# **Contents**

#### Preface ---- VII

## Acknowledgement —— IX

1	Introduction — 1
1.1	Mobility and electromobility —— 2
1.1.1	The fuel cell electric vehicle Hyundai ix35 — 3
1.1.2	Comparison of efficiency of the combustion engine and fuel
	cell <b>—— 10</b>
1.1.3	Some notes on the development of battery vehicles — 14
1.2	Hydrogen mobility —— 17
1.2.1	Hydrogen fuel cell busses and trucks —— 19
1.2.2	Vehicle range comparison 1994 versus 2017 —— 21
1.2.3	Hydrogen fuel cell bicycle —— 25
1.2.4	Hydrogen-powered submarines — 27
1.2.5	Fuel cell-powered airplanes —— 31
1.3	Solid oxide fuel cell for use in cars — 34
1.4	SOFC for laptops and cell phones — 34
1.5	Energy storage for stationary applications —— 35
1.5.1	Solid oxide fuel cell power plants —— 36
1.5.2	Hydrogen for stationary and residential applications —— 38
1.6	Driving with water? —— 42
2	The electrochemical double layer —— 45
2.1	Estimation of the capacitance by geometrical considerations — 49
2.2	Electrochemical double layer capacitors (supercapacitors) —— 51
2.2.1	Simple design of an electrochemical double layer capacitor —— 51
2.2.2	Operation principle of electrochemical double layer
	capacitors —— 53
2.2.3	Arrangement of charges and ions between supercapacitor electrodes —— 55
2.3	Ragone diagram —— 57
2.3.1	A supercapacitor with carbon powder electrodes — 61
2.3.2	Supercapacitors with monolithic carbon electrodes — 66
2.4	Activation of glassy carbon electrodes — 69
2.5	Electrical characteristics of the double layer capacitor —— 71
2.6	Determination of the time constant — 76
2.7	Determination of electric charge and capacitance — 78
2.8	Equivalent series resistance of capacitors — 79



2.8.1	Determination of the ESR with an ESR Meter —— 80
2.9	Determination of energy density —— 80
2.9.1	A word on electrolytes and electrolyte decomposition —— 81
2.10	Determination of power and power density —— 81
2.11	Fine structure of the double layer —— 82
2.11.1	Helmholtz' approach —— 82
2.11.2	The improved model for the double layer by Gouy and
	Chapman —— 84
2.11.3	The model by Otto Stern —— 85
2.11.4	Bockris-Müller-Devanathan Model —— 87
2.11.5	Dependency from the electrode material —— 88
2.11.6	The pseudocapacitance in RuO <sub>2</sub> — 88
2.12	The electrolytic capacitor —— 96
2.13	The Interface between semiconductors and electrolytes —— 97
3	The electrochemical cell —— 103
3.1	The lemon battery —— 103
3.2	The Daniell element —— 105
3.3	Reference cells —— 107
3.3.1	The Clark cell —— 107
3.3.2	The Weston cell —— 111
3.4	Faraday's law —— 112
3.5	The electrochemical equivalent —— 115
3.6	Electrolyzer cells —— 117
3.6.1	Hydrogen fuel from water electrolysis —— 117
3.7	Water electrolysis —— 118
3.7.1	Water electrolysis from renewable energy —— 118
3.7.2	Deuterium from water electrolysis —— 119
3.7.3	Three major water electrolysis concepts —— 120
3.7.4	Combined hydropower and PEM electrolyzer plant for hydrogen production —— 125
3.7.5	Electrolyzer powered with solar cells —— 127
3.7.6	SHINE – a project for a solar hydrogen electrolyzer —— 129
3.8	Ammonia synthesis for fertilizer production —— 129
3.8.1	Case study: Fertilizer production at the Assuan dam in Egypt —— 130
3.8.2	Electrochemical ammonium production —— 132
3.9	Chlor-alkali electrolysis —— 135
3.10	Aluminum production —— 136
3.11	Reactions and potential distribution in the electrochemical cell —— 136

