
Contents

Acronyms and Abbreviations	xi
1 PEM Fuel Cells and their Related Electrochemical Fundamentals	1
1.1 Fuel Cell Description.....	1
1.2 Fuel Cell Types.....	4
1.2.1 H ₂ /Air Fuel Cells	5
1.2.2 Direct Liquid Fuel Cells	8
1.2.3 Alkaline Fuel Cells	10
1.2.4 Phosphoric Acid Fuel Cells	11
1.3 Fuel Cell Challenges.....	12
1.4 PEM Fuel Cell Electrochemistry	13
1.4.1 Electrochemistry Fundamentals.....	13
1.4.2 Polarization Curves	20
1.4.3 Current Interruption.....	20
1.4.4 Chronoamperometry	21
1.4.5 Cyclic Voltammetry	22
1.4.6 Electrochemical Impedance Spectroscopy	26
1.5 Fuel Cell Analysis.....	28
1.5.1 Open Circuit Voltage.....	29
1.5.2 Cell Voltage Under Load.....	31
1.5.3 Ohmic Drop	34
1.5.4 Mass Transfer Drop.....	34
1.5.5 Fuel Cell Efficiencies	35
1.6 Chapter Summary	36
References.....	36
2 Electrical Fundamentals	39
2.1 Introduction.....	39
2.2 Direct Current Circuits.....	40
2.2.1 Ohm's Law	40
2.2.2 Series and Parallel Circuits.....	41
2.2.3 Kirchhoff's Laws.....	42
2.2.4 Resistors in DC Circuits	43
2.2.5 Capacitors in DC Circuits.....	45
2.2.6 Inductors in DC Circuits.....	49
2.3 Alternating Current Circuits	50
2.3.1 Sinusoidal Systems	50
2.3.2 Resistors in AC Circuits	52

2.3.3	Capacitors in AC Circuits.....	53
2.3.4	Inductors in AC Circuits.....	53
2.4	Complex Algebra and Impedance.....	54
2.4.1	AC Impedance of a Resistor–Capacitor Circuit.....	56
2.4.2	AC Impedance of a Resistor–Inductor Circuit	59
2.4.3	AC Impedance of a Capacitor–Inductor Circuit.....	61
2.4.4	AC Impedance of a Resistor–Capacitor–Inductor Circuit	63
2.5	Network Circuit Analysis	72
2.5.1	Topological Features of a Network	72
2.5.2	Network Theorems	73
2.5.3	Transient Network Analysis	78
2.6	Basic Knowledge for Understanding EIS	81
2.6.1	Introduction	81
2.6.2	Nyquist and Bode Plots	82
2.6.3	Equivalent Circuit Models.....	84
2.6.4	Data Fitting of EIS.....	89
2.6.5	Applications.....	92
2.7	Chapter Summary... ..	93
	References.....	93
3	Impedance and its Corresponding Electrochemical Processes	95
3.1	Electrode/Electrolyte Interfaces.....	95
3.1.1	Introduction	95
3.1.2	Equivalent Circuit of an Electrode/Electrolyte Interface.....	96
3.1.3	Differences Between Solid State and Aqueous Electrochemistry	97
3.2	Faradaic Impedance	98
3.2.1	Calculation of the Faradaic Impedance at the Equilibrium Electrode Potential.. ..	98
3.2.2	Kinetic Parameters from Z_f	104
3.2.3	Vectorgraphs of Faradaic Impedance.....	108
3.3	Total Impedance of an Electrochemical System	109
3.3.1	Calculated Z_f Based on Experimental Measurements.....	109
3.3.2	Graphic Presentations of the Total Impedance	112
3.3.3	Impedance Plots of Real Electrochemical Systems Using the Complex Plane	116
3.3.4	Semicircle Rotation of the Impedance.....	118
3.4	Correlation of EIS with Other Electrochemical Techniques.....	123
3.4.1	EIS and the Polarization Curve.....	123
3.4.2	EIS and Current Interruption	128
3.5	EIS Measurements	129
3.6	Advantages and Limitations of EIS	133
3.6.1	EIS Advantages	133
3.6.2	EIS Limitations.....	134
3.7	Chapter Summary	135
	References.....	136

4	EIS Equivalent Circuits.....	139
4.1	Electrochemical Elements.....	139
4.1.1	Lumped Elements.....	139
4.1.2	Frequency-Dependent Elements.....	140
4.1.3	Bounded Frequency-Dependent Elements.....	142
4.2	Basic Equivalent Circuits.....	143
4.2.1	Simple Combinations of Electrical Elements.....	143
4.2.2	Randles Cell.....	154
4.2.3	Structural Circuits.....	168
4.2.4	Other Circuits	177
4.3	Brief Discussion of Equivalent Circuits in PEM Fuel Cells	180
4.3.1	Gas Diffusion Layers.....	180
4.3.2	Catalyst Layers	180
4.3.3	Proton Exchange Membranes.....	184
4.3.4	Conductive Polymers.....	184
4.3.5	Membrane Electrode Assemblies	191
4.4	Chapter Summary	191
	References.....	191
5	EIS Diagnosis for PEM Fuel Cell Performance	193
5.1	Ex Situ Diagnosis.....	193
5.1.1	Electrode Characterization	193
5.1.2	Membrane Characterization	202
5.1.3	Comparison of Ex Situ and In Situ EIS Methods	212
5.2	In Situ Diagnosis.....	213
5.2.1	Different Gas Feeding Modes.....	214
5.2.2	Measurement Modes	237
5.2.3	Operating Conditions.....	239
5.2.4	Reference Electrodes	243
5.3	EIS Under Heavy Duty	250
5.3.1	Introduction	250
5.3.2	Grounded Mode.....	251
5.3.3	Floating Mode	254
5.4	Fast EIS.....	255
5.4.1	Principles and Measurements	255
5.4.2	Differences Between Frequency Domain and Time Domain	256
5.5	Chapter Summary	257
	References.....	258
6	EIS Applications	263
6.1	EIS Applications in PEMFCs	263
6.1.1	Optimization of MEA Structure	264
6.1.2	Ionic Conductivity	288
6.1.3	Contamination	295
6.1.4	Stack and Individual Cell Impedance	298
6.1.5	Localized EIS	307
6.1.6	EIS at High Temperatures	313

6.2	EIS Applications in DMFCs	323
6.2.1	Ex Situ Methanol Oxidation	323
6.2.2	In Situ Anode Reaction	335
6.2.3	Determination of the Ionic Resistance.....	338
6.2.4	In Situ Cathode Reaction.....	339
6.3	Chapter Summary	342
	References.....	342
Appendix A: Fourier Transform.....		347
Appendix B: Laplace Transform		353
Appendix C: Kramers–Kronig Transform		363
Appendix D: Effects of Equivalent Circuit Parameters on Nyquist Plots		371
Contributor Biographies.....		411
Index		413