ELECTROCATALYSIS IN SOLID ACID FUEL CELLS

Thesis by

Mary WC Louie

In Partial Fulfillment of the Requirements

for the degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2011

(Defended May 20, 2011)

© 2011

Mary WC Louie

All Rights Reserved

Acknowledgements

This work would not have been possible without financial support from the National Science Foundation (NSF), DMR-0906543, and from the Caltech Center for the Science and Engineering of Materials, an NSF Materials Research Science and Engineering Center (DMR-0520565). Additional funding has been provided by the Gordon and Betty Moore Foundation (via the Caltech Center for Sustainable Energy Research) and by the Department of Defense Multidisciplinary University Research Initiative (W911NF-07-1-0410) administered by the Army Research Office. I have been fortunate enough to be supported by the NSF Graduate Research Fellowship Program, the Baker Hughes Scholarship from the Society of Women Engineers, and the Ludo Frevel Crystallography Scholarship from the International Center for Diffraction Data.

I am grateful to my thesis advisor, Professor Sossina Haile, who has been a wonderful mentor both professionally and personally. She works tirelessly to provide all the resources her group members need to be productive, and all the while, her office door is always open and her patience, endless. I have always left her office with more clarity than when I entered. For these reasons, I owe a great portion of graduate career to Sossina.

I thank Professor Adrian Hightower, scientist and kickboxer extraordinaire, for our valuable discussions, scientific and nonscientific alike. His boundless enthusiasm and optimism have made the endless hours of AFM troubleshooting in his sub-basement laboratory more bearable.

I thank my thesis committee members, Professors Kaushik Bhattacharya, Konstantinos Giapis and William Goddard. Professor Bhattacharya first exposed me to the theory of martensite in ME260, and since then, I have had a good deal of fun pondering the implications of crystallographic compatibility on solid acid compounds. I have also shared many projects with Professor Giapis, including microplasmas and electrosprays. I thank him for the advice and support he has given me throughout the years. I would also like to acknowledge Professor David Goodwin for his time as a member of my candidacy committee.

There are many individuals to whom I owe my gratitude for their contributions to my research at Caltech. I am grateful to Calum Chisholm for our exchanges about anything and everything related to solid acid fuel cells and for his enthusiasm and energy. I thank Yoshihiro Yamazaki for our discussions on hydrogen transport and for letting me "borrow" his textbooks. Ayako Ikeda has been an invaluable resource; I thank her for the information she provides me regarding the stability of solid acid compounds. For the AFM work, Brian Sayers and Shijie Wu assisted a great deal with troubleshooting and instrumentation. I also would like to acknowledge Mikhail Kislitsyn for his work on the structural and thermal characterization of CRDP compounds, as well as Diana Smirnova and Manuj Swaroop who worked on initial twinning calculations for CDP in ME260.

There are many others I would like to thank for help along the way. Kenji Sasaki was my mentor when I first arrive in the Haile group, not to mention the first to explore the complexities of electrocatalysis in solid acid systems. Jeff Snyder exposed me to the world of lab equipment on eBay and kept me on my toes with his excited and loud utterances in the hallway. Eric Toberer not only gave me much needed advice over the years but also made our office fun. I am grateful to David Boyd for discussions and help with oxygen plasmas and Raman spectroscopy, Yong Hao for point electrode calculations, and Ali Saramat for our collaboration on nanoparticle synthesis. Peter Babilo never hesitated to offer a confused first-year student a helping hand in the lab. Nick Brunelli was a patient teacher; I am grateful to him for our many discussions early in my graduate career. I cannot thank William Chueh and Wei Lai enough for their many, *many* (somewhat underappreciated) hours spent writing LabVIEW programs from which the Haile group benefits on a daily basis. I would also like to acknowledge the hard work of the undergraduate students who have worked with me over the years: Tewodros Mamo, Helen Telila, Lauren Baranowski, Sarah Howell, and Xiuyuan Li.

The Haile lab is great group to work with; every member has always been ready to lend a hand to others. I also cannot forget the supportive staff on campus, including Rosie Sanchez, Kathy Bubash, Fenton Harvey, Fran Matzen, Irene Loera, Mike Vondrus, Mike Roy, Rick Gerhart and Rick Germond.

I owe a great deal to individuals who have shaped my career and have been, and still are, mentors to me. As an undergraduate student at Berkeley, I was fortunate to have befriended Jessica Preciado who is truly an inspiring individual; if not for her, I probably would not have gone to graduate school. I must also thank my first research mentor, Andy Malec, who put up with the many blunders of a novice in the laboratory and who patiently taught me how to count the number of hydrogen in organic compounds (or, at the time, what looked to me like “random zig-zags”). Loddie Foose never ceases to offer me advice; at times, I think she knows me better than I do. And finally, Lisa Cowan is a dear friend, without whom I would not have survived my early years here.

