The Chemistry of Membranes Used in Fuel Cells

Degradation and Stabilization

Edited by Shulamith Schlick

Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, MI, USA

WILEY

Contents

Preface *xiii* About the Editor *xvii* List of Contributors *xix*

- 1 The Evolution of Fuel Cells and Their Components 1 Thomas A. Zawodzinski, Zhijiang Tang, and Nelly Cantillo
- 1.1 Overview: A Personal Perspective of Recent Developments 1
- 1.2 Basics of Fuel Cell Operation 3
- 1.3 Types of Fuel Cells 5
- 1.3.1 Phosphoric Acid Fuel Cell 5
- 1.3.2 Molten Carbonate Fuel Cell and Solid Oxide Fuel Cell 5
- 1.3.3 Proton Exchange Membranes Fuel Cell 6
- 1.3.4 Alkaline Fuel Cell 6
- 1.3.5 Solid Acid Fuel Cell 8
- 1.4 Low Temperature Fuel Cells: Components 8
- 1.4.1 Membranes in PEM Systems 9
- 1.4.2 Electrocatalysts in PEM Systems 11
- 1.4.2.1 Catalyst Layer Structure in PEM Systems 13
- 1.5 Summary 16 Acknowledgments 16 References 16
- 2 Degradation Mechanism of Perfluorinated Membranes 19
 - Marek Danilczuk, Shulamith Schlick, and Frank D. Coms
- 2.1 Introduction 19
- 2.2 Fluoride Release Rate 22
- 2.3 Nuclear Magnetic Resonance 26
- 2.4 Fourier Transform Infrared Spectroscopy 30
- 2.5 Electron Spin Resonance 37
- 2.5.1 Direct ESR Radical Detection in Perfluorinated Membranes 37
- 2.5.2 Spin Trapping ESR 40

viii Contents

2.5.3	In Situ ESR Fuel Cell 41
2.5.4	Chemical Reactions and Crossover Processes in a Fuel Cell 43
2.5.5	Effect of Membrane Thickness 46
2.6	Conclusions 49
	Acknowledgments 51
	References 51
3	Banking the Stability of Perfluorinated Membranes to Attack
5	by Hydroxyl Badicals 55
	Marek Danilczuk and Shulamith Schlick
3.1	Introduction 55
3.2	The Chemical Stability of Perfluorinated Ionomers 57
3.3	Electron Spin Resonance Studies of PFSAs Exposed
	to Hydroxyl Radicals 61
3.3.1	Spin-Trapping ESR 61
3.3.2	Competitive Kinetics: Perfluorinated Ionomers as Competitors
	for HO [•] Radicals 62
3.3.3	Ce(III) as Competitor 68
3.4	Conclusions 70
	Acknowledgments 72
	References 72
4	Stabilization of Perfluorinated Membranes Using Ce ³⁺ and Mn ²⁺
	Redox Scavengers: Mechanisms and Applications 75
	Frank D. Coms, Shulamith Schlick, and Marek Danilczuk
4.1	Introduction 75
4.2	Oxidant Chemistry 76
4.3	Degradation Mechanisms of PFSA 79
4.4	Mitigation of Chemical Degradation by
	Redox Quenchers 81
4.4.1	Mitigation Mechanisms of Ce ³⁺ and Mn ²⁺ 82
4.4.1.1	Cerium Mitigation and Chain Scission Processes 89
4.4.2	ESR Spin Trapping Studies 89
4.4.3	Oxidative Stress and Ce ³⁺ Mitigation 91
4.4.3.1	MEA Design 96
4.4.4	Cerium Distribution and Migration 97
4.4.5	CeO ₂ Mitigation 100
4.4.6	Synergistic Mitigation Strategies 101
4.5	Conclusions 103
	Acknowledgments 104
	keierences 104

- 5 Hydrocarbon Proton Exchange Membranes 107
 - Lorenz Gubler and Willem H. Koppenol
- 5.1 Introduction 107
- 5.2 Radical Intermediates in Fuel Cells 108
- 5.3 Hydrocarbon Membranes 114
- 5.4 Chemical Stabilization by Antioxidants 119
- 5.4.1 Regenerative Radical Scavenging in PFSA Membranes 119
- 5.4.2 Hydrocarbon Membranes Doped with Organic Antioxidants 121
- 5.4.3 Polymer-Bound Antioxidants 122
- 5.5 The Challenge of Regeneration 125
- 5.5.1 Learnings from Mother Nature 125
- 5.5.2 Approaches for the Fuel Cell 126
- 5.6 Concluding Remarks 133 References 134
- 6 Stabilization of Perfluorinated Membranes Using Nanoparticle Additives 139

