Contents

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

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
    2.1.2 Selection Criteria for Operating Temperature  35
    2.1.3 Electrochemical Water Splitting  36
    2.1.4 pH Dependence of Water Dissociation Voltage  37
    2.1.5 Temperature Dependence of Water Dissociation Voltage  39
    2.1.6 Pressure Dependence of Water Dissociation Voltage  41
    2.1.6.1 General Pressure Dependence  42
    2.1.6.2 Detailed Pressure Dependence  44
  2.2 Efficiency of Electrochemical Water Splitting  46
    2.2.1 Water Splitting Cells: General Characteristics  46
    2.2.2 Main Sources of Energy Dissipation in Electrochemical Cells  48
    2.2.3 Energy Efficiency of Water Electrolysis Cells  50
    2.2.4 Faradaic Efficiency of Water Electrolysis Cells  51
  2.3 Kinetics of the Water Splitting Reaction  52
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
4.4 Markets for Electrolysers
4.4.1 Small-Scale Electrolyser Market (Less than 1 Nm³H₂ h⁻¹) 147
4.4.1.1 Medium-Scale Electrolysers Market (1–10 Nm³H₂ h⁻¹) 147
4.4.1.3 Large Scale Electrolysers (10 to More than 100 Nm³H₂ ·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
5.2.2 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
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
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
8.3 Electrolysis Powered by Intermittent Energy: Technical Challenges, Impact on Performances and Reliability 327
8.3.1 Effect of Intermittency on System Design and Operation 327
8.3.1.1 Impact on Power Electronics and Process Control 329
8.3.1.2 Requirements to Allow Dynamic Operation 332
8.3.1.3 Impact on Downstream Elements 334
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
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