I consider myself lucky to have entered Caltech with a great chemical engineering class; they managed to make my first year of classes and exams, I dare say, fun. In particular, Yvonne Chen, Diana Smirnova, and Havala Pye have become my good friends. I will miss our girls' game nights, not to mention repeatedly losing to Yvonne in bowling. Also, Diana kept me sane with our long runs and long conversations. Yvonne was my roommate for almost three years and is like a sister to me; to this day, she lends her patient ear for my ramblings.

I was fortunate enough to befriend many wonderful individuals: Puneet Chhabra, Glenn Garrett, Amy Fu, Peter Agbo, Arthur Chan, Eric Olmon, Chethana Kulkarni, Andrew Metcalf, and Nick Heinz. I also have not forgotten Alem and Hanu who always manage to put a smile on my face.

My husband, William, has been supportive and ever so patient with me. I thank him and his family for their love and support. Last but most definitely not least, I thank my family. My parents are the only reason why I have enjoyed the opportunities that they have only dreamt of; I still do not know how to express my appreciation of the sacrifices they have made. Also, Carrie, my "twin" sister and partner in crime (not to mention Dr. Louie No. 1), who despite being only one year older, was always the first to venture into the unknown when we were growing up. She has paved the way for me; she is and will always be my older, wiser sister.

Abstract

Solid state electrochemical reactions play a crucial role in many energy conversion devices, yet the pathways of many reactions remain unknown. The elusiveness of the reaction mechanisms is due, in part, to the complexity of electrochemical reactions; because electrochemical reactions require the interaction of many species (e.g., ions, electrons, and adsorbates) across multiple phases (e.g., electrolyte, catalyst, and gas phases), elucidation of the reaction pathway can quickly become complicated. In this work, we develop and utilize model catalyst | electrolyte systems, that is, structures of reduced complexity, to study electrode reactions in solid acid fuel cells which operate at intermediate temperatures of ~ 250 ºC. We employ AC impedance spectroscopy to explore the reaction pathway for hydrogen electro-oxidation over Pt thin films sputter-deposited atop the proton-conducting solid acid electrolyte CsH_2PO_4. We observed that hydrogen electro-oxidation occurs by diffusion of hydrogen through Pt, taking advantage of the entire Pt | CsH_2PO_4 interfacial area rather than being confined to the triple-phase sites. This insight opens up new avenues for developing high performance electrodes with low Pt loadings by eliminating the requirement that Pt-based electrodes be comprised of high triple-phase site densities long considered to be critical for Pt electrocatalysis. Indeed, even for flat, planar electrodes of very thin Pt films, we obtained a Pt utilization that is significantly higher than in typical composite electrodes.

We also demonstrate the efficacy of a new tool for probing the spatial heterogeneity of electrochemical reactions at the metal | electrolyte interface. We characterized oxygen electro-reduction kinetics at the nanoscale Pt | $CsHSO_4$ interface at ~ 150 ºC using conducting atomic force microscopy in conjunction with cyclic

voltammetry and AC impedance spectroscopy. Not only did we find the electrochemical activity for oxygen electro-reduction to vary dramatically across the electrolyte surface but the current-voltage data, when analyzed in the Butler-Volmer framework, exhibited a strong counter-correlation between two key kinetic parameters, the exchange coefficient and exchange current. Specifically, the exchange current spanned five orders of magnitude while the exchange coefficient ranged between 0.1 and 0.6. Such a correlation has not been observed before and points to the power of atomic force microscopy for electrochemical characterization at electrolyte | metal | gas boundaries in general.

As reduction in microstructural complexity is a key advantage in model electrode | electrolyte systems, we also sought to understand the bulk properties of solid acid compounds, specifically, the relationship between microstructure and the superprotonic phase transition, the latter of which lends solid acid compounds their high proton conductivities at intermediate temperatures. We found a correlation between phase transformation hysteresis and crystallographic compatibility of the high- and low-temperature phases of the $Cs_{1-x}Rb_xH_2PO_4$ solid solution series. Therefore, it is to be expected that hysteresis, and therefore microcrack formation, can be minimized during phase transformation via the principle of crystallographic compatibility. This is confirmed in single crystals of $CsHSO_4$, which was found to have higher crystallographic compatibility, lower hysteresis, and significantly fewer microcracks formed during phase transition compared to CsH_2PO_4. The apparent applicability of the theory of crystallographic compatibility implies a new tool for identifying solid acid compounds with suitable microstructures for fuel cell application and for model electrode | electrolyte systems.

