

Contents

Preface	v
Introduction	xiii
1 Fuel cell basics	1
1.1 Fuel cell thermodynamics	1
1.1.1 The physics of the fuel cell effect	1
1.1.2 Open-circuit voltage	4
1.1.3 Nernst equation	4
1.1.4 Temperature dependence of OCV	6
1.2 Potentials in a fuel cell	6
1.3 Rate of electrochemical reactions	9
1.3.1 Butler-Volmer equation	9
1.3.2 Butler-Volmer and Nernst equations	13
1.3.3 Tafel equation	15
1.4 Mass transport in fuel cells	16
1.4.1 Overview of mass transport processes	16
1.4.2 Stoichiometry and utilization	18
1.4.3 Quasi-2D approximation	19
1.4.4 Mass conservation equation in the channel	20
1.4.5 Flow velocity in the channel	22
1.4.6 Mass transport in gas-diffusion/backing layers	24
1.4.7 Mass transport in catalyst layers	27
1.4.8 Proton and water transport in membranes	28
1.5 Sources of heat in a fuel cell	32

1.6	Types of cells considered in this book	34
1.6.1	Polymer electrolyte fuel cells (PEFCs)	34
1.6.2	Direct methanol fuel cells (DMFCs)	36
1.6.3	Solid oxide fuel cells (SOFCs)	37
2	Catalyst layer performance	39
2.1	Basic equations	41
2.1.1	The general case	41
2.1.2	First integral	44
2.2	Ideal oxygen and proton transport	44
2.3	Ideal oxygen transport	45
2.3.1	Basic equations	45
2.3.2	Integral of motion	45
2.3.3	Equation for proton current	46
2.3.4	Low cell current	47
2.3.5	High cell current	48
2.3.6	The general polarization curve	51
2.3.7	Condition of negligible oxygen transport loss	53
2.4	Ideal proton transport	53
2.4.1	Basic equations	53
2.4.2	The x -shapes and polarization curve	53
2.4.3	Large cell current ($\zeta \gg 1$)	54
2.4.4	Small cell current ($\zeta \ll 1$)	55
2.5	Optimal oxygen diffusion coefficient	55
2.5.1	Reduction of the full system	55
2.5.2	Optimal oxygen diffusivity	56
2.6	Gradient of catalyst loading	58
2.6.1	Model	58
2.6.2	Polarization curve	62
2.7	DMFC anode	64
2.7.1	The rate of methanol oxidation	64
2.7.2	Basic equations and the conservation law	65
2.7.3	The general form of the polarization curve	67
2.7.4	Small variation of overpotential in the active layer	68
2.7.5	Active layer of variable thickness	71

2.8	Heat balance in the catalyst layer	74
2.8.1	Heat transport equation in the CL	75
2.8.2	Reduction to the boundary condition	76
2.8.3	Solution to the heat transport equation	77
2.9	Remarks on Chapter 2	79
3	One-dimensional model of a fuel cell	83
3.1	Voltage loss due to oxygen transport in the GDL	84
3.2	1D polarization curve of a cell	86
3.3	1D model of DMFC	87
3.3.1	Feed molecule concentration in the active layers . . .	88
3.3.2	1D polarization curve of DMFC	92
3.4	Heat transport in the MEA of a PEFC	93
3.4.1	General assumptions	93
3.4.2	Equations	94
3.4.3	Exact solutions	97
3.4.4	Temperature profiles	98
3.4.5	How to measure thermal conductivities of MEA layers	100
3.4.6	One-sided fluxes from the MEA	102
3.4.7	Heat crossover through the membrane	104
3.5	Heat transport in the MEA of a DMFC	105
3.5.1	Assumptions	106
3.5.2	Equations	107
3.5.3	Heat transport under open-circuit conditions	110
3.5.4	How to measure thermal conductivities of MEA layers	111
3.5.5	Temperature profiles and discussion	113
3.5.6	Exact solutions for finite current	114
4	Quasi-2D model of a fuel cell	117
4.1	Gas dynamics of channel flow	118
4.1.1	Momentum balance in the cathode flow	119
4.1.2	The limit of low flow velocity	120
4.2	A model of PEFC	123
4.2.1	Oxygen concentration and local current along the channel	124

