THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

# Sputtered Platinum and Platinum-Rare Earth Metal Alloy Nanocatalysts for Proton Exchange Membrane Fuel Cells

Björn Lönn

Department of Physics CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden, 2025 Sputtered Platinum and Platinum-Rare Earth Metal Alloy Nanocatalysts for Proton Exchange Membrane Fuel Cells

Björn Lönn

© Björn Lönn, 2025

ISBN 978-91-8103-229-1 Doktorsavhandlingar vid Chalmers tekniska högskola, Ny serie nr 5687. ISSN 0346-718X

Department of Physics Division of Chemical Physics Chalmers University of Technology SE-412 96 Göteborg, Sweden Phone: +46(0)31 772 1000

Cover:

Gas aggregation sputtering (left) and unbalanced magnetron sputtering (right) synthesis of platinum-based PEMFC nanocatalysts. TEM images show the difference in nanocatalyst size and morphology for the two different techniques. The chemical reaction (middle) is an illustration of the oxygen reduction reaction on a platinum-rare earth metal alloy surface.

Printed by Chalmers Digitaltryck, Gothenburg, Sweden 2025. Sputtered Platinum and Platinum-Rare Earth Metal Alloy Nanocatalysts for Proton Exchange Membrane Fuel Cells

Björn Lönn

Department of Physics Chalmers University of Technology

# Abstract

Proton exchange membrane fuel cells (PEMFCs) have the potential to become an integral technology in future sustainable energy systems, offering lowemission energy and transport solutions. Carbon-supported platinum (Pt) and Pt-based alloy nanoparticles constitute not only the most used PEMFC catalyst materials, but also the most promising future candidates. Among these, platinum-rare earth alloys (Pt-REs) stand out because of their enhanced oxygen reduction reaction (ORR) activities compared to Pt. However, the complicated synthesis of Pt-RE nanoparticles and an overall growing demand for Pt-based nanocatalysts, motivates development of clean, scalable ultra-high vacuum fabrication techniques.

This thesis explores sputtering and sputtering onto liquids (SoL) as potential synthesis methods for Pt-based nanocatalysts. Emphasis is placed on understanding the growth processes of Pt and Pt-RE nanoparticles during sputtering and post-sputtering treatments, as well as ORR performance of Pt-based nanoparticles and thin films. A combination of transmission electron microscopy, X-ray techniques, and electrochemical testing reveals how synthesis parameters influence nanocatalyst composition, morphology and performance. Key findings include a weak dependence of Pt primary particle size on substrate temperature during sputtering, a trend also observed during post-sputtering heat-treatment of unsupported particles. Conversely, heat-treatment with an added carbon support allows tuning of particle agglomeration and growth by adjusting the liquid substrate molecular weight. The performance of these catalysts is similar to conventional Pt ORR catalysts; however, SoL-synthesized Pt-RE primary particles are too small to provide enhanced ORR activities. By means of gas aggregation sputtering onto liquid polyethylene glycol, we demonstrate both synthesis and efficient collection of  $Pt_3Y$  nanoparticles with promising sizes for ORR applications. Future work should optimize the electrode preparation using these particles to maximize their catalytic performance. For sputtered Pt<sub>3</sub>Y thin films, vttrium leaching during fuel cell accelerated stress tests decreases their ORR activity; however, electron microscopy indicates that this leaching does not significantly alter the thin film surface morphology. The presented work expands the current knowledge of sputter-synthesized Pt-based nanocatalysts, gives new insights into the growth processes of SoL-synthesized Pt nanoparticles, and constitutes an important step towards implementation of the SoL technique for the fabrication of high-performance PEMFC nanocatalysts.

Keywords: Fuel cells, ORR, Pt-RE nanocatalysts, Sputtering onto liquids

# List of Publications

# Appended publications

This thesis is based on the following publications:

I Plasma-Induced Heating Effects on Platinum Nanoparticle Size During Sputter Deposition Synthesis in Polymer and Ionic Liquid Substrates,

R. Brown, <u>B. Lönn</u>, R. Pfeiffer, H. Frederiksen, B. Wickman Langmuir 37.29 (2021), 8821-8828.

 $\begin{array}{ll} {\rm II} & {\rm ORR} \mbox{ activity and stability of carbon supported $Pt_3Y$ thin films in $PEMFCs$,} \end{array}$ 

E. Marra, G. Montserrat-Sisó, B. Eriksson, <u>B. Lönn</u>, R. Wreland Lindström, G. Lindbergh, B. Wickman, C. Lagergren *Electrochimica Acta* 472 (2023) 143436.

- III Fuel Cell Catalyst Layers with Platinum Nanoparticles Synthesized by Sputtering onto Liquid Substrates, <u>B. Lönn</u>, L. Strandberg, V. Roth, M. Luneau, B. Wickman ACS Omega 9.43 (2024), 43725–43733.
- IV Platinum Nanoparticles Sputtered onto Liquid Polyethylene Glycol: Insights into Growth Processes for Supported and Unsupported Nanoparticles, <u>B. Lönn</u>, M. Luneau, B. Wickman Manuscript.

# My contributions

#### Paper I

I performed the substrate temperature, TGA, and parts of the SAXS experiments, analyzed the results, authored parts of the paper, and implemented a majority of the review comments.

#### Paper II

I performed the TEM analysis and wrote the corresponding section of the paper.

#### Paper III

I performed the synthesis, electrochemical analysis, and parts of the physical characterization and analysis (TEM and XPS). I prepared the first draft of the manuscript, finalized the paper together with the co-authors and implemented review comments.

#### Paper IV

I performed the synthesis, characterization, and analysis and prepared the manuscript.

"I have not failed. I've just found 10,000 ways that won't work." - Thomas A. Edison

# Contents

Abstract iii										
List of Publications v										
1	<b>Intr</b> 1.1	roduction Thesis scope	$\frac{1}{2}$							
<b>2</b>	Electrochemistry 5									
	2.1	Redox reactions	$5 \\ 6$							
	2.2	Electrochemical systems	7 8 10							
	2.3	2.2.5       Overpotential         (Electro-) catalysis	11 14 14 16							
	2.4	Applications	17							
3	Proton exchange membrane fuel cells									
	3.1	Fuel cell types	19							
	3.2	Components	20							
	3.3	Reactions	23							
		3.3.1Hydrogen oxidation reaction3.3.2Oxygen reduction reaction3.3.3Cell potential	23 24 25							
	3.4	Losses	26							
	3.5	Catalyst materials	27							
		3.5.1       Thin films	29 29 30							
4	Met	thods and experimental techniques	<b>31</b>							
	4.1	Nanocatalyst synthesis	31							
		4.1.1 Magnetron sputtering	31							
		4.1.2 Gas aggregation sputtering	34							

	4.1.3 Attachment of nanocatalyst particles on carbon suppor									
			material	36						
	4.2	4.2 Physical characterization								
		4.2.1	Transmission electron microscopy	36						
		4.2.2	Small-angle X-ray scattering	37						
		4.2.3	X-ray photoelectron spectroscopy	37						
		4.2.4	X-ray diffraction	39						
	4.3	Electr	ochemical characterization	39						
		4.3.1	Cell setup	39						
		4.3.2	Electrode preparation	41						
		4.3.3	Cyclic voltammetry	41						
		4.3.4	Evaluation of electrochemical surface area	42						
		4.3.5	Rotating disk electrode	43						
5	Growth processes of sputtered Pt-based nanoparticles 4'									
	5.1	Influe	nce of synthesis parameters	48						
		5.1.1	Substrate parameters	48						
		5.1.2	Gas environment	52						
		5.1.3	Sputtering parameters	55						
	5.2	sputtering treatments	57							
		5.2.1	Heat-treatment	57						
		5.2.2	Microwave-treatment	58						
	5.3	Perspe	ectives on nanoparticle growth $\ldots \ldots \ldots \ldots \ldots$	59						
6	Plat	tinum-	based nanocatalysts for the oxygen reduction							
	read	$\operatorname{ction}$		61						
	6.1	Nanop	particles sputtered in PEG	61						
		6.1.1	Standard DC magnetron sputtering	61						
		6.1.2	Gas aggregation sputtering	64						
	6.2	Sputte	ered thin films	65						
7 Conclusions										
•	1									
A	Acknowledgements									
Bibliography										

# Chapter 1 Introduction

Climate change represents one of the most pressing challenges of humanity. It is well established that the rising global temperatures observed during the recent century originate from human activities, particularly increasing greenhouse gas emissions [1]. This has led to severe impacts on terrestrial ecosystems [2], as well as in the oceans and the cryosphere [3]. To mitigate these effects and reduce the risks of escalating climate issues, urgent preventive action is needed. Governments [4] and intergovernmental organizations [5, 6] around the world are actively working to facilitate a transition to a fossil-free energy system. The 2015 United Nations Climate Change Conference (COP 21), held in Paris, saw the implementation of the latest global UN treaty on climate change. Known as the Paris Agreement, the treaty was signed by 196 parties and has the primary goal of limiting the increase in global average temperature to below 2 °C above preindustrial levels [7]. However, several recent reports show that the Nationally Determined Contributions (NDCs) pledged by the signatories are far from meeting the emission targets required to reach the 2  $^{\circ}$ C goal [8, 9], clearly emphasizing the importance of large-scale collaboration and stronger climate initiatives.

The recent commitment of the European Union to become "the first climateneutral continent" by 2050, under the European Green Deal [5], marks an important step toward net zero emissions of greenhouse gases. Part of this exertion involves shifting from a fossil-based energy system to one predominantly powered by renewable energy sources, such as wind and solar. While this transition is essential, it presents several challenges. A major challenge for green energy based on solar and wind power is its intermittency, which can lead to occasional mismatches between electricity supply and demand. This factor, along with the ongoing increase in global electricity use, embodies the need for higher degrees of electricity security during the transition to clean energy [10]. One promising approach to improve energy grid stability is the use of hydrogen as an energy carrier. In a system heavily reliant on variable renewable electricity sources, hydrogen could be produced through a process known as electrolysis, utilizing surplus renewable electricity to split water into its elements, hydrogen and oxygen. Hydrogen produced this way can serve multiple purposes; for example as a base chemical in the chemical and fertilizer industries, a reducing agent in the production of fossil-free steel, a sustainable fuel for transportation, or as temporary energy storage to balance the electricity grid. This concept, known as the Hydrogen Economy, is in fact an important component of the European Green Deal [11].

In an energy system partly based on hydrogen, the ability to convert the chemical energy stored in hydrogen back into electricity is of utmost importance. Fuel cells are the most efficient technology for this back-conversion. Commonly, the chemical reaction between hydrogen and oxygen, for which water and heat are the only reaction products, is used to convert hydrogen-stored chemical energy to electricity. Intuitively, this type of fuel cells is referred to as hydrogen fuel cells. Compared to conventional combustion, hydrogen fuel cells offer several advantages, including higher efficiency and, if hydrogen is produced from renewable energy, zero emissions, which are crucial to a future sustainable energy system. Many reports highlight hydrogen fuel cells as a key technology to tackle the impending challenges of the ongoing energy transition [11–14], and with their increasing importance, there is a growing demand for commercially available alternatives.

The most widely used fuel cell type, especially for transport applications, is the proton exchange membrane fuel cell (PEMFC), which combines low weight and fast start-up times with high energy density and conversion efficiency. Currently, PEMFC technology is highly dependent on noble platinum (Pt) as catalyst material to ensure satisfactory performance and durability. The global demand for Pt is expected to increase rapidly in the coming decades, particularly for scenarios with high market penetration of electrolyzers and fuel cells [15]. Therefore, it is of great importance that the implementation of Pt and Pt-based catalysts is carried out responsibly, to prevent and minimize risks related to the supply of Pt [15], and environmental impacts throughout the catalyst life cycle [16]. To fulfill such requirements on responsible implementation, the catalyst synthesis step is crucial. Not only is it essential to ensure that the synthesis is clean and free of hazardous chemicals and impurities [17, 18], but also to minimize the amount of Pt needed to meet the application-specific power density requirements. One way to reduce the Pt loading is to increase its catalytic activity, which can be achieved by optimizing the catalyst size, shape, and nanostructure, or by alloying. As will be argued in chapter 3, there exists a need for new PEMFC catalyst materials, but traditional synthesis techniques are unsuitable for one of the most promising catalyst candidates, which are platinum-rare earth (Pt-RE) metal alloys.

## 1.1 Thesis scope

This thesis focuses on the investigation and further development of sputteringbased methods for the synthesis of Pt and Pt-RE alloy nanocatalysts, with the primary aim of enabling clean, efficient, and scalable nanoparticle fabrication routes. To reach this goal, the scientific questions that I am looking to answer are how the particles form, what parameters influence their growth and morphology, and how this relates to their catalytic performance. A large part of this work involves the fabrication and characterization of nanoparticles sputtered onto liquid substrates (SoL). SoL is a promising, ultra-high vacuum technique for nanoparticle synthesis, where the liquid plays a central role in either the nucleation and growth of nanoparticles or the collection and stabilization of sputtered nanoparticles, and in some cases, both, depending on the selected sputtering technique. Nanoparticle growth processes are given particular attention, as a broad understanding of the phenomena and the parameters involved in the growth is integral to the optimization of nanoparticle size and morphology. Furthermore, the materials are also studied in thin film model systems, to elucidate the influence of structure and overlayer composition on their catalytic activity and stability. In summary, this thesis adds new insight into the field of nanofabrication of catalyst materials and provides future guidelines for the implementation of SoL in the synthesis of PEMFC catalysts. Part of the work included in this thesis has previously been presented in a licentiate thesis by the same author [19].

The following chapters will introduce the fundamental concepts of electrochemistry and fuel cells and the experimental methods and techniques necessary to understand the work presented herein. The thesis concludes with two chapters discussing a selection of the key findings, including a perspective on the growth of sputtered Pt and Pt-RE nanoparticles, and an outlook for the implementation of the SoL technique in PEMFC nanocatalyst synthesis.

# Chapter 2 Electrochemistry

Electrochemistry is the scientific field devoted to the interplay between electric potentials and chemical reactions. This involves the study of redox reactions and their responses to applied electric potentials. An important consequence of their nature is that spontaneous redox reactions can be used to convert chemical energy into electricity. This is our main topic of interest when considering energy conversion in fuel cells. The aim of this chapter is to provide a fundamental understanding of the most important electrochemical concepts that govern fuel cell principles. We will start with a brief history followed by a detailed description of fundamental concepts, including redox reactions, catalysis, and electrochemical systems.

The widespread interest in fuel cells and the hydrogen economy can be considered relatively new; however, electrochemistry and basic fuel cell technology are, in fact, old. The history of electrochemistry spans multiple centuries of scientific discoveries [20, 21], from electricity-induced twitching of frog legs and the first electric battery in the late 1700s, to fuel cells in space during the 1960s, and the cutting-edge research in fuel cells, electrolyzers, and batteries of the modern day. The common feature that all of these discoveries and technologies share, is the fundamental type of chemical reaction on which they are all based, namely redox reactions.

# 2.1 Redox reactions

To understand electrochemical systems, a central concept is redox reactions, a certain class of chemical reactions in which electrons are transferred between chemical species, causing a change in their oxidation states. The name stems from reduction-oxidation, which is most easily explained as the two opposite processes of gaining and losing electrons, respectively. As a simple example of a redox reaction one can consider the expression given in equation 2.1 where transfer of n electrons occur between the chemical species X and Y.

$$X + Y \rightleftharpoons X^{n+} + Y^{n-} \tag{2.1}$$

Here, n+ and n- denotes electron loss and gain, respectively. X donates n of its electrons, oxidizing into  $X^{n+}$  and Y is reduced to  $Y^{n-}$  by accepting the n electrons from X. A specie that accepts electrons to become reduced (Y) is called an oxidant (Ox), while an electron donor (X) is denoted as a reductant (Red). We can therefore identify two types of pairs in equation 2.1; the *redox pair* X/Y and the two *redox couples* X/X<sup>n+</sup> and Y<sup>n-</sup>/Y, where each redox couple consists of a specie in its reduced form (X or Y<sup>n-</sup>) alongside its oxidized form (X<sup>n+</sup> or Y). The general redox reaction in equation 2.1 can be treated as two separate *half reactions*, one for the oxidation (2.2) and another for the reduction (2.3). When considering half reactions, it is advisable to include transferred electrons as separate terms in the expressions, as exemplified in equations 2.2 and 2.3.

$$X \rightleftharpoons X^{n+} + ne^{-} \tag{2.2}$$

$$Y + ne^{-} \rightleftharpoons Y^{n-} \tag{2.3}$$

The two processes of oxidation and reduction always occur in pairs and simultaneously; however, they may be separated in space. This unique feature makes it possible to exploit a fundamental aspect of the thermodynamic laws governing all chemical reactions; to convert between chemical and electrical energy.

#### 2.1.1 Thermodynamics

According to thermodynamics, reactions can be either spontaneous, occurring naturally and releasing free energy to their surroundings, or non-spontaneous, requiring energy input from the surroundings [22]. As we already know, redox reactions involve the transfer of electrons from one reactant to another. When a spontaneous redox reaction occurs and its half-reactions are separated in space, part of the released energy becomes accessible as electrons, or more specifically, as an electric current. Electrochemical systems that utilize this principle are referred to as galvanic cells and include fuel cells and discharging batteries. Equally fascinating is that by externally applying a potential difference to the system, it is possible to force the electric current, and hence the redox reaction itself, to run in its non-spontaneous direction. Such systems are known as electrolytic cells.

If we consider a redox reaction in its most simple form, it consists of a reduction process in the forward direction and an oxidation in the backward direction, with n electrons transferred (equation 2.4).

$$Ox + ne^- \rightleftharpoons Red$$
 (2.4)

The overall direction and rate of the reaction may depend on several factors, including temperature, applied electric potential and mixture composition; however, the relative balance between oxidized and reduced forms at any given time can be expressed using the reaction quotient  $Q_r$ . For the simple reaction in equation 2.4, the reaction quotient is defined by:

$$Q_r = \frac{a_{Red}}{a_{Ox}} \tag{2.5}$$

where  $a_{\text{Red}}$  and  $a_{\text{Ox}}$  are the respective thermodynamic activities of the reduced and the oxidized species, respectively. The reaction quotient is useful because it allows us to express the change in Gibbs free energy during a reaction,  $\Delta G$ , as a function of the Gibbs free energy of reaction at standard conditions,  $\Delta G^{\circ}$ . Here, standard conditions are indicated by a °, and refer to a pressure of 1 bar, a temperature of 25 °C and a pH of 0.

$$\Delta G = \Delta G^{\circ} + RT ln Q_r \tag{2.6}$$

In equation 2.6, T is the temperature of the reaction and R is the ideal gas constant.  $\Delta G$  is a highly important property as it represents the maximum nonexpansion work,  $W_{max}$ , accessible from a chemical reaction. Remembering that in electrochemical cells, the main interest is to convert between chemical energy and electrical work, the relevance of  $\Delta G$  is further realized. The coming section will introduce the main principles of electrochemical cells, discuss the concepts of electrode and cell potentials and explain their connection with the thermodynamic principles just addressed, and introduce another central concept in electrochemistry, overpotential.