Table of Contents

Chapter 1 Introduction……………….. 1

1.1 Overview.. 1

1.2 Fuel Cells 1

1.2.1 Fuel Cell Basics.. 2

1.2.2 Overpotentials in Fuel Cells... 4

1.2.3 Component Requirements.. 6

1.2.4 Types of Fuel Cells 8

1.3 Solid Acid Fuel Cells 10

1.3.1 Solid Acid Compounds 10

1.3.2 CsH_2PO_4 as an Electrolyte: Benefits and Challenges............................. 13

1.3.3 Solid Acid Fuel Cell Performance.. 16

1.4 Electrode Reactions in Solid Acid Fuel Cells.. 17

1.4.1 Hydrogen Electro-oxidation and Oxygen Electro-reduction 17

1.4.2 Electrochemical Reaction Pathways 18

Chapter 2 Experimental Methods……………. 22

2.1 AC Impedance Spectroscopy.. 22

2.1.1 Basic Principles... 22

2.1.2 Data Analysis: Equivalent Circuit Models... 26

2.1.3 Data Analysis: Physical Models... 32

2.1.4 Experimental Corrections 34

2.2 Potential Sweep (DC) Methods 35

2.3 AC vs. DC Measurements... 37

2.4 Scanning Probe Microscopy for Electrochemistry 38

2.4.1 Atomic Force Microscopy 39

2.4.2 Electrical Atomic Force Microscopy 42

2.5 Cell Geometries for Probing Solid State Electrochemistry 43

2.5.1 Symmetric vs. Asymmetric Gas Environments 43

2.5.2 Electrode Symmetry and Geometry 46

2.5.3 Electrode Microstructure 50

2.6 Solid Acid Compounds for Electrode Studies: Challenges 51

2.6.1 Water Solubility 51

2.6.2 Mechanical Properties 52

2.6.3 Superprotonic Phase Transition 52

2.6.4 Thermal and Chemical Stability 54

Chapter 3 Hydrogen Electro-oxidation over Thin Film Pt Electrodes 55

3.1 Introduction 56

3.2 Experimental 57

3.2.1 Sample Preparation 57

3.2.2 Characterization 58

3.3 Results and Discussion 61

3.3.1 Film Morphology and Structure 61

3.3.2 Impedance Response: Effect of Platinum Film Dimension 65

3.3.3 Impedance Response: Impact of Gold Overlayers 70

3.3.4 Diffusion Analysis 71

3.3.5 Ultra-thin Platinum Films 74

3.4 Implications for Electrode Design 76

3.5 Summary 79

Chapter 4 Oxygen Electro-reduction at Nano-Pt | $CsHSO_4$ 80

4.1 Introduction 82

4.2 Experimental 85

4.2.1 Half-cell Fabrication 85

4.2.2 Experimental Conditions 86

4.2.3 Measurement Conditions 87

4.2.4 Data Analysis 88

4.3 Results and Discussion 89

4.3.1 Cyclic Voltammetry 89

4.3.2 Impedance Spectroscopy 92

4.3.3 Analysis of Oxygen Electro-reduction Kinetics 96

4.3.4 Heterogeneity of Electrochemical Kinetics 100

4.4 Summary 105

Chapter 5 Phase Transformation Hysteresis in Solid Acid Compounds 107

5.1 Introduction 109

5.2 Theory of Crystallographic Compatibility 111

5.3 Experimental 116

5.3.1 Synthesis and Fabrication 116

5.3.2 Characterization 117

5.3.3 Determination of Eigenvalues 119

5.4 Results and Discussion: $Cs_{1-x}Rb_xH_2PO_4$ 119

5.4.1 Phase and Chemical Characterization 119

5.4.2 Conductivity and Phase Transformation Hysteresis 123

5.4.3 Eigenvalues and Correlation to Hysteresis 126

5.5 Results and Discussion: Microstructure of CsH_2PO_4 and $CsHSO_4$ 128

5.5.1 Microcrack Formation 128

5.5.2 Microstructure of Single-crystal Surfaces 130

5.5.3 In situ Imaging of $CsHSO_4$ 134

5.6 Summary and Outlook 138

Appendix A Derivations 141

A.1 Kinetics of Electrode Reactions: Butler-Volmer Equation 141

A.2 Finite-Length Warburg with Reversible Bounds 146

A.3 Reaction Mechanism 152

A.3.1 Hydrogen Adsorption as a Rate-Limiting Step 154

A.3.2 Hydrogen Absorption as a Rate-Limiting Step 155

A.3.3 Hydrogen Diffusion as a Rate-Limiting Step 156

A.3.4 Charge Transfer as a Rate-Limiting Step 157

Appendix B Reactivity of Candidate Electrocatalysts with CsH_2PO_4 158

B.1 Motivation 158

B.2 Experimental 160

B.2.1 Sample Preparation and Heat Treatment 160

B.2.2 Characterization 160

B.3 Results and Discussion 160

Appendix C Platinum Thin Film Anodes 164

C.1 Experimental Setup 164

C.2 Platinum Film Quality 165

C.2.1 Before and After Electrochemical Characterization ... 165

C.2.2 Film Structure and Impedance Response of Sub-5 nm Films ... 168

C.2.3 Mechanical Integrity: 375 nm vs. Sub-8 nm Films ... 172

C.2.4 Effect of Mechanical Pressure from Current Collector ... 175

C.3 Non-electrode Impedance Responses ... 177

C.3.1 Origin of Spurious Electrical Effects ... 177

