

Table of Contents

Preface	xi
Chapter 1. Basic Concepts of Electrochemistry used in Electrical Engineering	1
1.1. Introduction	1
1.2. Brief description and principles of operation of electrochemical components	1
1.2.1. Principle of operation	1
1.2.2. Brief description of groups of components	4
1.3. Redox reaction	7
1.4. Chemical energy	9
1.4.1. Enthalpy, entropy and free energy	9
1.4.2. Enthalpy, entropy and free energy of formation	10
1.5. Potential or voltage of an electrode	10
1.6. Reversible potential of a cell	11
1.7. Faradaic current density and the Butler–Volmer equation	13
1.8. Butler–Volmer equation for a whole cell	15
1.9. From the Butler–Volmer equation to the Tafel equation	17
1.10. Faraday’s law	19
1.11. Matter transfer model: Nernst model	20
1.12. Concept of limit current	22
1.13. Expression of the polarization curve	24
1.14. Double-layer capacity	27
1.15. Electrochemical impedance	27
1.16. Reagents and products in the gaseous phase: total pressure, partial pressure, molar fraction and mixture	30

1.17. Corrected exercises	31
1.17.1. Calculation of the variation in enthalpy during the formation of a mole of water	31
1.17.2. Calculation of the variation in entropy for the formation of a mole of water	34
1.17.3. Calculation of the variation in free energy during the formation of a mole of water	36
1.17.4. Calculation of the Nernst potential for a cell in a PEM fuel cell (PEMFC)	38
1.17.5. Faraday equations for a Pb accumulator	39
1.17.6. Calculation of the mass of water consumed by an electrolysis cell	40
Chapter 2. Water Electrolyzers	41
2.1. Introduction	41
2.2. Principles of operation of the main water electrolyzers	44
2.3. History of water electrolysis	46
2.4. Technological elements	51
2.4.1. Alkaline technology	51
2.4.2. PEM technology	56
2.4.3. SO technology	61
2.4.4. Comparison of the three water electrolyzer technologies	64
2.4.5. Specifications of a commercial electrolyzer	65
2.5. Theoretical approach to an electrolyzer	67
2.5.1. Energy-related elements	67
2.5.2. Electrical behavior in the quasi-static state	80
2.5.3. Electrical behavior in the dynamic state with a large signal	95
2.5.4. Electrical behavior in a dynamic state with a small signal (impedance)	100
2.6. Experimental characterization of the electrical behavior of an electrolyzer	104
2.6.1. Polarization curve (quasi-static characterization)	106
2.6.2. Impedance spectroscopy (dynamic small-signal characterization)	108
2.6.3. Current steps	110
2.6.4. Current sweeping (large-signal dynamic characterization)	111
2.6.5. Combining the approaches to characterization (advanced approach)	111
2.7. Procedures for parameterizing the models	112
2.7.1. Minimal combinatorial approach to experimental characterizations	113
2.7.2. Multiple impedance spectra approach	114

2.7.3. Low-frequency multi-sweeping approach	114
2.7.4. Toward an optimal and systematic combinatorial exploitation of the experimental characterizations	115
2.8. Combination with a fuel cell. Concept of the “hydrogen battery”	116
2.8.1. General considerations.	117
2.8.2. Static characteristics of an H ₂ /O ₂ battery	119
2.8.3. Deadband of an H ₂ /O ₂ battery	120
2.8.4. Brief overview of situation with industrial developments	122
2.9. A few examples of applications for electrolyzers	123
2.9.1. Points about industrial hydrogen production by electrolysis.	124
2.9.2. State of the art on applications coupling solar photovoltaic and hydrogen; close examination of the French projects MYRTE, PEPITE and JANUS	126
2.10. Some points about the storage of hydrogen	135
2.11. Conclusions and perspectives	137
2.12. Exercises.	137
Chapter 3. Fuel Cells	151
3.1. Introduction.	151
3.2. Classification of fuel cell technologies.	152
3.2.1. Classification on the basic of the acid/basic medium	153
3.2.2. Classification on the basis of the operating temperature	154
3.2.3. Classification on the basis of the type of electrolyte	154
3.3. Proton Exchange Membrane Fuel Cells (PEMFCs)	157
3.3.1. Constitution	157
3.3.2. Characteristics.	160
3.4. Solid Oxide Fuel Cells (SOFCs)	168
3.5. Fuel-cell systems	171
3.5.1. General points	171
3.5.2. PEMFC systems	173
3.5.3. SOFC systems.	179
3.6. Applications for fuel cells	180
3.6.1. Mobile applications.	181
3.6.2. Stationary applications.	183
3.6.3. Applications in transport	184
3.7. Corrected exercises	190
3.7.1. Calculation of the cost of platinum for an electrode	190
3.7.2. Dimensions of a “standard” fuel cell module	191
3.7.3. Calculation of the flowrate of reactant gases entering the cell	191
3.7.4. Calculation of the water content of the air upon input and output of the cell. Calculation of the dew point at the cell output	193
3.7.5. Calculation of the yield of a PEMFC	197

