In-situ investigation of metal nanoparticle stability during electrocatalysis

vorgelegt von Diplom-Chemikerin Xenia Erler

Von der Fakultät II – Mathematik und Naturwissenschaften der Technische Universität Berlin zur Erlangung des akademischen Grades Doktorin der Naturwissenschaften Dr. rer. nat.

genehmigte Dissertation

Promotionsausschuss:

Vorsitzender:	Prof. Dr. rer. nat. Arne Thomas
Berichter:	Prof. Dr. rer. nat. Peter Strasser
Berichter:	Prof. Dr. rer. nat. Klaus Rademann

Tag der wissenschaftlichen Aussprache: 16. November 2012

Berlin 2012 D 83 Renewable energy conversion and storage using chemistry has become a pivotal issue in solving the global energy challenge. In particular fuel cells, owing to their high efficiency and fuel flexibility, will play a critically important part to use electrochemical energy for storage in molecular bonds. However, high catalyst cost and limited catalyst durability at the fuel cell electrodes have long hampered a broader technology deployment of fuel cells, in particular of low temperature Polymer Electrolyte Membrane Fuel Cells (PEMFC).

Typically, nanoscale materials such as nanoparticles are employed as catalytically active electrode components. This is because nanoparticles offer a large electrochemical surface area (ECSA), which is indispensable for useful electrochemical power densities. However, the large surface area of the nanoparticles also tends to be unstable due to their high surface energy. The proper mechanism of catalyst performance loss is poorly understood. The overall objective of this thesis was to determine the parameters, which control the activity and the durability of such fuel cell catalysts. To achieve that different strategies were developed: The structural dynamics and growth of particles with different shapes on a variety of carbon supports were compared and catalyst/support couples that exhibited improved structural stability were identified. Moreover the composition of the NP catalyst was modified by adding a less noble metal in the particle structure. The mechanism of intra particle dynamics was investigated in situ to obtain more information on the dramatically enhanced electrochemical catalyst performance. Additionally, an advanced approach of particle stability improvement by modification of the support structure with additional electron donor functional groups was developed.

In summary, this work has determined the dominant degradation mechanisms of metal nanoparticles during electrocatalysis and identified novel catalyst/support materials with improved stability and activity. Für den erfolgreichen globalen Energiewandel sind die Umrüstung auf erneuerbare Energien und ihre Speicherung in chemischen Bindungen stetig an Bedeutung gewinnende Kriterien. Hier zeichnen sich insbesondere Brennstoffzellen mit ihrer hohen Effizienz und flexiblen Betrieb im praktischen Einsatz aus, da die derartig genutzte Umwandlung der in chemischen Bindungen gespeicherten Energie in nutzbare Elektrizität eine Schlüsselrolle im globalen Energiewandel einnimmt. Allerdings erschweren die Kosten und Lebensdauer der in den Zellen verwendeten Katalysatoren eine übergreifende industrielle Implementierung dieser Technologie, speziell der Polymer-Elektrolyt-Membran Brennstoffzellen (PEMFC).

Die Implementierung von katalytisch aktiven Nanopartikeln an den Elektroden einer PEM-FC erhöht erheblich die elektrochemisch nutzbare Oberfläche und liefert einen unverzichtbaren Beitrag zu hohen elektrochemischen Stromdichten. Diese große Oberfläche scheint jedoch auf Grund der ebenfalls hohen Oberflächenspannung der Nanopartikel nicht stabil zu sein, was durch einen Verlust der katalytischen Leistung bemerkbar wird. Die genauen Abläufe dieses Leistungsabbaus sind nur in Ansätzen verstanden.

Diese Doktorarbeit beschäftigt sich hauptsächlich mit dem Bestimmen der relevanten Parameter, welche die Aktivität und die Langlebigkeit solcher Katalysatoren in Brennstoffzellen bedingen. Hierfür wurden mehrere Strategien verfolgt: Es wurden strukturelle Dynamiken und Wachstumsprozesse verschieden geformter Partikel auf einer gewissen Typenauswahl von Kohlenstoffträgern verglichen und Paare von Katalysator-Träger mit nachgewiesener hohen Langlebigkeit identifiziert. Außerdem wurde durch das Hinzufügen von weniger edlen Metallen zum Katalysator die chemische Zusammensetzung der Nanopartikel verändert. Die daraus resultierende deutlich gesteigerte elektrochemische katalytische Leistung wurde *in situ* untersucht, um die innerpartikulären dynamischen Abläufe aufzuklären. Zusätzlich wurde für eine verbesserte Katalysatorstabilität eine Methode zur Modifikation der Partikelträgerstrukturen mit erweiterten Elektronen-Donor funktionellen Gruppen entwickelt.

Zusammengefasst hat diese Arbeit die dominierenden Abläufe des elektrokatalytischen Leistungsabbaus von metallischen Nanopartikeln bestimmt und neuartige Katalysator-Träger-Kombinationen für eine mögliche Steigerung der Stabilität und Aktivität von Brennstoffzellen identifiziert.

Danksagung

Hiermit bedanke ich mich bei Herrn Prof. Dr. P. Strasser für die Möglichkeit der Durchführung dieser Dissertationsarbeit, die insbesondere durch die freie Gestaltungsfreiheit und das ausgeprägte Selbstbestimmungsrecht der Ausführung maßgeblich geprägt wurde. Ich danke Herrn Prof. Dr. K. Rademann für die freundliche Übernahme des Koreferats. Herrn Prof. Dr. A. Thomas danke ich für die freundliche Übernahme des Vorsitzes des Prüfungsausschußes.

Ein besonderer Dank gilt den Mitarbeitern der Arbeitsgruppe TC03 der Technischen Universität Berlin für die angenehme Arbeitsatmosphäre. Den Kollegen Herren Dipl.-Ing. S. Rudi, Dipl.-Ing. T. Reier und Prof. Dr. P. Strasser danke ich für ihr Engagement bei mehreren Synchrotron-Messzeiten. Ich bedanke mich herzlich bei den Herren Dipl.-Ing. S. Rudi und B. Sc. M. Neumann für die im Rahmen ihrer Abschlußarbeiten durchgeführten Synthesen, die diese Dissertation erheblich beeinflußten.

Ich danke Herrn Dr. A. Hoell, Dr. S. Haas und Dr. V. S. Raghuwanshi für die ausgiebige Unterstützung bei den am Helmholtz-Zentrum Berlin durchgeführten Experimenten.

Herrn Dipl.-Ing. S. Selve danke ich für die freundliche Unterstützung bei all den Fragen rund um TEM.

Herren Dr. J.-P. Paraknowitsch, Prof. Dr. A. Thomas und Dipl.-Chem. R. Illgen danke ich für die nette und erfolgreiche Zusammenarbeit.

Meinen Freunden M. Sc. S.-J. Tenne, Dipl.-Chem. A. Simo, Dipl.-Chem. U. Reinhardt, Dipl.-Chem. N. Abdulhanan, Dipl.-Ing. N. Hundertmark, Dipl.-Ing. R. Reske und Dipl.-Ing. R. Eichenauer und danke ich für den sooft dringend nötigen Ausgleich und die reichliche moralische Unterstützung.

Meiner Familie danke ich für all die Geduld, das Verständnis und das eiserne Rückgrad in allen Lebenssituationen. Meinem Ehemann, Robert, danke ich für einfach alles. Ohne ihn wäre diese Arbeit definitiv nicht das, was sie ist.

It ain't what you don't know that gets you into trouble. It's what you know for sure that just ain't so. *Mark Twain*

Contents

1.	Intro	duction		1	
	1.1.	Funda	mentals of fuel cell catalysis	1	
	1.2.	Challenges of PEMFC assemblies			
	1.3.	PEMFC catalyst degradation mechanisms and fuel cell catalyst durability			
		resear	ch	4	
	1.4.	Goals	of this thesis	8	
2.	Theoretical Aspects				
	2.1.	Transn	nission electron microscopy (TEM)	9	
	2.2.	Bruna	uer-Emmet-Teller (BET) adsorption isotherms	9	
	2.3.	Inducti	ively coupled plasma optical emission spectroscopy (ICP-OES)	11	
	2.4.	X-ray	photoelectron spectroscopy (XPS)	11	
	2.5.	X-ray	diffraction (XRD)	12	
	2.6.	Electro	ochemical methods	13	
		2.6.1.	Cyclic voltammetry (CV)	14	
		2.6.2.	Linear sweep voltammetry (LSV)	14	
	2.7.	Small	angle x-ray scattering (SAXS)	16	
		2.7.1.	Fundamentals	16	
		2.7.2.	Behaviour at q-values tending to 0 (forward scattering)	20	
		2.7.3.	Behaviour in the large q limit	21	
		2.7.4.	Formfactor for spherical particles	21	
		2.7.5.	Formfactor for parallelepiped particles	21	
		2.7.6.	Anomalous small angle x-ray scattering (ASAXS)	22	
		2.7.7.	Synchrotron radiation	24	
3.	Expe	erimenta	l procedures	26	
	3.1.	2-3 nm	n Pt nanoparticles	26	
		3.1.1.	Synthesis of spherical nanoparticles	26	
		3.1.2.	Deposition on carbon supports	26	

	3.2.	4-5 nm	Pt nanoparticles	27
		3.2.1.	Synthesis of spherical nanoparticles	27
		3.2.2.	Synthesis of cuboid nanoparticles	27
		3.2.3.	Deposition on carbon support	28
	3.3.	Synthes	sis of $PtNi_6$ /Vulcan(VC) and $PtNi_3$ /VC catalysts	28
	3.4.	Synthes	sis of nitrogen-doped coatings on MWCNT	28
	3.5.	TEM m	easurements	29
	3.6.	BET measurements		
	3.7.	ICP-OE	S measurements	29
	3.8.	XPS me	easurement	31
	3.9.	XRD an	alysis	31
	3.10.	High en	nergy XRD measurements	32
	3.11.	Electro	chemical characterization	33
		3.11.1.	Ink preparation	33
		3.11.2.	Electrode preparation	33
		3.11.3.	CV and LSV measurements	34
		3.11.4.	Error estimation	35
	3.12.	SAXS a	malysis	36
		3.12.1.	Preparation of dry powder samples	36
		3.12.2.	Preparation of catalyst containing carbon-sheet electrodes	36
		3.12.3.	In situ SAXS/ASAXS measurements	36
		3.12.4.	SAXS/ASAXS aquisition	39
		3.12.5.	General SAXS data treatment and mathematical fitting	39
		3.12.6.	SAXS fitting procedure for cuboid scatters	42
	3.13.	Chemica	als	44
4.	On t	he effect	of general parameters on particle growth trajectories	46
	4.1.	Electro	le surfaces	47
	4.2.	Effect o	f the gaseous environment	49
	4.3.	Effect o	f potential scanrate	51
	4.4.	Summar	ry	52
5.	Activ	vity and s	tability of shape selective nanoparticles	53
	5.1.	Introduc	tion	53
	5.2.	Structur	ral characterization of pristine catalysts	54
	5.3.	In situ o	degradation study	57

	5.4.	Conclusions	62
6.	Cata 6.1. 6.2. 6.3. 6.4. 6.5. 6.6. 6.7. 6.8.	lyst composition modification: activity and stability of PtNi alloy nanoparticles Introduction	 63 63 66 68 70 72 73 75 77
7.	Carb sphe 7.1. 7.2. 7.3. 7.4. 7.5. 7.6. 7.7.	on catalyst supports: The impact of the surface area on activity and stability of rical Pt nanoparticles Introduction	78 78 80 83 85 88 93 96
8.	Cata 8.1. 8.2. 8.3.	lyst support functionalization: Stability enhancement with ionic liquids Introduction	98 98 100 101 103 105 107 109 112
9.	Summary and outlook 11		
Α.	Appendix 135		

List of Figures

1.1.	Scheme of a PEMFC	2
1.2.	Scheme of particle coalescence	4
1.3.	Scheme of catalyst surface area loss due to dissolution of particles	5
1.4.	Scheme of Ostwald ripening driven particle growth	6
1.5.	Scheme of catalyst degradation by oxidation of particles and support \ldots	6
1.6.	Scheme of catalyst performance loss by particle detachment	7
2.1.	Visualization of Bragg equation	12
2.2.	Example of a CV measurement	15
2.3.	Example of a LSV measurement	16
2.4.	Scheme of of small angle x-ray scattering (SAXS) principle	17
2.5.	Principle of energy selections for ASAXS measurements	23
2.6.	Synchrotron facility BESSY II	25
3.1.	Scheme of electrochemical characterization procedure	34
3.2.	Experimental setup for <i>in situ</i> SAXS/ASAXS measurements	37
3.3.	Transmission measurements using a lab based SAXS equipment	40
3.4.	Illustration of SAXS estimates for cubic particles	42
4.1.	Comparison of different electrode surfaces	47
4.2.	Comparison of CV measurements performed on RDE and on CSh	48
4.3.	Comparison of catalyst degradation in N_2 and air saturated electrolyte $\ . \ .$	50
4.4.	Comparison of catalyst degradation induced by different scanrates	51
5.1.	Characterization via TEM and HRTEM of pristine spherical and cuboid Pt	
	nanoparticles supported on VC	55
5.2.	Characterization via SAXS of pristine spherical and cuboid Pt nanoparticles	
	supported on VC	56
5.3.	Electrochemical characterization of spherical and cubic Pt nanoparticles	
	supported on VC	57

5.4.	Illustration of the amount of atoms located in (111) and (100) crystal planes	
	for spherical and coboid particles	58
5.5.	Experimental CV curves and evolution of normalized ECSA of spherical and	
	cuboid Pt nanoparticles supported on VC	59
5.6.	In situ SAXS degradation study results for spherical and cuboid particles	61
6.1.	ECSA of PtNi/VC catalysts compared to a Pt/VC catalyst	64
6.2.	Experimental data for a pristine $PtNi_6/VC$ catalyst \ldots \ldots \ldots	66
6.3.	Characterization of a pristine $PtNi_6/VC$ catalyst \ldots \ldots \ldots \ldots	67
6.4.	Particle size trajectories during potential cycling of a $PtNi_6/{ m VC}$ catalyst .	69
6.5.	Comparison of particle size estimates using different calculation methods .	70
6.6.	Experimental data for a pristine $PtNi_3/VC$ catalyst $\ldots \ldots \ldots \ldots$	72
6.7.	Characterization of a pristine $PtNi_3/VC$ catalyst \ldots \ldots \ldots \ldots	73
6.8.	Particle size trajectories during potential cycling of a $PtNi_3/VC$ catalyst .	74
6.9.	Model of PtNi alloy nanoparticle evolution during electro-catalysis	75
7.1.	SEM images of different pristine carbon supports	80
7.2.	Characterization of pristine catalysts supported on VC, MWCNT, HSAC	
	and HCC	82
7.3.	Summary of the electrochemical characteristics of Pt nanoparticle catalysts	
	on different carbon supports	83
7.4.	Effect of carbon-surface area increase on particle separation	84
7.5.	Evolution of the electrochemical characteristics of Pt nanoparticle catalysts	
	on different carbon supports	86
7.6.	Electrochemical analytics of Pt nanoparticles supported on different carbons	87
7.7.	Structural dynamics of Pt/VC	89
7.8.	Structural dynamics of Pt/MWCNT	89
7.9.	Structural dynamics of Pt/HSAC	9
7.10.	Structural dynamics of Pt/HCC	92
7.11.	Scheme of the degradation mechanism of spherical Pt nanoparticles sup-	
	ported on different carbons	94
8.1.	Electrochemical stability study on Pt nanoparticles supported on high N-	
	containing carbon	100
8.2.	Comparison of catalyst degradation of Pt/meso-C and Pt/HSAC catalysts	102
8.3.	Schematic overview on synthesis strategy of Pt nanoparticles supported on	
	N-C coated MWCNT	104

Characterization of N–modified MWCNT	105
Characterization of pristine Pt/MWCNT and Pt/N–MWCNT catalysts $\ . \ .$	108
In situ electrochemical and SAXS experimental investigations of catalyst	
stability for Pt / MWCNT and Pt / N-MWCNT	110
Stability study on Pt/MWCNT and Pt/N–MWCNT catalysts	111
Effect of nitrogen in the carbon structure on particle size trajectories	114
Comparison of catalyst degradation in N_2 and air saturated electrolyte by	
absolute ECSA estimates	136
Characterization via XRD of pristine spherical and cuboid Pt nanoparticles	
supported on VC	136
Electrochemical analytics of PtNi catalysts	137
X-ray fluorescence analytics of PtNi catalysts	137
Experimental SAXS curve with the resulting LogNormal particle size prob-	
ability density function for a pristine Pt/meso-C catalyst	138
	Characterization of N-modified MWCNT

List of Tables

Potential protocol for electrochemical characterization of catalyst powders	34
Potential protocol for <i>in situ</i> SAXS/ASAXS characterization of catalyst	
powders	38
Mean particle size definitions for a distribution f(R)	41
List of used chemicals	44
Applied potential protocol for validation of general experimental parameters	47
Structural characterization of catalyst powders with differently shaped Pt	
nanoparticles supported on VC	57
Summary of electrochemical characterization of catalyst powders with dif-	
ferently shaped Pt nanoparticles supported on VC	60
Structural characterization of catalyst powders with different carbon supports	81
Electrochemical characterization of catalyst powders with different carbon	
supports	88
Structural characterization of catalyst powders Pt/MWCNT and Pt/meso-C	101
Peak fit parameter of the N_{1s} detail spectrum	106
Summary of used Pt-solutions for a standard calibration of the ICP-OES .	135
Example of weight-percentage determination of an ICP-OES sample	135
	Potential protocol for electrochemical characterization of catalyst powders Potential protocol for <i>in situ</i> SAXS/ASAXS characterization of catalyst powders

1. Introduction

1.1. Fundamentals of fuel cell catalysis

Renewable energy conversion and storage using chemistry has become a pivotal issue in solving the global energy challenge. In particular fuel cells, owing to their high efficiency and fuel flexibility, will play a critically important part to use electrochemical energy for storage in molecular bonds. However, high catalyst cost and limited catalyst durability at the fuel cell electrodes have long hampered a broader technology deployment of fuel cells, in particular of low temperature Polymer Electrolyte Membrane Fuel Cells (PEMFC).

A PEMFC is an electrochemical device that converts chemical energy into electricity. Chemical reactions provide the required electron flow that can be trapped by an external appliance.

Such an electrochemical device consists of two separated half cells, both including an electrode, as shown schematically in figure 1.1. On the one side of a fuel cell a cathode is integrated, where the reduction reaction occurs; on the other an anode is installed, where the oxidation reaction takes place. To afford mass transport of produced chemical ions a separator – an exchange membrane – must be positioned between the half cells. Several different types of fuel cell assemblies have been developed in the past, ^{1–3} such as *e.g.* Proton Exchange Membrane FC (PEMFC), Direct Methanol/Ethanol/Formic Acid FC, Solid Oxide FC (high temperature FC), Molten Carbonate FC.

The studies in this thesis focus on the hydrogen fuel cell, which is a PEMFC-type device that implements the two electrochemical reactions of interest: anodic hydrogen oxidation reaction (HOR) and cathodic oxygen reduction reaction (ORR):

$$HOR: \quad H_2 \rightleftharpoons 2H^+ + 2e^- \tag{1.1}$$

ORR:
$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$
 (1.2)

The conversion of hydrogen with oxygen contained in air produces water as the main product. Hence, protons produced on the anodic side of the FC migrate to the cathode in

order to react with oxygen anions and finally build water molecules. Simultaneous proton migration and half cell separation is usually realized by a semipermeable proton exchange membrane (PEM).



Figure 1.1.: Scheme of a PEMFC assembly. PEM separates the electrodes, which consist of conductive carbon nanoparticles loaded with catalytically active Pt nanoparticles, respectively. Gas diffusion layers guarantee a homogeneous distribution of reactant gases H₂ on the anode and O₂ on the cathode, which are converted during PEMFC performance to water.

1.2. Challenges of PEMFC assemblies

Slow kinetics of the ORR gives rise to a significant cathode overpotential, which acts to a decrease of the FC electrical efficiency. Hence, essential for a high rate of chemical conversion is the availability and development of highly active catalyst materials as electrode components.

Pt is one of the most favored materials in terms of its high hydrogen affinity. However, manufacture of electrodes must supply not only high rates and high quality, production cost efficiencies must be concerned also. The price of the scarce Pt is high and the amount of the metal on the electrodes are limiting factors in FC production. An advanced approach of cost minimization has been realized by replacing the bulk catalyst by nanoparticles acting as catalysts.

Metal nanoparticles offer a huge electrochemical surface area (ECSA) per mass unit compared to a bulk material. Especially Platinum-based catalysts at the nano scale have been developed for fuel cell applications. Studies on these scarce metal based catalysts have indeed evidenced high mass based ORR activity,^{4–10} however, stability tests evidenced a continuous ESCA loss. The mechanism of catalyst performance loss is poorly understood.^{6;9–11} Several processes, which contribute to the performance loss of a fuel cell, are introduced in the following section.

1.3. PEMFC catalyst degradation mechanisms and fuel cell catalyst durability research

Besides catalysts activity, one of the key issues for the commercialization of PEMFC is the durability of the used catalyst. Currently, the lifetime of the used catalysts does not satisfy the requirements for commercial technologies.^{3;9;12–14} Major processes, which contribute at the micro scale to the loss of the elecrochemical performance of a metal-nanoparticles based FC catalyst can be described as follows.

 Coalescence describes the process of aggregation of some particles leading to a decrease of overall particle number by the formation of bigger particles (figure 1.2).^{5;6;10;15-17} The mechanism can be described generally by 2D motion of Pt particles and coalescence when particles meet.¹⁸



Figure 1.2.: Scheme of particle coalescence.

Ruckenstein and Pulvermacher¹⁸ established equations for the time dependence of the distribution of crystallite sizes and for the decay of the exposed surface area of metal for both homogeneous and non-homogeneous surfaces. The results showed the rate of particle growth was found to depend on particle loading on the carbon support. Shao Horn *et al.* evidenced particle coalescence from transmission electron microscopy (TEM) measurements. The micrographs reflected several single crystals of Pt jointed together on the carbon support. However, the overall results of the performed degradation study showed that coalescence was accompanied by other processes, such as particle dissolution or Ostwald ripening.

2. Dissolution of Pt is one of the degradations mechanisms reported widely in literature (figure 1.3).^{5;6;10;17;19-23}

Holby *et al.*¹⁷ determined the Gibbs-Thomson energy, which gives the change in chemical potential as a function of particle diameter, to be a leading parameter in



Figure 1.3.: Scheme of catalyst surface area loss due to dissolution of particles by formation of metal ions Mⁿ⁺.

particle degradation and can be expressed as:

$$E_{GT} = \mu(d) - \mu(\infty) = \frac{4\gamma\Omega}{d} , \qquad (1.3)$$

where E_{GT} is the Gibbs-Thomson energy, $\mu(d)$ is the chemical potential of a particle with a diameter d, $\mu(\infty)$ is the chemical potential of a flat surface, γ is the surface energy of the particle ($\gamma_{Pt} = 0.148 \text{ eV}/\text{Å}^2$)²² and Ω is the volume per atom ($\Omega_{Pt} = 15.4 \text{ Å}^3/\text{atom}$)²².

The The Gibbs-Thomson energy contributes to the dissolution thermodynamics and kinetics of Pt nanoparticles in terms of increase of Pt solubility and enhancement of of the dissolution rates of Pt.^{10;22} Holby *et al.*¹⁷ developed simulations, which demonstrated that there is a critical enhancement in stability, due to rapidly changing Gibbs-Thomson energies, in the region from 2-3 nm to 4-5 nm particle sizes. Hence, particle size effect,^{20;23-27} which describes the relationship of surface area loss and particle size, was determined to play a key role in catalyst stability.

Darling *et al.*²² presented a mathematical model including the equation 1.3, which estimated the particle dissolution rate as a function of particle diameter. The results showed a very strong dependence of dissolution rates on the particle diameter and suggested that dissolution continues at a fixed flux until the particle is dissolved completely. Solely particles larger than 5 nm had the required stability to remain solid.

3. An Ostwald ripening^{28–33} mechanism can be described as inter particle transport of single ions: dissolution of small particles and redeposition of the produced species on the surface of bigger particles (figure 1.4) Overall increase of particle size is the consequence.^{28–30;32;34}

Bett *et al.*³¹ proposed Pt catalyst degradation by Ostwald ripening by their experimental investigation performed on 5%wt and 20%wt Pt/C, where neither the



Figure 1.4.: Scheme of Ostwald ripening driven particle growth. Small particle dissolve and form metal ions Mⁿ⁺, which subsequently depose on the surface of particles bigger in size.

effect of Pt loading nor the potential dependance on the Pt area loss was observed. Similar particle dynamics were assumed recently by Gilbert *et al.*³³. The authors concluded an Ostwald ripening mechanism (dissolution of small Pt nanoparticles and re-deposition on existing particles) in addition to the reflection of the contribution of Pt-oxide formation to particle growth. Additional reports in literature^{33;35–37} identified Pt oxidation to most likely contribute to surface area loss of such scarce metal nanoparticle catalysts.

4. Carbon support oxidation and a consequent loss of Pt nanoparticles by detachment from the conductive support and Pt oxidation. (figure 1.5).^{5;6;10;11;33;35;36;38-41} While Pt acts as a catalyst for HOR and ORR, it also enhances carbon oxidation. The corrosion reaction of carbon material in aqueous acid electrolytes can be generalized by:⁴²

$$C + 2H_2O \to CO_2 + 4H^+ + 4e^ E = 0.207 V$$
. (1.4)

Due to its high kinetic barrier (\leq 1.0 V) the reaction can be neglected at the the operating potentials of a FC. However, a long term durability can be affected by carbon corrosion. Such corroded carbon backbones collapse and weaken the interaction to supported particles, causing a particle detachment from the conductive support.



Figure 1.5.: Scheme of catalyst degradation by oxidation of particles and support.

Previous studies evidenced a direct relationship of catalyst stability and corrosion of the carbon support.^{5;6;10;11;39–41} Especially in a potential range above 1.2 V carbon

corrosion, has been attributed to be one of the main degradation mechanisms. The progress of carbon oxidation depends on the carbons properties, such as structure and porosity.^{25;39;41;43} Electrochemical treatment of a catalyst below 1.2 V also diminishes catalyst performance. However, in this potential range catalyst degradation is attributed more to particle degradation than to carbon oxidation.^{5;6;8–10;15;19;23;25;26;44;45} An *ex situ* method was used by Borup *et al.*⁵. The author conducted x-ray diffraction (XRD) measurements on electrochemically treated membrane-electrode-assemblies (MEA) to identify the cause of observed Pt surface area loss. Evolution of particle size evidenced particle growth, which was accelerated by potential cycling. Furthermore, the results clearly showed that the growth rate was increasing with increasing the upper potentials, where carbon corrosion was observed to increase as well.

5. Particle detachment from conductive support affects a loss of electrochemically available surface area even though the catalyst particles are still present in the cell (figure 1.6).^{33;39} One approach to characterize the processes affecting decreased catalyst performances is the employment of microscopy techniques, *i.e.* TEM.^{10;15}



Figure 1.6.: Scheme of catalyst performance loss by particle detachment.

Mayrhofer *et al.*¹⁵ implemented a TEM grid coated with a catalyst film in an electrochemical setup and characterized the catalyst particles after potential cycling. Particle size histograms were evaluated by *post mortem* micrographs from such grids. The authors suggested a corrosion mechanism, which involved particle detachment from carbon and a subsequent dissolution of Pt into the electrolyte without redeposition, and refuted the Ostwald ripening mechanism.

The detailed mechanisms of catalyst degradation and their relation to fuel cell performance loss is still poorly understood. A mechanism was typically suggested from *ex situ* investigations due to the isolation of the particles from experimental condition, such as electrolyte environment. Theoretical studies^{17;18;22;45–47} have implemented the electrochemical environment, though proper conditions could not be simulated due to the approximations, that had to be made for calculations. Hence, a coupling of *ex situ* and theoretical studies with an experimental *in situ* study provides a perspective approach to gain more relyable knowledge on durability mechanisms and the corresponding leading parameters.

1.4. Goals of this thesis

This thesis contributes to the understanding of PEMFC Pt and Pt-alloy catalyst instabilities. The overall objective was to determine the parameters that control the stability of a PEMFC cathode catalyst. To achieve this objective the following was studied:

Initially the dependence of catalyst stability and activity on the shape of nanoparticle catalysts was evaluated. For this purpose the performance of cubic and spherical Pt nanoparticles supported on Vulcan XC 72R carbon (VC) were compared.

Next, the elemental composition of the catalyst nanoparticles was changed in order to optimize the activity. The study was based on electrochemical performance comparison of pure Pt and PtNi alloy nanoparticles supported on VC, respectively.^{48;49} Alloy catalysts structure and intra particle dynamics and were linked to a modified catalyst performance affected by electrochemical treatment and afford conclusions on activity impacts.

Further focus was placed on catalyst degradation studies. In order to establish a clearer picture on the main degradation mechanisms Pt nanoparticles supported on different types of carbons were characterized. Catalyst degradation mechanisms and a resulting performance loss were considered in respect to the characteristics of the support, especially concentrating on the carbon surface area contributions.

Additionally, an advanced approach of particle stability improvement by modification of the support structure with additional electron donor functional groups was developed and discussed. Contributions of homogeneously embedded nitrogen atoms in a carbon graphite structure to nanoparticle stability were considered, followed by studies of the effect of N-containing coatings on an unmodified carbon backbone.

These investigations aimed to provision of an extended knowledge for PEMFC catalyst durability leading parameters and to enable optimization by a controlled particle synthesis, tailoring the desired catalyst stability, activity and costs.

2. Theoretical Aspects

This chapter provides an overview of theoretical backgrounds of used analytical methods. The techniques described in this chapter are introduced according to the contribution to the main objectives of the thesis. Occasionally used methods (TEM, ICP-OES, BET, XRD) are discussed briefly. Detailed theoretical background is given for methods giving results to the main subject of the thesis (LSV, CV, SAXS, ASAXS).

In case of a specialized technique the technique basics are given in the respective chapter. Experimental procedures including information on used experimental equipment are given in the following chapter 3.

2.1. Transmission electron microscopy (TEM)

TEM is a microscopic method that provides information on sample nature at high magnifications. The analytical technique provides visual insights in materials structure with resolutions up to few nanometers or Ångström.

The method is based on detection of transmitted electrons within a very thin specimen. Hence, TEM investigations require distinct sample preparations and thus are mainly used for *ex situ* characterizations of a material. TEM-images are visualizations of interactions of the electron beam with the atoms in the sample. At high magnifications used in highresolution TEM (HRTEM) complex wave interactions modulate the intensity on an image. This type of microscopy is based on a complex setup of various compounds, such as a stable high-vakuum systems, a designed electron gun, optical electron beam focusing system based on usage of electrostatic or magnetic lenses. An elaborate aperture provides the desired information on visible materials characteristics on nanometer scale.

2.2. Brunauer-Emmet-Teller (BET) adsorption isotherms

Physical adsorption of gas molecules can be used in order to determine several characteristic parameters of an analyzed solid material: specific area, pore volume and structure, mean pore size and pore distribution.⁵⁰ Governed by non-covalent van der Waals forces the approach of substrate coverage by gas molecules is based on a theoretical model developed by S. Brunauer, P. H. Emmett and E. Teller., which was named after the authors.⁵¹ The concept of BET-characterization is based on the following hypothesises:

- adsorption occurs at the lattice of a solid and the molecules direction is upwards;
- initially first monolayer is adsorbed on the bulk surface and each following layer can start only after its completed coverage;
- except the first layer, a molecule can be adsorbed on a n^{th} -layer center *, if such a center exists in the $(n-1)^{th}$ layer;
- at saturation pressure (p_0) the number of adsorption layers is infinite ($\lim_{x\to 1} n = \infty$ for $x = p/p_0$);
- except the first layer the adsorption enthalpy is equal for each layer.

The theory of gas molecules adsorption consisting of several defined layers requires additional assumptions: all of the adsorption centers * are equal; there is no interaction between the adsorbate molecules; adsorption centers * are statistically occupied.

Using the saturated pressure p_0 of an adsorbate gas $(p_0(N_2) \approx 1020 \text{ mbar}, p_0(Ar) \approx 260 \text{ mbar}, p_0(Kr) \approx 28 \text{ mbar})$ the BET-isotherm can be expressed as

$$\mathbf{x} = \frac{\mathbf{p}}{\mathbf{p}_0},\tag{2.1a}$$

$$c = \exp\left\{\frac{E_0 - E_L}{RT}\right\},$$
(2.1b)

$$V_{ads} = \frac{V_{m} \cdot c \cdot x}{(1 - x) \cdot (1 + (c - 1)x)}.$$
(2.1c)

Here, the variables are: p and p_0 are the equilibrium and the saturated pressure, c is the BET-constant, E_0 is the adsorption energy of one advorbate molecule in the first layer, E_L is the equivalent energy for the second and higher layers, V_{ads} is the adsorbed gas quantity in volume units and v_m is the gas volume in one adsorbed monolayer.

To determine v_m the adsorption cross section of the adsorbing species σ has to be given $(\sigma(N_2, 77K) = 0.162 \text{ nm}^2, \sigma(Ar, 77K) = 0.142 \text{ nm}^2, \sigma(Kr, 77K) = 0.202 \text{ nm}^2)$. To evaluate the values for the total surface area $S_{BET,total}$ and the specific area S_{BET} of the analyzed

solid material the BET-isotherms(2.1c) must be transformed into:

$$\frac{\mathbf{x}}{\mathbf{V}_{ads}(1-\mathbf{x})} = \frac{1}{\mathbf{v}_{m} \cdot \mathbf{c}} + \frac{\mathbf{c}-1}{\mathbf{v}_{m} \cdot \mathbf{c}} \cdot \mathbf{x}, \tag{2.2a}$$

$$S_{BET,total} = \frac{v_{m} \cdot N_{A} \cdot \sigma}{V},$$
 (2.2b)

$$S_{BET} = \frac{S_{total}}{a},$$
 (2.2c)

where N_A is the Avogadro number, a is the mass of adsorbent solid material (in g) and V is the molar volume of the adsorbate gas. The slope and the intercept reveal the values for gas volume in one adsorbed monolayer v_m and the BET-constant c, which additionally represents the quality of the measurement. (For 20 < c < 300 the BET approach is not valuable).

2.3. Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is a method used for detection of trace metals based on production of excited atoms and ions in a plasma that emit element specific electromagnetic radiation. The intensity of such emission gives quantitative information on concentration of a particular element.

2.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy characterizes a material in terms of its elemental composition, chemical state and electronical state of its contained elements. The material is excited with x-rays while the kinetic energy and the number of electrons that escape from the top 1–10 nm of the material is analyzed.

This surface chemical analysis technique is based on element characteristic set of x-ray photoelectrons, which are detected by counting the number of photoelectrons as a function of their binding energy. Peaks from a XP spectra reveal a direct identification of each element that exists on or in the top layers of a material. Those peaks correspond to the electron configuration of the electrons within the atoms (*e.g.* 1s, 2s, 2p etc.) and the number of electrons in each such peak is directly related to the amount of an element within the irradiated area.

2.5. X-ray diffraction (XRD)

X-ray diffraction is a powerful tool for crystalline particle characterization. The method provides data with elevated statistical relevances. With respect to the introduced microscopy technique TEM XRD provides several advantages, involving simple and fast sample preparation, uncomplicated experimental executions and statistically relevant easily interpretable results.

The method is based on elastic scattering of x-ray on a well ordered crystal structure. Crystals characteristics are governed by periodic atom arrangements defined by a unit cell of the crystal structure, which build crystal planes, as shown schematically in figure 2.1. The technique is based on studying the diffraction patterns, which result from interference of elastically scattered x-rays. Bragg's law⁵² gives a relationship between the incident irradiation wavelength λ , its scattering angle θ and the distance between the crystal lattice planes d, where n is an integer:

$$2d \cdot \sin \theta = n \cdot \lambda . \tag{2.3}$$



 $\Delta_1 + \Delta_2 = 2d\cos(90^\circ - \theta) = 2d\sin\theta$

Figure 2.1.: Visualization of Bragg equation. Maximum scattered intensity is only observed when the phase shift add to a multiple of the incident wavelength λ .

In terms of crystal characterization the observed diffraction patterns are integrated to exhibit scattering intensity as a function of scattering angle. The crystallite size is determined by studying the shape of the observed diffraction peaks.

The broadening of an observed diffraction peak can be characterized in a simplistic way by its Full Width at Half Maximum (FWHM) value at a particular 2θ angle. Because the apparent FWHM of a peak is a mathematical combination (convolution) of the specimen broadening FW_S and the instrumental broadening FW_I , it is necessary to characterize the goniometer in use to obtain the FW_I values as a function of 2θ angle, *i.e.* an FWHM curve. This can be done by acquiring a good scan pattern from a standard reference material that does not exhibit significant specimen broadening. These FWHM values can be considered to represent the instrument broadening FW_I , because the specimen broadening is negligible.