C.3.2 Appearance of Constriction Effect ... 178

C.3.3 Evidence of Constriction Effect ... 180

C.4 Layered Pt-Au Film Electrodes ... 183

C.5 Electrolyte Effects: $Cs_{0.25}Rb_{0.75}H_2PO_4$ vs. CsH_2PO_4 ... 188

C.5.1 150 nm Platinum Films ... 189

C.5.2 7.5 nm Platinum Films ... 191

C.6 Effect of Environmental Parameters ... 193

C.7 Role of the Superprotonic Phase Transition in Electrode Kinetics ... 199

C.7.1 Temperature Dependence ... 199

C.7.2 Platinum Film Geometry Dependence ... 201

C.7.3 Temperature Cycling and Crack Formation ... 202

Appendix D Hydrogen Electro-oxidation over Palladium Thin Films ... 207

D.1 Experimental ... 207

D.2 Results and Discussion ... 209

D.2.1 Palladium Film Characteristics ... 209

D.2.2 Characteristics of Impedance Spectra ... 214

D.2.3 Effect of Palladium Film Geometry ... 216

D.2.4 Effect of Environmental Parameters ... 217

D.2.5 Impedance Response of Layered Pt-Au Film Electrodes ... 220

D.2.6 10 nm Palladium Films *221*

D.2.7 Comparison to Platinum *222*

D.3 Summary 223

D.4 Recommendations for Future Studies 224

Appendix E Nickel Thin Films 225

Appendix F Pt | $CsHSO_4$ by Atomic Force Microscopy 229

F.1 Experimental Details 229

F.1.1 Instrumentation and Setup *229*

F.1.2 Sample Heating *230*

F.2 Data Analysis 232

F.2.1 Open- and Short-Circuit Corrections *232*

F.2.2 Measurement Stability *236*

F.2.3 Analysis of Cyclic Voltammograms *238*

F.2.4 Effect of Force on Electrochemical Measurements *239*

F.3 Nano-Pt | $CsHSO_4$ vs. Wire-Pt | CsH_2PO_4 240

F.4 Platinum Oxide Reduction at Pt | $CsHSO_4$ 242

F.4.1 Experimental *242*

F.4.2 Results and Discussion *243*

F.5 Oxygen Electro-Reduction at Pt | Single-crystal $CsHSO_4$ 246

F.5.1 Experimental *246*

F.5.2 Results and Discussion *249*

Appendix G Pt | $Ba_{3-x}K_xH_x(PO_4)_2$ by Atomic Force Microscopy 254

G.1 Introduction 254

G.2 Experimental 255

G.3 Results and Discussion 257

G.3.1 $Ba_{3-x}K_xH_x(PO_4)_2$ Characteristics 257

G.3.2 Fabrication of Microscale $Ba_{3-x}K_xH_x(PO_4)_2$ Half-cells 258

G.3.3 Oxygen Electro-reduction at Pt | $Ba_{3-x}K_xH_x(PO_4)_2$ 261

G.3.4 Troubleshooting 264

G.4 Recommendations for Future Studies 266

Appendix H Pd | $CsHSO_4$ by Atomic Force Microscopy 268

H.1 Experimental 268

H.2 Results and Discussion 269

H.2.1 Oxygen Electro-reduction 269

H.2.2 Transient Behavior of Pd | $CsHSO_4$ 274

H.2.3 Palladium Oxidation 276

H.2.4 Stability of Pd | $CsHSO_4$ 277

H.3 Summary 278

Appendix I Crystallographic Compatibility in $Cs_{1-x}Rb_xH_2PO_4$ 280

I.1 Visualization of the Cubic-to-Monoclinic Transformation in CsH_2PO_4 280

I.2 Calculation of Transformation Matrix 282

I.3 Calculation of Compatible Variant Pairs: Twinning Modes 283

I.4 Calculation of the Austenite-Martensite Interface 285

I.5 Results for CsH_2PO_4 287

Appendix J Microstructure of Solid Acid Compounds: Supplemental 292

J.1 Additional Images 292

Appendix K Pt | CsH_2PO_4 | Au as a Mixed Potential Hydrogen Sensor 294

K.1 Introduction 294

K.2 Mixed Potential Effect 295

K.3 Experimental 297

K.4 Results and Discussion 298

K.4.1 Sensor Response 298

K.4.2 Variability in the Sensor Response 303

K.5 Summary and Recommendations 304

References …………………………..…… ……………………………….……..305

List of Figures

Figure 1.1 Schematic of a fuel cell based on a proton-conducting electrolyte 3

Figure 1.2 Fuel cell polarization curve and overpotentials. 5

Figure 1.3 Schematic of a typical composite electrode... 8

Figure 1.4 Arrhenius plot of proton conductivity showing the superprotonic phase transition of select solid acid compounds...................................... 11

Figure 1.5 Superprotonic phase transition in CsH_2PO_4: Proton conductivity and corresponding unit cells. 12

Figure 1.6 Proton conduction mechanism in CsH_2PO_4. 13

Figure 1.7 Cartoon of triple-phase boundary pathways. 19

Figure 1.8 Comparison of triple-phase and two-phase boundary pathways 21

Figure 2.1 Basics of AC impedance 25

Figure 2.2 Nyquist representation of impedance response... 25

Figure 2.3 Depiction of ion movement due to an alternating electric field................ 26