4.2.2	Cell polarization curve	127
4.2.3	Water crossover and the polarization curve	128
4.2.4	Local polarization curves	131
4.3	A model of PEFC with water management	133
4.3.1	Model and governing equations	134
4.3.2	Solution at constant flow velocity	136
4.3.3	Close to the limiting current density ($\tilde{E}_0 \rightarrow \infty$)	137
4.3.4	The general case (finite $\tilde{E}_0$)	140
4.3.5	Model validation	141
4.3.6	Limiting current and optimal feed composition	142
4.3.7	Constant oxygen stoichiometry	143
4.4	Degradation wave	147
4.4.1	Model	147
4.4.2	Wave propagation	149
4.4.3	Cell potential	151
4.4.4	Two scenarios of cell performance degradation	153
4.4.5	Accelerated testing of ageing phenomena	154
4.5	Gradient of catalyst loading along the oxygen channel	156
4.5.1	Low cell current	157
4.5.2	High cell current	158
4.5.3	The effect of transport loss in the GDL	160
4.6	A model of SOFC anode	160
4.6.1	Basic equations and the local polarization curve	162
4.6.2	Hydrogen concentration in the channel	164
4.6.3	Cell voltage	165
4.6.4	Low current: z-shapes	166
4.6.5	Low current: Polarization curve	167
4.6.6	High current: z-shapes and polarization curve	169
4.6.7	Remarks	171
4.7	A model of DMFC	172
4.7.1	Continuity equations in the feed channels	173
4.7.2	Solution for the case of $\lambda^a = \lambda^c$	176
4.7.3	Cell depolarization at zero current: Mixed potential	178
4.7.4	Cross-linked feeding	181

4.7.5	Oxygen and methanol utilization, and mean crossover current density	183
4.7.6	Remarks	184
4.8	DMFC: The general case of arbitrary λ^a and λ^c	184
4.8.1	Equation for local current	184
4.8.2	Numerical solution	185
4.9	DMFC: Large methanol stoichiometry and small current	186
4.9.1	The shape of the jumper	186
4.9.2	Plateau	189
4.9.3	Critical air flow rate	190
4.9.4	Experimental verification	191
5	Modelling of fuel cell stacks	193
5.1	Temperature field in planar SOFC stacks	195
5.1.1	General assumptions	195
5.1.2	The general equation for bipolar plate temperature	196
5.1.3	Heat balance in the air channel	198
5.1.4	Heat balance in the BP	199
5.1.5	Cell polarization curve	201
5.1.6	Boundary conditions	202
5.1.7	Method of asymptotic expansion	203
5.1.8	Asymptotic solution	204
5.1.9	Local current	206
5.1.10	Example: Oxide-dominated stack resistivity	207
5.1.11	Remarks	208
5.2	Temperature gradient in SOFC stack	210
5.2.1	Stack and air temperatures	210
5.2.2	Temperature gradient	212
5.3	Thermal waves in SOFC stack	214
5.3.1	Basic equations	214
5.3.2	Stability analysis	216
5.3.3	Flow temperature is constant	217
5.3.4	Solution: The general case	218
5.3.5	Role of boundary conditions	222
5.3.6	Remarks	223

5.4	Heat effects in DMFC stack	226
5.4.1	General assumptions	226
5.4.2	Equations for stack and flow temperature	227
5.4.3	Asymptotic solution: The general case	231
5.4.4	Optimal stack temperature	234
5.5	Mirroring of current-free spots in a stack	236
5.5.1	Equation for bipolar plate potential	237
5.5.2	Cell polarization curve	239
5.5.3	Spot shape and numerical details	240
5.5.4	Numerical results	241
5.5.5	Analysis of equations: The length of mirroring	243
5.5.6	Remarks	248
5.6	Hybrid 3D model of SOFC stack	249
5.6.1	Thermal model	250
5.6.2	Electric problem	252
5.6.3	Numerical details	253
5.6.4	Numerical results	255
5.6.5	Analysis of governing equations	255
5.6.6	Temperature stratification	260
5.6.7	The mechanism of anomalous heat transport	261
5.7	Power generated and lost in a stack	262
5.7.1	The nature of voltage loss in bipolar plates	262
5.7.2	Power dissipated in a bipolar plate	263
5.7.3	Power dissipated in a thin bipolar plate	265
5.7.4	Useful power generated by the individual cell	267
5.7.5	Illustration: A 1D case	270
Bibliography		273
Abbreviations		283
Nomenclature		285
Index		293