	0.405	0.026
47.00	0.557	0.462	0.012	0.588	0.412	0.029
47.33	0.547	0.469	0.018	0.573	0.427	0.026
47.67	0.533	0.487	0.015	0.566	0.434	0.031
48.00	0.527	0.489	0.020	0.553	0.447	0.029
48.33	0.513	0.502	0.021	0.537	0.463	0.028
48.67	0.495	0.517	0.016	0.516	0.484	0.024
49.00	0.491	0.523	0.020	0.515	0.485	0.028
49.33	0.480	0.540	0.012	0.512	0.488	0.026
49.67	0.469	0.550	0.019	0.501	0.499	0.032
50.00	0.467	0.550	0.015	0.495	0.505	0.027
50.33	0.468	0.552	0.019	0.501	0.499	0.033
50.67	0.447	0.571	0.014	0.478	0.522	0.028
51.00	0.447	0.569	0.019	0.472	0.528	0.026
51.33	0.434	0.586	0.017	0.468	0.532	0.034

Table A.1 – *Continued on next page*

	2-D Model			1-D Model		
Time (hrs)	x_1	x_2	SSE_N	$1 - \gamma$	γ	SSE_N
51.67	0.424	0.596	0.014	0.459	0.541	0.033
52.00	0.424	0.596	0.012	0.458	0.542	0.029
52.33	0.412	0.605	0.013	0.442	0.558	0.025
52.67	0.408	0.608	0.020	0.433	0.567	0.027
53.00	0.404	0.613	0.017	0.431	0.569	0.025
53.33	0.398	0.623	0.018	0.434	0.566	0.033
53.67	0.401	0.620	0.011	0.437	0.563	0.032
54.00	0.696	0.307	0.030	0.702	0.298	0.030
54.33	0.763	0.247	0.024	0.780	0.220	0.028
54.67	0.833	0.177	0.023	0.849	0.151	0.027
55.00	0.874	0.134	0.017	0.887	0.113	0.021
55.33	0.912	0.098	0.014	0.929	0.071	0.022
55.67	0.930	0.077	0.012	0.942	0.058	0.016
56.00	0.948	0.058	0.017	0.959	0.041	0.020
56.33	0.971	0.036	0.012	0.982	0.018	0.016
56.67	0.970	0.035	0.016	0.979	0.021	0.018
57.00	0.980	0.026	0.019	0.990	0.010	0.021
57.33	0.994	0.012	0.017	1.004	-0.004	0.019
57.67	1.012	-0.006	0.017	1.023	-0.023	0.019
58.00	1.021	-0.017	0.019	1.028	-0.028	0.019
58.33	1	0	0.020	1	0	0.020

Table A.1: Best-fit parameter values along with normalized sum of squared error values for all polarization curve measurements.

APPENDIX B

LINEAR INTERPOLATIONS OF DEGRADATION AND RECOVERY TESTING
EIS PROFILES

In Chapter 6 the application of the linear interpolation analysis method was used to show that the progression in a fuel cell's measured electrochemical impedance spectroscopy (EIS) profile follows a predominantly linear trend with loading-induced degradation and recovery. Figures 6.11 - 6.15 showed comparisons of the one-dimensional and two-dimensional linear interpolator impedance profile predictions to those the measured impedance profiles for the DC operating point $V_{DC} = 430$ mV. This appendix contains the corresponding comparisons at the other two DC operating points of measurement, $V_{DC} = 670$ mV and $V_{DC} = 200$ mV. Values for the best-fit interpolator parameters and the normalized sum of squared errors for each prediction at all three operating points are given in Table 6.1.

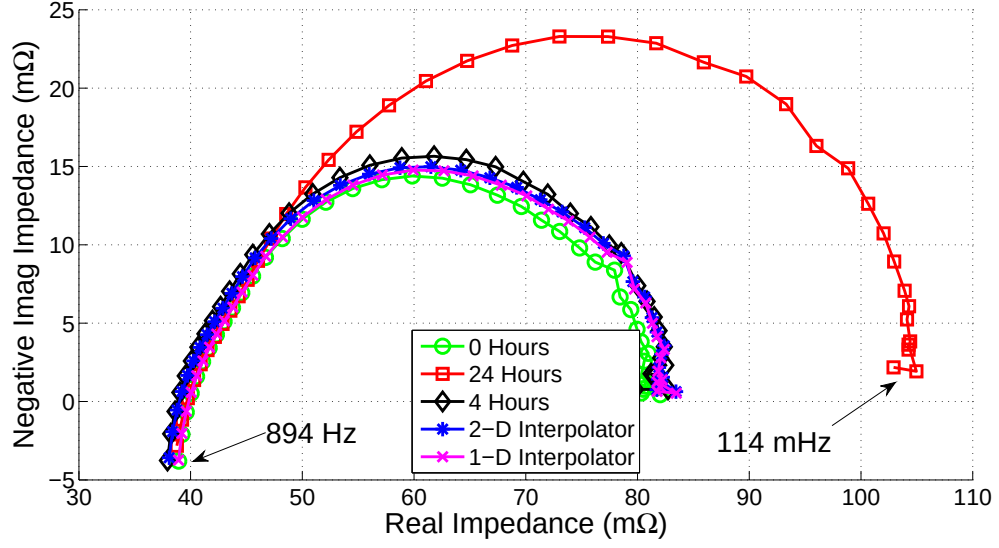


Figure B.1: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 4 hours of degradation.

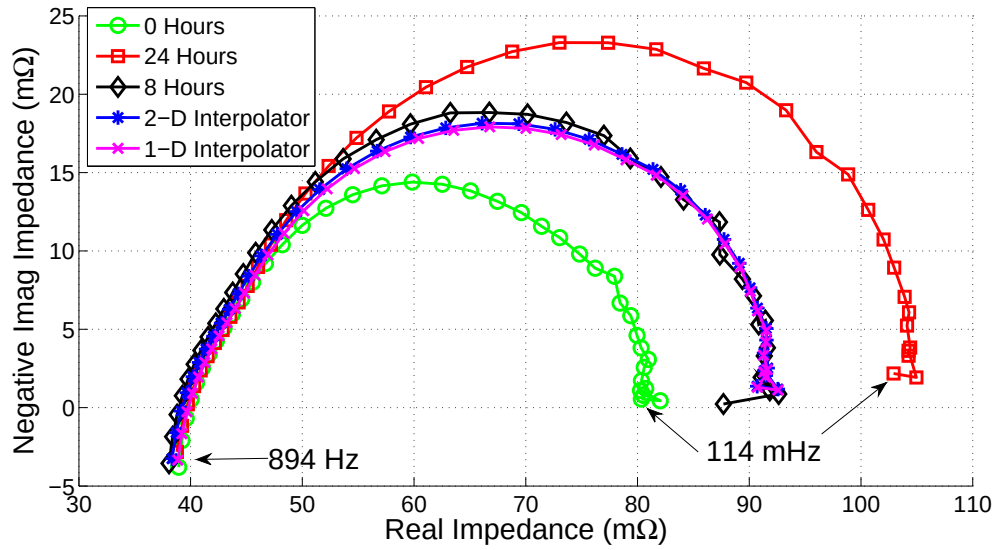


Figure B.2: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 8 hours of degradation.

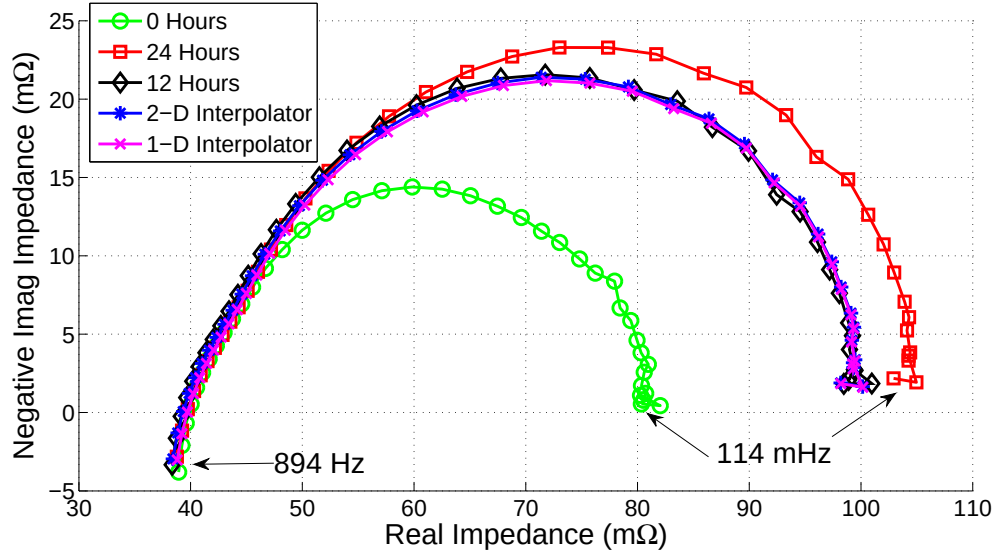


Figure B.3: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 12 hours of degradation.

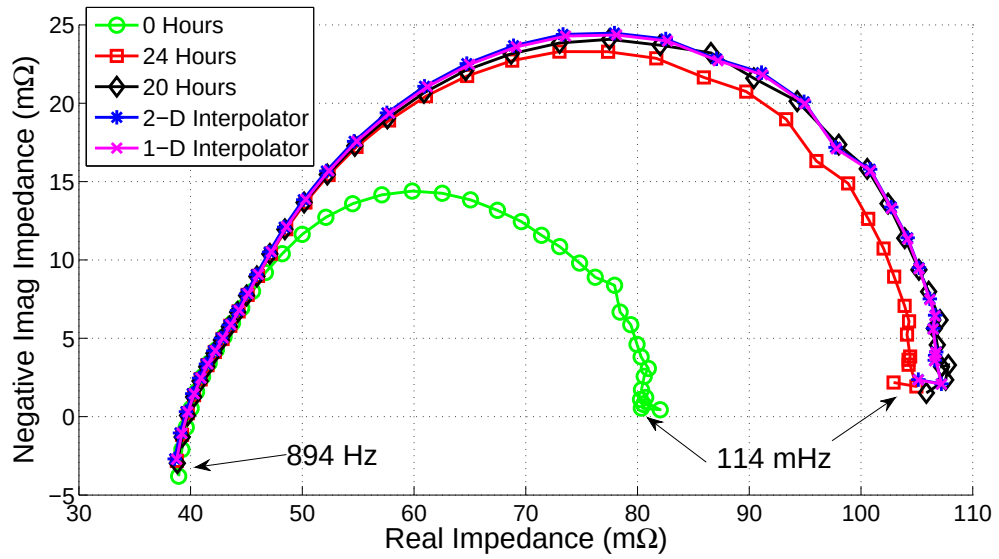


Figure B.4: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 20 hours of degradation.

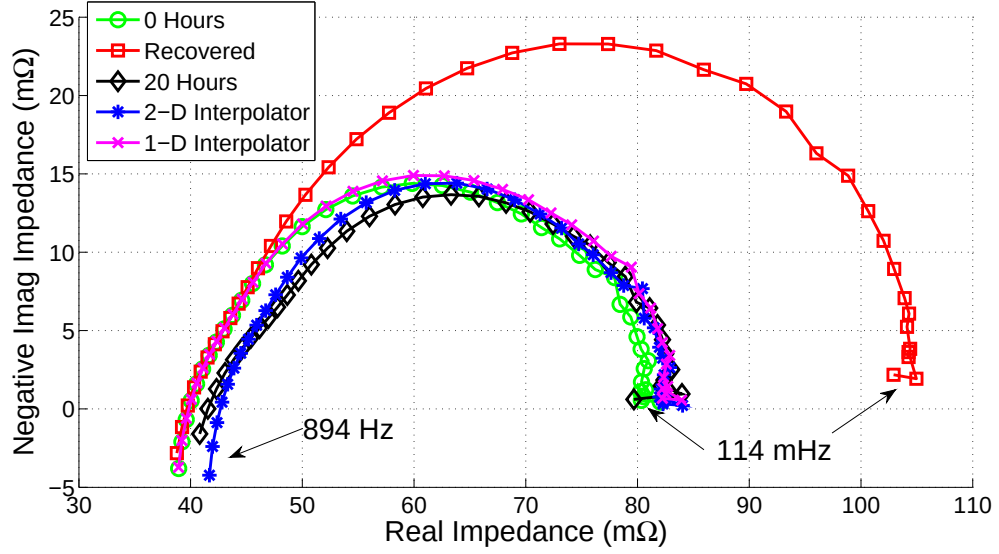


Figure B.5: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 24 hours of degradation followed by 40 hours of recovery.

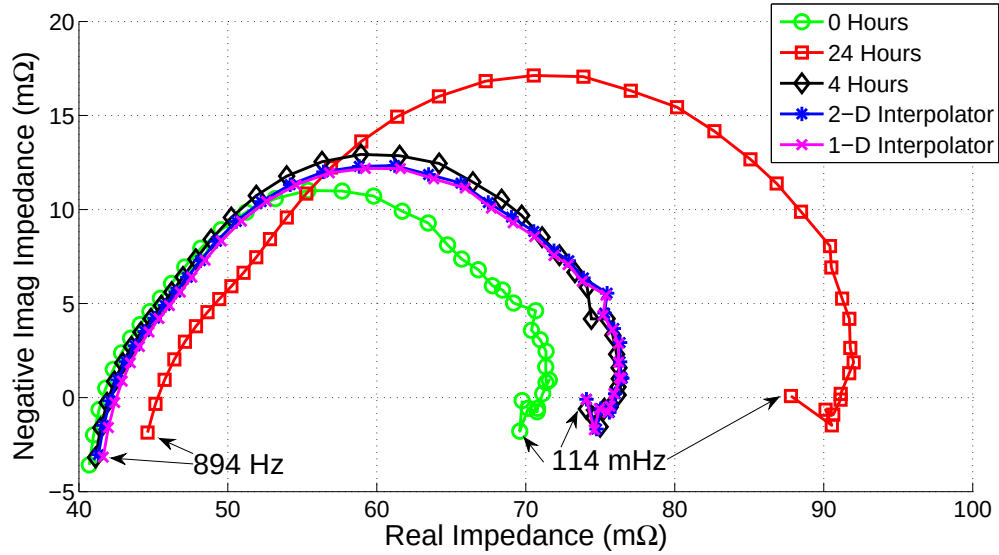


Figure B.6: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 4 hours of degradation.

