Contents

2.1.2 2.1.3 2.1.4 2.1.5 2.1.6 2.1.6.1 2.1.6.2 2.2 2.2.1 2.2.2

2.2.3 2.2.4 2.3

Foreword XIII Preface XV

List of Contributors XIX

_	
1	Introduction 1
	Agata Godula-Jopek
1.1	Overview on Different Hydrogen Production Means from a
	Technical Point of View 10
1.1.1	Reforming 13
1.1.2	Electrolysis 14
1.1.3	Gasification 16
1.1.4	Biomass and Biomass-Derived Fuels Conversion 16
1.1.5	Water Splitting 18
1.2	Summary Including Hydrogen Production Cost Overview 21
	References 28
2	Fundamentals of Water Electrolysis 33
	Pierre Millet
2.1	Thermodynamics of the Water Splitting Reaction 33
2.1.1	Thermodynamic Functions of State 33

Pierre Millet
Thermodynamics of the Water Splitting Reaction 33
Thermodynamic Functions of State 33
Selection Criteria for Operating Temperature 35
Electrochemical Water Splitting 36
pH Dependence of Water Dissociation Voltage 37
Temperature Dependence of Water Dissociation Voltage 39
Pressure Dependence of Water Dissociation Voltage 41
General Pressure Dependence 42
Detailed Pressure Dependence 44
Efficiency of Electrochemical Water Splitting 46
Water Splitting Cells: General Characteristics 46
Main Sources of Energy Dissipation in Electrochemical Cells 48
Energy Efficiency of Water Electrolysis Cells 50
Faradaic Efficiency of Water Electrolysis Cells 51
Kinetics of the Water Splitting Reaction 52



۷ı	Contents	
	2.3.1	Half-Cell Reaction Mechanism in Acidic Media 52
	2.3.1.1	HER 52
	2.3.1.2	OER 53
	2.3.1.3	Kinetics 54
	2.3.2	Half-Cell Reaction Mechanism in Alkaline Media 56
	2.3.3	Role of Operating Temperature on the Kinetics 56
	2.3.4	Role of Operating Pressure on the Kinetics 58
	2.4	Conclusions 59
		Nomenclature 59
		Greek symbols 60
		Subscripts or superscripts 60
		Acronyms 60
		References 61
	3	PEM Water Electrolysis 63
		Pierre Millet
	3.1	Introduction, Historical Background 63
	3.2	Concept of Solid Polymer Electrolyte Cell 65
	3.3	Description of Unit PEM Cells 67
	3.3.1	General Description 67
	3.3.2	Membrane Electrode Assemblies 68
	3.3.2.1	Electrocatalysts 68
	3.3.2.2	Coating Processes 69
	3.3.2.3	Electrocatalytic Layers 71
	3.3.3	Current – Gas Distributors 72
	3.3.4	Spacers 74
	3.3.5	Bipolar Plates 74
	3.4	Electrochemical Performances of Unit PEM Cells 76
	3.4.1	Polarization Curves 76
	3.4.2	Characterization of Individual Electrodes 78
	3.4.3	Charge Densities and Electrode Roughness 79
	3.4.3.1	Half-Cell Characterization 80
	3.4.3.2	Full-Cell Characterization 82
	3.4.4	EIS Characterization 84
	3.4.5	Pressurized Water Electrolysis and Cross-Permeation
		Phenomena 87
	3.4.5.1	Origins of Cross-Permeation Phenomena 87
	3.4.5.2	Hydrogen and Oxygen Solubility in SPEs 88
	3.4.5.3	Nafion Permeability to Hydrogen and Oxygen 89
	3.4.5.4	A Simple Model to Account for Gas Cross-Permeation 90
	3.4.6	Durability Issues: Degradation Mechanisms and Mitigation
		Strategies 92
	3.5	Cell Stacking 94
	3.5.1	Different Stack Configurations 94
	3.5.2	Design of PEM Water Electrolysis Stack 94