The first advanced concept on application of the line broadening technique was developed by Scherrer.⁵³ If the crystallites (i.e., crystalline domains) in the specimen are free of lattice strain, their average size D_{XRD} can be estimated from the specimen broadening FW_S of any single peak in the observed pattern according to the Scherrer formula (eq. 2.4), where K is the shape factor of the average crystallite with a typical value of 0.89 and λ is the wavelength of irradiating x-ray in Ångström.

$$D_{XRD} = \frac{K \cdot \lambda}{FW_S \cdot \cos\theta},\tag{2.4}$$

2.6. Electrochemical methods

Characterization of a catalyst in terms its electrochemically active surface area (ECSA) and its activity for a half cell reaction of interest (here ORR, as described in chapter1.1) is a key issue in fuel cell research.^{1–3;6} The as prepared catalyst powders, are usually tested on rotating disc electrodes (RDE) in order to determine the desired information. RDE technique allows accurate and reproducible electrochemical catalyst characterization.^{54;55} Each experiment requires preparation of a catalyst ink. Initially polished RDE is then coated with the catalyst suspension in order to build a homogeneous catalyst film. Such prepared RDE acts as working electrochemical cell in order to perform electrochemical investigations. The setup yields, depending on the selected potentiostate settings and experimental conditions, the electrochemically relevant parameters.

Commonly, stability tests of a fuel cell catalyst are performed using the cyclic voltammetry (CV) technique. Applying an accelerating stress test (AST) protocol and determining ECSA estimates after a certain number of CVs the ECSA change is observed as a function of potential cycles number. Correspondingly, the activity of a fuel cell catalyst for ORR is estimated from linear sweep voltammogramms (LSV).

In this section some relevant theoretical aspects on the mainly in this thesis applied electrochemical techniques CV and LSV will be given.

2.6.1. Cyclic voltammetry (CV)

Current density signal as a function of potential reveals the information on chemical processes taking place in an electrochemical cell. For CV experiments a triangular potential protocol is applied on the working electrode, whereas the the current is monitored. Figure 2.2 demonstrates a CV measurement performed on Pt nanoparticles supported on a high surface area carbon (HSAC) containing catalyst in 0.1 M $HClO_4$ with a potential scanrate of 50 $mV \cdot s^{-1}$.

Current signal identifies two main reversible reactions taking place on Pt nanoparticles surface: hydrogen underpotential ad- and desorption (0.05–0.40 V) and oxygen ad- and desorption (0.60–1.10 V).⁵⁴

ECSA of Pt can be determined by calculation the area under the H_{upd} -corresponding current peak (eq. 2.5a) and dividing this experimentally accessible value by the theoretical value Q_{theo} (eq. 2.5b) that is the amount of charge produced by hydrogen molecules covering a Pt surface, assuming one hydrogen occupying one Pt atom. Finally the Pt area estimate is divided by mass of Pt deposited on the RDE disk (2.5c).

$$Q_{exp} = \int_{\phi_1 = 0.05V}^{\phi_2 = 0.40V} I(\phi) dt , \qquad (2.5a)$$

$$Q_{\rm theo} = \frac{210\mu C}{\mathrm{cm}_{\mathrm{Pt}}^{-2}} , \qquad (2.5b)$$

$$ECSA = \frac{Q_{exp}}{Q_{theo} \cdot mass_{Pt}} .$$
 (2.5c)

2.6.2. Linear sweep voltammetry (LSV)

ORR activity can be estimated using the LSV technique.³ The reactant, O₂ is inserted in the electrolyte by saturating the solution with Oxygen gas. Current density is detected as a function of an anodically sweeped potential. The obtained polarization curve consists of three regions controlled mainly by: i) diffusion, ii) kinetics of the reaction and iii) mix of i and ii, as illustrated in figure 2.3. Such separation is deduced from the Koutecký-Levich



Figure 2.2.: Cyclic voltammogram of nanocrystalline Pt / HSAC in 0.1 M HClO₄. The solution was purged with N₂ and the measurement was cariied out at 25°C with 50 mVs⁻¹. Red region marks the area of H_{upd} -region used for ECSA calculations, where first the capacitive current j_c was subtracted.

equation (2.6a), which is valid for a rotating electrode:

$$\frac{1}{j_{sum}} = \frac{1}{j_{kin}} + \frac{1}{j_{diff}},
= \frac{1}{j_{kin}} + \frac{1}{BC_{\Omega}\omega^{\frac{1}{2}}};$$
(2.6a)

$$BC_{O}\omega^{\frac{1}{2}} = 0.62nFD_{O}^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}C_{O} .$$
(2.6b)

where the variables are: j_{diff} : diffusion limited current density, j_{kin} : kinetic limiting current density, $BC_0\omega^{\frac{1}{2}}$: Levich equation, C_0 : O_2 solubility of in the electrolyte $(1.18 \text{ mol m}^{-3})^{56}$, n: number of electrons required per mole of reactants, F: Farraday's constant (96485.341 C mol⁻¹), D_0 : diffusion coefficient of Oxygen in the electrolyte (= $1.9 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1.56}$), ν : viscosity of the electrolyte ($0.893 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$)¹³, ω : rotation rate of the RDE in rpm (1 rpm = $\pi/30 \text{ rad s}^{-1}$)⁵⁷.

In terms of a rotating working electrode, the mass transport limited current density can be neglected due to a high velocity and a consequent minimization of mass transport problems. The diffusion limited current density can easily be obtained by calculating the mean value



Figure 2.3.: Example of a LSV measurement performed in O_2 -saturated 0.1 M HClO₄ with a scanrate of 5 mVs⁻¹. Region used for determination of diffusion limited current density j_{diff} is red-coloured.

of the current density in the corresponding potential region (0.2–0.5 V vs RHE), as shown in figure 2.3. To calculate the kinetic limited current density j_{kin} the detected current density j_{sum} at a potential of 0.9 V vs RHE was established to be a suitable value.³ Subsequently, estimate j_{kin} from expression 2.6a is divided by Pt mass contained on a square centimeter of RDE in order to specify a quantitative Pt-mass based catalyst activity.

2.7. Small angle x-ray scattering (SAXS)

2.7.1. Fundamentals

Small angle x-ray scattering is a powerful analytical tool for characterization of nano scaled systems, such as nanoparticles of different shapes and sizes. An outstanding advantage of this non destructive technique is the possibility of probing samples in an unmodified environment during a reaction performance. In this research nanoparticles of different shapes and compositions were monitored in situ during electrochemical treatment in a fuel cell environment.

SAXS is based on elastic scattering of x-rays on the electron clouds of the particle's atoms.

Figure 2.4 illustrates schematically the basic principle of scattering: Two parallel incoming x-ray waves (wave-vector $\overrightarrow{k_0}$) are scattered (resulting wave vector \overrightarrow{k}) on two electrons of a particle with a distance \overrightarrow{r} . Scattering of two photons on different scattering centers results an interference of the out coming x-ray waves. A phase shift $\Delta \varphi$ is a consequence of the different path lengths x of the scattered photons. Hence, a detected signal is the scattering intensity as a function of scattering angle.

As it is valid for all kind of waves, the intensity per volume unit is proportional to the square of the amplitude magnitudes. To calculate a scattering amplitude a phase $\Delta \varphi$ has to be determined. To achieve that the wave vectors are used. As mentioned above, vector $\overrightarrow{k_0}$ defines the incident wave and \overrightarrow{k} the scattered one. The magnitudes of the wave vectors are:

$$\left| \overrightarrow{\mathbf{k}_0} \right| = \left| \overrightarrow{\mathbf{k}} \right| = \frac{2 \cdot \pi}{\lambda}$$
 (2.7)

The phase is therefore $\Delta \varphi$:

$$\Delta \varphi = \overrightarrow{\mathbf{r}} \left(\overrightarrow{\mathbf{k}} - \overrightarrow{\mathbf{k}_0} \right) = \frac{2\pi}{\lambda} r \left(k - k_0 \right) = \overrightarrow{\mathbf{q}} \overrightarrow{\mathbf{r}}.$$
(2.8)

Equation 2.8 introduces the scattering vector \overrightarrow{q} , which can be expressed as:

$$\overrightarrow{\mathbf{q}} = \left(\overrightarrow{\mathbf{k}} - \overrightarrow{\mathbf{k}_0}\right) =$$
 and $|\overrightarrow{\mathbf{q}}| = \frac{4\pi}{\lambda} \cdot \sin(\theta).$ (2.9)

The magnitude of the scattering vector (eq. 2.9) allows a comparison of the scattering curves obtained with different instruments or different excitation wavelengths. It is convenient to use a wavelength independent parameter, such as \overrightarrow{q} , because the wavelength λ of the incident beam is adjusted for every instrument depending on the selected x-ray source. Scattering patterns consist of the scattering intensity as a function of scattering vector.



Figure 2.4.: Scheme of small angle x-ray scattering (SAXS) principle.

The scattering intensity is the square of the wave amplitude and can directly be calculated using ($[A(\overrightarrow{q})]$) and the corresponding complex conjugate ($[A(\overrightarrow{q})]^*$) magnitude, which can be expressed as:

$$I(\overrightarrow{q}) = A(\overrightarrow{q}) \cdot [A(\overrightarrow{q})]^*.$$
(2.10)

The amplitude $A_{sum}(\vec{q})$, (the sum of all secondary waves A_j in phase, scattered with an angle θ at all present scattering centers), is given by the sum of all N outgoing spherical waves. Thus, the interference is only dependent on the phase shift of each secondara wave (eq.2.8), which is defined by the position of the scattering centers. Herewith the expression for A_{sum} is given as follows, assuming the atoms as scattering centers and defining the number of electrons at each atom j proportional to the scattering length density n_i :

$$A_{sum}\left(\overrightarrow{\mathbf{q}}\right) = \sum_{j=1}^{N} n_j A_j = A_0 \sum_{j=1}^{N} n_j exp\left(-i\Delta\varphi\right) = A_0 \sum_{j=1}^{N} n_j exp\left(-i\overrightarrow{\mathbf{r}_j} \overrightarrow{\mathbf{q}}\right).$$
(2.11)

The amplitude A_0 denotes the amplitude of the incident, corresponding to the scattering angle of 0. However, considering the enormous number of electrons and the fact that a single electron can not be exactly localized, it is convenient to introduce the electron density $\rho(\vec{r})$. The sum amplitude is then calculated using the electron density in the illuminated volume V. Consequently, equation 2.11 is replaced by:

$$A_{sum}\left(\overrightarrow{\mathbf{q}}\right) = A_0 \int_V \rho\left(\overrightarrow{\mathbf{r}}\right) exp\left(-i \overrightarrow{\mathbf{q}} \overrightarrow{\mathbf{r}}\right) d^3 \overrightarrow{\mathbf{r}}.$$
(2.12)

Similarly, the measured intensity, given by equation 2.10, can be converted to a double integral:

$$I(\overrightarrow{\mathbf{q}}) = \int_{V} \int_{V} \rho(\overrightarrow{\mathbf{r}_{1}}) \cdot \rho(\overrightarrow{\mathbf{r}_{2}}) \cdot exp(-i\overrightarrow{\mathbf{q}}(\overrightarrow{\mathbf{r}_{1}} - \overrightarrow{\mathbf{r}_{2}})) d^{3}\overrightarrow{\mathbf{r}_{1}} d^{3}\overrightarrow{\mathbf{r}_{2}}.$$
 (2.13)

Consequently, the intensity obtained from **all** inter and intra particular distanced scattering centers the probed volume V is given by equation 2.13. To solve the expression 2.13 it is plausible to first integrate over all scattering center pairs with an equal distance and subsequently over all vectors in the irradiated volume V. To achieve this an autocorrelation function $\gamma(\vec{r})$ (eq. 2.14a) can be defined with $\vec{r} = \vec{r_1} - \vec{r_2}$, which transforms the double

integral 2.13 to 2.14b:

$$\gamma(\overrightarrow{\mathbf{r}}) = \int_{V} \rho(\overrightarrow{\mathbf{r}_{1}}) \ \rho(\overrightarrow{\mathbf{r}_{1}} - \overrightarrow{\mathbf{r}}) \, \mathrm{d}^{3} \overrightarrow{\mathbf{r}_{1}}; \qquad (2.14a)$$

$$I(\overrightarrow{q}) = \int_{V} \gamma(\overrightarrow{r}) \rho(\overrightarrow{r}) \exp(-i\overrightarrow{q} \overrightarrow{r}) d^{3}\overrightarrow{r}.$$
 (2.14b)

Using the double integral 2.14b, the general expression 2.15 given 1915 by Debye:⁵⁸

$$\langle exp(-i\overrightarrow{q}\overrightarrow{r})\rangle = \frac{\sin(qr)}{qr}$$
; (2.15)

and assuming the structure being represented by the finite region only (the electron density is constant in the inner space of a scattering shape and $\Delta \rho = \rho_{\text{object}} - \rho_{\text{environment}}$ at the finite region) the expression 2.14b can be rewritten for such isotropic objects to:

$$\gamma(\overrightarrow{\mathbf{r}}) = \begin{cases} \mathbf{V} \cdot \gamma(\mathbf{r}); & \mathbf{r} \leq \mathbf{r}_{\max,\text{object}} \\ \text{const}; & \mathbf{r} > \mathbf{r}_{\max,\text{object}} \end{cases}$$
$$\langle \mathbf{I}(\overrightarrow{\mathbf{q}}) \rangle = \mathbf{I}(\mathbf{q}) = 4\pi \int_{\mathbf{V}} \gamma(\mathbf{r}) \mathbf{r}^2 \frac{\sin(\mathbf{qr})}{\mathbf{qr}} d^3 \mathbf{r} \quad .$$
(2.16a)

If the particles are separated from each other widely enough, it is plausible to assume that they will contribute independently to the total scattering intensity. Consequently, focusing on only **one** single particle is sufficient for further considerations.

In case of only **one** single particle with a volume V_p and a maximum distance between two scattering centers D, a function P(q) termed as formfactor, which includes the complete information on the structure of the scattering object, can be determined by:

$$P(q) = \frac{4\pi}{V_p} \int_0^D \gamma_p(r) r^2 \frac{\sin(qr)}{qr} dr \quad .$$
 (2.17)

In this thesis the solutions of formfactors for spherical and for cubic particles are of main interest and are given at the end of this section.

However, during a scattering experiment a huge number of particles are irradiated simultaneously. In the case of sufficiently distanced monodisperse particles, where the electron densities are widely enough separated and no electronic interactions occur (interaction free particles), the formfactor overlays with the scattering profiles of the probed particles. The scattering intensity of one particle is according to 2.16a

$$I_{p}(q) = V_{p}^{2} P(q).$$
(2.18)

Consequently the measured scattering intensity has to be multiplied by the number of scattering objects N_{obj} in the irradiated probed area with a probed volume V in order to obtain a final scattering pattern:

$$I(q) = \frac{N_{obj}}{V} \cdot V_p^2 \cdot P(q) = \Phi \cdot V_p \cdot P(q).$$
(2.19)

The introduced varible Φ is the volume fraction, which represents the total volume of scattering centers in the illuminated volume.

2.7.2. Behaviour at q-values tending to 0 (forward scattering)

If the scattering vector \overrightarrow{q} tends to 0 in a dilute system, the formfactor 2.17 is dependent only on the radius of gyration R_G . Guinier and Fournet developed 1955 an approximation to calculate the measured geometrical characteristics of an object accounting solely the limit behaviour $\overrightarrow{q} \rightarrow 0$. To extract such information a limited development of the formfactor 2.17 can be done. Hence, reaching the limit of q the total measured intensity for three dimensional objects 2.19 can be expressed as:

$$\lim_{q \to 0} I(q) = \Phi V_p \left[1 - \frac{(qR_G)^2}{3} + \cdots \right] = \Phi V_p exp \left\{ -\frac{(qR_G)^2}{3} \right\}.$$
 (2.20)

Transforming the measured intensity curve into a linear curve using the Guinier plot (ln I(q) vs. q^2) the radius of gyration can be obtained from the slope $R_G^2/3$.

The approximation can be extended also to rod-like and plane objects by expression 2.21. The apparent particle shape (also called dimensionallity) is then represented by α , which is an integer with values depending on object's structure: 0 (sheroid), 1 (rod-like) and 2 (plane). The preexponential factor A in 2.21 describes the excess differential cross-section per unit mass of a particle.

$$I(q) = \begin{cases} 1 & \text{for } \alpha = 0\\ \alpha \pi q^{-\alpha} & \text{for } \alpha = 1, 2 \end{cases} A \exp\left\{\left(-\frac{R_{\alpha}^2 q^2}{3-\alpha}\right)\right\}$$
(2.21)

2.7.3. Behaviour in the large q limit

If q tends to large limits, the measured scattering intensity must depend on the surface of the scattering objects in some way. For such case, Porod calculated the following approximation:⁵⁹

$$\lim_{q \to \infty} I(q) = \frac{2\pi (\Delta \rho)^2}{q^4} \frac{S}{V}.$$
 (2.22)

The variables S and V denote surface area (S) and volume (V) of an object. The experimental determination of the "Porod-limit" can be made easier using a plot $I(q)q^4$ versus q^4 . Indeed, when a constant background b_0 is present (due to the incoherent contribution for instance), this plot yields $I(q)q^4 = b_0 + b_1q^4$ and the background b_1 can be easily separated from the Porod-limit b_0 .

2.7.4. Formfactor for spherical particles

For the special case of a sphere (radius R_{sp} , volume V_{sp} of uniform density the formfactor of a sphere P_{sp} has been given by Rayleigh:⁶⁰

$$P_{sp}\left(q\right) = \left[\Delta\rho \cdot 3 \cdot \frac{\sin\left(qR_{sp}\right) - qR_{sp} \cdot \cos\left(qR_{sp}\right)}{\left(qR_{sp}\right)^3}\right]^2$$
(2.23)

2.7.5. Formfactor for parallelepiped particles

For the special case of a planar object the formfactor consists of two separate partial functions:⁵⁹ i) cross section formfactor $P_{cs}(q)$ for short dimensions and ii) shape factor P'(q) for larger dimensions, as shown in the expressions below. According to literature, the formfactors can be considered separately by assuming the shape factor to be a very thin disc. In case of a parallelepipendron, the radius of such thin disc is the spatial diagonal of an object, which equals to radius of gyration of a planar object. The value can be estimated

from extended Guinier's approximation for a planar object (eq. 2.21).

$$P_{\text{planar}}(q) = P'(q) \cdot P_{cs}(q)$$
(2.24a)

$$P'(q, R_{disc}) = \frac{2\pi^2 R_{disc}^4}{(qR_{disc})} \cdot \left(1 - \frac{J_1(2qR_{disc})}{qR_{disc}}\right) \approx R_{G,\alpha=2} , \qquad (2.24b)$$

labeleq : shape_factor_ppJ₁(x) =
$$\frac{\sin x}{x^2} - \frac{\cos x}{x}$$
; x = 2qR_{disc}, (2.24c)

$$P_{cs}(q;\Delta\rho,L) = \left(\Delta\rho L \frac{\sin\left(\frac{qL}{2}\right)}{\frac{qL}{2}}\right)^2 .$$
(2.24d)

Here, $J_1(x)$ is the first order spherical Bessel function, $P_{cs}(q, R_{disc})$ is the formfactor for an infinite thin disc, L is the length of the planar object.

2.7.6. Anomalous small angle x-ray scattering (ASAXS)

Anomalous SAXS is a modified approach of conventional SAXS method. The technique is based on sequent scattering measurements using different irradiation wavelengths. The aim of such implementation is the extraction of element specific scattering contributions of each element contained in the probed sample. An outstanding advantage is the possibility of scattering intensity isolation for different elements. Hence, characterization of nanoparticle alloy system, where several metals scatter simultaneously, or isolation of nanoparticles from a scattering matrix can be performed.

The essence of ASAXS is the amplification of a scattering experiment by precise selection of irradiation energies. The excitation of electrons to higher energetic states is strongly dependant on the elements electronic structure. Hence, each element can be characterized by in its specific x-ray absorption energies. Consequently, absorption of x-ray photons will become a preferred process the closer the irradiation energy is chosen to the absorption energy of the element and a suppressed scattering behavior will be the accompanying phenomenon. Figure 2.5 illustrates the context of scattering behavior, represented by the scattering factors, as a function of exciting energy.

To achieve precisely selectable excitation energies for an ASAXS measurement an appropriate x-ray source is needed. Presently, solely synchrotron facilities provide such an option (a detailed overview of synchrotron radiation specifications is described in the following section).



Figure 2.5.: ASAXS principle demonstrated for Ni and Pt resonant scattering bahaviours. Doted lines in the plots show an example of element specific set of selected energies, respectively.

An ASAXS experiment consists of a sequently detection of scattering profiles at different energies, which have to be selected in respect to the element of interest near by and additionally sufficiently far away from the x-ray absorption edge (doted lines in figure 2.5 show a set of selected energies). A correct extraction of the resonant scattering part requires absolute calibration of scattering curves. Furthermore, data acquisition must provide a low signal-to-noise ration in order to enable sufficient scattering pattern treatment.

A well established calculation method for resonant scattering curves is a calculation known as Stuhrmann-method.^{61;62} This method considers a mathematical relationship for several scattering curves obtained at different energies to extract the element of interest resonant term of scattering from the total scattering contribution. As reported in literature, an essential equation for this purpose is:

$$I(q; E_i) = I_0(q) + 2 \cdot f'(E_i) \cdot I_{0r}(q) + \left\{ (f'(E_i))^2 + (f''(E_i))^2 \right\} \cdot I_r(q) .$$
(2.25)

Here $I(q; E_i)$ is the scattering curve measured at energy E_i , $I_0(q)$ is the non resonant part of scattering, $I_r(q)$ the resonant part, $I_{0r}(q)$ a cross term of the resonant and non resonant scattering, $f'(E_i)$ and $f''(E_i)$ are the element specific scattering factors at the energy E_i . The expression can be rewritten as:

$$c_i = x + a_i \cdot y + b_i \cdot z \tag{2.26}$$

with given parameters

$$c_i = I(q; E_i) ; a_i = 2 \cdot f'(E_i) ; b_i = \{ (f'(E_i))^2 + (f''(E_i))^2 \}$$

and unknown values

$$x = I_0(q) ; y = I_{0r}(q) ; z = I_r(q) .$$

As it can be clearly seen from expression 2.26, minimum 3 different energies are required for determination of the resonant term $I_r(q)$, which is accessible by solving the system of 3 equation by z. Stuhrmann method reveals element specific scattering curves from multi component systems. Scattering contribution from each element is accurately determined using the expression 2.25 (or similar 2.26).

However, a simplified method for obtaining of element resonant scattering curves, based on subtraction of a curve measured with x-rays of energy near the absorption edge of the metal of interest from a curve measured with x-rays of energy far away from the edge, can be employed instead. This method is limited by number of elements contributing to scattering in the observed q-range. If, for instance, a trimetallic nanoparticle alloy is investigated and, hence, three elements scatter in the same q-range, this calculation method is not reliable. In the case of two scatters the method can be certainly used. Here termed as subtraction method (eq. 2.27), the calculation inspired by Haubold et al.,³⁶ can be used for determination of resonant scattering curves as well. The calculation relies on the following expression:

$$I_r(q) = I(q; E_2) - I(q; E_1); \qquad E_1 > E_2.$$
 (2.27)

Minimizing the number of required incident energies for calculations of resonant terms yields a suppressed data acquisition time and, hence, a shorter experiment procedure. Another advantage is that the calculation is much simpler compared to the Stuhrmann method.

In any case, using the Stuhrmann or the subtraction method, subsequent to the extraction of resonant scattering part, data treatment is performed similar to conventional SAXS. Details on determination of parameters of interest are given in section 3.12.5.

2.7.7. Synchrotron radiation

A synchrotron facility is an experimental station with an electron accelerator as radiation source. An electron gun produces electrons, which are injected into a circular channel. Using carefully adjusted undulators in an ultrahigh vacuum a circular self-supported movement of the injected beam is realized. Such accelerated electrons produce electromagnetic radiation tangential to the vector of the angular velocity. The as excited brilliant radiation is captured in a separate storage ring and is than used for experiments.
The advantages of synchrotron radiation in comparison to conventional radiation sources can be summarized as follows:

- an intensive and continuous spectrum from infrared to hard x-ray,
- high focus of the radiation up to 1 mrad (means: the beam expands only from 0.1 mm to 1 mm on a distance of 1 meter),
- linear polarization on the level of the accelerator,
- circular polarization above and below the level,
- high light density of the source,
- an exactly pulsed radiation source with light impulses up to 100 pico seconds,
- definite calculation of the radiation quality and properties,
- "'clean"' vacuum c Torr), no gas or plasma during radiation exciteme
- high stability of t

d synchrotron facilities.



Figure 2.6.: Assembly of a synchrotron facility BESSY II, adopted from⁶³.

Part of the experiments, especially ASAXS experiments, were carried out at BESSY II (Berlin Electron Storage Ring for Synchrotron Radiation, operated by the Helmholz Center Berlin). The assembly is illustrated in figure 2.6. Also parts of the experiments were performed at SLAC (National Accelerator Laboratory, operated by Stanford University for the Department of Energy Office of Science).

3. Experimental procedures

In this chapter routine experimental procedures are described. In case of a specialized method or setup the experimental procedure is described in the respective chapter. Used chemicals are listed in table 3.4, where also specifications of purity and providing company are given.

3.1. 2-3 nm Pt nanoparticles

3.1.1. Synthesis of spherical nanoparticles⁴⁴

Spherical nanoparticles were synthesized via a wet chemical route using the ethylen glycol reduction method: 5 mM of H₂PtCl₄ was dissolved in 50 ml of a 15 mM NaOHethylenglycol solution. (The alkaline solution of NaOH in ethylenglycol was prepared few day prior to synthesis, because the NaOH dissolution was a time consuming process.) After complete dissolution of metal salt in the alkaline medium, indicated by a homogeneous yellow colour, the mixture was overflown with nitrogen gas for 10 to 15 minutes in order to remove air. Subsequently the mixture was heated to 160°C with reflux under nitrogen atmosphere. The temperature was kept constant at 160°C for 20 minutes. Color change of the solution from yellow to dark brown indicated the formation of Pt nanoparticles. The reaction solution was cooled down immediately using a water bath to stop further nucleation. After this step protective atmosphere was not any more required. The as prepared nanoparticles remained stable for longer time: No change in mixture composition or particle size was observed even after few days of solution storage.

3.1.2. Deposition on carbon supports

Additionally, a propriate amount of support material, (depending on the desired catalyst weight loading, such as Vulcan or modified and unmodified multi walled carbon nanotubes), was dispersed in a 250 ml Erlenmeyer flask in 20 ml of water and sonified for 10 minutes. The as prepared Pt-NP solution was added at room temperature to the stirred support

suspension. 80 ml of a 2 M sulfuric acid were added slowly with stirring to the Particlescarbon mixture to change the pH from alkaline and enhance the nanoparticle deposition on the carbon support. The solvents were removed by centrifugation (5 minutes 7700 rounds per minute). The solid residue was washed with ultra pure water and the liquid was removed again by centrifugation. The washing procedure with a subsequent removal of liquid residuals by centrifugation was repeated three times and the remaining wet catalyst powder was freeze-dried afterwards (24 h, 0.035 mbar, -40°C, Labconco FreeZone6, Germany).

3.2. 4-5 nm Pt nanoparticles

3.2.1. Synthesis of spherical nanoparticles⁶⁴

In order to achieve a final Pt metal loading on carbon of 20% 0.20 mmol (80 mg) $Pt(acac)_2$ were dissolved in 18 ml of o-dichloro-benzol (DCB) at room temperature. Subsequently a mixture of 100 μ l oleic acid (OA) and a solution of 0.65 mmol (148.5 mg) tetradecane-1,2-diol (TDD) in 5.4 ml DCB was added to the metal-DCB solution. The mixture was sonicated for 10 minutes and overflown with a protective gas (N₂) for 10 min in order to remove excess of air. Following, the mixture was heated to 180°C. At this set temperature a solution of 3 μ mol (1.1 mg) $Co_2(CO)_8$ in 100 μ l DCB was injected to the hot mixture *via* a syringe, which was floated with N₂ several times prior to use, in order to prevent air contamination. The mixture was held at the set temperature of 180°C for further 30 min and then removed from the hot silicon bath in order to allow the solution to cool down to room temperature. After this step there was no need of protective gas usage. Next, the solution was washed with 20 ml ethanol and 5 ml diclormethane (DCM) and residuals were removed by centrifugation (5 min, 7700 rpm).

3.2.2. Synthesis of cuboid nanoparticles⁶⁵

In a glas vial equipped with a glas frit 40 mg (0.1 mmol) $Pt(acac)_2$ were added under N_2 atmosphere to a mixture of 3.68 ml (8 mmol) oleyl-amine (OAM), 0.63 ml (2 mmol) and 5 ml dibenzyl-ether (DBE). After complete dissolution of all components CO gas was bubbled for 10 min *via* the glas frit, which was immersed into the solution. Next, the mixture was heated up to 200°C and the temperature was held for further 18 min and then removed from the hot silicon bath in order to allow the solution to cool down to room temperature.

3.2.3. Deposition on carbon support

In both cases spherical and cuboid Pt nanoparticles were supported on Vulcan XC72 R (VC) immediately after finishing the last synthesis step.

For this purpose a defined amount of VC (depending on the desired catalyst weight loading) was suspended in 40 ml Toluol. The dispersion was stirred rigorously for 24 h. Then liquids were removed by centrifugation (10 min, 7700 rpm) and the solid portions were washed with ethanol in order to remove residuals of liquid organic compounds. After a further centrifugation the as cleaned catalyst powder was freeze dried (24 h, 0.035 mbar, -40°C, Labconco FreeZone6, Germany).

3.3. Synthesis of $PtNi_6/Vulcan(VC)$ and $PtNi_3/VC$ catalysts

Details on particle synthesis and electrochemical characterization are described in a previous work.^{48;49} A polyol method, previously described in literature, 9 was chosen to prepare PtNi alloy nanoparticles. In a 100-ml threeneck flasks with reflux 0.3 mmol $Ni(ac)_2 \cdot 4H_2O$, 0.4 mmol 1,2-tetradecanediol, 0.3 ml OAM and 0.3 ml OA were added to 25 ml diphenyl ether. The reaction mixture was stirred for 5 min under nitrogen atmosphere, followed by raising the temperature to 80°C. After about 30 min, the temperature was raised to 200°C. At this temperature, 0.1 mmol $Pt(acac)_2$ dissolved in 1.5 mL DCB was added, and the reaction mixture was stirred at 200°C for 1 h. Subsequently, the reaction mixture was cooled down to room temperature; 5 ml DCM and 20 ml ethanol were added to the cooled reaction mixture. Separately, 78.1 mg of Vulcan XC 72R was mixed with 40 ml toluene and was dispersed in an ultrasonic bath for 10 min. This suspension was added to the reaction mixture and was stirred for 24 h at room temperature. The product was centrifuged and washed three to four times with ethanol as above, followed by drying in a freeze dryer. The dried catalyst was heated in a furnace in a N_2 atmosphere of 230°C and was held there for 4 h to remove surfactants and enhance the atomic mixing of Ni and Pt.

3.4. Synthesis of nitrogen-doped coatings on MWCNT

3MBP-dca was acquired from VWR. MWCNTs were Baytubes purchased from the Bayer® company. Sulphuric acid was acquired from Sigma Aldrich. Ethanol was acquired from Carl Roth with a purity of 99.8%. The chemicals were entirely used without further treatment. Annealing of samples was accomplished in Nabertherm® box type furnaces, equipped with a continuous gas. CNTs were pre-oxidised by dispersion in sulphuric acid ($c = 2 \text{ mol} \cdot l^{-1}$)

by sonication. After stirring the dispersion vigorously overnight the black residue was isolated by centrifugation, frequently washed with deionised water and subsequently dried overnight in the vacuum drying oven. For the preparation of the coating the MWCNTs were dispersed in a 30 wt% solution of 3MBP–dca in deionised water by sonication. The resulting black slurry was filtered by vacuum filtration and the black residue in the filter was washed with 50 ml of ethanol to remove excess IL. The residue was subsequently placed in ceramic crucible and thermally treated in a furnace under constant argon flow to 1000°C applying a heating rate of 100 K \cdot h⁻¹. After 1 h at 1000°C the sample was allowed to cool down to room temperature and subsequently pestled for further use.

3.5. TEM measurements

For TEM sample preparation a small amount of the synthesized powder was dispersed *via* ultra sonication in 0.5 ml of ⁱPrOH. A Cu-grid with holey carbon film was impregnated with 2 μ l of the solution and air-dried. A FEI TECNAI G² 20 S-TWIN microscope, equipped with a GATAN MS794 P CCD-detector, was operated at an accelerating voltage of 200 kV.

3.6. BET measurements

A defined amount of a sample was filled into a BET glas tube. Samples were degassed at 150°C for 20 h at reduced pressure before measurement. Nitrogen adsorption isotherms (equation 2.1c) were measured using a Quadrasorb porosimetry device manufactured by Quantachrome. The calculation of the specific surface area was performed using equation 2.2a, as described in chapter 2.2.

3.7. ICP-OES measurements

The weight loading of Pt-NP on carbon support was determined using optical emission spectroscopy with inductive coupled plasma as ionization source (ICP-OES). Theoretical background of the method is described in the chapter 2.3. For spectroscopical measurements a defined amount in the range of $\sim 5 \text{ mg}$ of a dry powder (m_{powder}) was dissolved in a quartz tube in 10 ml of a mixture of concentrated acids: sulfuric (2 ml), nitric (2 ml) and chloric (6 ml) acids. Vigorously stirring the solution in a fume hood overnight allowed the acid mixture to degas. Prior to exposure of the residual solution to microwaves the

mass of the solution was determined (This value $m_{\rm ini}$ was important for calculation of the Pt weight-percentage after ICP-OES measurements).

The first step of the digestion *via* microwave treatment was a constant heat up to 180°C during 10 minutes with a constant heat gradient, which was adjusted automatically by the microwave accompanying software. The temperature was held for 20 min, whereas the pressure of evolvong gas was controlled to not exceed 18 bar. The solution was filtered to remove the remained carbon, diluted to 3 defined different concentrations and analyzed with ICP-OES Varian 715-ES. Several wavelengthes were chosen in the ICP-OES software to detect Pt emission: $\lambda_1 = 203.6$, $\lambda_2 = 204.9$, $\lambda_3 = 214.4$, $\lambda_4 = 265.9$, $\lambda_5 = 306.5$ nm, respectively.

Calculation of metal amount

The amount of a dissolved metal was determined using a standard calibration method. For this purpose a standard aqueous solution of Pt with a concentration of 999 mg \cdot l⁻¹ and a density of 1.034 kg \cdot l⁻¹ (\Rightarrow molality of Pt of 966.15 mg_{Pt} \cdot kg⁻¹_{water}) was diluted to 3 different concentrations as shown in detail in table A.2 using a balance. Additionally a blank standard with a Pt concentration of 0 was used as a first measurement for ICP-OES calibration. The as prepared powder digestion solution was diluted with water to achieve two different molalities of Pt in the range of standard molalities (2-10 mg_{Pt}/kg_{H₂O).}

The emissions of the fresh prepared standard solutions were measured with the ICP-OES software starting from the blank sample and following with the solutions with increasing metal amount. An automatically calculated linear calibration-curve was estimated by the software and used for the following measurements of sample molalities.

A mean value of the estimated molalities (5 wavelengthes were used for each sample) of Pt-aliquotes ($\overline{Pt_{ICP}}$) was used to calculate the Pt-weight percentage on the powder using the following equations:

m

$$m_{\rm solvent} = m_{\rm ini} - m_{\rm powder} \tag{3.1a}$$

$$M_{digestion} = \frac{m_{powder}}{m_{solvent}}$$
(3.1b)

$$ali_{digestion} = \frac{m_{digestion} \cdot M_{digestion}}{am_{Water}}$$
(3.1c)

$$wt\%_{Pt} = \frac{\overline{Pt_{ICP}}}{ali_{digestion}}$$
(3.1d)

The variables are assigned as:

 $\mathrm{m}_{\mathrm{solvent}}$: mass of pure solvents used for dissolution of Pt after degasing overnight,

 $\mathrm{m}_{\mathrm{ini}}$: determined mass of the powder solution after degasing overnight,

 $\mathrm{m}_{\mathrm{powder}}$: weighed quantity of catalyst powder,

 $\mathrm{M}_{\mathrm{digestion}}$: Pt amount in mg per kg acidic solvents,

ali_{digestion}: Pt-molality of an aliquote of the prepared digestion solution used for a diluted ICP-OES sample,

 $\mathrm{m}_{\mathrm{digestion}}$: weighed mass of an aliquote of the digestion solution,

 $\mathrm{am}_{\mathrm{Water}}:$ amount of water used for dissolution of the digestion solution

 $\mathrm{wt}\%_{\mathrm{Pt}}$: weight percentage of Pt in the catalyst powder,

 $\overline{\mathrm{Pt}_{\mathrm{ICP}}}$: mean of the estimated Pt molalities determined with ICP-OES at several wave-lengthes.

