



Content

Abstract	iii
Content	v
List of Acronyms & Abbreviations	vii
1. Introduction	9
2. Theoretical Concepts and Experimental Methods	15
2.1. Background on PEMFC Electrochemistry	15
2.1.1. Relevant Electrochemical Reactions and Thermodynamics	15
2.1.2. Reaction Kinetics and Electrocatalysis	18
2.1.3. Further Voltage Losses	19
2.1.4. Main Degradation Mechanisms in PEMFC electrodes	21
2.2. Electrochemical Methods	23
2.2.1. Electrochemical Impedance Spectroscopy.....	23
2.2.2. Cyclic Voltammetry.....	26
2.2.3. Rotating (Ring) Disk Electrode Voltammetry	30
2.2.4. Single Cell PEMFC Experiments	35
2.2.5. Start-Up/Shut-Down Experiments	37
2.2.6. Modeling Approach of Start-Up/Shut-Down Events.....	38
2.3. Preparation of R(R)DE Experiments	39
2.3.1. Glass Cell and Components	40
2.3.2. Catalyst Layers.....	42
2.4. Preparation of PEMFC Experiments	44
2.4.1. Single PEMFC Hardware and Components.....	44
2.4.2. Membrane Electrode Assembly (MEA) Fabrication	48
2.4.3. Electrode Preparation.....	49
2.5. Catalyst Powder Characterization	50
2.6. Advanced Analyses	52
2.6.1. MEA Cross-Sectional Imaging by SEM.....	52
2.6.2. Differential Electrochemical Mass-Spectrometry	53
3. Platinum-Free Oxygen Reduction Electrocatalysis	55
3.1. Monometallic Palladium for Oxygen Reduction in PEM Fuel Cells – Particle-Size Effect, Reaction Mechanism, and Voltage Cycling Stability	57
3.2. ZrO₂ Based Oxygen Reduction Catalysts for PEMFCs: Towards a Better Understanding	69
3.3. Platinum-Free ORR Catalysts – Conclusions	85
4. PEMFC Degradation by Start-Up/Shut-Down	87
4.1. PEM Fuel Cell Start-Up/Shut-Down Losses vs. Temperature for Non-Graphitized and Graphitized Cathode Carbon Supports	89



Content

4.2. PEM Fuel Cell Start-Up/Shut-Down Losses vs. Relative Humidity – The Impact of Water in the Electrode Layer During Carbon Corrosion	103
4.3. PEM Fuel Cell Start-Up/Shut-Down Degradation – Conclusions	121
5. Conclusions	123
References	125
List of Figures	139
Acknowledgements	142
Curriculum Vitae	143
List of Publications	145