4	Batteries —— 138
4.1	Batteries from the perspective of the consumer —— 138
4.2	Where does the name "battery" come from? —— 142
4.3	The Leclanché element —— 147
4.4	The rechargeable lithium ion battery —— 150
4.4.1	Some basic Li battery cathode chemistry —— 151
4.4.2	Excursion: Production of battery graphite with hydropower in
	Switzerland —— 155
4.4.3	Carbon materials in battery electrodes — 158
4.4.4	Assembly of the lithium ion battery — 159
4.4.5	Electrochemical characteristic of lithium battery spinel cathodes —— <b>161</b>
4.4.6	Operando and in situ X-ray spectroscopy on a lithium ion cell —— 168
4.5	Lead acid battery —— 174
4.5.1	Self-discharge —— 178
4.5.2	Jump starting a car —— 179
4.5.3	Lead acid battery for solar energy storage —— 180
4.6	Redox flow battery —— 183
4.7	Zinc air battery —— 191
4.7.1	Efforts for zinc air secondary batteries —— 197
4.7.1.1	The rechargeable high temperature lithium air battery —— 199
4.8	The ZEBRA battery —— 202
4.8.1	ZEBRA battery for submarines —— 204
4.8.2	ZEBRA batteries for stationary applications —— 206
4.8.3	Design of the ZEBRA battery —— 206
4.9	Zinc/silver oxide batteries — 210
4.10	Toxicity of batteries and their materials —— 217
4.11	Battery transportation —— 219
4.12	Recycling of batteries —— 219
4.12.1	Economical aspect of battery recycling — 222
4.13	Large-scale stationary batteries —— 224
5	Electroanalytical methods —— 226
5.1	Simplistic analogy of hydrodynamics and electricity —— 226
5.2	The Kirchhoff laws —— 228
5.2.1	Kirchhoff's current law —— 228
5.2.2	Kirchhoff's voltage law —— 229
5.2.3	Resistivities, capacities and inductivities in electric circuits —— 230
5.3	Redox processes —— 232
5.4	/–V curves <b>—— 233</b>
5.4.1	Metallic conductivity – Ohm's law —— 234

5.4.2	Semiconductor conductivity – the Shockley equation —— 234
5.4.3	lonic conductivity —— 237
5.4.4	Separation of electronic and ionic conductivity —— 238
5.4.5	Electrochemical kinetics – the Butler-Volmer equation —— 241
5.5	Cyclic voltammetry —— 244
5.5.1	Randles-Sevcik equation — 246
5.5.2	Determination of HOMO and LUMO from the cyclic
	voltammogram —— 247
5.5.3	Catalyst turnover frequency —— 249
5.5.4	The need for a reference electrode —— 253
5.6	Impedance spectroscopy —— 255
5.6.1	A word about the misnomer between resistivity and
	conductivity —— 257
5.6.2	Representation of electrochemical systems by electric
	circuits —— 257
5.6.3	Diffusive resistance of porous electrodes — 261
5.6.4	Flat band potential and Mott-Schottky plot — 262
5.6.5	Density of states —— 263
5.7	Chronoamperometry —— 263
5.7.1	The open circuit potential —— 264
5.8	Boundary layers: A trivial explanation —— 265
5.9	Rotating disk electrode —— 265
5.10	Probe beam deflection —— 266
5.11	The Nernst equation —— 266
5.11.1	The concentration cell —— 267
5.11.2	Nernst equation in biology —— 268
5.11.3	Lambda sensor —— <b>269</b>
5.12	Other supporting analysis methods —— 269
5.12.1	Gravimetric analyses —— 270
5.12.2	Particle size and pore size analysis —— 271
5.12.3	Structure analyses —— 271
5.12.4	Spectroscopic analyses —— 273
5.12.5	Dilatometry —— 273
5.12.6	Thermal conductivity —— 278
6	Fuel cells —— 280
6.1	A general remark about electric charge carriers —— 280
6.2	Variety of fuel cells —— 280
6.3	The proton exchange membrane fuel cell —— 283
6.4	Solid oxide fuel cell (SOFC) —— 285
641	An SOEC for residential home applications —— 285

6.4.2	Design and architecture of the SOFC stack —— 285
6.4.3	Operation principle of the SOFC —— 289
6.4.4	Electronic structure and conductivity of SOFC cathode materials —— 290
6.4.5	The temperature-dependent conductivity of an SOFC cathode —— 294
6.4.6	Chromium poisoning of cathodes — 296
6.4.7	Sulfur poisoning in SOFC anodes — 298
6.4.8	Cathode conductivity experiments —— 302
6.4.9	The triple-phase boundary —— 314
6.5	Biofuel cells, or bio fuel cells? —— 316
6.6	Direct methanol fuel cell —— 318
6.7	Phosphoric acid fuel cell —— 319
7	Solid electrolytes —— 323
7.1	Some words about liquid electrolytes —— 323
7.2	NAFION®, a polymer solid electrolyte —— <b>324</b>
7.3	Solid electrolytes —— 325
7.3.1	Influence of shape and porosity on the ionic conductivity —— 328
7.3.2	Lithium ion conductivity in LiNbO <sub>3</sub> thin films —— 331
7.4	Ceramic proton conductors —— 334
7.4.1	The barium zirconate and cerate proton conductors —— 334
7.4.2	Mass gain of ceramic proton conductors upon protonation —— 336
7.4.3	Thermogravimetric analysis (TGA) of hydration and proton loading —— <b>341</b>
7.4.4	Conductivity of ceramic proton conductors — 343
7.4.5	Determination of proton conductivity with neutron methods — 346
7.5	LiPON battery solid electrolytes —— 353
7.6	Some words about ceramic insulators —— 353
8	Photoelectrochemical cells —— 356
8.1	The oil crisis —— 356
8.2	The case for solar energy and solar fuels —— 359
8.3	PEC water splitting cells —— 360
8.3.1	Semiconductor Photoelectrochemistry —— 362
8.3.2	Photoelectrochemical workstation —— <b>364</b>
8.3.3	Photocurrent spectroscopy —— 366
8.3.4	Electronic defect states —— 371
8.4	Dye sensitized solar cells (DSSC) —— <b>377</b>
8.4.1	Sensitization of semiconductors with dye molecules — 377
8.4.2	The Grätzel cell —— 381
8.5	Excursion to noble metal mining and refining —— 385

