Novel Synthesis Routes of Platinum Rare Earth Metal Alloy Nanoparticles as Catalysts for Hydrogen Fuel Cells

Brandes, Benedikt Axel

Publication date: 2019

Novel Synthesis Routes of Platinum Rare Earth Metal Alloy Nanoparticles as Catalysts for Hydrogen Fuel Cells

PhD Thesis

December 2018

DTU Energy
Department of Energy Conversion and Storage
Title:
Novel Synthesis Routes of Platinum Rare Earth Metal Alloy Nanoparticles as Catalysts for Hydrogen Fuel Cells

Author:
Benedikt Axel Brandes
babra@dtu.dk

Principal supervisor:
Jens Oluf Jensen
Professor, DTU Energy
jojen@dtu.dk

Co-supervisor:
Qingfeng Li
Professor, DTU Energy
qfli@dtu.dk

Co-supervisor:
Lars Nilausen Cleemann
Professor, Head of Section, DTU Energy
lncl@dtu.dk

Date of submission:
14th December 2018

Department of Energy Conversion and Storage
Section for Electrochemistry
Technical University of Denmark
Electrovej, Building 375
2800 Kgs. Lyngby
Denmark
www.energy.dtu.dk
+45 46 77 58 00
Preface

This thesis is submitted to the Technical University of Denmark (DTU) in candidacy for a Ph.D. degree. The work presented and discussed in this thesis has been conducted over 3 years from December 2015 to December 2018 at the section of Electrochemistry (former: Proton Conductors). Additional research has taken place at the Korean Advanced Institute of Science and Technology (KAIST) in Daejeon, South Korea in the institute of material science and engineering with Prof. EunAe Cho from November 2017 to April 2018. The project was funded by DTU’s alliance stipend program.

Benedikt Axel Brandes

December 2018
Acknowledgements

I am very grateful for the past three years I could spend at DTU. I want to express my gratitude to everyone who contributed to make this project possible and enjoyable to work on.

First and foremost, I would like to thank Prof. Jens Oluf Jensen who has been an inspiring principal supervisor from the beginning. Without his engagement in the application process I would not have been part of DTU in the first place. Many thanks go to Prof. Qingfeng Li and Prof. Lars Nilausen Cleemann for the many fruitful discussions, support and scientific guidance.

I must praise the work of the (laboratory) technicians, namely Claus Burke Mortensen and Larisa Seerup for providing an excellent work environment. They maintain the laboratory equipment at the highest standard and are always supportive in bringing sometimes unusual experimental requests to reality.

I want to pay my gratitude to Yang Hu and Mikkel Rykær Kraglund for the insightful discussions and the help and advice they provided. Without them, my time at DTU would have not been as productive and enjoyable.

Special thanks go to the team of the section of electrochemistry and DTU energy that contributed to this project. I was delighted by the work of Thomas M Carpenter who was a fantastic student worker and made great contributions to this project.

I want to thank Prof. EunAe Cho of KAIST in South Korea for allowing me to be part of her laboratory and my colleagues in her group for the unforgettable and pleasant stay in Daejeon.

Last but not least I want to thank all of my friends and family that supported me during this project, especially during times when the progress was lower than I had hoped for.
Abstract

Hydrogen fuel cells promise to contribute to our future energy landscape by providing clean electricity to stationary and mobile applications. The main challenge of their application is their high cost compared to other energy systems. The main cost is the catalyst that facilitates one of the two main reaction within a fuel cell: the oxygen reduction reaction (ORR). The most active and stable material is platinum in form of nanoparticles, which is a scare and expensive element. Three approaches are investigated by researches to reduce its impact on the overall system cost: (1) Replace platinum with non-noble metals, that are cheaper but less active and less stable. (2) Gain control over the shape of the nanoparticles, increasing the share of the higher active platinum facets. (3) Mix platinum with other metals to form alloy nanoparticles with an increased surface activity. In this thesis the latter approach is chosen to obtain novel ORR catalysts.

DTU is the leader in the field of establishing rare earth metal platinum alloy nanoparticles as catalyst for the ORR. However, a cheap and scalable synthesis method is lacking so far. The main obstacle is the very negative reduction potential of the rare earths which prohibits the utilization of the common nanoparticle synthesis methods.

This thesis discusses and investigates several options of synthesizing Pt\textsubscript{x}Y and Pt\textsubscript{1-x}Y nanoparticles by novel synthesis routes.

First, sodium dissolved in liquid ammonia is used as a reducing agent and rapidly mixed with various early transition, rare earth metal salts and platinum on carbon. After an annealing treatment at high temperatures the respective platinum alloy nanoparticles are obtained. However, the size distribution of the nanoparticles does not meet the design criteria of ORR catalysts.