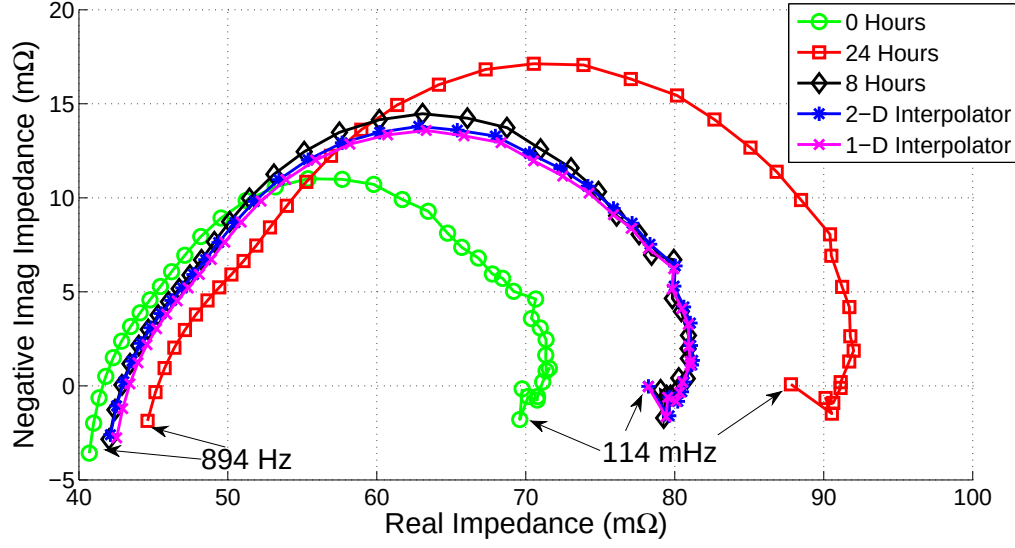


Figure B.7: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 8 hours of degradation.

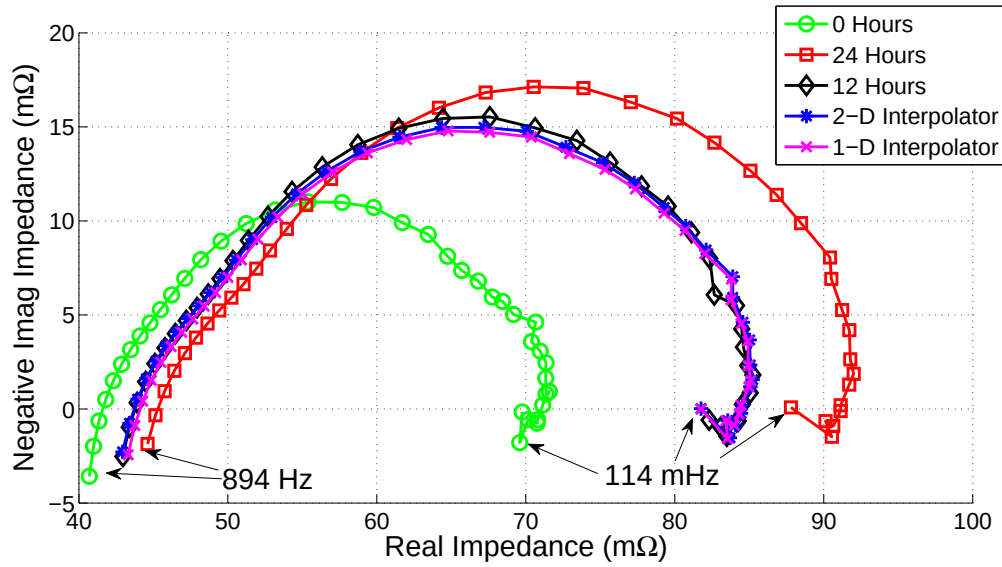


Figure B.8: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 12 hours of degradation.

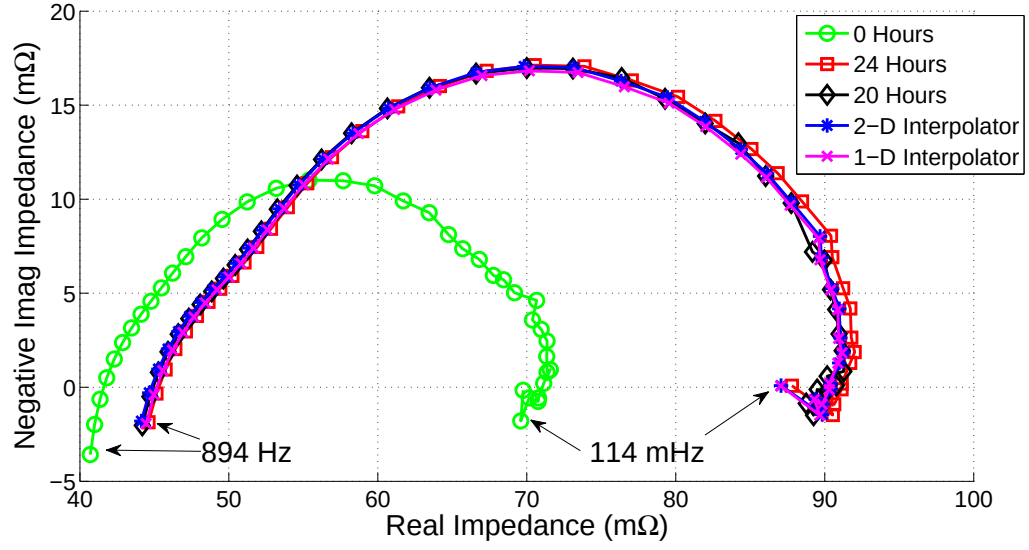


Figure B.9: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 20 hours of degradation.

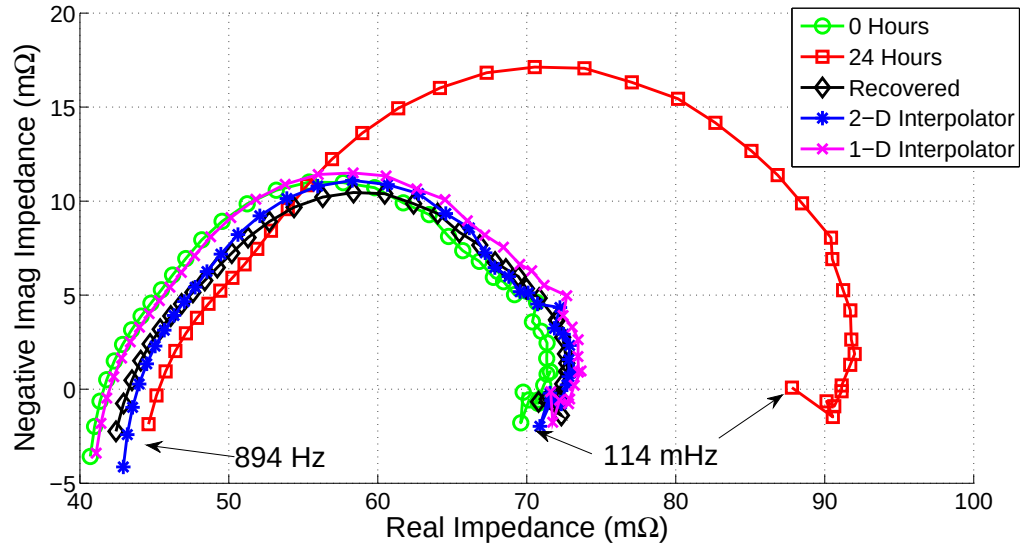


Figure B.10: Comparison of the 1-D and 2-D linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 24 hours of degradation followed by 40 hours of recovery.

APPENDIX C

SINGLE FREQUENCY-BASED LINEAR INTERPOLATIONS OF
DEGRADATION AND RECOVERY TESTING EIS PROFILES

In Chapter 6 the application of the linear interpolation analysis method to electrochemical impedance spectroscopy (EIS) measurements was used to show that EIS measurements progressed in a predominantly linear manor as the cell degraded due to current loading. Additionally, it was also shown that at certain frequencies, single impedance measurements provided good measures of the progression in the entire impedance profile. Figures 6.18 - 6.22 gave examples of the quality of the single-frequency predictions using the two-dimensional, one-dimension and magnitude-based impedance interpolation models to match measured impedance profiles at the DC operating point of $V_{DC} = 430$ mV. his appendix contains the corresponding comparisons at the other two DC operating points of measurement, $V_{DC} = 670$ mV and $V_{DC} = 200$ mV. Values for parameters and the normalized sum of squared errors for each prediction at all three operating points are given in Table 6.2.

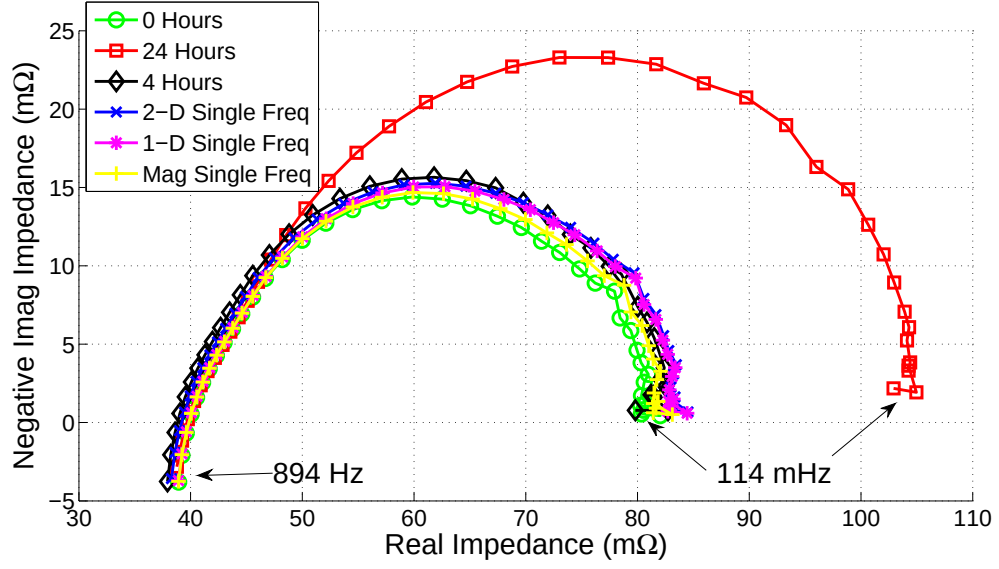


Figure C.1: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 4 hours of degradation.

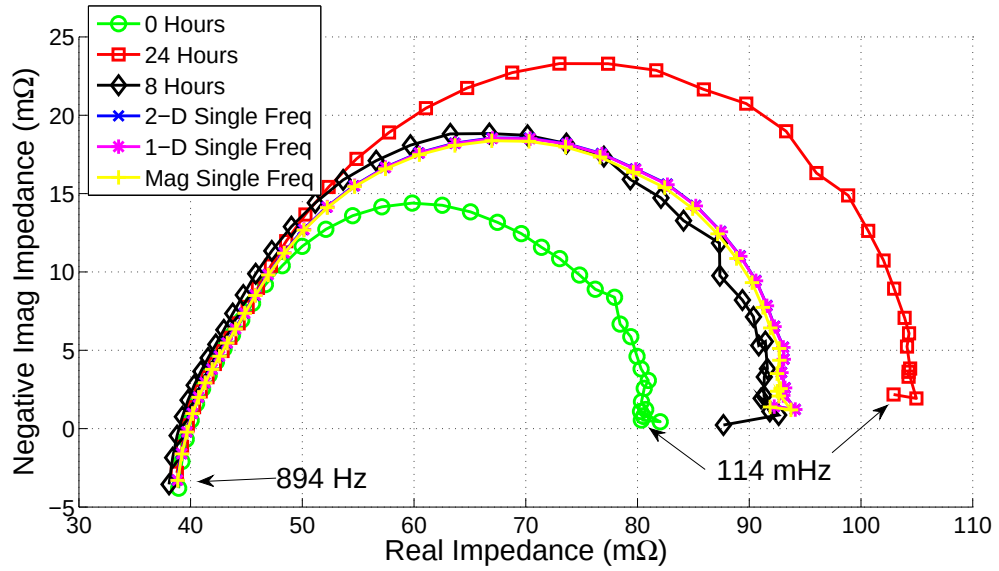


Figure C.2: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 8 hours of degradation.

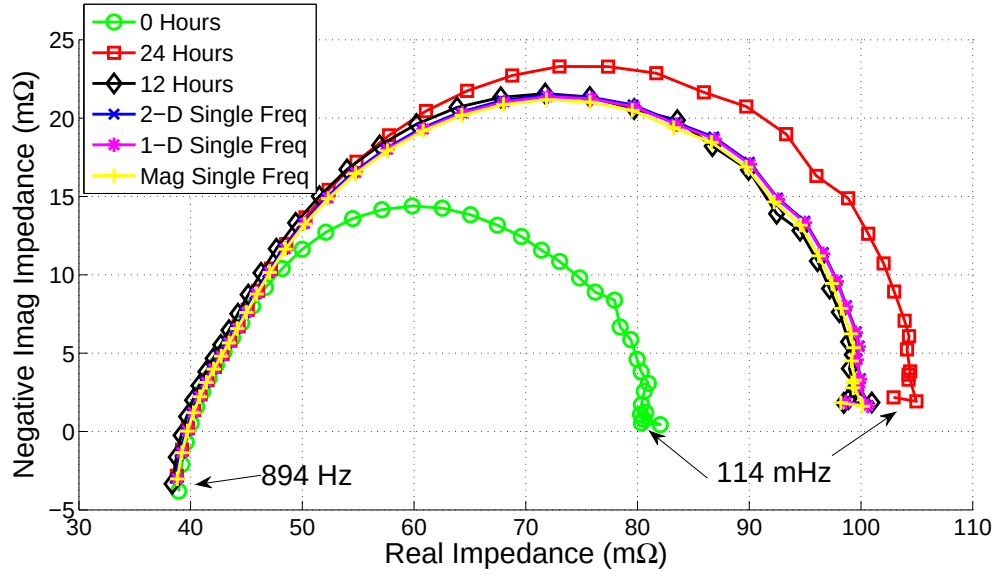


Figure C.3: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 12 hours of degradation.