#### 2.2 Electrochemical systems

An electrochemical system typically consists of two or more electrodes, separated in space and connected via an electric circuit and an ionic conducting medium, for example, a liquid electrolyte or an ion conducting membrane; see figure 2.1. At equilibrium, there is no electric current flowing through the external circuit, as the forward and backward directions of each half-reaction occur at the same rate. However, if the equilibrium is disturbed, each electrode will start to favor one of the directions of its associated half-reaction. At the anode, electrons released from the oxidation reaction are collected and supplied to the external circuit, while at the cathode, the electrons are resupplied to the reduction reaction. Hence, a flow of electrons will occur in the external electric circuit, from the anode to the cathode. Similarly, ions generated at one of the electrodes will flow through the ion-conducting media separating the two electrodes. Here, the direction of ionic flow depends on the cell chemistry and, more specifically, its corresponding half-reactions. Positive ions will move towards the cathode, whereas negative ions will move in the direction of the anode.



Figure 2.1: General schematic of an electrochemical cell containing two electrodes, a cathode and an anode. The electrodes are in electric and ionic contact with each other, allowing the flow of electric current and ions during the reaction.

#### 2.2.1 Electrode potentials and cell potential

Any electrode, inert or not, that is immersed in any kind of electrolyte will possess an electric potential. This arises from the way conduction electrons experience their surroundings, and the potential is therefore specific to the electrode material and the environment in which it is present. When an electrode is immersed in an electrolyte, the difference in electric potential  $\varphi$  between the electrode and the electrolyte is known as the Galvani potential difference [23].

$$\Delta \varphi_{Galvani} = \varphi_{Electrode} - \varphi_{Electrolyte} \tag{2.7}$$

A result of the Galvani potential difference is the formation of an electric double layer at the electrode surface, as the electrode charge attracts counter-ions within the solution. A simplified schematic of the electrical double layer is shown in figure 2.2, for a negatively charged electrode.

In reality, the composition of the double layer is highly complex, but here it is sufficient to visualize two oppositely charged layers over which the majority of the electrode-electrolyte potential drop occurs. It is not possible to experimentally determine  $\Delta \varphi_{Galvani}$ , but if a second electrode is introduced whose Galvani potential difference  $\Delta \varphi'_{Galvani}$  is constant, it is possible to measure the electrode potential E, relative to this second, reference electrode [23]:

$$E = \Delta \varphi_{Galvani} - \Delta \varphi_{Galvani}$$
(2.8)

Electrode	Double layer	Electrolyte
	++++++++	

Figure 2.2: Illustration of the electric double layer formed at the electrodeelectrolyte interface.

In a system with an active redox couple, E is decided by the reduction potential of the associated half reaction [22, 23]. The reduction potential is a measure of how easily the oxidizing agent of the redox couple is reduced, and corresponds to the potential at which the half reaction produces no net current, meaning that the forward and backward reaction rates are at equilibrium. When a redox reaction takes place in an electrochemical cell, the voltage of the cell, often referred to as just the cell potential,  $E_{cell}$ , will be the difference between its respective electrode potentials.

$$E_{cell} = E_1 - E_2 \tag{2.9}$$

At equilibrium, indicated from now on by a <sup>0</sup>, the cell potential  $E_{cell}^0$  gives the theoretical maximum amount of electric work  $W_{max}$  that can be obtained from a redox reaction involving the transfer of n electrons, through

$$W_{max} = -nFE_{cell}^0 \tag{2.10}$$

where the Faraday constant F (96 485 C/mol), corresponds to the electric charge of one mole of electrons.  $W_{max}$  is also the minimum amount of work that must be applied in order to force the reactions of 2.1-2.3 to occur in the opposite direction. In the case where all non-expansion work from an electrochemical reaction is in the form of electric work, equations 2.6 and 2.10 can be combined into

$$E_{cell}^{0} = -\frac{\Delta G}{nF} = -\frac{\Delta G^{\circ}}{nF} - \frac{RT}{nF} lnQ_{r} = E_{cell}^{\circ} - \frac{RT}{nF} lnQ_{r}$$
(2.11)

which is known as the Nernst equation, relating the equilibrium cell potential  $E_{cell}^0$  to its equilibrium potential at standard conditions,  $E_{cell}^{\circ}$ . In a similar manner, the equilibrium potential  $E^0$  of an individual electrode can be expressed as a function of its equilibrium potential at standard conditions,  $E^{\circ}$ .

$$E^0 = E^\circ - \frac{RT}{nF} lnQ_r \tag{2.12}$$

It should be noted that  $Q_r$  in the two last equations are specific for either the associated electrode half-reaction, or for the overall cell reaction. It further follows from the definition of the Nernst equation for the cell potential that the overall reaction quotient is the ratio between the reaction quotients from the two electrode reactions. For the simple general case discussed in section 2.1, these are obtained according to equation 2.5, and the reaction quotient for the overall reaction becomes:

$$Q_{r,overall} = \frac{Q_{r,1}}{Q_{r,2}} = \frac{\frac{a_{Y^{n-}}}{a_Y}}{\frac{a_X}{a_{Y^{n+}}}} = \frac{a_{X^{n+}}a_{Y^{n-}}}{a_X a_Y}$$
(2.13)

The Nernst equation is a central concept in electrochemistry, and can be extended to redox reactions with an arbitrary number of reactants and products. We will return to the Nernst equation in chapter 3 when discussing the redox reactions of PEMFCs.

#### 2.2.2 Reference potentials

It is virtually impossible to experimentally determine the absolute values of any practical electrode potential [24]. As a consequence, electrode potentials are typically reported relative to a reference potential. There are many possibilities to define a reference potential, of which the most common is the standard hydrogen electrode (SHE). The SHE is defined as the potential of a Pt electrode immersed in an ideal aqueous solution with an  $H^+(aq)$  ion activity of 1, bubbled with a hydrogen gas pressure of 1 bar [23]. This potential is purposely set as 0 V, at all temperatures, and is often used to compare the potential of electrode reactions in various electrolytes. The great strength of the SHE is that it provides a robust, well-defined universal potential, to which any electrode potential can be related. However, in many systems, operating far from ideal or standard conditions, it is more practical to define other types of reference potentials. The most useful for the work in this thesis, and the one that will be mainly referred to from now on, is the reversible hydrogen electrode (RHE). The reaction that provides the potential, known as the hydrogen electrode reaction, is the same for both SHE and RHE, and is highlighted in equation 2.14. In contrast to SHE, RHE is simply defined as the potential of the hydrogen electrode reaction on Pt in the electrolyte of interest. Hence, its value varies with pH in relation to SHE, but has the advantage that it can be determined directly in the same system as the electrode.

$$\frac{1}{2}H_2 \rightleftharpoons H^+ + e^- \tag{2.14}$$

In addition to these two reference potentials based on the hydrogen electrode reaction, other chemical equilibria can be used to provide a reliable potential reference value. Two example of reference electrodes based on other chemical reactions are those of the silver-silver chloride and mercury-mercury sulfate electrodes. The two electrode processes are given in equations 2.15 and 2.16, where the indicated electrode potentials vs. SHE are for the cases of saturated KCl and  $K_2SO_4$  electrolytes, respectively [23].

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$
 0.1976 V vs. SHE (2.15)

$$Hg_2SO_4 + 2e^- \rightleftharpoons 2Hg + SO_4^{2-}$$
 0.650 V vs. SHE (2.16)

Reference electrodes like the two explained here are commonly used when measuring potentials in practical electrochemical cells. A prominent advantage compared to the hydrogen electrodes is that they do not rely on bubbling of gases, meaning that they can simply be inserted into the cell, without the need for complex auxiliary equipment.

#### 2.2.3 Overpotential

When an electrochemical system is used for the conversion of chemical energy into electricity (galvanic cell) or vice versa (electrolytic cell), the conversion efficiency will always be less than 1 [23, 25]. The explanation is that every real system is associated with various types of losses throughout the system. For a galvanic cell, the power output at a specific current depends on the cell potential. Due to the different system losses, there will always be a difference between the actual cell potential of the cell  $E_{cell}$ , and the theoretical maximum derived from the reduction potentials of the half-reactions,  $E_{cell}^0$ . This difference  $\eta_{cell} = E_{cell} - E_{cell}^0$  is known as the cell overpotential. Similarly, the overpotential at a specific electrode is defined as the difference between its observed potential and the reversible equilibrium potential,  $\eta = E - E^0$ .

The implication of the overpotential for a galvanic cell is that its cell potential, and hence its power output, will decrease as the current increases. In contrast, electrolytic cells need to operate at cell potentials larger than the reversible cell potential to facilitate the reactions, and the cell potential increases with



Current / A

Figure 2.3: Schematic illustration of current-voltage dependence of galvanic (turquoise) and electrolytic (pink) cells. Electrode potentials are indicated by solid lines, while equilibrium potentials are shown as dashed lines. Coloured areas between the solid lines display how the respective cell voltage of galvanic and electrolytic cells change with increasing currents.

increasing current. These behaviors are qualitatively shown in figure 2.3. In reality, the current-voltage dependence is not linear as in figure 2.3, and a single model of this dependence would require simultaneous account of all different types of losses. Instead, the overpotential-dependencies of redox reactions are often broken down into specific scenarios, which are modeled individually. A commonly used approximation for low to moderate currents is the Butler-Volmer equation (2.17) [26, 27]. This description relates the current density j to the electrode overpotential  $\eta$  while assuming negligible mass transport losses and rate-limiting electron transfer kinetics [23].

$$j = j_0 \left( e^{\frac{(1-\alpha)nF\eta}{RT}} - e^{\frac{-\alpha nF\eta}{RT}} \right)$$
(2.17)

The first exponential term in the Butler-Volmer equation corresponds to an anodic current contribution, while the second is the cathodic contribution. In the expression, the pre-exponential factor  $j_0$  is the so called exchange current density and  $\alpha$  is a symmetry factor, describing the relationship between electron transfer in the forward and backward directions. Figure 2.4a shows typical current-overpotential responses for different values of  $j_0$ , when n = 1 and  $\alpha = 0.5$ . At zero overpotential, the two contributions cancel out, but for non-zero deviations from the equilibrium potential, it is possible to identify two different limiting cases [27]. If we first consider the case of very small overpotentials around the equilibrium, figure 2.4a indicates a linear relationship between the current and the overpotential. This trend can be further elucidated by performing a Taylor expansion of the equation around the equilibrium potential. Neglecting terms of the second order and above, the following relationship is obtained:

$$j = j_0 \frac{nF}{RT} \eta \tag{2.18}$$

This linear relationship typically holds only for very small overpotentials (<10 mV). If, on the other hand, the overpotential is of moderate size, either the anodic or the cathodic term will dominate the current response, depending on the sign of the overpotential. If one of the terms can be neglected, the anodic and cathodic cases are represented by equations 2.19 and 2.20 respectively.

$$j = j_0 e^{\frac{(1-\alpha)nF\eta}{RT}} \tag{2.19}$$

$$j = j_0 e^{\frac{-\alpha n F \eta}{RT}} \tag{2.20}$$

Equations 2.19 and 2.20 can also be expressed in their logarithmic forms (with base 10), for which linear dependencies of the logarithmic anodic and cathodic current densities on the overpotential are obtained:

$$log(j) = log(j_0) + \frac{(1-\alpha)nF}{2.3RT}\eta \qquad \text{for positive } \eta \qquad (2.21)$$

$$log(|j|) = log(j_0) - \frac{\alpha n F}{2.3RT} \eta \qquad \text{for negative } \eta \qquad (2.22)$$



Figure 2.4: a) The Butler-Volmer equation represented in its general form, with n = 1 and  $\alpha = 0.5$  for three different values of  $j_0$ : (i)  $j_0 = 0.1$ , (ii)  $j_0 = 0.01$ , (iii)  $j_0 = 0.001$ . b) Logarithmic representation of the Butler-Volmer equation and its limiting cathodic and anodic cases when n = 1,  $j_0 = 0.1$  A cm<sup>-2</sup>, and  $\alpha = 0.5$ . The corresponding Tafel slopes are indicated by dashed lines.

Figure 2.4 b) plots equations 2.21 and 2.22 together with the Butler-Volmer equation (2.17), for the case where n = 1,  $j_0 = 0.1$  A cm<sup>-2</sup>, and  $\alpha = 0.5$ . The plot shows that for overpotentials larger than  $\pm 50$  mV, equations 2.21 and 2.22 are exceptional approximations of the Butler-Volmer equation. Additionally, the slopes of the linear sections in figure 2.4 b), known as Tafel slopes, tell us that the current density increases by one order of magnitude for every 120 mV increase in the overpotential, showing the strength of the overpotential as a driver for electrochemical reactions [27].

From both the general expression and the two limiting cases of the Butler-Volmer equation, it is clear that in situations where the equation is valid, the current is directly proportional to the exchange current density  $j_0$ . Looking once again at the three current density-overpotential responses of figure 2.4 a), the significance of  $j_0$  is clearly realized from how it affects the onset potential of the reaction. In essence,  $j_0$  represents the rate of electron transfer at equilibrium. A large value of  $j_0$  is highly beneficial for the overall rate of electrochemical reactions, and the magnitude of  $j_0$  is the principal quantity that can be increased by introducing a catalyst [23].

# 2.3 (Electro-) catalysis

Catalysis is a central concept for many chemical reaction technologies [28–30], and so also for many electrochemical systems. In its pure essence, catalysis is the act of changing the rate of a reaction, performed by a material or chemical specie (i.e. the catalyst) which is not itself consumed by the reaction.

The main field of catalysis can be subdivided into two branches, homogeneous and heterogeneous catalysis. What separates the two branches from each other is the phases in which the reactants and the catalyst are present. In homogeneous catalysis, the catalyst is in the same phase as the reactants, typically in the liquid phase. In contrast, in heterogeneous catalysis, the catalyst is in a phase different from that of the reactants. Typically, solid catalysts are used to increase the rate of gas- or liquid-phase reactions. Hydrogen fuel cells utilize heterogeneous catalysis through a solid-phase catalyst and gas-phase reactants.

#### 2.3.1 Heterogeneous catalysis

The reaction rate of a catalytic reaction is determined by the interactions occurring between the reactants and the catalyst surface. To understand the reaction rate, it is necessary to mention the concept of activation energy. According to the Arrhenius equation (2.23) [22], the rate constant of a reaction k, is determined by a pre-exponential factor (A) and an exponential expression containing the activation energy of the reaction  $E_a$ , the gas constant R, and the temperature T.

$$k = Ae^{-\frac{E_a}{RT}} \tag{2.23}$$

The rationale behind the Arrhenius activation energy is that, for a set of reactants to transform into reaction products, an energy barrier  $(E_a)$  must be overcome. Activation barriers originate from breakage of chemical bonds, producing transition states with higher energy, before new bonds are created as the product is formed [31]. Although statistically possible if the final reaction products have lower energy than the reactants, such activated processes proceed exceptionally slow unless sufficient energy is supplied. The reaction rate constant can be thought of as the number of collisions between reactants that result in a reaction, during some unit of time. The pre-exponential factor reflects the total amount of collisions between reactants per unit time and has a temperature dependence. The exponential term instead indicates the probability that such collisions will result in a reaction and is strongly dependent on both temperature and activation energy. From the Arrhenius equation it

is evident that increasing the temperature and/or decreasing the activation energy improves the reaction rate.



Reaction coordinate

Figure 2.5: Qualitative energy diagram of a chemical reaction showcasing both the catalysed, and the uncatalysed reaction path.

A catalyst functions by providing an alternative reaction pathway that lowers the transition state energies. This typically involves a chain of events (elementary steps) in which the reactants are first bonded to various active sites on the catalyst surface during the adsorption and diffusion steps. Subsequent elementary steps typically consist of surface reactions into intermediate states and/or the final product, followed by the desorption of the product. Associated with each elementary step is, to varying degrees, an energy barrier. Figure 2.5 illustrates how such a catalyzed reaction pathway could look, compared to the uncatalyzed reaction. As depicted in the figure, all individual elementary steps of the catalyzed pathway exhibit energy barriers smaller than the one of the uncatalyzed reaction, which results in a faster overall reaction rate.

When evaluating the potential of a material to catalyze a specific chemical reaction it is common to investigate the binding energies of the different species participating in the reaction. For a catalyst to perform well, it is important that its binding strength with any such specie is neither too high nor too low. If the binding is too weak, reactants and intermediates will either not bind, or desorb before any reaction takes place, while if too strong, efficient blocking of active sites will arise by products or intermediates. The concept of relating binding strength to catalytic activity is called Sabatier's principle [32], and results in a volcano-shaped plot as shown in figure 2.6. The best catalysts for the reacton in question, are found close to the top of the volcano at a corresponding optimum binding energy  $E_{opt}$ .

Another important factor to consider in catalyst development, is the catalysts



Figure 2.6: Sabatier's principle illustrated in the form of a volcano plot of catalytic activity versus binding energy of an arbitrary specie.

ability to selectively promote the wanted reaction(s), while suppressing the unwanted ones. While a deeper discussion on PEMFC catalysis is left for chapter 3, it is at this stage sufficient to stress the importance of developing cheaper and more efficient PEMFC catalysts. To succeed, the target catalyst should approach the top of the volcano in terms of activity towards the relevant reactions, while exhibiting both good selectivity, promoting water formation over hydrogen peroxide, and long-term stability.

#### 2.3.2 Electrocatalysis

When an electrochemical reaction is catalyzed, it is referred to as electrocatalysis. Many of the elementary steps in an electrocatalyzed reaction are the same as those in heterogeneous catalysis; however, unique for electrocatalysts are that they also need to assist the electron transfer to or from the specific halfreaction. The oxygen reduction reaction (ORR) is an important example of electrochemical reactions that require a catalyst to run efficiently, as well as the most relevant for this thesis. A more detailed description of the catalytic mechanisms of ORR will be given when we return to it in chapter 3 on PEMFCs. Now, it is sufficient to note that ORR is a relatively complicated reaction involving the transfer of up to 4 electrons and the breakage of an O-O bond. Without a catalyst, the reaction runs very slowly, but introducing a catalyst surface with an affinity for adsorbing oxygen can significantly speed up the reaction. Here, the magnitude of this affinity, in terms of oxygen binding energy, becomes important. Figure 2.7 highlights the dependence of ORR activity as a function of oxygen binding energy for a wide range of metals [33]. Indeed, they appear to follow the Sabatiers principle, as indicated by the characteristic volcano plot. Pt is located close to the top of the volcano, and a small weakening (0.1 eV) of its binding energy with oxygen would result in an optimal binding strength.



Figure 2.7: Volcano plot for the ORR activity as a function of O binding energy. Data is from [33].

An electrocatalyst can be employed in many different ways. In some applications, the electrode itself is the catalyst, whereas in fuel cells the catalyst material is often coated on top of the electrode in the form of highly dispersed, carbon-supported Pt nanoparticles, as will be discussed in the next chapter.