Secondly, the same principle is used by replacing liquid ammonia with a suitable organic solvent. Platinum rare earth metal alloy nanoparticles with an improved particle size distribution are obtained.

Eventually, it is found for the first time that platinum and the respective rare earth metal salts alloy at elevated temperatures in the presence of potassium vapor. This method allows a fairly good control over the phase composition and size distribution of the nanoparticles. The obtained Pt\textsubscript{3}Y/C and Pt\textsubscript{2}Gd/C nanocatalysts were electrochemically tested and found to exhibit a higher ORR activity than the responding commercial Pt/C catalyst. The importance of the
annealing temperature, precursor stoichoiometry and acid leaching is further investigated to complete the understanding the role of the potassium vapor.

This method has the potential to be commercialized and eventually reduce the necessary amount of platinum in fuel cell systems and thus progressing their application and contribution towards a sustainable energy future.
Publications and patents

Scientific contribution

Synthesis of Pt-Rare Earth Metal Alloy Nanocatalysts
Yang Hu, Jens Oluf Jensen, Lars Nilausen Cleemann, Benedikt Axel Brandes, Qingfeng Li
Publication, submitted

Pt$_3$Y Nanoparticles Supported on Carbon
Benedikt Axel Brandes, Yang Hu, Lars Nilausen Cleemann, Qingfeng Li, Jens Oluf Jensen
Talk, AiMES 2018 Cancun

Patents

Process for producing metal alloy nanoparticles
Main inventor, priority date obtained

Process for producing alloy nanoparticles
Coinventor, priority date obtained
Contents

1 Introduction ......................................................... 1
   1.1 The present day energy sector .................................. 1
   1.2 Challenges within the present day energy landscape ............ 3
      1.2.1 Limited resources ........................................ 4
      1.2.2 Dependence on foreign powers .......................... 4
      1.2.3 Climate Change .......................................... 6
      1.2.4 Local Pollution and other impacts ........................ 9
      1.2.5 The challenges regarding renewable energy sources ........ 11
   1.3 The hydrogen economy ....................................... 12
      1.3.1 Hydrogen fuel cell technologies .......................... 14
   1.4 PEMFC ....................................................... 14
      1.4.1 DOE targets ........................................... 18
   1.5 Thesis outline ............................................... 18

2 The oxygen reduction reaction .................................... 21
   2.1 Current understanding ....................................... 21
      2.1.1 Mechanism ............................................. 21
      2.1.2 The scaling relationship ................................. 23
   2.2 Platinum on carbon ......................................... 26
      2.2.1 Preparation ............................................ 26
   2.3 Platinum free catalysts ...................................... 27
   2.4 Platinum alloys of the late transition metals ................ 28
      2.4.1 Preparation ............................................ 28
   2.5 Platinum alloys of the early transition metals ............... 29
   2.6 Platinum alloys of the rare earth metals .................... 31
      2.6.1 Motivation ............................................. 31
      2.6.2 Synthesis ............................................. 35
         Molten Salt .............................................. 35
         Ultrapure hydrogen reduction .............................. 36
         Very high temperature annealing of yttrium and platinum
         salts mixed with carbon .................................. 37
         Author’s remarks to the synthesis attempts in literature ... 38
   2.7 Platinum alloys of other metals ............................. 38
      2.7.1 PtPb .................................................. 38
Contents

2.7.2 Shape controlled metal doped platinum alloy nanoparticles 39

3 Techniques 41
3.1 Characterization ................................................. 42
  3.1.1 XRD ...................................................... 43
  3.1.2 EDS ...................................................... 47
  3.1.3 TEM ...................................................... 49
  3.1.4 XPS ...................................................... 51
  3.1.5 TGA ...................................................... 53
3.2 Electrochemical testing ........................................... 54
  3.2.1 RDE ...................................................... 54
  3.2.2 The electrochemical reaction .............................. 54
    Thermodynamics ............................................. 55
  3.2.3 Kinetics .................................................. 56
    Mass transport ............................................. 58
  3.2.4 How to measure kinetics .................................. 59
    The counter electrode ...................................... 60
    The reference electrode .................................... 60
    Special reference electrodes ............................... 61
  3.2.5 The ORR case ............................................ 62
    Comparing catalyst activities ................................ 64
    Mass transport and RDE .................................... 64
    ECSA determination ......................................... 66
  3.2.6 Typical experiment protocol ................................ 67
    Electrode preparation ...................................... 68
    Cell preparation ........................................... 69
    Protocol .................................................... 70