3.5.3	Stack Performances 96
3.5.4	Diagnosis Tools and Maintenance 97
3.6	Balance of Plant 100
3.6.1	General Description 100
3.6.2	Cost Analysis 100
3.7	Main Suppliers, Commercial Developments and Applications 102
3.7.1	Commercial Status 102
3.7.2	Markets and Applications 104
3.8	Limitations, Challenges and Perspectives 105
3.8.1	Replacement of Platinum with Non-Noble Electrocatalysts 107
3.8.2	Replacement of Iridium with Non-Noble Electrocatalysts 108
3.8.3	New Polymeric Proton Conductors for Operation at More Elevated
	Temperatures 109
3.8.4	Operation at Elevated Current Densities 110
3.8.5	Operation at Elevated Pressures 110
3.9	Conclusions 111
	Nomenclature 113
	Greek symbols 113
	Subscripts or superscripts 114
	Acronyms 114
	References 114
4	Alkaline Water Electrolysis 117
	Nicolas Guillet and Pierre Millet
4.1	Introduction and Historical Background 117
4.2	Description of Unit Electrolysis Cells 121
4.2.1	General Description 121
4.2.2	Electrolyte 123
4.2.3	Electrodes and Catalysts 124
4.2.4	Diaphragm/Separator 128
4.2.4.1	Zero-Gap Assembly 131
4.2.4.2	Anionic Membranes 132
4.3	Electrochemical Performances of Alkaline Water Electrolysers 137
4.3.1	Polarization Curves 137
4.3.2	Comparison of Electrolyser Performances 138
4.3.3	Operation at Elevated Temperatures 139
4.3.3.1	Thermodynamics 140
4.3.3.2	Kinetics 142
4.3.3.3	Electrolyte Conductivity 142
4.3.4	Operation at Elevated Pressures 142
4.3.4.1	Hydrogen Compression 143
4.3.4.2	Pressurized Electrolysers 144
4.3.4.3	Advantages and Disadvantages 144
4.3.4.4	Best Solution? 146
4.4	Main Suppliers, Commercial Developments and Applications 147

VIII	Contents	
	4.4.1	Markets for Electrolysers 147
	4.4.1.1	Small-Scale Electrolyser Market (Less than 1 Nm ³ H ₂ h ⁻¹) 147
	4.4.1.2	Medium-Scale Electrolysers Market $(1-10 \text{ Nm}^3\text{H}_2 \text{ h}^{-1})$ 147
	4.4.1.3	Large Scale Electrolysers (10 to More than 100 Nm ³ H ₂ · h ⁻¹) 148
	4.4.2	Commercially Available Electrolyser Designs 150
	4.4.2.1	Oerlikon-Type Electrolyser 150
	4.4.2.2	Norsk Hydro-Type Electrolyser 154
	4.4.2.3	Zdansky/Lonza-Type Electrolyser 155
	4.4.3	Advanced Designs 156
	4.4.3.1	Metal Foam as Electrodes 156
	4.4.3.2	Gas Diffusion Electrodes 159
	4.4.3.3	Very High-Pressure Electrolysers 160
	4.5	Conclusions 161
		Nomenclature 162
		Greek Symbols 162
		Subscripts or Superscripts 162
		Acronyms 163
		References 163
	5	Unitized Regenerative Systems 167 Pierre Millet
	5.1	Introduction 167
	5.2	Underlying Concepts 168
	5.2.1	Thermodynamics 168
		•

5.1	Introduction 167
5.2	Underlying Concepts 168
5.2.1	Thermodynamics 168
5.2.2	Half-Cell Reactions 171
5.2.3	Process Reversibility 172
5.3	Low-Temperature PEM URFCs 174
5.3.1	Principles 174
5.3.2	Cell Structure and URFC Stack 175
5.3.3	Performances 176
5.3.3.1	Water Electrolysis Mode 176
5.3.3.2	Fuel Cell Mode 177
5.3.3.3	URFC Mode 178
5.3.4	Limitations and Perspectives 180
5.4	High-Temperature URFCs 182
5.4.1	Principles 182
5.4.2	Cell Structure 182
5.4.3	Performances 184
5.4.3.1	Water Electrolysis Mode 184
5.4.3.2	Fuel Cell Mode 184
5.4.3.3	URFC Mode 185
5.4.4	Limitations and Perspectives 186
5.5	General Conclusion and Perspectives 187
	Nomenclature 187
	Greek Symbols 188