# 2.4 Applications

Electrochemical principles are the basis for several fundamental energy technologies, including batteries, fuel cells, and electrolysers. A fuel cell converts chemical energy stored in a fuel to electricity according to the mechanisms described for a galvanic cell above. Electrolysers are instead electrolytic cells, in which electrical energy is supplied to drive a chemical reaction. In this way, hydrogen can be produced for subsequent deployment using a fuel cell. Batteries are, similarly to fuel cells and electrolysers, energy converters. The main difference between batteries and fuel cells, is that batteries act directly as energy storage, while fuel cells require external storage and continuous supply of fuel to produce electricity. Furthermore, rechargeable batteries acts as electrolytic cells while charging and galvanic cells during discharge. In general, batteries offer exceptional energy conversion efficiencies, outperforming both fuel cells and electrolysers in this regard. However, batteries suffer from low gravimetric energy density, making them heavy and not well suited for heavy-duty and long-range transport. Fuel cells offer both lighter weights and faster refuelling, compared to batteries, making them an attractive alternative for these types of applications.

# Chapter 3

# Proton exchange membrane fuel cells

The history of fuel cells is almost as old as that of electrochemistry. Credited with the invention of the first fuel cell in the late 1830s is William Robert Grove [20, 34, 35]. Later, in the early 1930s, Francis Thomas Bacon started developing the first practical alkaline fuel cell, and his technology was later proven useful in the Apollo space missions [20, 21]. Fuel cell technology has developed tremendously since its early days, and today many different types of fuel cells exist. The proton exchange membrane fuel cell (PEMFC) is the most widely used type thanks to its wide range of applications [36], particularly within the transport sector. It is also the fuel cell technology towards which the main focus of this thesis is directed. Before going further into the details of PEMFCs and their fundamental theory, a brief review of other important fuel cell technologies, and the advantages of PEMFCs, is presented.

## 3.1 Fuel cell types

Fuel cells come in many different designs, all of which have their specific, inherent advantages and disadvantages. Furthermore, what aspects and traits are most crucial is most often application-dependent. One way to categorize fuel cells is to group them by their operating temperature, leading to the identification of two main classes: low-temperature- and high-temperature fuel cells. High-temperature fuel cells are mainly aimed at stationary applications [36] where better utilization of their high heat output is possible and the need for start-stop situations is few. Two examples of high-temperature fuel cell chemistries are solid oxide and molten carbonate fuel cells. As their names suggest, electrolytes in these types of cells consist of a solid oxide, often a mix of zirconia and yttria, or a molten carbonate, typically sodium and potassium carbonate, supported by a ceramic matrix [36]. The reactions of these types of fuel cells are facilitated at elevated temperatures in the range of 600–1000 °C and utilize a wider range of fuels than low-temperature systems.

Low-temperature fuel cells, on the other hand, are typically based on aqueous electrolytes and therefore operated below 100  $^{\circ}$ C. Different cell chemistries are possible, and the two main groups consist of acidic and alkaline fuel cells, respectively, where PEMFCs belong to the former. Within the two groups, one can further distinguish between fuel cells with liquid electrolytes (for example alkaline fuel cells (AFCs)) and fuel cells based on ion conducting membranes (for example PEMFCs, anion exhange membrane fuel cells (AEMFCs), and direct methanol fuel cells (DMFCs)). The latter type of fuel cells are highly suitable for applications within mobility and other areas where a high power output per weight is important [36, 37]. Regardless of the type and chemistry, all fuel cells share the same overall function and components, although the nomenclature sometimes differs.

#### Advantages of PEMFCs

The fact that PEMFCs operate at low temperatures is accompanied by several advantages compared to their high-temperature relatives. At high temperatures, both the thermal and mechanical properties of the fuel cell components become increasingly important. Hence, PEMFCs offer lighter weights and more flexibility in material selection and modularity [36]. Another advantage is the fast start-up times, which, together with their high energy density, makes PEM-FCs the most widely considered fuel cell technology for transport applications, where weight and start-up time are some of the most important aspects [36, 37]. Compared to low-temperature fuel cells based on liquid electrolytes, a crucial advantage of the membrane-based fuel cells is that both the membrane and the cell can be made very thin, reducing cell resistance and improving the overall power density significantly. Compared to its alkaline equivalent, the AEMFC. PEMFCs are less sensitive to  $CO_2$ -poisoning, which readily reduces the performance and durability of AEMFCs [38, 39]. Furthermore, PEMFCs exhibit better ionic conductivity, due to the faster transport of H<sup>+</sup> ions compared to OH<sup>-</sup> for AEMFCs.

# 3.2 Components

The general components of a PEMFC are its two electrodes (cathode and anode) and a proton exchange membrane (PEM). To the electrodes belong an assembly of carbon-supported catalyst layers, gas diffusion layers (GDLs) and flow field plates for transport of reactants and products, current collectors, and a frame for stability. An overall schematic of a single cell is shown in figure 3.1. Many single cells are generally stacked in series to form a fuel cell stack and boost the power output. Then reactant and product transport, current collection and mechanical stability are all provided by one single component called a bipolar plate. Although fuel cell stacks are the most relevant configuration for real applications, I will limit this discussion to the components of a single-cell PEMFC.



Figure 3.1: PEMFC schematic, showcasing the different components. Directions of electron-, ion-, reactant-, and product flows are indicated with arrows.

#### Proton exchange membrane

The heart of a PEMFC and the origin of its name, is the proton conducting membrane, specifically constructed to allow transport of protons from the anode to the cathode, while acting as an impermeable barrier for electrons and reactant gases [40]. The most common PEM types are different kinds of perfluorosulfonic acids, consisting of perfluorinated polymer backbones with sulfonic acid functionalized sidechains grafted onto the backbone. The perfluorinated backbone gives the membrane its mechanical strength and prevents excess swelling when exposed to water, while the hydrofilic sulfonic acid groups allows absorption of water, which is necessary for ion conduction through the membrane [41]. Proton conduction in these types of membranes occurs via two distinct mechanisms [42]: (1) vehicular diffusion of  $H_3O^+$  ions induced by the concentration difference between the cathode and the anode, and (2) the Grotthuss mechanism in which "proton hopping" occurs between the absorbed water molecules in the membrane. Which mechanism contributes the most to the overall proton conductivity of perfluorinated sulfonic acid membranes is mainly decided by the membrane hydration level [42].

### Electrodes

When referring to the electrodes of a fuel cell, one generally means the catalyst layer, situated closest to the membrane. This is where the reactions occur, and it is between the two catalyst layers at the anode and cathode sides of the fuel cell that the voltage arises. The most common configuration of the catalyst layer is that of Pt nanoparticles supported on a highly porous, large surface area carbon structure, as depicted in figure 3.2. To ensure good contact with protons in the membrane and allow transport of reactants to the catalyst surface, high porosity and surface area, as well as good dispersion of catalyst particles over the support, are key [43]. In addition, the catalyst layer needs to provide electrical contact to facilitate efficient electron transport to and from the respective electrode reactions, and ionic contact with the membrane for efficient proton transport. The latter is typically ensured by covering the catalyst layer particles with a thin ionomer coating, often in the form of perfluorosulfonic acid [43].

On the other side of the catalyst layer from the perspective of the membrane, there are a GDL, a flow field, and a current collector, see figure 3.1. The flow field and current collector are most often combined into a single component, called a bipolar plate, which typically consists of a metal plate with incorporated channels that simplify the flow of gases and water. The GDL, typically in the form of a fibrous carbon paper or cloth, is situated between the bipolar plate and the catalyst layer [25]. Its purpose is to provide an even distribution of reactant gases and electric current to the catalyst layer, efficiently remove the water produced in the reaction, and add mechanical stability to the catalyst layer [25, 44].



Figure 3.2: An illustration of Pt catalyst nanoparticles (white) supported on a porous structure of high surface area carbon (black). Practical catalyst layers are typically covered by a thin ionomer layer as explained in the text. Hence, for clarity, I want to point out that the ionomer layer is not displayed in this illustration.

## 3.3 Reactions

The overall reaction of a PEMFC consists of the reaction between gaseous hydrogen and oxygen, forming water as the sole product.

$$2H_2(g) + O_2(g) \to 2H_2O(l)$$
 (3.1)

The reaction can, in similarity to all other redox reactions, be described by its two half reactions, oxygen reduction (equation 3.6) and hydrogen oxidation (equation 3.2). These two half-reactions are inherent to all types of hydrogen fuel cells, however, the species participating in the half-reactions differ depending on the cell chemistry. The reaction pathways described here are the ones valid in acidic media.

#### 3.3.1 Hydrogen oxidation reaction

At the anode side of a PEMFC, hydrogen is oxidized by the dissociative splitting of hydrogen molecules into protons and electrons, in a half reaction denoted as the hydrogen oxidation reaction (HOR) [45].

$$H_2 \to 2H^+ + 2e^-$$
 (3.2)

The reaction involves only one adsorbed intermediate,  $H^*$ . The possible reaction pathways are presented in equations 3.3–3.5 including three different elementary reaction steps, that can be combined into two different HOR pathways, the Tafel-Volmer and Heyrovsky-Volmer [45].

Tafel 
$$H_2 + 2^* \to 2H^*$$
 (3.3)

Heyrovsky 
$$H_2 + * \rightarrow H^* + H^+ + e^-$$
 (3.4)

Volmer 
$$H^* \to H^+ + e^- + *$$
 (3.5)

In the Tafel-Volmer pathway, a hydrogen molecule adsorbs dissociatively to the catalyst surface, followed by two individual one-electron oxidations of the adsorbed hydrogen atoms into protons and electrons. The Heyrovsky-Volmer pathway, however, involves instead the chemisorption of one hydrogen atom and a one-electron oxidation of the second hydrogen atom, in the first step. The first step is followed by another one-electron oxidation of the adsorbed hydrogen atom. The hydrogen adsorption free energy,  $\Delta G_H$ , largely determines the overall rate of the HOR reaction, although kinetic barriers also influence the rate [45]. The latter can be dependent on reaction conditions such as pH, as exemplified by the decrease in exchange current density with increasing pH observed on Pt catalysts [46]. However, in the acidic environment inherent to PEMFCs, the HOR is efficiently catalyzed by Pt already at very low overpotentials [45].

#### 3.3.2 Oxygen reduction reaction

The oxygen reduction reaction (ORR) is the cathode-side half-reaction in a PEMFC. In acidic media, ORR consists of the combination of oxygen, protons, and electrons to form water.

$$O_2 + 4H^+ + 4e^- \to 2H_2O \tag{3.6}$$

This is called the four-electron pathway, as it involves four electrons for every oxygen molecule being reduced. A competing reaction pathway exists, in which an oxygen molecule combines with two electrons and two protons, forming hydrogen peroxide.

$$O_2 + 2H^+ + 2e^- \to H_2O_2$$
 (3.7)

For fuel cell applications, this two-electron pathway is unfavorable because it results in less current, and  $H_2O_2$  degrades the ionomer and the membrane. The four-electron route can follow several potential mechanisms [33, 45, 47], including the dissociative mechanism (equations 3.8–3.10) and the associative mechanism (equations 3.11–3.15).

Dissociative: 
$$O_2 + 2^* \to 2O^*$$
 (3.8)

$$2O^* + 2H^+ + 2e^- \to 2OH^* \tag{3.9}$$

$$2OH^* + 2H^+ + 2e^- \to 2H_2O + 2^* \tag{3.10}$$

Associative: 
$$O_2 + {}^* \to O_2^*$$
 (3.11)

$$O_2^* + H^+ + e^- \to OOH^*$$
 (3.12)

$$OOH^* + H^+ + e^- \to H_2O + O^*$$
 (3.13)

$$O^* + H^+ + e^- \to OH^* \tag{3.14}$$

$$OH^* + H^+ + e^- \to H_2O + *$$
 (3.15)

In the dissociative mechanism, the oxygen molecule dissociates into two adsorbed oxygen atoms, which combines with two protons and two electrons into adsorbed OH. The adsorbed OH combines with another two proton-electron pairs, forming water. The associative reaction pathway has instead the adsorption of an oxygen molecule as the first elementary step, which then combines with a proton-electron pair into adsorbed OOH. In the third step, OOH reacts with another proton-electron pair, releasing water from the surface, leaving behind an adsorbed oxygen atom. The adsorbed oxygen atom then reacts according to the two last steps of the dissociative pathway. The actual reaction mechanism is decided by the dissociation barrier of oxygen on the specific catalyst surface.

Pt is the best elemental catalyst for the ORR, however, recalling the volcano plot presented in figure 2.7, its binding energy with oxygen is approximately 0.1 eV too strong. A consequence of this suboptimal binding to oxygen species is that proton-electron transfer to  $O^*$  or  $OH^*$  limits the activity at high potentials (1-1.23 V) [33, 45]. Hence, it is of high interest to develop catalysts with more beneficial oxygen interactions, in order to minimize these activity limitations.

#### 3.3.3 Cell potential

The equilibrium electrode potentials of the HOR and ORR half reactions follow directly from the Nernst equation (2.12, and are 0 V and 1.23 V vs. SHE at standard conditions, respectively. For other values of pH, the corresponding reduction potentials can be visualized in a so-called Pourbaix diagram, as shown in figure 3.3. It is evident from the diagram that the equilibrium potential of both HOR and ORR decreases with increasing pH, however, both with the slope of -0.059 V/pH, consistent with the Nernst equation. As a result, the theoretical maximum cell potential of a PEMFC at ambient temperature and pressure is 1.23 V, for any pH. As we shall see, because of various types of losses, the current-voltage behavior of PEMFCs is far from the ideal case, particularly when the cell produces current.



Figure 3.3: Pourbaix diagram of water, showing its stability region at different pH, and the corresponding reduction potentials of the hydrogen and oxygen electrodes. The data was retrieved from reference [48].

# 3.4 Losses

The concept of overpotential was introduced in chapter 2, and here, different types of losses causing the cell potential drop in operating fuel cells are discussed. Generally, three types of losses can be described, namely *activation losses* in the electrode, *ohmic losses* in the membrane, electrodes and external circuitry, and losses due to inefficient *mass transport* of reactants and products [25].

## Activation losses

Recalling the concept of activation energy introduced in chapter 2, for a chemical reaction to occur, it must overcome an activation energy barrier. Catalysts are used to effectively decrease these barriers and speed up the reactions, however, a certain energy barrier will always remain. In a PEMFC, the main source of overpotential is due to activation losses in the ORR half-reaction, which results in an instant drop of the cell potential at zero current according to figure 3.4. The reason for the large overpotential has been described theoretically [33, 45, 47], and is related to the many intermediates  $(O^*, OH^*, OOH^*)$  involved in the reaction. The binding energies of these intermediates are highly correlated according to scaling relations [33], and cannot be optimized simultaneously by a single catalyst, leading to the considerable overpotential observed in fuel cells at low currents. As we start to draw current from the PEMFC, the voltage response roughly follows the one predicted by the Butler-Volmer equation. At lower potentials, the reaction rate is no longer limited by electrode activation. Eventually, the current-voltage behavior shifts from an exponential form to a more linear one, suggesting that something else is dominating the response.

# Ohmic losses

Any electric or ionic conductor is associated with a certain amount of resistance to the flow of electrons and ions, respectively. In a PEMFC, resistive losses occur in the electrolyte membrane, the electrode materials, and the electrical interconnections. The response, in the form of a cell potential drop, is linear with increasing currents. Hence, as reflected in figure 3.4, its impact is small for low currents, but becomes a concern in higher power situations, and explains the linear behavior of the performance curve in the 500–1500 mA/cm<sup>2</sup> region.

#### Mass transport losses

As the current in a fuel cell increases, so does the consumption of reactants at the electrodes. According to the Nernst equation (2.12), reactant and product concentrations affect electrode potentials. Therefore, inefficient supply of fresh reactants to the electrodes decreases the overall cell potential of the cell. In a PEMFC cathode, where oxygen is supplied in the form of air, inert nitrogen, not consumed by the reaction, can effectively block the transport of fresh oxygen to the electrode, at high currents [25]. Further blocking can arise if the reaction product, water in the case of PEMFCs, is not removed at an adequate rate. Furthermore, mass transport losses are responsible for the voltage breakdown at


Figure 3.4: Qualitative illustration of a PEMFC performance curve (black). Approximate activation, ohmic and mass transport losses are indicated (dark blue) along with the reversible cell voltage (light blue).

high currents indicated in figure 3.4, and as a consequence, these high-current regions are normally avoided in fuel cell operation.

### 3.5 Catalyst materials

The PEMFC is, because of its acidic nature along with fluctuating operating potentials, a very harsh environment for catalyst particles. As a result, noble Pt is the most widely used PEMFC catalyst material, exhibiting both good chemical stability and high catalytic activity toward the HOR and ORR reactions. However, Pt is scarce and expensive, which is an obstacle to large-scale commercialization of PEMFCs. To facilitate a widespread transition of heavy duty long-range transport into a fuel cell-based sector, Pt utilization must be improved.

### Alternatives

When alternative replacements for Pt in PEMFCs or any other type of catalyst material are discussed, there are three main aspects to consider: catalytic activity, stability, and selectivity.

The catalytic activity is a measure of the rate at which a catalyst facilitates a certain reaction, and it is naturally of high importance when designing new

catalysts. The better intrinsic catalytic activity a material has, the less material is needed to obtain satisfactory performance. However, high catalyst stability is equally important to ensure that the catalytic activity is maintained over time. Finally, selectivity is crucial in promoting the preferred reaction and preventing the unwanted ones. In PEMFCs, as mentioned in 3.3.2, a competing reaction to the main four-electron cathode side reaction is the two-electron pathway, which results in less current as only half the number of electrons are involved in this type of ORR. Hence, a good PEMFC catalyst material should promote the four-electron ORR pathway.

Catalytic activity can be defined in different ways, but the two most relevant definitions for practical PEMFC catalysts are the specific activity of the active surface and the mass activity of the full catalyst ensemble. The specific activity is an average measure of the contributions from all individual active sites and is therefore normalized by the total electrochemical surface area (ECSA) of the catalyst. As mentioned in chapter 2, the catalytic activity of a material depends on its adsorption free energies with the relevant chemical species. For Pt ORR catalysts, both theoretical and experimental investigations have shown that terrace sites with a larger coordination number (typically the Pt (111)-surface) exhibit more favorable binding energies with oxygen adsorbates than under-coordinated step and edge sites [49, 50]. The relative portion of terrace sites tend to increase with particle size and is maximized for a flat, extended surface. As a consequence, Pt specific ORR activity typically increase with particle size, until it reaches the specific activity of an extended Pt surface [49, 51]. The mass activity, on the other hand, relates the catalytic performance to the total catalyst mass. For scarce and expensive materials, like Pt and its alloys, the mass activity is crucial to ensure high material utilization and reduce cost. While specific activity mainly depends on the available active sites at the catalyst surface, the mass activity is highly sensitive to the catalyst shape, size, and morphology. Inevitably, to obtain the highest possible Pt ORR mass activity, there will be a trade-off between the specific activity and the surface-to-volume ratio [51].

One way to improve the ORR activity of a catalyst is to alter its binding energy to oxygen species, which can be done by alloying. For Pt, which is already close to the top of the volcano plot in figure 2.7, a weakening of the oxygen binding energy of approximately 0.1 eV is needed to reach the optimum. The two main groups of Pt alloying agents that have been reported for ORR are late transition metals, with cobalt and nickel being the most studied [52–56], and rare earth metals, including yttrium [57–64] and the lanthanides [58, 65–67].