4 Synthesis strategies 71
4.1 Challenges in the synthesis of platinum rare earth metal alloy nanoparticles ................................. 71
  4.1.1 Reducing agents ......................................... 71
  4.1.2 Solvents ................................................ 72
    Dissolving rare earth metal salts .......................... 72
  4.1.3 The ammonia route ...................................... 74
  4.1.4 Difference in reducing potentials ....................... 74
  4.1.5 Phase and particle size control ......................... 74
  4.1.6 Water and oxygen impurities ........................... 75
  4.1.7 Experimental outline .................................... 75
Contents

6.4.4 Optimized deposition of gadolinium nanoparticles on commercial Pt/C ........................................... 113
Concepts ........................................................................ 113
Experimental .................................................................. 114
Results .......................................................................... 115
Discussion ...................................................................... 115

6.4.5 Effect of annealing temperature on the THF/naphthalene/air-free transfer samples .......... 116
Experimental .................................................................. 116
Results .......................................................................... 116
Discussion ...................................................................... 116

6.4.6 General observations and interpretation ...................................................................................... 118

6.4.7 Conclusion .............................................................. 119

7 Synthesis involving Rieke metals 121
7.1 Concept ..................................................................... 121
7.2 Procedure ................................................................... 122
7.3 Results and discussion ............................................... 123
7.4 Conclusion .................................................................. 124

8 Synthesis using potassium vapor as reducing agent 125
8.1 Precursor preparation using THF ................................. 127
8.1.1 Experimental .......................................................... 127
8.1.2 Results .................................................................... 127
8.2 Precursor preparation using hexane ............................ 129
8.2.1 Concept ................................................................... 129
8.2.2 Procedure ................................................................. 129
8.2.3 Results .................................................................... 129
8.2.4 Discussion ................................................................. 131
8.3 Precursor preparation using water and ammonium chloride ...................................................... 132
8.3.1 Concept ................................................................... 132
8.3.2 Procedures ............................................................... 134
8.3.3 Results .................................................................... 134
8.3.4 Discussion ................................................................. 135
8.4 Potassium vapor induced platinum growth ............... 135
8.4.1 Concept ................................................................... 135
8.4.2 Procedure ............................................................... 135
8.4.3 Results .................................................................... 136
8.4.4 Discussion ................................................................. 136
8.5 Precursor preparation using water and optimized potassium source ................................. 137
8.5.1 Concept ................................................................... 137
Contents

8.5.2 Procedure ................................................. 139
8.5.3 Results ..................................................... 140
8.5.4 Detailed results and discussion ......................... 141
ORR activity measurement results .......................... 141
Mechanism of alloy formation ............................... 142
Effect of acid washing ........................................ 144
Phase control ..................................................... 146

9 Discussion and conclusion ............................... 149
9.1 Early transition metal platinum alloy nanoparticles .... 149
9.2 Rare earth metal platinum alloy nanoparticles ......... 150
Correlation between the preferred nanoparticle phase and
its melting point ...................................................... 152
9.3 Final remarks ................................................. 154

List of figures ..................................................... 155
List of tables ..................................................... 159
References ......................................................... 161
1 Introduction

This PhD thesis aims to contribute to a solution of the dominant present day challenge: Allowing the transformation of our current energy landscape by replacing the dominating fossil fuels by renewable energy. A great challenge is the impermanent nature of most renewable energy sources and the energy density demands in the mobility sector. In both cases hydrogen fuel cells promise a smooth transition towards a sustainable future without sacrifice.

This introduction aims to draw a brief overview over mankind’s current energy system and its present influence on society and environment. Finally the hydrogen economy as one possible future scenario is presented of which the objective of this work can be a piece of.

1.1 The present day energy sector

Mankind utilized in 2017 about 13500 Mio toe\(^1\) (157000 TWh) (including conversion losses) of primary energy in three sectors: Industry, residential and commercial businesses and transportation. The consumption pattern differs between these sectors: While industry consumes mostly natural gas, oil and electricity, the transport sectors consumes almost entirely oil products. The household and commercial sector rely on energy in the form of electricity and natural gas. The dominant sources of energy are fossil fuels with a 85 % share, see figure 1.1.

The three main types of fossil fuels are coal, oil and natural gas. Oil and its products are ideal cases for the transportation sector due to their liquid form and high energy density, making them rather easy to handle. Natural gas re-

\(^1\)Mio toe = Million tons of oil equivalent = 11.63 MWh
1 Introduction

quires a more advanced transportation system, but it combusts rather clean and is ideal for stationary and decentralized applications. This leads to the dominant use of natural gas for heating and cooking in the residential and commercial sector. It is also used as a feed stock in the chemical industry. Coal combustion is comparably dirty, but can be cheaply mined, is abundant in most places and can be easily transported and stored in vast quantities. These properties make it an ideal case for the central generation of electricity which is almost solely used by the residential and commercial sector and the industry.