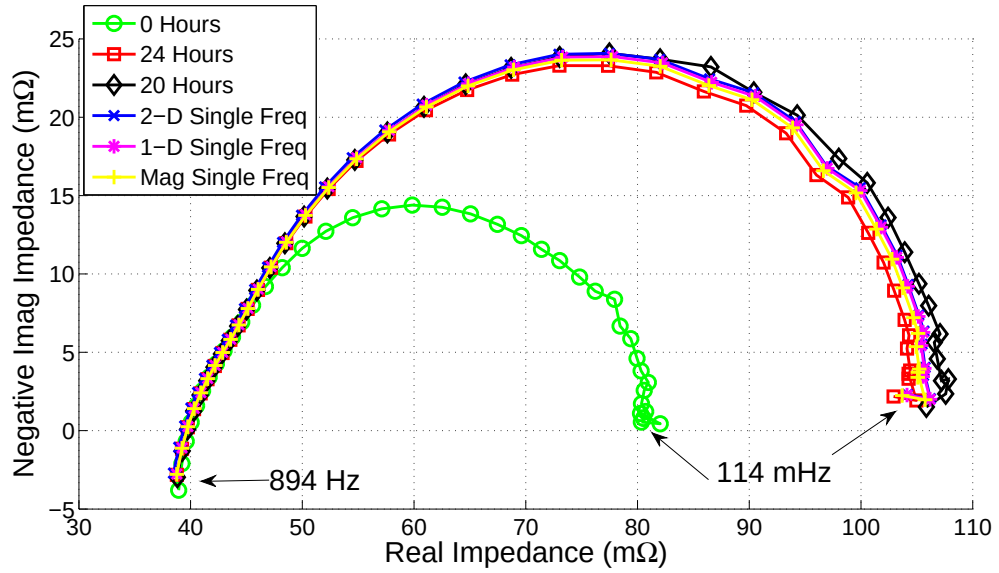


Figure C.4: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 20 hours of degradation.

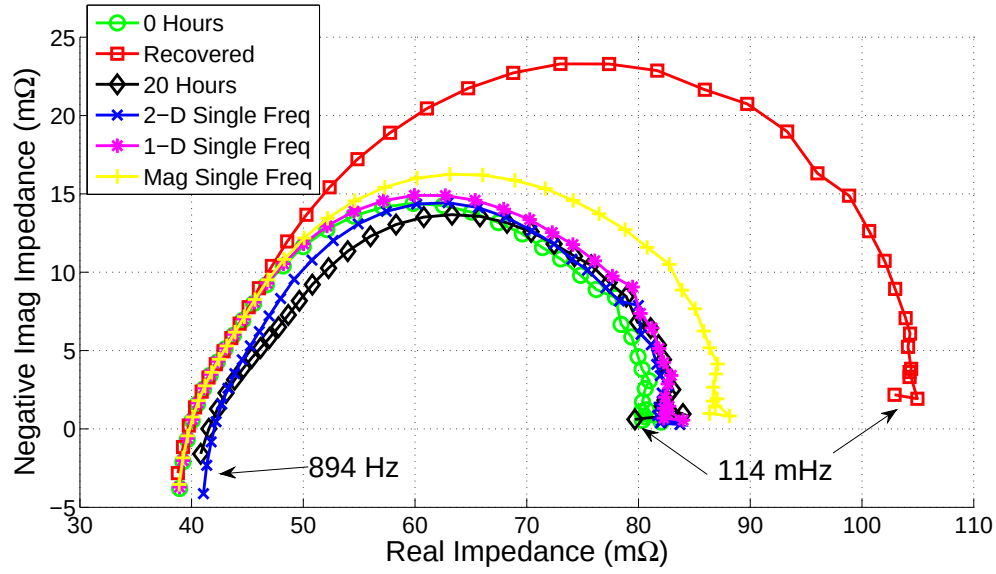


Figure C.5: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 670$ mV after 24 hours of degradation and 40 hours of recovery.

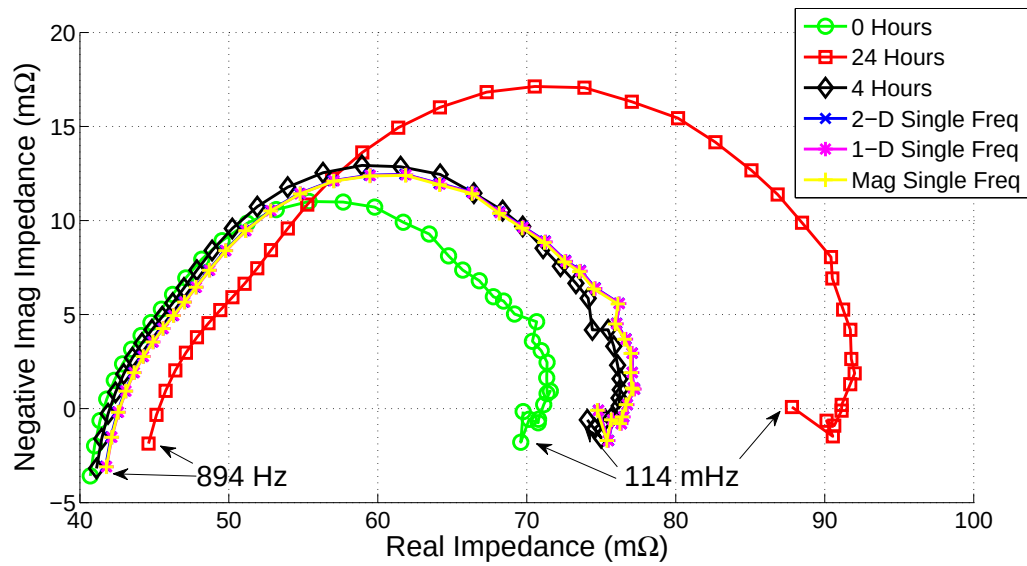


Figure C.6: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 4 hours of degradation.

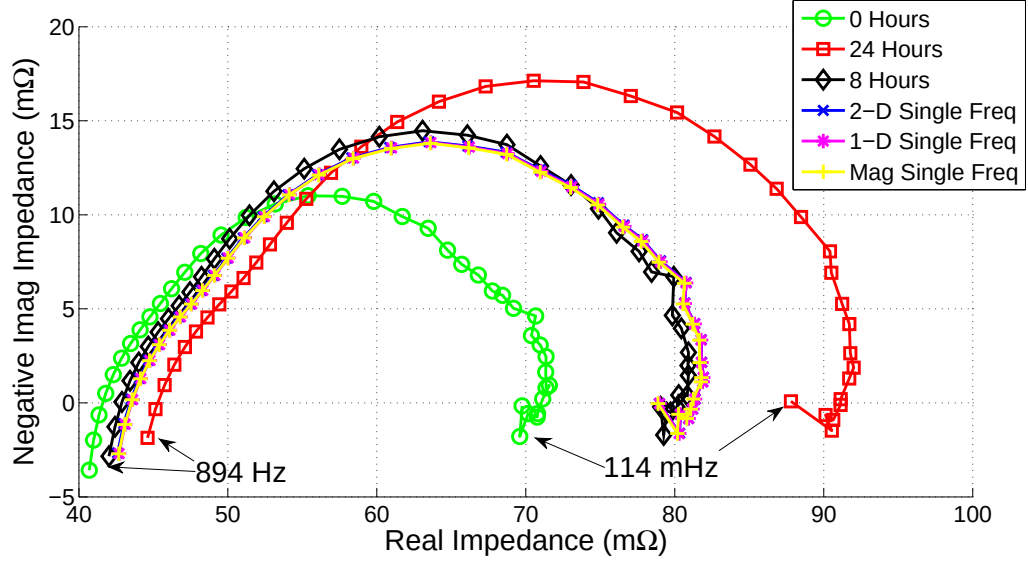


Figure C.7: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 8 hours of degradation.

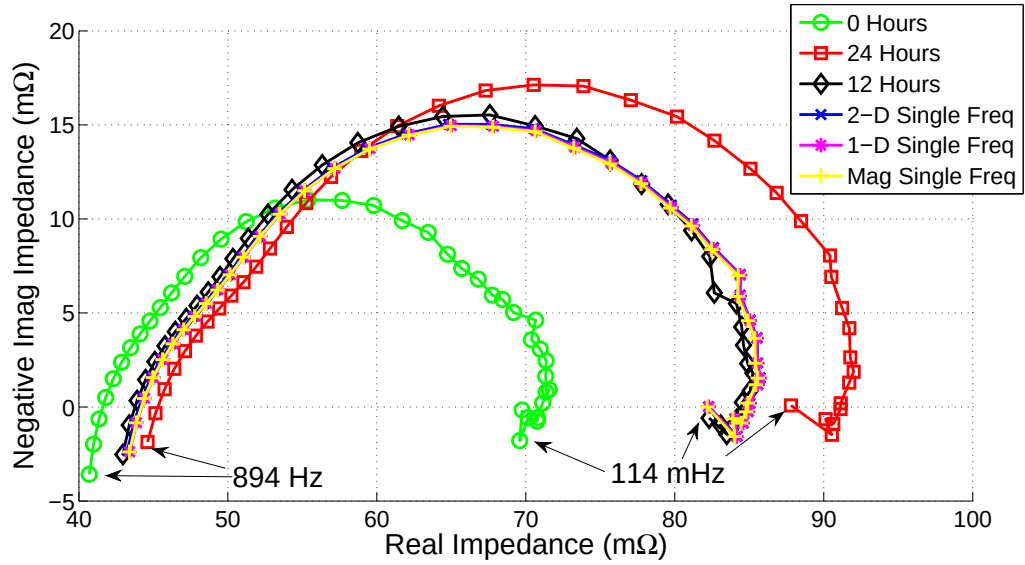


Figure C.8: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 12 hours of degradation.

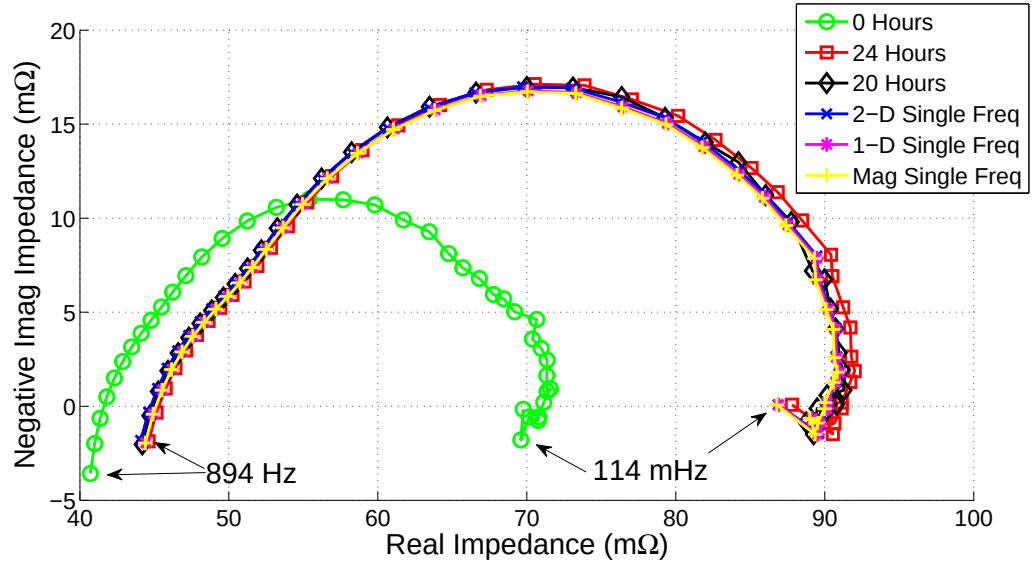


Figure C.9: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 20 hours of degradation.

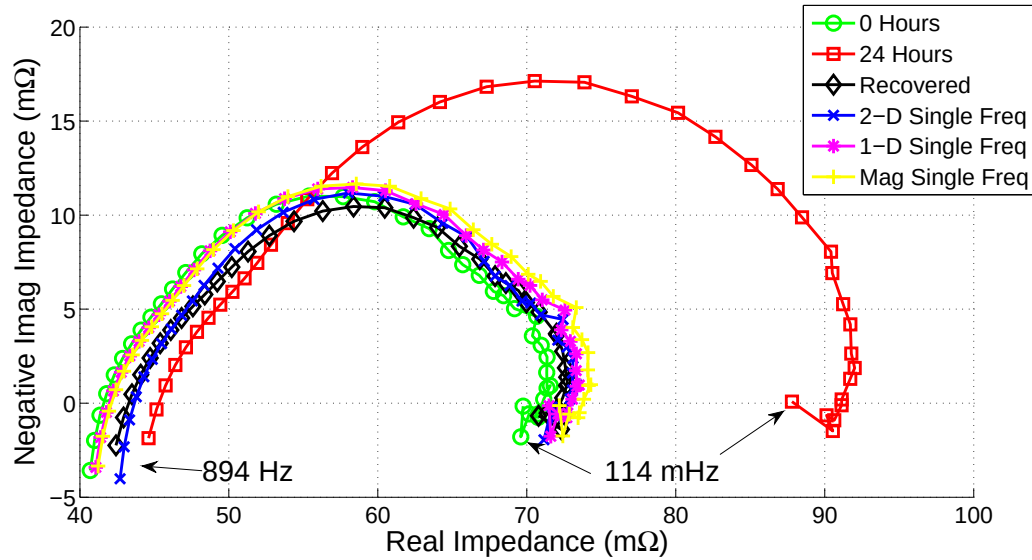


Figure C.10: Comparison of the 2-D, 1-D and magnitude-based linear interpolator predictions to the measured impedance at $V_{DC} = 200$ mV after 24 hours of degradation and 40 hours of recovery.

APPENDIX D

LINEAR INTERPOLATIONS OF PWM CONTROL EIS PROFILES

In Chapter 7 the one-dimensional linear interpolation analysis method and the single-frequency impedance magnitude based interpolation analysis method are applied to the electrochemical impedance spectroscopy (EIS) measurements taken during the PWM Control testing. Figure 7.10 is given as a representative example of the predicted $I_{EIS} = 6\text{A}$ impedance profiles for these methods. In this appendix, the remaining interpolation predictions are compared to the measured data at all other time instances of EIS measurement performed during the test. Best-fit parameter values and the normalized sum of squared errors for each prediction are given in Table 7.3.

