


San Ping Jiang · Qingfeng Li

Introduction to Fuel Cells

Electrochemistry and Materials

 Springer

Contents

Part I Fundamentals

1	Introduction	3
1.1	Fuel Cells in the Hydrogen Chain	3
1.2	A Brief History of Fuel Cells	5
1.3	Types, Construction, and Components of Fuel Cells	8
1.3.1	Fuel Cell Classification	8
1.3.2	Construction and Components of Fuel Cells	9
1.3.3	Brief Summary of Each Type of Fuel Cells	12
1.4	Fuel Cells Versus Batteries	16
1.5	Unitized Regenerative Fuel Cells and Reversible Fuel Cells	17
1.6	Applications and Prospect of Fuel Cell Technologies	19
1.7	Summary	23
1.8	Questions	24
1.9	General Readings	25
	References	25
2	Fuel Cell Thermodynamics	27
2.1	Internal Energy, Heat, Work, and Entropy	27
2.2	Enthalpy and Gibbs Free Energy	31
2.2.1	Definition of Enthalpy and Gibbs Free Energy	31
2.2.2	Gibbs Free Energy from First and Second Thermodynamics Laws	32
2.2.3	Enthalpy of Formation	33
2.2.4	Effect of Temperature on the Change in Enthalpy and Entropy	36
2.2.5	Effect of Temperature on Gibbs Free Energy	40
2.2.6	Gibbs Free Energy and Electrical Work	41
2.2.7	Thermodynamic Reversible Potential and Thermoneutral Potential	43

2.2.8	Effect of Temperature and Pressure on Reversible Potential	46
2.3	Nernst Equation	48
2.4	Comparison of Work Done by a Heat Engine and Fuel Cell	51
2.4.1	Work Done in a Heat Engine and Carnot Efficiency	52
2.4.2	Fuel Cell Efficiency, Stoichiometry Number, Fuel and Oxygen Utilization Efficiency	54
2.4.3	Other Attributes of ICE and Fuel Cells	60
2.5	Thermodynamics and Efficiency of Water Electrolysis	60
2.5.1	Basic Thermodynamics of Water Electrolysis	61
2.5.2	Thermal Balance of Electrolysis Cells	62
2.5.3	Energy Efficiency of Water Electrolysis	63
2.5.4	High-Temperature Electrolysis	64
2.6	Summary	65
2.7	Questions	66
2.8	General Readings	68
3	Fuel Cell Electrochemistry	69
3.1	Electrochemistry at the Interface	69
3.1.1	Origin of Double Layer Structure	70
3.1.2	Standard Hydrogen Reference Electrodes	72
3.1.3	Other Reference Electrodes	75
3.1.4	Electrode Potential and Standard Reduction Potential	77
3.1.5	Concentration Cells	79
3.2	Activation and Activation Polarization Loss	81
3.2.1	Why Charge Transfer at the Interface	81
3.2.2	Butler–Volmer Equation	83
3.2.3	Tafel Plot	86
3.2.4	Effect of Exchange Current Density	88
3.2.5	Effect of Tafel Slope	91
3.3	Ohmic Polarization Loss	92
3.4	Mass Transport and Concentration Polarization in Steady State	95
3.5	I-V Characteristics	99
3.5.1	Cell Voltage and Various Types of Voltage Losses	99
3.5.2	Open-Circuit Voltage Loss	101
3.5.3	I-V Characteristics and Materials Issues	104
3.6	Basic Electrochemical Techniques	106
3.6.1	Rotating Disk and Rotating Ring Disk Electrodes	106
3.6.2	Linear Sweeping and Cyclic Voltammetry Techniques	112
3.6.3	Electrochemical Impedance Spectroscopy (EIS)	114
3.7	Summary	119