Renewable energies (Hydropower, biomass, wind and solar energy) and nuclear power contribute to the generation of electricity with a 36 % share after the fossil fuels, dominated by coal. In 2017, 25500 TWh of electricity have been generated, representing about a third of the total usage of the utilized primary energy that, conversion losses included.

Affordable energy has been a key factor in the development of our society. The correlation between income, the index of human development (HDI) and energy consumption is very strong regardless of population size, see figure 1.2.

Until the year 2100 the human population will grow to about 11 billion [3]. If the trend of human development continues approaching that of the development countries, which must be in the interest of us all, the energy consumption

Figure 1.1: Breakdown of the world primary energy and electricity consumption by fuel sources. Created with data from [1].
1.2 Challenges within the present day energy landscape

Figure 1.2: Displaying the correlation between energy consumption and wealth and human development. Generated with data from gapminder tools [2].

is destined to grow as well. Likely scenarios suggest that the energy consumption until year 2100 will double to about 30000 Mio toe [4].

1.2 Challenges within the present day energy landscape

Major concerns regarding our present energy landscape have been articulated. It must be discussed if these concerns justify the efforts that come with the transition envisioned by many. The following section represent a rather subjective view of the author of this thesis on this topic.
1 Introduction

1.2.1 Limited resources

It is well known that only a finite amount of fossil fuels exist on earth. The exploitation of coal, natural gas and oil becomes more energy intensive and expensive year by year. Despite rising fossil fuel prices, the share of income the average person spends on energy has been decreasing ever since due to technology advancements and economic growth. Figure 1.3 shows exemplary for crude oil how negligible its price is before refining in comparison to the world's GDP: The share of the world income spent on oil has stayed constant in the past 20 years after a steady decline, despite rising prices and costs for exploitation costs. Merely 4% of the world GDP has been spent on ca. 34 billion barrels of crude oil that have been extracted in 2013. Another angle on the limits of fossil fuel resources gives the resource to production ratio (RPR). This number suggests how many years the current production level can be maintained using only proven and at current prices exploitable reserves. In case of rising prices and new technologies, the RPR can increase significantly. Historically, this number has stayed rather constant of around 50 years for oil and natural gas and over 100 years for coal.

Conclusively, no shortage of fossil fuels can be expected in the midterm (> 100 years). Putting these numbers in perspective: Mankind has very likely more years left using fossil fuels than it had been using them. From the exploitation standpoint of view a transformation of our fossil fuel based energy landscape is only necessary in the long term. Countries that attempt an energy transformation based solely on the argument of limited resources will encounter a competitive disadvantage, thus sacrificing possible gains in wealth in life standards in a globalized world economy.

1.2.2 Dependence on foreign powers

Indeed most oil and natural gas reserves are found in countries with a questionable stand towards human rights and fair market practices. However, these regimes rely on a constant influx of foreign currency and their economy is often completely depended on the export of fossil fuels.

Table 1.1 ranks the top ten producers in crude oil, natural gas and coal: The
1.2 Challenges within the present day energy landscape

Figure 1.3: Fraction of the world and US GDP that is spent on oil and its price and consumption since the 1970s. Created from data of [5]

top ten oil producers are dominated by oppressive regimes, however oil can be stored easily and many countries have tremendous reserves. Many of these reserves had been established as an answer to the oil crisis in the seventies.

The situation seems to be more relaxed looking at the biggest natural gas producers, the share of USA, Canada, Norway and Australia exceeds 40% within the top ten. The second biggest producer, Russia, is as of 2018 completely depended on its main European customers due to its pipeline network and lack of liquefaction terminals. Using natural gas as a leverage is unlikely, especially after Europe has invested heavily in natural gas terminals since the Ukrainian gas crisis in 2006.

At the first look, China dominates the production market in coal. But it is also the greatest consumer. Coal in general is rather abundant and its greatest consumers can source it themselves.

Scenarios in which fossil fuel exporting countries threaten their costumers using their resources as a leverage appear to be very unlikely in our globalized economy.
1 Introduction

Table 1.1: Top ten producers of oil, natural gas and coal. Reproduced from [5].