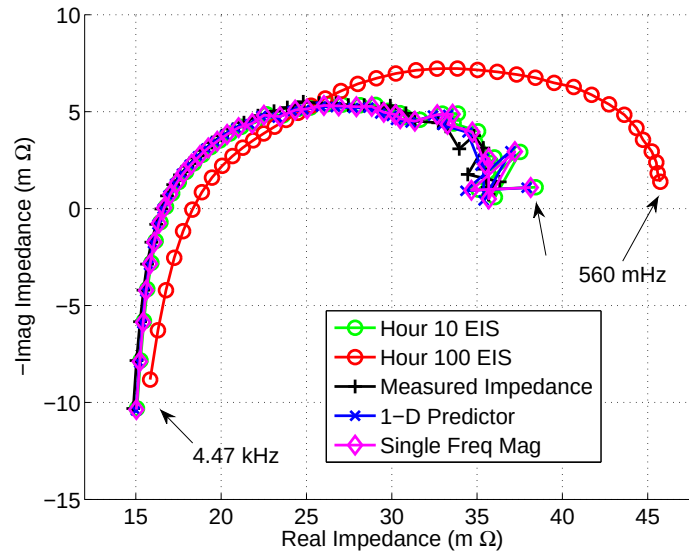


Figure D.1: Comparison of the one-dimensional full profile linear interpolation and the magnitude-based single frequency impedance interpolation of the EIS profile measured after 20 hours of PWM control testing. Impedance measurement taken at a DC current of 6 A.

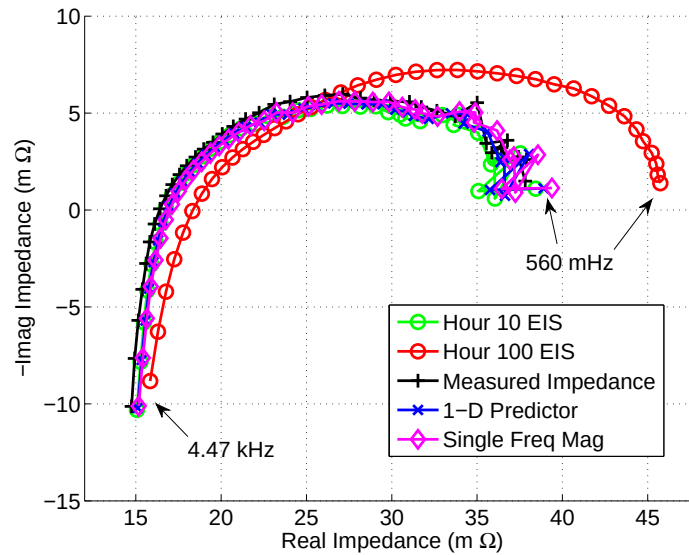


Figure D.2: Comparison of the one-dimensional full profile linear interpolation and the magnitude-based single frequency impedance interpolation of the EIS profile measured after 30 hours of PWM control testing. Impedance measurement taken at a DC current of 6 A.

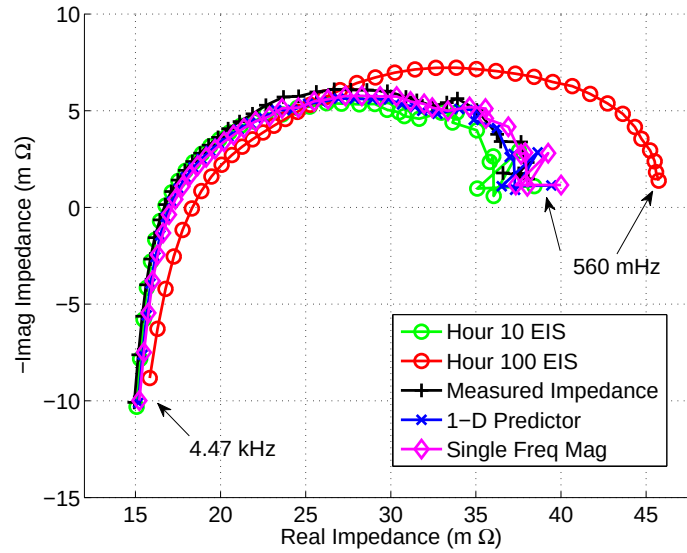


Figure D.3: Comparison of the one-dimensional full profile linear interpolation and the magnitude-based single frequency impedance interpolation of the EIS profile measured after 40 hours of PWM control testing. Impedance measurement taken at a DC current of 6 A.

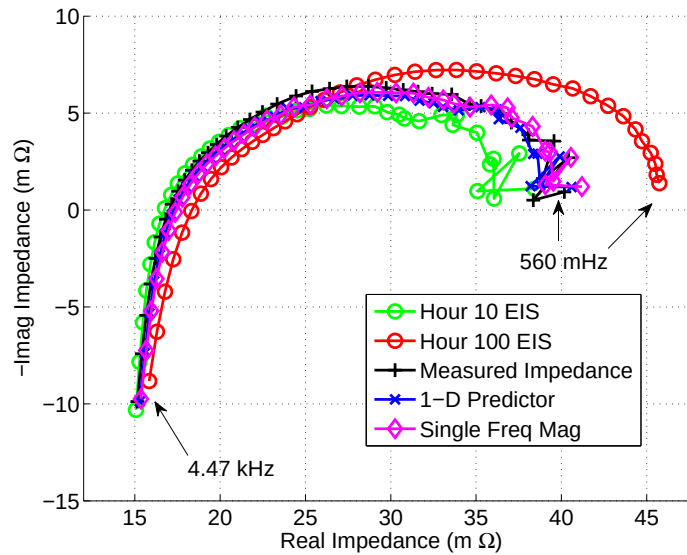


Figure D.4: Comparison of the one-dimensional full profile linear interpolation and the magnitude-based single frequency impedance interpolation of the EIS profile measured after 50 hours of PWM control testing. Impedance measurement taken at a DC current of 6 A.

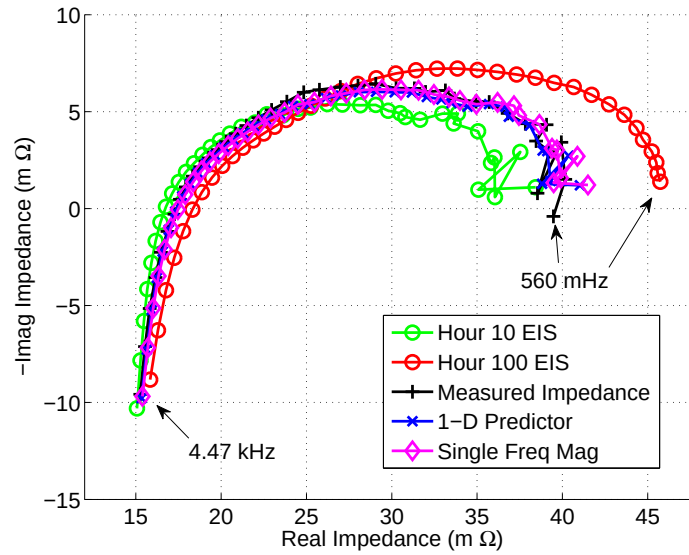


Figure D.5: Comparison of the one-dimensional full profile linear interpolation and the magnitude-based single frequency impedance interpolation of the EIS profile measured after 60 hours of PWM control testing. Impedance measurement taken at a DC current of 6 A.

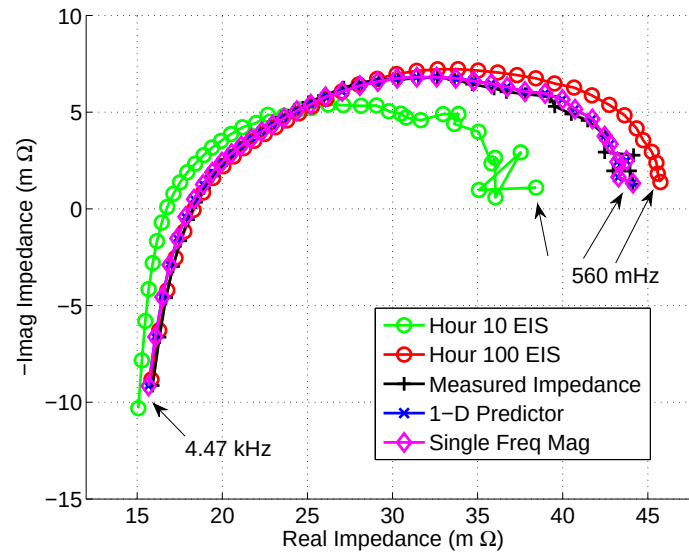


Figure D.6: Comparison of the one-dimensional full profile linear interpolation and the magnitude-based single frequency impedance interpolation of the EIS profile measured after 80 hours of PWM control testing. Impedance measurement taken at a DC current of 6 A.

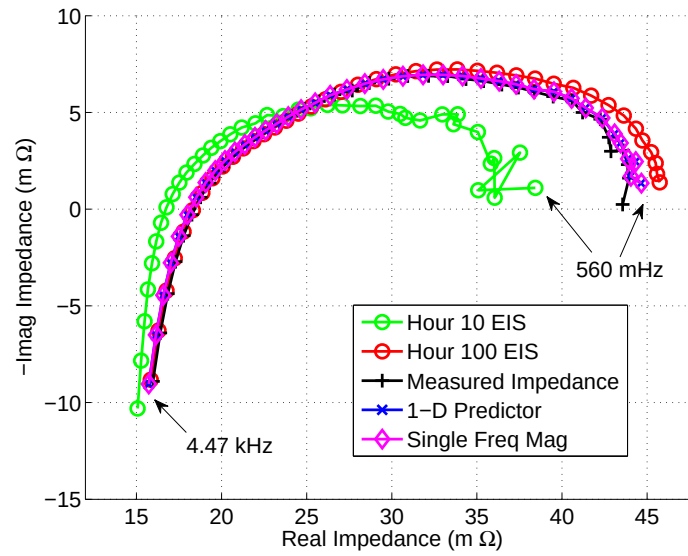
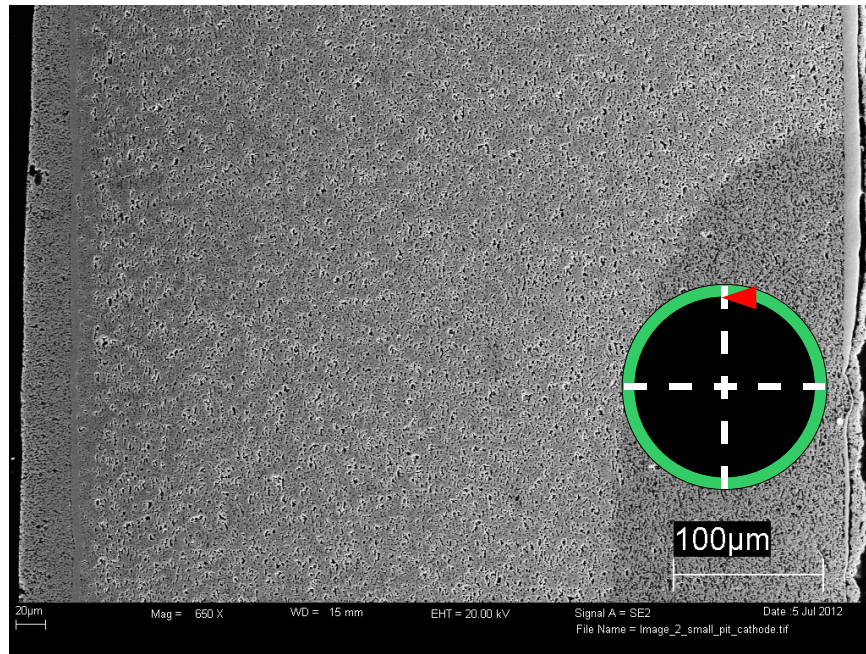


Figure D.7: Comparison of the one-dimensional full profile linear interpolation and the magnitude-based single frequency impedance interpolation of the EIS profile measured after 90 hours of PWM control testing. Impedance measurement taken at a DC current of 6 A.

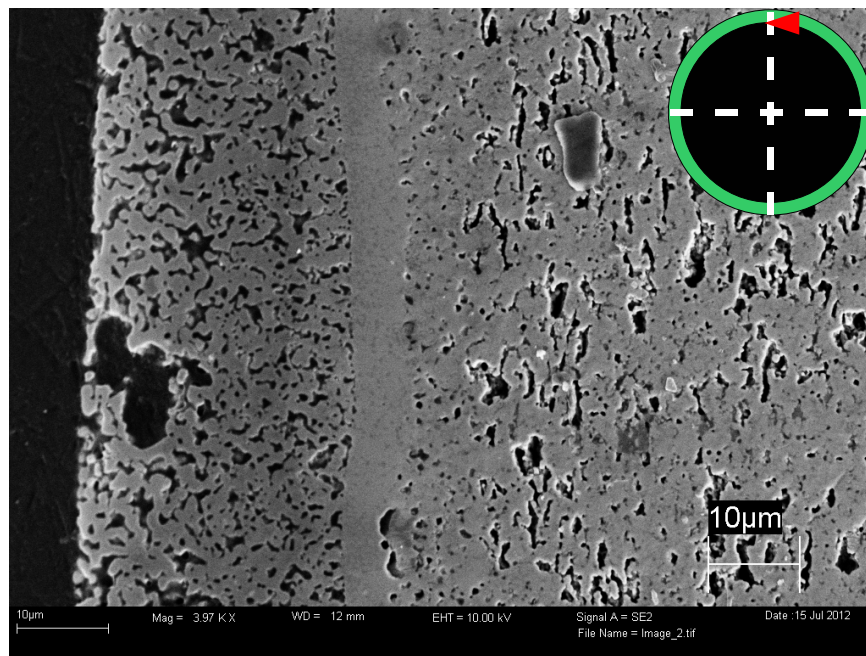
APPENDIX E

SEM IMAGES FROM PWM CONTROL TEST

In Chapter 7, Figures 7.11 and 7.12 give SEM images of the two most prominent forms of defects observed in the post-test analysis of the SOFC used in the PWM control experiment. Figure 7.11 shows an image well representative of the many voids within the lanthanum strontium manganite (LSM) structure of the cathode, while Figure 7.12 shows representative images of cracking observed in the cathode between the LSM layer and the LSM-YSZ (yttria stabilized zirconia) layer. This appendix serves to compile further examples of these two defects. The red arrow in the SOFC diagram accompanying each SEM image indicates the quartered sample imaged and location along the break plane corresponding to the image.