Subscripts or Superscripts		188
Acronyms	188	
References	189	

6	High-Temperature Steam Electrolysis 191
	Jérôme Laurencin and Julie Mougin
6.1	Introduction 191
6.2	Overview of the Technology 191
6.3	Fundamentals of Solid-State Electrochemistry in SOEC 197
6.3.1	Cell Polarization Curve 198
6.3.1.1	Expression of the Cell Voltage $U(i)$ 198
6.3.1.2	Ohmic Losses and Contact Resistances 199
6.3.1.3	Anode and Cathode Polarization: Role of the Electrochemical
	Process on the Cell Polarization Curve 200
6.3.1.4	Global Decomposition of the Cell Polarization Curve 206
6.3.2	Fundamental for Electrochemistry, Mass and Charge Transfer in SOEC Electrodes 209
6.3.2.1	Electronic and Ionic Charge Transport into the Electrode 209
6.3.2.2	Gas Transport in the Electrode 215
6.3.2.3	Expression of the Source Terms: Kinetic of the Electrochemical
	Process 219
6.3.2.4	Specific Operating Mechanisms of Single-Phase SOEC Anode 223
6.3.2.5	Role of Microstructure in the Electrode Behaviour 228
6.3.3	Role of Temperature in SOEC Operation 236
6.3.3.1	Cell Thermal Regimes 236
6.3.3.2	Impact of Cell Temperature on Polarization Curve 239
6.3.4	Summary and Concluding Remarks 243
6.4	Performances and Durability 244
6.4.1	Performances 244
6.4.2	Durability 249
6.4.3	Stack Electrochemical and Thermal Management 252
6.5	Limitations and Challenges 253
6.5.1	Degradation Issues 254
6.5.2	System Integration and Economical Considerations 257
6.6	Specific Operation Modes 259
6.6.1	Pressurized Operation 259
6.6.2	Reversible Operation 260
6.6.3	Co-Electrolysis 261
	List of Terms 262
	Roman symbols 262
	Greek Symbols 263
	Abbreviations 264
	References 264

x	Contents	
	7	Hydrogen Storage Options Including Constraints and Challenges 273 Agata Godula-Jopek
	7.1	Introduction 273
	7.2	Liquid Hydrogen 276
	7.2.1	Liquid Hydrogen Storage Systems 279
	7.3	Compressed Hydrogen 281
	7.3.1	Compressed Hydrogen Storage Systems 282
	7.4	Cryo-Compressed Hydrogen 284
	7.4.1	Cryo-Compressed Hydrogen Storage Systems 284
	7.5	Solid-State Hydrogen Storage Including Materials and System-Related Problems 286
	7.5.1	Physical Storage - Overview 290
	7.5.2	Chemical Storage - Overview 297
	7.5.2.1	Solid-State Hydrogen Storage System Coupled with Electrolyser 301
	7.6	Summary 304 References 306
	8	Hydrogen: A Storage Means for Renewable Energies 311
		Cyril Bourasseau and Benjamin Guinot
	8.1	Introduction 311
	8.2	Hydrogen: A Storage Means for Renewable Energies (RE) 312
	8.2.1	Renewable Energy Sources: Characteristics and Impacts on Electrical Networks 312
	8.2.1.1	Intermittency and Limited Forecast of Renewable Production and Electrical Load 312
	8.2.1.2	Impacts of Non-Dispatchable Power Sources on Electrical Networks 314
	8.2.1.3	Solutions for Higher Penetration of Renewable Energies 316
	8.2.2	Energy Storage on Electrical Networks 318
	8.2.2.1	Technologies Characteristics 318
	8.2.2.2	Past, Present and Future Technology Choices 319
	8.2.2.3	Possible Roles of Energy Storage on the Grid 320
	8.2.3	Hydrogen for Energy Storage 323
	8.2.3.1	Power to Hydrogen: Use of Electrolysis to Store Electrical Energy 323
	8.2.3.2	Attractiveness of Hydrogen: Not Only an Energy Carrier 324
	8.2.3.3	Use of Hydrogen to Produce Electricity 326

