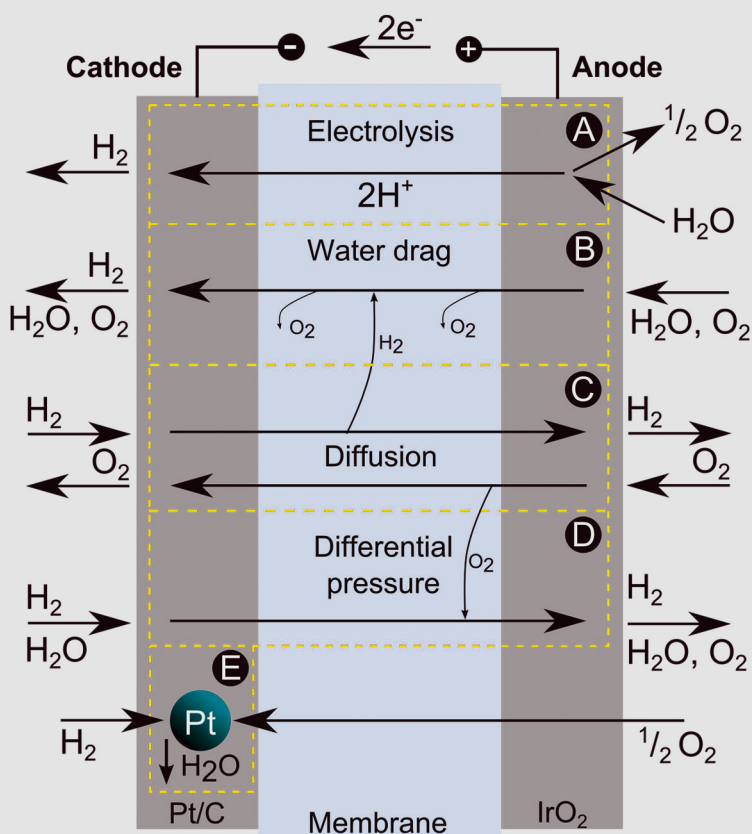




Proton Conduction and Gas Permeation through Polymer Electrolyte Membranes during Water Electrolysis

Maximilian Schalenbach

Energie & Umwelt / Energy & Environment

Band / Volume 426

ISBN 978-3-95806-333-4

Forschungszentrum Jülich GmbH
Institut für Energie- und Klimaforschung
Elektrochemische Verfahrenstechnik (IEK-3)

Proton Conduction and Gas Permeation through Polymer Electrolyte Membranes during Water Electrolysis

Maximilian Schalenbach

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment

Band / Volume 426

ISSN 1866-1793

ISBN 978-3-95806-333-4

Contents

1	Introduction	1
2	Fundamentals	5
2.1	Water electrolysis	5
2.1.1	Thermodynamics	5
2.1.2	Voltage-current characteristic	9
2.1.3	Setup	12
2.1.4	Cell efficiency	14
2.1.5	Gas crossover and safety issues	16
2.2	Proton conduction in aqueous solutions and PEMs	16
2.2.1	Physical description of the ionic conductivity	18
2.2.2	Ionic conductivities at ACs and DCs	19
2.3	Gas diffusion	21
2.3.1	Permeability, diffusion and solubility	21
2.3.2	Polymers	22
2.3.3	Water	23
2.4	Characteristics of polymer electrolyte membranes	25
2.5	Thermodynamics of gas compression	27
3	Overview of current literature	30
3.1	Structure and water content of Nafion®	30
3.2	Conductivity of Nafion®	31
3.3	Gas permeability of Nafion®	32
3.4	Gas purities during water electrolysis	33
4	Methods	35
4.1	Impedance spectroscopy	35
4.2	Electrochemical monitoring technique	37
4.2.1	Measurement principle	37
4.2.2	Setups	38
4.3	Resistor network modeling	42
4.4	Measurement of the anodic hydrogen content	42
5	Proton conduction in Nafion®	46
5.1	Scattering of protons at pore walls	46
5.1.1	Impedance spectra of Nafion®	46
5.1.2	Movement of the protons in the water channels	48
5.2	Conductivities of Nafion® membranes and aqueous solutions	50