An example for such a calculation, where the digestion was diluted to 2 different molalities, is given in detail in table A.2 in appendix A.

3.8. XPS measurement

The XPS-measurement was performed using a VG ESCALAB 200 X xp-spectrometer, manufactured by VG Scientific, East Grinstead, UK. Using this spectrometer, electron spectra were recorded using polychromatic Al – K_{α} excitation (15 kV, 20 mA) and an emission angle of 0 degree. The spectrometer energy scale was calibrated following ISO 15472.⁶⁶ The survey scans were measured in constant retardation ratio (CRR) mode, while narrow scans were done in constant analyser energy (CAE) 20 mode. In order to correct the binding energy scale for static charging, an electron binding energy of 285.0 eV⁶⁷ for the C 1s reference level of aliphatic hydrocarbon was used. The samples were fixed nonconductively on a double sided silicon free carbon tape. The analysis of XPS spectra was done with the Unifit 2011 software, developed by R. Hesse, Unifit Scientific Software GmbH, Leipzig, Germany. As fitting strategy for the peak-shape analysis the convolution with a fully fitable Tougaard background correction was chosen.^{68;69}

3.9. XRD analysis

Diffraction patterns were collected with a Bruker D8 Advance Diffractomer operated with 40 kV, 40 mA in a 2θ -range of 15–100°. Angular resolution was set to 0.05° and diffraction signal at each step was collected for 5 s. XRD curves of catalyst containing particles were corrected by subtraction of corresponding blank samples XRD patterns. Such blank

measurements were conducted on samples with same composition, but excluding the presence of nanoparticles (*e. g.* carbon support only). The size of crystalline particles was calculated using a software package MDI Jade 8, . In particular, for this purpose each diffraction peak from a background-corrected pattern was fitted with a Pearson Voigt type distribution. Peak positions were selected by overlaying a selected reference pattern (PDF data files, National Institute for Science and Technology). Using the Scherrer equation (eq. 2.4) crystallite size was estimated for each peak fit. All estimates for single peaks of a diffraction pattern were averaged by mean and additionally the corresponding error of mean was calculated (similar to eq. 3.3b).

3.10. High energy XRD measurements

High-energy XRD measurements were performed at the beam line 11IDC, at the Advanced Photon Source, Argonne using x-rays of energy 115 keV (λ =0.1078 Å⁻¹). The diffraction data were reduced to the so-called structure factors, S(q), and then Fourier transformed to the corresponding atomic PDFs G(r), using the relationship:

$$G(r) = \frac{2}{\pi} \int_{q=0}^{q_{max}} q \ S(q) \ \sin(qr) \ dq$$
(3.2)

where $q_{max} = 28$ Å⁻¹ in the present experiments. The scattering vector q is defined as given by the expression 2.9.

Note, as derived, atomic PDFs G(r) are experimental quantities that oscillate around zero and show positive peaks at real space distances, r, where the local atomic density $\rho(\mathbf{r})$ exceeds the average one ρ_0 . This behavior can be expressed by the equation $G(\mathbf{r}) = 4\pi\rho_0(\rho(\mathbf{r})/\rho_0 - 1)$, which is the formal definition of the PDF G(r). High-energy XRD and atomic PDFs have already proven to be very efficient in studying the atomic-scale structure of nanosized materials,⁷⁰ including chemical order-disorder effects.^{71;72}

Modeling details

The experimental PDFs were fit with structure models based on chemically disordered (S.G. Fm-3m) and chemically ordered (S.G. Pm-3m) cubic-type atomic arrangements found in noble-transition metal alloys. In this type of Bravais lattices based modeling a PDF for an infinite cubic lattice is first computed. Then each of the coordination spheres of the perfect lattice is broadened by a convolution with a Gaussian function to take into account the presence of thermal and static local atomic displacements in real nanoparticles. At

the same time the computed PDF is multiplied by a particle shape (spherical in our case) dependent function which is zero for distances longer than the size of the nanoparticles being modeled. It is a simplistic approximation to the structure of real NPs but is useful since it allows i) to verify the type of their atomic ordering and ii) obtain a set of structural parameters (e.g. lattice constants and atomic displacement amplitudes) that may be compared directly with those for the corresponding bulk materials. The computations were done with the help of the program PDFgui.⁷³

3.11. Electrochemical characterization

Electrochemical characterizations were conducted with a Biostat SP-200 potentiostate in a glass cell. A PINE glassy carbon (GC) rotating disc electrode (RDE) with a total surface area of 0.1963 cm^2 was used as working electrode. A saturated calomel electrode (SCE) was implemented *via* a Luggin-capillary into the experimental setup for setting desired overpotentials. All potentials in this thesis are given in respect to a reversible hydrogen electrode (RHE) in 0.1 M HCLO₄. A wraped 5x5 cm² Pt mesh fixed on a Pt wire acted as high surface counter electrode.

3.11.1. Ink preparation

For electrochemical measurements inks of the synthesized powders were prepared as following: ~ 5 mg of the powder, (the exact amount was determined with a highly precise balance and documented for each ink), was dispersed in a mixture of 2490 μ l of water, 2490 μ l iso-propanol and 20 μ l of a 5 wt-% Nafion solution in iso-propanol. The mixture was ultra sonified for 15 minutes using a Branson sonifier with an output power of 6 W in a cooling water bath.

3.11.2. Electrode preparation

The GC rotating disc electrodes were polished manually in two steps: first with Buehler "Alpha micropolish 1" solution on a Nylon sheet and second after rinsing with ultrapure water (to remove the residues of the micropolish solution) with Buehler "Alpha micropolish 0.05" solution on a Microloth® sheet. Electrodes were then sonicated in water, acetone and again water, each procedure for 5 minutes, to remove the polishing solution residues. The as prepared electrodes were coated with 10-20 μ l of an ink solution and air dried.

According to literature,³ the amount of catalyst ink was elected to adjust a Pt loading on the GC disc to 12-20 μ g/cm².

3.11.3. CV and LSV measurements

Electrochemical characterization was performed in 0.1 M $HClO_4$, saturated with N_2 for CVs and with O_2 for LSV. The potential step protocol is shown schematically in figure 3.1, details are summarized in table 3.1.



Figure 3.1.: Scheme of electrochemical characterization procedure: Chronoamperommetry, CA (solid grey); linear sweep voltammetry, LSV (solid blue); cyclic voltammetry, CV for H_{upd} estimation (solid red), activation cycles (dashed red) and accelerating stress test (doted red). Numbers give the amount of forward-backward scans.

Table 3.1.: Potential protocol for electrochemical characterization of catalyst powders. Hupd: CVsmeasured for calculation of the Pt surface area; Act: CVs for surface cleaning; LSV:LSV measured for determination the ORR-activity; AST: acceleration stress test CVs.

Technique	$\mathrm{H}_{\mathrm{upd}}$	Act	$\mathrm{H}_{\mathrm{upd}}$	LSV	AST	$\mathrm{H}_{\mathrm{upd}}$
# of cycles	3	200	3	0.5	100	3
Range / V	0.05-1.10	0.05-1.10	0.05-1.10	0.06-1.02	0.50-1.10	0.05-1.10
Rate $mV \cdot s^{-1}$	50	500	50	5	50	50
					\leftarrow Loopin	g sequence $ ightarrow$

ECSA was determined from CV (0.050 – 1.100 V, 50 mV s⁻¹) in the H_{upd} -range of 0.050 – 0.400 V, as described in chapter 2.6. The calculation of the ECSA has been performed with a script ECLab_v4.ogs (appendix A), which was developed for this purpose and executed by the Origin 8.1 (or newer) software.

The script evaluates the H_{upd} -area from a single measurement or from a looping sequence (see table 3.1) according to expressions 2.5c. In order to run the script a specified import filter for experimentally obtained .mpt-files was configured in the Origin-software. (A detailed description of filter configuration, data import and script execution is given in the appendix A.) Additionally, after an import of a LSV-measurement as .mpt-file into Origin software using the same mpt-Filer as for H_{upd} -calculation, the Pt-mass based activities were estimated using the LSV.ogs script (see appendix A).

Pt-mass based activities of the catalyst for the oxygen reduction reaction (ORR) were determined at 0.9 V from LSV (0.060 – 1.020 V, 5 mVs⁻¹) by factoring the geometric area of the glassy carbon disk (0.1963 cm^2), according to calculation introduced in chapter 2.6.2

3.11.4. Error estimation

Ink preparation and film formation on a glassy carbon electrode cause measurement uncertainties. To calculate representative values⁷⁴ the measurements were carried out two or three times for each catalyst powder, respectively. Presented results contain the mean value \bar{x} (equation 3.3a) and the corresponding error of mean e_j (eq. 3.3b), obtained using the empirical standard deviation σ (equation 3.3c). A definite number of measurements causes errors of the calculated mean value. The standard error in the calculated mean value e_j , which represents the expectation interval of a true mean value (e.g. $\bar{x_j} \pm e_j$), was calculated using equation 3.3b.

$$\bar{\mathbf{x}}_{j} = \frac{\sum_{i=1}^{n} \mathbf{x}_{i}}{n} , \qquad (3.3a)$$

$$e_j = \frac{1}{\sqrt{n}} \cdot \sigma_j$$
 with (3.3b)

$$\sigma_{j} = \sqrt{\frac{\sum_{i=1}^{n} (x_{i} - \bar{x})^{2}}{n - 1}}$$
(3.3c)

(3.3d)

Here, x_i is an estimated ECSA-value at each point j of the measurement (e.g. after activation cycles \bar{x}_{act} and 25 loops of AST cycles \bar{x}_{end}) and n is the number of values that have been averaged to a mean value \bar{x}_j ; σ_j is the empiric standard deviation and e_j is the

corresponding error of mean.

Calculation of a relative ECSA loss requires a consideration of error propagation. Hence, following relationship yields a resulting error (e_{loss}) for division of the two estimates e_{act} and e_{end} , which correspond to ECSA estimated after the activation regime (\bar{x}_{act}) and ECSA after all AST-cycles (\bar{x}_{end}) of the acceleration stress test regime (see table 3.1):

$$\bar{\mathbf{x}}_{\text{loss}} = (1 - \bar{\mathbf{x}}_{\text{end}} : \bar{\mathbf{x}}_{\text{act}}) \cdot 100 ,$$
 (3.4a)

$$e_{\rm loss} = \sqrt{\left(\frac{e_{\rm end}}{\bar{x}_{\rm end}}\right)^2 + \left(\frac{e_{\rm act}}{\bar{x}_{\rm act}}\right)^2 \cdot \bar{x}_{\rm loss}} .$$
(3.4b)

3.12. SAXS analysis

Synthesized and benchmark catalysts powders were characterized *ex situ* after preparation and *in situ* during an electrochemical protocol using SAXS.

3.12.1. Preparation of dry powder samples

Pristine catalysts were characterized using the as prepared powder after finishing all synthesis steps described in the section 3.1 of this chapter. A small amount of the powders was deposed on an adhesive Kapton pad, which was discharged electro statically prior to use. A second Kapton pad was used for coverage. A concomitant advantage of the sample preparation was the conservation of the fresh catalyst and isolation from any contaminants. Sample containing Kapton pad was used for SAXS profile measurements. A second, solely carrier powder containing, (depending on the catalyst powder the corresponding carbon background was chosen, *e.g.* MWCNT for Pt/MWCNT), prepared Kapton pad was used for background scattering detection.

3.12.2. Preparation of catalyst containing carbon-sheet electrodes

For each electrode a carbon sheet (25 x 25 cm sheets, 175 thick, Fuel cell store) was cut in \sim (1 x 4) cm piece and impregnated 10 times with 10 μ l of an ink solution (see section 3.11.1) to maximize the amount of Pt nanoparticles in the x-ray spot.

3.12.3. In situ SAXS/ASAXS measurements

Such prepared working electrodes were inserted into the *in situ* electrochemical cell, which was additionally equipped with a Pt-wire counter electrode and a 3 molar Ag/AgCl

reference electrode, as shown in figure 3.2. The overpotentials were set with a Gamry Ref-600 potentistate.



Figure 3.2.: Experimental setup for in situ SAXS/ASAXS measurements.

Characterization of catalyst powders was performed *in situ* during electrochemical treatment as follows:

- 1. Working and counter electrodes were inserted in the electrochemical cell and secured by tightening the alligator clips in the respective holder.
- 2. The position of a dry ink droplet was determined *via* Nanogarphy (included in the lab based machine software) or by transmission measurements at synchrotron beamlines (transmission decrease indicates the ink droplet).
- 3. At determined position a scattering pattern was collected for 2 seconds to ensure the presence of the catalyst (high count number compared to different location on electrode).
- 4. The maximum measurement time was calculated from the scattering pattern obtained in point 3 of this list in terms of detector saturation prevention. Maximum count number per second per unit of detector area was specified by manufacturer for each

used detecting unit.

- 5. A scattering pattern of a dry catalyst-loaded electrode was collected for the determined amount of time at the same position as identified in 3.
- 6. Reference electrode was mounted and subsequently the cell was filled with \sim 3 ml of a fresh prepared electrolyte. Immediatly, the potential protocol described in table 3.2 was started to prevent catalyst dynamics in acidic environment.
- 7. Chronoamperometry (technique 0) was performed for 2 minutes to let the system equilibrate and a first test SAXS pattern was collected for 10 seconds to determine the maximum number of counts, as described in point 4.
- 8. Further in situ SAXS measurements were performed according to table. 3.2.

Table 3.2.: Potential protocol for in situ SAXS/ASAXS characterization of catalyst powders. Electrochemical techniques are abbreviated as: CA (chronoamperommetry), CV (cyclic voltammetry), AST-CV (acceleration stress test potential cycles), n = [0:12]. All potentials are given in respect to a RHE, 0.1 M HClO₄.

# of technique	Technique	# of	Potential range	Scan rate	# of
		cycles	/[V]	$/[mV \cdot s^{-1}]$	loops
0	CA	-	0.50	-	_
1	SAXS/CA	-	0.50	-	_
3	Act-CV	200	0.05-1.10	500	_
4	SAXS/CA	-	0.50	-	_
5 + 2n	AST-CV	100	0.50-1.10	50	25
6 + 2n	SAXS/CA	_	0.50	_	25

In a special case of ASAXS experiments reference samples (GC, silver behenate and empty hole) were mounted at same distance to the detector as working electrode on side of the electrochemical cell holder, as shown in figure 3.2. The samples were measured before collection of each SAXS pattern in order to calibrate to an absolute scale. As described

in chapter 2.7.6 the isolation of an element specific part of scattering requires precise and absolutely calibrated data collection.

Metal foils (depending on the measured metal components of the probed catalyst, *e.g.* Pt and Ni foil in case of PtNi alloy nanoparticles) were located next to reference samples described above in terms of energy calibration. Prior to each ASAXS experiment the transmission of each foil was detected as a function of energy in order to determine experimentally element secific x-ray absorption edge. The shift of experimentally exhibited value in respect to the theoretical value was used for energy calibration. The difference between the experimental and theoretical value provided the information on energy scale shift of the experimental setup.

All reference data were recorded for ASAXS evaluation performed by beamline specific software SASred Tool. A detailed description is given in the software corresponding manual and in the doctoral thesis from Dr. rer. nat. S. Haas.⁷⁵

3.12.4. SAXS/ASAXS aquisition

SAXS experiments were conducted using three different setups:

- 1. Scattering data were collected with a Bruker AXS NanoStar lab system, equipped with a rotating Cu-target anode operated with 45 kV, 110 mA. The scattered x-rays of a Cu- K_{α} wavelength (0.154 nm) were detected with a 2D HiStar photon counter detector.
- Portions of the research were carried out at the SLAC National Accelerator Laboratory, a national user facility operated by Stanford University, at the beamline 1-4. Data were collected with a CCD of type MAR165 from Rayonix using the energy of 8333 eV as irradiation source.
- 3. Anomalous small angle x-ray scattering experiments were performed at Berlin synchrotron facility BESSY II, operated by the Helmholtz Zentrum Berlin, at the 7T-MWP-SAXS beamline. Data were collected with a CCD of type MAR165 from Rayonix using the energies 11490 and 11560 eV near below the Pt-L₃ absorption edge; as well as 8101 and 8330 eV that is near below the Ni-K edge.

3.12.5. General SAXS data treatment and mathematical fitting

Experimental scattering patterns were integrated in order to obtain I(q) *vs.* q scattering curves. Additional to each measurement transmission of each sample was determined: i)



Figure 3.3.: Transmission measurements using a lab based SAXS equipment.

using a glassy carbon (GC) plate, as shown in figure 3.3 for the lab based setup and ii) using an in the beamstop implemented diode at synchrotron facilities.

Transmission of probed samples was required for background correction of the scattering curves to isolate the scattering portions of interest, namely the scattering contribution $I_{NP}(q)$ of nanoparticles only. Background subtraction was performed using equation 3.5a with the respective determined transmission coefficients:

$$I_{NP}(q) = \frac{I_{NP+S}(q)}{\tau_{NP+S}} \quad \frac{I_S(q)}{\tau_S} , \quad \text{with}$$
(3.5a)

$$\tau_{\rm NP+S} = \frac{I_{\rm NP+S+GC} \quad \tau_{\rm GC} \cdot I_{\rm NP+S}}{I_{\rm GC} \quad \tau_{\rm GC} \cdot I_{\rm air}} , \qquad (3.5b)$$

$$\tau_{\rm S} = \frac{I_{\rm S+GC} \quad \tau_{\rm GC} \cdot I_{\rm S}}{I_{\rm GC} \quad \tau_{\rm GC} \cdot I_{\rm air}} \ . \tag{3.5c}$$

Here the symbols are:

 $I_{NP+S}(q)$: scattering curve from sample containing nanoparticles (NP) on support (S); $I_{S}(q)$: scattering curve from a background sample containing same scattering components as $I_{NP+S}(q)$, except nanoparticles;

 $\tau_{\text{NP+S}}$ and τ_{S} : transmission coefficients from samples (NP+S) and (S);

 $\tau_{\rm GC}$: transmission coefficient of the GC plate, (in the used configuration 0.035);

I_{air}, I_{NP+S} and I_S: total number of counts detected per second without GC plate;

 $I_{\rm GC}$, $I_{\rm NP+S+GC}$ and $I_{\rm S+GC}$: total number of counts detected per second with inserted GC plate. Such background corrected curves were fitted using SASfit software (version 0.93.2).⁷⁶

If a sample contains particles with different sizes (termed as a polydisperse sample), several contributing formafactors are added in order to produce a scattering pattern of the probed sample. This approach is essential for mathematical modeling of scattering curves. Hence,

a distribution function $f(R; \mu, \sigma)$ of objects with different sizes R completes the correct expression for the total scattering intensity by weighting in respect to diverse particle sizes:

$$I(q) = N_{obj} \int_{0}^{V} f(R; \mu, \sigma) V_{p}^{2} P(q) dV,$$
(3.6a)

$$f(R;\mu,\sigma) = \frac{1}{\sqrt{2\pi\sigma}R} \exp\left(-\frac{\ln\left(\frac{R}{\mu}\right)^2}{2\sigma^2}\right)$$
(3.6b)

 N_{obj} is the number of scattering particles in the probed volume V (as introduced in eq. 2.19), V_p is volume of a single particle, $f(R; \mu, \sigma)$ is a LogNormal distribution function, where μ and σ are the mean and standard deviation.

The mean value of a distribution can be defined in respect to the corresponding moments in different ways, whereas the n^{th} moment of a LogNormal distribution is given by:

$$\langle \mathbf{R}^{\mathbf{n}} \rangle = \frac{\int_{0}^{\infty} \mathbf{f}(\mathbf{R}; \mu, \sigma) \mathbf{R}^{\mathbf{n}} d\mathbf{R}}{\int_{0}^{\infty} \mathbf{f}(\mathbf{R}; \mu, \sigma) d\mathbf{R}}$$

$$= \exp\left(\mathbf{n}\mu + \frac{\mathbf{n}^{2}\sigma^{2}}{2}\right)$$

$$(3.7)$$

Table 3.3.: Mean particle size definitions for a distribution f(R) of particle radii R.

Name	Definition
Mean length or mean radius	$\mu = \langle \mathbf{R}^1 \rangle$
Area weighted or intersection length radius	$R_{li} = \frac{3}{4} \left< R^3 \right> / \left< R^2 \right>$
Volume weighted or correlation length radius	$R_{lc} = \frac{2}{3} \left< R^4 \right> / \left< R^3 \right>$
Guinier radius	$R_{G} = \sqrt{\left< R^{8} \right> / \left< R^{6} \right>}$

The software revealed from each scattering curve the parameters mean particle radius (μ) and number density of particles in the probed volume V (N_{SASFit} = N_{obj}/V). Using equation 3.7 the definitions for the mean value determined from SAXS data can be given as shown in table 3.3.^{77–79} Furthermore, equation 3.7 gives the opportunity to calculate the volume fraction Φ of the scattering centers in the sample area, according to expression

2.19, with:

$$\Phi = N_{SASfit} \cdot V_p = N_{SASfit} \cdot \frac{4\pi}{3} \left\langle R^3 \right\rangle . \tag{3.8}$$

3.12.6. SAXS fitting procedure for cuboid scatters

SAXS curves were obtained for both catalyst samples according to the standard procedure, as described in chapter 3.12. Mathematical fitting of experimental scattering curves was performed using corresponding formfactors for spherical and cubic particles (chapters 2.7.4, 2.7.5).

An extended data processing was required in case of the catalyst containing cubic nanoparticles. Due to the complex expression of the formfactor (expression 2.24a), a two step estimation of fitting parameters was required. First the shape factor P'(q) was considered. The value can be determined by assuming the shape factor being a very thin disc. In case of a parallelepipendron, the radius of such thin disc is equals to radius of gyration of a planar object. According to literature,⁷⁷ radii of gyration of a sphere $R_{g,sphere}$ and a homogeneous planar object $R_{g,planar}$ are

$$\begin{split} R_{g,sphere} &= R_{G,\alpha=0} = R_{R_{G,\alpha=0}} \cdot \sqrt{\frac{3}{5}} , \\ R_{g,planar} &= R_{G,\alpha=2} = \sqrt{\frac{a^2 + b^2 + L^2}{12}} . \end{split}$$
(3.9)

where $R_{G,\alpha}$ are the radii of gyration obtained from Guinier approximations 2.21, α is the dimensionality of a particle, $R_{R_{G,\alpha=0}}$ is a sphere radius determined from Guinier approximation, a is the width, b is the length of a parallelepiped particle and L is the respective thickness, as illustrated in figure 3.4. The radius of gyration of such cubic particle



Figure 3.4.: Illustration of SAXS estimates for cubic particles, as described in text.

 $(\mathrm{R}_{\mathrm{g}}=\mathrm{R}_{\mathrm{G},\alpha=2})$ can be determined using the extended Guinier's approximation for a planar

object (eq. 2.21). The estimate $R_{G,\alpha=2}$ can be correlated to the space diagonal D of a cubic particle:

$$D = \sqrt{a^2 + b^2 + L^2} = R_{G,\alpha=2} \cdot \sqrt{12} .$$
(3.10)

The space diagonal D is a fixed parameter, which represents the contribution of the shape factor P'(q). The value of D was determined with Origin-software from Porod-background corrected scattering curves using the script Guinier_correct.ogs (see appendix A). The estimate of D had to be defined in the fitting software SASFit for further data processing. Second, a lognormal distribution of particles thickness L was estimated considering the cross section formfactor $P_{cs}(q)$. The distribution of L exhibited a corresponding lognormal distribution of face diagonals $d = \sqrt{a^2 + b^2}$ by application Pythagoras' theorem,

$$d = \sqrt{D^2 - L^2} . (3.11)$$

All SAXS estimates from fitting (L, d) were mean values of lognormal-type value distributions. According to expression 3.7 volume-weighed values were calculated. Final, volume-weighed estimates are marked with an index lc.

In summary, following steps were performed in order to extract quantitative information on cuboid particle dimensions:

- From transmission and background corrected SAXS curves Porod backgrund was subtracted and the resulting curve was plotted as ln(I(q)) vs. q².
- Guinier plot was fitted with a linear function and the slope was estimated.
- In respect to the extended Guinier approximation, radius of gyration was estimated using the appropriate dimensionallity ($\alpha = 2$ for flat particles).
- From radius of gyration (equivalent to Guinier radius $R_{G,\alpha=2}$) the space diagonal length D was calculated. This value reflected the contribution of the shape factor P'(q).
- D was set as constant and a lognormal distribution of cuboid thickness L was estimated by accounting the contribution of the cross section formfactor $P_{cs}(q)$.
- Using Pythagoras' theorem, the corresponding distribution of particle face diagonal d was calculated.
- Finally, from resulting lognormal distributions intercorrelation length based parameters L_{lc} and d_{lc} were calculated using the desired moments of the distribution.

3.13. Chemicals

Chemichal formula	Compound	Purity / %	Providing company	Abbreviation
H ₂ O	Water	Millipore	100	-
$H_2PtCl_4 \cdot 6H_2O$	Dihydrogen hexachloroplatinat hexahydrat	99.95	Alfa Aesar	_
$\mathrm{Pt}(\mathrm{C_5H_7O_2})_2$	Platinum acetyl acetonat	97	ACS	$Pt(acac)_2$
$Co_2(CO)_8$	Dicobalt octacarbonyl	94	Sigma Aldrich	-
$C_2H_6O_2$	Ethylenglycol	99.5, p.a.	Carl Roth	_
NaOH	Natriumhydroxid	≥ 99	Carl Roth	-
H_2SO_4	Sulfuric acid	95-98	Sigma Aldrich	-
HCl	Chloric acid, 37%	99	VWR	_
HNO_3	Nitric acid, 65%	99	Carl Roth	_
HClO_4	Perchloric acid, 70%	99.999	Sigma Aldrich	-
$\mathrm{CH}_{2}\mathrm{Cl}_{2}$	Dichloromethane	99.5	ACS	DCM
$\mathrm{C}_{14}\mathrm{H}_{14}\mathrm{O}$	Dibenzylether	98	Fluka	DBE
$\rm CH_6O$	Ethanol	99.8	Carl Roth	-
$C_6H_4Cl_2$	o-Dichlor-benzol	99	Fluka	DCB
$\mathrm{C}_{14}\mathrm{H}_{30}\mathrm{O}_{2}$	Tetradecan-1,2-diol	90	Sigma Aldrich	TDD
C_7H_8	Toluol	99.5	Sigma Aldrich	-
$\mathrm{C_{18}H_{37}N}$	Oleyl amine	70	Sigma Aldrich	OAM
$\mathrm{C}_{18}\mathrm{H}_{34}\mathrm{O}$	Oleic acid	99	Sigma Aldrich	OA
$\mathrm{C}_{12}\mathrm{N}_{4}\mathrm{H}_{16}$	3-methylN-butyl- pyridinium- dicyanamide		VWR	3-MBP-dca
C_3H_8O	Isopropanol	≥99.5	Sigma Aldrich	_

Table 3	3.4.: 1	List o	f used	chemicals.

Chemichal	Compound	Purity / %	Providing	Abbreviation
formula			company	
N ₂	Nitrogen gas		Linde	_
O_2	Oxygen gas		Air Liquid	-
CO	Carbon monoxide gas	99.97	Linde	_
С	Multi walled carbon	-	Bayer	MWCNT
	nanotubes			
С	Vulcan XC 72R	-	Cabot	VC
С	High surface area	-	TKK Japan	HSAC
	carbon			
С	Hollow core	-	Korea	HCC
	mesoporous shell		University	
	carbon			

4. On the effects of general experimental parameters on particle growth trajectories

In this chapter contributions of general experimental parameters, such as used electrode surface, gaseous environment and scanrate of cyclic voltammogramms, will be validated and discussed.

Investigations presented in this thesis are based on two different strategies for studying nanoparticle behavior during electrochemical treatment: First, after a substantial structural characterization of pristine powder catalysts are characterized electrochemically for their ORR activity and electrochemical stability during potential testing. Therefore, information on ECSA change is extracted to monitoring catalyst degradation. Second catalysts are characterized *via in situ* SAXS in order to gain more detailed insights on particle trajectories during electrochemical treatment.

Experimental environments for electrochemical measurements and SAXS investigations different: for LSV measurements a RDE with a well polished bulk GC surface was used. Such rotating electrode had to be positioned vertically to guarantee minimization of mass transport limitations during electron transfer processes. In contrast, for SAXS experiments x-ray transparent electrodes were required, because the scattering signal was detected in a transmission mode. Hence, different electrochemical cells were used for selected experimental investigations. In order to ensure that both study strategies supplement each other and a correlation of results obtained with unequal setups evidence correct conclusions, a general investigation of experimental setup parameters was performed.

For this purpose CV measurements were conducted in 0.1 M $HClO_4$ electrolyte applying an electrochemical protocol summarized in table 3.1. ECSA was determined from H_{upd} -CV in the potential-range of 0.005 – 0.400 V, as described in chapter 2.6.

Table 4.1.: Applied potential protocol for validation of general experimental parameters. Hupd: CVsmeasured for calculation of Pt-ECSA; Act: activation CVs for catalyst-surface cleaning;AST: acceleration stress test CVs.

Technique	$\mathrm{H}_{\mathrm{upd}}$	Act	$\mathrm{H}_{\mathrm{upd}}$	AST	$\mathrm{H}_{\mathrm{upd}}$
# of cycles	3	200	3	100	3
Range / mV	5-1100	5-1100	5-1100	500-1100	5-1100
Rate $mV \cdot s^{-1}$	50	500	50	50	50
ι	← Looping	sequence \rightarrow			

4.1. Electrode surfaces: Rotating disc electrode (RDE) vs. carbon sheet electrode (CSh)

As mentioned above, monitoring of ECSA altering and size trajectories of catalyst particles required different experimental assemblies, which were introduced in detail in chapter 3. Here, a comparison of two degradation behavior of a catalyst supported on electrodes with different surfaces (figure 4.1), namely a GC disc (smooth) and a carbon sheet (rough) will be discussed. The contribution of electrode surface nature to particle degradation during electrochemical treatment will be established.

In order to isolate this parameter, experiments were performed in the same experimental setup – in a classical electrochemical glass cell. RDE and CSh electrodes were treated corresponding to standard electrode preparation procedures. It is important to note that



Figure 4.1.: Comparison of different electrode surfaces. a) Photograph of a smooth glassy carbon rotating disc electrode used for electrochemical catalyst characterization. b) Scanning electron micrograph of a rough carbon sheet electrode used for in sit SAXS measurements.

the amount of catalyst ink on CSh was always set to tenfold volume applied on a GC disc, as described in chapter 3. This concomitant requirement must be included in a correct study of effects of measurements using different electrodes.

RDE and CSh electrodes were coated simultaneously with the same freshly prepared ink solution of a commercially available benchmark catalyst 21.5wt-% Pt / VC. CV measurements were conducted in permanently N₂-saturated electrolyte applying an electrochemical protocol summarized in table 4.1.

Experimental CV curves are presented in figure 4.2a. As expected from a tenfold Pt loading on the CSh as compared to a GC-RDE, the CSh-measurement exhibited much higher current values as in case of RDE.



Figure 4.2.: Comparison of CV measurements of 21.5wt-% Pt / VC catalyst, performed on RDE and on CSh. a) Experimental data collected in N₂-saturated 0.1 HClO₄ at 25°C with a scanrate of 50 mV s⁻¹. b) Calculated ECSA estimates from RDE (black) and CSh (red) experiments as function of potential cycles.

ECSA values were evaluated for each experiment according to expression 2.5c. Figure 4.2b illustrated the evolution of ESCA as a function of potential cycles. Initially significantly different ECSA estimates, which were determined before 200 activation cycles (ECSA_{RDE}(-2) = $67.5 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1} \text{ vs ECSA}_{\text{CSh}}(-2) = 24.3 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$), converge with a proceeding potential stress. A coincidence of curves is observed 200 potential cycles after activation (ECSA_{RDE}(2) = $63.9 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1} \text{ vs. ECSA}_{\text{CSh}}(2) = 61.4 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$). Subsequently, ECSA curves remain overlayed.

The initially low ECSA value determined on CSh electrode could be attributed to the removement of impurities on electrodes surface. In contrast to RDE, it was not possible to polish a CSh electrode and remove embedded impurities from the electrodes surface prior to experiment. Consequently, instead of hydrogen-atoms, impurities-molecules naturally covering such paper electrodes were able to occupy Pt atoms of the catalyst. Hence, ECSA values, which were determined from the amount of deposited H-molecules on Pt-atoms,

were likely to be low. A certain number of potential cycles (activation cycles and additional 200 AST cycles) was required to remove undesirable molecules and obtain "clean" Pt nanoparticles surfaces. Consequently, ECSA values on CSh merged to the values obtained on an initially clean RDE subsequent to removement of impurities from Pt-atoms, even though the ink-film thickness of CSh is assumed to be significantly higher compared to RDE. This finding is in agreement with assumption valid for fuel cell assemblies (figure 1.1), which consist of thick catalyst layers on both sides of a PEM.

In summary, experimental findings evidenced that catalyst nanoparticles were electrified equally on RDE and on CSh from begin of the applied electrochemical treatment. As discussed in the introduction section 1.3, fuel cell catalyst degradation is mainly affected by processes caused by electron transfer. Hence, surface characteristics of a used electrode had an effect solely on ECSA evolution of observed catalysts. However, no significant contribution to degradation of particles was concluded. Additionally, this study points out the advantages of application RDE for ECSA determination besides to its essential use for ORR activity measurements.

4.2. Effect of the gaseous environment: N_2 vs. air

All performed electrochemical characterizations of catalysts consisted of a combination of LSV and CV techniques. As introduced in chapter 3.11, those voltammetry methods required saturation of electrolyte with N_2 or O_2 , depending on method selection. Hence, alteration of catalyst was proceeding in N_2 saturated electrolyte and only for LSV measurements the gas was exchanged to O_2 . However, structural *in situ* analysis with SAXS was performed in air saturated electrolyte due to the open-cell assembly of the used *in situ* SAXS-cell (figure 3.2).

In regard to catalyst degradation mechanism introduced in chapter 1.3, such as oxidation of Pt or carbon support corrosion, alteration of a catalyst in an electrolyte containing different gases was investigated. Experiments were performed using a RDE/glass cell setup in 0.1 M HClO₄. Measurements were conducted following the electrochemical protocol shown in table 4.1. First, experiments were performed in a "classical" way, which means that the electrolyte was permanently saturated with nitrogen. Next, same catalyst was probed in air-saturated electrolyte, which means that N_2 was used only during H_{upd} -CV (of cause, for this purpose prior to H_{upd} -CV to remove air the acid was bubbled with N_2). Besides, after each H_{upd} -CV measurement the electrolyte was bubbled for 10 minutes with O_2 gas in order to remove N_2 . Following accelerating stress test cycles were performed without

any external influence, hence, in air saturated electrolyte.

Aiming to extract the influence of the gas dissolved in the electrolyte a benchmark catalyst 21wt-% Pt/VC and a synthesized catalyst 17wt-% Pt/MWCNT were selected. The support structure of these catalyst is completely different, as shown in figure 7.1).

Hence, if carbon oxidation is enhanced by the oxygen contained in the electrolyte and affects Vulcan and multi walled carbon nanotubes in a different manner, loss of ECSA of the catalysts strongly reflects this.



Figure 4.3.: Comparison of catalyst degradation in N₂ (black) and air (red) saturated electrolyte by normalized ECSA as a function of potential cycles for a) benchmark catalyst 21% Pt/VC and b) synthesized catalyst 17% Pt/MWCNT.

Normalized ECSA curves of Pt/VC and Pt/MWCNT are shown in figure A.1; corresponding CV and absolute ECSA values as function of potential cycles are reported in figure A.1 (appendix A). The calculated estimates were normalized to the value obtained immediately after activation cycles in order to clarify the differences between catalysts treated in N₂-electrolyte (black curves) and in air-electrolyte (red curves). Results evidence a similar normalized ECSA decay curve for either catalyst. A comparison of total ECSA losses does not represent a quantitave relevance to this study and will not be discussed here, but later in the chapter 7, which subjects to a comparison of degradation of Pt nanoparticles supported on diverse carbons.

Based on experimental finding, it was concluded, that gas content in the electrolyte does not play a significant role in particles trajectories during electrochemical treatment. Data exhibited equal ESCA losses in case of Pt nanoparticles supported on carbons with different structures, independently of N_2 or air content in the catalyst environment. Hence, a very similar catalyst degradation during electrochemical characterization in a glass cell and in an *in situ* SAXS-cell could be concluded.

4.3. Effect of potential scanrate

Fuel cell catalyst degradation was simulated by an electrochemical accelerating stress test (AST). Particle catalysts were subjected to AST-protocol(4.1) and the resulting particle size trajectories were monitored after every 100 cycles. Hence, the duration of each degradation experiment was mainly controlled by the selected CV-scanrate.