<table>
<thead>
<tr>
<th>Rank</th>
<th>Country</th>
<th>Oil, 2013 Production</th>
<th>Natural Gas, 2017 Production</th>
<th>Coal, 2016 Production</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>bio B</td>
<td>bio m³</td>
<td>mio tons</td>
</tr>
<tr>
<td>1</td>
<td>Russia</td>
<td>3.8 12%</td>
<td>734.5 20%</td>
<td>3411 46%</td>
</tr>
<tr>
<td>2</td>
<td>Saudi Arabia</td>
<td>3.8 12%</td>
<td>635.6 17%</td>
<td>692 9%</td>
</tr>
<tr>
<td>3</td>
<td>USA</td>
<td>3.2 10%</td>
<td>223.9 6%</td>
<td>661 9%</td>
</tr>
<tr>
<td>4</td>
<td>Iraq</td>
<td>1.6 5%</td>
<td>176.3 5%</td>
<td>493 7%</td>
</tr>
<tr>
<td>5</td>
<td>Iran</td>
<td>1.5 4%</td>
<td>175.7 5%</td>
<td>434 6%</td>
</tr>
<tr>
<td>6</td>
<td>China</td>
<td>1.5 4%</td>
<td>149.2 4%</td>
<td>385 5%</td>
</tr>
<tr>
<td>7</td>
<td>Canada</td>
<td>1.4 4%</td>
<td>123.2 3%</td>
<td>251 3%</td>
</tr>
<tr>
<td>8</td>
<td>UAE</td>
<td>1.1 3%</td>
<td>113.5 3%</td>
<td>176 2%</td>
</tr>
<tr>
<td>9</td>
<td>Kuwait</td>
<td>1.1 3%</td>
<td>111.4 3%</td>
<td>131 2%</td>
</tr>
<tr>
<td>10</td>
<td>Brazil</td>
<td>0.9 3%</td>
<td>91.2 2%</td>
<td>102 1%</td>
</tr>
</tbody>
</table>

|      | Rest    | 12.9 35.4%           | 1145.5 31%                   | 723 10%               |
|      | World   | 32.9 100%            | 3680 100%                    | 7460 100%             |

1.2.3 Climate Change

In the past 170 years a rise of the earth surface temperature (water and land) has been observed and that has in that pace never occurred on the planet. This development is called global warming and its underlying mechanism is the greenhouse effect. This mechanism is well understood and without it, life on earth would not be possible. The main contributor to the greenhouse effect is atmospheric water vapor, among other greenhouse gases (CO₂, CH₄, N₂O, etc.) These greenhouse gases reflect heat radiation back to the earth and thereby increasing its surface temperature by about 33 °C [6] to an average surface temperature of about 15 °C.

The content of water within the atmosphere is in equilibrium with its temperature and the heat radiation towards and from the earth is in balance. However, if a rise in the concentration of the other greenhouse gases increase the temperature, a positive feedback loop is established, so that the atmosphere can contain more water vapor. It is also evident that human activities have increased the emission of greenhouse gases, mainly CO₂. Both observations, the rise in temperature and the content of CO₂ in the atmosphere are summarized in figure 1.4. This correlation together with complex simulations leads to the conclusion in the overwhelming majority of the scientific community that the observed global warming is of anthropological origin.
1.2 Challenges within the present day energy landscape

Moreover, the majority of publications suggest that the anthropological global warming will affect mankind and the earth ecosystems negatively. Among possible and observed consequences are the rise of sea levels, intensified storms and weather extremes, disruption of ecosystems and a decrease in biodiversity and negative consequences on agriculture activities. It is generally agreed upon to take measures to prevent climate change or limit its extent to below 2°C compared to preindustrial levels.

The dominant origin of anthropological greenhouse gas emissions is the energy sector (including mobility), see figure 1.5 and within it, the use of fossil fuels. A transformation towards low carbon emitting energy sources can significantly reduce the forecasted global warming and its suggested negative effects on the environment of the earth.

It is projected that humanity will grow to a population of about 11 billion [9] by year 2100. Additionally it is unarguably of great importance that the living
1 Introduction

Figure 1.5: Composition of anthropological greenhouse gas emissions (left). Contribution of different fossil fuels to CO\textsubscript{2} emissions (right). [8].

standard of currently about 6 billion people to has to reach sooner rather than later the level of the 1 billion people living in developed nations. It appears to be very difficult to achieve the reduction of greenhouse gas emission in an environment where the majority of mankind does still live in relative poverty to the developed world. Since using fossil fuels still provide in most places the cheapest path towards proving energy and mobility, it is morally questionable to limit the use of fossil fuels in underdeveloped nations. The benefit of reduced greenhouse gas emissions and a reduced global warming does not rank higher than the benefit of affordable energy to the majority of humanity yet. In case a low carbon emission energy system can actually provide energy more cost effectively, it would prevail and the argument of global warming would simply not be needed.
1.2 Challenges within the present day energy landscape

1.2.4 Local Pollution and other impacts

While global warming is, as the name suggests, a global phenomena and CO₂ by itself is not a pollutant, there are direct consequences to our environment and human health by any energy source. Quantifying the impact of different energy sources is difficult, but this section attempts to give a brief overview.

Crude Oil  The effect of crude oil on our environment and humans can be split in two parts: Effects from its exploitation and from its main use in the transport sector. Oil spills have become more rare in the recent years. However, when they happen, they are devastating and ecological systems, especially within the sea, take decades to regenerate from these disasters. This is especially concerning since most crude oil is transported on the ocean and an increasing share is produced in deep waters.