Electrolysis Powered by Intermittent Energy: Technical Challenges,

Effect of Intermittency on System Design and Operation 327

Impact on Power Electronics and Process Control 329

Requirements to Allow Dynamic Operation 332

Impact on Performances and Reliability 327

Impact on Downstream Elements 334

8.3

8.3.1

8.3.1.1

8.3.1.2 8.3.1.3

8.3.2	System Performances and Reliability under Dynamic Operation 334
8.3.2.1	Impact on Hydrogen Production Characteristics 335
8.3.2.2	Impact on System Efficiency 337
8.3.2.3	Impact of Intermittency on Reliability and Durability 341
8.3.2.4	Specificities of High-Temperature Steam Electrolysis 343
8.3.3	Improvements on Design and Operation to Manage
	Intermittency 345
8.3.3.1	Improvements on System Design 345
8.3.3.2	Improvements on Operating Strategies 347
8.3.3.3	Which Technology Best Suited to Intermittent Sources? 349
8.4	Integration Schemes and Examples 351
8.4.1	Autonomous Applications 351
8.4.1.1	Production of Renewable Hydrogen 352
8.4.1.2	Stand-Alone Power System with Hydrogen as Storage of Electrical
	Energy 353
8.4.2	Grid-Connected Applications 356
8.4.2.1	Production of Renewable Hydrogen with Grid Assistance 356
8.4.2.2	Electrolysis for Renewable Energy Storage 357
8.4.2.3	Renewable Source, Grid and Electrolysis Integrated Energy
	System 358
8.4.3	High-Temperature Steam Electrolysis Integration with Renewable Source 361
8.5	Techno-Economic Assessment 362
8.5.1	Hydrogen from Electrolysis: Future Markets 362
8.5.1.1	Hydrogen for Off-Grid Applications 363
8.5.1.2	Hydrogen for Mobility 363
8.5.1.3	Power to Hydrogen - A Way to Provide Services to the
	Network 364
8.6	The Role of Simulation for Economic Assessment 365
8.6.1	Objectives of the Simulation 365
8.6.2	Simulation's Main Input Data – Impact on the Robustness of the
	Results 367
8.6.2.1	Components, Architectures and Component Models 368
8.6.2.2	Control Strategies 371
8.6.2.3	Simulation Temporal Characteristics 372
8.6.2.4	Simulation Results 373
8.6.3	Optimization and Sensitivity Analysis 375
8.6.3.1	Principles 375
8.6.3.2	Objectives 375
8.6.3.3	Main Difficulty and Solutions Related to Simulation 376
8.6.4	Example of Existing Software Products for Techno-Economic
	Assessments of Hydrogen-Based Systems 376
8.7	Conclusion 378
	References 379

XII Contents	
9	Outlook and Summary 383
	Agata Godula-Jopek and Pierre Millet
9.1	Comparison of Water Electrolysis Technologies 387
9.2	Technology Development Status and Main Manufacturers 387
9.2.1	Alkaline Water Electrolysis 387
9.2.2	PEM Water Electrolysis 389
9.2.3	Solid Oxide Water Electrolysis 390
9.3	Material and System Roadmap Specifications 390
9.3.1	Alkaline Water Electrolysis 392
9.3.2	PEM Water Electrolysis 392
9.3.3	Solid Oxide Water Electrolysis 393
	References 393

Index 395