In order to estimate, if experiment duration can be optimized, degradation studies of the benchmark catalyst 21% Pt/VC were conducted at 200 and 50 mV s⁻¹. Using a NanoStar lab based setup samples were measured using *in situ* SAXS. For a quantitative comparison of size trajectories the estimates were plotted *vs.* time of AST cycles, which was calculated by

$$t_{AST} = \frac{N_{AST} \cdot 2(r_{AST})}{Scanrate} \frac{1}{3600}$$

where t_{AST} is the time of treating the catalyst with accelerating potential stress CVs, N_{AST} is the number of applied AST between single SAXS measurements, r_{AST} is the potential range of a AST wave (this value has to be accounted twice for back and forward scans of a CV), all according to table 4.1

Experimental results are shown in figure 4.4. Curves of particle diameter, normalized number density and normalized volume fraction of one scanrate overlay with the corresponding estimates of the second scanrate.



Figure 4.4.: Comparison of catalyst degradation of 21% Pt/VC induced by AST potential cycles with scanrates of 200 mV s⁻¹ (hollow symbols) and 50 mV s⁻¹ (full symbols). Particle size evolution (circles), change of norm. number density of particles (triangles) and of norm. volume fraction (squares) as a function of t_{AST} , respectively.

Obviously, particle degradation is likely to depend solely on the absolute amount of time of AST duration. No significant difference in particles trajectories was observed treating the

catalyst with 50 mV s⁻¹-AST and 200 mV s⁻¹-AST. Hence, all experements in this thesis were performed using 50 mV s⁻¹ in order to minimize the number of SAXS-measurements and consequently the total time of *in situ* observations.

4.4. Summary

Experimental investigations presented in this chapter aimed to check how sensitive the time evolution of catalyst stability descriptors were to chages in electrode surface and loading, scanrate and gas environments. This was necessary for a correct correlation of results obtained from analytical methods performed under different conditions, such as electrochemical catalyst characterization and *in situ* SAXS degradation studies.

First, two different types of electrodes were compared: a smooth, polished glassy carbon rotating disc electrode and porously structured carbon-paper sheet electrodes. Experimental investigation were conducted using a benchmark catalyst Pt/VC. The results revealed that particles were electrified in the same way on both types of electrodes, within the error of measurements. Additionally, it was pointed out, that a tenfold amount of catalyst on a CSh, compared to RDE coverage, does not affect particle degradation.

Second, the role of gas environment in the electrolyte was determined. The study was based on the differences in conditions between electrolyte consistence in a glass cell (N_2 -saturation) compared to a SAXS-cell (air-saturation). For that purpose Pt nanoparticles supported on two different types of carbon were probed on a RDE. CSatalyst degradation by oxidation is attributed also to carbon structure. Hence, oxygen contained in the electrolyte by saturation with air was suggested to affect carbon corrosion and consequently, catalyst performance loss. In contrast to this, experimental findings evidenced that ECSA loss trajectories are not significantly affected by the gas content in the electrolyte.

Finally, the effect of potential scanrate on particle degradation rate was estimated. To achieve that a benchmark catalyst was probed electrochemically and simultaneously particles trajectories as a function of potential cycles were monitored with *in situ* SAXS. AST cycles were conducted with 50 mV s⁻¹ and 200 mV s⁻¹ in order to proof, if any change in particle structural development depending on scanrate can be deduced. Experimental results clearly demonstrated that solely the absolute time of AST-application affects particles degradation.

5. Activity and stability of shape selective nanoparticles

5.1. Introduction

The design of fuel cell catalysts aims at creating surfaces that balance the adsorption of reactants and desorption of products, and at same time lower the activation energy of reactions. Both theoretical and experimental studies have shown that electronic structure and surface atom arrangement are two key factors to determine the performance of electrocatalysts.³

Catalytically active platinum nanoparticles with various shapes, such as cube, cubooctahedron, octahedron, nanorod and various multipods have been synthesized in the past years.^{80–82} Platinum tubes and hollowed structures can also been obtained using templates or through galvanic replacement.^{83;84} Previous studies on electrochemical activities of differently shaped Pt nanoparticles, (such as spherical, polyhedron, truncated cubes and cubes),^{81;82} evidenced an enhancement of ORR activity in case of cubic catalyst particles. Besides catalyst activity, its stability is one of the key issues for application in state-of-the-art technologies.

In this chapter the presented studies subject to identification of contribution of particle shape on particle degradation during electrochemical performance. To achieve this two types of Pt nanoparticles were selected: spherical and cuboid noble metal catalysts.

Aiming at extracting the dependence of degradation of the electrocatalysts on shape, spherical and cuboid Pt nanoparticles were synthesized with comparable sizes and subsequently supported on same conductive carbon support. Subsequent to *ex situ* characterization, catalyst samples were probed for their elctrochemical performance and stability. Additional structural degradation studies were performed to exhibit the desired relationship of catalyst stability on the geometry of used nanoparticles.

5.2. Structural characterization of pristine catalysts

Catalyst powders were synthesised as described in chapter 3.2. The catalysts were characterized before electrochemical testing with ICP-OES, TEM, XRD and SAXS, all estimates are summarized in table 5.1 at the end of this chapter section.

A reliable comparison of electrochemically induced degradation of nanoparticle Pt catalysts can only be realized in case of similar metal weight-loadings on conductive support. Hence, the amount of particle loading on the conductive support was determined with ICP-OES. The measurements exhibited comparable Pt weight-% loadings for both catalysts: 7.63% in case of spherical particles and 6.3% for parallelepipeds.

TEM images (figure 5.1) of the synthesized spherical and cubic Pt nanoparticles supported on VC, respectively, identify different particle shapes. Besides, a homogeneous distribution of Pt NP on the conductive support was approved and first information on particle dimensions was revealed. Information on particle size was not extracted from microscopic measurements due to impracticalities of dimensioning parallelepiped shapes. For this purpose x-ray diffraction and small angle scattering experiments were conducted.

Experimental diffraction curves are given in figures A.2 (appendix A). First statistically representative crystallite size estimates were revealed from x-ray reflex-broadening using the Scherrer equation 2.4.⁵³ Similar crystallite size estimates for spherical (4.5 ± 0.1 nm) and cubic (4.9 ± 0.4 nm) nanoparticles qualified the samples for competitive studies. However, XRD is an analytical method that is applicable for characterization of crystalline structures only.



Figure 5.1.: Characterization via TEM and HRTEM of a1), a2)pristine spherical and b1), b2)cubic Pt nanoparticles supported on VC, respectively.

In contrast to XRD, SAXS does not require a crystalline structure to obtain structural information. Hence, additional SAXS experiments on pristine powder samples were performed to gain more detailed and representative information on nanoparticle dimensions. First, background corrected experimental SAXS curves were transformed to Guinier plots (see chapter 2.7.2), as shown in figures 5.2a2 and b2. Linear fits in the initial regions of such Guinier plots revealed desired radii of gyration by choosing correct dimensionalities α . From relationships given in expression 3.9 sphere diameter of 4.0 nm and space diagonal of 5.6 nm were calculated for the corresponding samples. The estimates are in agreement with values determined by XRD analysis. Mathematical fitting of experimental

SAXS curves evaluated volume-weighted particle size estimates (for reference see table 3.3). Corresponding to determined values probability density functions (pdf) of particle sizes were evaluated. The resulted plots are shown as inset graphs in figures 5.2a3 and b3, together with experimental data including fit curves.

In particular, detailed structural analysis of cubic nanoparticles was realized exclusively using SAXS: TEM was limited by depth analysis due to a 2-dimensional imaging, whereas XRD was limited by required condition of crystallinity. SAXS was found to be a powerful analytical tool that allowed statistically accurate characterization of a 3-dimensional structure of cuboid particles independently of a presence of crystalline domains.



Figure 5.2.: Characterization via SAXS of pristine spherical (images a) and cuboid (images b) Pt nanoparticles supported on VC, respectively. Numbers 1 correspond to experimental SAXS curves with respective Guinier functions. Insets are Guinier plots of data. Numbers 2 correlate a mathematical fit function with experimental data. Inset shows the obtained pair distribution functions.

Table 5.1.: Structural characterization of catalyst powders with differently shaped Pt nanoparticles supported on VC after coating with spherical and cubic Pt nanoparticles via ICP-OES, XRD, SAXS. Guinier sizes are estimated by equation 3.9 and given as $2 \cdot R_{R_{G,\alpha=0}}$ and $R_{g,planar} \cdot \sqrt{12}$. Particle sizes are given as $2 \cdot R_{lc}$ for spherical particles and L_{lc} for cubes.

Particle	Pt-loading	Crystallite size	Guinier size	Particle size	Poly- dispersity
Shape	in %wt,	in nm,	in nm,	in nm,	in %,
	ICP-OES	XRD	SAXS	SAXS	SAXS
Spherical	7.6	4.5 ± 0.1	6.7	5.0	0.25
Cuboid	6.3	4.9 ± 0.4	5.6	3.3	0.35

5.3. In situ degradation study

Electrochemical testing

Structurally characterized catalysts were tested in terms of their electrochemical performances. From LSV and CV measurements (introduced in chapter 3.11) catalyst activities for ORR and ECSA development during an extended electrochemical treatment were evaluated. For this purpose, a defined standard electrochemical protocol, as summarized schematically in 3.1, was applied to prepared RDEs. Exact potential settings are given in 3.1. All results from electrochemical characterization are summarized in table 5.2 at the end of this chapter.



Figure 5.3.: Electrochemical characterization of spherical (black curves) and cubic (red curves) Pt nanoparticles supported on VC, respectively. LSV curves were measured in O_2 saturated 0.1 M HClO₄ at 25°C with a scanrate of 5 mV s⁻¹.

Experimental LSV polarization curves are shown in part a of figure 5.3. Pt-mass based value for ORR activity of spherical catalyst (0.095 A mg_{Pt}^{-1}) differ significantly from the estimates for cubic nanoparticles (0.059 A mg_{Pt}^{-1}). Based on previous studies reported in literature,^{20;26;80} this experimental findings could be attributed to the shape diversity of particles. Markovic et al. reported that ORR activity, observed in different types of electrolyte, varies with geometric structure of particles.²⁰ The authors conclude from experimental findings performed in perchloric acid an ORR mass activity trend of Pt crystal faces as follows: (100) < (110) \cong (111). A closer look on structures of spherical and parallelepiped particles and corresponding prefered orientations of respective (100) and (111) planes, as illustrated in figure 5.4, reveals the link of observed ORR activity to crystal structure. Regarding a significantly different amount of atoms located in (111) surfaces of differently shaped particles and refering to literature an unequal ORR due to a higher number of (111)-located Pt atoms compared to a cuboid structure.



Figure 5.4.: Illustration of amount of atoms located in (111) and (100) crystal planes for spherical and cuboid particles. Model particles are based on fcc structure of Pt with diameter/hight of 4 nm. Dark grey atoms indicate atoms located in (111)-surface. Light orange plane denotes the orientation of the (100) face.

These findings refuted previously reported ORR activity enhancement of cubic particles.^{81;82} It is important to notice that those investigations were based on electrochemical measurements performed in H_2SO_4 , in contrast to the experiments presented here (only $HCLO_4$ was used as electrolyte). As mentioned above, ORR activity is strongly dependant on the nature of used electrolyte.²⁰ In case of H_2SO_4 the dependence of ORR activity on crystal face orientation is different as for a non adsorbing acid $HCLO_4$. Due to a different preference of SO_4^- anion adsorption on atoms located in (111), (100) or (110), the respective crystal faces are occupied differently by acid anions. Consequently, these atoms are more or less blocked and not fully available for oxygen deposition.^{20;26;27} Hence, these results reported in literature cannot be directly correlated to the finding observed in this study. Besides ORR activity the catalysts were characterized in terms of electrochemical stability during AST cycles. In order to exhibit the information on degradation behaviour, ECSA values were calculated from CVs (experimental curves are shown in figure 5.5a), as described in chapter 2.6.1. Absolute ECSA values at the beginning of potential protocol were determined for spherical nanoparticles (48.7 m² · g⁻¹_{Pt}) to be significantly higher than for cuboid particles (31.5 m² · g⁻¹_{Pt}). Apparently, spherical particles offered higher surface area per mass unit Pt for hydrogen chemisorption.



Figure 5.5.: a) CV for spherical and cuboid Pt nanoparticles supported on VC, respectively. Black curves was obtained after completing the activation cycles, red curves were detected after finishing the AST protocol of 2400 potential cycles. Measurements were conducted in N₂-saturated 0.1 M HClO₄ with a scanrate of 50 mV s⁻¹. b) Corresponding evolution of normalized ECSA as function of potential cycles for spherical (circles) and cuboid (squares) Pt nanoparticles.

In respect to the main subject of the performed study, normalized ECSA values were plotted as functions of potential cycles, as shown in figure 5.5b in order to compare degradation of spherical and cuboid particles. ECSAs were normalized to the value estimated after 200 AST cycles (Nr. of AST-CV = 2). The reason for choosing this point was an observed ECSA rise until completing 200 AST cycles, affected by removement of organic residuals from synthesis.

Time resolved ECSA behaviour was very similar for the probed catalyst samples, according to the overlay of normalized ECSA curves. Consequently comparable electrochemical stability could be concluded for spherical and cuboid Pt nanoparticles with comparable sizes. To gain more details on structural stability, *in situ* SAXS experiments were conducted.

Structural in situ characterization

SAXS experiments were performed in the *in situ* SAXS-cell. Measurements of scattering curves were conducted using the lab system NanoStar (Bruker), equipped with a gas

Catalyst	ORR-activity	ECSA 200 CV	ECSA 2400 CV
shape	in $\mathrm{A} \cdot \mathrm{mg}_{\mathrm{Pt}}^{-1}$,	in $\mathrm{m}^2 \cdot \mathrm{g}_{\mathrm{Pt}}^{-1}$,	in $\mathrm{m}^2 \cdot \mathrm{g}_{\mathrm{Pt}}^{-1}$,
	LCV	$\mathrm{H}_{\mathrm{upd}}CV$	$\mathrm{H}_{\mathrm{upd}}CV$
Spherical	0.095	48.7	46.7
Cuboid	0.059	31.5	29.6

Table 5.2.:	Summary	of	electrochemical	characte	rization	of	catalyst	powders	with	spherical	and
	cuboid Pt	na	noparticles supp	orted on	VC, resp	bec	tively.				

detector. Details on experimental performance and curve evaluation are given in chapter 3.12.

Figure 5.6 illustrates the results obtained from SAXS measurements. In case of spherical particles no significant change in particles size was observed (part a1 of the figure). Similarly, the size of cuboid particles remained stable during a complete AST protocol. The estimates for particles thickness L_{lc} did not change dimensions during potential cycling. Some fluctuations in particles face diameter curve d_{lc} (hollow circles in part b1 of the figure) were observed. Concerning the procedure of d_{lc} calculation (equation 3.11), these fluctuation were attributed to the required calculations of the radius of gyration $R_{G,\alpha=0}$. Guinier radii were estimated using linear fits of adapted plots of scattering curves. Hence, resolution of the detector influenced the precision of $R_{G,\alpha=0}$ determination. However, a clear trend could be extracted from plot 5.6b1: cuboid Pt nanoparticles did not significantly grow.

In order to verify these suggestions, it was important to take a closer look on additional SAXS parameters, such as normalized particle number density N_0 an normalized volume fraction Φ . The estimates for N_0 and Φ for spherical and cuboid particles suggest particles stability. Despite the observed fluctuation of the estimates, no indications for particle dissolution could be extracted from the presented results. Resulting lognormal probability density functions of particle sizes illustrate the stability of particle size in case of cuboid particles (figure 5.6a2). Besides, plot 5.6b2 showed that the face diagonal of cuboid particles shifted to higher size values, whereas a slight shift in the opposite direction was observed for particle thickness. However, both variables L_{lc} and d_{lc} are related to each other (eq. 3.11) and were likely to mutually influence the corresponding counterpart.

These findings were in agreement with comparable studies reported in literature.^{27;85;86} Kikuchi et al. and Onochi et al.^{85;86} reported on AFT shape stability studies of large


Figure 5.6.: In situ SAXS degradation study results for spherical (images a) and cuboid particles (images b). Numbers 1: Evolution of normalized number density of particles, normalized volume fraction and particle size as functions of potential cycles, respectively. Numbers 2: Resulting LogNormal distributions of determined size values.

cuboid nanoparticles (\sim 30 nm) probed in non acidic electrolyte. They observed a slight increase of particles hight upon the onset potential of 1.2 V, which was attributed to Pt-oxide formation. However, in the here conducted study the applied potential did not exceed 1.1 V. Komanicky et al.²⁷ investigated dissolution of Pt atoms located in different crystal planes. The authors deduced that in the low-index surfaces, the platinum oxide formation passivated the surfaces, resulting in a lower dissolution rates at a potential of 0.95 V. These findings support the results obtained in the *in situ* SAXS degradation study presented here.

5.4. Conclusions

The investigations presented here aimed at correlation fuel cell catalyst stability with respect to the geometric structure of Pt nanoparticle catalysts. To achieve this, catalyst samples consisting of spherical and cuboid Pt nanoparticles, supported on carbon (VC), were synthesized.

The preparation procedure was tailored to obtained particles with comparable dimensions. Indeed, structural characterization methods, such as ICP-OES, TEM, XRD and *ex-situ* SAXS revealed that the synthesized samples were appropriate for a competitive degradation study.

Next, catalyst samples were characterized electrochemically under same experimental conditions. ORR-activities, extracted from LSV measurements, identified spherical Pt nanoparticles as a significantly more suitable catalyst, compared to cuboid catalysts. This finding was attributed to the different ratio of (111) and (100) crystal facets.²⁰ Besides, absolute ECSA values indicated that spherical Pt nanoparticles offer a higher surface area for H-chemisorption than cuboid particles with comparable sizes. However, ECSA loss affected by potential cycling was similar in case of both samples. Consequently, same electrochemical stability was concluded.

Additionally, *in situ* SAXS experiments were conducted to exhibit structural particle stability. In cases of spherical and cuboid nanoparticles size estimates remained constant for the total duration of potential stress protocol, respectively. Corresponding values for normalized number density of particles and normalized volume fraction did not indicate particle dissolution. The results were in agreement with previously reported studies on stability of cuboid nanoparticles.^{27;85;86} Hence, structural stability of the compared samples did not differ significantly.

In summary, overall catalyst stability of nanoparticles in the size range of 4–5 nm seemed to be independent on particles geometry. Solely, electrochemical performance of the catalyst was attributed to the geometry of used Pt nanoparticles.

6. Catalyst composition modification: activity and stability of PtNi alloy nanoparticles

6.1. Introduction

In the past decade a great research effort has been underway aiming at the optimization of electrochemical catalysis for renewable energy conversion. Polymer electrolyte membrane fuel cell (PEMFC) technology is a promising approach for a replacement of fossil fuels with environmental friendly alternatives.^{5;8;9;13;45;87–89}. Fuel cell performance, however, depends strongly on the activity and stability of the catalyst used at the electrodes. Considering the acid ambience in a PEMFC the usage of noble metal catalysts, such as Pt nanoparticles, is indispensable for attaining of sufficient activities for the oxygen reduction reaction (ORR). Platinum, however, is very scarce which impedes large-scale applications slowing down the development of PEMFC technology. An approach of reducing the amount of Pt is alloying it with other, mostly transition metals.^{3;7;90–99}.

Using a single crystal as a model system⁹⁶ Stamenkovic et al. showed that a Pt₃Ni(111) crystal surface exhibits orders of magnitude higher ORR-activities in PEMFC applications compared to Pt(111) crystal surface and to conventional nanoparticle Pt catalysts supported on carbon. Single crystals, however, do not represent a practical and useful catalyst class of materials. Recently, PtNi nano-sized alloys,in, particular with >50% initial Ni abundance, have emerged as the most attractive bimetallic nanoparticle alloys for achieving both high activity and stability while reducing the amount of Pt used.⁸³ Due to the high initially Ni content the active form of the catalyst is obtained through a Ni dissolution and particle dealloying process.

The detailed structure of such dealloyed nanocatalysts is still poorly understood. This is largely in part due to the fact that many of the powerful surface characterization techniques do not offer a required combination of high resolution and statistical accuracy. An overwhelming number of studies have employed Transmission Electron Microscopy (TEM) before and after the electrochemical testing.^{84;100} uch studies are limited in accuracy by

the facts that only few selected nanoparticles are analyzed reducing the statistical significance of the results. More statistically representative results can be obtained when the whole ensemble of nanoparticles is probed at once. The experimentally observed catalytic properties are also a result of the cooperative action of a large number of nanoparticles so comparing assembly-averaged morphological and structural characteristics of nanoparticles with an assembly averaged property puts the comparison on the same footing.

In a previous work $^{48;49}$ we synthesised and electrochemically characterized several Pt_xNi_{1-x} (1.00 < x < 0.14) alloy particles aiming at optimizing their catalyst activity for the ORR(experimental data is shown in the appendix figure A.3).

This study concentrates on Pt₁₄Ni₈₆ (denoted here as PtNi₆) and Pt₂₆Ni₇₄ (PtNi₃) supported on Vulcan XR32 carbon. These two systems showed remarkable catalyst activities for ORR.⁴⁸ Both catalysts also showed an increase in the electrochemical surface area (ECSA) during a potential stress protocol tests as compared to a reference pure Pt catalyst that showed a 20%-decrease of ECSA, as shown in figure 6.1. To better understand the enhanced catalytic activity, in particular structural changes associated in respect to the dealloying of Ni, the two alloy nanoparticle systems were characterized by synchrotron x-ray diffraction and *in situ* anomalous small angle scattering. The premises of this study lie in the fact that the catalytic properties are, to a great extent, influenced by the type of atomic and chemical ordering the nanoparticles exhibit.



Figure 6.1.: Normalized ECSA-evaluation as a function of potential cycles for synthezised $PtNi_6 / VC$ and $PtNi_3$ compared to a commercial Pt/VC catalyst.

In this study a report will be given on novel atomic-scale insights in the dominant structural transformations during the electrochemical catalytic activation, that is, Ni dissolution, of bimetallic Pt-Ni alloy nanoparticles. Using anomalous SAXS¹⁰¹ and PDF analysis⁷⁰ a structural transformation from disordered to ordered alloy phases accompanied by increased catalytic activity was observed. It will be also shown that the formation of Pt multilayer particle shells^{84;102–105} is increasingly suppressed with higher initial Ni content. ASAXS and PDF are powerful, but relatively rarely used analytical tools complementing TEM. The insights will aid further efforts to understand nanoscale Pt based electrocatalysts. They will also help design activation protocols and suitable precursor compositions to arrive at structurally optimized catalysts.

6.2. Structural characterization of pristine $PtNi_6$ /Vulcan

ASAXS experiments were conducted at the 7T-MPW-SAXS beamline of a synchrotron facility BESSY II. Two different calculation methods were used to extract the resonant terms of scattering, the Stuhrmann-method^{61;62} and a simplified but very efficient subtraction method³⁶ (a detailed description is given in the chapter 2.7.6). Both analysis yielded similar results. Particle sizes in the presented studies on PtNi alloys were monitored at q-values between 0.35 and 3.5 nm. The scattering of carbon support particles (approx. 100 nm in size) appeared at much lower wave vector values. Hence, data processing using the simplified subtracting method turned out to be very reliable.



Figure 6.2.: Characterization of a pristine PtNi₆/VC catalyst: a) Experimental resonant ASAXS curves for Pt (circles) and Ni (triangles) with mathematical fits (solid lines), respectively; b) XRD profile (line) and theoretical reflex positions for Pt (dotted bars) and Ni (solid bars); c) selected TEM image and d) to electron micrographs corresponding particle size results from counting 200 particles with a lognormal particle size distribution.

Anomalous, Pt and Ni resonant scattering profiles of pristine $PtNi_6$ catalyst (figure 6.2a) were fitted using a lognormal particle size distribution, assuming spherical particles. Information on particles sizes were extracted from the estimated element specific scattering curves by calculating the volume weighted correlation length diameters $(2 \cdot R_{lc})$, which is obtained using $R_{lc} = \langle R^4 \rangle / \langle R^3 \rangle \cdot 2/3 = lc \cdot 2/3$, where R_{lc} is the correlation length radius, $\langle R^n \rangle$ is the nth moment of the size distribution.^{78;79} In contrast to the mean value of a distribution, the correlation length radius R_{lc} represents a more accurate estimate due to a direct relation to the correlation length lc, which is a hypotheses free characteristic constant of a scattering curve and is extractable without any information on the scattering system.⁵⁹

The fits to the experimental scattering curves (Figure 6.2a) yielded a diameter of 4.6 ± 0.1 nm for Nickel and 3.6 ± 0.1 nm for Platinum. These values suggest an enrichment of Ni near the surface of the alloy nanoparticles, which is consistent with recent STEM/EELS measurements.⁹⁹ Lab based XRD patterns are shown in Figure 6.2b. Broad peaks appear at Bragg angles between the theoretically estimated positions of the Bragg peaks for bulk Pt and Ni, suggesting the formation of a homogeneous PtNi alloys. Particle size estimated using the Scherrer equation⁵³ range around of 4.3 ± 0.4 nm, which are in good agreement with the estimates obtained by ASAXS. To cross check the SAXS and XRD results we also conducted TEM experiments (Figures 6.2c and 6.2d). TEM (based on counting about 200 particles) revealed an average particles size of 2.3 ± 1 nm. Figure 6.3b compares the particle size estimates obtained from the several techniques we employed. The differences can be explained in terms of the unequal averaging methods of the different techniques. TEM provides a particle-number averaged size, while XRD and ASAXS yield a particlevolume weighted size information. Also, in contrast to SAXS and XRD, TEM is limited by the usually small probe area that is often limited to few particles of the sample studied. In contrast, ASAXS gives an element specific correlation length diameter estimates



Figure 6.3.: Characterization of a pristine PtNi₆/VC catalyst: a) probability density functions of particle sizes, obtained from resonant ASAXS curves for Pt (dotted line) and Ni (solid line), respectively. b) Comparison between particle sizes obtained by different techniques.

6.3. Structural evolution of $PtNi_6$ during activation, catalysis and potential cycling

Structural changes of the $PtNi_6$ nanoalloys on the colloidal scale during an extensive electrochemical potential cycling protocol involving activation, ORR catalysis and stability testing using in situ ASAXS characterizations of the $PtNi_6$ catalyst in liquid electrolyte under potential cycling were investigated. Figure 6.4a shows the measured continuous particle size evolution in terms of Pt and Ni as a function of the number of potential cycles. In particular, Pt and Ni species show only a slight overall particle size change during the potential cycling. The space occupied by Pt species, measured by the Pt correlation diameter $2 \cdot R_{lc}$, increases with the progress of the electrochemical treatment from an initial value of 3.4 ± 0.1 nm to 3.7 ± 0.1 nm. This progress can be an evidence for lattice relaxation in the particle affected by Ni dissolution. An interesting evolution during the first 500 cycles of the Ni based parameter from 3.9 ± 0.1 nm to 3.6 ± 0.1 nm, followed by increase to 4.0 ± 0.1 nm, indicates a Ni dissolution and a subsequent particle growth.

Additionally, structural changes of the PtNi₆ nanoalloys on the atomic scale were investigated. To probe the atomic scale rearrangements, in particular ordering/disordering transitions *ex situ* high-energy XRD experiments were conducted and coupled to atomic PDFs analysis on pristine and electrochemically treated/cycled samples. Atomic PDF analysis has recently proven to be a very powerful tool for structural characterization of nanosized particles,⁷⁰ yet has rarely been applied to Pt alloy fuel cell cats.

High energy x-ray diffraction experiments were carried out at the beamline 11ID at the Advanced Photon Source, Argonne using x-rays of energy 115 keV. The higher energy x-rays allow to collect data to higher wave vectors which is crucial for obtaining good quality atomic PDFs. With the present experiments XRD data up to wave vectors of 28 $^{-1}$ were collected. The XRD data was reduced to atomic PDFs shown in Figure 6.4b. The PDF of the fresh PtNi₆ particles is well approximated with a model based on the face centred cubic (fcc) lattice of Ni, where some Pt atoms have been randomly accommodated resulting in a chemically disordered solid solution single phase. A surprising finding was that the calculated atomic PDF for the used catalysts reveals characteristic features of Ni phase segregation, namely a pronounced shoulder on the left hand side of the first PDF peak (Figure 6.4c). This intra atomic distance is consistent with metallic Ni-bond lengths, suggesting a formation of Ni rich domains. The residual part of the atomic PDF represents an fcc phase (CuAu₃-type).



Figure 6.4.: a) Particle size evolution during potential stress cycling of PtNi₆ catalyst, derived from in-situ ASAXS measurements: Pt (black hollow cycles), Ni (red triangles). b) Experimental (black dots) and model atomic PDFs (red lines) for pristine and used PtNi₆, c) represents an extended region of plot b. PDF models feature chemically ordered (Pm-3m) and disordered (Fm-3m) cubic-type lattices.

Apparently, dealloying of a solid solution leads to an ordered alloy structure. The HEXRD and PDF analysis show clear evidence for i) leaching of Ni, ii) rearrangement of the atomic species across the nanoparticles and iii) massive ordering of the crystal structure of the nanoparticles. In particular, Ni atoms seem to leach out of the nanoparticles during the voltage cycles, resulting in an unexpected change of the atomic arrangement from an initial solid solution of Pt in a Ni matrix to chemically ordered $PtNi_3$ -type alloy structure.

In order to quantify the elemental composition change during potential cycling we performed x-ray fluorescence (XRF) analysis from the fresh and electrochemically treated catalysts (experimental data is shown in fig. A.4a). Initially Ni rich alloy nanoparticles with a composition of $Pt_{14}Ni_{86}$ transform to Pt rich $Pt_{76}Ni_{23}$ alloys. This estimates are in agreement with a recent study by Wang et al.,¹⁰³ who reported on electrochemically treated Pt_3Ni , PtNi and $PtNi_3$ alloy nanoparticles and modelled the Ni loss of catalysts. The author's model predicted a PtNi-core/Pt-shell structure formation where the shell thickness scales directly with initial Ni atomic-% catalyst composition. However, experimental data for particles with Ni content higher than 75 at.-% is not provided.

In summary, the particle crystal structure was exhibited as one leading parameter of the catalytic performance of transition metal rich Pt-alloy nano catalysts and extend the previously reported model of core-shell formation by our findings evidenced by intra particle atomic rearrangements. The results establish a clear relationship between the $PtNi_6/Vulcan$ nanoparticles catalytic activity, size, composition evolution and structure-type evolution during electrochemical performance.

6.4. ASAXS data evaluation methods: A comparison

At this point it is necessary to discuss different ASAXS experimental data evaluation processes. A well established calculation method for resonant scattering curves is a calculation termed as Stuhrmann-method^{61;62}. Besides, a reduced method for determination of element resonant scattering curves, based merely on subtraction of a curve measured at x-ray energy near the absorption edge of the metal of interest from a curve measured in an energy range far away from the edge, can be used as well. The element specific curve results then from the obtained intensity contrast. Both methods are described in detail in the chapter 2.7.6 of this thesis.

The results for the determined sizes obtained from both methods are shown in figure 6.5. Part a of the figure demonstrates the particle sizes estimated for Pt, part b the estimates for Ni.



Figure 6.5.: Comparison of particle size values for a PtNi₆/VC catalyst, obtained from ASAXS using the Stuhrmann method and the subtraction method for a) Pt resonant values and b) Ni resonant values.

Obviously, some of the points are missing for the Stuhrmann-method based values for Pt and Ni, respectively. One of the reasons is that the method is very sensitive to energy fluctuations of the incident x-rays. If any process during the absolute calibration process fails or any instability of the measuring equipment occurs, Stuhrmann based calculation does not offer any resonant scattering curve. Additionally, the sensitivity of the aperture and the monitoring setup differs in respect to the energy variation. Concerning this it is obvious, that the error of calculation is not neglect able and falls heavily into account by calculation Stuhrman resonant curves due the necessity of at least minimum three scattering curves measured at different x-ray energies. Hence, a precise measuring equipment and high brilliant synchrotron radiation are indispensable to gain a significant ASAXS effect.

In this work ASAXS experiments were carried out at a BESSY beamline completely optimized for the sensitive ASAXS technique. However, as shown in figure 6.5, the Stuhrmannmethod estimates aver overlapping nicely with the values termed by the very basic subtraction method. For Pt and Ni resonant values it is clearly shown that there is no significant difference in particle size estimates, respectively. A remarkable disadvantage of the Stuhrmann method is that the estimates for Pt and Ni were not obtained at the same stages of the electrochemical treatment protocol. Hence, detailed conclusions on particle structure during electrocatalysis can hardly be realized in this study using the Stuhrmann method. Nevertheless, a detailed insight is available by the subtraction method. Usually, one has to be very carefull by interpreting scattering curves obtained by the less complicated method, because the background scattering can still contribute to the scattering curve. However, particle size in the presented study on PtNi alloys was monitored by q-values between 0.35 and 3.5 nm^{-1} . Concerning the size of support pieces (\approx 100 nm) the scattering of carbon is expected to be observed at much lower scattering vector values (see also chapter 2). Hence, data processing using a subtracting method is reliable. In the reported study ASAXS results obtained form the subtraction method are discussed mainly in the in-situ sections. Characterization of pristine catalysts via ASAXS was performed by application the Stuhrmann method.

6.5. Structural characterization of pristine $PtNi_3$ /Vulcan catalyst

The study on the relationship of activity enhancement of the catalyst to its structural transformation during potential cycling was complemented by focusing on a second catalyst $PtNi_3/Vulcan$. This catalyst showed remarkable catalytic activity, which was enhanced significantly by an electro-chemical treatment.^{48;49}

 $PtNi_3$ /Vulcan catalyst was studied first *ex situ* as prepared fresh. In Figure 6.6a the resonant ASAXS curves with the corresponding fits for both Pt and Ni metallic species are shown. The particle size probability density function was extracted from the experimental ASAXS data (experimental resonant curves are shown in in Fig. 6.6a).



Figure 6.6.: Characterization of a pristine PtNi₃/VC catalyst: a) Experimental resonant ASAXS curves for Pt (circles) and Ni (triangles) with mathematical fits (solid lines), respectively; b) XRD profile (line) and theoretical reflex positions for Pt (dotted bars) and Ni (solid bars); c) selected TEM image and d) to electron micrographs corresponding particle size results from counting 200 particles with a lognormal particle size distribution.

The estimated ASAXS particle size values, based on the correlation length, for Pt (3.1 ± 0.1 nm) and Ni (3.3 ± 0.1 nm) species, shown in Fig. 6.7a, do not differ significantly. Analysis of the in house XRD patterns yielded a particle diameter of 3.7 ± 0.3 nm (experimental data is shown in Figure 6.7b).

Again, broad Bragg peaks are located between the theoretical positions for bulk Pt and Ni. Hence, single alloy particles are expected for the synthesized $PtNi_3/VC$ sample. Particles size estimated from TEM images (shown in Figure 6.6c), showed a lognormal size distribution (fig. 6.6d)) centered to about 4.7 \pm 0.8 nm. Figure 6.7b shows a comparison between the size estimates obtained by the three different techniques employed here. Again, particles sizes estimated by TEM deviate most from those determined with the statistically more representative XRD and ASAXS.



Figure 6.7.: Characterization of a pristine PtNi₃/VC catalyst: a) probability density functions of particle sizes, obtained from resonant ASAXS curves for Pt (dotted line) and Ni (solid line), respectively. b) Comparison between particle sizes obtained by different techniques.

6.6. In situ study of the atomic scale dynamics of $PtNi_3$ /Vulcan

Applying the same electrochemical potential stress protocol tests as for $PtNi_6/VC$ catalyst the structural rearrangement of the $PtNi_3$ alloy particles was also studied. A clear difference compared to $PtNi_6$ can be seen in the in situ ASAXS data of $PtNi_3$ catalyst (Figure 6.8a). The analysis of the resonant correlation length diameters follows a different trend. Here both Pt and Ni diameters increase over the first 1000 potential cycles. The Pt and Ni diameters, however, differ indicating that the Pt and transition metals (Ni) species follow somewhat different rearrangement paths within the nanoparticles.

Concerning the ASAXS resonant diameters the information extracted from the PDFs of a $PtNi_3$ catalyst suggests a reformation of a homogeneous alloy particle to a core-shell structure. Ni atoms do not leach out of the particle completely, in addition the thickness of Pt on the particle surface increases. Consequently, a PtNi-core/Pt-shell structure of a treated catalyst can be assumed. These results are in full agreement with previous studies



on PtCu and PtCo alloy nanoparticles.^{84;104;105}

Figure 6.8.: a) Particle size trajectories during potential stress cycling of a PtNi₃ catalyst, derived from in-situ ASAXS measurements, b) experimental (dots) and model atomic PDFs (lines) for pristine and used PtNi₃. PDF models feature chemically ordered (Pm-3m) and disordered (Fm-3m) cubic-type lattices.