Pt-late transition metal alloys have the advantage of exceptional ORR activities, reaching enhancement factors of up to 10 times that of polycrystalline Pt [52], but they suffer from dealloying during long-term operation [68, 69]. Pt-rare earth metal (Pt-RE) alloy activity enhancements have been reported as comparable to those of Pt-late transition metal alloys. The reason for their enhanced activities is the formation of a thin, pure Pt skin at the material surface [67] when exposed to acidic environment. The Pt overlayer, about a



Figure 3.5: Illustration of a  $Pt_3RE$  alloy material, showcasing the compressed overlayer caused by the larger atomic radii of RE atoms in the alloy core. The schematic is not supposed to reflect the exact crystal structure of a specific  $Pt_3RE$  alloy, but to highlight the general trend(s) for the whole group of Pt-RE materials.

nm thick, is affected by the lattice mismatch with the alloy core underneath, which induces a compressive strain in the shell [66], as illustrated in figure 3.5. This strain has been attributed to cause a slight weakening of the binding energy with oxygen species, and hence to increase the specific ORR activity [57]. Furthermore, with more favorable alloy formation energies, Pt-REs provides better catalyst stability than Pt-late transition metal alloys [59].

### 3.5.1 Thin films

Thin films are convenient model systems when studying a material's catalytic performance, as they are easily produced in a reproducible manner and can be coated directly onto half-cell electrodes or fuel cell microporous layers. They do not provide the same amount of material utilization as well-dispersed nanoparticle catalysts, but have, regardless, found some commercial success [70].

### 3.5.2 Nanoparticles

As we have already argued, Pt nanoparticles supported on a microporous carbon support are the most common catalyst used in PEMFCs. Pt-RE nanoparticles could potentially become a serious contender to Pt, if the enhanced ORR activity is successfully implemented in practice. The amplitude of the overlayer strain and the associated enhancement of specific ORR activity have been shown to increase with nanoparticle size [57]. When the size of a particle is increased, the surface-to-volume ratio decrease is inversely proportional to the radius. To ensure high utilization of catalyst materials, it is desirable to maximize the mass activity of the nanoparticle catalyst.

### 3.5.3 The Dream Particle

The trade-off between specific activity and surface-to-volume ratio is not unique to Pt-REs, but the fact that the specific activity enhancement compared to Pt also increases with size means that the optimal Pt-RE nanoparticle size will differ from the optimal Pt nanoparticle size. This allows us to introduce the idea of a "Dream Particle", which exhibits the highest ORR activity enhancement compared to that of Pt. By mass-selection of sputtered nanoparticles, the optimal nanoparticle sizes for  $Pt_x Y$  [57] and  $Pt_x Gd$  [65] has been shown to be in the range of 8–10 nm, compared to the optimum of 3 nm found for pure Pt particles [49].

Although various techniques have been used to display the excellent ORR activities of Pt-RE nanoparticles, no technique has yet been able to provide scalability while maintaining the ultra-high catalytic performance in terms of activity and stability. The extreme reduction potentials and oxygen affinities of rare earth elements effectively prevent the use of conventional nanoparticle synthesis routes [71, 72]. Hence, a gap exists in the arsenal of synthesis techniques in order to meet the high requirements of the rare earth metals and enable fabrication of high-performance fuel cell catalyst layers. If Pt-RE alloys are to become a competitor to Pt as a standard PEMFC catalyst, this gap needs to be addressed.

### Chapter 4

# Methods and experimental techniques

This chapter provides a brief background on the techniques used for the work performed. The main focus is on central concepts for nanocatalyst synthesis and electrochemical characterization.

### 4.1 Nanocatalyst synthesis

To fill the Pt-RE nanoparticle synthesis gap mentioned in previous sections, this thesis investigates techniques based on magnetron sputtering. This includes several efforts involving sputtering onto liquid substrates, and is an attempt to address both the low-oxygen partial-pressure requirement and the issue of catalyst layer fabrication.

### 4.1.1 Magnetron sputtering

Sputtering is a physical vapor deposition (PVD) technique utilizing the impact energy of an ionized sputter gas, such as argon or krypton, to knock out atoms and clusters of a target material [73, 74]. This is done through the application of a voltage across the gas, eventually forcing it to ionize, forming a plasma glow [74]. Without the addition of any further restricting equipment, this plasma will simply fill the space between the negatively biased sputter target (cathode) and the substrate. The positively charged ions, are attracted by the cathode, forcing an acceleration towards the target plate. Upon impact, depending on the applied voltage, one or more atoms and atomic clusters may be ejected from the surface as a result of the collision [73, 74]. The principle, called sputtering, was discovered in 1852, [75] by the same W.R. Grove also credited for inventing the fuel cell. On a personal note, the thought that we are now, almost two centuries later, trying to implement one of Grove's techniques in the fabrication of catalyst materials for use in another of his inventions is truly thrilling.



Figure 4.1: Schematic of the two different magnetron configurations, balanced and unbalanced.

In magnetron sputtering, an arrangement of magnets behind the target plate, typically one central magnet surrounded by a ring of magnets of opposite polarity, give rise to a magnetic field. Depending on the strengths of the individual magnets, two different configurations of the magnetic field may arise, as depicted in figure 4.1. If the strength of the center magnet is as high as its surrounding magnets, all field lines exiting the outer magnets will pass through the middle magnet. Such a configuration is called a balanced magnetron, and leads to confinement of the plasma close to the target plate, as its electrons are trapped by the magnetic field lines, and prevented from ionizing gas molecules in the rest of the chamber [74, 76]. If instead the center magnet is weaker than its surrounding counterparts, it will not be able to close all field lines. As a result, electrons will escape the confinement, ionize neutral gas molecules further away from the target, and hence, allowing the protrusion of plasma onto the substrate [74, 76]. This type of configuration is called an unbalanced magnetron and is often used in thin film sputtering to increase the interaction between the plasma and the film, which can have an effect on the film growth. In this work, the plasma protrusion of our unbalanced magnetron setup is used to control the heating effect of the substrate during sputtering, which, as we will later show, has an effect on the size of sputtered nanoparticles. In summary, the magnetron sputtering technique is widely used for thin films within micro- and nanofabrication, but its application is not limited to various types of layered structures and coatings.

#### Liquid substrates

Pioneering work in the mid 1990's [77] on using low vapor pressure liquids as substrates for sputtering, quickly developed into a new, facile and multi-



Metal target plate

Figure 4.2: Schematic illustration of the SoL technique.

purposed method for nanoparticle synthesis. The advantages of sputtering onto liquids (SoL) are several, including long term stabilization of nanoparticles provided by the liquid, the lack of capping agents needed as well as the use of a pure target plate over chemical precursors, which are often difficult to remove and sometimes hazardous.

The practice of SoL generally consists of the insertion of a low vapor pressure liquid into a vacuum chamber. The liquid substrate is mounted underneath the magnetron gun equipped with the target plate, at some target-to-substrate distance. Low vapor pressures of the liquid substrates are required in order to prevent vaporization under the ultra-high vacuum (UHV) conditions inherent to the magnetron sputter chamber. In this work, evacuation to base pressures of less than  $5 \cdot 10^{-7}$  mbar, is obtained by turbomolecular pumping. UHV conditions are especially important when considering synthesis of Pt-RE allow nanoparticles, to prevent oxidation of the rare-earth metal. A simplified schematic of the SoL procedure is shown in figure 4.2, illustrating the plasma shape resulting from an unbalanced magnetron configuration. During sputtering, the protruding plasma causes the liquid substrate to heat up. Heating the substrate ultimately decreases its viscosity and increases the diffusion rate of immersed particles, clusters and single atoms, which can be used to tailor the size of nanoparticles [78] by controlling the temperature. Sputtered atoms and clusters are ejected in a complicated emission pattern, depending on ion energies and incident angles as well as target texture [79]. Here, it is sufficient

to understand that a portion of the ejected atoms and clusters will propagate through the target-to-substrate gap, and impinge on the liquid surface. Due to collisions between, and subsequent coalescence of atoms and clusters within the sputter gas, the population of sputtered species arriving at the substrate surface will be a mix of atoms and clusters depending on the pressure.

Further nucleation, growth, and sometimes aggregation may occur inside the liquid [80, 81]. Except for viscosity, nanoparticle growth and aggregation are also governed by the interactions between the substrate and submerged particles [80]. The interaction is highly dependent on the type of substrate. Two notable examples are those of ionic liquids and polymers. An ionic liquid consists of an ion pair, a positively charged cation, and a negative anion. These ions can, depending on the charge of the submerged nanoparticles, arrange themselves in an electric double layer around the particles. Polymers, on the other hand, are long chains of hydrocarbons that can surround the nanoparticles and provide steric stabilization. The exact amount of stabilization provided by both groups of substrates depends on the specific choice of liquid [80]. To summarize the applicability of liquid substrates in nanoparticle synthesis, a correctly chosen liquid will act both as a combined collection and growth medium, and provide the stabilization needed for aggregation prevention.

### 4.1.2 Gas aggregation sputtering

In standard magnetron sputtering, thin films or nanoparticles are grown on a substrate from sputtered atoms and smaller clusters. However, the sputtering gas itself can be used for the nucleation and growth of sputtered nanoparticles by decreasing the mean free path of the sputtered atoms. The gas aggregation sputtering (GAS) approach utilizes thermalization of magnetron-sputtered material in an aggregation zone [82], with a locally elevated gas pressure. The higher pressure facilitates three-body collisions between two sputtered atoms and an atom (or ion) of the sputtering gas (typically argon), which are necessary to induce particle nucleation in the gas phase [83]. The subsequent growth of the nuclei is dependent on several factors, including the residence time within the aggregation zone and the concentration of sputtered atoms, clusters, and nuclei. Adjusting process parameters such as the flow of the sputter gas, the deposition current, and the aggregation length allows control over these factors, and hence the final nanoparticle size [83, 84].

A simplified schematic of the experimental GAS-setup used in this work is presented in Figure 4.3. The gas and cooling water connections (a) facilitate simple external control of the pressure within the aggregation zone (c) and the temperature of its walls. The aggregation length  $L_a$  between the magnetron gun (d) and the aggregation zone exit aperture  $d_1$  can be altered by adjusting the length of the expandable bellow (b). A T-piece (f) allows differential pumping of the aggregation zone by a turbomolecular pump (e), and connects it to the deposition chamber (g) through the second aperture  $d_2$ . The deposition chamber is directly pumped by a second turbomolecular pump (e), and contains the sample (h) located on a stage (i) underneath the two apertures, at a distance



Figure 4.3: Schematic of the GAS setup highlighting the gas and cooling connection (a), expandable bellow (b), aggregation chamber (c), magnetron gun (d), turbomolecular pumps (e), T-piece (f), deposition chamber (g), sample (h), and stage (i). Indicated are also the two apertures  $d_1$  and  $d_2$ , and the adjustable aggregation length  $L_a$ .

of approximately 30 cm from  $d_1$ . The pressure in the aggregation zone both before and during sputtering is surveyed by a full-range pressure gauge through one of the VCR gas connections. The typical base pressures used in this work were in the 10<sup>-7</sup> mbar and 10<sup>-9</sup> mbar ranges for the aggregation zone and the T-piece, respectively.

Gas aggregation is one of few methods that has been shown to produce Pt-RE nanoparticles of optimal size and with greatly enhanced ORR activity. However, previous work has relied on the mass selection of nanoparticles, which greatly limits the scalability of the technique [72].

### 4.1.3 Attachment of nanocatalyst particles on carbon support material

For real applications within fuel cells, the immobilization of nanocatalyst particles on a high surface area carbon support material and the addition of an ionomer is required to facilitate reliable electrical and ionic contact, as well as transport of reactants and products. Common carbon support materials are various types of Vulcan<sup>®</sup> and Ketjenblack<sup>®</sup>, while the most common ionomer is Nafion<sup>®</sup>. It is essential to find a route for catalyst particle transfer from the liquid substrates, and attachment to the carbon support.

One method for nanoparticle transfer and attachment has been used in this thesis, and consists of a heat treatment of the liquid stabilized nanoparticles, along with Vulcan<sup>®</sup> XC-72. The support material is simply ground and added to the nanoparticle-liquid substrate dispersion, after which the mixture is heated to 150 °C in an oil bath for 19 hours, under constant magnetic stirring. After the heat treatment, a supported catalyst powder was extracted by repeated washing in isopropanol and separation by centrifugation, followed by a drying step in an oven at 80 °C overnight.

### 4.2 Physical characterization

Physical characterization is used to investigate important properties of the SoLsynthesized nanoparticles, including size and morphology as well as chemical states and composition.

### 4.2.1 Transmission electron microscopy

The resolution limit of an optical microscope, commonly known as the Abbe limit of diffraction [85], states that the minimum resolvable distance d is directly proportional to the wavelength of transmitted light  $(\lambda)$  by

$$d = \frac{\lambda}{2NA} \tag{4.1}$$

where NA is the numerical aperture of the objective lens. Assuming a wavelength in the shorter region of visible light (400 nm), and a typical numerical aperture for modern optical microscopes of around 1.5, equation 4.1 predicts the minimum resolved distance to 133 nm. Considering that the typical size of practical fuel cell catalyst nanoparticles is in the range of 3-10 nm, another imaging technique is required to obtain a sufficient spatial resolution. As a consequence of the wave-particle duality, electrons can be used for imaging in a manner similar to that of light, but due to their considerably shorter wavelengths, electron microscopy offers supreme spatial resolution compared to its optical counterpart, on the order of Ångströms [85]. In transmission electron microscopy (TEM), thin specimens (up to 100 nm) are subjected to a high-energy electron beam [86]. A collection of electromagnetic lenses ensures that the electron beam is collimated and focused into a small spot on the sample. Due to the high energy of the incident beam, electrons will, to a large extent, be transmitted or forward scattered by the sample, allowing their use for imaging in an analogous manner to light in traditional optical microscopes. In standard bright-field TEM imaging, electron-dense regions scatter more than domains with low electron density, and therefore appear darker in the formed image [86]. It is primarily this electron density contrast that is used to image nanoparticle samples in TEM. Synthesized nanoparticle samples are typically deposited on Au lacey carbon TEM grids, where the holes in the lacey carbon support film are covered with an ultra-thin carbon film. This enables imaging of the nanoparticles with almost no interference from the background.

### 4.2.2 Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) is a technique for characterization of small objects, such as nanoparticles or polymers, using a collimated X-ray beam [87]. When the beam hits the sample, it interacts with the atoms of the particles, and any scattering or absorption events are thence reflected in the resulting output signal. The scattering pattern obtained is an average of all the particles within the sample hit by the beam. By looking at the scattered signal at small detection angles, information about the average size and shape of nanoparticles in the sample can be retrieved, which is particularly useful when concerned with structure and morphology of nano-objects.

### 4.2.3 X-ray photoelectron spectroscopy

While SAXS utilizes X-ray scattering directly, X-ray photelectron spectroscopy (XPS) is based on an indirect effect of X-ray interactions with the sample [88]. The photoelectric effect, as it is called, was first studied during the later decades of the 19<sup>th</sup> century [88], and later famously explained mathematically by Albert Einstein in 1905 [88, 89]. Photoelectrons are produced when an incident photon with sufficient energy is absorbed by an atom or ion, causing the emission of one of its electrons. These electrons contain specific information about the atoms or ions from which they originate, and can therefore be used for detailed material characterization. Building on these foundational principles, Kai Siegbahn and his co-workers pioneered the XPS analysis technique in the 1960's [88, 90], exploiting that the kinetic energy of a photoelectron is a function of its binding energy. Since the binding energy is both element- and environment-specific, the detection and analysis of photoelectron kinetic energies offer a way to determine the chemical states and compositions of materials [88].

Another feature of photoelectrons within a solid material is their tendency to scatter inelastically, loosing energy in the process. Although the mean free paths of X-rays are typically on the order of micrometers in most materials,



Figure 4.4: Photoelectron emission by X-ray irradiation. The leftmost X-ray produces a photoelectron that participates in an inelastic scattering event, losing parts of its kinetic energy. The other two X-rays result in escaping photoelectrons. Due to the difference in photon energies, the maximum depth from which these two X-rays generate detectable photoelectrons differ.

the mean free paths of photoelectrons are not [88]. In fact, for photoelectrons with kinetic energies larger than  $\sim 100 \text{ eV}$ , the inelastic mean free path (IMFP) increases with increasing kinetic energy (and hence increasing photon energy). However, in most XPS applications, the IMFP is in the range of 1-10 nm, rather than micrometers. A photoelectron that loses parts of its energy in an inelastic scattering event will, provided that it later escapes into the vacuum, become part of the spectral background [88]. This means that only photoelectrons from the absolute top surface layer will escape into the vacuum and reach the detector without losing energy, making XPS a highly surface sensitive technique. Figure 4.4 illustrates the principles of escape depths in XPS. The two leftmost X-rays show how the production of detectable photoelectrons from X-rays of an arbitrary energy depends on where in the sample volume they are emitted. The rightmost X-ray of higher energy results in a longer IMFP.

An XPS instrument allows for the creation of material-specific binding energy spectra. Photoelectrons of different kinetic energies and momentums are separated laterally in an electrostatic analyzer, and are detected and counted as a function of their kinetic energies by a detector situated on the exit side of the analyzer [91]. The binding energy spectra are directly extracted from the kinetic energy data by the equation

$$E_B = \hbar\omega - \phi_{XPS} - E_k \tag{4.2}$$

relating binding energy  $E_B$  to the photon energy  $\hbar\omega$ , the work function of the instrument  $\phi_{XPS}$ , and the kinetic energy  $E_k$  [88, 91].

Lab-scale XPS instruments typically use nearly monochromatic K $\alpha$  radiation from aluminum or magnesium to induce photoelectron emission in materials. It constitutes an excellent tool for fast and reliable screening of nanomaterial surface compositions and oxidation states.

### 4.2.4 X-ray diffraction

When an X-ray beam is directed onto a crystalline material, the crystal planes within the material acts as a diffraction grating, if the X-ray wavelength is similar to the plane spacing [92]. This leads to constructive interference, for the specific criteria known as Bragg's law:

$$n\lambda = 2dsin(\theta) \tag{4.3}$$

In equation 4.3, n is an integer,  $\lambda$  the wavelength of the X-ray, d the interplanar spacing, and  $\theta$  the angle of diffraction [93]. Due to the differences in lattice structures and interplanar distances of materials, the Bragg diffraction pattern provides a fingerprint of any crystalline material [93]. Furthermore, the technique is powerful in the sense that it can provide information not only of the crystal structure, but also of other factors including crystal orientations, crystallite sizes, crystal defects, and strain [93]. Hence, it is an important tool for studying the physical properties of crystalline materials.

### 4.3 Electrochemical characterization

Electrochemical characterization allows evaluation of the catalytic performance of synthesized catalysts, which can be subsequently linked to the physical properties. This section discuss the electrochemical methods used in this thesis.