3.8	Questions	121
3.9	General Readings	122
	References	122
4	Fuels for Fuel Cells	123
4.1	Introduction	123
4.2	Hydrogen Production	126
4.2.1	Steam Reforming	128
4.2.2	Water Electrolysis	130
4.3	Hydrogen Storage	141
4.3.1	Physical Storage of Hydrogen	141
4.3.2	Reversible and Irreversible Hydrides	142
4.4	Methanol, Ethanol, Formic Acid, and Other Liquid Fuels	144
4.4.1	Electrochemical Oxidation of Alcohols	145
4.4.2	Effect of pH and Temperature on Alcohol Oxidation Reactions	153
4.4.3	Energy Density, Environment Effect, and By-Products of Various Fuels	157
4.5	Ammonia, Urea, and Hydrazine	159
4.5.1	Ammonia Oxidation Reaction	159
4.5.2	Hydrazine Oxidation Reaction	162
4.5.3	Toxicity Issues	164
4.6	Natural Gas, Hydrocarbons, and Biomass-Derived Synthetic Fuels	164
4.7	Summary	166
4.8	Questions	167
	References	168

Part II Polymer Electrolyte Membrane Fuel Cells

5	Polymer Electrolyte Membrane Fuel Cells: Principles and Materials	173
5.1	Introduction	173
5.2	Proton-Conducting Electrolytes	174
5.2.1	Electrolytes for Low-Temperature Fuel Cells	174
5.2.2	Proton Conduction Mechanisms and Materials	177
5.3	Proton Exchange Membranes	181
5.3.1	Poly(Perfluorosulfonic Acid) Membranes	182
5.3.2	Short Side-Chain PFSA Membranes	190
5.3.3	PFSA Composite Membranes	191
5.3.4	Alternative Membranes	195
5.4	Electrocatalysts	196
5.4.1	Anode Catalysts	197
5.4.2	Cathode Catalysts	198
5.4.3	Carbon Supports	207
5.5	Electrodes and Membrane Electrode Assembly	214

5.5.1	Gas Diffusion Layer	214
5.5.2	Microporous Layers	218
5.5.3	Catalyst Layer	219
5.6	Bipolar Plates and Seals	222
5.7	Summary	223
5.8	Questions	224
5.9	General Readings	226
	References	227
6	Polymer Electrolyte Membrane Fuel Cells: Fabrication and Characterization	229
6.1	Proton Exchange Membranes	229
6.1.1	PFSA Membrane Fabrication	229
6.1.2	Ion-Exchange Capacity and Equivalent Weight	231
6.1.3	Water Uptake and Swelling	232
6.1.4	Proton Conductivity	235
6.1.5	Electroosmotic Drag of Water	238
6.1.6	Water and Methanol Diffusion	241
6.1.7	Solubility and Diffusion of Oxygen	242
6.1.8	Permeability of Hydrogen	244
6.1.9	Methanol Crossover—Liquid and Vapor	248
6.1.10	Fenton Test	252
6.1.11	Mechanical Properties	254
6.1.12	Thermal Stability Test	256
6.2	Catalyst Synthesis	257
6.2.1	Impregnation–Reduction Method	257
6.2.2	Colloidal Adsorption Method	259
6.2.3	Self-assembly Method on CNT and Graphene Supports	261
6.3	Ex Situ Characterization of Catalysts	262
6.3.1	Catalyst Ink and Thin Catalyst Film	263
6.3.2	Three-Electrode Cell Configuration	263
6.3.3	Preconditioning and ORR Activity Measurement	265
6.3.4	Determination of the ECSA	266
6.3.5	Analysis of the Polarization Curves	268
6.3.6	Stability Test	271
6.3.7	Half-Cell Characterization	272
6.4	Fuel Cell Test for in Situ Characterization	275
6.4.1	Cell Assembling and Pretest Conditioning	275
6.4.2	Determination of ECSA	276
6.4.3	Membrane Durability Test	277
6.4.4	Catalyst Stability Test	279
6.5	Summary	285
6.6	Questions	286
6.7	General Readings	287
	References	288