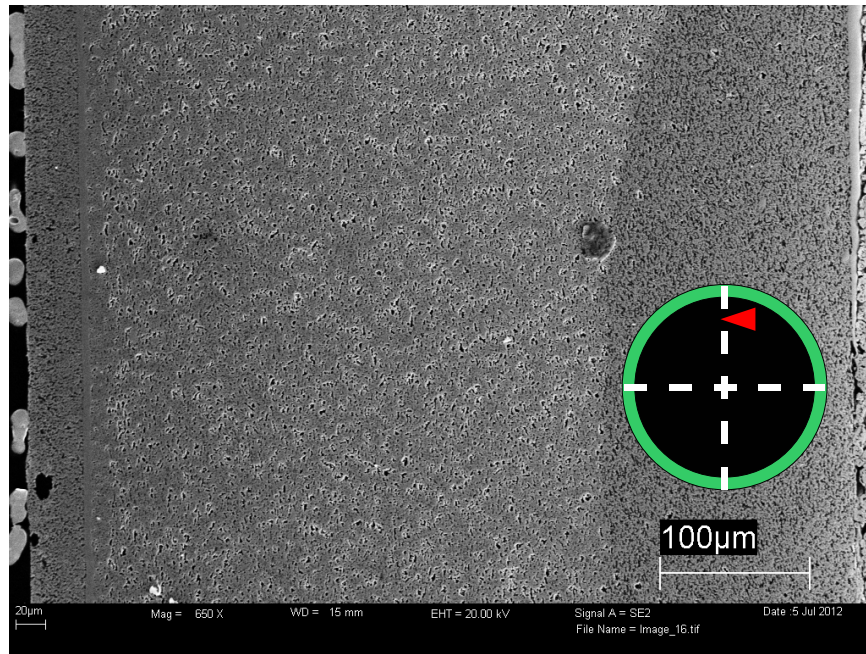


(a) Full Cross-section Image

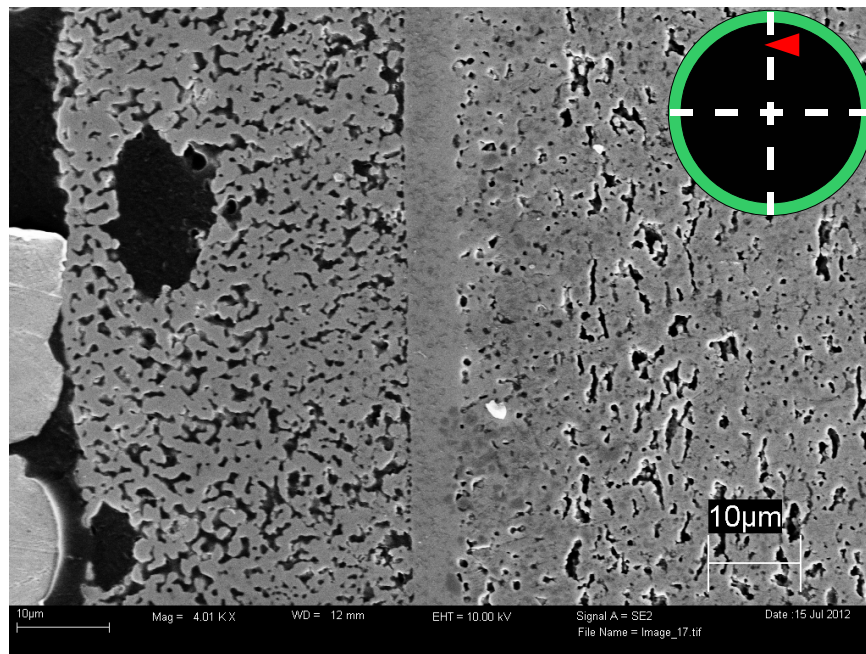


(b) Close Up

Figure E.1: Images show two voids in the cathode near the outer edge of the cell which explains the tapering of the cathode layer at the top of the image. (a) Shows a cross-sectional image that spans the entire width of the cell, while (b) shows a close-up image around the void area.

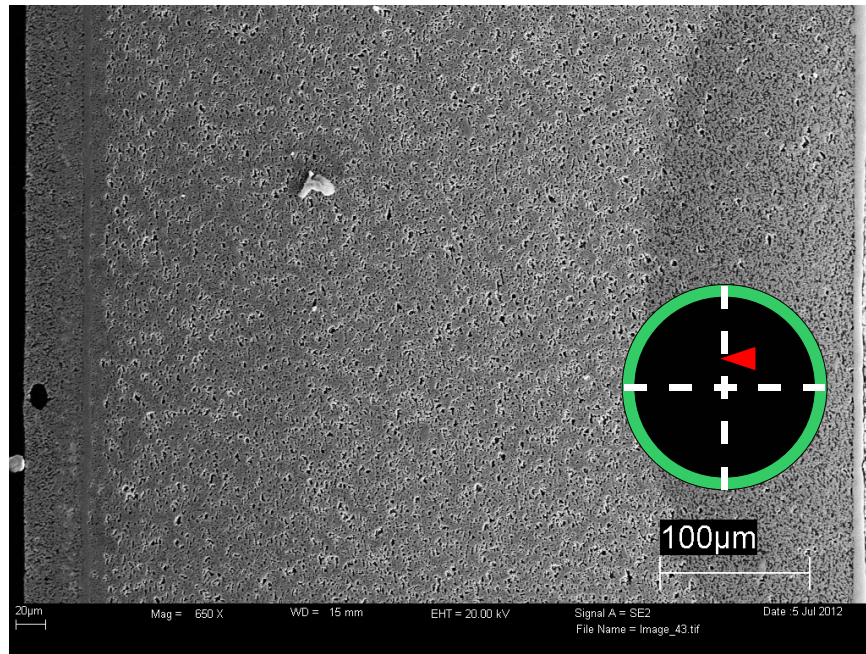


(a) Full Cross-section Image

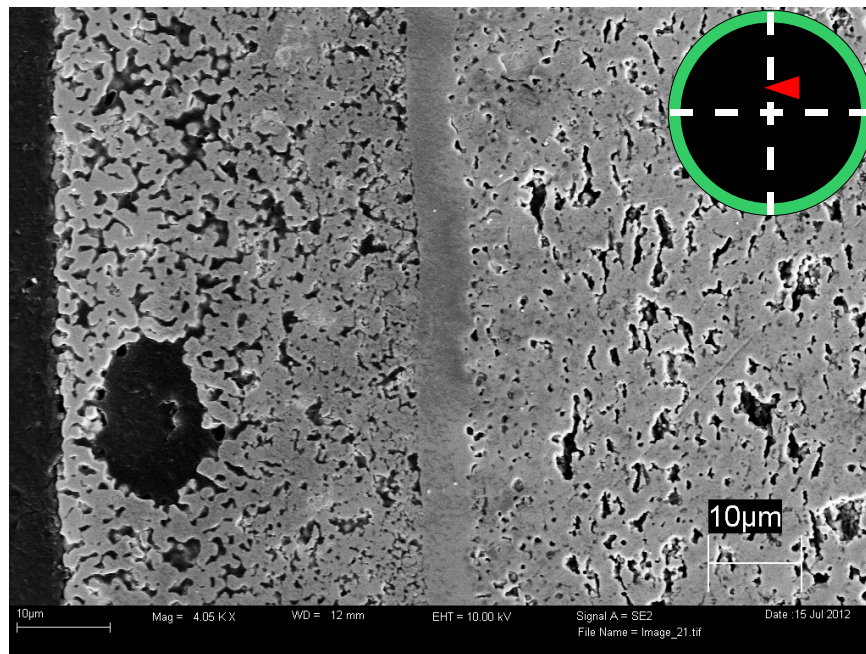


(b) Close Up

Figure E.2: Images shows a large and small void in the cathode. (a) Shows a cross-sectional image that spans the entire width of the cell, while (b) shows a close-up image around the void area.



(a) Full Cross-section Image



(b) Close Up

Figure E.3: Images show a large void in the cathode. (a) Shows a cross-sectional image that spans the entire width of the cell, while (b) shows a close-up image around the void area.

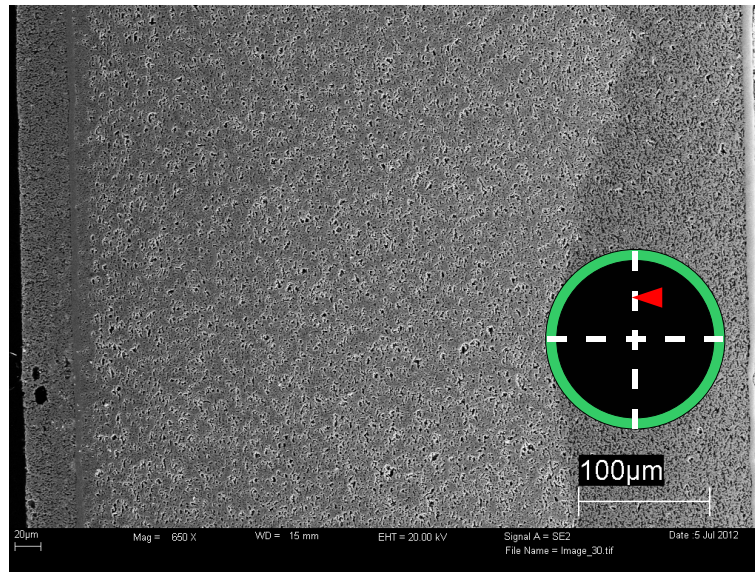


Figure E.4: Sample image showing two large voids in the cathode. No close-up image of these voids were taken.

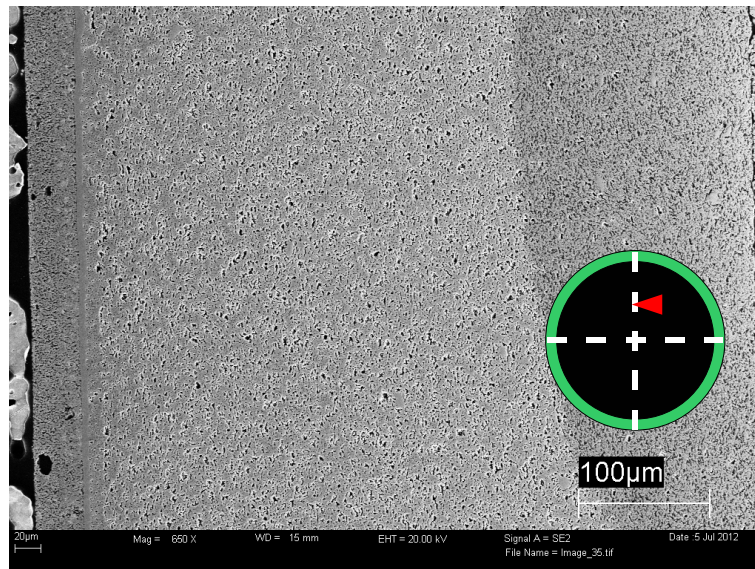


Figure E.5: Sample image showing a large void in the cathode. No close-up image of this void was taken.

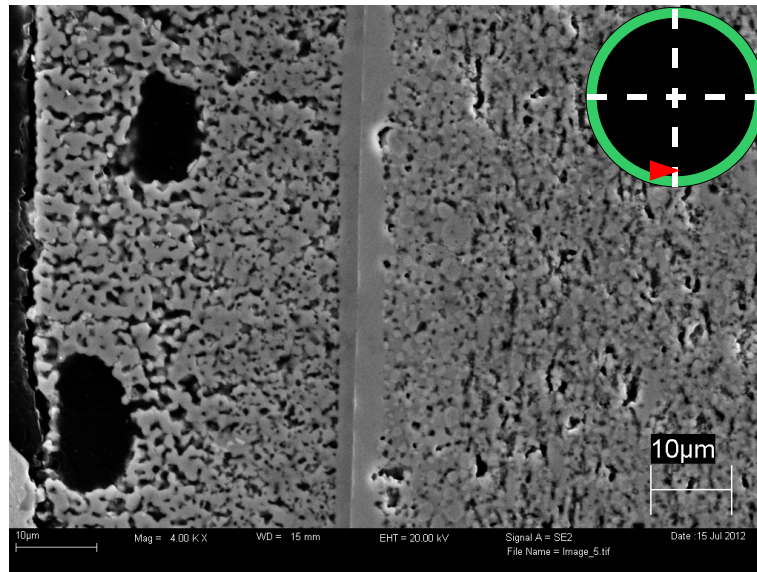


Figure E.6: Sample image showing two large voids in the cathode. No full-width image of these voids were taken.

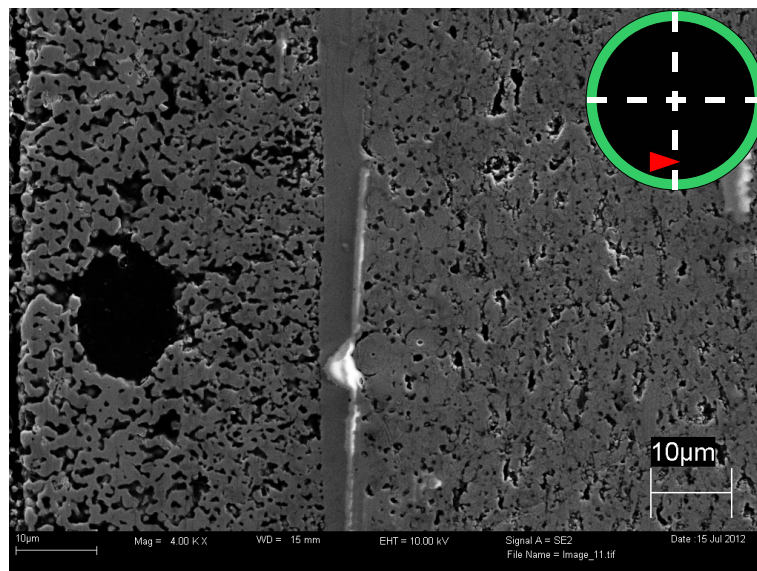


Figure E.7: Sample image showing a large void in the cathode. No full-width image of this void was taken.