### 4.3.1 Cell setup

In this work, all electrochemical characterization was performed using a rotating disk electrode (RDE) setup, including a potentiostat, a rotator and an electrolyte-filled three-electrode glass cell. The operating principles of the potentiostat is left out of this thesis, however, it can be understood as an instrument for controlling and measuring potentials and currents. The three electrodes of the glass cell are denoted as working (WE), counter (CE) and reference (RE) electrodes, respectively. As WE in the measurements conducted here, a certain type of electrodes called glassy carbon electrodes (GCE) is used, with the purpose of constituting a simple platform for electrochemical



Figure 4.5: Combined three-electrode RDE cell setup employing a Pt wire CE, catalyst-coated glassy carbon WE and an RE.

evaluation of electrocatalysts. The GCE geometry chosen was that of small cylinders, typical for RDE, which can be coated by deposition of a catalyst thin film or as in this work, by a layer of catalyst nanoparticles on microporous carbon, which will be described in 4.3.2. The coated WE is mounted at the end of a Teflon head connected to a rotatable shaft according to figure 4.5. The WE provides the location for the half reaction of interest, while the other half reaction is facilitated at the CE. Upon application of a potential over the two electrodes, a resulting current will start to flow in the external connection between them, which can be measured by an amperemeter in the potentiostat. As electrons are either added or removed at the WE, the CE needs to perform the opposite action in order to balance the overall charge of the system. In doing so, the CE potential will vary considerably and is therefore not a suitable reference point for the WE. Instead, the exact potential of the WE is measured relative to that of the RE, in which a well-defined redox reaction equilibrium fixes its potential at a stable, known value. This technique is ideally unaffected by the reactions on the other two electrodes, as no current passes through the RE.

### 4.3.2 Electrode preparation

The most common process for preparation of nanocatalyst layers on GCEs is via drop casting of a catalyst ink. The ink is typically made by dispersion of the supported catalyst powder in a solvent, by ultrasonication. A Nafion solution is added to the ink, acting both as a glue and ion conductor in the final electrode. Catalyst ink is drop casted onto small (5 mm in diameter), cylindrical GCEs under slow rotation, to provide more homogeneous coverage of the electrode surface, and heating from a heat gun facilitates faster drying of the catalyst layer. No material is lost in this process, meaning that catalyst loading can be derived directly from the concentration in the ink.

### 4.3.3 Cyclic voltammetry

Cyclic voltammetry (CV) is a technique used to characterize the nature of redox reactions [23]. By measuring the current while continuously sweeping the potential between two limiting values, the current response can be plotted as a function of the potential. When a Pt WE is cycled between 0.05 and 1V vs. RHE in an electrolyte saturated with an inert gas, typically nitrogen or argon, the voltammogram will exhibit a current-voltage behavior governed by the adsorption and desorption of oxygen and hydrogen species from the electrolyte onto the catalyst surface. The CV curve in figure 4.6 illustrates the redox behavior of hydrogen and oxygen species on Pt nanoparticles in a 0.1 M perchloric acid (HClO<sub>4</sub>) electrolyte saturated with argon, cycled between 0.05and 1.0 V vs. RHE at 50 mV/s scan rate. In the CV, positive currents are denoted as anodic by convention, which means that the WE acts as an anode. with a flow of electrons from the electrolyte to the electrode as species are being oxidized. Similarly, negative currents (cathodic) represent the reduction of electrolytic species, requiring the transfer of electrons from the electrode into the electrolyte. Here, the WE acts as a cathode. Looking at the curve in figure 4.6, three main potential regions can be identified, showing distinct characteristics, these being below 0.4 V, 0.4–0.6 V, and above 0.6 V vs. RHE.

At lower potentials, a set of distinct peaks are observed. These belong to what is usually called under-potential deposition (UPD), or adsorption and desorption of hydrogen. As we move towards higher potentials in the plot, a flat region of comparably low currents appears, the so-called double-layer region. Here, there are no active redox reactions and all currents belong to the charging of the electric double layer at the electrode surface. This capacitance layer is not unique to the double-layer region, and is always present when sweeping or cycling the potential. Above 0.6 V, another set of peaks develop, which originate from the adsorption/desorption of oxide species and the oxidation of Pt. Two important features, not visible in the CV of figure 4.6, is the evolution of hydrogen (HER) and oxygen (OER), respectively. HER would be reached by sweeping the potential slightly further in the cathodic direction, passing 0 V, while oxygen evolution typically requires potentials closer to 1.6 V, where the onset potential for OER on Pt is located.



Figure 4.6: Typical CV of Pt nanoparticles in argon saturated 0.1 M HClO<sub>4</sub>, indicating the directions of anodic and cathodic sweeps, as well as the hydrogen UPD integral area used for ECSA calculations.

The adsorption and desorption of the oxygen and hydrogen species from the electrolyte, as well as the charging of the electric double-layer capacitance, are artifacts of the potential cycling. This means that as soon as the potential cycling is stopped, there will be no currents produced from these processes. Continuous electrochemical reactions, on the other hand, are not dependent on potentials being swept or cycled to produce current. Currents produced in this manner are called Faradaic currents, while currents from the other processes are denoted as non-Faradaic currents. An example of a continuous electrochemical reaction is when the electrolyte is bubbled with oxygen, for which ORR takes place for potentials below 1 V. It is worth noting that in a CV, the contribution of non-Faradaic currents will always be added as an overlay to the Faradaic currents.

### 4.3.4 Evaluation of electrochemical surface area

There are many techniques for measuring electrochemical surface area (ECSA) in acidic medium [94]. For measurements on Pt fuel cell catalysts, underpotential deposition (UPD) of hydrogen and CO-stripping are two commonly used methods. The first can be performed directly using the CV in argon presented in figure 4.6. The currents involved in either the adsorption (marked in grey) or desorption (not marked) of hydrogen on the catalyst surface can be related to the total charge of hydride film formation via

$$Q = \frac{1}{\nu} \int I dE \tag{4.4}$$

where  $\nu$  is the scan rate. It is important to stress that only the contribution from hydrogen adsorption is used, and the double layer capacitance current is therefore subtracted beforehand. Typically, the integration is made from the double layer region, to the local maxima right before hydrogen evolution starts (figure 4.6). The charge obtained from integration over this range, is generally considered to corresponds to a hydrogen coverage of 77% [95]. On obtaining the charge from the hydrogen layer, it can be compared to the theoretical value of hydrogen monolayer formation on the specific catalyst. For hydrogen on Pt, this charge  $\theta_{Pt}$  is assumed to correspond to one electron per Pt site, giving a monolayer charge of  $\theta_{H-Pt} = 210 \ \mu \text{C cm}_{Pt}^{-2}$  [95]. Hence, an estimation of the ECSA is attained from:

$$A_{ECSA} = \frac{Q_H}{0.77 \cdot \theta_{H-Pt}} \tag{4.5}$$

A second approach to estimate the ECSA is by the process of CO-stripping. The idea is analogous to that of hydrogen UPD, but instead of hydrogen, the catalyst surface is saturated with adsorbed carbon monoxide (CO). Then, the electrolyte is purged of excess CO by extensive bubbling with inert argon. After argon purging, only a monolayer of CO is left on the surface, upon which a standard CV is initiated. Adsorbed CO will become oxidized into CO<sub>2</sub> and desorb from the surface, from which a CO-stripping current peak is formed somewhere within the 0.5-0.9 V vs. RHE potential range. Via subtraction of the following CV, and subsequent integration, the charge related to the CO oxidation is obtained in the same manner as for the hydrogen UPD. Then, the ECSA is again estimated by the monolayer charge. As CO oxidation involves the transfer of two electrons, the monolayer charge will be twice that of hydrogen UPD,  $\theta_{CO-Pt} = 420 \ \mu \text{C cm}_{Pt}^{-2}$ , giving the ECSA as:

$$A_{ECSA} = \frac{Q_{CO}}{\theta_{CO-Pt}} \tag{4.6}$$

### 4.3.5 Rotating disk electrode

In a fuel cell, with continuous supply of gases to the electrodes, mass transport losses arise first at rather high currents, as shown in figure 3.4 of chapter 3. However, in a three-electrode cell, the system will experience mass-transport losses already at low currents because of the low solubility of the reactant gases in the electrolyte. When a liquid-immersed electrode starts to draw a current, dissolved reactants in its close vicinity are consumed by the reaction. This causes a depletion of reactants in the volume closest to the electrode and gives rise to a concentration gradient between the electrode and the liquid bulk. For the reaction to proceed, the reactants need to diffuse through this low concentration region, which can therefore be considered as a diffusion layer (see figure 4.7a). If the reaction kinetics at the electrode is faster than the transport of reactants, the reaction becomes mass-transport limited. This complicates the characterization of the kinetic performance of the catalyst.

To decrease the influence of the mass-transport losses, rotating disk electrode (RDE) setups are often used. In RDE, the electrode is mounted at the end of a rotating shaft. The rotational motion of the shaft induces a well-defined



Figure 4.7: Cross-section of the RDE shaft and GCE, with the difference in diffusion layer thickness illustrated for the case of a) no rotation and b) with rotation. A bottom view of the electrode mount is given in c), and the electrolyte flow-patterns due to rotation are indicated in b-c).

flow pattern in the solution [96]. Due to non-slip boundary conditions at the electrode-liquid interface, the only velocity component present at the surface is the azimuthal velocity  $(v_{\theta})$  caused by the rotation. This angular velocity gradually decreases the further away from the electrode we come. As the electrode spins, it exerts a dragging force on the liquid close to it, and a radial velocity component forms as we move away from the non-slip conditions at the surface into the liquid. The radial velocity  $(v_r)$  first increases with increasing distance from the electrode, but eventually reaches a maximum before dying away as the effective influence of the electrode rotation on the liquid decreases. The liquid that is radially thrown outwards in the electrode vicinity is replaced by an axial flow of electrolyte from the bulk solution, with velocity  $v_x$ . Figure 4.7b-c show qualitative schematics of the flow pattern around a rotating disk electrode.

Within a certain volume near the electrode, the velocity distribution consists of all three velocity components  $(v_{\theta}, v_r, \text{ and } v_x)$ . Defining clear limits of this region is difficult. However, a so-called hydrodynamic boundary layer is often defined, with a thickness  $\delta_H$  approximately related to the kinematic viscosity of the solution  $(\nu)$  and the angular rotation rate  $(\omega)$  according to equation 4.7 [96]. The thickness of  $\delta_H$  corresponds roughly to where the radial velocity distribution has its maximum. As a result, transport of reactants into the hydrodynamic boundary layer occurs mainly through convection; however, closer to the electrode surface, diffusion becomes increasingly important. In fact, closest to the electrode, transport of reactant ions and molecules is dominated by the diffusion across a thin, relatively stagnant layer of electrolyte, known as the diffusion layer [23, 96]. Similarly to the hydrodynamic boundary layer, the thickness approximation  $\delta_D$  of the diffusion layer is inversely proportional to



Figure 4.8: Current density-voltage response for a generic reduction reaction in RDE ( $E < E_0$ ), illustrating the linear relationship between  $j_{lim}$  and  $\omega^{\frac{1}{2}}$  as well as the potential-regions with diffusion-, kinetic- and mixed control of the current density.

the square root of the rotation rate, as shown in equation 4.8, where  $D_F$  is the diffusion coefficient of the ion or molecule [23, 97].

$$\delta_H = \left(\frac{\nu}{\omega}\right)^{\frac{1}{2}} \tag{4.7}$$

$$\delta_D = 1.61 D_F^{\frac{1}{3}} \nu^{\frac{1}{6}} \omega^{-\frac{1}{2}} \tag{4.8}$$

The fact that the diffusion layer thickness decreases with increasing rotation rates has important implications for the study of electrochemical reactions and is the main motivation behind using RDE to study half-cell reactions. For a diffusion-limited reaction, the maximum retrievable current density  $j_{lim}$  on a disk electrode can be calculated as

$$j_{lim} = \frac{nFD_F c_0}{\delta_D} = 0.62nFD_F^{\frac{2}{3}} \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}} c_0 \tag{4.9}$$

where  $c_0$  is the reactant concentration of the bulk solution [23, 97]. Typical current density-voltage responses for an arbitrary reduction reaction, at three different rotation rates are illustrated in figure 4.8, showing the linear relationship between  $j_{lim}$  and  $\omega^{\frac{1}{2}}$  in the diffusion controlled [98–100], low potential region. Closest to the equilibrium potential, in the kinetically controlled region, the current density follow the exponential trend predicted by the Butler-Volmer equation (2.17) [98–100]. In between these two regions, both diffusion and electrode kinetics limits the reaction rate, and we say that we are in the region of mixed control [98–100].

When evaluating the catalytic activity of materials in half-cell setups, it is sometimes of interest to extract the so-called kinetic current density  $j_k$  from the measured current density j in the mixed region. Theoretically,  $j_k$  is defined as the current density in a situation with infinite mass transport, when the only limitation is the kinetics at the electrode [97]. The relationship between the actual measured current density and the limiting current densities due to kinetic and mass-transport limitations can be described by the Koutecký-Levich equation (4.10). Using the definition of  $j_{lim}$  introduced in equation 4.9, the reciprocal current density j becomes a linear function of  $\omega^{-\frac{1}{2}}$ , with  $\frac{1}{j_k}$  corresponding to the intercept with the y-axis, at infinite rotation rates. Furthermore, from this relationship, it is evident that  $j_k \to \infty$  in the diffusioncontrolled region, where  $j = j_{lim}$ , which is consistent with the insight from chapter 2 that the overpotential is an exceptionally strong driver for electrode kinetics.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_{lim}} \tag{4.10}$$

The main focus of this thesis is the study of various Pt-based materials and their ORR activities. A commonly used benchmark for the ORR activity of these materials in RDE is  $j_k$ , evaluated at 0.9 V vs. RHE, in an oxygen-saturated electrolyte [49, 57, 61, 62, 66]. For the studies presented in the two upcoming chapters and appended papers, in which ORR activities have been studied using RDE,  $j_k$  at 0.9 V vs. RHE has been the activity benchmark of choice.

### Chapter 5

## Growth processes of sputtered Pt-based nanoparticles

The duration of this thesis work has seen a number of ways to influence the size of SoL-synthesized Pt-based nanoparticles, but also many unsuccessful attempts. With such a clear specification of a "dream particle" as the one defined in section 3.5.3, the importance of these "failures" is easily overlooked. Much can be learned from them, and therefore I would like to return to the quote on page vii:

"I have not failed. I've just found 10,000 ways that won't work."

This quote may be a modern paraphrasing of Thomas A. Edison; nevertheless, it captures the scientific process in detail. Progress requires a certain number of failures, and consequently, along with the successful attempts, I would like to present some of mine. Together, they contribute to the general knowledge of nanoparticle formation in SoL.

As discussed in chapter 3, the particle size of Pt-RE nanoparticles has a major effect on the ORR activity. As we investigate alternative techniques for the synthesis of these materials, it is important to obtain an understanding of the fundamental processes behind nanoparticle nucleation and growth. In an effort to do so, we have studied the behavior of both Pt, which is a more widely studied material that allows easier comparison with the literature, and the Pt<sub>3</sub>Y system, being one of the most active ORR catalyst materials and the one we ultimately aim to synthesize.

### 5.1 Influence of synthesis parameters

The many different parameters which may influence nanoparticle nucleation and growth in SoL can be categorized into three main groups: Those of the substrate (viscosity, surface tension, temperature, liquid type, etc.), the sputter gas environment (pressure, sputter gas species, etc.) and magnetron gun parameters (voltage, sputtering current, etc.). The following sections summarize our findings on how these different types of parameter affect or do not affect nanoparticle growth.

### 5.1.1 Substrate parameters

The two main substrate parameters that have been investigated in this work are the type of liquid and the temperature during sputtering. Naturally, it is unavoidable that some of these parameters correlate with other parameters. As an example, both temperature and choice of liquid have or may have an influence on the substrate viscosity and surface tension. The reason behind our choice of parameters is that they are easily controlled and have been shown to have a significant influence on the size of nanoparticles in other materials [78, 101–106]. However, the results presented in this section should be viewed with the correlation effect in mind.

### Liquid type

In **paper I**, four different low-temperature liquids were used as sputtering substrates, three imidazolium-based ionic liquids (Emim Tf, Dmim Tf and Dmim Tf<sub>2</sub>N), and the polymer, PEG 600. The ionic liquids were carefully chosen in order to compare two things; 1) the contribution of the alkyl chain length to the nanoparticle growth for the two ionic liquids with triflate (Tf) anions and 2) the influence of a similar but larger anion (Tf<sub>2</sub>N), for ionic liquids with identical cations (Dmim). Nanoparticle sizes were studied using both TEM and SAXS. **Paper III** also presented TEM size data on Pt nanoparticles sputtered in PEG 600, and the mean diameters of the two works are shown in figure 5.1.

TEM indicates that the variations in size of the nanoparticles produced in the four liquids are small, as they all produce particles of around 2 nm in size. The mean size of particles produced in Dmim Tf is slightly smaller than those produced in Emim Tf. This may agree with the previously reported trend that the size of Au nanoparticles decreases with increasing alkyl chain length [103, 104], however, the difference observed here is not statistically significant. Hence, it does not allow for any conclusion other than that the influence of the alkyl chain length on the Pt nanoparticle size is not large. The same relationship appears to hold for the two different anions, and when using a completely different type of liquid (PEG 600). Slightly different behavior is observed in SAXS, which indicates smaller nanoparticle sizes in general. Nevertheless, the mean diameters are all within one standard deviation of each



Figure 5.1: Mean Pt nanoparticle sizes, sputtered in four different liquids, evaluated using TEM (red) and SAXS (blue), obtained in **papers I** and **III**. Error bars indicate standard deviations.

other, and therefore there are no clear trends on the nanoparticle size sputtered in different liquids to report from the work in **papers I** and **III**.

A final attempt was made to study the influence of substrate type on the size of  $Pt_3Y$  nanoparticles as a response to the report by Orozco et al. [107], who found that sputtering in liquid glycerol led to increased Pt nanoparticle sizes. The synthesis consisted of sputtering of  $Pt_3Y$  onto both pure glycerol and a glycerol dispersion containing a high surface area carbon support. TEM micrographs of the two samples are shown in figure 5.2.

While Orozco reported the formation of a Pt film on the glycerol surface after sputtering, we observed an interesting, highly branched structure of aggregated particles, highlighted by light pink curves in figure 5.2a. In addition to these branched structures, a second sample domain consisting of smaller particle agglomerates, indicated by dark pink curves, is present. Looking at the higher magnification micrograph of figure 5.2a, both types of structures consist of smaller individual particles. The fact that these particles tend to agglomerate or even aggregate makes their size estimation very difficult. Qualitatively, they are slightly larger than the particles sputtered in PEG and ionic liquids, but the difference is not very distinct. Furthermore, the high degrees of agglomeration and aggregation are not beneficial for catalytic performance.

Surprisingly, when the nanoparticles were sputtered onto the PEG/carbon dispersion, no such branched structures were observed. Instead, a catalyst powder decorated with well-dispersed nanoparticles could be retrieved, as shown in figure 5.2b. TEM indicates that these carbon-supported particles are still of a size of around 2-2.5 nm, which is considerably smaller than the optimal size of  $Pt_3Y$  nanoparticles discussed in chapter 3. Further investigations of these samples were aborted after it was revealed that they exhibited very poor ORR activity. We are unaware of the reason for the poor activity, but glycerol has a significantly higher vapor pressure compared to PEG and the ionic liquids



Figure 5.2:  $Pt_3Y$  nanoparticles sputtered onto a) pure PEG 600 and b) high surface area carbon support dispersed in PEG 600, as observed in TEM.

studied, which meant that the sputtering background pressure could not be lowered further than  $5 \cdot 10^{-5}$  mbar. We hypothesize that this is too high a background pressure for Pt-RE nanocatalyst sputter synthesis.