7	Polymer Electrolyte Membrane Fuel Cells: Performance and Operation	291
7.1	Performance and Analysis	291
7.1.1	Analysis of i-V Curves	293
7.1.2	Ohmic Losses	294
7.1.3	ORR Kinetic Parameters	295
7.1.4	Mass Transport Losses	298
7.2	Fueling Options and CO Poisoning	299
7.2.1	CO Adsorption on Pt	300
7.2.2	CO Poisoning Effect	301
7.2.3	Relative Activity and Temperature Effect	302
7.2.4	CO Poisoning Mitigation and Bifunctional Mechanism	302
7.2.5	Catalysts for Methanol Electro-Oxidation	304
7.2.6	Other Effects of CO	304
7.3	Water Management	305
7.3.1	Water Balance and Transport	305
7.3.2	Saturated Water Vapor Pressure and Relative Humidity	306
7.3.3	Self-Humidification	307
7.3.4	External Humidification	309
7.3.5	Modified and Thinner Membranes	310
7.4	Thermal Management	311
7.4.1	Heat Generation	311
7.4.2	Cooling Duty and Radiator Area	312
7.4.3	Air Cooling Versus Water Cooling	313
7.4.4	Operating Points and Stack Calculation	314
7.5	Durability Issues and Mitigation	314
7.5.1	Status and Target of Durability	314
7.6	Summary	321
7.7	Questions	322
	References	323
8	High-Temperature Polymer Electrolyte Membrane Fuel Cells	325
8.1	Why and How High Temperatures	325
8.2	Polybenzimidazoles and Their Interactions with Phosphoric Acids	326
8.2.1	Synthesis and Molecule Weight Determination	326
8.2.2	Membrane Casting from DMAc Solutions and Acid Doping	328
8.2.3	Direct Cast Membranes	329
8.2.4	Membrane Characterization	330
8.2.5	PBI Variants	332
8.2.6	Cross-linking, Blends, and Thermal Curing	332
8.2.7	PBI Composite Membranes	336

8.3	Catalysts and Electrodes	336
8.3.1	Catalysts	336
8.3.2	Gas Diffusion Electrodes	341
8.3.3	Membrane Electrode Assemblies	341
8.4	Fuel Cell Performance and Operation	344
8.4.1	Performance and Pt Loading	344
8.4.2	Impact of Fuel Impurities and Water	345
8.5	Alternative High-Temperature Membranes	346
8.5.1	Non-PBI Based High-Temperature Membranes	346
8.5.2	Inorganic High-Temperature Membranes	347
8.6	Durability and Commercialization	349
8.7	Summary	351
8.8	Questions	351
8.9	General Readings	352
	References	352

Part III Solid Oxide Fuel Cells

9	Solid Oxide Fuel Cells: Principles and Materials	357
9.1	Introduction	357
9.1.1	Operation Principles	357
9.1.2	Charge Transport in Oxide Materials	360
9.2	Electrolyte	369
9.2.1	Zirconium Oxides	372
9.2.2	Cerium Oxides	375
9.2.3	Lanthanum Strontium Magnesium Gallate Perovskites	377
9.2.4	Apatite Oxides	379
9.2.5	Bismuth Oxides	380
9.3	Anode	381
9.3.1	Ni-Based Cermet Anode	383
9.3.2	Cu/CeO ₂ /YSZ-Based Anode	387
9.3.3	Ceramic Oxide Anode	387
9.4	Cathode	389
9.4.1	Lanthanum Strontium Manganite	390
9.4.2	Lanthanum Strontium Cobalt Ferrite	395
9.4.3	Other Perovskites, Double Perovskites, and Ruddlesden-Popper Structured Oxides	396
9.4.4	Composite Cathode	400
9.5	Interconnect and Sealant	403
9.5.1	Interconnect	403
9.5.2	Sealants	410
9.6	Cell Structures and Stack Design	412
9.6.1	Cell Structures	412
9.6.2	Stack Design	413