Figure 2.4 Impedance spectrum for three serial RC sub-circuits and comparision of RQ and RC response... 30

Figure 2.5 Equivalent circuit for three serial electrochemical 31

Figure 2.6 Schematic for Warburg diffusion.. 33

Figure 2.7 Potential profile for cyclic voltammetry 36

Figure 2.8 Cyclic voltammograms for some common circuit elements..................... 37

Figure 2.9 Atomic force micoscope probes: tip and cantilever description............... 40

Figure 2.10 Operation of atomic force microscopy. 41

Figure 2.11 Asymmetric and symmetric gas configurations for electrode studies 45

Figure 2.12 Electrode geometries for solid state electrochemical measurements........ 48

Figure 2.13 Requirements of asymmetric electrode geometries 49

Figure 2.14 Different electrode microstructures for a catalyst-electrolyte system 51

Figure 2.15 Fuel cell open-circuit voltage with temperature cycling........................... 53

Figure 3.1 XRD pattern of Pt film on a CsH_2PO_4 substrate...................................... 61

Figure 3.2 Representative SEM micrographs of Pt films.. 63

Figure 3.3 Schematic of the Pt | CsH_2PO_4 | Pt system 63

Figure 3.4 SEM micrographs of Pt grain size for various film thicknesses............... 64

Figure 3.5 XRD patterns showing correlation of grain size with Pt film thickness... 65

Figure 3.6 Impedance spectra for Pt film electrodes of different thicknesses 66

Figure 3.7 Plots of Pt film electrode resistance as a function of film geometry 68

Figure 3.8 Dependence of pH_2 reaction order and activation energy on film thickness.. 69

Figure 3.9 Schematic of the Au | Pt | CsH_2PO_4 | Pt | Au cell 71

Figure 3.10 Impedance spectra: Au | Pt | CsH_2PO_4 | Pt | Au vs. Pt | CsH_2PO_4 | Pt 71

Figure 3.11 Extracted hydrogen diffusivity as a function of film................................ 74

Figure 3.12 Area-normalized electrode resistance of Pt films as function of thickness.. 76

Figure 4.1 Schematic of nano-electrode setup using an atomic force microscope 83

Figure 4.2 Cyclic voltammograms: Au | $CsHSO_4$ vs. Pt | $CsHSO_4$ 90

Figure 4.3 AC impedance spectra for Pt | $CsHSO_4$ as a function of overpotential 93

Figure 4.4 Impedance spectra for Pt | $CsHSO_4$ at –1.0 and –0.9 V............................ 93

Figure 4.5 Resistance of Pt | $CsHSO_4$ as a function of overpotential......................... 96

Figure 4.6 Tafel plot for Pt | $CsHSO_4$. 98

Figure 4.7 Image of typical $CsHSO_4$ surface by SEM and AFM 101

Figure 4.8 Tafel plots and extracted i_0 and α values as a function of position 103

Figure 4.9 Semi-log plot of i_0 as a function of α, showing correlation 103

Figure 5.1 Schematic of austenite-to-martensite transformation for CsH_2PO_4 113

Figure 5.2 Room temperature XRD patterns of $Cs_{1-x}Rb_xH_2PO_4$ 120

Figure 5.3 XRD patterns for CsH_2PO_4 as a function of temperature 122

Figure 5.4 Thermal expansion of CsH_2PO_4: lattice parameters and cell volume 122

Figure 5.5 Temperature dependence of the proton conductivity of CsH_2PO_4 124

Figure 5.6 Reproducibility of $Cs_{1-x}Rb_xH_2PO_4$ upon repeated temperature cycling 124

Figure 5.7 Phase transition temperature and hysteresis width as functions of Rb content. 126

Figure 5.8 Middle eigenvalue, λ_2, as a function of Rb content, and hysteresis width as a function of λ_2 127

Figure 5.9 SEM images of cracks in CsH_2PO_4 and $CsHSO_4$ after heat treatment 129

Figure 5.10 Optical clarity of CsH_2PO_4 and $CsHSO_4$ crystals after heat treatment 129

Figure 5.11 SEM images of polished CsH_2PO_4 crystal before and after heat treatment. 131

Figure 5.12 SEM images of fractured CsH_2PO_4 crystal before and after heat treatment 131

Figure 5.13 SEM images of fractured CsH_2PO_4 crystal after heat treatment 131

Figure 5.14 SEM images of as-grown $CsHSO_4$ crystal before and after heat treatment. 132

Figure 5.15 SEM images of polished $CsHSO_4$ crystal before and after heat treatment. 133

Figure 5.16 Topography of fractured $CsHSO_4$ crystal at elevated temperatures 135

Figure 5.17 Topography of fractured $CsHSO_4$ crystal as function of temperature.... 137

Figure 5.18 Plot of phase transition hysteresis as a function of middle eigenvalue and volume change for three classes of solid acid compounds. 140

Figure A.1 Effect of potential on free energy profiles for charge transfer reaction.. 143

Figure A.2 Effect of exchange current on the current-overpotential behavior. 145

Figure A.3 Warburg diffusion: schematic of diffusion of species through a film 147