viii Electrochemical Components

3.7.6. Autonomy of an exploration submarine	198
3.7.7. Power supply to an isolated farm site	199
3.7.8. Fuel-cell generator for a private vehicle	204
Chapter 4. Electrical Energy Storage by Supercapacitors	209
4.1. Introduction	209
4.2. Operation and energy characteristics of EDLCs	211
4.2.1. Structure and operation of supercapacitors	211
4.2.2. Electrical and energetic characterization of supercapacitors	214
4.3. Supercapacitor module sizing	219
4.3.1. Power-based design	220
4.3.2. Dimension design based on the energy stored by the supercapacitor	222
4.3.3. Balancing the supercapacitors	224
4.4. Supercapacitor modeling	226
4.5. DC/DC converter associated with a supercapacitor module	233
4.6. Thermal behavior of supercapacitors	234
4.6.1. Thermal modeling of supercapacitors	235
4.6.2. Modeling by thermal/electrical analogy	237
4.7. Hybrid electricity storage device: the LIC (Lithium Ion Capacitor)	238
4.8. Exercises – statements	240
Chapter 5. Electrochemical Accumulators	253
5.1. Introduction	253
5.2. Lead accumulators	253
5.2.1. Operational principle	253
5.2.2. Advantages and disadvantages to this technology	254
5.3. Nickel accumulators	255
5.3.1. Nickel-Cadmium (Ni-Cd) accumulator	255
5.3.2. Nickel Metal Hydride (Ni-MH) accumulator	256
5.3.3. Nickel-Zinc accumulator	258
5.4. Lithium accumulators	259
5.4.1. Why lithium?	259
5.4.2. Principle of their function	259
5.4.3. Advantages and disadvantages to these technologies	260
5.4.4. Lithium-ion technology	261
5.4.5. Lithium-metal-polymer technology	262
5.4.6. Other technologies	263
5.5. Characteristics of an accumulator or battery	264
5.5.1. Capacity	264
5.5.2. Internal resistance	266

5.5.3. Voltages	267
5.5.4. Energy	268
5.5.5. State of charge of a battery	268
5.6. Modeling of a battery	269
5.6.1. Thévenin model	269
5.6.2. Improved Thévenin model	270
5.6.3. FreedomCar model	271
5.7. Aging of batteries	272
5.8. Exercises	273
Chapter 6. Hybrid Electrical System	277
6.1. Introduction	277
6.2. Definitions	277
6.2.1. General points	277
6.2.2. Particular case of a hybrid electric vehicle	278
6.2.3. Hybrid electric system	279
6.3. Advantages to hybridization	279
6.3.1. Ragone plot	280
6.3.2. Different types of energy?	284
6.3.3. Taking account of non-energy-related criteria in the choice of a hybrid electricity storage solution	287
6.4. Management of the energy flows in a hybrid system	289
6.4.1. Optimization-based strategies	290
6.4.2. Rule-based strategies	291
6.4.3. Criteria for the supervision of the energy flows	292
6.5. Example of application in the domain of transport: the ECCE platform (<i>Evaluation des Composants d'une Chaine de traction Electrique – Evaluation of the Components</i> in an Electric Powertrain)	293
6.6. Corrected exercises	296
6.6.1. Ragone plot of an ideal battery	296
6.6.2. Ragone plot of an ideal capacitor	299
6.6.3. Design of an electric vehicle	302
6.6.4. Energy management in an electric vehicle	306
Bibliography	309
Index	321