To obtain a better insight on the structural rearrangement in $PtNi_3$ caused by electrochemical treatment a fresh and used $PtNi_3$ samples were probed with high-energy XRD. The respective atomic PDFs are shown in Figure 6.8b. That of fresh $PtNi_3$ particles is well approximated with a single phase model based on the archetypal $AuCu_3$ -type structure. The PDF of the used $PtNi_3$ particles may only be explained in terms of a mixture of two nanophases. A clear signature of plenty of Ni-Ni distances (Figure 6.8c) was observed. Those are not seen as much in the fresh sample which, therefore, may be called a typical alloy. One may call the observation of excess of Ni-Ni bonds in the used $PtNi_3$ a signature of de-alloying or phase segregation.

Furthermore, the element compositions of fresh $PtNi_3$ and electrochemically treated alloy nanoparticles were estimated. XRF study revealed an evolution of the $Pt_{27}Ni_{73}$ pristine catalyst to a Pt-rich $Pt_{73}Ni_{27}$ alloy (fig. A.4b). Again, we compared a model reported by Wang et al.¹⁰³ with our findings. The simulated function, which includes an experimentally estimated value for an initial $Pt_{25}Ni_{75}$ homogeneous alloy, reveals a formation of a Pt rich ${\rm Pt}_{87}{\rm Ni}_{13}$ catalyst. A PtNi-core/Pt-skeleton-shell structure with a shell thickness of >1 nm was deduced from experimental investigations and supported by the calculated model. Our results exhibit similar tendency of a PtNi-core/Pt-shell structure formation in case of catalyst with same initial composition. Additionally we determined a shell thickness of approximately 1 nm.

6.7. Correlation of nanoparticle structure evolution with catalytic activity for ORR

Supported by the investigation of $PtNi_6$ particle evolution better understanding of the Pt-Ni alloy nanoparticles transformation mechanism during electrochemical catalysis can be achieved. A scheme of a proposed particle evolution is given in Figure 6.9.

In particular, pristine $PtNi_6$ alloy nanoparticles feature a fcc-type ordering of Ni-atoms with randomly distributed Pt atoms in the particles. Part of Ni atoms leach out under electrochemical stress turning the structure type of the nanoparticles into a more or less single-phase $PtNi_3$ type ordering (Figure 6.9a). Electrochemical treatment of as prepared



Figure 6.9.: Model of PtNi alloy nanoparticle evolution during electro-catalysis.

PtNi₃ single-phase alloy results in a PtNi-core/Pt-shell type particles (Figure 6.9b). Compared to a model reported by Wang et al.¹⁰³ similar element composition changes were found. The results reported here confirmed a similar trend for Ni catalyst containing up to 75at.-% of the non noble metal. However, a diverse inra particle reformation mechanism was found for nanoparticles with a higher initial Ni content, drawn predominantly by a massive ordering of the crystal lattice. Rearrangement of crystal structure has not been considered as an activation mechanism of PtNi alloys yet, in contrast to numerous reports on activity increase affected by a formation of a core-shell^{7;95;100;104;106} or skeleton structure^{83;84;103} for Pt-alloy nanoparticles.

In this study, unique supplementary information on particle structure evolution caused by electrochemical potential cycling were provided by application of statistically relevant x-ray techniques. Hence, accounting for other studies reported in literature,^{107;108} an increasing ORR activity from PtNi₆ to PtNi₃ can be explained related to a structural rearrangement process as described above. Electrochemical treatment of a PtNi catalyst first stabilizes an ordered alloy structure and subsequently boosts an enrichment of Pt species on the surface of the particles. The resulted structure of with Pt enriched surface also features compressed Pt-Pt inter atomic distances affected by the underlying PtNi core.

6.8. Conclusions

In summary, the morphological, chemical and atomic-scale structural evolution of two alloy fuel cell catalysts during electrochemical treatment have been investigated with *in situ* and *ex situ* x-ray diffraction/scattering techniques. A previous study on the electrochemical properties of Pt_xNi_{1-x} catalysts with various alloy compositions^{48;49} indicated particle evolution affecting their performance.

The results obtained here give a clearer picture of how the nanoparticles evolve under electrochemical treatment: According to our data the Pt atoms in a PtNi₆ catalyst are more or less uniformly distributed in a matrix of Ni atoms. Then Ni-atoms leach out accompanied with some nanoparticles coarsening resulting in structure of an ordered PtNi₃ type. Resulting single phase PtNi₃ particles show increased activity compared to the initial PtNi₆ alloy catalyst. Electrochemical treatment of a homogeneous alloy PtNi₃ catalyst produces PtNi-core/Pt-shell particles, where geometric lattice strain effect on surface Pt atoms are likely to contribute to the catalytic activity enhancement.

Additional catalyst performance leading parameters, which affect ORR activity increase of electrochemically treated alloy nanoparticle fuel cell catalysts, were investigated. It was possible to show that objectives assigned to Pt content minimization by enrichment of an alloy catalyst with a non noble metal must account the ordering of atoms in the catalyst's structure in order to accompany the desired reduction of Pt with an enhanced ORR activity. The results provide detailed insights into intra particle atomic structure and aim to a controlled tailor made catalyst improvement.

7. Carbon catalyst supports: The impact of the surface area on activity and stability of spherical Pt nanoparticles

7.1. Introduction

Platinum nanoparticles supported on carbons, which can offer high conductivity owing to their graphitic structure in addition to high surface area, have evidenced enhanced catalytic activity for fuel cell applications. Studies of such scarce metal based catalysts have indeed shown high ORR activity, however, stability tests exhibited a continuous ESCA loss.^{4–10} The mechanism of ESCA loss is poorly understood. Especially in a potential range above 1.2 V, carbon corrosion has been found suspected to be one of the main degradation mechanisms. The progress of carbon oxidation is dependent on the carbons properties, such as structure and porosity.^{25;39;41;43} Electrochemical treatment of a catalyst below 1.2 V diminishes catalyst performance, too. However, in this potential range catalyst degradation is attributed more to nanoparticle degradation than to carbon oxidation. ^{5;6;8–10;15;19;23;25;26;44;45} Additionally, previous studies evidenced a direct relationship of catalyst mass activity and the surface area of the carbon support.^{109–112} Hence, support morphology influences the electrochemical properties of Pt catalysts. Consequently, the structure of the support can be suggested to affect the electrochemical durability of a fuel cell catalyst. In order to determine supports contribution to degradation, catalysts with different supports were selected, aiming at investigating the contribution of supports structure to particle degradation in the potential range below 1.2 V.

In this chapter the main objective is to distinguish between the possible particle degradation mechanism. As introduced in chapter 1.3, particles can migrate and coalesce; they can dissolve completely due to their Gibbs-Thomson energy (see equation 1.3) and the produced metal ions can redeposit on particles surface (Ostwald mechanism). Furthermore, particles can detach from the conductive support and consequently suppress the electrocatalytic performance of a fuel cell catalyst. Here a conclusion will be made on the particle stability as a function of support morphology. To achieve that, several Pt nanoparticle catalysts supported on various carbons with different morphological properties were selected. Subsequent to a detailed *ex situ* characterization of pristine powders the identification of the dominant degradation behavior of these catalysts as a function of support characteristics will be discussed.

7.2. Structural characterization of pristine catalyst powders

Two commercially available reference catalysts 20.5% wt Pt on Vulcan XC-72 (VC, BASF) and 28.0% wt Pt on High Surface Area Carbon (HSAC, TKK Japan) and on two synthesized catalysts 17.2% wt Pt on Multi Walled Carbon Nanotubes (MWCNT, Bayer) and 20.1% wt Pt on Hollow Core Carbon (HCC, Korea University) were selected for this study, because of their different morphologies. Catalyst powder synthesis is described in detail in chapter 3.1. These catalyst were selected in respect to their diverse morphology and a consequent varying support surface area, as it can be suggested by figure 7.1.



Figure 7.1.: SEM images of different pristine carbon supports: a) MWCNT, b) VC, c) HSAC, d) HCC.

Nitrogen-adsorption measurements were performed before coating the carbon supports with nanoparticles. The amount of area per mass unit of carbon powders was calculated with the Brunauer-Emmett-Teller equations, as introduced in chapter 2.2. Results show a clear trend of BET estimates: VC < MWCNT < HSAC < HCC.

Subsequent to particle synthesis and their deposition on carbon, fresh catalyst samples were analyzed with ICP-OES, as described in chapter 3.7 for the determination of the exact metal loading. Particle sizes were determined *via* x-ray diffraction and small angle x-ray scattering (XRD and SAXS). A homogeneous particle distributions on carbon supports

were deduced from TEM migrographs. All experimental data are shown in figure 7.2 and respective results are summarized in table 7.1.

Diffraction patterns (figures 7.2a1-d1) showed broad Bragg-peaks at positions corresponding to pure Pt. According to 2.5 the broad peak width indicated the presence of small particles. Calculations of particle sizes based on the Scherrer equation confirmed this suggestion. Particle size estimates were in great agreement with the values obtained from SAXS.

In regard to the calculated errors of particle sizes, the estimated particle sizes of each catalyst powder were found to be in the same dimension range. Consequently, experimental investigations on catalyst size trajectories could give the information on the relationship of nanoparticle stability and supports characteristics.

Table 7.1.: Summary of experimental characterization of carbon supports multi-walled carbon nanotubes (MWCNT), Vulcan (VC, commercial catalyst), high surface area carbon (HSAC, commercial carbon), and hollow core carbon (HCC) before coating with Pt nanoparticles via N-sorption measurements and after coating via ICP-OES, XRD, SAXS.

Catalyst	Surface area	Pt-loading	Crystallite size	Particle size	Poly- dispersity
support	in $\mathrm{m}^2 \cdot \mathrm{g}^{-1}$,	in %wt,	in nm,	in nm,	in %,
	N-sorption	ICP-OES	XRD	SAXS	SAXS
VC	170	21.5	2.7 ± 0.4	2.5	25
MWCNT	230	17.2	2.0 ± 0.2	1.8	35
HSAC	545	28.0	2.6 ± 0.5	2.7	30
HCC	1470	20.1	1.6 ± 0.3	1.6	35



7. Carbon catalyst supports: The impact of the surface area on activity and stability of spherical Pt nanoparticles 82

Figure 7.2.: Characterization of pristine Pt nanoparticles catalysts supported on a) MWCNT, b) VC, c) HSAC, d) HCC, respectively. Results were obtained using the analytical tools 1) XRD, 2) SAXS, 3) TEM with scale bars corresponding to 10 nm, respectively. Images b3 and c3 were adopted from Hasché et al.^{7;113}

83

7.3. Electrochemical characterization

All catalysts were characterized electrochemically, as described in chapter 3.11, to determine the ORR mass and specific activities and to obtain information on catalyst durability in terms of ECSA-time behavior.

Results for ORR mass activity and ECSA of particles estimated after the activation step $(ECSA_{act})$ and after 2500 potential $(ECSA_{end})$ cycles are plotted in figure 7.3. (Respective experimental data of electrochemical characterization are shown in figure 7.6 at the end of this section. Calculated values were determined according to the procedure described in chapter 2.6 and are given in detail in table 7.2 at the end of this section.)

Both electrochemical parameters, ORR and ECSA, were correlated to BET surface area of the C-supports, as shown in figure 7.3a. Obviously, the values of the estimated electrochemical parameters increase with an increasing BET surface area of the carbon support, except in the case of Pt/HCC (this will be discussed later).



Figure 7.3.: Summary of the electrochemical characteristics of Pt nanoparticle catalysts on different carbon supports. a) ORR mass activity (full circles), ECSA (hollow squares) and ORR specific activity (red stars) of the catalysts as function of BET-surface area of the carbon supports. b) ORR mass and specific activities as function of ECSA_{act} of the catalysts.

The ECSA and the Pt mass based ORR activities of the catalysts (Pt/VC, Pt/MWCNT, Pt/HSAC) increased with an increase of carbon BET-surface area, despite similar catalyst nanoparticle sizes (see table 7.1). This trend was attributed to a different separation of the Pt nanoparticles due to a different amount of pores of the supports, as shown schematically in figure 7.4, which demonstrates, that in case of a sufficient separation of a Pt crystallite from a neighbour Pt crystallite, almost the full surface area of a particle can be utilized for

ORR. In contrast, when Pt particles are close together within some critical region, there must be a mutual influence on the diffusion. Consequently, not all of the present Pt surface area is usable for ORR.



Figure 7.4.: Effect of carbon-surface area increase on particle separation. Illustration of accessible (blue) and chemically unusable (red) surface area of supported nanoparticles. The increase of particle separation and a consequent increase of chemically accessible area is achieved by the increase of the carbon-surface area. However, if carbon consists of pores of particle size dimensions (as in the case of Pt/HCC), unusable area is predominating.

The discrepancy observed for the catalyst with the highest BET-surface area (Pt/HCC) could be attributed to the well defined morphology of the support. The C-shells of HCC contained meso pores with well defined sizes in the range of 3-4 nm.¹¹⁴ According to literature, ^{112;115;116} pores sizes of 3-8 nm were found to be useful for the fuel diffusion. Uchida et al.^{115;116} could show that the current density of methanol oxidation increased with increasing the volume of 3-8 nm pores. On the other hand, considering the fact that the ionomer particles are larger than pore diameters, Pt nanoparticles located inside such pores were likely to not contribute completely to chemical reactions due to a partially missing contact to the ionomer. Obviously, in the case of Pt/HCC catalyst this negative effect of fractional Pt-ionomer contact absence due to pore limitations overacted the positive effect of fuel distribution in such 3-8 nm pores. Due to the observed dramatically low electrochemically accessible surface area of the catalyst, the major portion of particles was likely located inside pores and the minor on the surface of such hollow carbon spheres. Consequently, a significant amount of catalytically active Pt nanoparticles surface was excluded from chemical reactions and thus the ECSA values was low compared to the other observed catalyst samples. Additionally, the particles located inside pores were not fully accessible due to the ratio of the active and inactive areas, as defined previously and illustrated in figure 7.4.

However, the rate of chemical reaction occurring per square centimeter of Pt should not be influenced by the amount of such usable/active Pt area. This relationship was reflected by

the estimates of the specific ORR activities. The red curve in figure 7.3a illustrates the the behavior of ORR specific activities as a function of carbon BET-Surface area. The values are comparable for Pt/VC, Pt/MWCNT and Pt/HCC, reflecting that chemical conversion rates were not depending on the support morphology, but on the nature of catalytically active atoms (in all cases it was Pt). A significant increase of ORR specific activity was observed for Pt/HCC. However, the origin of such high specific ORR activity in the case of Pt nanoparticles supported on the carbon with the highest BET surface area could not be identified from the experimental data.

A closer look on the electrochemical characteristics exhibited a direct proportional relationship of ORR mass activity and ECSA, as shown in figure 7.3b. Obviously, the ORR activity per mass unit of Pt increased with increasing electrochemically available surface area. This observation was expected due to its simply logical origin: a consequence of a high amount of ECSA is a higher amount of ORR-performing Pt atoms per mass unit. This finding is in agreement with the hypothesis made from figure 7.4, that illustrated the importance of the available surface of particles resulting from their separation.

These observed results were also in agreement with literature: Supported by experimental investigations from Sattler and Ross¹¹⁰ and Bregoli¹⁰⁹, Watanabe et al.^{111;112} reported, that Pt mass based ORR activity can directly be correlated with the surface area of the supporting material. The authors identified catalyst particle-separation as a key parameter for their catalytical performance. Similar to results presented in this study, they found that a higher Pt-particles separation resulted an increase of ECSA and a simultaneous increase of ORR activity.

7.4. Degradation stability studied using electrochemical characterization

For the durability study, ECSA values were determined for each catalyst as a function of potential stress cycles (experimental data is shown in figure 7.6), respectively. In order to quantify the durability of the catalysts, relative ECSA losses were calculated, as described in chapter 3.11.4. The absolute values of the used ECSA values (ECSA_{act} and ECSA_{end}) and the respective ECSA losses are shown in the bar diagram 7.5a. From this plot a similar significant ECSA loss in the case of Pt/VC, Pt/MWCNT and Pt/HSAC was evidenced, even though the absolte initial ECSA values were dependent on the carbon's morphology, as discussed before.

For the three catalysts Pt/VC, Pt/MWCNT, and Pt/HSAC the value differs max. 3% from



Figure 7.5.: Evolution of the electrochemical characteristics of Pt nanoparticle catalysts on different carbon supports. a) Absolute values of ECSA estimates after activation cycles (hollow bars) and after 2500 AST-cycles (dashed bars) are plotted on the left y-axis. Relative values for ECSA-loss (grey bars) are related to the right y-axis. b) ORR specific activities (red stars) and relative ECSA loss (grey squares) as function of BET-surface area of the carbon supports.

each other. In case of the carbon with the highest BET surface area (HCC) the observed ECSA loss differed from the other catalysts, which again was attributed to the ratio of active and inactive Pt surface (figure 7.4). Consequently, even though the initial values of ECSA were directly correlated with supports structure (for Pt/VC, Pt/MWCNT and Pt/HSAC), catalyst degradation proceeded with similar rates.

An explanation of the equal degradation behavior of Pt nanoparticles supported on carbons, which offered a sufficient amount of usable Pt area (VC, MWCNT and HSAC), was found by correlating the ECSA loss estimates with the specific ORR activities of the catalysts. Figure 7.5b illustrates that the ECSA loss curve as a function of BET-surface area of the carbon supports progressed parallel to the specific ORR activities curve. Obviously, solely the rate of chemical reactions during the AST per area-unit of Pt, which is defined by the specific ORR activity, controlled the degradation of the Pt nanoparticles. Consequently, atoms that interacted with a higher amount of molecules were predominantly subjected to degradation mechanisms.

In order to specify the degradation mechanisms and the respective role of carbons morphology and to gain more detailed information on particle size trajectories, structural investigations *via in situ* SAXS were performed.



Figure 7.6.: Electrochemical characterization of Pt / Carbon. Letters specify the support structure: a) MWCNT, b) VC, c) HSAC, d) HCC. Numbers show to each support corresponding CVs(1) and LSV (2). ECSA (3) loss was calculated from the H_{upd}-range (0.05-1.10 V vs. RHE) of the plotted CVs.

Catalyst	ORR-activity	$\mathrm{ECSA}_{\mathrm{act}}$	$\mathrm{ECSA}_{\mathrm{end}}$	ECSA-loss
support	in $\mathrm{A} \cdot \mathrm{mg}^{-1}$,	in $\mathrm{m}^2 \cdot \mathrm{g}_{\mathrm{Pt}}^{-1}$,	in $\mathrm{m}^2 \cdot \mathrm{g}_{\mathrm{Pt}}^{-1}$,	in %,
	LCV	$\mathrm{H}_{\mathrm{upd}}CV$	$\mathrm{H}_{\mathrm{upd}}CV$	$\mathrm{H}_{\mathrm{upd}}CV$
VC	0.097 ± 0.023	61.2 ± 0.5	43.9 ± 1.0	28.2 ± 1.7
MWCNT	0.133 ± 0.015	74.5 ± 4.2	55.2 ± 2.4	25.9 ± 5.3
HSAC	0.168 ± 0.015	91.2 ± 0.0	68.2 ± 0.8	25.2 ± 0.8
HCC	0.083 ± 0.001	26.5 ± 1.4	15.5 ± 2.4	41.5 ± 9.6

Table 7.2.: Electrochemical characterization of catalyst powders with different carbon supports.

7.5. Degradation stability studied using in situ SAXS

Particle degradation was studied *in situ* at a synchrotron facility SLAC. SAXS working procedure and a detailed description of data processing is given in chapter 3.12. From experimental scattering curves the information on volume weighted particle size $(2 \cdot R_{lc})$, number density of particles (N_0) and the volume fraction of scattering centers (Φ) were extracted. Additionally, according to the expressions introduced in chapter 3.12.5 Lognormal-type probability density functions (pdf) were calculated using the estimates from mathematical fits of SAXS data, namely the mean particle size $\mu = < R^1 >$, the corresponding standard deviation σ and the number density of particles in the probed volume $N_{SASfit} = N_{obj}/V$. Here, first the SAXS results for each catalyst will be discussed separately and subsequently a conclusion will be made on particle size trajectories as a function of carbon morphology. Furthermore, the contribution of different degradation mechanisms, evidenced from the combination of electrochemical and structural investigations, will be discussed in regard to the support's structure.

Structural dynamics of Pt/VC

Figure 7.7a summarized the SAXS estimates for the PT/VC catalyst as a function of potential stress cycles. Particles diameter increased during the AST from 3.4 nm to 5.0 nm with an initial growth rate of 0.06 nm/100CV. Simultaneously, N_0 dropped after 2500 AST cycles to 30% of the initial value, whereas Φ remained almost constant for the duration of the AST. According to these findings, coalescence was deduced from the experimental data. However, the process of Ostwald ripening cannot be excluded.





Figure 7.7.: Structural dynamics of Pt/VC. a) Evolution of particle diameter (black circles), number density of particles (red triangles) and volume fraction of scattering centers (red squares). b) Resulting Lognormal-type probability density function of particle sizes with progress of AST protocol (from black to red).

A closer look on the Lognormal-type pdf (figure 7.7b) indicated a significantly reduced probability of small particles sizes. The probability for big particle sizes increases also, but not with the same magnitude. These observations suggested that coalescence was accompanied by Ostwald ripening, because the probability for big particles was not found to be proportional to the amount of the small particle loss.

Structural dynamics of Pt/MWCNT



Figure 7.8.: Structural dynamics of Pt/MWCNT. a) Evolution of particle diameter (black circles), number density of particles (red triangles) and volume fraction of scattering centers (red squares). b) Resulting Lognormal-type probability density functions of particle sizes with progress of AST protocol (from black to red).

Figure 7.8a summarized the SAXS estimates for the PT/MWCNT catalyst as a function of potential stress cycles. Particles diameter increased during the AST from 3.2 nm to 5.9 nm

with an initial growth rate of 0.12 nm/100CV, which represented a twice faster growth of particles than in the case of Pt/VC catalyst.

Simultaneously, N_0 dropped after 2500 AST cycles to 10% of the initial value. Compared to Pt/VC the decrease of particle number was higher, as it could be predicted from the faster growth rate of particles. However, the degradation of nanoparticles supported on MWCNT was likely to be different from Pt/VC, as indicated by the evolution of Φ . In contrast to Pt/VC, the volume fraction of Pt/MWCNT did not remain constant for the entire AST duration. After 1000 potential cycles the value decreased to 70%, suggesting particle dissolution.

Consequently, Pt nanoparticles supported on MWCNT predominantly coalesced in the first instance. Further catalyst stability was controlled by dissolution of particles. Again, the process of Ostwald ripening cannot be excluded for the Pt/MWCNT. Even though particles were likely to dissolve, the volume weighted size still increased, which indicated Ostwald ripening.

The calculation of Lognormal-type pdfs (figure 7.8b) for each recorded step of the AST and their evolution revealed that small nanoparticles dissolved completely, whereas the probability of larger particle sizes was not scaled proportionally to the loss of small particles.

These findings were attributed to the morphology of the carbon, which was represented by "smooth" surface in the case of MWCNT and porous surface in the case of VC. Particle motion and coalescence on a smooth surface is expected to be higher than on a porous one. Hence, particle growth rate must be higher. Furthermore, particles, which do not coalesce dissolve due to the Gibbs-Thomson energy. Pt ions produced by dissolution can diffuse to the electrolyte (smooth carbon) or are caught in the carbon pores (porous carbons). The experimental data for Pt/VC and Pt/MWCNT support these suggestion. Additional particle dynamics study on Pt/HSAC and Pt/HCC were performed in order to validate the made conclusions.

Structural dynamics of Pt/HSAC

Figure 7.9a summarized the SAXS estimates for the PT/HSAC catalyst as a function of potential stress cycles. Particles diameter increased during the AST from 2.4 nm to 4.2 nm with an initial growth rate of 0.10 nm/100CV. Simultaneously, N_0 dropped after 2500 AST cycles to 20% of the initial value, whereas Φ remained almost constant for the duration of the AST.

These findings were very similar to the observation obtained from the durability study of



Figure 7.9.: Structural dynamics of Pt/HSAC. a) Evolution of particle diameter (black circles), number density of particles (red triangles) and volume fraction of scattering centers (red squares). b) Resulting Lognormal-type probability density functions of particle sizes with progress of AST protocol (from black to red).

Pt/VC. The difference was the growth rate of particles. In regard to the conclusions made for Pt/VC and Pt/MWCNT, coalescence and particle dissolution defined the particles dynamics. In the case of Pt/HSAC, which represented a porous carbon, dissolution did not dominate at any point of degradation, as deduced from a constant value Φ .

However, particles final size after finishing the AST was significantly smaller compared to Pt nanoparticles supported on VC, whereas the size estimates of pristine particles were in the same size range (Pt/VC: $2.5 \pm 25\%$ and Pt/HSAC: $2.7 \pm 30\%$) Consequently, the BET surface area of the carbon support was likely to contribute the particle size trajectories.

A closer look on the Lognormal-type pdf (figure 7.9b) evidenced similar evolution of probabilities for small and large particle sizes compared to Pt/VC. In agreement to the made suggestions, that Pt ions produced by dissolution were caught in the pore-cages of the carbon, it was deduced that the amount and the size of such pores were the limiting factors for particle growth. In order to clarify this relationship, the dynamics of electrochemically treated Pt/HCC, where the pores were in a defined size range of 3–4 nm, were studied.

Structural dynamics of Pt/HCC

Figure 7.10a summarized the SAXS estimates for the PT/HCC catalyst as a function of potential stress cycles. Particles diameter increased during the AST from 2.4 nm to 4.2 nm with an initial growth rate of 0.06 nm/100CV. Simultaneously, N_0 dropped after 2500 AST cycles to 10% of the initial value. A continuous decrease of Φ to 60% suggested particle dissolution.

As mentioned above, a combination of coalescence and particle dissolution with a subse-



Figure 7.10.: Structural dynamics of Pt/HCC. a) Evolution of particle diameter (black circles), number density of particles (red triangles) and volume fraction of scattering centers (red squares). b) Resulting Lognormal-type probability density functions of particle sizes with progress of AST protocol (from black to red).

quent redeposition of produced ions (in the cases of porous carbons) was likely to control the durability of Pt nanoparticles during electrochemical treatment. Especially in the case of Pt/HCC the effect of dissolution and redeposition (Ostwald ripenening) was clearly observed. Particles dissolved (Φ decreased) and the the ions were caught in the carbon pores with the defined sizes of 3–4 nm. Exactly this size range was observed as the final size of Pt nanoparticles on HCC. Consequently, the redeposition of ions was limited by the pore size of the carbon support. The calculated pdfs (figure 7.10b) for Pt/HCC pointed out this relationship: In contrast to Pt/VC, Pt/MWCNT and Pt/HSAC catalysts, the calculated pdfs for Pt/HCC evidenced a slight increase of the probabilities of larger particle sizes, but no complete shift of the functions.

7.6. Proposed degradation mechanisms

It is apparent that due to a different nature of graphite planes orientation of VC, HSAC and HCC (resulting in carbon pores), compared to MWCNT (smooth surface), the influence of carbon surface to catalyst degradation mechanisms is suggested to be controlled not solely by BET surface area, but also by the kind of particle anchoring on the carbon. In case of MWCNT Pt nanoparticles are located on nearly smooth surface of C-tubes. In contrast, Pt nanoparticles supported on "classically" porous carbons with randomly oriented graphite planes the deposition of Pt nanoparticles on the carbon carrier could not be localized. The structure of such catalyst supports allowed the Pt particles to deposit during synthesis on the carbon surface and inside the pores and even inside the hollow cores of HCC.

Different particles locations were evidenced from the ECSA estimates. According to literature, ^{25;109–111} ECSA increase resulted by carbon surface area increase was found to be a consequence of particle separation controlleed by the porous structure of the support, as demonstrated in figure 7.4. Especially the determined ECSA of Pt/HCC catalyst support suggested particle deposition inside pores of the carbon particles and resulting good separation of particles. However, ECSA values of the Pt/HCC catalyst were determined to be low. This finding was attributed to the ratio of effectively usable to unusable Pt nanoparticle surface. In the special case of HCC, the carbon morphology consisted mainly of pores in the size range of 3–4 nm, whereas the ionomer was larger in size. Hence, solely portions of Pt nanoparticles were available for chemical reactions.

Focusing on the corresponding SAXS data a mechanism of particle degradation could be proposed (a scheme is given in figure 7.11). SAXS estimates for particle size increased rapidly at the beginning (first 1300 AST-CV) and rose slowly with further number of potential stress cycles. Besides, number density of particles supported on porous carbons (VC, HSAC, HCC) decreased with similar rates. Combining the size rise and the loss of particles amount, coalescence was exhibited as the main degradation mechanism. However, Ostwald ripening was likely to accompany the coalescence process.

In regard to a previously reported study by Gruver *et al.*⁴⁶ coalescence and Ostwald ripening could be distinguished by the shape of particle size probability density function. The authors could correlate pdf with a tail towards higher particle sizes to coalescence process and a contrary course was attributed to Ostwald ripening driven processes. This advanced approach of steady-state particle size distribution correlated with the coarsening process has been used later by Wilson *et al.*¹¹⁷ and Tada *et al.*¹¹⁸ in understanding the degradation of Pt nanoparticles supported on Vulcan. The pdf obtained from experimental SAXS results tailed towards higher particle values. Besides, the probability density of

large particles was found to increase slightly, indicating that coalescence was not defining the particle size trajectories alone. If this was the case, the amount of larger particles would have scaled directly proportionally to the loss of small particles. However, the presence of Ostwald ripening could not be completely excluded. From the experimental data, it was only possible to conclude, that coalescence was not the single mechanism of nanoparticle growth.

The observed result correlated with previously reported observations by K. More and K. Reeves.³² The authors applied TEM and XRD techniques on Pt/VC catalysts before and after the usage as FC catalysts. Pt size distributions measured during cycling potential (0.1 - 1.2 V) changed form: A greater tendency to a bimodal distribution was observed. The calculated pdf curves did not shift entirely to larger particle sizes, instead the distribution became broader, besides, the fraction of small particles remained. Experimental findings presented here revealed similar pdfs evolutions, except in the case of Pt/MWCNT. Hence, the growth of Pt nanoparticles was best described by a combination of coalescence and Pt dissolution/re-precipitation.

Additionally, according to figure 7.11, dependence of particle durability on particle separation reasoned by carbon porosity, which was defined by the BET-surface area estimates, was evidenced. The final size of particles was achieved by the space limitation of the corresponding pore sizes of the carbon supports. In case of VC and HSAC particles grew to larger diameters, reasoned by a broader distribution of pore-sizes. HCC pores were in



Figure 7.11.: Scheme of degradation mechanism of spherical Pt nanoparticles supported on a) MWCNT with tubular oriented graphite planes and b) porous carbons, such as VC, HSAC, HCC. Portions of particles migrate on the smooth carbon surface and coalesce, accompanied by simultaneous dissolution of other particles. Particles inside the pores coalesce and grow, particles on the outer surface grow or dissolve. Subsequent to achievement of the size limit for encapsulated particles due to the defined pore-size of carbon, particles dissolve.

the size range of 3–4 nm, final nanoparticle size was clearly observed in this range and consequently attributed to the pore-limitation effect.

In contrast, particles supported on MWCNT did not achieve any final size due to absence of such pore-limitation. As reported by Serp et al.¹¹⁹, pores in MWCNT can be mainly divided into inner hollow cavities of small diameter (narrowly distributed, mainly 3-6 nm) and aggregated pores (widely distributed, 20-40 nm) formed by interaction of isolated MWNT. Even though the BET-surface area indicated porous structure, the estimate was originated by intra and inter tubular pores, which meant that Pt nanoparticles were generally not embedded by carbon.

However, the degradation of particles did not stop after a final particle size controlled by pore-limitation was reached. (Especially in the case of Pt/HCC catalyst, this evolution was observed clearly.) Despite, degradation of catalyst particles (see chapter 1.1) progressed with the increasing number of potential cycles in terms of dissolution of Pt nanoparticles, as indicated by the descending volume fraction curves. As reported in literature, Pt dissolution is a common degradation process.^{10;15;22} Mayrhofer et al. demonstrated that whole Pt particles detached from the support and dissolved into the electrolyte without re-deposition.¹⁵ Darling et al. presented a theoretical model, which simulated the relationship of onset potential in a PEMFC and its effect on Pt dissolution.²² A summary of comparable studies was given by Shao-Horn et al.¹⁰ Overall, based on previously reported results, dissolution of Pt atoms was expected to be the second step of degradation mechanism.

However, dissolution of particles was likely to contribute to particle degradation over the entire potential stress due to the Gibbs-Thomson energy, which could be expected to be similar for initial particles with comparable sizes. In case of "classically" porous dissolution was not observed directly due to a constant volume fraction curve until the limiting size of particles was achieved, because formed Pt ions were captured inside the pores. A resulting increase of Pt ion concentration in such "pore-cages" was balanced by redeposition of these ions on the surfaces of particles existing also inside the cage. This process describes the Ostwald ripening mechanism.

96

7.7. Summary

In this chapter the relationship between the catalyst degradation behavior and the structure of a conductive support was investigated. Initially, spherical Pt nanoparticles supported on different carbon carriers with various N-sorption surface areas were characterized ex-situ with TEM, XRD, SAXS and ICP-OES. Pristine powders revealed similar metal contents and particle sizes, respectively.

Next, the electrochemical properties of the observed catalysts were analyzed. Catalytic activities for the oxygen reduction reaction were estimated using linear sweep voltammetry. Information on particle stability was gained from cyclic voltamogramms in the H_{upd} -region. For this purpose electrochemical surface area (ECSA) has been calculated assuming a coverage of one H-atom per Pt-atom.

An increase of ECSA was observed with an increasing BET-surface area of the carbon support. This finding was in agreement with literature.^{109–112} This relationship was not observed for Pt/HCC (the carbon with the higher BET-surface area) and the discrepancy was attributed to the pore sizes in the range of 3–4 nm. Referring to previously reported studies,^{112;115;116} these pore sizes were identified to limit catalyst performance by an insufficient Pt-ionomer contact.

ECSA decrease was independent from the supports structure in the cases of Pt/VC, Pt/MWCNT and Pt/HSAC. For each of these catalysts ESCA loss was estimated in a range of 25-30%. A relationship between the relative ECSA loss and the specific ORR activity of the catalysts was established. The values suggested, that solely the chemical conversion rate per area Pt (which is reflected by the specific ORR activity), defined the relative loss of chemically usable nanoparticle area, independently from the total initially available Pt-ECSA. A discrepant behavior was observed for Pt nanoparticles supported on HCC (ECSA loss of 41.5%) and, again, the difference was connected to the limitations caused by pore sizes of HCC. Overall, ECSA decrease provoked by electrochemical treatment of catalysts suggested catalyst degradation. The identification of degradation affected by the supports structure required further detailed investigations.

To better understand catalyst degradation and performance losses, the applied electrochemical treatment was coupled to *in situ* structural investigation on particle dynamics *via* SAXS. The advanced technique exhibited information on particle size, number density of particles and volume fraction of scattering centers in a probed area as functions of potential cycles, respectively, and additionally extended the results obtained for the ECSA evolution. Experimental results afforded a study and understanding of degradation directly associated with Pt particle parameters (size, number density, volume fraction) as a func-
tion of the nature and surface area of the C-support. Even though the increasing surface area of the carbon limited particle growth, ECSA losses remained similar. Combining the information obtained from SAXS and ECSA conclusion on mechanisms were made.

First step of catalysts degradation was identified as formation of bigger particles as a result of coalescence. However, dissolution of particles due to Gibbs-Thomson energy was expected to occur over the entire duration of the AST protocol. The process was observed by experimental results only subsequent to coalescence, as it will be discussed below. Particle durability was likely controlled by the surface of the support. Experimental findings evidenced that porous structure was significantly affecting particle dynamics. The final size of the particles increased with a decreasing BET surface area of the carbon. Pt nanoparticles supported on carbons with randomly distributed graphite sheets (VC, HSAC and HCC) specified final particle sizes by the corresponding pore-sizes of carbon. This conclusion was also supported by observing the Pt nanoparticles supported on tubular oriented graphite sheets, namely Pt/MWCNT. This type of carbon was identified to be completely different compared to the other observed carbons VC, HSAC and HCC. Hence, final size of Pt nanoparticles was not reached by completing the AST-protocol.

Second step of the degradation mechanism was dissolution of Pt, which also was controlled by carbon support characteristics. In case of carbons with "classical" porosity (VC, HSAC and HCC) dissolution of Pt started to dominate subsequent to the achievement of final particle sizes limited by pore dimension of the support. In case of MWCNT, the supported Pt nanoparticles dissolution of particles was observed constantly during the entire ASTprotocol. Regarding the different particle anchoring as on VC, HSAC and HCC, Pt ions produced from particles supported on MWCNT were not captured by "pore-cages". Hence, the volume fraction dropped continuously. In contrast, Pt ions produced by dissolution of particles supported on VC, HSAC and HCC were caught. An increase in Pt ion concentration inside a pore was likely counterbalanced by redeposition of these ions on particle located inside the pores. This Ostwald ripening process turned into pure dissolution after a limiting particle size affected by the pore size was achieved.