#### Temperature

Substrate temperature is well known to affect nanoparticle size in SoL [78, 102], but not much specific data on Pt particles is present in literature. Therefore, in **paper I**, experiments were performed using our unbalanced magnetron to achieve varying degrees of substrate heating by adjusting the sputtering power, while measuring the liquid temperature carefully. Size estimations for Pt nanoparticles sputtered in PEG 600 using 20 W (for 3.300 s), 65 W (for 3.300 s) and 50 W (for 30 s) are shown in figure 5.3. The variations in nanoparticle size, due to sputtering power alteration, is small, evident when comparing the mean size of particles sputtered at 20 W (2.1 nm) and 65 W (2.4 nm). Between particles sputtered at 65 W for 3.300 s and at 50 W for 30 s, the mean sizes differ more, from 2.4 and 1.8 nm, respectively. These results should be viewed in the light of their accompanying temperature data, displayed in figure 5.4. As clearly visible, temperature increases rapidly during the first 100 s of each sputter cycle, after which the increase rate slows down and eventually approaches plateau values closer to the end of each cycle. The



Figure 5.3: TEM micrographs of Pt nanoparticles sputtered into PEG 600, using a) 20 W for 3.300 s, b) 65 W for 3.300 s, and c) 50 W for 30 s. The corresponding size distributions are displayed in d-f), respectively.

heating is considerably faster for the 65 W case, and the maximum temperature reached is just below 200 °C for the high power case, and only 120 °C in the low power case. The temperature development during the 30 s sputtering at 50 W, coincides with the first 30 s of the 65 W cycles, reaching a final temperature of 80 °C at the end of the sputtering experiment.

The effect of substrate temperature on Pt nanoparticle size indicated by these results is small in comparison with what was previously reported for gold [78], a trend similar to what has been observed for gold and Pt grain sizes



Figure 5.4: Temperature development during sputtering, performed at 20 W (3.300 s), 50 W (30 s) and 65 W (3.300 s), measured using a K-type thermocouple immersed in the liquid.

when sputtered onto flat, solid surfaces [108]. Furthermore, it should be mentioned that our unbalanced magnetron setup is utilized for controlled substrate heating, by applying a range of sputtering powers. Hence, the size effect seen from heating the substrate in this work, is a combined effect, consisting of contributions from both altering the sputter power, and the associated substrate heating.

### 5.1.2 Gas environment

The investigations of the gas environment studied two different aspects: 1) the effect of different sputter gases in standard magnetron sputtering and 2) gas aggregation nanoparticle synthesis.

### Sputter gas

First, the influence of the type of sputter gas on nanoparticle size was explored. From the results obtained in **papers I** and **III**, it is known that argon sputtering produces small particles with diameters around 1.5–2.5 nm, depending on the liquid temperature, and hence in our case, sputtering power. These may be favorable sizes in the case of Pt ORR catalysts, but for Pt-RE alloys, increasing the size is crucial to obtain enhanced ORR activity. Therefore, a heavier sputtering gas, krypton, was chosen in the hope that by increasing the momentum of the impacting sputter ions, larger clusters of atoms would be ejected, leading to an increase in the final nanoparticle size. Figure 5.5 shows a TEM micrograph and size distribution of Pt nanoparticles sputtered into PEG 600 using krypton, at a sputtering power of 50 W.



Figure 5.5: TEM micrograph and size distribution of Pt nanoparticles sputtered onto PEG 600 using krypton as sputter gas.

From the size distribution it can be observed that the mean size of Pt particles sputtered using krypton is roughly 1.6 nm, which is slightly smaller than particles obtained using argon. This result, while surprising, can be connected back to the previous discussion of sputtering power and substrate temperature: A similar effect was reported by Hatakeyama et al. [101], who used higher sputtering voltages to increase the impact momentum (and energy) of argon ions. They found that smaller gold particles were produced at higher voltages. Our results from **paper I** rather indicate a small size increase for higher sputtering powers, despite the fact that the highest sputtering power in that work (65 W) also had the highest sputtering voltage. Hence, the temperature dependence reported in **paper I** may have been underestimated if the increasing power is, in fact, counteracting the increase in nanoparticle size. If so, a potential route to increase the size of Pt-RE nanoparticles could be to reduce the sputtering power while keeping substrate temperatures at an elevated level by external heating. In summary, the influence of the sputter gas type observed in this work, is not large.

#### Gas aggregation

As already discussed, gas aggregation is one of few techniques that have been successfully applied in the synthesis of highly active Pt-RE nanoparticles [57, 65]. However, the referenced works relied on mass-selection of nanoparticles, which heavily reduces the deposition rate, and hence the scalability of the technique. Another requirement to enable scalability is an efficient way of collecting the synthesized nanoparticles, and a potential way could be to sputter onto a liquid substrate, for example PEG.

In contrast to the studies on mass-selected particles which used liquid nitrogen for aggregation zone cooling, we are limited to water cooling. A few previous studies have been conducted regarding mass-selection-free gas aggregation synthesis of Pt nanoparticles using water-cooled aggregation zones [109, 110]. These works saw the production of 4 nm diameter Pt clusters, which is too small for the intended applications of this thesis. As a consequence, our efforts have aimed at optimizing the synthesis parameters to reach the required  $Pt_3Y$ nanoparticle size and morphology. To get a basic idea of the system and its nanoparticle production, our first attempt implemented a selection of reasonable synthesis parameters. We used the shortest possible aggregation length that our system (NC200U-B Nanocluster source, Oxford Applied Research) allows



Figure 5.6: TEM micrographs of gas aggregated nanoparticles, synthesized using 5 cm aggregation length, 0.45 mbar aggregation pressure, and 155 mA sputtering current.

(5 cm), an argon flow rate of 30 sccm which resulted in a pressure of 0.45 mbar in the aggregation zone, and a sputtering current of 155 mA giving a total sputtering power of 34 W. The particles were deposited directly on a TEM grid, and the resulting particles are displayed in figure 5.6. It is clearly seen that the produced particles form large, branched structures under these conditions and that most individual particles exhibit diameters well below 10 nm.

After this first attempt, the main goal was to increase the size of individual particles while limiting the formation of larger aggregates. The main parameters affecting the nucleation and growth of individual nanoparticles in gas aggregation are the aggregation length, the sputtering power, the argon flow rate, and the residence time of the clusters within the aggregation zone [83], where the residence time depends on both the aggregation length and the argon pressure. The formation of aggregates, on the other hand, mainly depends on the residence time, and the particle concentration in the volume [83]. For the following two experiments, we increased the argon flow to 50 sccm, resulting in an aggregation pressure of 0.64 mbar. The aggregation lengths in these two experiments were also increased, to 10 and 15 cm, respectively, while the sputtering currents were maintained at 155 mA in both cases.



Figure 5.7: TEM micrographs of gas aggregated nanoparticles, synthesized using a) 10 cm aggregation length and b) 15 cm aggregation length. In both experiments, the aggregation pressure was 0.64 mbar, and the sputtering current 155 mA.

Figure 5.7 shows typical TEM images of nanoparticles produced with the two longer aggregation lengths. Both samples display larger individual particles and considerably lower tendencies to form branched structures, compared to the case with the shortest aggregation length. However, most particles are still present as part of larger aggregates. According to the TEM results, the size of these aggregates decreases with increasing aggregation length, whereas the individual particles are of similar size in the two samples. These trends are intuitive and can be explained by separating the complete process into two steps; the nucleation and growth of individual nanoparticles and the aggregation of individual particles into larger aggregates. The initial nucleation and growth of individual nanoparticles should behave in a similar manner in the two cases, considering that the sputtering currents and argon pressures are identical. However, the aggregation of particles should be more extensive for the shorter aggregation length, since the concentration of individual particles is larger in the smaller volume, which is also what we observe.

### 5.1.3 Sputtering parameters

We cannot separate the effect of the sputtering power from the substrate temperature for the nanoparticles sputtered using the unbalanced magnetron setup. However, for  $Pt_3Y$  particles formed by gas aggregation, there is a direct effect of sputtering power on their size and morphology. With a basis in the particles produced in figure 5.7b (155 mA sputter current, 50 sccm argon flow, 15 cm aggregation length), we decided to study the size and morphology of particles produced at two other sputter currents, one lower (100 mA) and one higher (300 mA). All other synthesis parameters were left unchanged; however, a small variation of the sputter voltage between 200 to 215 V was required to facilitate the difference in sputter current. The resulting sputtering powers were 20, 32, and 64 W, for the 100, 155 and 300 mA cases, respectively.

TEM imaging of the three samples revealed an interesting trend. We expected that higher currents would lead to larger individual particle sizes [83] due to a higher concentration of sputtered atoms in the volume. This does indeed seem to be the case, based on our TEM observations shown in figure 5.8. However, what we did not expect is that sputtering using the highest current also results in a larger portion of non-aggregated single particles in the deposit, and formation of smaller aggregates in general. We can only speculate as to why these do not aggregate as much as the smaller particles produced at lower currents. Possibly, they are more efficiently trapped and removed by the gas flow exiting the aggregation zone, but we do not have any clear evidence supporting such a counterintuitive effect.

Regardless of which underlying process that determines the particle formation in figure 5.8, this is the first result of  $Pt_3Y$  nanoparticles with promising size and morphology obtained under the umbrella of this thesis. Furthermore, a deposition rate of more than 0.7 mg/min was estimated for the high current case, a massive increase compared to mass-selected nanoparticles [57, 65, 72]. In addition, energy dispersive x-ray spectroscopy (EDX) suggests a platinuma) Sputter current 100 mA



Figure 5.8: TEM micrographs of gas aggregated nanoparticles synthesized using a sputter current of a) 100 mA, b) 155 mA, and c) 300 mA. In all three experiments, the aggregation pressure was 0.64 mbar, and the aggregation length 15 cm.

yttrium ratio of 3.22 in the sputtered particles, which is very close to the composition of the sputter target, as well as the desired ratio of 3. This is in contrast to previous work on gas aggregation synthesis of mass-selected Pt-RE nanoparticles reported in the literature, for which an excess of Pt in the sputter target (Pt<sub>9</sub>RE) has been claimed necessary to obtain the right composition in the sputtered particles.

### 5.2 Post-sputtering treatments

In addition to varying the synthesis parameters, nanoparticle growth can be achieved through post-sputtering treatment of the samples. The next two sections present and discuss what we have learned regarding the specific types of post-treatment studied; those of heat- and microwave-treatment.

### 5.2.1 Heat-treatment

Heat-treatment of unsupported nanoparticles leads merely to particle aggregation and only little growth, as shown in **papers I** and **III**. However, two parameters have been observed to influence the stability and post-sputtering growth of Pt nanoparticles in PEG; 1) the presence of a carbon support in PEG during heat-treatment (**paper III**) and 2) the molecular weight of PEG (**paper IV**).

### Effect of carbon support

The heat-treatment was initially used as a method to transfer sputtered nanoparticles from the liquid to the carbon support. However, after increasing its duration from four to nineteen hours, we observed that the treatment also induced significant growth of the sputtered Pt particles. Interestingly, the effect does not apply to the whole ensemble of particles. Instead, two distinct populations of particles are present in the heat-treated catalyst samples. As presented in **paper III**, the first population consists of small (2.5 nm) particles nicely dispersed on the support. In contrast, the second population displays considerably larger (6.7 nm) particles, typically present within or in the very close vicinity of larger particle agglomerates. Thermal-induced growth and agglomeration of carbon-supported Pt nanoparticles has been observed in both inert and reducing atmospheres [111], with clear indications that the carbon support facilitates this growth, especially under a reducing atmosphere. Furthermore, liquid PEG can provide a reducing atmosphere, as exemplified by the chemical reduction of a Pt precursor into nanoparticles, reported by Cheng et al. [112]. We therefore attribute the continued growth and agglomeration of Pt particles during the heat-treatment to the combination of a reducing PEG environment and the presence of a carbon support, concluding that the actual mechanism of this growth would be an interesting topic of a future study.

### Effect of PEG molecular weight

The study by Cheng [112] became the inspiration for our next investigation of post-sputtering heat-treatments. Their work showed a clear relationship between the effectiveness of the Pt reduction and the PEG molecular weight, with larger nanoparticles produced in heavier PEGs. As a response, we set out to determine whether a similar effect exists for the heat-treatment of sputtered nanoparticles. The experiments, which are presented in the **paper IV** manuscript, were based on identical heat-treatments as in **paper III** but were performed in a range of PEG mixtures between PEG 600 and two heavier PEGs (PEG 1500 and PEG 4000). In contrast to the chemical reduction of a Pt precursor, heat-treatment of sputtered Pt nanoparticles show the opposite dependence on the PEG molecular weight. Particles produced and treated in the heavier PEG 4000 mixtures exhibit both smaller sizes and less particle agglomeration than particles in PEG 1500 mixtures and pure PEG 600. This suggests that agglomeration is in fact necessary for the carbon-mediated growth observed in **paper III**, and the longer PEG chains contribute to better stabilization, effectively preventing such particle agglomeration and growth. In extension, these observations led us to suspect that the amount of sputtered Pt atoms and ions that dissolve in the liquid substrate is likely not very large, which could be an effect of nanoparticle formation occurring predominantly at the liquid surface during sputtering. Further indications and discussion on the role of the surface in the formation of sputtered Pt nanoparticles are given in the **paper IV** manuscript.

### 5.2.2 Microwave-treatment

58

A second post-treatment to further grow sputtered nanoparticles attempted in this thesis is that of microwave-assisted particle growth. The method has been used as a green nanoparticle synthesis route for a range of materials, using ethylene glycol as a reducing agent and microwaves to induce high local temperatures. The technique was performed for Pt and Pt<sub>3</sub>Y nanoparticles sputtered in PEG. Here, only the latter is presented, but the results were very similar for the two samples. Figure 5.9 shows a typical TEM micrograph of the treated particles. When analyzing the TEM images, a small tendency of particle coalescence could be seen, which is reflected by a slightly extended distribution tail, which could be an effect of the microwave treatment. However, except for these few larger, coalesced particles, the size distribution is very similar to the as-sputtered nanoparticles reported in **papers I** and **III**.



Figure 5.9: TEM micrographs of sputtered  $Pt_3Y$  nanoparticles after postsputtering microwave-treatment. A slight tendency of particle coalescence is observed compared to as-sputtered particles, but only for a minor portion of the particle population.

### 5.3 Perspectives on nanoparticle growth

To summarize the results presented in this chapter, the growth of Pt-based nanoparticles produced by SoL is a complex subject. Nevertheless, we have been able to pinpoint a set of parameters and post-sputtering treatments that show little to no influence on the nanoparticle size: type of liquid, choice of sputter gas, substrate temperature, microwave post-treatment, and heat-treatment in the absence of a carbon support. In addition to these "negative" results, we have shown that Pt-based nanoparticle growth post-sputtering is possible, facilitated by a high surface area carbon support in the reducing PEG environment during heat-treatment at 150 °C. Furthermore, the extensive agglomeration of particles that occur during the heat-treatment can be controlled and mitigated by adjusting the PEG molecular weight. We believe that these results are mainly of relevance for SoL-synthesis of Pt nanoparticles, since the mentioned post-treatments are incompatible with Pt-RE alloys.

If the unsuccessful attempts to increase Pt and Pt-RE nanoparticle size in standard magnetron sputtering on liquid substrates are discouraging from the perspective of a "Dream Particle", the results from gas aggregation experiments are more positive. We have seen that tuning of the nanoparticle size as well as the degree of particle aggregation is possible, even without the use of a mass-filter. Moreover, these particles have been successfully collected by sputtering into PEG 600, and transferred to a carbon support for electrochemical evaluation in RDE. Their catalytic performance will be discussed in the next chapter, but looking forward, it is desirable to achieve better control over the aggregation of particles, and ensure preferential fabrication of single particles with diameters of roughly 10 nm. Doing so likely requires decreasing the residence time in the chamber. Increasing the argon pressure leads to a shorter residence time, but also to a larger number of three-body collisions that may promote aggregate formation. Introducing a flow of helium gas, on the other hand, decreases residence time without significantly inducing additional three-body collisions and could therefore be used to control the particle size and limit aggregate formation [83, 84]. This would be an appropriate next step in the development of gas aggregation sputtering of Pt-RE nanoparticles onto liquid substrates.

### Chapter 6

# Platinum-based nanocatalysts for the oxygen reduction reaction

In the previous chapter, we focused on the growth of Pt-based nanoparticles. This chapter provides a summary and discussion of the key results concerning the electrocatalytic performance of the studied nanomaterials and how these relate to structure and morphology.

### 6.1 Nanoparticles sputtered in PEG

This section presents the electrochemical evaluation of SoL-synthesized nanoparticles from both standard magnetron sputtering and gas aggregation sputtering. Supporting XPS results have been included where appropriate, to strengthen the discussion.

### 6.1.1 Standard DC magnetron sputtering

The electrochemical evaluation of Pt and Pt<sub>3</sub>Y catalyst nanoparticles synthesized by standard DC magnetron sputtering onto liquid PEG, supported on high surface area carbon support (Vulcan<sup>®</sup> XC-72) is presented in figures 6.1 and 6.2. Cyclic voltammetry (figure 6.1) reveals a larger electrochemical surface area in the Pt<sub>3</sub>Y sample. We do not fully understand this incoherence in the final catalyst area, but possible explanations include varying collection efficiencies during transfer to carbon support and extraction from the PEG substrate, slight differences in ink preparation and drop casting, or leaching of oxidized yttrium leading to a more porous material. We consider the first and last explanations to be the most likely. After separation of the catalyst samples



Figure 6.1: Cyclic voltammograms of Pt and  $Pt_3Y$  nanoparticles in argon saturated 0.1 M HClO<sub>4</sub> electrolyte, recorded at 50 mV/s scan rate.

from the PEG in a centrifuge, the supernatant PEG of the Pt sample exhibited a significantly more yellow color than its  $Pt_3Y$  counterpart, which could suggest residual Pt nanoparticles in the liquid and lower extraction efficiency.

Despite the larger surface area of the  $Pt_3Y$  catalysts, the geometric ORR activity (figure 6.2a) is not considerably increased compared to Pt. As a consequence, after the influence of mass transport limitations is removed and the current density normalized by the ECSA, the kinetic current densities shown in figure 6.2b demonstrate that the Pt catalyst performs better than the  $Pt_3Y$ . We believe that the size of the primary sputtered particles is so small that no metallic yttrium remains in the particle core after acid leaching of the oxidized yttrium. This assumption is confirmed by XPS analysis of the  $Pt_3Y$  catalyst before and after ORR measurements. Figure 6.3a clearly shows the presence of



Figure 6.2: Catalytic ORR activity of Pt and  $Pt_3Y$  carbon supported nanoparticles obtained in oxygen-saturated 0.1 M HClO<sub>4</sub>, represented as a) geometric activities and b) kinetic current densities corrected for mass transport losses. The data was recorded using 50 mV/s scan rate.