9.7	Variations of SOFCs	414
9.7.1	Single-Chamber Solid Oxide Fuel Cells	415
9.7.2	Metal-Supported Solid Oxide Fuel Cells	416
9.7.3	Direct Carbon Fuel Cells	417
9.8	Summary	418
9.9	Questions	420
	References	422
10	Solid Oxide Fuel Cells: Reactions	425
10.1	Surface Segregation of Oxide Electrodes	425
10.1.1	Surface Segregation Under Open Circuit	426
10.1.2	Surface Segregation Under Polarization	428
10.1.3	A Note	435
10.2	Reactions at the Cathode	436
10.2.1	Activation Process	436
10.2.2	Oxygen Reduction Reaction	439
10.2.3	Effect of Oxygen Vacancies	444
10.3	Reactions at the Anode	446
10.3.1	Hydrogen Oxidation Reaction	446
10.3.2	Hydrocarbon Fuel Oxidation Reaction	454
10.3.3	Redox Reaction	457
10.4	Interface and Interface Reactions	458
10.4.1	LSM and YSZ (Doped Ceria) Systems	458
10.4.2	Interface and Interaction Between LSCF and YSZ	462
10.4.3	LSCF/GDC/YSZ Interface	466
10.4.4	Other Interfaces	466
10.5	Reaction with Contaminants	467
10.5.1	Reactions Between Cathode and Contaminants	468
10.5.2	Reaction Between Anode and Contaminants	478
10.5.3	Contaminant-Tolerant Electrodes	483
10.6	Summary	487
10.7	Questions	490
	References	492
11	Solid Oxide Fuel Cells: Techniques and Characterization	497
11.1	Electrode Arrangement and Test Stations	497
11.1.1	Test Station Design and Arrangement	497
11.1.2	Electrode Arrangements	501
11.1.3	Comparative Experimental Approach	504
11.2	Cell Configurations and Performance Scalability	505
11.2.1	Cell Configurations	505
11.2.2	Symmetric Cell	506
11.2.3	Polarization Performance Analysis	509
11.3	Equipotential Line and Constriction Effect	517
11.3.1	Equipotential Line	517

11.3.2	Special Voltage Probe and Resistance Distribution	518
11.3.3	Relationship Between Validity of Reference Electrode and Electrolyte Thickness	525
11.3.4	Constriction Effect	527
11.4	Equivalent Circuit Analysis in Electrochemical Impedance Spectroscopy	529
11.4.1	Equivalent Circuit for Capacitance Impedance	531
11.4.2	Equivalent Circuit for Inductance Impedance	533
11.4.3	Physical Significance of Equivalent Circuit Elements	535
11.4.4	Impedance Measurement in SOFCs	537
11.5	Galvanostatic Current Interruption Technique	539
11.5.1	Comparison of EIS and GCI Techniques	541
11.6	Conductivity Measurement of SOFC Components and Materials	543
11.6.1	Two-Probe and Four-Probe Methods	543
11.6.2	Conductivity Measurement of Porous Electrode Coating	545
11.6.3	Contact Resistance Between Electrode and Current Collector	547
11.6.4	Ionic Conductivity of Electrolyte by EIS	548
11.7	Other Properties	550
11.7.1	Oxygen Surface Diffusion and Exchange Coefficient Measurements	550
11.7.2	Porosity and Density Measurement	552
11.7.3	Focus Ion Beam and Scanning Transmission Electron Microscopy (FIB-STEM)	553
11.8	Summary	557
11.9	Questions	558
	References	559
12	Solid Oxide Fuel Cells: Fabrication and Microstructure	561
12.1	Introduction	561
12.2	Powder Synthesis Methods	562
12.2.1	Solid-State Reaction and Physical Mixing Methods	562
12.2.2	Solution Combustion Method	563
12.2.3	Co-precipitation Method	566
12.2.4	Pechini and Polymeric Complexing Method	568
12.2.5	Sol-Gel Method	570
12.2.6	Gel-Casting Method	571
12.3	Fabrication Techniques for Electrolyte and Electrode Coatings	574
12.3.1	Die Pressing Method	575

12.3.2	Tape-Casting Method	576
12.3.3	Screen-Printing Method	579
12.3.4	Chemical Vapor Deposition and Atomic Layer Deposition	580
12.3.5	Electrochemical Vapor Deposition	580
12.3.6	Magnetron Sputtering Techniques	581
12.3.7	Pulsed Laser Deposition	584
12.3.8	Plasma Spray Deposition	584
12.3.9	Slurry-Coating, Spin-Coating and Dip-Coating Methods	586
12.3.10	Electrophoretic Deposition	589
12.3.11	Spray Pyrolysis and Flame-Assisted Vapor Deposition	591
12.4	High-Temperature Sintering Process	592
12.4.1	Anode	593
12.4.2	Cathode	595
12.4.3	Sintering Profile	597
12.4.4	High-Temperature Sintering Aids and Solid-State Reactive Sintering	599
12.5	Direct Assembly and Polarization-Induced Interface	600
12.6	Nano-Structured Electrodes	603
12.6.1	Wet-Infiltration Techniques	603
12.6.2	Decoration and Polarization-Induced Phase Migration	608
12.6.3	Nanosized Catalysts by in Situ Exsolution	611
12.6.4	Microstructure and Microstructure Stability	612
12.7	Cell Fabrication	614
12.7.1	Planar Cells	614
12.7.2	Tubular Cells	615
12.8	Summary	616
12.9	Questions	618
	References	619