In summary, nanoparticle degradation mechanisms were estimated to be dependent on the carrier structure especially on the origin of porosity. Furthermore, the results encouraged a study of support modification in terms of degradation prevention of the electrochemical catalyst.

8. Catalyst support functionalization: Stability enhancement with ionic liquids

8.1. Introduction

Metal nanoparticles (NPs) are a frequently employed catalytically active component of industrial catalysts such as three-way catalysts in catalytic converters, reforming catalysts in refinery processes or electrode catalysts in electrochemical devices. This is because nanoparticles offer a large catalytically active surface area, which is indispensable for cost- and material efficient product yields. In electrocatalytic electrodes, such as polymer electrolyte membrane (PEM) fuel cell electrodes or PEM electrolyzer electrodes, highly dispersed metal nanoparticles ensure sufficient electrochemical surface areas (ECSA) and hence viable electrochemical power densities and hydrogen yields, respectively. However, the dispersed nanoparticles show structural instabilities due to their high surface energy.^{4–10;120}

Ex situ transmission electron microscopy (TEM) studies^{6;10;15–17} have evidenced that electrocatalytic Pt nanoparticles quickly grow and coarsen; this manifests itself as degradation of cell voltage and loss in the ECSA. The growth rate was found to be dependent on the surface area of the carbon support with high surface area carbons showing a slower Pt coarsening rate than low surface area supports (chapter 7).^{7;8} In parallel to the particle coarsening, carbon supports corrode and degrade due to the high cathodic electrode potentials. Much has been learned about the molecular scale degradation mechanisms of fuel cell cathodes,¹⁰ however, to date, robust and practical material-design strategies to mitigate the structural degradation of carbon-supported Pt nanoparticle catalysts has remained scarce.

Here, a simple, but very effective strategy to mitigate Pt NP coarsening in supported high surface area fuel cell electrodes is presented. The study is based on the hypothesis that surface heteroatoms, such as nitrogen, mediate the enhancement of platinum adsorption on the surface of carbon materials and slow down or even suppress its growth and surface

area degradation.^{121–126}

Nitrogen doping of carbon electrodes can be achieved via a variety of methods including pyrolysis and CVD of nitrogen rich precursors and post-synthetic methods like ion bombardment or thermal treatment in the presence of reactive nitrogen compounds such as ammonia.¹²⁶

lonic liquids are established precursor compounds in the field of materials chemistry, ^{127–131} but just recently they have been applied as precursors for nitrogen-doped carbon.^{132–137} As liquids with negligible vapour pressure, such precursors can be easily processed and transformed into N-doped carbon materials by simple annealing under inert gas atmosphere.^{134;135} N-doped carbons derived from 3–methyl–N–butyl–pyridinium–dicyanamide (3–MBP–dca) exhibit interesting properties: even at carbonisation temperatures of 1000°C a high nitrogen content of approx. 10 wt% is observed in the resulting carbon material. The nitrogen atoms are incorporated into the carbon backbone in pyridinic or quaternary graphitic bonding environments within a structure that is dominated by graphitic microdomains. Furthermore, remarkable electric conductivities were reported, reaching the range of highly ordered graphite.^{134;135} Thus IL-derived N-doped carbons have been envisaged as interesting materials for electrochemical applications.

One interesting example has recently been presented using IL-derived N-doped carbon- ${\rm Li}_4{\rm Ti}_5{\rm O}_{12}$ composites as cathode material in lithium ion batteries.¹³⁸

8.2. Nitrogen-containing graphites

A study on N-doped carbon reported in literature inspired the investigation of the stabilizing effect of support structure on catalyst particles. To achieve that a carbon support with a high nitrogen content was prepared by pyrolysis using an IL-precursor (3–MBP–dca). Synthesis procedure and characterization of the material, which will be termed here as "'meso-C"', are reported elsewhere.¹³⁹



Figure 8.1.: Electrochemical stability study on Pt nanoparticles supported on high N-containing carbon. Evolution of the Pt ESCA (inset: normalized ECSA trend) for Pt/meso-C (squares) and Pt/HSAC (circles) during voltage cycling from 0.5 to 1.0 V versus RHE with 50 mV \cdot s⁻¹ in deaerated 0.1 M HClO₄ electrolyte at room temperature. Figure is adapted from literature.¹¹³

The most relevant characterization for the presented study is elemental analysis, which revealed a Nitrogen content of 14 wt% assembled in the meso-C carbon structure. Pt nanoparticles were deposed on the modified conductive material in order to obtain the information on stabilizing effects of the increase of hetero atoms in the particle support. The catalyst powder was tested under potential cycling to determine the electrochemical stability¹¹³ and compared to a commercially available Pt/HSAC catalyst. In this section the investigations will focus on the same comparison. Results on particle stabilizing effect of the N-doped material will be presented *versus* the degradation behaviour of the commercial

benchmark catalyst Pt/HSAC.

Figure 8.1 compares the reported ECSA estimates for Pt/HSAC and Pt/meso-C. The results suggest a very similar behaviour in terms of ECSA loss. A significant stability enhancement is observed in case of nanoparticles supported on the N-containing carbon after 4000 voltage cycles. Hasché et al. conclude a two step degradation mechanism, "where the ECSA loss curve can be split into two regimes." In "the earlier stage (up to 4000 voltage cycles) particle growth controls primarily the degradation mechanism while in the later stage carbon (support) corrosion associated with particle detachment is dominant."¹¹³ This chapter focuses on the comparison of Pt supported on the N-containing meso-Carbon

and Pt/HSAC. Prior to stability study a summary on detailed characterization of the pristine catalysts is given in table 8.1.

Table 8.1.: Summary of experimental characterization of carbon supports multi-walled carbon nanotubes (MWCNT), and N-doped mesoporous carbon (meso-C) before coating with Pt nanoparticles via N-sorption measurements and after coating via ICP-OES, XRD, SAXS.

Catalyst	Surface area	Pt-loading	Crystallite size	Particle size	Poly- dispersity
support	in $\mathrm{m}^2 \cdot \mathrm{g}^{-1}$,	in %wt,	in nm,	in nm,	in %,
from	N-sorption	ICP-OES	XRD	SAXS	SAXS
MWCNT	377	17.2	2.0 ± 0.2	1.8	35
meso-C	320 ¹³⁹	17.1	1.9 ± 0.1	2.7	35

The commercial benchmark powder was already introduced in chapter 7.2 of this thesis. For a better conspicuity the determined values are adopted and presented together with the estimates for the Pt/meso-C catalyst. The characterization of the second catalyst of interest are reported in literature and accompanied with further structural analysis with SAXS (experimental data is shown in figure A.5 in the appendix A).

8.2.1. Stability study of Pt/meso-C compared to Pt/HSAC

In order to determine the degradation mechanism during the first stage of degradation in detail, as described in the introduction section of this chapter, *in situ* SAXS experiments were carried out at the synchrotron facility SLAC. Working electrodes were prepared following the standard procedure described in the experimental section (chapter 3.12).

Stability study of the Pt/HSAC catalyst was reported in chapter 7.5. For a better visualization and comparison of the SAXS results the estimates for particle diameter, number density of particles and the volume fraction of scattering centers are plotted in figure 8.2 together with the values for Pt/meso-C.

Figure 8.2 summerizes the results obtained from *in situ* SAXS measurements. The evolution of particle diameter (fig. 8.2a) as a function of potential stress emphasizes a significantly enhanced particle stability in case of Pt/meso-C catalyst. Platinum nanoparticles with an initial size of 2.5 nm grow to 2.7 nm, representing a rise of 8%. At the first glance, an optimal fuel cell catalyst is represented by supporting Pt nanoparticles on meso-C. A closer look on the additional parameters determined from SAXS, the number density of particles and the volume fraction of scattering centers, reveals a more complex correlation to the



Figure 8.2.: Comparison of catalyst degradation of Pt/meso-C (red stars) and Pt/HSAC catalysts (black triangles), during potential cycling derived from SAXS estimates a) diameter, b) normalized number density of particles and c) normalized volume fraction of scattering centers) as functions of potential cycles, respectively. Resulting LogNormal probability density functions for d) Pt/meso-C and e) for Pt/HSAC. Color change indicates the estimates after the activation cycles (black) up to 2500 potential cycles (bright red).

assumed particle stabilization. Figure 8.2b indicates a loss in particle number density for the Pt/meso-C catalyst, even though the size of the particles does not change significantly during the electrochemical stress regime. A consolidation of the stable particle size and a dramatic loss in particle number density suggests particle dissolution. A more detailed insight in degradation mechanism can be extracted concerning the contribution of the volume fraction of scattering centers. The normalized values for Pt nanoparticles supported on the hetero-atoms containing carbon decreases to 50% with progress of potential stress. Hence, particle dissolution can be assumed for the Pt/meso-C catalyst as the main process of catalyst degradation.

Obviously, a certain size of nanoparticles is favoured on a Nitrogen-containing carbon support. No indication of significant particle growth was observed *via in situ* SAXS. How-ever, the electrochemical surface area loss, as observed in literature,¹¹³ and the decrease of particle number density with a simultaneous loss of volume fraction of scattering centers suggest a continuous particle dissolution.

In contrast, particles supported on HSAC grow and coarsen during the whole potential stress protocol. Initial particle size of 2.5 nm increases to 4.2 nm (fig. 8.7a). This relative particle growth of 68% subjects to an extended particle degradation. Whereas the number density of particles for the commercial catalyst decreases dramatically to 20% in respect to the initial value, volume fraction of scattering centers remains almost constant. Refered to the particle size increase, a counterbalanced number density decrease and a constant volume fraction, catalyst degradation mainly affected by particle growth is deduced, as discussed more in detail in chapter 7.

To emphasise the role of modification of the carrier's nature, the LogNormal-type probability density functions (pdf) were calculated using SAXS estimates (details on calculation are given in the chapter 3.12.5). Figure 8.2d presents the pdf for the Pt/meso-C catalyst, part e) for the benchmark catalyst Pt/HSAC. A distinct evolution of pdf is revealed for the compared catalysts. The pdf of the commercial catalyst Pt/HSAC shifts towards higher particle size values with increasing number of cycles. In contrast, no change in pdf mode is indicated in case of Pt/meso-C.

8.3. Nitrogen-doped coatings on MWCNT

The method used throughout this part of study does, in contrast, not change the backbone of the material itself, but applies a thin coating of N-doped carbon on the surface of the electrocatalyst support via a post-synthetic method (figure 8.3).



Figure 8.3.: Schematic overview on synthesis strategy of Pt nanoparticles supported on N-C coated MWCNT.

On the one hand, this allows for the use of cheap and widely available bulk carbons as host material and on the other hand offers the possibility of a more direct comparison of doped and non-doped catalyst supports. Herein it is shown that by this method, growth and coarsening of Pt nanoparticles during electrochemical potential cycling are largely suppressed. Furthermore, it is shown that the presence of N-C coatings does not compromise the electrocatalytic activity of Pt nanoparticles. The N-C coatings were formed from ionic liquid precursors, which can wet the surface of the pristine carbon support and subsequently be pyrolyzed into nitrogen-rich carbon coatings. Particle growth on the pristine and N-C coated carbons was monitored using time-resolved *in situ* SAXS,^{101;106} a non-invasive powerful, yet rarely used method, to monitor growth trajectories of electrocatalytic particles in real time.

Thus to exploit the favourable properties of IL derived carbons in a most economical way, it was envisaged to prepare just thin coatings of the IL derived carbons on a convenient bulk carbon material. Such a coating also offers the opportunity to combine the properties of the IL derived carbon with the ones of the host.

In this study the IL 3–MBP–dca was used to prepare a N–doped carbon (N-C) coating on the walls of carbon nanotubes (MWCNTs).^{134;135} MWCNTs have been selected as a host, as their defined morphology allows for a good control of the homogeneity of the coating. Furthermore a preferable interaction of MWCNTs with ILs is known from the recent literature.¹⁴⁰ It should be however noted that in principle all other forms of carbons, like activated charcoal, should be as well feasible as host materials. Prior to the application of the N-doped carbon coatings, the MWCNT supports were surface oxidised using sulfuric acid in order to increase the number of polar end groups. This served to even further enhance the interaction between the polar ILs with the MWCNT surface. IL precursor concentrations were carefully adjusted to enable a homogeneous coating and to minimize any intertubular residues.

8.3.1. Support characterization

An optimized 30 mol% of 3MBP-dca in water was applied in the wetting of the MWCNTs and subsequent formation of an N-doped carbon layer by thermal treatment under inert gas at 1000°C. Higher concentrations of ILs or even pure ILs led to strong intertubular bulk carbon contributions, while lower concentrations did not yield sufficiently and homogeneously coated materials. The resulting composite material (henceforth referred to as "N-MWCNT") was analyzed by means of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and nitrogen sorption. Nitrogen sorption isotherms (see



Figure 8.4.: a) Transmission electron micrographs of N–MWCNTs with a chemical formula of the IL– coating precursor. b) XP survey spectrum of coated nanotubes with a highly resolved N1s spectrum. c) Nitrogen–sorption isotherms of raw MWCNT and N–C functionalised MWCNT in comparison.

Fig. 8.4c) reveal a decrease of the surface area upon hydroxylation of the CNTs, probably due to increased intertubular interactions. In N–MWCNTs this effect is no longer observed due to the N–C modified MWCNT surfaces. The micrograph in Fig. 8.4a further evidences no significant amounts of excess intertubular bulk residue. A similarly heat treated non–modified CNTs material, henceforth referred to as MWCNT, were used as a benchmark support in this study.

The XPS survey scan in Fig. 8.4b shows peaks for C, O and N with concentrations of 97, 2 and 1 at.%, respectively. The spectral parameters are shown in table 8.2.

Peakname	Graphitic N	Pyridinic N	ox. N-species
Gaussian width / eV	2.1	2.1	2.1
Lorentzian width / eV	0.35	0.35	0.35
Asymmetry α	0.09	-	-
Binding energy / eV	401.1	398.7	404.0
Relative amount / %	61.8	35.7	2.5
Total amount / at-%	0.6	0.4	_

Table 8.2.: Peak fit parameter of the N_{1s} detail spectrum in inset of figure 8.4c.

The nitrogen content may seem small at first glance. Nevertheless it has to be considered that a coating of carbon doped with ca. 10 wt% N has been applied on a carbon surface; thus higher N-contents can hardly be expected. High resolution analysis of the N_{1s} region shows three components with binding energies of 398.7 eV, 401.1 eV and 404.0 eV and with relative N-intensities of 35.7, 61.8 and 2.5%. Based on a previous study¹³⁴ it was possible to identify these three components as pyridinic, graphitic and oxidised N-species. The high resolution C_{1s} region shows two loss- and the sp2- and sp³-carbon peaks, as they are typical for MWCNTs. Additionally there were three component peaks with additional components with binding energies of 286.8 eV, 287.9 eV and 288 eV. A specific assignment to functional groups, however, was not possible, because oxygen and nitrogen-containing groups lead to very similar chemical shifts in that region.

8.3.2. Characterization of the pristine catalyst powders Pt/MWCNT and Pt/N-MWCNT

To study the effect of N-doped interlayers on the electrochemically induced growth and surface area degradation of catalytic NPs, Pt nanoparticles were deposited^{104;141} on the benchmark MWCNTs as well as on the N–MWCNTs support materials. Particle growth trajectories were measured in situ using SAXS. SAXS offers a time resolved analysis of the particle size distribution, characterized by the mean diameter and dispersion, the number density and the volume fraction of scattering centers.⁷⁹ Fig. 8.5a shows the high resolution TEM images of the as–prepared Pt–NP supported on the uncoated MWCNTs. The particles are homogeneously distributed on the support; a mean particle size of 1.4 nm was obtained from the log-normal distribution of the particle size resulting from counting 200 particles on TEM images (Fig. 8.5b).

Probing a much larger particle population than TEM, SAXS provides statistically more reliable size information. Fig. 8.5c shows the background-corrected scattering curve of the pristine powder and its fit using a spherical particle form factor. The inset presents the corresponding particle size distribution (psd). The psd is characterized by a narrow distribution of smaller (~ 1.8 nm) particles. A similar analysis for the as-prepared Pt–NP supported on the N–MWCNTs is shown in Fig. 8.5d, e and f. The TEM derived mean particle size of the NPs was 1.6 nm, while SAXS data suggested a bimodal size distribution clustering around 2.6 nm and 5.8 nm.

The crystallinity of the supported particles was probed by x-ray diffraction (Fig. 8.5d and 8.5h). Crystallite mean size analyses (2.1 nm for Pt-NPs on MWCNTs and 2.8 nm for Pt-NPs on N-MWCNTs) are reasonably consistent with TEM and SAXS-derived values.



Figure 8.5.: High resolution TEM images of a) 17 wt% Pt/(unmodified) MWCNTs and e) a 17 wt% Pt/N-MWCNTs catalysts. b) and f) show the TEM based size histograms together with a log-normal fit. Histograms were based on 200 particles. c) and g) show experimental SAXS profiles with a log-normal fit for the 17 wt% Pt/MWCNTs and the 17 wt% Pt/N-MWCNTs, respectively. Insets in c) and g) show the extracted particle size distributions plotted on two separate y scales in case of Pt/N-MWCNT catalyst. d) and h) show the corresponding XRD patterns for the catalysts.

8.3.3. Stability study of the catalysts under electrochemical cycling

Finally, the as-prepared MWCNT and N-MWCNT supported PtNPs powder catalysts were used to prepare a liquid catalyst ink suspension, cast into a thin catalyst electrode film and subsequently subjected to an electrochemical voltage cycling protocol to evaluate differences in the stability of the two nanoparticle catalystsupport couples. Emphasis was placed on the evolution of the mean particle size, the ECSA and the Pt-mass based catalytic activity for the oxygen reduction reaction (ORR) to water. This reaction occurs at fuel cell cathodes, the electrode potential of which can vary between 0.5 V and 1.5 V versus the hydrogen anode depending on the fuel cell operating conditions.⁶

Linear sweep voltammetry (Fig. 8.6a and 8.6d) revealed Pt-mass based activities of $0.127 \text{ A} \cdot \text{mg}^{-1}$ for Pt-NPs supported on MWCNTs and $0.123 \text{ A} \cdot \text{mg}^{-1}$ for Pt-NPs on N–MWCNTs, which are in agreement with those of commercial carbon-supported Pt electrocatalysts (see table 7.2). This shows that the NC coatings had no significantly detrimental effect on the electrocatalytic ORR activity. Cyclic voltammetry (CV) (Fig. 8.6b and 8.6e) of catalyst electrode films in a degassed electrolyte yielded time-resolved ECSA trajectories shown in Fig. 8.7a and d. The ECSA loss is a macroscopic descriptor for the total catalytically active surface area and is affected by a large number of different factors, such as particle dispersion, support structure, and the accessibility of particles on the support surface. With initial ECSA values in the 50 - 60 m² · g⁻¹ range,^{7;8} both catalysts showed similar ECSA losses over the 2400 potential cycles of 33% for the uncoated MWCNT and somewhat reduced 27% for the N-MWCNT supported particles.

To test our hypothesis of decreased particle coarsening on N-MWCNT supports, we performed in situ SAXS measurements monitoring particle size changes during voltage cycling. Background-corrected scattering I(q) curves of Pt–NPs on WMCNTs and N–MWCNTs are given in Fig. 8.6c and 8.6f, respectively. Shifts of the decreasing portions of the scattering profiles towards smaller q values over time, seen in Fig. 8.6c, evidence particle coarsening.^{101;142}

Using the I(q) data, time-resolved particle size distributions, time trajectories of correlation length particle diameters $(2 \cdot R_{lc})$ and normalized number densities of scattering centers (N₀) were extracted and compared for the MWCNT and N-MWCNT supports (see Fig. 8.7b, c, e, and f, respectively).



Figure 8.6.: LSV for specific activity calculation (O_2 -saturated 0.1 M HClO₄, 0.06 - 1.02 V, 5 mV · s⁻¹), CVs for H_{upd} calculation (N_2 -saturated 0.1 M HClO₄, 0.05 - 1.10 V, 50 mV · s⁻¹) and in-situ monitored SAXS curves for 20 wt% Pt on MWCNTs (a, b and c) and for 17 wt% Pt on N-MWCNTs (d, e and f). Evolution of scattering curves is given by color change from black (after activation) to red (after 2500 CVs).

Pt-NP number density normalized diameters on unmodified MWCNTs rapidly increased from 3.2 nm to about 6.0 nm during the voltage cycling test. Simultaneously the normalized number density of particles decreased dramatically by about 90%, suggesting a reduction in the number of particles due to coarsening. The normalized volume fraction of scattering centers in the probed area of the Pt/MWCNT catalyst reveals a constant curve progression

up to 1000 voltage cycles and a subsequent decrease to 70% of the initial value. The probability density function (8.7c) of the nanoparticles supported on unmodified carbon shows a continuous shift towards higher particle sizes and a descent evolution of the mode of the distribution.

The time trajectories of the N-MWCNT supported nanoparticles offer a strong contrast to those supported on the unmodified MWCNT. The mean particle size increased from 3.2 nm to only 3.9 nm, a mere 22% growth compared to the 88% growth of the MWCNT-supported



Figure 8.7.: Stability study on Pt/MWCNT (a, b, c) and Pt/N–MWCNT catalysts (d, e, f). a, d) Experimental active surface area (ECSA); b, e) in situ particle diameter change (black circles), normalized number density of particles (hollow triangles) and normalized volume fraction of scattering centers (red squares) during potential cycling. c, f) Calculated LogNormal distribution functions.

particles. Also, rather than a steep exponential drop, the particle number density exhibited a gradual decrease by only 30%. The behaviour of the volume fraction is comparable to that observed for the benchmark catalyts Pt/MWCNT. In the initial stage (0-1000 cycles) the volume fraction remains nearly unchanged and then drops to 70%. The size distribution function remains nearly unchanged during the potential protocol (Fig. 8.7f) in contrast to the distribution determined for Pt/MWCNT catalyst (8.7c).

8.4. Conclusions

Particle stabilization with N-modified graphites

This study was focused on optimizing the stability of Pt nanoparticles by modification the support structure. In the previous chapter a relationship between the support characteristics in terms of its BET surface area and the durability of the supported nanoparticles during potential cycling was exhibited. Thus, a dependency of durability of nanoparticles on support structure provoked a detailed investigation of particle trajectories on a carbon support with a modified backbone. Inspired by a study of Hasché et al.¹¹³, that compared the electrochemical stability of a commercial benchmark catalyst Pt/HSAC with a catalyst consisting of Pt nanoparticles supported on Nitrogen-modified carbon derived from pyrolysis of an ionic liquid, the particle trajectories for the two catalysts were investigated *in situ* with SAXS.

Supported by the evolution of particle diameter as a function of potential cycles a distinct stabilizing effect was observed for Pt/meso-C. However, beyond a significantly reduced particle growth and a suppressed particle number density loss compared to Pt/HSAC, corresponding estimates for the volume fraction of scattering centers indicate a pronounced particle dissolution on the meso-C carbon. Referring to a similar electrochemical surface area loss¹¹³ of Pt nanoparticles supported on an unmodified graphite (HSAC) and on N-containing carbon (meso-C) the hypothesis of catalyst degradation prevention was not confirmed.

It was apparent that an advanced concept of a support modification strategy is needed for stability improvement of an electrochemical fuel cell catalyst. Hence, the results shifted the focus towards an extended application of heteroatoms containing supports.

Particle stabilization with N-doped carbon coatings on MWCNT

The advanced approach of support modification in terms of implementation of N-atoms into carbon structure was consisted of the synthesis of N-doped carbon coatings on MWCNT. The observed evolution of the SAXS-derived structural parameters of the Pt nanoparticles strongly suggested that, owing to its IL pyrolysis coating, the N-MWCNT support provided an improved structural stability of a Pt particle ensemble and reduced Pt particle coarsening during potential cycling.

Based on the measured ECSA values, a mere increase in the surface area of the N-MWCNT support could be excluded as the origin of the stabilization. For the given initial particle diameters, the observed ECSA losses of about 30% appeared to be poorly correlated with particle growth, and rather controlled by structure of the catalyst and the support as well as the interaction with the electrolyte, respectively. The pyrolysis of ILs is known to form pyridinic, pyrrolic, and other nitrogen containing functional surface sites, often at graphene sheet edges.^{143–147} A stabilizing interaction between such nitrogen-containing surface regions and small Pt nanoparticles could be the explanation for reduced migration and coalescence.

On the general effect of Nitrogen

A durability controlling parameter was identified by the performed studies of nanoparticles supported on with heteroatoms modified carbons: The results suggest a strong interaction of the heteroatoms contained in the modified carbon with Platinum, indicated by a finite size of particles achieved irrespected to the progress of potential cycling. According to the previous study discussed in chapter 7, the BET surface area of the carbon support controls the mechanism of particle degradation, as shown in 7.11. Referring to the proposed two step mechanism consisting of coalescence and dissolution, the concept could be adopted for particles supported on "classicaly" porous N-graphite (meso-C) and on "smooth" surface of tubular oriented graphite planes of the N-carbon coated carbon nanotubes (N-MWCNT). Despite the anticipated particle growth, a stable final nanoparticle size around 3–4 nm was estimated, which led to the conclusion that pore-size limitation is not valid for the catalysts doped with heteroatoms.

As shown in figure 8.8 N-containing domains immobilized particles, inhibited migration of particles and consequently prevented coalescence. This conclusions were supported by the fact, that these observations were revealed for particles supported on "classicaly" porous N-graphite (meso-C) and on "smooth" N-MWCNTs. Furthermore, the hypothesis



Figure 8.8.: Effect of nitrogen in the carbon structure on particle size trajectories for Pt nanoparticles supported on a) N-CNT and b) meso-C. Immobilization of particles by Ncontaining domains inhibit migration of particles and consequently prevents coalescence.

that particle dissolved on each carbon support irrespective to the BET surface area, solely driven by the Gibbs-Thomson energy, was supported by particle degradation study on N-containing grpahites. Dissolution process was observed as a dominant mechanism from the beginning of the AST cycles in the case of Pt/meso-C. In contrast to Pt/HSAC, where coalescence dominated and dissolution was balanced by ion redeposition, particles on N-carbon were immobilized and a stable particle size prevented redeposition of Pt ions. Hence, smaller particles dissolved completely. In the case of Pt/N-MWCNT dissolution process remained comparable to Pt/MWCNT (similar Φ decreae). Obviously, in the case of N-containing carbon particle migration and a subsequent coalescence were suppressed by immobilization of the nanoparticles, which was also indicated by a suppressed N₀ decay rate for Pt/N-MWCNT.

9. Summary and outlook

This thesis is about improved understanding of PEMFC catalyst stability. The overall objective was to determine the PEMFC-catalyst performance and stability controlling parameters to obtain better understanding of nanoparticle stability on a fundamental level. To achieve this objective the following subjects were studied and discussed:

 Sensitivity of catalyst activity and stability on nanoparticle shape was investigated. Spherical and cuboid shaped Pt nanoparticles with comparable sizes were synthesized and supported on the same carbon carrier Vulcan XC72 R (VC). Subsequent to the characterization of the pristine powder, catalysts were electrochemically analyzed to reveal information about activity and stability during an accelerating stress test (AST) protocol.

A significantly higher catalyst ORR mass activity was observed for spherical particles in comparison to cuboid nanoparticles. Referring to literature, this observation was attributed to the ratio of (100) and (111) crystal facets, which is significantly different for spherical and cuboid particles with comparable dimensions. Stability the catalyst samples,however, was very similar, as judged by the comparable decays of the respective normalized ECSA curves.

In situ SAXS measurements supported these experimental findings. Stability of nanoparticles was found not to be influenced by particles shape. From particle size trajectories it was concluded, that the strategy of changing the particle shape is not significant in terms of fuel cell catalyst optimization, if the particles dimensions are 4–5 nm. Regarding a higher ORR mass activity of spherical Pt nanoparticles, further investigations were focused on similarly shaped particles. Hence, all following experiments were performed using catalysts consisting of spherical nanoparticles supported on conductive carbons.

 Further investigations were performed on 4–5 nm diameter spherical catalyst nanoparticles with modified elemental compositions. Several studies reported in literature have evidenced that bimetallic alloys of Pt, especially PtNi, are a promising class of fuel cell catalysts due to their enhanced ORR activities. Indeed, experimental investigations of Pt_xNi_{1-x} (0.14 $\leq x \leq$ 0.86) alloys with various elemental compositions reflected these findings. Electrochemical measurements pointed out that $PtNi_3$ and $PtNi_6$ -type alloy nanoparticles exhibited increasing ORR activity during the applied potential stress protocol.

This activity enhancement was found to be higher with diminishing the Ni content in the alloy composition. The precise atomic scale structure of such nanoalloys is still poorly understood. Here a study of alloy nanoparticle catalysts using two previously rarely applied, yet statistically representative x-ray scattering techniques was presented.

The morphological, chemical and atomic-scale structural evolution of two alloy fuel cell catalysts during electrochemical treatment was investigated with *in situ* and *ex situ* x-ray diffraction/scattering techniques.

The results obtained here gave a clearer picture of how the nanoparticles evolve under electrochemical treatment: According to experimental findings the Pt atoms in a PtNi₆ catalyst were more or less uniformly distributed in a matrix of Ni atoms. As a result of potential cycling, Ni-atoms leach out accompanied with some coarsening of nanoparticles, resulting in a structure of an ordered PtNi₃ type. Resulting single phase PtNi₃ particles showed increased activity compared to the initial PtNi₆ alloy catalyst. Electrochemical treatment of a homogeneous alloy PtNi₃ catalyst produces PtNi-core / Pt-shell particles, where the geometric lattice strain effect on surface Pt atoms are likely to contribute to the catalytic activity enhancement. Additional catalyst performance leading parameters, which affect increasing ORR activity of electrochemically treated alloy nanoparticle fuel cell catalysts, were investigated.

It was shown that the change of elemental composition of a catalyst must take into account the ordering of atoms in the catalyst's structure The transition between a disordered and ordered structures need to be taken into consideration in the understanding of non-noble metal rich alloyed/dealloyed particles. The results provided detailed insights into intra particle atomic structure and aimed to a controlled tailor made catalyst synthesis.

3. In the next chapter the relationship between the catalyst degradation behavior and the structure of a conductive support was investigated. Initially, spherical Pt nanoparticles supported on different carbon carriers (VC, MWCNT, HSAC and HCC) with various N-sorption surface areas were structurally characterized. The BET- results, (obtained from nitrogen-sorption measurments), evidenced a carbon surface area trend: VC < MWCNT < HSAC < HCC. Comparable nanoparticle sizes ensured a competitive study of catalyst durability as a function of the nature of the carbon supports and their surface area.

Next, the electrochemical properties of the catalysts were analyzed. ORR activities correlated largely with the BET-trend: Pt/VC < Pt/MWCNT < Pt/HSAC. The discrepancy in the case of Pt/HCC was attributed to the sizes of the carbon-pores (3–4 nm). Previously reported investigation evidenced that these pore sizes limited catalyst performance by an insufficient Pt-ionomer contact.

ECSA estimates reflected the same trend in terms of value increase with increase of carbons BET surface area. Consistent with ORR activity estimates, ECSA values of Pt/HCC differed from other catalysts. Again, this observation was attributed to insufficient Pt-ionomer contact. The identification of degradation affected by the supporting structure required further detailed investigations. Combining the information obtained from SAXS and ECSA conclusions on degradation mechanisms were made. In summary, the degradation mechanism consisted of the following processes:

- Particles dissolved due to their Gibbs-Thomson energy. The contribution of dissolution to particle degradation was depending on carbon structure/porosity. Pt supported on "smooth" MWCNT showed a constant volume fraction loss, indicating a constant dissolution of particles. Pt supported on "classically" porous carbons (VC, HSAC, HCC) were likely to dissolve, but the formed ions were captured inside the pores. A resulting increase of Pt-ions concentration was compensated by redeposition of ions on surface of particles located inside the pore-cages. Hence, no significant indication for dissolution was experimentally monitored in the cases of carbons with large pore sizes (VC, HSAC). The pore sizes of the carbon were found to limit the final size of the supported nanoparticles. Especially, the catalyst with well defined carbon-pore sizes (Pt/HCC) evidenced that the final size of the nanoparticles was controlled by the dimensions of pores. Subsequent to achievement of the final limited particle size, the dissolution of particles was not longer balanced by re-deposition of ions on particle surfaces. Consequently, experimental data exhibited a significant loss of the volume fraction of scattering centers.
- Particles coalesced and the rate was found to depend on carbons structure/porosity. Growth rate of particles indicated that on "smooth" carbon surface the mobility of particles was higher than on porous carbons reasoned by dif-

ferent degree of particle anchoring on the carbon's surface. Furthermore, a dependency of coalescence rate on BET surface area of porous carbons was extracted: A suppressed particle growth with increasing surface area of carbon evidenced a slower particle migration affected by longer pathways. The final size of coalesced particles was found to be controlled by the pore sizes of carbon.

4. The final study was focused on optimizing the stability of Pt nanoparticles by modification of the support structure. Here, the conclusions obtained from investigation of the effect of carbon morphology were adapted.

First part of the study aimed to modify the nature of anchoring nanoparticles on the carbon surface. To achieve this, a hetero atoms containing carbon support was selected. According to literature, the embedding of N-atoms in graphene edges was hypothesized to enhance Pt-support interactions. As a result of this, Pt nanoparticles were immobilized. Consequently particle growth due to coalescence was prevented.

A previously reported study on comparison of Pt/HSAC and Pt supported on a N-containing carbon (Pt/meso-C) revealed similar electrocatalytic properties of the catalysts. Electrochemical testing suggested a two step mechanism, where initially catalyst degradation was controlled by particle growth and after a certain number of AST cycles by carbon corrosion.

In order to specify the degradation mechanism, particle size trajectories were observed with structural analysis. A stabilizing effect of nitrogen in terms of particle immobilization was deduced from *in situ* SAXS experiments. In regard to the preliminary evidenced particle degradation mechanism dependence on carbon structure it was hypothesized that coalescence of particles was suppressed by immobilization.

An accompanying study of particles supported on nitrogen containing graphite with tubular oriented graphite planes (Pt/N-MWCNT) revealed similar results. Compared to Pt nanoparticles supported on conventional MWCNT, the electrochemical performance was found to be equivalent. Particle trajectories probed with *in situ* SAXS pointed out a suppressed coalescence process.

In general, the effect of nitrogen in the carbon backbone can be summarized as follows: N-containing domains immobilized the nanoparticles, inhibited migration of particles and consequently prevented coalescence. This conclusions were supported by the fact, that these observations were revealed for particles supported on "classically" porous N-graphite (meso-C) and on "smooth" N-MWCNTs. Furthermore, the hypothesis that particle dissolved on each carbon support irrespective to the BET surface area, solely driven by the Gibbs-Thomson energy, was supported by particle degradation study on N-containing graphites. Dissolution process was observed as a dominant mechanism from the beginning of the AST cycles in the case of Pt/meso-C. In contrast to Pt/HSAC, where coalescence was clearly observed and dissolution was balanced by ion redeposition (resulting in Ostwald ripening driven particle growth), particles on N-carbon were immobilized and a stabilizing particle size prevented redeposition of Pt ions. Hence, smaller particles dissolved completely, resulting ECSA loss. In the case of Pt/N-MWCNT dissolution remained comparable to Pt/MWCNT (similar Φ decrease). Obviously coalescence was suppressed, indicated by a suppressed N_0 decay rate for Pt/N-MWCNT.

Outlook

In regard to all studies performed in this thesis, a deeper insight in Pt and Pt-alloy FC catalyst degradation was obtained. Overall, the main objective was achieved and several controlling parameters of fuel cell catalyst performances were identified. According to the obtained knowledge, the most promising strategy in further research concentrating on PEMFC catalyst optimization would be:

- The usage of spherical nanoparticles for higher ORR activities in non-adsorbing electrolytes.
- The application of Pt-alloy catalyst nanoparticles with a defined, stable crystal structures, which guarantees an optimized atom-arrangement, in order to enhance ORR activity and minimize the amount of the scarce Pt.
- Advancing the approach of support modification for particle stability enhancement. A combination of a heteroatom embedding in the carbon structure, which suppresses particle dissolution, with N-containing carbon materials, which suppress particle migration, would further improve the stability of a FC catalyst. Further studies on a fundamental level are required to identify such additional component. Additionally, the stabilizing effect of such additional component needs to be proven by an *in situ* investigation of particle trajectories.
- A combination of cost reducing Pt-alloys with stability improving support materials would make a substantive step towards the goal of FC catalyst stabilization.