Figure 6.3: Y3d and S2p narrow scan of the  $Pt_3Y$  catalyst powders a) before, and b) after ORR measurements in RDE. The yttrium signal is completely removed after ORR, indicating complete oxidation and leaching of yttrium from the catalyst.

an yttrium phase in the as-prepared sample before ORR measurements. The position of the  $Y3d_{5/2}$  peak at 160 eV binding energy suggests that this yttrium phase is not metallic (156 eV) [113], but in a considerably higher oxidation state. In fact, the high binding energy does not match that of  $Y_2O_3$  oxide (156.4-157 eV) either [113]. Most likely, yttrium bonds with fluorine from the ionomer during ink preparation, forming YF<sub>3</sub>, which is consistent with literature values reported for the  $Y3d_{5/2}$  peak position [114, 115]. After ORR measurements, the Y3d peaks are completely annihilated as seen in figure 6.3b. The small feature to the right of the sulfate S2p (169.4 eV) peaks is attributed to a reduced sulfur phase (164.3 eV), not yttrium [113]. Hence, we can conclude that the yttrium is completely oxidized and leached during the ORR measurements. The only way to prevent this is to ensure the formation of larger Pt-RE nanoparticles before introducing the catalyst to oxidizing environments.

The activities showcased in figure 6.2, are high in regards to commercially available Pt catalysts, which typically possess specific activities well below 1  $\text{mA/cm}^2$  at 0.9 V. Both Pt and Pt<sub>3</sub>Y samples exhibit kinetic current densities

of over 1.5 mA/cm<sup>2</sup><sub>Pt</sub> at this potential, roughly corresponding to the activity reported for mass-selected Pt nanoparticles with sizes of around 6–8 nm [49, 116]. The TEM imaging of the supported Pt nanoparticle catalysts summarized in figure 2 of **paper III** explains this behavior, as it portrays the existence of two distinct nanoparticle populations in the heat treated, carbon supported catalyst samples. Based on these images, it is evident that the population with the largest particle size (6.6 nm mean diameter), is dominating both in terms of incorporated material, as well as surface area, which is further supported by the electrochemical results. Furthermore, heat treatment of sputtered Pt nanoparticles in the absence of carbon support (**papers I** and **III**), suggest only minor influence on the nanoparticle growth, leaving the presence of carbon particles as the sole explanation for this increase in particle size.

#### 6.1.2 Gas aggregation sputtering

The results presented here are merely preliminary and, therefore, the discussion has been constructed in a way that reflects this. In an effort to evaluate the gas aggregated  $Pt_3Y$  particles electrochemically, sputtering was performed onto PEG 600 to collect a larger amount of material, on the order of milligrams. The synthesis parameters were adjusted slightly, as an instability of the sputtering voltage was observed for longer deposition times using the highest sputtering current (300 mA) and argon flow (50 sccm). The adjusted parameter values were 200 mA sputter current and 30 sccm of argon flow. A similar heattreatment to the one in **paper III** was performed for transfer of particles to a high surface area carbon support. However, both the time and temperature parameters were decreased (1 h, 100 °C) with the intention of not causing any further growth of the nanoparticles. After the heat-treatment, the cleaning procedure, ink preparation, and electrode preparation followed the protocol used in **paper III**. The prepared electrodes were dipped in  $0.1 \text{ M HClO}_4$  to facilitate the leaching of oxidized yttrium from the surface layer and allowing the formation of a Pt skin, followed by electrochemical characterization in RDE.

Unfortunately, the initial test does not indicate an enhancement in ORR activity, but rather a small decrease. Figure 6.4 shows  $j_k$  of the gas aggregated Pt<sub>3</sub>Y catalyst sample. The value of  $j_k$  at 0.9 V vs. RHE is just below 1.5 mA/cm<sup>2</sup><sub>Pt</sub>, which is very similar to the smaller Pt<sub>3</sub>Y particles in figure 6.2b. At this point, we do not have a clear explanation for the lack of activity enhancement for our larger Pt<sub>3</sub>Y particles, and we can only state that there are many potential factors that could influence the observed activity. Possibly, the heat-treatment used for the transfer to the carbon support has a detrimental effect on the material. The ink preparation is another potential candidate for the poor activity. As an example the ionomer-catalyst ratio (I/C) has been shown to greatly influence the specific activity of Pt<sub>x</sub>Y nanoparticles [117], where higher I/C ratios can lead to ionomer poisoning of the catalyst particles.



Figure 6.4: Kinetic current density of gas aggregated Pt<sub>3</sub>Y nanoparticles.

### 6.2 Sputtered thin films

In addition to the work on Pt and Pt<sub>3</sub>Y nanoparticles, the activity and stability of sputtered Pt<sub>3</sub>Y thin films were investigated in **paper II**. Consistent with previous studies [63, 118], the initial ORR activity of Pt<sub>3</sub>Y thin films outperforms that of Pt. The activity was shown to decrease during accelerated stress tests (AST) inside a PEMFC for both the alloy and the Pt thin films, however, after AST, the Pt<sub>3</sub>Y activity is similar to the Pt activity before AST. Furthermore, the decrease in Pt<sub>3</sub>Y ORR activity was attributed to an increasing Pt overlayer thickness, due to gradual leaching of yttrium from the core alloy during AST. Electron microscopy further suggests that the yttrium leaching does not significantly alter the film morphology of the alloy samples, explaining why the ORR activity of the alloy thin films after AST are still on par with that of as-sputtered Pt.

# Chapter 7 Conclusions

This thesis has extensively studied the growth processes of Pt and Pt-RE metal alloy nanocatalysts and explored their implementation in catalyst layers for the ORR reaction, relating the size, structure, and morphology of the materials to their catalytic activity. We have found that many of the SoL synthesis parameters, including substrate type and temperature, sputter gas type, and sputtering power, have only a small, if any, influence on the growth of Ptbased nanoparticles synthesized using magnetron sputtering in the unbalanced configuration (**papers I** and **III**). Hence, Pt-based nanoparticle growth in SoL is considerably less sensitive to parameters such as substrate type and temperature than many other frequently studied metallic systems; for example Au, Ag, Cu, and their alloys.

Post-sputtering treatments of synthesized nanoparticles have also been proven to be relatively ineffective in promoting particle growth, with one clear exception: heat-treatment of Pt nanoparticles in a dispersion of high surface area carbon in PEG 600 (**paper III**). These nanoparticles exhibit significant growth, accompanied by partial agglomeration and aggregation, resulting in a bimodal nanoparticle size distribution (2.5 and 6.7 nm mean diameters). Their catalytic ORR activity is high, and comparable to mass-selected nanoparticles with diameters around 6–8 nm, indicating that the ORR activity is dominated by the larger particle population. We have also shown that the degree of agglomeration and aggregation during heat-treatment can be controlled by varying the molecular weight of PEG, with heavier PEGs offering more efficient particle stabilization and smaller sizes in general (**paper IV**).

Nanoparticles that exhibit promising size and morphology have been synthesized and collected using gas aggregation sputtering onto liquid PEG, without the use of any mass-filtering equipment. This allows for increased deposition rates and is therefore an important step towards a scalable Pt-RE synthesis method. Future studies should further explore the influence of the synthesis parameters, with the final goal of achieving the optimal nanoparticle size and morphology for the ORR. Finally, the long-term stability and activity of Pt and  $Pt_3Y$  thin films have been studied in the PEMFC environment (**paper II**). The alloy thin films showed higher activity both before and after aging; however, a significant decrease in activity was observed for both sample types. For  $Pt_3Y$ , the decrease in activity was caused by continued leaching of yttrium during the aging process, leading to a thicker Pt overlayer with very similar atomic spacing to bulk Pt. Furthermore, physical characterization using electron microscopy revealed that the yttrium leaching does not significantly change the  $Pt_3Y$  thin film morphology, and in combination with the other results this explains why the  $Pt_3Y$  activity after aging is similar to that of Pt before aging.

Looking ahead, it is difficult to deny the great potential that Pt-RE metal alloys have for the catalysis of the ORR. Yet, it has proven exceptionally difficult to implement a functional, highly active, and stable Pt-RE nanoparticle catalyst layer in practice. We are still hopeful that these materials will see commercial success and contribute to improved fuel cell efficiencies in the future; however, before that can become a reality, several issues remain to be addressed, some of which have ties to this thesis. On the positive note, we have seen clear evidence that Pt<sub>3</sub>Y nanoparticles of promising size and morphology can be produced and efficiently collected by gas aggregation sputtering onto liquid PEG. So far, we have not been able to demonstrate any enhanced ORR activity of these nanoparticles compared to Pt. Further studies are needed for the electrode preparation, which includes several sensitive steps. For example, we have seen that the typical yttrium oxide in as-sputtered  $Pt_3Y$  nanocatalysts [62], is replaced by a fluoride phase during the ink preparation procedure. It would be of interest to study the chemical processes during ink preparation in more detail, and specifically to determine if acid-leaching of the yttrium oxide before the ink preparation could have a positive effect on the catalytic activity. In general, we believe that hydrocarbon-based, fluorine-free PEMs and ionomers could be a possible key in preventing the ionomer poisoning of Pt-RE nanoparticles. Currently, there are considerable research activities invested in these types of membranes and ionomers [119, 120], and a future study that compares the effect of their chemistry on the ORR activity of Pt-RE nanoparticle catalysts would be of greatest interest.

In conclusion, this work has demonstrated the viability of using SoL for production of high-performance PEMFC catalyst layers, with potential to be extended to Pt-RE alloy nanoparticles using gas aggregation sputtering instead of standard magnetron sputtering. More work should be directed towards the optimization of catalyst layer preparation procedures, in order to unlock the enhanced ORR activities inherent to these materials. If successful, such a technological breakthrough could significantly alter the sustainable transport arena, in favor of hydrogen fuel cells.

## Acknowledgments

The work in this thesis has been funded by the Swedish Energy Agency, Energimyndigheten.

First and foremost, I would like to thank my supervisor **Björn Wickman**, and my examiner **Henrik Grönbeck**, for support and guidance, and for always taking their time to address any questions or issues related to my work.

Then, I would like to express gratitude towards my two co-supervisors, **Rose-mary Brown** and **Mathilde Luneau**, who supported me and shared their knowledge, at different stages during this work.

Working on this thesis, I have come in contact with a great number of people who have helped me in some way, of which I especially want to thank the following: **Henrik Frederiksen** - for helping me with anything related to sputtering and for showing genuine interest in my work. **Lasse Urholm** and **Lennart Norberg** - for all the practical assistance in the lab. **Stefan, Ludvig**, and **Michal** at CMAL - for valuable help and discussions on electron microscopy and x-ray diffraction techniques. **Linnéa** and **Vera** in the Electrochemistry group - for helping me with experiments during crucial moments of the PhD and co-authoring paper III with me.

I would also like to thank everyone at the Chemical physics division, with a special mention to the past and current members of the Electrochemistry group. You all made this journey fun and pleasant.

Finally, to my wife **Hanna**, my family, and my friends who supported and encouraged me through good and bad, I want to express my greatest appreciation. Without you, none of this would have been possible.

Thank you, everyone!

## Bibliography

- [1] IPCC. Synthesis Report of the IPCC Sixth Assessment Report. 2023. URL: https://www.ipcc.ch/report/ar6/syr/ (cit. on p. 1).
- [2] IPCC. Special Report on Climate Change and Land. 2019. URL: https: //www.ipcc.ch/srccl/ (cit. on p. 1).
- [3] IPCC. Special Report on the Ocean and Cryosphere in a Changing Climate. 2019. URL: https://www.ipcc.ch/srocc/ (cit. on p. 1).
- [4] Naturvårdsverket. Begränsad Klimatpåverkan. 2022. URL: https://www. naturvardsverket.se/om-oss/publikationer/7000/begransadklimatpaverkan/ (cit. on p. 1).
- [5] European Commission. A European Green Deal. 2020. URL: https:// commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal\_en (cit. on p. 1).
- [6] IEA. Net Zero by 2050. 2021. URL: https://www.iea.org/reports/ net-zero-by-2050 (cit. on p. 1).
- [7] UNFCCC. The Paris Agreement. 2015. URL: https://unfccc.int/ process-and-meetings/the-paris-agreement (cit. on p. 1).
- [8] UNEP. Emissions Gap Report 2021. 2021. URL: https://www.unep. org/resources/emissions-gap-report-2021 (cit. on p. 1).
- UNFCCC. NDC Synthesis Report. 2022. URL: https://unfccc.int/ ndc-synthesis-report-2022#Projected-GHG-Emission-levels (cit. on p. 1).
- [10] IEA. Power Systems in Transition. 2020. URL: https://www.iea.org/ reports/power-systems-in-transition (cit. on p. 1).
- [11] European Commission. EU Hydrogen Strategy. 2020. URL: https:// energy.ec.europa.eu/topics/energy-systems-integration/ hydrogen\_en#eu-hydrogen-strategy (cit. on p. 2).
- [12] Iain Staffell et al. "The role of hydrogen and fuel cells in the global energy system". In: *Energy & Environmental Science* 12.2 (2019), pp. 463–491 (cit. on p. 2).
- [13] Matteo Genovese et al. "Power-to-hydrogen and hydrogen-to-X energy systems for the industry of the future in Europe". In: International Journal of Hydrogen Energy 48.44 (2023), pp. 16545–16568 (cit. on p. 2).

- [14] Thanh Tuan Le et al. "Fueling the future: A comprehensive review of hydrogen energy systems and their challenges". In: *International Journal of Hydrogen Energy* 54 (2024), pp. 791–816 (cit. on p. 2).
- [15] Kasper Dalgas Rasmussen et al. "Platinum demand and potential bottlenecks in the global green transition: a dynamic material flow analysis". In: *Environmental science & technology* 53.19 (2019), pp. 11541–11551 (cit. on p. 2).
- [16] Thomas E Graedel et al. "Criticality of metals and metalloids". In: Proceedings of the National Academy of Sciences 112.14 (2015), pp. 4257– 4262 (cit. on p. 2).
- [17] Jae Yong Song, Eun-Yeong Kwon and Beom Soo Kim. "Biological synthesis of platinum nanoparticles using Diopyros kaki leaf extract". In: *Bioprocess and biosystems engineering* 33 (2010), pp. 159–164 (cit. on p. 2).
- [18] Prashant Mohanpuria, Nisha K Rana and Sudesh Kumar Yadav. "Biosynthesis of nanoparticles: technological concepts and future applications". In: *Journal of nanoparticle research* 10 (2008), pp. 507–517 (cit. on p. 2).
- [19] Björn Lönn. Platinum-Based Nanocatalysts for Proton Exchange Membrane Fuel Cells. Chalmers Tekniska Högskola (Sweden), 2023 (cit. on p. 3).
- [20] G Sandstede et al. "Handbook of fuel cells. Fundamentals, technology, applications". In: ed. by W Vielstich, A Lamm and Gasteiger HA. John Wiley & Sons, Ltd Chichester, UK, 2003. Chap. 12. History of low temperature fuel cells, pp. 145–218 (cit. on pp. 5, 19).
- [21] F.T. Bacon. "Fuel cells, past, present and future". In: *Electrochimica Acta* 14.7 (July 1969), pp. 569–585. DOI: 10.1016/0013-4686(69) 87042-8. URL: https://doi.org/10.1016%2F0013-4686%2869% 2987042-8 (cit. on pp. 5, 19).
- [22] P. W. Atkins and L Jones. *Chemical principles*. en. 5th ed. W.H. Freeman, 2010. ISBN: 1-4292-1955-6 (cit. on pp. 6, 9, 14).
- [23] Carl H. Hamann, Andrew Hamnett and Wolf Vielstich. *Electrochemistry*.
  2nd ed. Wiley-VCH, 2007. ISBN: 978-3-527-31069-2 (cit. on pp. 8–12, 14, 41, 44, 45).
- [24] Sergio Trasatti. "The absolute electrode potential: an explanatory note (Recommendations 1986)". In: *Pure and Applied Chemistry* 58.7 (1986), pp. 955–966 (cit. on p. 10).
- [25] Andrew L Dicks and David AJ Rand. Fuel cell systems explained. John Wiley & Sons, 2018 (cit. on pp. 11, 22, 26).
- [26] Edmund JF Dickinson and Andrew J Wain. "The Butler-Volmer equation in electrochemical theory: Origins, value, and practical application". In: *Journal of Electroanalytical Chemistry* 872 (2020), p. 114145 (cit. on p. 12).

- [27] Derek Pletcher. A first course in electrode processes. Royal Society of Chemistry, 2009 (cit. on pp. 12, 13).
- [28] Carl A Busacca et al. "The growing impact of catalysis in the pharmacentrical industry". In: Advanced Synthesis & Catalysis 353.11-12 (2011), pp. 1825–1864 (cit. on p. 14).
- [29] Ib Chorkendorff and Johannes W Niemantsverdriet. Concepts of modern catalysis and kinetics. John Wiley & Sons, 2017 (cit. on p. 14).
- [30] M Shelef and R.W McCabe. "Twenty-five years after introduction of automotive catalysts: what next?" In: *Catalysis Today* 62.1 (Sept. 2000), pp. 35–50. DOI: 10.1016/s0920-5861(00)00407-7. URL: https: //doi.org/10.1016%2Fs0920-5861%2800%2900407-7 (cit. on p. 14).
- [31] Emil Roduner. "Understanding catalysis". In: Chemical Society Reviews 43.24 (2014), pp. 8226–8239 (cit. on p. 14).
- [32] R. O'Hayre et al. Fuel Cell Fundamentals. 3rd ed. John Wiley & Sons, 2016 (cit. on p. 15).
- [33] Jens Kehlet Nørskov et al. "Origin of the overpotential for oxygen reduction at a fuel-cell cathode". In: *The Journal of Physical Chemistry* B 108.46 (2004), pp. 17886–17892 (cit. on pp. 16, 17, 24–26).
- [34] William Robert Grove. "LVI. On a new voltaic combination: To the editors of the Philosophical Magazine and Journal". In: *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* 13.84 (1838), pp. 430–431 (cit. on p. 19).
- [35] Eduardo I. Ortiz-Rivera, Angel L. Reyes-Hernandez and Rey A. Febo.
  "Understanding the history of fuel cells". In: 2007 IEEE Conference on the History of Electric Power. 2007, pp. 117–122. DOI: 10.1109/HEP.
   2007.4510259 (cit. on p. 19).
- [36] Omar Z Sharaf and Mehmet F Orhan. "An overview of fuel cell technology: Fundamentals and applications". In: *Renewable and sustainable energy reviews* 32 (2014), pp. 810–853 (cit. on pp. 19, 20).
- [37] Jung-Ho Wee. "Applications of proton exchange membrane fuel cell systems". In: *Renewable and sustainable energy reviews* 11.8 (2007), pp. 1720–1738 (cit. on p. 20).
- [38] Hydrogen and Fuel Cell Technologies Office part of U.S. Department of Energy. *Types of Fuel Cells*. URL: https://www.energy.gov/eere/ fuelcells/types-fuel-cells (cit. on p. 20).
- [39] Hydrogen and Fuel Cell Technologies Office part of U.S. Department of Energy. Comparison of Fuel Cell Technologies. URL: https://www. energy.gov/eere/fuelcells/comparison-fuel-cell-technologies (cit. on p. 20).
- [40] VM Vishnyakov. "Proton exchange membrane fuel cells". In: Vacuum 80.10 (2006), pp. 1053–1065 (cit. on p. 21).