Figure A.4 Two-phase boundary pathway for hydrogen electro-oxidation. 153

Figure B.1 Plot of Gibbs free energy for metal oxide formation at 240 ºC in air for various metal oxides. 159

Figure B.2 Plot of Gibbs free energy of select metal carbides and nitrides in air at 240 ºC........ 163

Figure C.1 Drawing of test station for symmetric cell measurements. 165

Figure C.2 SEM micrographs of 375 nm Pt films on top of CsH_2PO_4 before and after electrochemical characterization. 166

Figure C.3 SEM micrographs of 75 nm Pt films on top of CsH_2PO_4 before and after electrochemical characterization 167

Figure C.4 SEM micrographs of 7.5 nm Pt films on top of CsH_2PO_4 before and after electrochemical characterization. 167

Figure C.5 SEM micrographs of 7.5, 22.5, 37.5 and 52.5 nm Pt films on top of CsH_2PO_4 after electrochemical characterization. 168

Figure C.6 SEM micrographs of sub-5 nm thin Pt films before and after electrochemical characterization 170

Figure C.7 Nyquist spectra for 1.5, 3, and 4.5 nm thick Pt films and the corresponding area-normalized electrode resistances in comparison to thicker films 171

Figure C.8 SEM micrographs of the undersides of as-deposited 4.5 and 7.5 nm Pt films 174

Figure C.9 SEM micrographs of the undersides of as-deposited 1.5, 3, and 4.5 nm Pt films. 174

Figure C.10 Cross-section image showing delamination of an intact 375 nm Pt film from CsH_2PO_4 174

Figure C.11 SEM micrographs of a 375 nm Pt film deposited onto CsH_2PO_4, after electrochemical testing, showing buckling 175

Figure C.12 Pt film quality, after electrochemical characterization, as a function of film thickness and mechanical pressure applied to the cell 176

Figure C.13 The constriction effect: ion movement at various frequencies. 178

Figure C.14 Impedance spectra: Solartron 1250 vs. 1260 FRA. 180

Figure C.15 Representative impedance spectra for a Pt | CsH_2PO_4 | Pt showing no effect of pH_2 on ohmic offset and high frequency arc. 182

Figure C.16 Temperature dependence of the ohmic offset and the width of the high frequency arc 183

Figure C.17 Impedance response of Pt-Au layered thin film electrode system 185

Figure C.18 Impedance spectra of a Au | CsH_2PO_4 | Au symmetric cell 188

Figure C.19 Nyquist plot for 150 nm Pt films on CsH_2PO_4 and $Cs_{0.25}Rb_{0.75}H_2PO_4$ electrolytes 190

Figure C.20 Nyquist plots for 7.5 nm Pt films on CsH_2PO_4 and $Cs_{0.25}Rb_{0.75}H_2PO_4$ electrolytes 193

Figure C.21 pH_2 and pH_2O dependence plots for Pt | CsH_2PO_4 | Pt (75 nm). 196

Figure C.22 pH_2 and pH_2O dependence plots for Pt | CsH_2PO_4 | Pt (7.5 nm). 196

Figure C.23 Arrhenius behavior of Pt | CsH_2PO_4 | Pt (75 nm) 198

Figure C.24 Arrhenius behavior of Pt | CsH_2PO_4 | Pt (7.5 nm) 198

Figure C.25 Pt | CsH_2PO_4 | Pt across the phase transition: plot of cell temperature and resistance as functions of time, and corresponding Arrhenius plot. 200

Figure C.26 Dependence of electrode resistance on film geometry below the phase transition temperature 202

Figure C.27 Effect of the superprotonic phase transition on cracking in polycrystalline CsH_2PO_4 discs, with application of mechanical pressure 203

Figure C.28 The effect of the superprotonic phase transition on cracking in polycrystalline CsH_2PO_4 discs *without* application of mechanical pressure applied 204

Figure C.29 Impedance spectra for Pt | CsH_2PO_4 | Pt symmetric cells (7.5 and 150 nm Pt) before and after a cool-heat cycle through the phase transition. 206

Figure C.30 Effect of thermal cycling on the impedance response of Pt | CsH_2PO_4 | Pt symmetric cell 206

Figure D.1 XRD pattern of 100 nm Pd films on top of CsH_2PO_4 before and after electrochemical characterization 210

Figure D.2 SEM images of the cross sections of Pd | CsH_2PO_4 | Pd cells. 210

Figure D.3 SEM micrographs of 10 nm Pd films deposited on top of CsH_2PO_4 before and after electrochemical characterization 211

Figure D.4 SEM micrographs of 100 nm Pd films deposited on top of CsH_2PO_4 before and after electrochemical characterization 212

Figure D.5 SEM micrographs of 100 nm Pd films deposited on top of CsH_2PO_4: lateral variation in film structure.. 213

Figure D.6 Impedance spectrum for a Pd | CsH_2PO_4 | Pd cell (100 nm Pd films) 214

Figure D.7 Equivalent circuit model for the Pd | CsH_2PO_4 | Pd symmetric cell. 215