Similarly, the emissions of NOₓ and particular matter of gasoline and diesel engines have been declining since the introduction of emission control mechanisms. However, they are still higher than what most health organizations suggest and a further decrease seems to be necessary, however increasingly more difficult to achieve.

Natural Gas  Due to its gaseous form, records of ecological disasters are almost absent. Nevertheless, gas explosions from gas leaks still occur and claim many lives every year.

Coal  The use of coal has without doubt the most impact on the environment and human well being:

- Exploitation in underground mines leads regularly to disasters, leading to many fatalities, especially in Asia. Open pit or mountain top removal mining is safer to humans, but its environmental impact is significant.

- Coal contains significant amounts of sulfur that leads to acidic rain when fired in power plants and deforestation if not filtered properly. Other toxins are heavy metals, including a couple of thousand tons of radioactive uranium and thorium, that are released into the environment every year.
1 Introduction

**Nuclear Energy** Nuclear energy is not a fossil fuel and its reserves are essentially endless \(^2\), it is still included in this list. Its impacts on the environment arise mostly from uranium mining and how nuclear waste will be treated and stored. The environmental and effects during the operation of a nuclear power plant are very limited. However, in case of accidents the impact on humans and the environment can be significant. The risk profile also changes drastically with reactor type and its location determining the influence of possible natural disasters.

<table>
<thead>
<tr>
<th>Electricity Source</th>
<th>Deaths per TWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>2-100</td>
</tr>
<tr>
<td>Oil</td>
<td>(50)*</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>(20)*</td>
</tr>
<tr>
<td>Biofuels/Biomass</td>
<td>-</td>
</tr>
<tr>
<td>Solar (rooftop)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Wind</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Hydro</td>
<td>0.1 (1 with catastrophes)</td>
</tr>
<tr>
<td>Nuclear</td>
<td>0.05 (1 with catastrophes)</td>
</tr>
</tbody>
</table>

Many of the ecological impacts and health risks to humans can only be minimized and not completely avoided when using fossil fuels as a primary energy source. It becomes increasingly difficult when the emissions do not occur centralized, but rather in the places where people live - e.g. by using gasoline and diesel as dominant part of our individual mobility.

The author strongly believes that avoiding local pollution, possible oil spills and impacts from coal mining are the strongest arguments for new energy technologies. A local transformation of our energy system can provide the highest short-term improvement to our environment and to human health. Eventually

\(^2\)Using breeder reactors: Just 545 t/year of non-enriched uranium would be needed to satisfy the world primary energy demand at 2017 levels. The current operational mines could provide this amount for about 20000 years. If the more abundant thorium is used at a fuel or/and other unconventional reserves (such as in seawater) are to be used the resources are virtually endless.
1.2 Challenges within the present day energy landscape

the transformation of our energy system occurs just by being more competitive in terms of price and by providing lower local emissions and therefore being demanded as a part of high standard of living.

1.2.5 The challenges regarding renewable energy sources

Renewable energy can be divided into two groups: While energy output of hydro-power plants and biomass/fuels are predictable and can be stored to a certain extent, solar and wind energies are entirely dependent on the weather, they may be forecast but need to be "stored". With the exception of biomass/fuels, renewable energy is produced in the form of electricity, while a major part of our energy consumption is in the form of heat and liquid fuels.

Energy storage is crucial if renewable energy should penetrate the mobility sector and replace fossil fuels in the electricity sector. Looking at the case of stationary energy storage, the highest round trip efficiencies can be achieved by pumped hydro and batteries, see figure 1.6. However, pumped hydro power plants have a rather low volumetric energy density, a significant landscape and environmental impact and possible locations are scare. Batteries are superior, but rather expensive and might become resource constrained when using it as seasonal energy storage.

Hydrogen, synthesized by electrolysis from electricity and transformed back via hydrogen fuel cells exhibits a round trip efficiency significantly lower than that of pumped hydro and batteries. However, it offers nearly limitless storage capacity via underground caverns (as are currently used for natural gas). Additionally, the expensive part of a electrolysis fuel cell system does not scale with capacity, only by peak power. This is a tremendous benefit over battery systems in case of seasonal energy storage.

In case of the mobile sector, batteries and hydrogen fuel cells can complement each other. The battery can be utilized for short distances and power peaks during acceleration, providing rather cheap and efficient local transport. Longer trips can be covered by the fuel cell without being limited of the battery size and long charging times. Modest efficiency losses are offset by convenience and fast refueling. Local pollution is virtually non existing and the energy effi-
1 Introduction

Figure 1.6: Volumetric energy density and round trip efficiency of major energy storage media.

ciency is significantly higher than of combustion engine vehicles in either case.