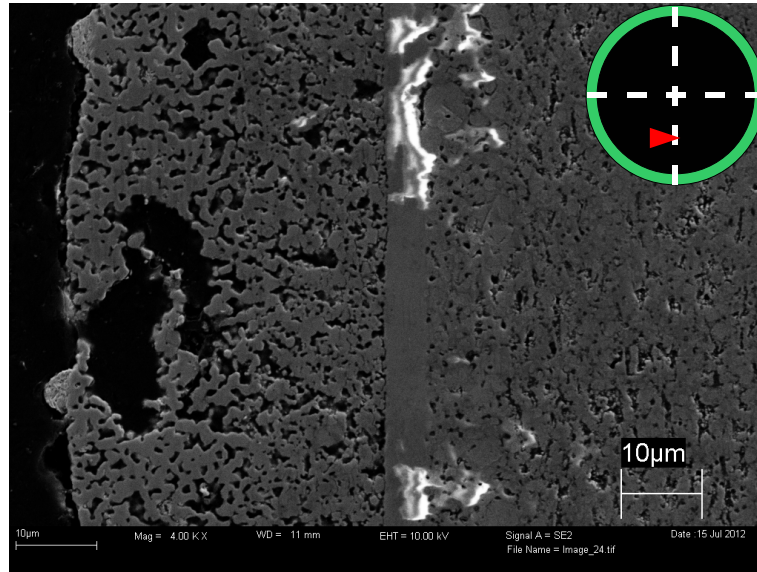


Figure E.8: Sample image showing a void in the cathode that breaks the outer edge of the cathode. No full-width image of this void was taken.

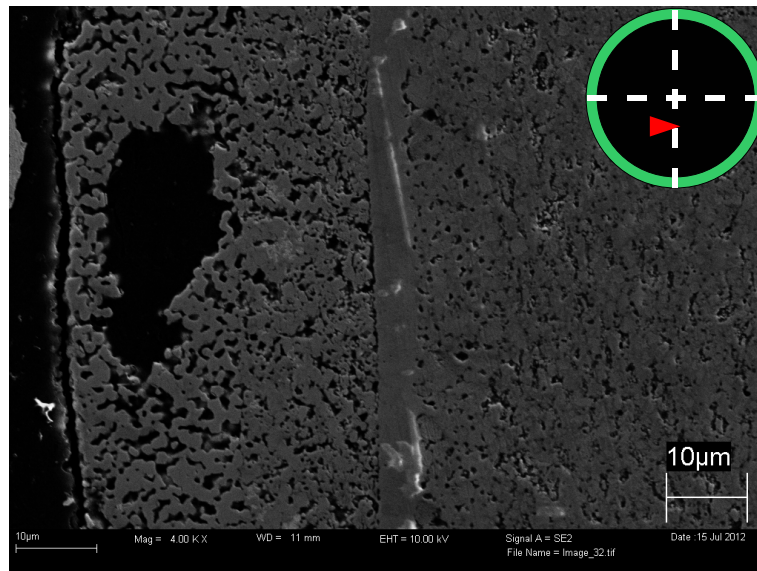
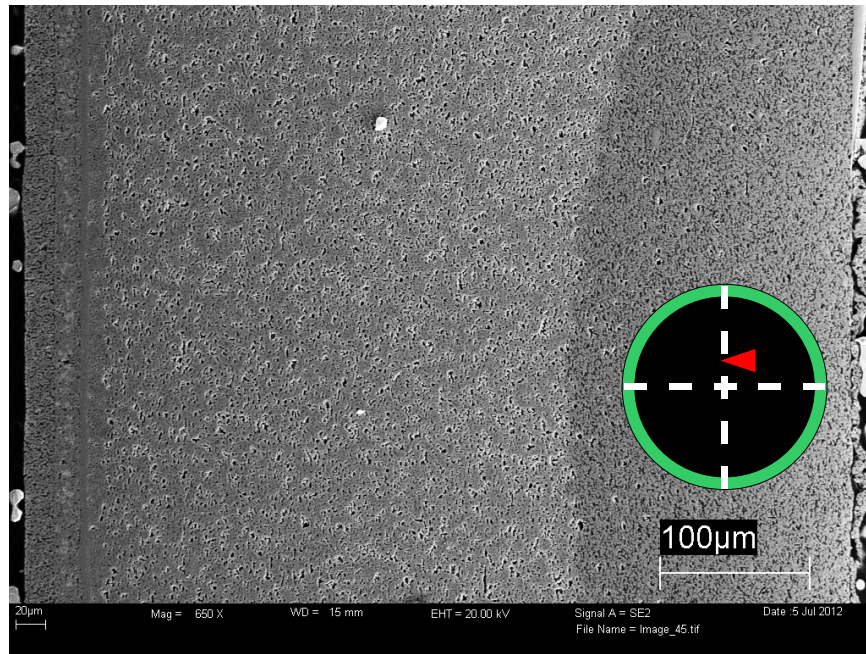
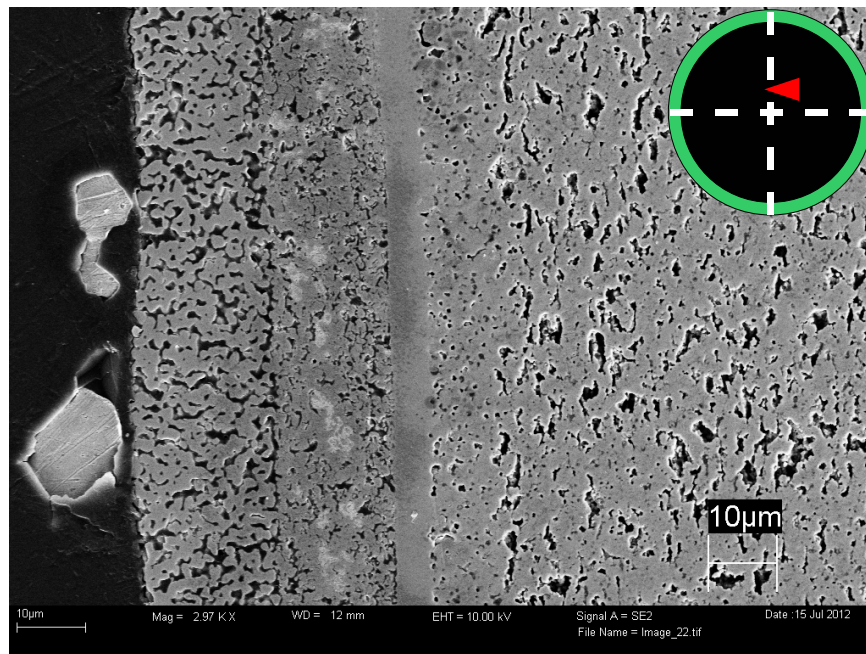


Figure E.9: Sample image showing a very large void in the cathode. No full-width image of this void was taken.

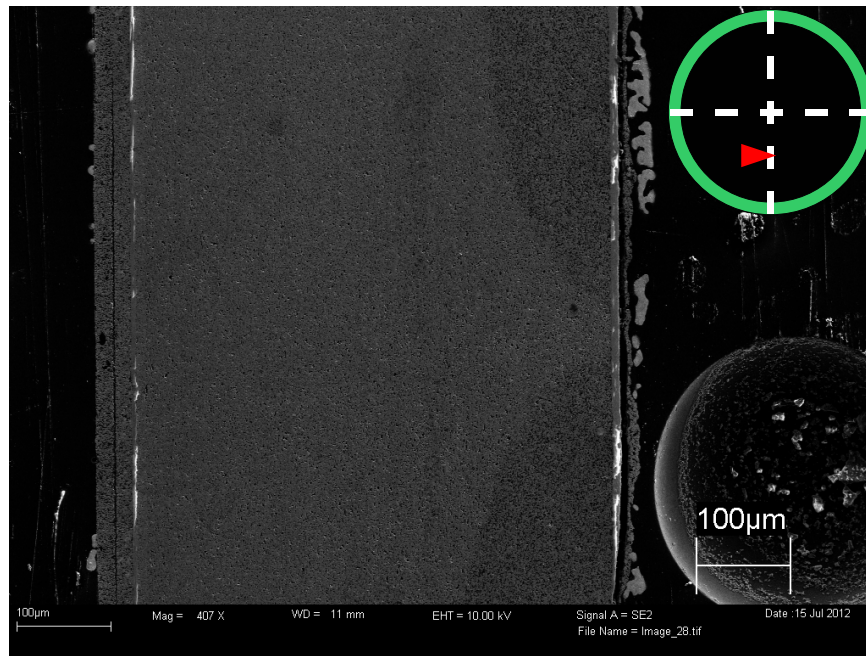


(a) Full Cross-section Image

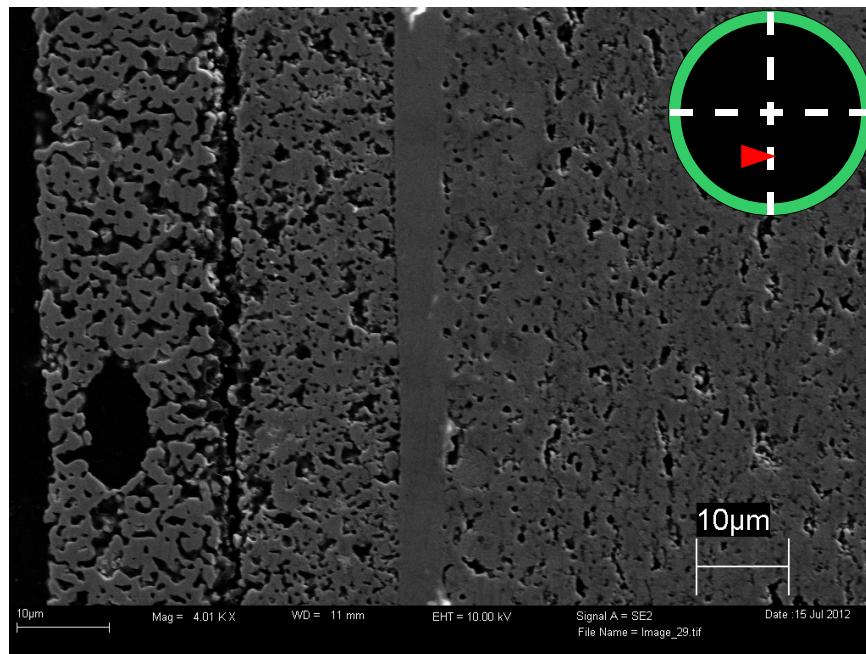


(b) Close Up

Figure E.10: Images show a very thin, and only partially formed, crack in the cathode. The total length of the affected area is about $100\ \mu\text{m}$. (a) Shows a cross-sectional image including this crack that spans the entire width of the cell, while (b) shows a close-up image around the crack area.



(a) Full Cross-section Image



(b) Close Up

Figure E.11: Images show a crack in the cathode with a total length of around 500-600 μm . (a) Shows a cross-sectional image including this crack that spans the entire width of the cell, while (b) shows a close-up image around the crack area.

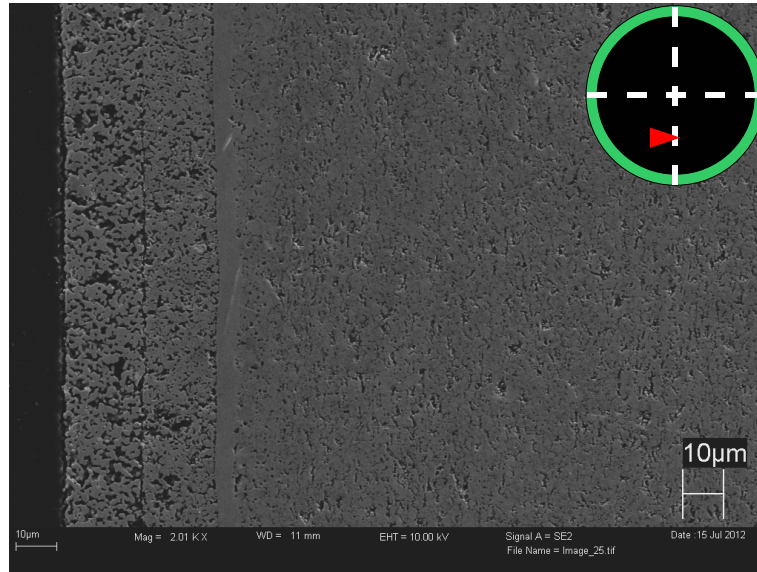


Figure E.12: Image shows a thin crack in the cathode. No full-width image of this crack was taken.

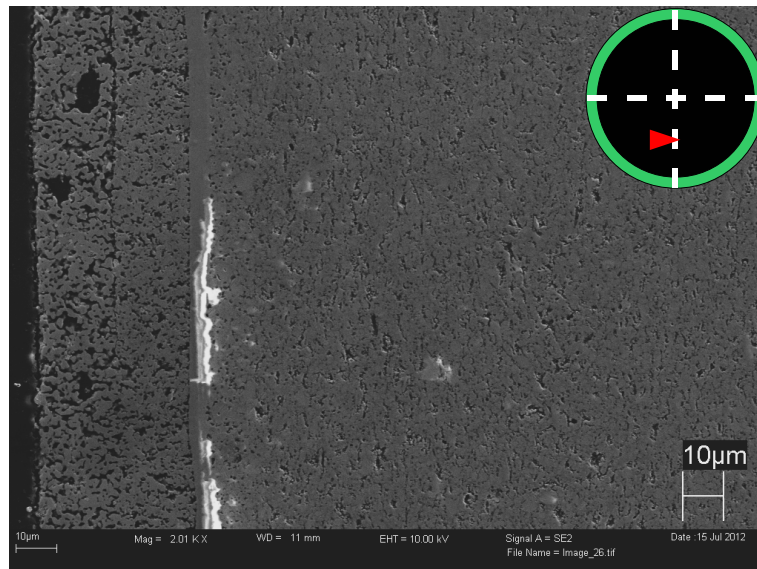


Figure E.13: Image shows the continuation of the thin crack in the cathode of Figure E.12. The total length of the crack is around 200 μm . No full-width image of this crack was taken.