8.6	Solar cells on flexible substrates —— 389
8.7	Some diagnostics mathematics on DSSC —— 395
8.8	Some remarks on design —— 397
9	Electricity in nature —— 401
9.1	The electricity between air and earth —— 401
9.2	Some words on reproducibility and stability of biological systems —— 401
9.3	Electric properties of the earth subsurface — 406
9.4	Natural electric field —— 408
9.5	Electricity in the atmospheres —— 408
9.6	Excursion to energy storage in wood —— 411
9.7	Generator gas: fuel gas produced from wood —— 422
10	Electricity and biology —— 427
10.1	Electrocultures —— 427
10.2	"Wires in bugs" —— 429
10.3	Early and historic studies on animal electricity —— 434
10.4	Electrophysiology in the nineteenth century —— 440
10.5	The "electric branch" of analytical psychology —— 441
10.6	The biological cell —— 444
10.7	Coating electrodes with biological components —— 447
10.7.1	Coating porous photoelectrodes with proteins —— 450
10.7.2	Protein films drop casted on single crystal metal oxides —— 451
10.7.3	Thylakoid films deposited on gold electrodes —— 451
10.8	Biofilms on photoelectrodes —— 455
10.8.1	How to get biofilms —— 455
10.8.2	In situ photoelectrochemical biofilm studies at the synchrotron —— 457
10.9	Thylakoid membrane electrochemistry —— 458
10.9.1	Extraction of electrons from photosynthetic cells —— 458
10.10	Solar cell assembly from bilayer lipid membrane and nanoparticles —— 462
10.11	Other nano-biohybrid systems —— 462
10.12	Enhancement of photocurrent by light harvesting proteins —— 464
10.12.1	, , , , , , , , , , , , , , , , , , , ,
	his-tag — 464
10.12.2	<u> </u>

10.13		Impedance spectra of bilayer membranes with rhodopsin —— 467
10.14		Impedance spectra of electrodes coated with proteins and with biofilms —— 469
10.15		Microbial fuel cells —— 472
11	Land	use and power plants —— 475
11.1		Coal power plants —— 483
11.2		Wind power plants (wind parks) —— 485
11.3		The biosphere —— 488
12	Elect	rochemical engineering and reactor design —— 497
12.1		Safety and security issues in electrochemical reactors — 497
12.2		Role of mathematics in electrochemical engineering — 497
12.3		Parallel electrode plates in car starter battery —— 499
12.4		Primary and secondary current distribution —— 501
12.5		Solar hydrogen reactor concepts —— 502
12.5.1		The EPFL cappuccino cell —— 502
12.6		PEC reactor for sealed GC measurements —— 505
12.7		Large scale PEC reactors —— 509
12.7.1		Starting from scratch: Design of a primitive structural model —— 509
12.7.2		A functional model of a PEC reactor —— 523
12.7.3		More advanced structures —— 524
12.8		Energy harvesting with window facades —— 526
12.9		An artificial photosynthesis carpet rolled out in the desert — 528
12.10		Test cell for separator measurements under pressure and
		temperature —— 530
12.10.1		Conductivity of separators for various thicknesses — 531
12.10.2		Conductivity of the electrolyte —— 534
12.10.3		Pressure dependence of the thickness of a separator —— 535
12.10.4		Selection of separators and membranes —— 537
12.10.5		Temperature dependence of the conductivity —— 537
13	Reac	hing for the inner of the sun — by nuclear fusion —— 540
13.1		Reaching for the inner of the sun —— 540
13.1.1		How fossil are fossil fuels? —— 540
13.1.2		Some remarks on the "scientificness" of science —— 541
13.1.3		The power of the sun —— 542
13.2		Energy from the nuclear forces —— 544
13.2.1		The nuclear fusion reactions —— 544
13.2.2		The TOKAMAK —— 547
13 3		The cold fusion —— 548

#### XVIII — Contents

13.3.1	Electrochemists go nuclear —— 548
13.3.2	The experiment by Pons and Fleischmann — 549
13.3.3	Other electrochemists aid to help —— 553
13.4	About reproducibility of experiments: some personal remarks —— 557
13.5	When the sun sets —— 559

## Appendix Resistor Color Code — 561

Bibliography —— 562

Index ---- 630