Part IV Other Fuel Cells

13	Alkaline Fuel Cells	623
13.1	Introduction	623
13.2	Alkaline Fuel Cells	624
13.2.1	Electrolyte for AFC	624
13.2.2	Catalysts	625
13.2.3	Gas Diffusion Electrodes for Liquid Electrolytes	627
13.2.4	Electrolyte Configuration	632
13.2.5	Stack Design	636
13.2.6	Carbonization and CO ₂ Scrubbing	636
13.2.7	Performance and Durability	638

13.3	Anion Exchange Membrane Fuel Cells	639
13.3.1	AEM Electrolyte	640
13.3.2	Catalyst Development	643
13.3.3	Performance	644
13.4	Summary	646
13.5	Questions	647
	References	648
14	Phosphoric Acid Fuel Cells	649
14.1	Introduction	649
14.2	Phosphoric Acid	649
14.2.1	Acid Chemistry	649
14.2.2	Conductivity and Mechanism	651
14.2.3	Vapor Pressure and Thermal Stability	653
14.3	Cell Components	654
14.3.1	Catalysts	654
14.3.2	Gas Diffusion Electrodes	660
14.3.3	Matrix and Acid Reservoir	661
14.3.4	Bipolar or Separate Plates	663
14.3.5	Seals and Coolers	663
14.4	Performance and Cell Management	664
14.4.1	Performance and Lifetime	664
14.4.2	Acid Evaporation and Mitigation	667
14.4.3	Migration of Acid and Management	667
14.5	Summary	668
14.6	Questions	669
	References	670
15	Molten Carbonate Fuel Cells	673
15.1	Introduction	673
15.2	Electrolytes	676
15.2.1	Alkali Metal Carbonates	676
15.2.2	Acid—Base Chemistry	677
15.2.3	Properties of Molten Carbonate Systems	678
15.2.4	Comparison of Li/K and Li/Na Systems	679
15.3	Cathode Reactions and Materials	680
15.3.1	Oxygen Reduction Reaction in Molten Carbonates	680
15.3.2	Cathode Materials	681
15.3.3	NiO Dissolution and Precipitation	681
15.3.4	Electrolyte Additives and Alternative Materials	682
15.4	Anode Reactions and Materials	683
15.5	Matrix and Immobilization of Molten Carbonate Electrolyte	685
15.5.1	Matrix Materials	685
15.5.2	Immobilization and Distribution of Electrolyte	685
15.5.3	Matrix Stability and Fabrication	686

15.6	Construction Materials	688
15.7	Performance and Durability	689
15.8	Summary	691
15.9	Questions	692
	References	692
16	Protonic Ceramic Oxide Fuel Cells, Microbial Fuel Cells, and Biofuel Cells	695
16.1	Protonic Ceramic Oxide Fuel Cells	695
16.1.1	Operation Principle of Protonic Ceramic Oxide Fuel Cells	696
16.1.2	Proton-Conducting Oxides	698
16.1.3	Electrode Materials for PCFCs	701
16.1.4	Other Applications of Proton-Conducting Oxides	703
16.1.5	Proton Conductivity Measurement	705
16.2	Microbial Fuel Cells	708
16.2.1	Microbial Fuel Cell Configuration	708
16.2.2	Catalysis in Microbial Fuel Cell Anode	710
16.2.3	Catalysis in Microbial Fuel Cell Cathode	712
16.2.4	Electron Transfer Mechanism	714
16.2.5	Challenges in MFCs	716
16.3	Biofuel Cells	716
16.4	Summary	718
16.5	Questions	719
	References	719