Figure D.8 Select impedance spectra for 100, 200, and 300 nm thick Pd films 216

Figure D.9 Plots of the electrode resistances as functions of film diameter. 217

Figure D.10 Plots of the area-normalized electrode resistances as functions of film thickness.. 217

Figure D.11 Representative plots for extracting $p\mathrm{H}_2$ reaction order and activation energy.. 218

Figure D.12 Impedance spectra for the Pd-Au thin film system: Pd | CsH_2PO_4, Au | Pd | CsH_2PO_4, and Pd | Au | CsH_2PO_4... 221

Figure D.13 Impedance spectra for Pd | CsH_2PO_4 | Pd cell (10 nm Pd films). 222

Figure E.1 SEM micrographs of Ni films deposited on top of CsH_2PO_4 before and after electrochemical characterization.. 226

Figure E.2 Images of 100 nm Ni films after heat treatment compared to those after electrochemical characterization 227

Figure E.3 XRD patterns of 100 nm Ni films on top CsH_2PO_4 before and after testing. 228

Figure E.4 XRD patterns of as-deposited 400 nm Ni films on top CsH_2PO_4 fabricated by thermal evaporation and by sputter deposition. 228

Figure F.1 Photographs of experimental setup for electrochemical AFM. 230

Figure F.2 Schematic of the $CsHSO_4$ cell configurations for AFM. 231

Figure F.3 Analysis of the temperature gradient across $CsHSO_4$ in AFM 232

Figure F.4 Illustration of how stray capacitance affects two arbitrary processes..... 233

Figure F.5 Open-circuit impedance response as a function of the current range selected in instrumentation 234

Figure F.6 Representative Nyquist and Bode-Bode plots before and after open-circuit correction. 235

Figure F.7 Short-circuit measurement for a Pt-coated AFM probe in contact with Au foil 236

Figure F.8 AFM image of a $CsHSO_4$ surface: effect of thermal drift 237

Figure F.9 Measurement stability: two impedance spectra collected with frequency sweeps in opposite directions.. 238

Figure F.10 Cyclic voltammograms for Pt | $CsHSO_4$ at various scan rates and the corresponding α values 239

Figure F.11 Effect of force and of probe withdrawal/reapproach on cyclic voltammograms for Pt | $CsHSO_4$. 240

Figure F.12 i_0-α correlation: Pt | $CsHSO_4$ vs. Pt | CsH_2PO_4 242

Figure F.13 Pt oxide reduction peak as a function of chemical and electrochemical oxidation time 245

Figure F.14 Pt oxide reduction peak voltage, current and area as a function of chemical and electrochemical oxidation time... 246

Figure F.15 Cyclic voltammograms for a Pt probe in contact with as-grown $CsHSO_4$ single-crystal surface 248

Figure F.16 Cyclic voltammograms for a Pt probe in contact with single-crystal $CsHSO_4$, contaminated with acidic solution 249

Figure F.17 Cyclic voltammogram and Nyquist spectra for Pt probe in contact with fractured $CsHSO_4$ crystal 250

Figure F.18 Tafel plots for Pt | fractured $CsHSO_4$ and i_0-α correlation...................... 251

Figure F.19 AFM topography image of a single-crystal $CsHSO_4$ surface 253

Figure F.20 AFM images of $CsHSO_4$ crystal surfaces showing damage caused by probe 253

Figure G.1 Schematic of experimental setup for electrochemical AFM measurements of $Ba_{3-x}K_xH_x(PO_4)_2$ electrolytes..................................... 257

Figure G.2 SEM images: $Ba_{3-x}K_xH_x(PO_4)_2$ powder vs. $CsHSO_4$ powder 258

Figure G.3 SEM images of $Ba_{3-x}K_xH_x(PO_4)_2$ platelets on a Pt-coated Si wafer....... 259

Figure G.4 SEM images showing wafer-to-wafer transfer of $Ba_{3-x}K_xH_x(PO_4)_2$ platelets 261

Figure G.5 Electrochemical AFM measurements at Pt | $Ba_{3-x}K_xH_x(PO_4)_2$ and corresponding cyclic voltammograms 262

Figure G.6 Cyclic voltammograms for Pt | $Ba_{3-x}K_xH_x(PO_4)_2$ obtained by wafer-to-wafer platelet transfer 263

Figure G.7 Short-circuit measurements on Pt-coated silicon wafer.......................... 264

Figure G.8 Raman spectrum for $Ba_{3-x}K_xH_x(PO_4)_2$ platelets deposited on Si wafer . 266

Figure H.1 Cyclic voltammograms and impedance spectra for nano-Pd | $CsHSO_4$. 270

Figure H.2 Electrode resistances plotted as functions of overpotential, and Tafel plot for the Pd | $CsHSO_4$ system 272

Figure H.3 Variation of Tafel plot with position across a $CsHSO_4$ surface.............. 273

Figure H.4 i_0-α correlation: Pd | $CsHSO_4$ vs. Pt | $CsHSO_4$ 273

Figure H.5 Polycrystalline $CsHSO_4$ damaged by AFM probe................................. 274