5.3	Physical effects that reduce the proton conductivity of Nafion®	54
5.4	Synopsis of the chapter	55
6	Hydrogen and Oxygen Permeabilities of Nafion®	57
6.1	Influence of ambient conditions	57
6.1.1	Pressure	57
6.1.2	Relative humidity	59
6.1.3	Temperature	61
6.2	Influence of the solubilities	65
6.3	Pathways for the gas permeation	66
6.4	Synopsis of the chapter	67
7	Resistor network modeling of the gas permeation through Nafion®	69
7.1	Model development	69
7.1.1	Resistor network model	70
7.1.2	Permeabilities of the aqueous and solid phase	76
7.1.3	Simulation of the gas permeability	79
7.2	Application of the model to the experimental data	82
7.2.1	Variation of the intermediate phase	82
7.2.2	Variation of the solid phase	84
7.2.3	Deviations from the Boltzmann distribution	85
7.3	Discussion	87
7.3.1	Increased permeability of the intermediate phase	88
7.3.2	Softening of the solid phase	89
7.3.3	Influence of the water content on the modeled permeability . .	90
7.3.4	Impact of the different phases	90
7.3.5	Improvement of PEMs	91
7.4	Synopsis of the chapter	93
8	Characterization of different polymer electrolyte membranes	95
8.1	Conductivities	96
8.2	Permeabilities	97
8.3	Ratios of conductivities to permeabilities	98
8.4	Synopsis of the chapter	99
9	Gas permeation through the membrane during water electrolysis	100
9.1	Partial pressure increase in the catalyst layer	101
9.1.1	Influence of concentration and differential pressure differences	102
9.1.2	Quantitative description	103

9.2	Gas permeation fluxes	105
9.2.1	Separate description of the permeation fluxes	105
9.2.1.1	Diffusion	106
9.2.1.2	Proton permeation	107
9.2.1.3	Ratio of the permeation fluxes	110
9.2.2	Interacting description of the permeation fluxes	114
9.2.2.1	Mathematical description of the interaction	114
9.2.2.2	Concentration profiles of the gases in the aqueous phase	117
9.2.3	Comparison of the separated and interacting description	117
9.3	Anodic hydrogen content	119
9.3.1	Hydrogen oxidation at the anodic catalyst	120
9.3.2	Experimental evaluation of the model	122
9.3.2.1	Influence of the cathodic partial pressure increase factor	122
9.3.2.2	Influence of the proton permeation	123
9.3.3	High-pressure electrolysis	125
9.4	Synopsis of the chapter	126
10	Efficiency of pressurized water electrolysis	128
10.1	General remarks and reaction kinetics	128
10.2	Cell efficiency and membrane thickness optimization	129
10.2.1	Model	129
10.2.2	Balanced and differential pressure operation	130
10.2.3	Influence of parameters	131
10.3	Pressurized electrolysis <i>vs.</i> subsequent compression	133
10.3.1	Details of the comparison	134
10.3.2	Energy consumption of a compressor	135
10.3.3	Comparison of the efficiencies	136
10.4	Synopsis of the chapter	139
11	Electrochemical mitigation of hydrogen crossover	141
11.1	Introduction	141
11.2	Electrochemical characterization	143
11.2.1	Potential and current density of the additional electrode	143
11.2.2	Influence of the additional electrode on the cell voltage	144
11.3	Efficiency and anodic gas purity	146
11.4	Challenges for application	149
11.5	Synopsis of the chapter	151
12	Discussion	152
12.1	Microscopic geometry and macroscopic properties of PEMs	152
12.2	Efficiency and operation parameters	155

13 Summary	157
14 Attachment	160
14.1 Electrode preparation	160
14.2 Additional information to the conductivity measurements	160
14.2.1 Capacitances between the water channels	161
14.2.2 Procedure to determine the proton conductivity of HCl	162
14.2.3 Fitting procedure and error calculation	163
14.2.4 Derivation of the geometric restrictions factor	164
14.2.5 Influence of the water content on the estimated values	168
14.3 Additional information to the permeability measurements	168
14.3.1 Electrochemical half-cell with sulfuric acid electrolyte	169
14.3.2 Electrochemical cell with Nafion [®] electrolyte	170
14.3.3 Cell for the measurement of the dry PEMs	171
14.3.4 Saturation current density	172
14.4 Resistor network modeling	173
14.4.1 Simulated oxygen permeability of fully hydrated Nafion [®] . . .	173
14.4.2 Codes	175
14.5 Relation of adiabatic compression to isothermal compression	179
14.6 Setup to mitigate hydrogen crossover	181
List of figures	182
List of tables	189
Nomenclature	192
Bibliography	195

Energie & Umwelt / Energy & Environment
Band / Volume 426
ISBN 978-3-95806-333-4