- [41] Steven J Hamrock and Michael A Yandrasits. "Proton exchange membranes for fuel cell applications". In: *Journal of Macromolecular Science*, *Part C: Polymer Reviews* 46.3 (2006), pp. 219–244 (cit. on p. 21).
- [42] S Jamai Peighambardoust, Soosan Rowshanzamir and Mehdi Amjadi. "Review of the proton exchange membranes for fuel cell applications". In: *International journal of hydrogen energy* 35.17 (2010), pp. 9349–9384 (cit. on p. 21).
- [43] Muhamad Ariff Amir Hamzah et al. "Microporous layer in proton exchange membrane fuel cells: Advancement in materials and properties". In: Journal of Environmental Chemical Engineering 12.6 (2024), p. 114220. ISSN: 2213-3437. DOI: https://doi.org/10.1016/j.jece. 2024.114220. URL: https://www.sciencedirect.com/science/ article/pii/S2213343724023510 (cit. on p. 22).
- [44] L Cindrella et al. "Gas diffusion layer for proton exchange membrane fuel cells—A review". In: *Journal of Power Sources* 194.1 (2009), pp. 146– 160 (cit. on p. 22).
- [45] Zhi Wei Seh et al. "Combining theory and experiment in electrocatalysis: Insights into materials design". In: *Science* 355.6321 (2017), eaad4998 (cit. on pp. 23–26).
- [46] CM Zalitis et al. "Properties of the hydrogen oxidation reaction on Pt/C catalysts at optimised high mass transport conditions and its relevance to the anode reaction in PEFCs and cathode reactions in electrolysers". In: *Electrochimica Acta* 176 (2015), pp. 763–776 (cit. on p. 23).
- [47] Heine A Hansen, Venkatasubramanian Viswanathan and Jens K Nørskov. "Unifying kinetic and thermodynamic analysis of 2 e-and 4 e-reduction of oxygen on metal surfaces". In: *The Journal of Physical Chemistry C* 118.13 (2014), pp. 6706–6718 (cit. on pp. 24, 26).
- [48] Marcel Pourbaix. "Atlas of electrochemical equilibria in aqueous solutions". In: NACE (1974) (cit. on p. 25).
- [49] Francisco J Perez-Alonso et al. "The effect of size on the oxygen electroreduction activity of mass-selected platinum nanoparticles". In: Angewandte Chemie International Edition 51.19 (2012), pp. 4641–4643 (cit. on pp. 28, 30, 46, 64).
- [50] GA Tritsaris et al. "Atomic-scale modeling of particle size effects for the oxygen reduction reaction on Pt". In: *Catalysis letters* 141 (2011), pp. 909–913 (cit. on p. 28).
- [51] Hubert A Gasteiger et al. "Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs". In: *Applied Catalysis B: Environmental* 56.1-2 (2005), pp. 9–35 (cit. on p. 28).
- [52] Vojislav R Stamenkovic et al. "Improved oxygen reduction activity on Pt3Ni (111) via increased surface site availability". In: *science* 315.5811 (2007), pp. 493–497 (cit. on p. 28).

- [53] Xiaoqing Huang et al. "High-performance transition metal-doped Pt3Ni octahedra for oxygen reduction reaction". In: *Science* 348.6240 (2015), pp. 1230–1234 (cit. on p. 28).
- [54] UA Paulus et al. "Oxygen reduction on carbon-supported Pt- Ni and Pt- Co alloy catalysts". In: *The Journal of Physical Chemistry B* 106.16 (2002), pp. 4181–4191 (cit. on p. 28).
- [55] V Stamenković et al. "Surface composition effects in electrocatalysis: Kinetics of oxygen reduction on well-defined Pt3Ni and Pt3Co alloy surfaces". In: *The Journal of Physical Chemistry B* 106.46 (2002), pp. 11970–11979 (cit. on p. 28).
- [56] Vojislav Stamenkovic et al. "Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure". In: *Angewandte Chemie International Edition* 45.18 (2006), pp. 2897–2901 (cit. on p. 28).
- [57] Patricia Hernandez-Fernandez et al. "Mass-selected nanoparticles of Pt x Y as model catalysts for oxygen electroreduction". In: *Nature chemistry* 6.8 (2014), pp. 732–738 (cit. on pp. 28–30, 46, 53, 55).
- [58] Ifan EL Stephens, Alexander S Bondarenko and Bech. "Oxygen electroreduction activity and x-ray photoelectron spectroscopy of platinum and early transition metal alloys". In: *ChemCatChem* 4.3 (2012), pp. 341–349 (cit. on p. 28).
- [59] J Greeley et al. "Alloys of platinum and early transition metals as oxygen reduction electrocatalysts". In: *Nature chemistry* 1.7 (2009), pp. 552–556 (cit. on pp. 28, 29).
- [60] Sung Jong Yoo et al. "Pt3Y electrocatalyst for oxygen reduction reaction in proton exchange membrane fuel cells". In: *International journal of hydrogen energy* 37.12 (2012), pp. 9758–9765 (cit. on p. 28).
- [61] Niklas Lindahl et al. "High specific and mass activity for the oxygen reduction reaction for thin film catalysts of sputtered Pt3Y". In: Advanced Materials Interfaces 4.13 (2017), p. 1700311 (cit. on pp. 28, 46).
- [62] Rosemary Brown et al. "Unraveling the surface chemistry and structure in highly active sputtered Pt3Y catalyst films for the oxygen reduction reaction". In: ACS applied materials & interfaces 12.4 (2019), pp. 4454– 4462 (cit. on pp. 28, 46, 68).
- [63] Niklas Lindahl et al. "Fuel cell measurements with cathode catalysts of sputtered Pt3Y thin films". In: *ChemSusChem* 11.9 (2018), pp. 1438– 1445 (cit. on pp. 28, 65).
- [64] R Brown et al. "Surface composition of a highly active Pt3Y alloy catalyst for application in low temperature fuel cells". In: *Fuel Cells* 20.4 (2020), pp. 413–419 (cit. on p. 28).
- [65] Amado Velázquez-Palenzuela et al. "The enhanced activity of massselected PtxGd nanoparticles for oxygen electroreduction". In: *Journal* of Catalysis 328 (2015), pp. 297–307 (cit. on pp. 28, 30, 53, 55).

- [66] María Escudero-Escribano et al. "Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction". In: *Science* 352.6281 (2016), pp. 73–76 (cit. on pp. 28, 29, 46).
- [67] Kim Degn Jensen et al. "X-ray absorption spectroscopy investigation of platinum–gadolinium thin films with different stoichiometry for the oxygen reduction reaction". In: *Catalysts* 10.9 (2020), p. 978 (cit. on p. 28).
- [68] Shuo Chen et al. "Platinum-alloy cathode catalyst degradation in proton exchange membrane fuel cells: nanometer-scale compositional and morphological changes". In: *Journal of the Electrochemical Society* 157.1 (2009), A82 (cit. on p. 28).
- [69] F Maillard et al. "Durability of Pt3Co/C nanoparticles in a protonexchange membrane fuel cell: Direct evidence of bulk Co segregation to the surface". In: *Electrochemistry Communications* 12.9 (2010), pp. 1161– 1164 (cit. on p. 28).
- [70] Mark K Debe, Radoslav T Atanasoski and Andrew J Steinbach. "Nanostructured thin film electrocatalysts-current status and future potential". In: *ECS transactions* 41.1 (2011), p. 937 (cit. on p. 29).
- [71] Brian Peter Knudsen. "Synthesis of Platinum Rare Earth Alloy Catalysts for Fuel Cells". In: (2016) (cit. on p. 30).
- [72] Ningjing Tang, Hui Wang and Tao Zhang. "Synthesis of Pt-Rare Earth Metal Alloys and Their Applications". In: *Chemistry–A European Journal* 30.67 (2024), e202402750 (cit. on pp. 30, 35, 55).
- [73] Ioan Valentin Tudose et al. "Chapter 2 Chemical and physical methods for multifunctional nanostructured interface fabrication". In: Functional Nanostructured Interfaces for Environmental and Biomedical Applications. Ed. by Valentina Dinca and Mirela Petruta Suchea. Micro and Nano Technologies. Elsevier, 2019, pp. 15–26. ISBN: 978-0-12-814401-5. DOI: https://doi.org/10.1016/B978-0-12-814401-5.00002-5. URL: https://www.sciencedirect.com/science/article/pii/B9780128144015000025 (cit. on p. 31).
- [74] Jon Tomas Gudmundsson and Daniel Lundin. "Introduction to magnetron sputtering". In: *High power impulse magnetron sputtering*. Elsevier, 2020, pp. 1–48 (cit. on pp. 31, 32).
- [75] William Robert Grove. "VII. On the electro-chemical polarity of gases". In: *Philosophical Transactions of the Royal Society of London* 142 (1852), pp. 87–101 (cit. on p. 31).
- Jindrich Musil, Jaroslav Vlcek and Pavel Baroch. "Chapter 3 Magnetron Discharges for Thin Films Plasma Processing". In: Materials Surface Processing by Directed Energy Techniques. Ed. by Yves Pauleau. European Materials Research Society Series. Oxford: Elsevier, 2006, pp. 67-110. ISBN: 978-0-08-044496-3. DOI: https://doi.org/10.1016/B978-008044496-3/50004-6. URL: https://www.sciencedirect.com/science/article/pii/B9780080444963500046 (cit. on p. 32).

- [77] Gao-xiang Ye et al. "Structural and electrical properties of a metallic rough-thin-film system deposited on liquid substrates". In: *Physical Review B* 54.20 (Nov. 1996), pp. 14754–14757. DOI: 10.1103/physrevb. 54.14754 (cit. on p. 32).
- [78] Yoshikiyo Hatakeyama et al. "Synthesis of gold nanoparticles in liquid polyethylene glycol by sputter deposition and temperature effects on their size and shape". In: *The Journal of Physical Chemistry C* 115.8 (2011), pp. 3279–3285 (cit. on pp. 33, 48, 50, 51).
- [79] Jaydeep Sarkar. "Sputtering and Thin Film Deposition". In: Sputtering Materials for VLSI and Thin Film Devices. Elsevier, 2014, pp. 93– 170. DOI: 10.1016/b978-0-8155-1593-7.00002-3. URL: https: //doi.org/10.1016%2Fb978-0-8155-1593-7.00002-3 (cit. on p. 33).
- [80] Anastasiya Sergievskaya, Adrien Chauvin and Stephanos Konstantinidis. "Sputtering onto liquids: a critical review". In: *Beilstein Journal of Nanotechnology* 13.1 (2022), pp. 10–53 (cit. on p. 34).
- [81] Michael Meischein, Xiao Wang and Alfred Ludwig. "Unraveling the formation mechanism of nanoparticles sputtered in ionic liquid". In: *The Journal of Physical Chemistry C* 125.43 (2021), pp. 24229–24239 (cit. on p. 34).
- [82] C Xirouchaki and RE Palmer. "Deposition of size-selected metal clusters generated by magnetron sputtering and gas condensation: a progress review". In: *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences* 362.1814 (2004), pp. 117–124 (cit. on p. 34).
- [83] Malak Khojasteh and Vitaly V Kresin. "Influence of source parameters on the growth of metal nanoparticles by sputter-gas-aggregation". In: *Applied Nanoscience* 7 (2017), pp. 875–883 (cit. on pp. 34, 54, 55, 59).
- [84] Rasmus Munksgård Nielsen et al. "The morphology of mass selected ruthenium nanoparticles from a magnetron-sputter gas-aggregation source". In: *Journal of Nanoparticle Research* 12 (2010), pp. 1249–1262 (cit. on pp. 34, 59).
- [85] Peter W. Hawkes and John C. H. Spence, eds. Springer Handbook of Microscopy. Springer Cham, 2019. ISBN: 978-3-030-00069-1 (cit. on p. 36).
- [86] Brent Fultz and James M Howe. Transmission electron microscopy and diffractometry of materials. Springer Science & Business Media, 2012 (cit. on p. 37).
- [87] L. A. Feigin and D. I. Svergun. Structure Analysis by Small-Angle X-Ray and Neutron Scattering. en. Springer, 2013. ISBN: 978-1-4757-6624-0 (cit. on p. 37).
- [88] Paul Van der Heide. X-ray photoelectron spectroscopy: an introduction to principles and practices. John Wiley & Sons, 2011 (cit. on pp. 37–39).

- [89] Albert Einstein. "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt". In: Annalen der Physik 322 (1905), pp. 132–148 (cit. on p. 37).
- [90] Kai Siegbahn. "ESCA: atomic, molecular and solid state structure studies by means of electron spectroscopy". In: Nova Acta Regiae Societatis Scientiarum Upsaliensis (1967) (cit. on p. 37).
- [91] Stephan Hüfner. Photoelectron spectroscopy: principles and applications. Springer Science & Business Media, 2013 (cit. on p. 39).
- [92] Walther Friedrich, Paul Knipping and Max Laue. "Interferenzerscheinungen bei roentgenstrahlen". In: Annalen der Physik 346.10 (1913), pp. 971–988 (cit. on p. 39).
- [93] Andrei A Bunaciu, Elena Gabriela UdriŞTioiu and Hassan Y Aboul-Enein. "X-ray diffraction: instrumentation and applications". In: *Critical reviews in analytical chemistry* 45.4 (2015), pp. 289–299 (cit. on p. 39).
- [94] S Trasatti and OA Petrii. "Real surface area measurements in electrochemistry". In: *Pure and applied chemistry* 63.5 (1991), pp. 711–734 (cit. on p. 42).
- [95] T Biegler, DAJ Rand and R Woods. "Limiting oxygen coverage on platinized platinum; relevance to determination of real platinum area by hydrogen adsorption". In: *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 29.2 (1971), pp. 269–277 (cit. on p. 43).
- [96] Richard G. Compton and Craig E. Banks. Understanding Voltammetry. World Scientific Publishing Europe Ltd., 2018 (cit. on p. 44).
- [97] Allen J Bard, Larry R Faulkner and Henry S White. *Electrochemical methods: fundamentals and applications*. John Wiley & Sons, 2022 (cit. on pp. 45, 46).
- [98] Juan Wang et al. "Quantitative kinetic analysis on oxygen reduction reaction: A perspective". In: *Nano Materials Science* 3.3 (2021), pp. 313– 318 (cit. on p. 45).
- [99] Priscila Vensaus et al. "Enhancement of electrocatalysis through magnetic field effects on mass transport". In: *Nature Communications* 15.1 (2024), p. 2867 (cit. on p. 45).
- [100] Wenlong Chen et al. "Reconsidering the benchmarking evaluation of catalytic activity in oxygen reduction reaction". In: *IScience* 23.10 (2020) (cit. on p. 45).
- [101] Yoshikiyo Hatakeyama, Kei Onishi and Keiko Nishikawa. "Effects of sputtering conditions on formation of gold nanoparticles in sputter deposition technique". In: *RSC advances* 1.9 (2011), pp. 1815–1821 (cit. on pp. 48, 52).
- [102] Yoshikiyo Hatakeyama, Satoshi Takahashi and Keiko Nishikawa. "Can temperature control the size of Au nanoparticles prepared in ionic liquids by the sputter deposition technique?" In: *The Journal of Physical Chemistry C* 114.25 (2010), pp. 11098–11102 (cit. on pp. 48, 50).

- [103] Yoshikiyo Hatakeyama et al. "Small-angle X-ray scattering study of Au nanoparticles dispersed in the ionic liquids 1-alkyl-3-methylimidazolium tetrafluoroborate". In: *The Journal of Physical Chemistry C* 113.10 (2009), pp. 3917–3922 (cit. on p. 48).
- [104] Yoshikiyo Hatakeyama et al. "Anion and cation effects on the size control of Au nanoparticles prepared by sputter deposition in imidazolium-based ionic liquids". In: *Physical Chemistry Chemical Physics* 18.4 (2016), pp. 2339–2349 (cit. on p. 48).
- [105] Yoshikiyo Hatakeyama et al. "Temperature-independent formation of Au nanoparticles in ionic liquids by arc plasma deposition". In: *Chemical Physics Letters* 658 (2016), pp. 188–191 (cit. on p. 48).
- [106] Susann Wegner and Christoph Janiak. "Metal nanoparticles in ionic liquids". In: *Topics in Current Chemistry* 375 (2017), pp. 1–32 (cit. on p. 48).
- [107] Vanessa Orozco-Montes et al. "Synthesis of platinum nanoparticles by plasma sputtering onto glycerol: Effect of argon pressure on their physicochemical properties". In: *The Journal of Physical Chemistry C* 125.5 (2021), pp. 3169–3179 (cit. on p. 49).
- [108] Rod Heu et al. "Target material selection for sputter coating of SEM samples". In: *Microscopy Today* 27.4 (2019), pp. 32–36 (cit. on p. 52).
- [109] O Kylián et al. "Deposition of Pt nanoclusters by means of gas aggregation cluster source". In: *Materials Letters* 79 (2012), pp. 229–231 (cit. on p. 53).
- [110] Ondřej Kylián et al. "Deposition and characterization of Pt nanocluster films by means of gas aggregation cluster source". In: *Thin Solid Films* 571 (2014), pp. 13–17 (cit. on p. 53).
- [111] Rémy Sellin et al. "Effects of temperature and atmosphere on carbonsupported platinum fuel cell catalysts". In: *The Journal of Physical Chemistry C* 113.52 (2009), pp. 21735–21744 (cit. on p. 57).
- [112] Haiyang Cheng et al. "Polyethylene glycol-stabilized platinum nanoparticles: The efficient and recyclable catalysts for selective hydrogenation of o-chloronitrobenzene to o-chloroaniline". In: *Journal of colloid and interface science* 336.2 (2009), pp. 675–678 (cit. on p. 57).
- [113] Jill Chastain and Roger C King Jr. "Handbook of X-ray photoelectron spectroscopy". In: *Perkin-Elmer Corporation* 40.221 (1992), p. 25 (cit. on p. 63).
- [114] N Yu Kirikova et al. "XPS studies of the energy band structure of three Y3+-based fluoride compounds". In: *Journal of electron spectroscopy* and related phenomena 122.1 (2002), pp. 85–89 (cit. on p. 63).
- [115] Dae-Min Kim et al. "The erosion behaviors of Y2O3 and YF3 coatings under fluorocarbon plasma". In: *Thin Solid Films* 519.20 (2011), pp. 6698–6702 (cit. on p. 63).

- [116] Chao Wei et al. "Recommended practices and benchmark activity for hydrogen and oxygen electrocatalysis in water splitting and fuel cells". In: Advanced Materials 31.31 (2019), p. 1806296 (cit. on p. 64).
- [117] Paulette A Loichet Torres et al. "ORR Activity and Voltage-Cycling Stability of a Carbon-Supported PtxY Alloy Catalyst Evaluated in a PEM Fuel Cell". In: *Journal of The Electrochemical Society* 170.12 (2023), p. 124503 (cit. on p. 64).
- [118] Björn Eriksson et al. "Enhanced oxygen reduction activity with rare earth metal alloy catalysts in proton exchange membrane fuel cells". In: *Electrochimica Acta* 387 (2021), p. 138454 (cit. on p. 65).
- [119] Emmanuel Balogun et al. "Catalyst layers for fluorine-free hydrocarbon PEMFCs". In: *Electrochimica Acta* 401 (2022), p. 139479 (cit. on p. 68).
- [120] Xin Wang et al. "Proton exchange membrane water electrolysis incorporating sulfo-phenylated polyphenylene catalyst coated membranes". In: *Journal of The Electrochemical Society* 170.2 (2023), p. 024502 (cit. on p. 68).