Guanxiong Wang, Javier Parrondo, and Vijay Ramani

- 6.1 Nanoparticle Additives as a Stabilizer for Perfluorinated Membranes 139
- 6.2 CeO₂ and Modified CeO₂ Nanoparticles as FRSs 141
- 6.3 Platinum-Supported Ceria as FRS 152
- 6.4 Manganese Oxide and Manganese Oxide Composite as FRSs 154
- 6.5 Metal Nanoparticles as FRSs 160
- 6.6 Experimental Techniques for the Detection of Free Radicals and Measurement of the Membrane Degradation Rates *163*
- 6.6.1 Fluoride Emission Rate 163
- 6.6.2 Fluorescence Spectroscopy as a Tool for the Detection and Quantification of Free Radical Degradation in PEMs *163*
- 6.7 Conclusions 164 Acknowledgments 165 References 166
- 7 Degradation Mechanisms in Aquivion® Perfluorinated Membranes and Stabilization Strategies 171 Vincenzo Arcella, Luca Merlo, and Alessandro Ghielmi
- 7.1 Introduction 171
- 7.2 Properties of SSC Ionomers 173
- 7.3 Properties of Aquivion[®] Ionomers 173
- 7.4 The Need for High Stability of PFSA Membranes 177
- 7.5 PFSA Membrane Degradation in Fuel Cell 177

x Contents

- Generation of Radical Species in the Fuel Cell Environment 178 7.6
- Degradation Studies on Aquivion[•] Membranes 181 7.7
- Stabilization Procedures on Aquivion[•] Membranes 185 7.8
- Conclusions 190 7.9
 - References 190
- Anion Exchange Membranes: Stability and Synthetic Approach 195 8 Dongwon Shin, Chulsung Bae, and Yu Seung Kim
- Introduction 195 8.1
- Chemical Degradation Mechanisms 196 8.2
- Degradation of Cationic Groups 196 8.2.1
- 8.2.1.1 Alkyl Ammoniums 196
- 8.2.1.2 N-Based Cyclic Cations 199
- 8.2.1.3 Other Cationic Groups 202
- Degradation of Polymer Backbones 204 8.2.2
- 8.2.2.1 Polyolefins 205
- 8.2.2.2 Polyaromatics 205
- 8.2.2.3 Polyacrylates 207
- 8.2.2.4 Polybenzimidazoles 208
- Perfluorinated Polymers 208 8.2.2.5
- Synthetic Approaches 210 8.3
- Polyolefins 210 ·8.3.1
- 8.3.1.1 Polyethylene and Polypropylene 211
- 8.3.1.2 Polystyrene 212
- 8.3.1.3 Others 215
- Polyaromatics 217 8.3.2
- 8.3.2.1 Cationic-Group-Tethered Poly(arylene)s 217
- 8.3.2.2 Poly(arylene)-Containing Cationic Polymer Backbones 219
- 8.3.2.3 Multication-Tethered Poly(arylene)s 219
- 8.3.3 Other Polymers 221
- 8.3.3.1 Polybenzimidazoles 221
- 8.3.3.2 Polynorbornenes 223
- 8.3.3.3 Perfluorinated Polymers 224
- 8.4 Conclusions 225 Acknowledgments 225 References 226
- Profiling of Membrane Degradation Processes in a Fuel Cell 9 by 2D Spectral–Spatial FTIR 229
 - Shulamith Schlick and Marek Danilczuk
- 9.1 Introduction 229
- Optical Images of Nafion[•] Cross Sections 231 9.2

- 9.3 Line Scan Maps of the Membranes 232
- 9.4 FTIR Spectra of Nafion[•] MEAs 232
- 9.5 Abstraction of a Fluorine Atom on a Carbon in the Nafion[•] Main Chain by H[•] 235
- 9.6 Conclusions 237 Acknowledgments 237 References 238
- 10 Quantum Mechanical Calculations of the Degradation in Perfluorinated Membranes Used in Fuel Cells 241 Tod H. Yu. Poris V. Mariney, and William A. Coddard III

Ted H. Yu, Boris V. Merinov, and William A. Goddard III

- 10.1 Introduction 241
- 10.2 Computational Methods 244
- 10.3 Results and Discussion 244
- 10.3.1 Generation of Radicals 244
- 10.3.1.1 Hydroxyl Radicals 244
- 10.3.1.2 Hydrogen Radicals, H[•] 247
- 10.3.1.3 Hydroperoxyl Radicals, HOO* 249
- 10.3.2 Concentrated HO[•] Conditions versus Fuel Cell Conditions 249
- 10.3.3 Degradation under Concentrated HO[•] Conditions 249
- 10.3.3.1 R-CF₂H Polymer Main Chain Defect Initiation 249
- 10.3.3.2 R-CF=CF₂ Polymer Main Chain Defect Initiation 250
- 10.3.3.3 R-COOH Polymer Main Chain Defect Initiation 250
- 10.3.3.4 Propagating Polymer Main Chain Degradation 250
- 10.3.3.5 Side-Chain Degradation 252
- 10.3.4 Degradation under Fuel Cell Conditions with Fuel Crossover 256
- 10.3.4.1 Polymer Main Chain End-Group Initiation 256
- 10.3.4.2 Propagating Polymer Main Chain Degradation 256
- 10.3.4.3 Side-Chain Degradation 257
- 10.3.5 Degradation under Fuel Cell Conditions without Crossover 259
- 10.3.5.1 Degradation at the Cathode without H₂ Crossover 259
- 10.3.5.2 Degradation at the Anode without O₂ Crossover 261
- 10.4 Summary 265
- 10.4.1 Concentrated HO[•] Conditions 265
- 10.4.2 Fuel Cell Conditions 265
- 10.4.2.1 Fuel Cell Conditions without Crossover at Cathode 266
- 10.4.2.2 Fuel Cell Conditions without Crossover at Anode 266 Acknowledgments 267 References 267

Index 271