Figure H.6 Transient features in the cyclic voltammograms of Pd | $CsHSO_4$ 275

Figure H.7 Behavior of reduction peaks in Pd | $CsHSO_4$ as a function of chemical and electrochemical oxidation time 277

Figure H.8 Spatial (and time) dependence of Pd | $CsHSO_4$ response 278

Figure I.1 Visualization of the phase transformation in CsH_2PO_4 281

Figure I.2 Schematic of parallel twins separating two alternating variants............. 284

Figure I.3 Schematic of the interface between austenite and two variants of martensite 286

Figure J.1 SEM images of CsH_2PO_4 crystal before and after heat treatment 292

Figure J.2 SEM images of a polished CsH_2PO_4 crystal after heat treatment........... 292

Figure J.3 Twins in $CsHSO_4$: SEM image after heat treatment and AFM image at superprotonic conditions. 293

Figure K.1 Schematic polarization curves for determining mixed potentials in Au | CsH_2PO_4 | Pt hydrogen sensor 296

Figure K.2 Plot of open-circuit voltage as a function of time for a Pt | CsH_2PO_4 | Au sensor at 235 ºC for various pH_2 299

Figure K.3 Mixed potential response of Pt | CsH_2PO_4 | Au sensor at 235 ºC plotted against pH_2 300

Figure K.4 Schematic showing how mass transport effects can result in a large change in mixed potential for a small change in gas composition.. 301

Figure K.5 Mixed potential response of multiple Pt | CsH_2PO_4 | Au sensors at 235 ºC plotted against pH_2.. 302

Figure K.6 Plot of open-circuit voltage as a function of time for a Pt | CsH_2PO_4 | Au sensor at 235 ºC for various pH_2 302

List of Tables

Table 1.1 Common fuel cell types and their primary characteristics 9

Table 2.1 Impedance response of frequently encountered circuit elements..................27

Table 2.2 Impedance response of frequently encountered sub-circuits..........................28

Table 2.3 Impedance response for bounded and unbounded Warburg diffusion...........33

Table 3.1 Experimentally-determined parameters for hydrogen transport in Pt 74

Table 3.2 Comparison of platinum-based anodes for solid acid fuel 79

Table 4.1 Conducting AFM probes employed in this study..88

Table 5.1 Lattice parameters and chemical compositions for $Cs_{1-x}Rb_xH_2PO_4$ 120

Table 5.2 Thermal expansion parameters for CsH_2PO_4 123

Table B.1 Reactivity of CsH_2PO_4 with metal oxides at 150 ºC and 240 ºC.................162

Table B.2 Reactivity of CsH_2PO_4 with metal nitrides and carbides at 240 ºC.............163

Table C.1 Summary of parameters extracted from the low frequency arc generated by addition of Au films to the Pt | CsH_2PO_4..186

Table C.2 Comparison of fitted parameters for 150 nm Pt films on CsH_2PO_4 and $Cs_{0.25}Rb_{0.75}H_2PO_4$. 191

Table C.3 Comparison of fitted parameters for 7.5 nm Pt films on CsH_2PO_4 and $Cs_{0.25}Rb_{0.75}H_2PO_4$. 193

Table C.4 pH_2 and pH_2O dependences of electrolyte-related processes......................194

Table D.1 Pd thin films: area-normalized resistance, pH_2 and pH_2O reaction order and activation energy..218

Table H.1 AFM probes employed for comparing Pd | $CsHSO_4$ and Pt | $CsHSO_4$. 269

Table I.1 Lattice parameters and atomic positions for monoclinic CsH_2PO_4.............281

Table I.2 Lattice parameters and atomic positions for cubic CsH_2PO_4.......................281

Table I.3 Twelve martensite variants for transformation of CsH_2PO_4 288

Table I.4 Allowed twinning modes of CsH_2PO_4 martensite..289

Table I.5 CsH_2PO_4 martensite variant pairs that can form an interface with the austenite phase..290

List of Acronyms

ACIS	alternating current impedance spectroscopy
AFC	alkali fuel cell
AFM	atomic force microscopy
BKHP	barium potassium hydrogen phosphate, $Ba_{3-x}K_xH_x(PO_4)_2$
CDP	cesium dihydrogen phosphate, CsH_2PO_4
CHS	cesium hydrogen sulfate, $CsHSO_4$
CRDPn	cesium rubidium dihydrogen phosphate, $Cs_{1-x}Rb_xH_2PO_4$, where $n = 100x$
CV	cyclic voltammetry
dFLW	distributed finite-length Warburg
EDS	energy dispersive spectroscopy
FRA	frequency response analyzer
MCFC	molten carbonate fuel cell
OCV	open-circuit voltage
PAFC	phosphoric acid fuel cell
RMS	root mean square
SAFC	solid acid fuel cell
PEMFC	polymer electrolyte membrane or proton exchange membrane fuel cell
SEM	scanning electron microscopy
SOFC	solid oxide fuel cell
XRD	X-ray diffraction