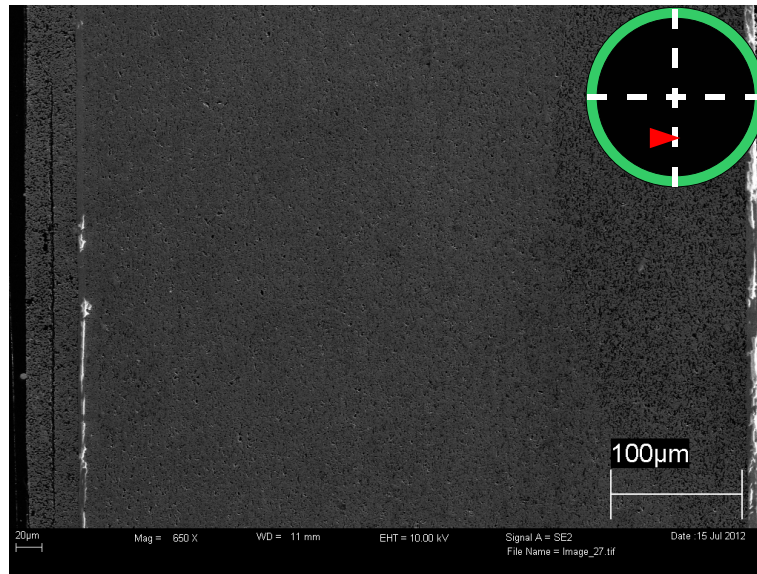


Figure E.14: Image shows a crack in the cathode with a total length of around 350 μm . No full-width image of this crack was taken.

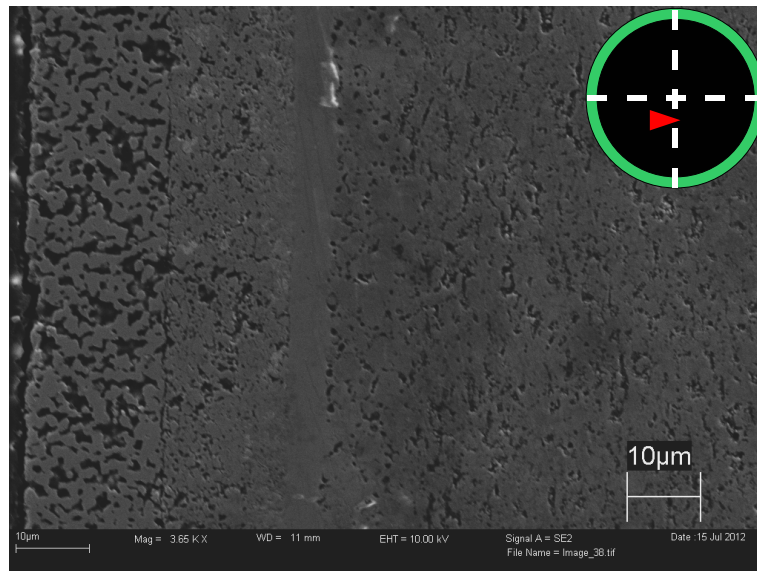


Figure E.15: Image shows a very thin crack in the cathode with a total length of around 40 μm . No full-width image of this crack was taken.

APPENDIX F

SEM IMAGES FROM CONTINUOUS CURRENT CONTROL TEST

In Chapter 8, Figures 8.24 - 8.26 give SEM images of the two most prominent forms of defects observed in the post-test analysis of the SOFC used in the continuous control experiment. Figure 8.24 shows an image well representative of the voids within the lanthanum strontium manganite (LSM) structure of the cathode, while Figures 8.25 and 8.26 show representative images of cracking observed in the cathode between the LSM layer and the LSM-YSZ (yttria stabilized zirconia) layer. This appendix serves to compile further examples of these two defects. The red arrow in the SOFC diagram accompanying each SEM image indicates the quartered sample imaged and location along the break plane corresponding to the image.

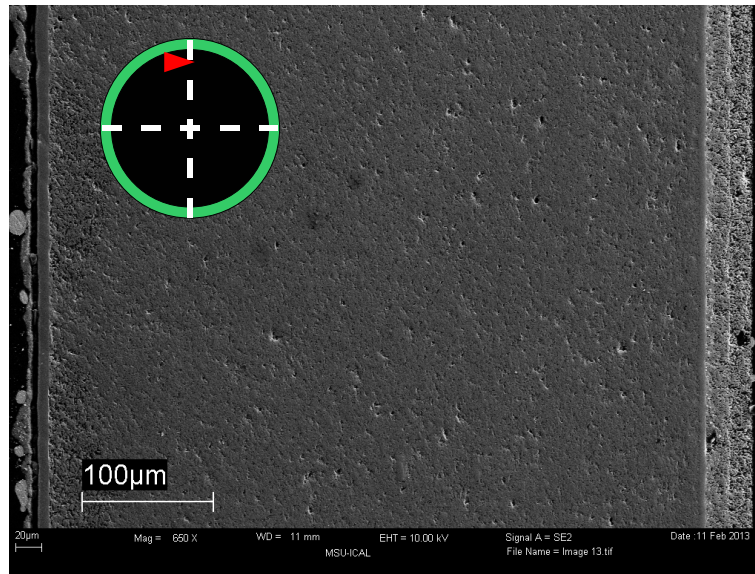


Figure F.1: Sample image showing a void in the cathode. No close-up image of this void was taken.

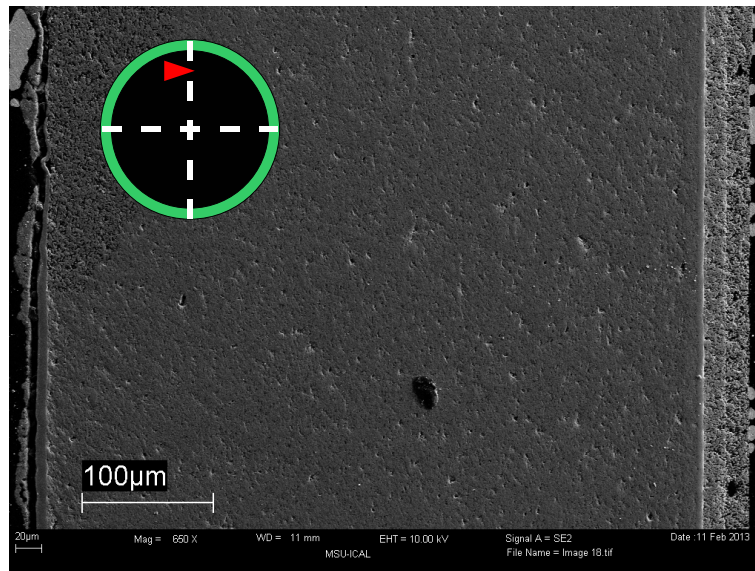


Figure F.2: Sample image showing a void in the cathode. No close-up image of this void was taken.

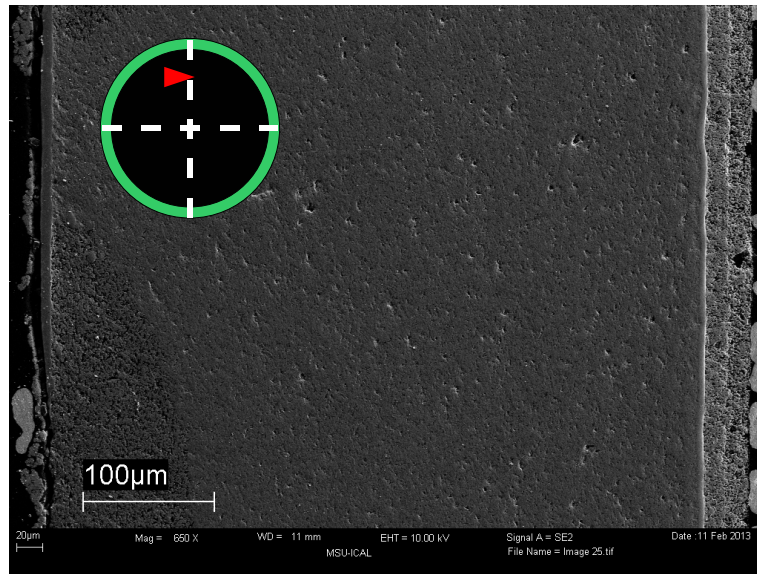


Figure F.3: Sample image showing a void in the cathode. No close-up image of this void was taken.

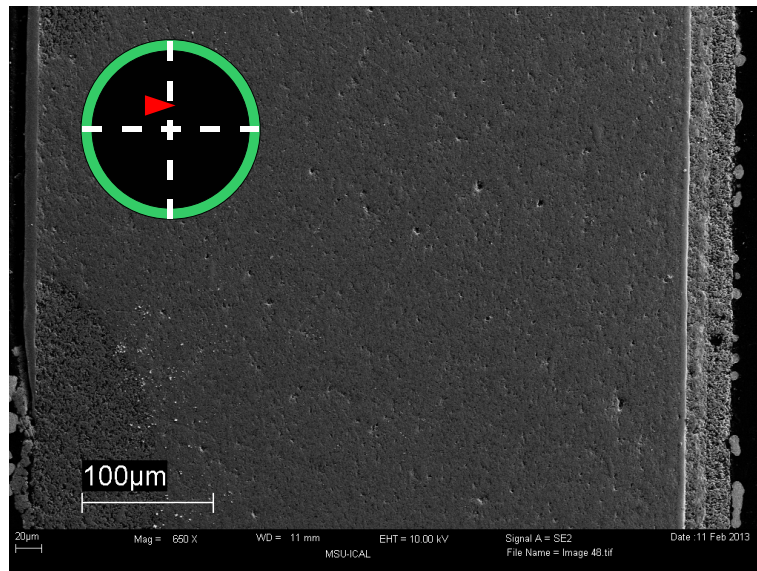
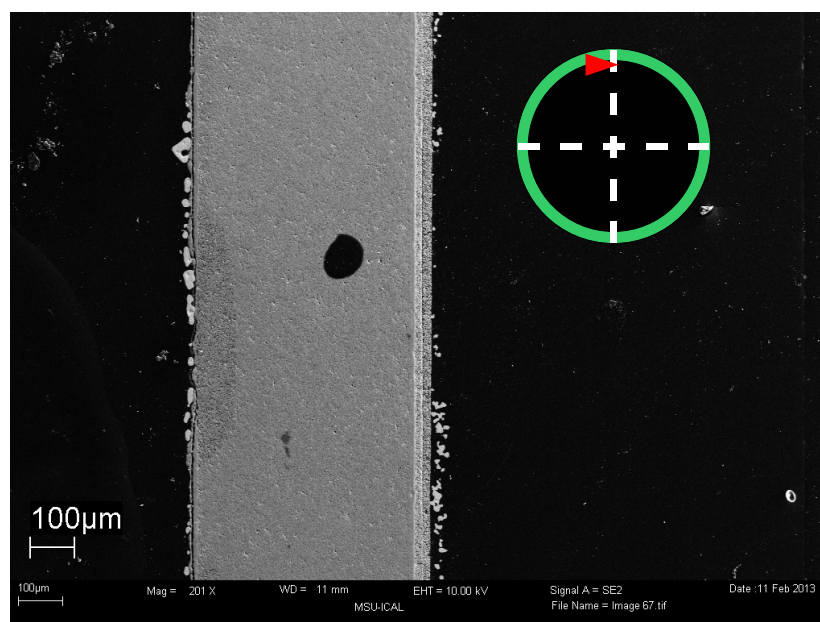
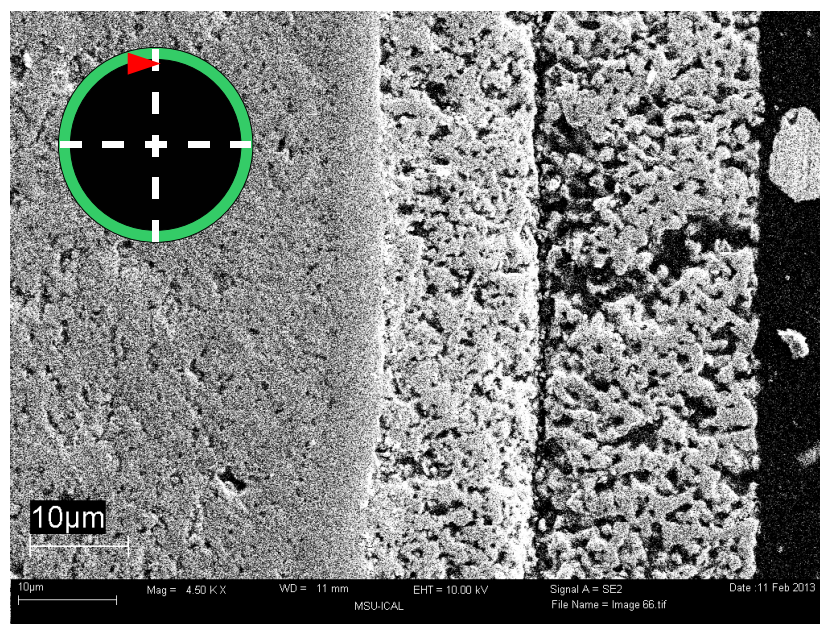


Figure F.4: Sample image showing a void in the cathode. No close-up image of this void was taken.