References

- [1] L. Carrette, K. A. Friedrich, and U. Stimming. Fuel cells: Principles, types, fuels, and applications. *Chemphyschem*, 1(4):162–193, 2000.
- [2] L. Carrette, K. A. Friedrich, and U. Stimming. Fuel cells fundamentals and applications. *Fuel Cells*, 1(1):5–39, 2001.
- [3] H. A. Gasteiger, S.S. Kocha, B. Sompalli, and F. T. Wagner. Activity benchmarks and requirements for pt, pt-alloy, and non-pt oxygen reduction catalysts for pemfcs. *Applied Catalysis B: Environmental*, 56(1-2):9–35, 2005.
- [4] P. J. Ferreira, Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, and H. A. Gasteiger. Instability of pt/c electrocatalysts in proton exchange membrane fuel cells – a mechanistic investigation. J. Electrochem. Soc., 152(11):A2256–A2271, 2005.
- [5] R. L. Borup, J. R. Davey, F. H. Garzon, D. L. Wood, and M. A. Inbody. Pem fuel cell electrocatalyst durability measurements. J. Pow. Sourc., 163:76–81, 2006.
- [6] R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. I. Kimijima, and N. Iwashita. Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chemical Reviews*, 107(10):3904–3951, 2007.
- [7] F. Hasché, M. Oezaslan, and P. Strasser. Activity, stability, and degradation mechanisms of dealloyed ptcu₃ and ptco₃ nanoparticle fuel cell catalysts. *ChemCatChem*, 3(11):1805–1813, 2011.
- [8] F. Hasché, M. Oezaslan, and P. Strasser. Activity, stability and degradation of multi walled carbon nanotube (mwcnt) supported pt fuel cell electrocatalysts. *Physical Chemistry Chemical Physics*, 12(46):15251–15258, 2010.

- [9] S. S. Zhang, X. Z. Yuan, J. N. C. Hin, H. J. Wang, K. A. Friedrich, and M. Schulze. A review of platinum-based catalyst layer degradation in proton exchange membrane fuel cells. *Journal of Power Sources*, 194(2):588–600, 2009.
- [10] Y. Shao-Horn, W. C. Sheng, S. Chen, P. J. Ferreira, E. F. Holby, and D. Morgan. Instability of supported platinum nanoparticles in low-temperature fuel cells. *Top. Catal.*, 46:285–305, 2007.
- [11] E. Antolini. Carbon supports for low-temperature fuel cell catalysts. *Applied Catalysis B-Environmental*, 88(1-2):1–24, 2009.
- [12] U.S. Department of Energy. Multi-year research, development and demonstration plan. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf, 2011.
- [13] F. T. Wagner and S. G. Yan. Catalyst and catalyst-support durability. In W Vielstich, Yokokawa H, and H A Gasteiger, editors, *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, volume 5, pages 250–263. John Wiley Sonsm, Ltd., 2009.
- [14] W. Vielstich, H. A. Gasteiger, and H. Yokokawa, editors. Handbook of Fuel Cells:Advances in Electrocatalysis, Materials, Diagnostics and Durability, volume Volumes 5 6. John Wiley Sons Ltd, Chichester, West Sussex, UK, 2009.
- [15] K. J. J. Mayrhofer, J. C. Meier, S. J. Ashton, G. K. H. Wiberg, F. Kraus, M. Hanzlik, and M. Arenz. Fuel cell catalyst degradation on the nanoscale. *Electrochemistry Communications*, 10(8):1144–1147, 2008.
- [16] P. J. Ferreira and Y. Shao-Horn. Formation mechanism of pt single-crystal nanoparticles in proton exchange membrane fuel cells. *Electrochem. Solid State Lett.*, 10: B60–B63, 2007.
- [17] E. F. Holby, W. C Sheng, Y. Shao-Horn, and D. Morgan. Pt nanoparticle stability in pem fuel cells: influence of particle size distribution and crossover hydrogen. *Energy Environ. Sci*, 2:865–871, 2009.
- [18] E. Ruckenstein and B. Pulvermacher. Growth kinetics and size distributions of supported metal crystallites. *Journal of Catalysis*, 29(2):224–245, 1973.
- [19] K. Kinoshita. Particle size effects for oxygen reduction on highly dispersed platinum in acid electrolytes. *Journal of the Electrochemical Society*, 137(3):845–848, 1990.

- [20] N. Markovic, H. Gasteiger, and P. N. Ross. Kinetics of oxygen reduction on pt(hkl) electrodes: Implications for the crystallite size effect with supported pt electrocatalysts. *Journal of the Electrochemical Society*, 144(5):1591–1597, 1997.
- [21] S. Mukerjee. Particle size and structural effects in platinum electrocatalysis. *Journal of Applied Electrochemistry*, 20(4):537–548, 1990.
- [22] Robert M. Darling and Jeremy P. Meyers. Kinetic model of platinum dissolution in pemfcs. *Journal of the Electrochemical Society*, 150(11):A1523–A1527, 2003.
- [23] K. J. J. Mayrhofer, B. B. Blizanac, M. Arenz, V. R. Stamenkovic, P. N. Ross, and N. M. Markovic. The impact of geometric and surface electronic properties of pt-catalysts on the particle size effect in electrocatalysis. *The Journal of Physical Chemistry B*, 109(30):14433–14440, 2005.
- [24] K. Kinoshita, D. R. Ferrier, and P. Stonehart. Effect of electrolyte environment and pt crystallite size on hydrogen adsorption .5. *Electrochimica Acta*, 23(1):45–54, 1978.
- [25] M. Watanabe, H. Sei, and P. Stonehart. A breakthrough to the crystallite size effect of platinum catalysts supported on carbon. *Journal of the Electrochemical Society*, 135(3):C157–C157, 1988.
- [26] N. M. Markovic and P. N. Ross. Surface science studies of model fuel cell electrocatalysts. Surface Science Reports, 45(4-6):121–229, 2002.
- [27] V. Komanicky, K. C. Chang, A. Menzel, N. M. Markovic, H. You, X. Wang, and D. Myers. Stability and dissolution of platinum surfaces in perchloric acid. *Journal* of the Electrochemical Society, 153(10):B446–B451, 2006.
- [28] P. W. Voorhees. The theory of ostwald ripening. *Journal of Statistical Physics*, 38 (1-2):231–252, 1985.
- [29] M. Volmer and A. Weber. Germ-formation in oversaturated figures. Zeitschrift Fur Physikalische Chemie–Stochiometrie Und Verwandtschaftslehre, 119(3/4):277–301, 1926.
- [30] V. K. Lamer. Nucleation in phase transitions. *Industrial and Engineering Chemistry*, 44(6):1270–1277, 1952.

- [31] J. A. S. Bett, K. Kinoshita, and P. Stonehart. Crystallite growth of platinum dispersed on graphitized carbon-black .2. effect of liquid environment. *Journal of Catalysis*, 41 (1):124–133, 1976.
- [32] K. L. More and K. S. Reeves. Microstructural characterization of pem fuel cell meas. http://www.hydrogen.energy.gov/pdfs/review05/fc39_more.pdf, 2005.
- [33] J. A. Gilbert, N. N. Kariuki, R. Subbaraman, A. J. Kropf, M. C. Smith, E. F. Holby, D. Morgan, and Myers D. J. In-situ anomalous small-angle x-ray scattering studies of platinum nanoparticle fuel cell electrocatalyst degradation. *Journal of American Chemical Society*, 2012. doi: 10.1021/ja3038257.
- [34] Matt C. Smith, James A. Gilbert, Jennifer R. Mawdsley, Sonke Seifert, and Deborah J. Myers. In situ small-angle x-ray scattering observation of pt catalyst particle growth during potential cycling. J. Am. Chem. Soc., 130(26):8112–8113, 2008.
- [35] H G Haubold and X H Wang. Asaxs studies of carbon supported electrcatalysts. Nucl. Instr. and Meth. in Phys. Res. B, 97:50–54, 1995.
- [36] H.-G. Haubold, X.H. Wang, G. Goerigk, and W. Schilling. In situ anomalous small angle x ray scattering investigation of carbon supported electrocatalysts. J. Appl. Cryst., 30:653–658, 1997.
- [37] M. Tada, S. Murata, T. Asakoka, K. Hiroshima, K. Okumura, H. Tanida, T. Uruga, H. Nakanishi, S. Matsumoto, Y. Inada, M. Nomura, and Y. Iwasawa. In situ timeresolved dynamic surface events on the pt/c cathode in a fuel cell under operando conditions. *Angewandte Chemie-International Edition*, 46(23):4310–4315, 2007.
- [38] F. Maillard, S. Schreier, M. Hanzlik, E. R. Savinova, S. Weinkauf, and U. Stimming. Influence of particle agglomeration on the catalytic activity of carbon-supported pt nanoparticles in co monolayer oxidation. *Physical Chemistry Chemical Physics*, 7 (2):385–393, 2005.
- [39] D. A. Stevens and J. R. Dahn. Thermal degradation of the support in carbon-supported platinum electrocatalysts for pem fuel cells. *Carbon*, 43(1):179–188, 2005.
- [40] Paul T. Yu, Wenbin Gu, Rohit Makharia, Fredrick T. Wagner, and Hubert A. Gasteiger. The impact of carbon stability on pem fuel cell start up and shutdown voltage degradation. ECS Transactions, 3(1):797, 2006.

- [41] J. J. Wang, G. P. Yin, Y. Y. Shao, S. Zhang, Z. B. Wang, and Y. Z. Gao. Effect of carbon black support corrosion on the durability of pt/c catalyst. *Journal of Power Sources*, 171(2):331–339, 2007.
- [42] K. Kinoshita. Carbon: Electrochemical and Physicochemical Properties. Wiley, New York, 1988.
- [43] D. A. Stevens, M. T. Hicks, G. M. Haugen, and J. R. Dahn. Ex situ and in situ stability studies of pemfc catalysts. *Journal of the Electrochemical Society*, 152(12): A2309–A2315, 2005.
- [44] X. Tuaev, J. P. Paraknowitsch, R. Illgen, A. Thomas, and P. Strasser. Nitrogendoped coatings on carbon nanotubes and their stabilizing effect on pt nanoparticles. *Physical Chemistry Chemical Physics*, 14(18):6437–6440, 2012.
- [45] S. G. Rinaldo, J. Stumper, and M. Eikerling. Physical theory of platinum nanoparticle dissolution in polymer electrolyte fuel cells. *Journal of Physical Chemistry C*, 114 (13):5773–5785, 2010.
- [46] G. A. Gruver. Corrosion of carbon-black in phosphoric-acid. Journal of the Electrochemical Society, 125(10):1719–1720, 1978.
- [47] G. Madras and B. J. McCoy. Ostwald ripening with size-dependent rates: Similarity and power-law solutions. *The Journal of Chemical Physics*, 117(17):8042–8049, 2002.
- [48] S. Rudi, X. Tuaev, and P. Strasser. Electrocatalytic oxygen reduction on dealloyed $pt_{1-x}ni_x$ alloy nanoparticle electrocatalysts. *Electrocatalysis*, 2012.
- [49] Rudi S. Synthese und strukturelle untersuchung von platin-nickel bimetallischen nanopartikelkatalysatoren f
 ür polymer elektrolyt membran brennstoffzellen. Master's thesis, Technichal University Berlin, 2011.
- [50] A. J. Lecloux. Texture of catalysis. In *Catalysis Science and Technology*, volume 2, pages 171–230. Akademie-Verlag Berlin, 1983.
- [51] S. Brunauer, P. H. Emmett, and E. Teller. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2):309–319, 1938.
- [52] W. L. Bragg. The diffraction of short electromagnetic waves by a crystal. Proceedings of the Cambridge Philosophical Society, 17:43–57, 1913.

- [53] P. Scherrer. Bestimmung der grösse und der inneren struktur von kolloidteilchen mittels röntgenstrahlen. Nachr. Ges. Wiss. Göttingen, 2(26):98–100, 1918.
- [54] C. H. Hamann, A. Hamnett, and W. Vielstich. Methods for the study of the electrode/electrolyte interface. In *Electrochemistry*, volume 2, page 262. Wiley-VCH Verlag GmbH Co. KGaA, 2007.
- [55] A. J. Bard and L. R. Faulkner. Electrochemical Methods Fundamentals and Applications, volume 2. John Wiley Sons, Inc., 2001.
- [56] U. A. Paulus, A. Wokaun, G. G. Scherer, T. J. Schmidt, V. Stamenkovic, V. Radmilovic, N. M. Markovic, and P. N. Ross. Oxygen reduction on carbon-supported pt-ni and pt-co alloy catalysts. *Journal of Physical Chemistry B*, 106(16):4181–4191, 2002.
- [57] H. A. Gasteiger, N. M. Markovic, and P. N. Ross. H-2 and co electrooxidation on well-characterized pt, ru, and pt-ru .1. rotating-disk electrode studies of the pure gases including temperature effects. *Journal of Physical Chemistry*, 99(20):8290– 8301, 1995.
- [58] P. Debye. Zerstreuung von roentgenstrahlen. Annalen der Physik, 351(6):809–823, 1915.
- [59] G. Porod. Die rontgenkleinwinkelstreuung von dichtgepackten kolloiden systemen .1. *Kolloid-Zeitschrift and Zeitschrift Fur Polymere*, 124(2):83–114, 1951.
- [60] Lord J. W. S Rayleigh. Proc. Roy. Soc. (London), 25:A–84, 1911.
- [61] H.B. Stuhrmann. Adv. Polym. Sci., 67:123, 1985.
- [62] H. B. Stuhrmann, G. Goerigk, and B. Munk. Anomalous x-ray scattering. In S Ebashi, M Koch, and E Rubinstein, editors, *Handbook of Synchrotron Radiation*, volume 4, page 557. Elsevier, Amsterdam, 1991.
- [63] http://www.helmholtz-berlin.de/angebote/arbeiten-lernen/info/beschleunigerphysikfuer-anfaenger/der-speicherring_de.html.
- [64] S. I. Lim, I. Ojea-Jimenez, M. Varon, E. Casals, J. Arbiol, and V. Puntes. Synthesis of platinum cubes, polypods, cuboctahedrons, and raspberries assisted by cobalt nanocrystals. *Nano Letters*, 10(3):964–973, 2010.

- [65] Y. J. Kang, X. C. Ye, and C. B. Murray. Size- and shape-selective synthesis of metal nanocrystals and nanowires using co as a reducing agent. *Angewandte Chemie-International Edition*, 49(35):6156–6159, 2010.
- [66] ISO 15472:2001. Iso 15472:2001 surface chemical analysis x-ray photoelectron spectrometers calibration of energy scales, 2001.
- [67] B. G. Briggs. volume 26. Wiley, Chichester, 1992.
- [68] R. Hesse and R. Denecke. Improved tougaard background calculation by introduction of fittable parameters for the inelastic electron scattering cross-section in the peak fit of photoelectron spectra with unifit 2011. Surface and Interface Analysis, 2011.
- [69] R. Hesse, P. Streubel, and R. Szargan. Produkt or sum: comparative tests of voigt, and produkt or sum of gaussian and lorentzian functions in the fitting of synthetic voigt-based x-ray photoelectron spectra. *Surface and Interface Analysis*, 39:381 – 391, 2007.
- [70] V. Petkov. Nanostructure by high-energy x-ray diffraction. *Materials Today*, 11(11): 28–38, 2008.
- [71] V. Petkov, T. Ohta, Y. Hou, and Y. Ren. Atomic-scale structure of nanocrystals by high-energy x-ray diffraction and atomic pair distribution function analysis: Study of fexpd100-x (x=0, 26, 28, 48) nanoparticles. *Journal of Physical Chemistry C*, 111 (2):714–720, 2007.
- [72] T. Proffen, V. Petkov, S. J. L. Billinge, and T. Vogt. Chemical short range order obtained from the atomic pair distribution function. *Zeitschrift Für Kristallographie*, 217(2):47–50, 2002.
- [73] C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Bozin, J. Bloch, T. Proffen, and S. J. L. Billinge. Pdffit2 and pdfgui: computer programs for studying nanostructure in crystals. *Journal of Physics-Condensed Matter*, 19(33), 2007.
- [74] M. Grabe. *Measurement Uncertainties in Science and Technology*. Springer, 2005.
- [75] S. Haas. Nanochemische Zusammensetzungsanalyse mittels anomaler Röntgenkleinwinkelstreuung (ASAXS): Erbium und Ytterbium dotierte Oxyfluorid-Glaskeramiken. PhD thesis, Helmholtz Zentrum Berlin, 2010.

- [76] J. Kohlbrecher and Bressler I. Software package sasfit for fitting small-angle scattering curves. http://kur.web.psi.ch/sans1/SANSSoft/sasfit.html, 2010.
- [77] Mittelbach.P and G. Porod. Zur rontgenkleinwinkelstreuung kolloider systeme die mittleren durchschusslangen und die koharenzlange eines kolloiden systems – kennzahlen zur ermittlung von teilchenform und polydispersitatsgrad. *Kolloid-Zeitschrift* and Zeitschrift Fur Polymere, 202(1):40–49, 1965.
- [78] G. Damaschun, J. J. Muller, H. V. Purschel, and G. Sommer. Computation of shape of colloid particles from low-angle x-ray scattering. *Monatshefte Fur Chemie*, 100(5): 1701–1714, 1969.
- [79] G. Walter, R. Kranold, T. Gerber, J. Baldrian, and M. Steinhart. Particle size distribution from small-angle x-ray scattering data. *Journal of Applied Crystallography*, 18(4):205–213, 1985.
- [80] Z. M. Peng and H. Yang. Designer platinum nanoparticles: Control of shape, composition in alloy, nanostructure and electrocatalytic property. *Nano Today*, 4(2): 143–164, 2009.
- [81] Chao Wang, Hideo Daimon, Youngmin Lee, Jaemin Kim, and Shouheng Sun. Synthesis of monodisperse pt nanocubes and their enhanced catalysis for oxygen reduction. *Journal of the American Chemical Society*, 129(22):6974–6975, 2007.
- [82] Chao Wang, Hideo Daimon, Taigo Onodera, Tetsunori Koda, and Shouheng Sun. A general approach to the size- and shape-controlled synthesis of platinum nanoparticles and their catalytic reduction of oxygen. *Angewandte Chemie International Edition*, 47(19):3588–3591, 2008.
- [83] M. K. Carpenter, T. E. Moylan, R. S. Kukreja, M. H. Atwan, and M. M. Tessema. Solvothermal synthesis of platinum alloy nanoparticles for oxygen reduction electrocatalysis. *Journal of the American Chemical Society*, 134(20):8535–8542, 2012.
- [84] M. Oezaslan, M. Heggen, and P. Strasser. Size-dependent morphology of dealloyed bimetallic catalysts: Linking the nano to the macro scale. *Journal of the American Chemical Society*, 134(1):514–524, 2012.
- [85] H. Kikuchi, W. Ouchida, M. Nakamura, C. Goto, M. Yamada, and N. Hoshi. Atomic force microscopy of cubic pt nanoparticles in electrochemical environments. *Electrochemistry Communications*, 12(4):544–547, 2010.

- [86] Y. Onochi, M. Nakamura, and N. Hoshi. Atomic force microscopy of the dissolution of cubic and tetrahedral pt nanoparticles in electrochemical environments. *Journal of Physical Chemistry C*, 116(28):15134–15140, 2012.
- [87] C. He, S. Desai, G. Brown, and S. Bollepalli. Pem fuel cell catalysts: Cost, performance, and durability. *The Electrochemical Society Interface*, pages 41–44, 2005.
- [88] A. B. Ofstad, M. S. Thomassen, J. L. G. de la Fuente, F. Seland, S. Moller-Holst, and S. Sunde. Assessment of platinum dissolution from a pt/c fuel cell catalyst: An electrochemical quartz crystal microbalance study. *Journal of the Electrochemical Society*, 157(5):B621–B627, 2010.
- [89] H. P. Yuan, H. Q. Song, X. P. Qiu, W. T. Zhu, and L. Q. Chen. Electrochemical characters and structure changes of electrochemically treated pt nanoparticles. *Electrochemistry Communications*, 12(1):14–17, 2010.
- [90] K. Ahrenstorf, O. Albrecht, H. Heller, A. Kornowski, D. Gorlitz, and H. Weller. Colloidal synthesis of ni_xpt_{1-x} nanoparticles with tuneable composition and size. *Small*, 3(2):271–274, 2007.
- [91] K. Ahrenstorf, H. Heller, A. Kornowski, J. A. C. Broekaert, and H. Weller. Nucleation and growth mechanism of ni_xpt_{1-x} nanoparticles. *Advanced Functional Materials*, 18(23):3850–3856, 2008.
- [92] M. K. Debe, A. J. Steinbach, G. D. Vernstrom, S. M. Hendricks, M. J. Kurkowski, R. T. Atanasoski, P. Kadera, D. A. Stevens, R. J. Sanderson, E. Marvel, and J. R. Dahn. Extraordinary oxygen reduction activity of pt₃ni₇. *Journal of the Electrochemical Society*, 158(8):B910–B918, 2011.
- [93] C. Du, M. Chen, W. Wang, and G. Yin. Nanoporous pdni alloy nanowires as highly active catalysts for the electro-oxidation of formic acid. ACS Applied Materials Interfaces, 3(2):105–109, 2011.
- [94] S. Koh and P. Strasser. Electrocatalysis on bimetallic surfaces: Modifying catalytic reactivity for oxygen reduction by voltammetric surface de-alloying. J. Am. Chem. Soc., 129:12624–12625, 2007.
- [95] M. Oezaslan and P. Strasser. Activity of dealloyed ptco₃ and ptcu₃ nanoparticle electrocatalyst for oxygen reduction reaction in polymer electrolyte membrane fuel cell. *Journal of Power Sources*, 196(12):5240–5249, 2011.

- [96] V. R. Stamenkovic, B. Fowler, B. S. Mun, G. F. Wang, P. N. Ross, C. A. Lucas, and N. M. Markovic. Improved oxygen reduction activity on pt₃ni(111) via increased surface site availability. *Science*, 315(5811):493–497, 2007.
- [97] H. Yano, M. Kataoka, H. Yamashita, H. Uchida, and M. Watanabe. Oxygen reduction activity of carbon-supported pt-m (m = v, ni, cr, co, and fe) alloys prepared by nanocapsule method. *Langmuir*, 23(11):6438–6445, 2007.
- [98] C. H. Cui, H. H. Li, and S. H. Yu. Large scale restructuring of porous pt-ni nanoparticle tubes for methanol oxidation: A highly reactive, stable, and restorable fuel cell catalyst. *Chemical Science*, 2(8):1611–1614, 2011.
- [99] Lin Gan, Marc Heggen, Stefan Rudi, and Peter Strasser. Core-shell compositional fine structures of dealloyed ptxni1-x nanoparticles and their impact on oxygen reduction catalysis. *Nano Letters*, 2012. doi: 10.1021/nl302995z.
- [100] F. Hasché, M. Oezaslan, and P. Strasser. Activity, structure and degradation of dealloyed ptni₃ nanoparticle electrocatalyst for the oxygen reduction reaction in pemfc. *Journal of the Electrochemical Society*, 159(1):B25–B34, 2012.
- [101] X. Tuaev and P. Strasser. Small angle x-ray scattering (saxs) techniques for polymer electrolyte membrane fuel cell characterisation. In C Roth and C. Hartnig, editors, *Polymer electrolyte membrane and direct methanol fuel cell technology*, volume II: In situ characterization techniques for low temperature fuel cells. Woodhead Publishing Series in Energy, London, 2011.
- [102] J. Snyder, I. McCue, K. Livi, and J. Erlebacher. Structure/processing/properties relationships in nanoporous nanoparticles as applied to catalysis of the cathodic oxygen reduction reaction. *Journal of the American Chemical Society*, 134(20):8633–8645, 2012.
- [103] Chao Wang, Miaofang Chi, Guofeng Wang, Dennis van der Vliet, Dongguo Li, Karren More, Hsien-Hau Wang, John A. Schlueter, Nenad M. Markovic, and Vojislav R. Stamenkovic. Correlation between surface chemistry and electrocatalytic properties of monodisperse ptxni1-x nanoparticles. *Advanced Functional Materials*, 21(1):147– 152, 2011.
- [104] P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. F. Yu, Z. C. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney, and A. Nilsson. Lattice-strain control of the

activity in dealloyed core-shell fuel cell catalysts. *Nature Chemistry*, 2(6):454–460, 2010.

- [105] Chao Wang, Nenad M. Markovic, and Vojislav R. Stamenkovic. Advanced platinum alloy electrocatalysts for the oxygen reduction reaction. ACS Catalysis, 2(5):891–898, 2012.
- [106] C. F. Yu, S. Koh, J. E. Leisch, M. F. Toney, and P. Strasser. Size and composition distribution dynamics of alloy nanoparticle electrocatalysts probed by anomalous small angle x-ray scattering (asaxs). *Faraday Discussions*, 140:283–296, 2008.
- [107] M. Mavrikakis, B. Hammer, and J. K. Norskov. Effect of strain on the reactivity of metal surfaces. *Physical Review Letters*, 81(13):2819–2822, 1998.
- [108] V. Stamenkovic, Bongjin S. Mun, K. J. Mayrhofer, P. N. Ross, N. M. Markovic, J. Rossmeisl, J. Greeley, and J. K. Nørskov. Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. *Angewandte Chemie International Edition*, 45(18):2897–2901, 2006.
- [109] L. J. Bregoli. Influence of platinum crystallite size on electrochemical reduction of oxygen in phosphoric-acid. *Electrochimica Acta*, 23(6):489–492, 1978.
- [110] M. L. Sattler and P. N. Ross. The surface-structure of pt crystallites supported on carbon-black. Ultramicroscopy, 20(1-2):21–28, 1986.
- [111] M. Watanabe, H. Sei, and P. Stonehart. The influence of platinum crystallite size on the electroreduction of oxygen. *Journal of Electroanalytical Chemistry*, 261(2B): 375–387, 1989.
- [112] M. Watanabe, S. Saegusa, and P. Stonehart. High platinum electrocatalyst utilizations for direct methanol oxidation. *Journal of Electroanalytical Chemistry*, 271(1-2): 213–220, 1989.
- [113] F. Hasché, T. P. Fellinger, M. Oezaslan, J. P. Paraknowitsch, M. Antonietti, and P. Strasser. Mesoporous nitrogen doped carbon supported platinum pem fuel cell electrocatalyst made from ionic liquids. *ChemCatChem*, 4(4):479–483, 2012.
- [114] B. Z. Fang, J. H. Kim, M. Kim, M. Kim, and J. S. Yu. Hierarchical nanostructured hollow spherical carbon with mesoporous shell as a unique cathode catalyst support in proton exchange membrane fuel cell. *Physical Chemistry Chemical Physics*, 11 (9):1380–1387, 2009.

- [115] M. Uchida, Y. Aoyama, N. Eda, and A. Ohta. Investigation of the microstructure in the catalyst layer and effects of both perfluorosulfonate ionomer and ptfe-loaded carbon on the catalyst layer of polymer electrolyte fuel cells. *Journal of the Electrochemical Society*, 142(12):4143–4149, 1995.
- [116] M. Uchida, Y. Fukuoka, Y. Sugawara, N. Eda, and A. Ohta. Effects of microstructure of carbon support in the catalyst layer on the performance of polymer-electrolyte fuel cells. *Journal of the Electrochemical Society*, 143(7):2245–2252, 1996.
- [117] M. S. Wilson, F. H. Garzon, K. E. Sickafus, and S. Gottesfeld. Surface-area loss of supported platinum in polymer electrolyte fuel-cells. *Journal of the Electrochemical Society*, 140(10):2872–2877, 1993.
- [118] T. Tada and T. Kikinzoku. In W. Vielstich, H. Gasteiger, and A. Lamm, editors, Handbook of Fuel Cells - Fundamentals, Technology and Applications, volume 3, page 481. John Wiley and Sons, 2003.
- [119] P. Serp, M. Corrias, and P. Kalck. Carbon nanotubes and nanofibers in catalysis. *Applied Catalysis a-General*, 253(2):337–358, 2003.
- [120] J. Xie, L. Wood, K. L. More, P. Atanassov, and R. L. Borup. Microstructural changes of membrane electrode assemblies during pefc durability testing at high humidity conditions. *Journal of the Electrochemical Society*, 152(5):A1011–A1020, 2005.
- [121] T. Holme, Y. Zhou, R. Pasquarelli, and R. O'Hayre. First principles study of doped carbon supports for enhanced platinum catalysts. *Physical Chemistry Chemical Physics*, 12(32):9461–9468, 2010.
- [122] Y. Chen, H. Wang, J.and Liu, R. Li, X. Sun, S. Ye, and S. Knights. Enhanced stability of pt electrocatalysts by nitrogen doping in cnts for pem fuel cells. *Electrochem. Commun.*, 11(10):2071–2076, 2009.
- [123] Y.-H. Li, T.-H. Hung, and C.-W. Chen. A first-principles study of nitrogen- and boronassisted platinum adsorption on carbon nanotubes. *Carbon*, 47(3):850–855, 2009.
- [124] C. E. Chan-Thaw, A. Villa, P. Katekomol, D. Su, A. Thomas, and L. Prati. Covalent triazine framework as catalytic support for liquid phase reaction. *Nano Lett.*, 10(2): 537–541, 2010.

- [125] C. E. Chan-Thaw, A. Villa, L. Prati, and A. Thomas. Triazine-based polymers as nanostructured supports for the liquid-phase oxidation of alcohols. *Chem.-Eur. J.*, 17 (3):1052–1057, 2011.
- [126] Y. Zhou, K. Neyerlin, T. S. Olson, S. Pylypenko, J. Bult, H. N. Dinh, T. Gennett, Z. Shao, and R. O. Hayre. Enhancement of pt and pt-alloy fuel cell catalyst activity and durability via nitrogen-modified carbon supports. *Energy Environ. Sci.*, 3(10): 1437–1446, 2010.
- [127] M. Antonietti, D. B. Kuang, B. Smarsly, and Z. Yong. Ionic liquids for the convenient synthesis of functional nanoparticles and other inorganic nanostructures. *Angewandte Chemie International Edition*, 43(38):4988–4992, 2004.
- [128] S. Lee. Functionalized imidazolium salts for task-specific ionic liquids and their applications. *Chemical Communications*, (10):1049–1063, 2006.
- [129] Z. Ma, J. H. Yu, and S. Dai. Preparation of inorganic materials using ionic liquids. *Advanced Materials*, 22(2):261–285, 2010.
- [130] S. Zhu, Y. Wu, Z.and Wang C. Chen, Q.and Yu, S. Jin, Y. Ding, and G. Wu. Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chemistry*, 8(4):325–327, 2006.
- [131] D. Carriazo, M. C. Gutierrez, M. L. Ferrer, and F. del Monte. Resorcinol-based deep eutectic solvents as both carbonaceous precursors and templating agents in the synthesis of hierarchical porous carbon monoliths. *Chemistry of Materials*, 22 (22):6146–6152, 2010.
- [132] M. C. Gutierrez, D. Carriazo, C. O. Ania, J. B. Parra, M. L. Ferrer, and F. del Monte. Deep eutectic solvents as both precursors and structure directing agents in the synthesis of nitrogen doped hierarchical carbons highly suitable for co₂ capture. *Energy Environmental Science*, 4(9):3535–3544, 2011.
- [133] J. S. Lee, X. Q. Wang, H. M. Luo, and S. Dai. Fluidic carbon precursors for formation of functional carbon under ambient pressure based on ionic liquids. *Advanced Materials*, 22(9):1004–+, 2010.
- [134] J. P. Paraknowitsch, A. Thomas, and M. Antonietti. A detailed view on the polycondensation of ionic liquid monomers towards nitrogen doped carbon materials. *Journal* of Materials Chemistry, 20(32):6746–6758, 2010.
- [135] J. P. Paraknowitsch, J. Zhang, D. S. Su, A. Thomas, and M. Antonietti. Ionic liquids as precursors for nitrogen-doped graphitic carbon. *Advanced Materials*, 22(1):87–+, 2010.
- [136] J. P. Paraknowitsch, Y. Zhang, and A. Thomas. Synthesis of mesoporous composite materials of nitrogen-doped carbon and silica using a reactive surfactant approach. *Journal of Materials Chemistry*, 21:15537, 2011.
- [137] J. S. Lee, X. Q. Wang, H. M. Luo, G. A. Baker, and S. Dai. Facile ionothermal synthesis of microporous and mesoporous carbons from task specific ionic liquids. *Journal of the American Chemical Society*, 131(13):4596-+, 2009.
- [138] L. Zhao, Y. S. Hu, H. Li, Z. X. Wang, and L. Q. Chen. Porous li(4)ti(5)o(12) coated with n-doped carbon from ionic liquids for li-ion batteries. *Advanced Materials*, 23 (11):1385–1388, 2011.
- [139] T. P. Fellinger, F. Hasché, P. Strasser, and M. Antonietti. Mesoporous nitrogendoped carbon for the electrocatalytic synthesis of hydrogen peroxide. *Journal of the American Chemical Society*, 134(9):4072–4075, 2012.
- [140] T. Fukushima and T. Aida. Ionic liquids for soft functional materials with carbon nanotubes. *Chemistry A European Journal*, 13(18):5048–5058, 2007.
- [141] K. Yaccato, R. Carhart, A. Hagemeyer, A. Lesik, P. Strasser, A. F. Volpe, H. Turner, H. Weinberg, R. K. Grasselli, and C. Brooks. Competitive co and co2 methanation over supported noble metal catalysts in high throughput scanning mass spectrometer. *Applied Catalysis a-General*, 296(1):30–48, 2005.
- [142] H. Schnablegger and Y. Singh. A Practical Guide for SAXS. Graz, 2006.
- [143] F. Jaouen, J. Herranz, M. Lefevre, J. P. Dodelet, U. I. Kramm, I. Herrmann, P. Bogdanoff, J. Maruyama, T. Nagaoka, A. Garsuch, J. R. Dahn, T. Olson, S. Pylypenko, P. Atanassov, and E. A. Ustinov. Cross-laboratory experimental study of non-noblemetal electrocatalysts for the oxygen reduction reaction. *Acs Applied Materials Interfaces*, 1(8):1623–1639, 2009.
- [144] D. Villers, X. Jacques-Bedard, and J. P. Dodelet. Fe-based catalysts for oxygen reduction in pem fuel cells – pretreatment of the carbon support. *Journal of the Electrochemical Society*, 151(9):A1507–A1515, 2004.

- [145] G. Lalande, R. Cote, D. Guay, J. P. Dodelet, L. T. Weng, and P. Bertrand. Is nitrogen important in the formulation of fe-based catalysts for oxygen reduction in solid polymer fuel cells? *Electrochimica Acta*, 42(9):1379–1388, 1997.
- [146] G. Wu, Z. Chen, K. Artyushkova, F. H. Garzon, and P. Zelenay. Polyaniline-derived non-precious catalyst for the polymer electrolyte fuel cell cathode. *ECS Transactions*, 16(2):159–170, 2008.
- [147] R. Bashyam and P. Zelenay. A class of non-precious metal composite catalysts for fuel cells. *Nature*, 443(7107):63–66, 2006.

A. Appendix

	Desired molality	Pt-standard	Water	Resultig molality
Units	$\mathrm{mg}_{\mathrm{Pt}}/\mathrm{kg}_{\mathrm{H}_{2}\mathrm{O}}$	mg	g	$\rm mg_{Pt}/kg_{\rm H_2O}$
Blank	0	0	10	0
Standard 1	2.0	20	9.980	1.936
Standard 2	4.5	45	9.955	4.376
Standard 3	7.0	70	9.930	6.810
Standard 4	10.0	100	9.900	9.759

Table A.1.: Summary on used Pt-solutions for a standard calibration of the ICP-OES.

Table A.2.: Example of weight-percentage determination of an ICP-OES sample, which was diluted to two different molalities before IPC-OES measurements.

Variable	Unit	Sample 1	Sample 2	
$\overline{\mathrm{Pt}_{\mathrm{ICP}}}$	${\rm mg}_{\rm Pt}/{\rm kg}_{{\rm H}_2{\rm O}}$	8.1	14.9	
m _{powder}	mg	6.0	6.0	
m _{ini}	mg	13986.0	13986.0	
m _{solvent}	mg	13980.0	13980.0 429.2	
M _{digestion}	mg/kg	429.2		
$m_{digestion}$	mg	1350	2500	
$\mathrm{am}_{\mathrm{Water}}$	mg	15000	15000	
ali _{digestion}	mg/kg	38.6	71.5	
$wt\%_{Pt}$	%	20.97	20.83	



Figure A.1.: Comparison of catalyst degradation in N_2 (squares) and air (triangles) saturated electrolyte by absolute (black) and normalized ECSA (red) as a function of potential cycles for a) benchmark catalyst 21% Pt/VC and b) synthesized catalyst 17% Pt/MWCNT.



Figure A.2.: Characterization via XRD of pristine spherical and cuboid Pt nanoparticles supported on VC, respectively.



Figure A.3.: Cyclic and Linear Sweep voltammograms for a) and c) PtNi₆ and b) and d) PtNi₃, respectively.



Figure A.4.: X-ray fluorescence analytics of a) catalyst with the initial elemental composition of $PtNi_6$ and b) catalyst with the initial elemental composition $PtNi_3$.