1.3 The hydrogen economy

Hydrogen is the most abundant element on earth. As an energy carrier it is non-toxic and its explosion risks are mitigated by its tendency to escape quickly into the atmosphere. If burned or reacted with oxygen, the only product is water vapor.

However, it does not occur in elemental form on earth but can be produced in various ways. The two most common hydrogen production methods are the reforming of natural gas, often produced on site for the fertilizer and petroleum refining industry and the electrolysis of water. The latter uses electricity as the source of energy and would be one of the key components in a hydrogen economy, sketched in figure 1.7.

The fluctuating electricity output of mainly wind and solar energy would be
1.3 The hydrogen economy

Figure 1.7: Diagram of a possible future hydrogen economy and its major components.

transformed into hydrogen which then can be distributed to various consumers or stored in e.g. underground caverns. This allows an affordable seasonal storage option. The distribution network could eventually use the existing natural gas network with little modification, noting that e.g. in Germany the so called city gas in the early 20th century consisting of > 50 % hydrogen was widely used.

Eventually hydrogen from storage or directly from the production side can be transformed into electricity and heat by hydrogen fuel cells, either stationary or in the mobility sector featuring fuel cell vehicles. Additionally together with biomass or CO$_2$ from carbon capture technologies, hydrogen can be utilized as a feed stock in the chemical industry.

During a transition phase hydrogen can be sourced by fossil fuels directly over steam reforming and other technologies, allowing a smooth transition towards a sustainable hydrogen economy.

The key components of a hydrogen economy are the electrolysis system, in which water and electricity is transformed into hydrogen (and oxygen) and hydrogen fuel cells, on which this work is concerned, which transforms the hydrogen together with atmospheric oxygen back into electricity and water.
1 Introduction

1.3.1 Hydrogen fuel cell technologies

Principally two ways exist to release the energy from the reaction of hydrogen and oxygen: First, burning hydrogen in a combustion engine or turbine. The maximum thermal efficiency of such a process is theoretically limited and does rarely exceed 50%, often significantly lower in practice. Second, by electrochemically reacting hydrogen and oxygen. This process can be efficiently carried out at room temperature, up to several hundred degrees Celsius. Principally, the thermal efficiency can approach 84% and typically lies above 45%.

The operating conditions are mainly determined by the electrolyte used in an hydrogen fuel cell. At lower temperature the electrolyte is liquid or a polymer, at medium temperatures up to 200°C polymer membranes with immobilized phosphoric acid are used [11] and at temperatures above 200°C solid oxides are used. An overview over different fuel cell types commercialized or close to being commercialized are presented in figure 1.8. Other types of fuel cells exist, using methane, methanol, ethanol, formic acid, formaldehyde, etc. as a fuel. These are referred to as direct fuel [fuel type] cells (e.g. direct methanol fuel cell). There chemical efficiencies are rather low due to the high barriers in splitting carbon bonds or excessive crossover.

The most promising fuel cell type is the low temperature polymer electrolyte membrane fuel cell (LT-PEMFC or simply PEMFC). At typical operating conditions (80°C its thermal efficiency can reach up to 60%. The temperature level allow the excess heat to be used (e.g. cabin heating in cars).

1.4 PEMFC

A simplified scheme of a PEMFC is presented in figure 1.9. Hydrogen and oxygen (air in the application case, which has minor changes on the fuel cell system) are supplied homogeneously via flow-fields (FF) into a gas diffusion layer (GDL) from which the gas molecules diffuse to the catalyst. Catalyst particles are mixed with high surface area carbons and an ion-conductive polymer (typically Nafion). This mixture is coated onto both sides of a Nafion membrane as catalyst layers, forming the electrodes. The assembly of the GDL, the elec-
1.4 PEMFC

Figure 1.8: Different fuel cell types are grouped depending on their typical operating temperature and the conducted ionic species through their membrane/electrolyte. Note that the fuel cell names indicate which membrane/electrolyte is used: Solid oxide fuel cells (SOFCs), alkaline fuel cells (AFCs), solid acid fuel cells (SAFCs), phosphoric acid fuel cells (PAFCs), low and high temperature polymer electrolyte/proton exchange membrane fuel cells (LT,HT-PEMFCs).

trodes and the membrane is called membrane electrode assembly (MEA). The cell is sealed by gaskets while the electric current is conducted through current collectors (CC) to a load.