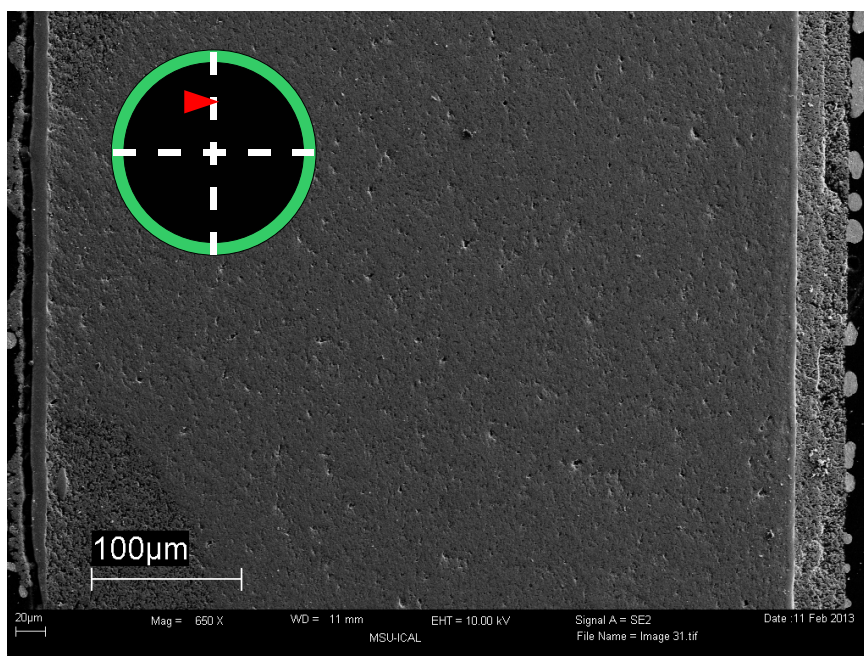


(a) Full Cross-section Image

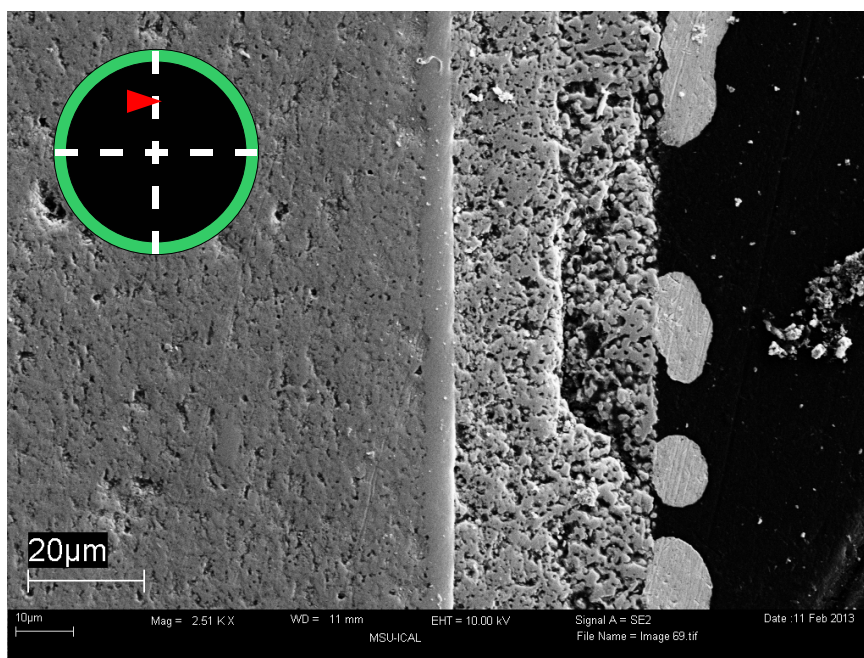


(b) Close Up

Figure F.5: Images show a thin crack in the cathode between the LSM and LSM-YSZ layers. The total length of the crack is about $700\text{ }\mu\text{m}$. (a) Shows a cross-sectional image including this crack that spans the entire width of the cell. The black mark in the anode is a misplaced drop of carbon paint applied to the sample epoxy to reduce sample charging. (b) shows a close-up image of the crack.

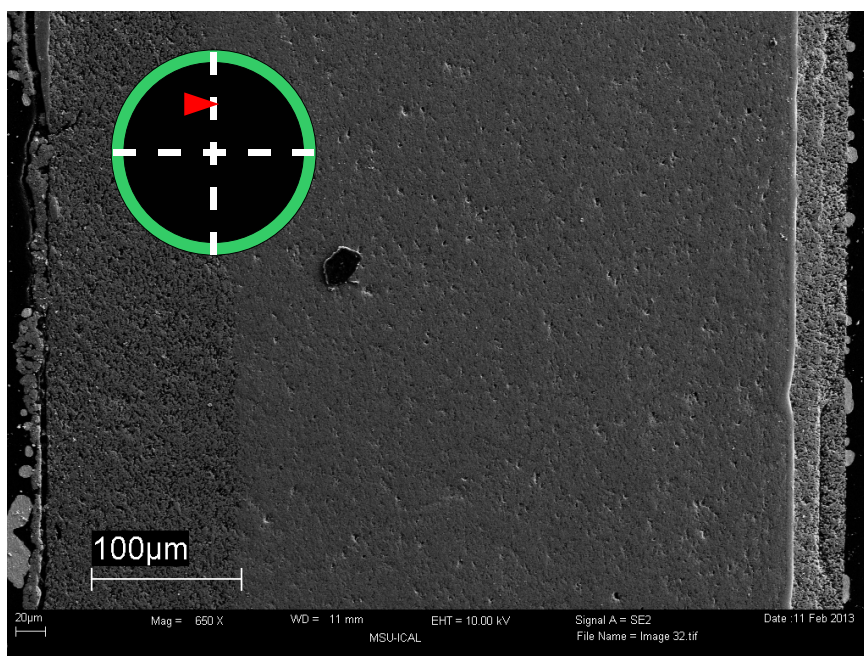


(a) Full Cross-section Image

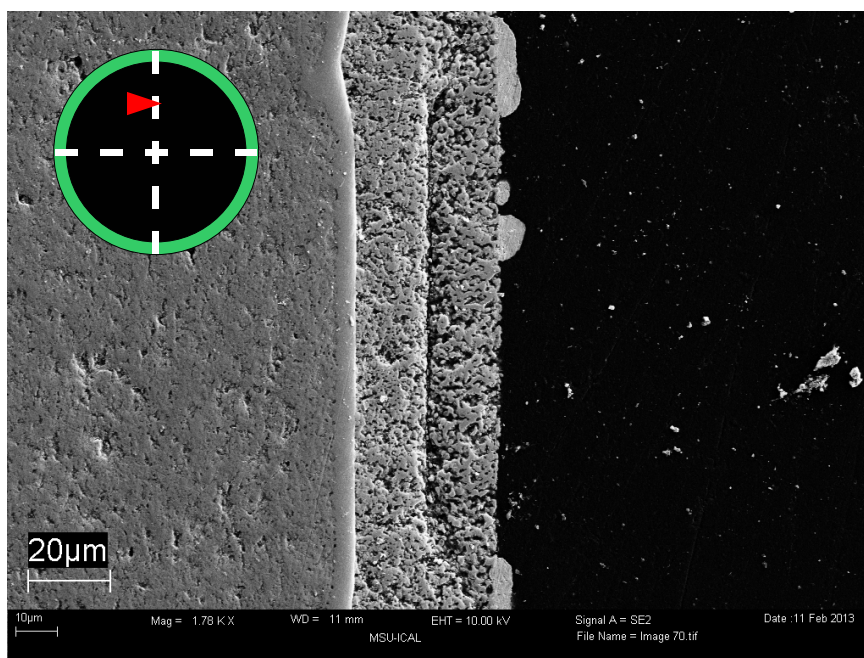


(b) Close Up

Figure F.6: Images show a short crack in the cathode that extends from the LSM / LSM-YSZ boundary to the exterior of the LSM layer. (a) Shows a cross-sectional image including this crack that spans the entire width of the cell, while (b) shows a close-up image of the crack.

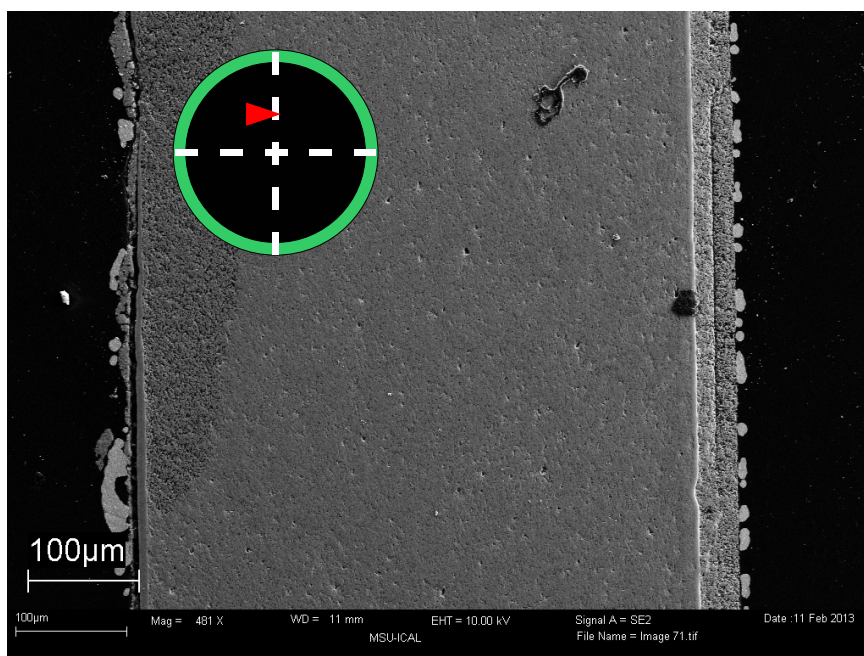


(a) Full Cross-section Image

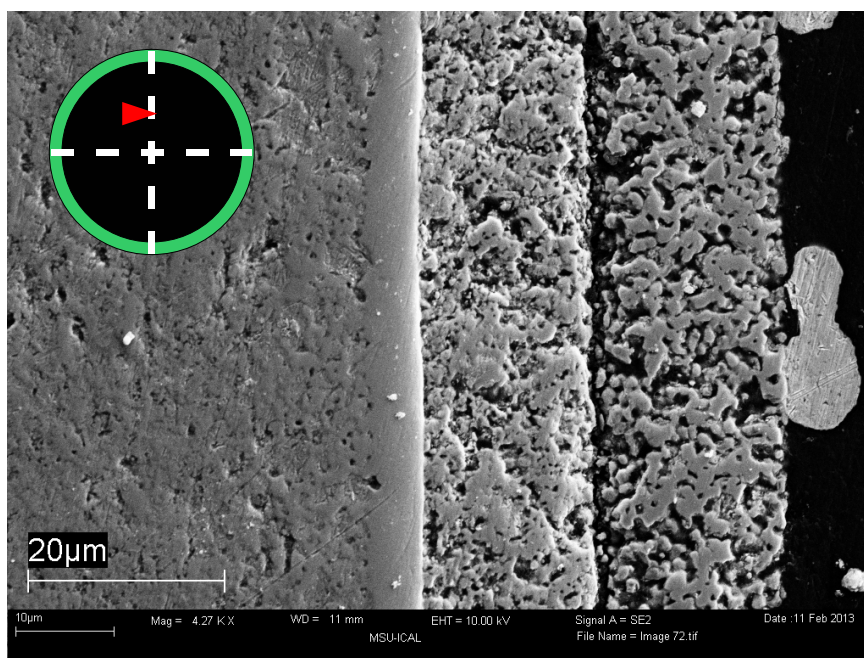


(b) Close Up

Figure F.7: Images show a thin crack in the cathode between the LSM and LSM-YSZ layers. The total length of the crack is about $100\ \mu\text{m}$. (a) Shows a cross-sectional image including this crack that spans the entire width of the cell, while (b) shows a close-up image of the crack.

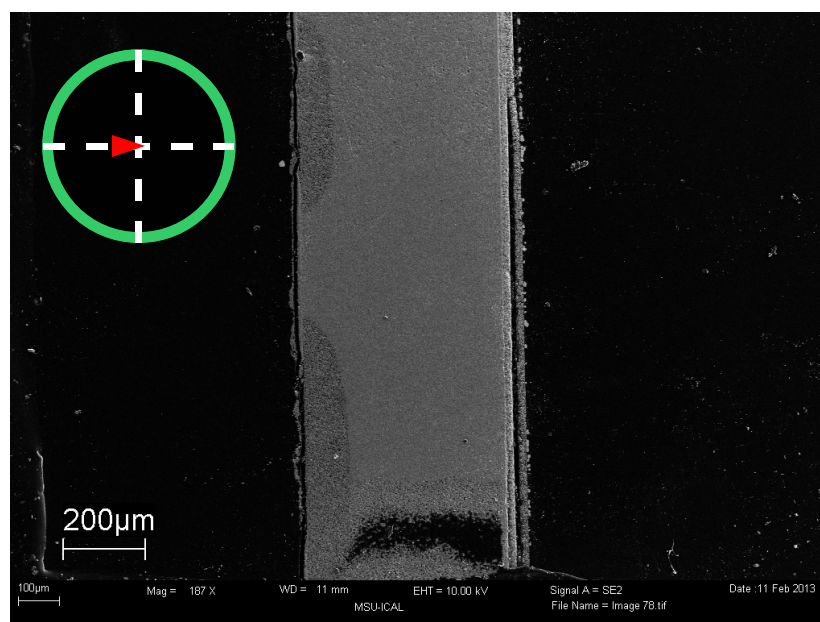


(a) Full Cross-section Image

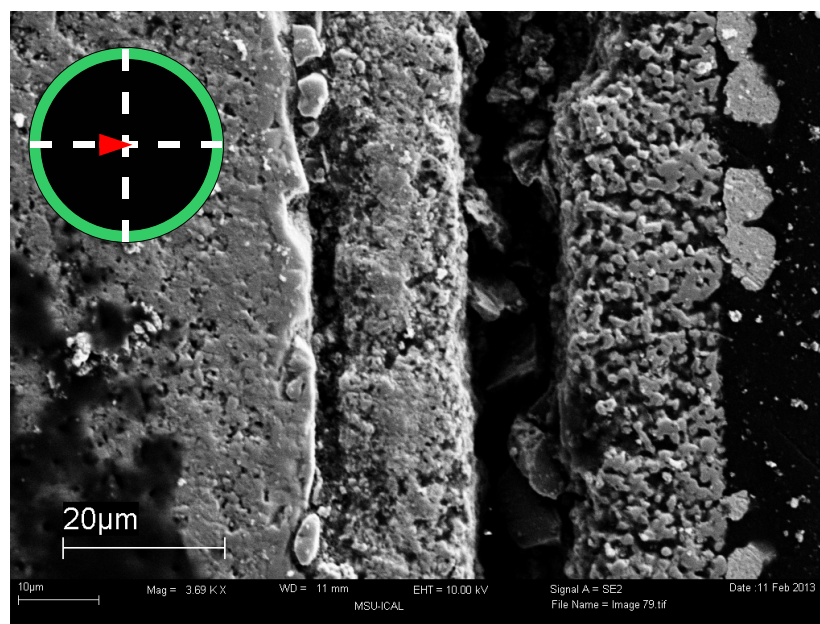


(b) Close Up

Figure F.8: Images show a thin crack in the cathode between the LSM and LSM-YSZ layers. The total length of the crack is about $300\ \mu\text{m}$. (a) Shows a cross-sectional image including this crack that spans the entire width of the cell, while (b) shows a close-up image of the crack.



(a) Full Cross-section Image



(b) Close Up

Figure F.9: Images show massive cracking in the cathode. The total length of the crack is about 1.1 mm, and shows cracking between the LSM and LSM-YSZ layers as well as LSM-YSZ layer and the YSZ electrolyte. (a) Shows a cross-sectional image including this crack that spans the entire width of the cell, while (b) shows a close-up image of the crack.