Figure A.5.: Experimental SAXS curve (black dots) with a corresponding fit (red line) for a pristine Pt/meso-C catalyst. Inset shows the resulting LogNormal particle size probability density function.

Scripts

To apply the script it is necessary to treat the files in the following way: The original .mpr-files must be exported as ASCII-files in the EC_Lab Software (Experiment \rightarrow Export as text). The resulting .mpt-files must be imported *via* drag-and-drop into the origin-software, using an import-filter, which has to be written in the Origin software (detailed description is given in the appendix A). The procedure is listed in the following graphs below. After finishing creating the filter the option for automatic execution has to be disabled. To achieve that choose the "'Tools"' toolbar and select "'Import Filter Manager'' to disable the option (last 2 graphs in the procedure below). To start the LSV script it must be accessed *via* the command window in Origin.

Import Assist	ent - Quelle		
Oatentyp O ASCII	O Binär	◯ Anwender-definiert	
Datenquelle			
💿 Datei	D:\Promotion\B	Experimentell_ab53\bioanalytical\120724_MMS2_x263_RDE363\x263_RD 💌 🔜	
◯Zwischen	ablage		
Importfilter Passende	Filter für Datenty	yp und Dateinamen anzeigen	
Importfilter für	aktuellen Daten	typKeine> ▼	
Beschreibung	,		
Zielfenster			-
Workshee	et 🔿 M	fatrix 🔷 Keine (Anwender-definierter Filter muß Fenster erzeugen)	
Vorlage	<standard< th=""><th></th><th></th></standard<>		
Vorlage für ei	n neues Blatt od	ler eine neue Mappe	
Import Modus	Neue Arbeit	tsmappen öffnen	
Abbrechen		<< Zurück Weiter >> Fertigstel	len

port Assistent - Da	iteinamenoptionen			
Umbenennen				
Auto				
	ateiname			
Arbeitsblatt mit V	ariable			
	t Dateiname			
Arbeitsmappe mi	t Variable			
Langname nur fü	ir die Mappe umbenennen			
Den Dateiptad e	inbinden, wenn die Arbeits	mappe umbenannt wird		
Anhängen				
Dateiname zu A	rheitsmannenkommentare			
Dateiname zu Si				
	Jakenkunnnenkare			
Einbinden des P	fads, wenn der Dateiname	angehängt wird		
		24.5	Zunitale Mitaitar SS	Fortigatellon
Abbrechen			weiter >>	rengstellen
Abbrechen			weiter >>	rengstellen
oort Assistent - He	eaderzeilen		weiter >>	rengstellen
port Assistent - He	eaderzeilen		Curuck Weiter >>	rengstellerr
port Assistent - He	eaderzeilen zeilen (ohne Subheaderzei	ilen) 🚺 💌 🗢	Zeilennummern von u	unten beginnen
port Assistent - He nzahl der Hauptheader nzahl der Subheaderze	zaderzeilen Izeilen (ohne Subheaderzei vilen 10 💽 😥	ilen) 🚺 💽 ⊄	Zeilennummern von u gung der Subheaderzeilen	inten beginnen
Abbrechen port Assistent - He Inzahl der Hauptheader Inzahl der Subheaderze Spaltenheaderzuordnu	eaderzeilen Izeilen (ohne Subheaderzei Iilen (O) 💽 🜮 ng von Subheaderzeilen	ilen) 1 💽 🖍	gung der Subheaderzeilen	Inten beginnen
Dort Assistent - He nzahl der Hauptheader nzahl der Subheaderze Spaltenheaderzuordnu Kurznamen	eaderzeilen Izeilen (ohne Subheaderzei Vilen 10 💽 🞸 Ing von Subheaderzeilen Keine V	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 v bis 17	Inten beginnen
Dort Assistent - He nzahl der Hauptheader nzahl der Subheaderze Spaltenheaderzuordnu Kurznamen	eaderzeilen izeilen (ohne Subheaderzei silen 0 von Subheaderzeilen Keine> von Subheaderzeilen	ilen) 1 💽 🖍 🕫 Automatische Festler Kommentare Systemparameter	Zeilennummern von u gung der Subheaderzeilen 3 bis (Keine> bis	Inten beginnen
Abbrechen port Assistent - He nzahl der Hauptheader nzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten	eaderzeilen Izeilen (ohne Subheaderzei eilen 0 voi Subheaderzeilen Keine> voi Subheaderzeilen Keine> voi Subheaderzeilen	ilen) [] 💽 🖍 Automatische Festler Kommentare Systemparameter 3enutzerdefinierte Paramet	gung der Subheaderzeilen 3 v bis 17 <keine> bis 0 er <keine> v bis 0</keine></keine>	
Abbrechen port Assistent - He nzahl der Hauptheader nzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin	eaderzeilen rzeilen (ohne Subheaderzei silen 0 von Subheaderzeilen Keine> von Subheaderzeilen Keine> von Subheaderzeilen Keine> von Subheaderzeilen Egen in jeder Zeile	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 4 Keine> bis 0 bis 0 er Keine> bis 0	Inten beginnen
Abbrechen port Assistent - He nzahl der Hauptheader nzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin	eaderzeilen Izeilen (ohne Subheaderzei eilen 0 V V V I V Subheaderzeilen Keine V V V 1 V V V V V V 2 V V V V V V V V V gen in jeder Zeile	ilen) I V Construction I Constructio I Construction I Construction I Construction I Constructio	gung der Subheaderzeilen (Keine> bis 0 (Keine> bis 0 50	Inten beginnen
Dort Assistent - He nzahl der Hauptheader nzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin	eaderzeilen Izeilen (ohne Subheaderzei Ing von Subheaderzeilen Keine> V III 2 V IIII 2 V IIII 2 V IIII 2 V IIII 2 V IIII 2 V IIII 2 V IIIII 2 V IIIII 2 V IIIIII 2 V IIIIII 2 V IIIIIII 2 V IIIIIIII 2 V IIIIIIIIII	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis (Keine> bis bis 0 er Keine> 50	Inten beginnen
Abbrechen port Assistent - He Inzahl der Hauptheader Inzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin Ieichensatzvorschau	eaderzeilen Izeilen (ohne Subheaderzei Isilen 10 V V IN Subheaderzeilen Keines V III 2 V III V gen in jeder Zeile	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis 7 keine> bis 0 er Keine> 50	Inten beginnen
Abbrechen port Assistent - He unzahl der Hauptheader unzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin eichensatzvorschau	eaderzeilen rzeilen (ohne Subheaderzei ng von Subheaderzeilen Keine> V III 2 V III gen in jeder Zeile System Langname, U=Einheiten, P	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis 7 keine> bis 0 er Keine> 50	Inten beginnen
Abbrechen port Assistent - He unzahl der Hauptheader unzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin eichensatzvorschau räfix: S=Kurzname, L= 181	eaderzeilen rzeilen (ohne Subheaderzei ng von Subheaderzeilen Keine> V V 1 V V gen in jeder Zeile System Langname, U=Einheiten, P EC-Lab ASCII	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis 7 keine> bis 0 er Keine> 50	Inten beginnen
Abbrechen port Assistent - He Inzahl der Hauptheader Inzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin Zeichensatzvorschau Yäfix: S=Kurzname, L= 101 102	eaderzeilen rzeilen (ohne Subheaderzei ilen 0 V V ng von Subheaderzeilen Keine> V V 1 V V gen in jeder Zeile System Langname, U=Einheiten, P EC-Lab ASCII Nb header 1in	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis 4 keine> bis 0 50	Inten beginnen
Abbrechen port Assistent - Ho unzahl der Hauptheader unzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin Zeichensatzvorschau Yäfix: S=Kurzname, L= 101 102 103	eaderzeilen rzeilen (ohne Subheaderzei silen 0 • • • • ng von Subheaderzeilen Keine> • • • 1 • • • • gen in jeder Zeile 0 System Langname, U=Einheiten, P EC-Lab ASCII Nb header 1in Cuclic Voltam	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis 4 Keine> bis 0 50	Inten beginnen
Abbrechen port Assistent - He Inzahl der Hauptheader Inzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin Zeichensatzvorschau Täfix: S=Kurzname, L= 101 102 103 104 105	eaderzeilen rzeilen (ohne Subheaderzei eilen 0 V V rg von Subheaderzeilen Keines V V gen in jeder Zeile 0 System Langname, U=Einheiten, P EC-Lab ASCII Nb header 1in Cyclic Voltam	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis (Keine> bis 0 bis 50	Inten beginnen
Abbrechen port Assistent - He inzahl der Hauptheader inzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin Zeichensatzvorschau Yräfix: S=Kurzname, L= 101 102 103 104 105 106	eaderzeilen rzeilen (ohne Subheaderzei eilen 0 V V rg von Subheaderzeilen Keine> V V gen in jeder Zeile 0 System V Langname, U=Einheiten, P EC-Lab ASCII Nb header 1in Cyclic Voltam Run on channe	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis 4 keine> bis 0 50	Inten beginnen
Abbrechen port Assistent - He mzahl der Hauptheader mzahl der Subheaderze Spaltenheaderzuordnu Kurznamen Langnamen Einheiten Zeichen zum Übersprin Zeichensatzvorschau Präfix: S=Kurzname, L= 101 102 103 104 105 106 197	eaderzeilen rzeilen (ohne Subheaderze eilen 0 V V ng von Subheaderzeilen Keine> V V 1 V V 2 V V gen in jeder Zeile 0 System Langname, U=Einheiten, P EC-Lab ASCII Nb header 1in Cyclic Voltam Run on channe Grouped chann	ilen)	Zeilennummern von u gung der Subheaderzeilen 3 bis 3 bis 4 keine> bis 0 50	Inten beginnen

Anzahl der Hauptheader	aderzeilen zeilen (ohne Subhead		□ 7 -1				
Anzahl der Subheaderze	ilen 0	Automatische Festleru	ing der Subb	eaderze	eilen	en begir	inen
Spaltenheaderzuordnur	ng von Subheaderzeil	en	ing der e der	0000120			
Kurznamen	<keine> 🗸</keine>	Kommentare	<keine></keine>	🖌 bis	17	~	\$
Langnamen	1	Systemparameter	<keine></keine>	🖌 bis	0	~	\$
Finhaitan		Benutzerdefinierte Parameter	<keine></keine>	✓ bis	0	~	\$
	Langname, U=Einheite	en, P=Parameter, C=Kommentar, I	MH=Hauptko	opfzeile,	SH=Ne	benkopf	zeile
^p räfix: S=Kurzname, L=I							
⁹ räfix: S=Kurzname, L=1 048 048MH 049 049MH 050 050MH	Ef (V) vs.	-0.211 Ref					^
Präfix: S=Kurzname, L= 948 048MH 949 049MH 950 050MH 951	Ef (V) Vs. mode ox/red	-0.211 Ref 1 error control chan	iges cou	nter	inc.	time	 Image: A start of the start of
Präfix: S=Kurzname, L= 348 048MH 349 049MH 350 050MH 351 352 352	Ef (V) Vs. 2 1 0 0 0 2 2 1 0 1 0 0	-0.211 Ref d error control chan 38.86840 -0.66297292 38.87140 -0.66292308	1985 cou	nter 23138	inc. 319 -2	time .4741	× 33
Präfix: S=Kurzname, L= 948 048MH 949 049MH 950 050MH 951 952 953 954	Ef (V) vs. 2 1 0 0 0 2 1 0 1 0 2 1 0 0 0	-0.211 Ref d error control chan 38.86840 -0.66297292 38.87140 -0.66282308 38.87640 -0.66257321	1985 COU 17 -0.66 11 -0.66 8 -0.66	nter 23138 21613	inc. 319 -2 35 -2.	fime 2.4741 .3977	► 33 13 14 ▼
Präfix: S=Kurzname, L= 348 048 MH 349 049 MH 350 05 0MH 351 352 353 354 4	Ef (V) vs. 2 1 0 0 0 2 1 0 1 0 2 1 0 0 0 2 1 0 0 0	-0.211 Ref d error control chan 38.86840 -0.66297292 38.87140 -0.66282308 38.87640 -0.66257321	ges cou 7 -0.66 1 -0.66 8 -0.66	nter 23138 21613 18906	inc. 319 -2 35 -2. 386 -2	time. 2.4741 .3977 2.277	

Import Assistent - Spalten mit Daten			$\mathbf{\overline{X}}$
Dateistruktur Image: Trennzeichen Aufeinanderfolgende Trennzeichen als e Feste Breite Anzahl Spalten Image: Textvermerk	a Leerzeichen ; eins behandeln Anderes Anwer Benutzerdefiniertes Datumsfo en Numerische Trennzeir	Zuordnung der <unverändert> Rechter Mausklin spaltenüberschrif Setzen von Form rmat <keine></keine></unverändert>	Spalten Anwenden k auf die ift zum individuellen hat und Zuordnung. Anwenden
Führende Nullen in Zahlen entfernen Zeilen durch Auffüllen mit fehlenden Wert Vorschau Spaltenbreite (Ändern der Spalt A(Y) (T&N) B(Y) (T&N)	Add Sparklines Ja(wen en gleich groß machen enbreite durch Klicken und 2 C(Y)(T&N)	n kleiner als 50 Spalten) Das Ziel-Spaltenformat be Ziehen mit der Maus) D(Y)(T&N)	Alten Spalte hinzufügen halten Spalte löschen E(Y)(T&N)
mode ox/red 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1	error 0 0 0 0 0 0	control change 0 1 0 1 0 1	scounter inc. 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
Abbrechen	ĺ	<< Zurück Weiter >>	Fertigstellen

Import Assistent - Filter Spe	chern 🗧					
Einstellungen des Import Assistenten können als Filter gespeichert und erneut verwandt werden. Filter können auf der ersten Seite des Assistenten ausgewählt werden.						
Einmal gespeichert, können Impo von Dateien auf Origin und beim	Einmal gespeichert, können Importfilter auch zum automatischen Setzen der Importeinstellungen beim Drag and Drop von Dateien auf Origin und beim Öffnen der Dateien über das Datei:Öffnen Menu verwandt werden.					
Filter Speichern						
🔘 Im Ordner Daten	:\Promotion\Experimentell_ab53\bioanalytical\120724_MMS2_x263_RDE363\					
🔘 m Ordner Anwender Dateie	D:\Drigin User Files\origin8.1\Filters\					
◯ in das Fenster □ Zeige Filter in Liste Datei:Ŭ	◯ in das Fenster □ Zeige Filter in Liste Datei:Üffnen					
Beschreibung Filter						
Dateiname Filter (.01F Erweiter	ing wird angehängt) mpt_import					
Geben Sie Dateinamen an, mit welchen der Filter verknüpft wird. Sie können Platzhalter verwenden, mehrere Namen können durch ¹ / ¹ getrennt werden z.B.: *.txt or *.txt; *.dat; mydata????.*						
Fortgeschrittene Filteroption	en setzen					
Abbrechen	<< Zurück Weiter >> Fertigstellen					

Import Assistent - Fortgeschrittene (Optionen	×
Per Drag&Drop in Diagramm importieren	Daten in das Layer in welches die Daten gezogen werden Zeichnen 💌	
Per Drag&Drop in Arbeitsbereich importieren	Dateien in Worksheet/Matrix öffnen	
Folgender LabTalk Code wird nach erfolgreic	hem Import ausgeführt:	
cd %yScripte;		
EcLab_v4;		
Create a folder "Sc	ripte" in the OriginUserFiles folder	
And save there the	Eclab v4.ogs and the LSV.ogs	
Abbrechen	<< Zurück Weiter >> Fertigstellen	

1 🖻 🖬 🏫		a 63 [🔁 [/	a c	2 🗃	- R		B	1	123-	123-	C	J	Optionen	Strg+U
				21-		~~~	1	• <u>•</u> ••		2	- -	2	1	Protection	•
1 🕒 🗟 🖗	2	T St		rd::		×	в	1	Ū	x2	x ₂ 3	¢1	<u> </u>	Eit Funktion Manager	F9
	-	_	_	<u> </u>	1								1	Template-Bibliothek	
Fold	o er1					111	Boo	k						Design Manager	F7
									ACX	^		B		Importfilter-Mapager	
						T	angn		Avy	<u> </u>	+-	-		Dackdatei Manager	
						T	nhei				+		1	Editualer manager	
							Kom				-		-	Custom Menu Organizer	
1							1	_			-		1	\underline{X} -Funktion Builder	F10
							2						1	X-Funktion Skriptbeispiele	F11
						F	3	-			_			Kopieren von Origin Sub- <u>V</u> I to L	abVIEW User.lib
							5				+	\neg	1	Gruppenordnerspeicherort einri	chten
							6	<u> </u>			+	-	1	Gruppenordner Manager	
							7				-		1	Change User Files Folder	
4							8						1	Anwenderdateien übertragen	
2							9						1	Politica Editor	
2							10	-			-	_	(—	Paletten-Editor	
p							12	_			+-	\rightarrow	1	MATLAB Konsole	
-							13	_			+-	\neg	1	Mathematica Link	
							14	_			+		_		
							15	1							
			_	_	_	_	_	_	_	_	_	_	_		
Filtermar	nager														
F *b	0.														O.d.u.
Filter	Dia	19&DTO	p une		zen	De ×	Atelei	IWer	iterur	ngen	1				Didner
ASUI				1		t	- lui	Jat							Benutzer
Chi-import				1			shi								Benutzer
DIF_read				1		u *	ATC.								Benutzer
gamry				1		5.L 8	DTA								Benutzer
gamry_LSV				1		1.L *	DIA								Benutzer
import_bcr			1	-		<u>_</u> .r	loct								Benutzer
mpt_import		_	Y	<u></u>		*.r	npt								Benutzer
par_sastit				1		*.F	par								Benutzer
plt_import			~	1		*.r	plt								Benutzer
SASfit			~	1		*.0	dat								Benutzer
SAXS_SLAC			~	1		*.t	axt;*.c	dat							Benutzer
ASCII			~			*.t	xt;*.c	dat							System
CDF			V			× ,	cdf								System
			_	•											
CSV			~	i		*.(CSV								System
CSV DiademDAT				1		*.[*.[CSV DAT								System System

ECLabv4.ogs

DT

Excel

Famos

HDF5

EarthProbe

win -a %H;

//%F ist nötig für die Hupd-Berechnung; %O für die Loop-Trennung %F=%H;

.dcf;.hpf

*.epa; *.xls;*.xlsx *.dat; *.raw

× h5·×he5·×hdf5

System

System

System

System

Sustem

Anwenden

Bearbeiten

~

Abbrechen

```
Appendix
```

renameBook\$=%E; renameBook\$=renamebook.right(8)\$; renameBook\$=renamebook.left(5)\$ page.label\$=renameBook\$; nrows=wks.nrows;

getn

```
(Scanrate in mV/s) sr
(Ref-Potential vs RHE in mV) rf
(V für Baseline in mV) ca
(welchen Cycle Für weitere Rechnung?) cv
(Oberfläche Elektrode in cm<sup>2</sup>:) ele
(die Nötigen Parameter für Hupd bitte eingeben);
```

```
getyesno "sollen Loops aufgeteilt werden?" looppos;
if(looppos==1){run.section(%yScripte\ECLab_v4.ogs, Loop_separate)};
if(looppos==0){run.section(%yScripte\ECLab_v4.ogs, noLoop)};
```

```
[Loop_separate]
//%F ist nötig für die Hupd-Berechnung; %O für die Loop-Trennung
%O=%E;
for (ii = 1; ii<=nrows; ii++)
{if (Cell(ii,1)$ ==--) break;}
{if (Cell(ii,1)$ ==--) aa=$(ii);}</pre>
```

```
wrcopy iw:=%0! r1:=1 r2:=aa ow:=Loops!;
wrcopy iw:=%0! r1:=aa+2 r2:=nrows ow:=allData!;
```

```
col(1)[L]$=mode#;
col(2)[L]$=ox/red;
col(3)[L]$=error;
col(4)[L]$=control;
col(5)[L]$=changes;
col(6)[L]$=counter inc.;
col(7)[L]$=time;
```

```
col(7)[U]$=s;
col(8)[L]$=Ewe;
col(8)[U] =V;
col(9)[L]$=<I>;
col(9)[U]$=mA;
col(10)[L]$=cycle#;
page.active$=Loops;
loop(ii,1,aa)
{start$(ii)=wcol(6)[ii]+1;end$(ii)=wcol(8)[ii]+1;}
page.active$=alldata;
repeat 6{delete col(1)};
//damit die richtige Anzahl der Loops entsteht,
//denn aa beinhaltet auch die Leerzeile
aa=aa-1:
nrows=wks.nrows;
loop(ii,1,aa)
{wrcopy iw:=[%H]alldata! r1:=start$(ii) r2:=end$(ii) ow:=Loop$(ii)!;
col(1)[L]$=time;
col(1)[U]$=s;
col(2)[L]$=Ewe;
col(2)[U]$=V;
col(3)[L]$=<I>;
col(3)[U]$=mA;
col(4)[L]$=cycle#;
wks.col2.type=4;}
getyesno "Soll Hupd bestimmt werden?" antw;
if(antw==1){run.section(%yScripte\ECLab_v4.ogs, Hupd)};
[Hupd]
for(li=1; li <=aa; li++)</pre>
 {page.active$=Loop$(li);
```

```
//kopiere die Daten und erstelle gleichzeitig die passenden Sheets:
//Wo beginnen die einzellnen Cycles?
//curve eins im bereich a1 bis e1
a1=1;
for (ii = 2; ii<=wks.nrows; ii++)</pre>
{if (Cell(ii,4) ==cell($(ii-1),4)) test=1; else break;}
{if (test ==1) a2=$(ii)};
e1=a2-1:
//curve eins im bereich a2 bis e2
for (ii = a2+1; ii<=wks.nrows; ii++)</pre>
{if (Cell(ii,4) ==cell($(ii-1),4)) test=1; else break;}
{if (test ==1) a3=$(ii)};
e2=a3-1;
//curve eins im bereich a3 bis e3
for (ii = a3+1; ii<=wks.nrows; ii++)</pre>
{if (Cell(ii,4) ==cell($(ii-1),4)) test=1; else break;}
{if (test ==1) e3=$(ii-1)};
newbook Loop$(li) sheet:=0;
wrcopy iw:=[%F]Loop$(li)! r1:=a1 r2:=e1 ow:=curve1!;
wrcopy iw:=[%F]Loop$(li)! r1:=a2 r2:=e2 ow:=curve2!;
wrcopy iw:=[%F]Loop$(li)! r1:=a3 r2:=e3 ow:=curve3!;
win -r %H Loop$(li);
doc -e LW
{col(1)[L]$=time;
col(1)[U]$=s;
col(2)[L]$=Ewe;
col(2)[U]$=V;
col(3)[L]$=<I>;
col(3)[U]$=mA;
col(4)[L]$=cycle#;
wks.col2.type=4;}
run.section(%yScripte\ECLab_v4.ogs, umrechnen);
//hier kommt die Berechnung:
```

```
run.section(%yScripte\ECLab_v4.ogs, integration);
ECSA$(li)=cell(1,2);
win -a \%F;}
run.section(%yScripte\ECLab_v4.ogs, new);
[new]
newbook ECSA;
wks.ncols=4:
if(looppos==1)
\{col(1)=\{-1:\$(aa)\};\
loop(ii,1,aa){cell($(ii+2),2)=ECSA$(ii)};
run.section(%yScripte\ECLab_v4.ogs, ECSA);};
if(looppos==0)
{ getn (wieviele loops insgesamt?) bb;
col(1)={-1:$(bb)};
loop(ii,1,bb){cell($(ii+2),2)=ECSA$(ii-1)};
run.section(%yScripte\ECLab_v4.ogs, ECSA);};
[ECSA]
col(3)[L]$= active area;
col(3)[U] = m<sup>2</sup>:
col(4)[L] = ECSA;
col(4)[U] = m^2/g;
wks.col4.width=15;
//dividieren durch die theoretische Ladungsdichte von Pt und umrechnen in m^2
col(3)=col(2)/210*1000/10000;
getn
(Einwaage Pulver in mg?) ee
(Massenprozent M?) mp
(wieviele \mul auf Elektrode?) ml
(InkVolumen angesetzt in ml:) vv
(Bitte . und nicht , als Trennzeichen nehmen);
// Berechnung der Masse von reinem Metall auf der Elektrode = rm:
rm = ee/(vv*1000)*ml/100*mp;
//mit $(double, .2) werden 2 signifikante Stellen angegeben
```

```
col(4) [C] = Beladung Metall (rm*1000/ele, .2) \mu g cm + (-2);
//Berechnung der tatsächlichen ESCA:
col(4) = col(3)/rm/0.001;
//zum Zeichnen:
plotxy iy:=(1,4) plot:=192 ogl:=[<new template:=HUPD_AREA name:=ESCA>];
// Set symbol size; %C is the active dataset
set %C -z 7;
//wenn keine Loops vorhanden sind, dann wird nur der Header weggeschnitten:
[noLoop]
win -a %H;
cell(2,1)= ;
//%F ist nötig für die Hupd-Berechnung; %O für die Loop-Trennung
%O=%E;
for(ii=1; ii<=wks.nrows; ii++)</pre>
{if (Cell(ii,1)$ ==mode) break;}
{if (Cell(ii,1)$ ==mode) aa=$(ii);}
wrcopy iw:=%0! r1:=aa+1 r2:=wks.nrows ow:=alldata!;
col(1)[L]$=mode#;
col(2)[L]$=ox/red;
col(3)[L]$=error;
col(4)[L]$=control;
col(5)[L]$=changes;
col(6)[L]$=counter inc.;
col(7)[L]$=time;
col(7)[U]$=s;
col(8)[L]$=Ewe;
col(8)[U]$=V;
col(9)[L]$=<I>;
col(9)[U]$=mA;
col(10)[L]$=cycle#;
wks.col8.type=4;
repeat 6{delete col(1)};
```

```
a1=1;
for (ii = 2; ii<=wks.nrows; ii++)</pre>
{if (Cell(ii,4) ==cell($(ii-1),4)) test=1; else break;}
{if (test ==1) a2=$(ii)};
e1=a2-1:
//curve eins im bereich a2 bis e2
for (ii = a2+1; ii<=wks.nrows; ii++)</pre>
{if (Cell(ii,4) ==cell($(ii-1),4)) test=1; else break;}
{if (test ==1) a3=$(ii)};
e2=a3-1;
//curve eins im bereich a3 bis e3
for (ii = a3+1; ii<=wks.nrows; ii++)</pre>
{if (Cell(ii,4) ==cell($(ii-1),4)) test=1; else break;}
{if (test ==1) e3=$(ii-1)};
wrcopy iw:=[%H]alldata! r1:=a1 r2:=e1 ow:=curve1!;
wrcopy iw:=[%H]alldata! r1:=a2 r2:=e2 ow:=curve2!;
wrcopy iw:=[%H]alldata! r1:=a3 r2:=e3 ow:=curve3!;
doc -e LW
{col(1)[L]$=time;
col(1)[U]$=s;
col(2)[L]$=Ewe;
col(2)[U]$=V;
col(3)[L]$=<I>;
col(3)[U]$=mA;
col(4)[L]$=cycle#;
wks.col2.type=4;};
//wieder reinnehmen:
//plotxy iy:=(1,2) plot:=200;
run.section(%yScripte\ECLab_v4.ogs, umrechnen);
getyesno "Soll Hupd bestimmt werden?" antw1;
if(antw1==1)
{renameBook$=%L;
renameBook$=renameBook.between("CV_","mpt")$;
```

```
renameBook_new$=renameBook.between("_",".")$;
%K = renameBook.between("loop",".")$;
page.label$=renameBook_new$;
run.section(%yScripte\ECLab_v4.ogs, integration);
ECSA$(%K)=cell(1,2);};
[umrechnen]
//win -a %H;
page.active$ = curve$(cv);
col(3)[L]$= umgerechnetesV;
col(3)[U]$= auf RHE mit + $(rf/1000);
col(4)=col(c);
col(4)[L]$= I gemessen;
col(4)[U] = mA;
col(5)=col(d)/ele;
col(3)=col(2) + rf/1000;
col(5)[L]$=J\-(geo);
col(5)[U] =mA/cm<sup>2</sup>;
col(5)[C] = A(geo) = $(ele) cm^{2};
wks.col3.type = 4;
[integration]
copydata irng:=[%H]curve$(cv)!3:4 orng:=[%H]kopiertCurve$(cv)!1:2;
wks.col1.type = 4;
for(ii=1; ii<= wks.nrows; ii++)</pre>
{if(cell($(ii),2) < 0) break;}</pre>
cn=ii;
for(ii=cn; ii<= wks.nrows; ii++)</pre>
{if(cell($(ii),2) > 0) break;}
cn=ii-1;
wrcopy iw:=[%H]%C! r1:=cn r2:=wks.nrows ow:=Curve$(cv)auf0!;
for(ii=1; ii<= wks.nrows; ii++)</pre>
{if(cell($(ii),1) > ca/1000) break;}
```

```
cn=ii;
col(2)[L]$=BaselineCreate;
col(3)=col(BaselineCreate)-col(BaselineCreate)[cn];
col(3)[L]$=done;
wks.col1.type=4;
//nc = normiereungswert
nc = cell(cn,3);
nrows = wks.nrows;
wrcopy iw:=[%H]Curve$(cv)auf0! r1:=1 r2:=cn ow:=nurPositiv!;
delete col(2);
col(1)[L]$= Potential;
col(1)[U]$= V;
col(2)[L]$= Current;
col(2)[U] = mA;
wks.col1.type=4;
//kleine Korrektur, damit der erste Punkt auch auf 0 sitzt:
cell(1,2)=0;
integ1 iy:= (Col(1),Col(2)) type:=math area:=1;
double area = integ1.area;
type The calculated area is $(integ1.area);
newsheet name:=berechneteoberfläche cols:=2;
//hier ist der Wert für die oberfläche:
col(1)[L]$= Oberfläche berechnet aus dem Integral;
col(2)[L]$= durch scanrate dividiert;
col(2)[C]$= scanrate $(sr) mV/s;
col(2)[U] = mC;
//mV muss nicht umgerechnet werden, da mA als Scala
//dann aber das Ergebnis in C noch *1000, damit am Ende mC rauskommt:
cell(1,1)= $(integ1.area);
cell(1,2)= $(integ1.area)/(sr)*1000;
```

LSV.ogs

```
F=96485.341;
D=1.9e-9;
nue=8.93e-7;
C0=1.18;
w=1600;
n=4;
```

it =-0.62*n*F*D^(2/3)*nue^(-1/6)*C0*w^(1/2)*(pi/30)^(1/2);

getn

(Which cycle should be used?) cv (Electrode surface in cm²:) ele (Full metal mass on electrode [mg]) rm (Theoretical diff. lim. cur.) it (Please enter the parameters);

```
page.active$=curve$(cv);
// die Grenzen für die Bestimmung von i_d:
for(ii=1; ii<= wks.nrows; ii++)
{if(cell($(ii),3) > 0.9) break;}
{if (Cell($(ii),3) > 0.9) ia=cell($(ii),5);}
for(ii=1; ii<= wks.nrows; ii++)
{if(cell($(ii),3) > 0.2) break;}
{if (Cell($(ii),3) > 0.2) ja=$(ii);}
for(ii=1; ii<= wks.nrows; ii++)
{if(cell($(ii),3) > 0.2) ja=$(ii);}
for(ii=1; ii<= wks.nrows; ii++)
{if(cell($(ii),3) > 0.5) break;}
{if (Cell($(ii),3) > 0.5) jb=$(ii);};
```

getn
(electrons/mol:) n
(Faradayconst. [C/mol]) F
(Diff-const. [m²/s]) D
(Viscosity [m²/s]) nue
(conc. oxi-species [mol/m³]) C0

```
(Rotation in rpm) w
(Read value j [mA/cm^2] at 0.9V) ia
(Calculation of diffusions current density at 0.9V; im = mass activity);
range aa = col(e)[$(ja)]:col(e)[$(jb)];
id = mean(aa);
ik=(ia*id)/(id-ia);
im =ik/rm*ele;
newsheet name:=MassActivityCalc;
cell(1,1)= "Diffusion curr.dens. in mA/cm<sup>2</sup>";
cell(1,2)= id/10;
cell(2,1) = "kinetic in mA/cm<sup>2</sup>";
cell(2,2) = ik;
cell(3,1)= "Mass activity in mA/mg";
cell(3,2) = im;
cell(4,1) = "Mass metal in \mu g";
cell(4,2) = rm*1000;
wks.col1.width=20;
page.active$=curve$(cv);
col(5)[U]$= "j\-(mass) = $(im, .2) mA/mg";
wks.col5.width=15;
//if a graph template for LSV measurements is saved in the template
//library of Origin, it shoud be named as LSV and the following % \mathcal{T}_{\mathrm{S}}
//line should be enabled in the script:
//plotxy iy:=(3,5) plot:=192 ogl:=[<new template:=LSV name:=LSV>];
Guinier correct.ogs
```

getn
(q column) qc
(I(q) column) qi
(Specify the column numbers!);

```
win -a %H;
cell(1,1) = ;
renameBook$=%H;
ncols = wks.ncols;
col((ncols+1)) = col((qc))^2;
col($(ncols+2)) = ln(col($(qi)));
wks.col$(ncols+1).type=4;
col((ncols+1))[L] = q^2;
col($(ncols+2))[L]$ = ln(intensity);
//Suche die x-Werte für den Fit
for(ii=1; ii<= wks.nrows; ii++)</pre>
{if(cell($(ii),$(ncols+1)) > 0.2) break} aa=ii;
for(ii=1; ii<= wks.nrows; ii++)</pre>
{if(cell($(ii),$(ncols+1)) > 0.4) break} bb=ii;
//Fitte die Werte
fitLR iy:=($(ncols+1),$(ncols+2))[$(aa):$(bb)];
//fass die Parameter zusammen
newsheet name:= fitParameter;
cell(1,1)= "Intercept";
cell(1,2)= fitLR.a;
cell(2,1)= "Slope";
cell(2,2)= fitLR.b;
cell(3,1)= "Intercept error";
cell(3,2)= fitLR.aerr;
cell(4,1)= "Slope error";
cell(4,2)= fitLR.berr;
cell(5,1)= "Sum squares";
cell(5,2)= fitLR.r;
cell(6,1)= "number of points";
cell(6,2)= fitLR.pts;
cell(8,1)= "Rg";
cell(8,2) = sqrt(-cell(2,2));
cell(9,1)= "D=Rg*12^0.5";
cell(9,2) = cell(8,2)*sqrt(12);
```

```
wks.col1.width=10;
//und erstelle eine neue Funktion mit den berechneten Werten
page.active=1;
col($(ncols+3))[L]$=FitX;
col($(ncols+4))[L]$=FitY;
cell(1,$(ncols+3))=0.1;
for (ii=2; ii<=21; ii ++)</pre>
{kk=ii-1:
cell(ii,$(ncols+3))=cell(kk,$(ncols+3))+0.02;}
wks.col$(ncols+3).type=4;
col($(ncols+4)) = fitLR.a + fitLR.b*col($(ncols+3));
//mache einen Graph daraus
plotbylabel iy:=(($(ncols+1),$(ncols+2)),($(ncols+3),$(ncols+4)))
group:=Units plottype:=line rows:=1 cols:=1;
//Set the start value
layer.x.from = 0.1;
//Set the end value
layer.x.to = 0.8;
//Set the increment value
layer.x.inc = 0.05;
//Set the start value
layer.y.from = $(fitLR.a-2);
//Set the end value
layer.y.to = $(fitLR.a);
//Set the increment value
layer.y.inc = 0.001;
page.label$= renameBook$;
```

Abbreviations

Abbreviation	Declaration
(A)SAXS	(Anomalous) Small Angle X-Ray Scattering
AST	Accelerating stress test
a. u.	arbitrary units
BESSY	Berliner Elektronspeicherring-Gesellschaft für Synchrotronstrahlung
CA	Chronoamperommetry
CV	Cyclic voltammetry
ECSA	Electro-chemical surface area
EDX	Energy Dispersive X-Ray Analysis
FC	Fuel cell
GC	Glassy carbon
HOR	Hydrogen oxidation reaction
(HR)TEM	(High Resolution) transmission electron microscopy
IL	Ionic liquid
LSV	Linear sweep voltammetry
meso-C	Carbon material synthesized by pyrolysis of 3-MBP-dca
MWCNT	Multi walled carbon nano tubes
N-MWCNT	MWCNT coated with a Nitrogen-doped carbon
norm.	normalized
NP	nanoparticle/s
ORR	Oxygen reduction reaction

Δn	nor	Ъ	i٧
γΨ	per	iu	١٨

Abbreviation	Declaration
PDF	Pair distribution function
pdf	Probability density function
PEMFC	Polymer electrolyte membrane fuel cell
psd	particle size distribution
SEM	Scanning electron microscopy
SLAC	Stanford Linear Accelerator Center, National Accelerator Laboratory
XANES	X-Ray Absorption Near Edge Structure
XPS	X-ray photo electron spectroscopy
XRD	X-ray Diffraction