The MEA is the most significant part of a PEMFC. The platinum nanoparticles are in contact with the electric conductive carbon, the ionomer, the humidified gas phase and condensed liquid water. This so called three-phase interface is very sensitive and needs to be designed carefully. The following reactions take place at the two electrodes:

Anode: \( 2 \text{H}_2 \rightarrow 4 \text{H}^+ + 4 e^- \)  \hspace{1cm} Hydrogen Oxidation Reaction (HOR)
Cathode: \( \text{O}_2 + 4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O} \)  \hspace{1cm} Oxygen Reduction Reaction (ORR)

Hydrogen splits within the anodic three-phase interface into electrons and
protons. The electrons are conducted through the carbon and FF to the CC. The protons migrate through the ion-conductive membrane to the cathodic three-phase interface where they combine with oxygen and electrons conducted from the cathodic CC to water. This reaction exhibits a Gibbs free energy gain per mole of hydrogen of 237.14 kJ, corresponding to an equilibrium potential of $\Delta E = 1.23 \text{V}_{\text{SHE}}$ between cathode and anode. However, each of the reaction and conduction steps has an energetic barrier associated with it. These barriers need to be overcome by an additional potential that reduces the equilibrium potential, hence called overpotential $\eta$. The higher the reaction rate (corresponding to the drawn current $i$) the higher the loss of efficiency by overpotentials:

$$\text{Exergeticefficiency} = \frac{\Delta E - \sum \eta(i)}{\Delta E}$$ (1.1)

In addition to overpotentials, other potential loses include those associated with the conduction of electrons and protons, diffusion and convection of reactant gases, contact resistances. A overview over typical values of losses is given in table 1.3.

The aim of fuel cell research is to reduce these losses, primarily from the ORR and increase the stability of the used materials at a reasonable cost. Significant
Table 1.3: Breakdown of the losses in a fuel cells. Overpotentials reduce the usable cell voltage from 1229 mV to ca. 760 mV corresponding to a thermal efficiency of ca. 50%. The values given are ballpark numbers and vary with the actual system and operating conditions. Without reference.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact and electric Resistances</td>
<td>40 mV</td>
</tr>
<tr>
<td>H⁺ Conduction</td>
<td>100 mV</td>
</tr>
<tr>
<td>H₂ and O₂ supply mV</td>
<td></td>
</tr>
<tr>
<td>HOR</td>
<td>30 mV</td>
</tr>
<tr>
<td>ORR</td>
<td>300 mV</td>
</tr>
<tr>
<td>Sum</td>
<td>470 mV</td>
</tr>
</tbody>
</table>

work and research efforts are spent on finding better catalyst materials for the ORR where advancements promise the biggest gains in terms of efficiency and overall system cost. The cost of a typical fuel cell system for vehicles is broken down in figure 1.10.

The two biggest contributors to the overall costs are the bipolar plates and the catalyst. The high cost of the bipolar plates arises from its manufacturing from either graphite or gold coated metal plates. In an automotive stack the pattern of the flow fields are milled into the bipolar plates in contrast to the separate units shown in figure 1.9. The biggest cost however is the catalyst and its production.
1 Introduction

1.4.1 DOE targets

In order to guide the development of fuel cells, the US Department of Energy (DOE) has set performance targets for the components of the PEMFC for 2020. If these targets are reached, fuel cell vehicles are believed to become competitive with combustion engine vehicles. The set targets specifically for the catalyst performance can be found in table 1.4.

<table>
<thead>
<tr>
<th>Target for 2020</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Performance at 0.8 V</td>
<td>0.3 A/cm²</td>
</tr>
<tr>
<td>Performance at the rated power</td>
<td>1 W/cm²</td>
</tr>
<tr>
<td>Start-up/shutdown durability</td>
<td>5000 Cycles</td>
</tr>
<tr>
<td>Durability with Cycling</td>
<td>5500 h</td>
</tr>
</tbody>
</table>
| MEA Cost | $14/kW

The reason for the high price of the catalyst is that only platinum and its alloys are sufficiently active and stable materials both for the HOR and the ORR. In order to maximize its surface area and hence maximize its mass activity the catalyst is synthesized in the form of nanoparticles. Next to the high platinum price advanced and costly production methods are necessary to control the particle size distribution. A fuel cell performance curve of a state of the art platinum alloy catalyst (PtCo/HSC) is shown in figure 1.11 on the next page.

1.5 Thesis outline

The work described in this thesis is concerned with finding a viable and scaleable way in synthesizing novel platinum alloy nanoparticles with a focus on the rare earth metals. Therefore the following chapter will discuss the ORR, the understanding of its mechanism and the implication on possible catalyst materials. It follows an examination of the state of the art catalysts and how they are synthesized. Other catalyst materials will be described followed by the introduction to platinum rare earth metal catalyst.
The next chapter displays the used analyzing techniques that have been used in this work to monitor the progress of our approaches to the synthesis.

The following chapters give a detailed overview over the synthesis methods that were investigated, motivation and conclusions. It will become clear that experiments with undesired outcome can lead to a synthesis method which promises to be viable method in synthesis highly ORR-active platinum rare earth metal alloys.

Finally, the work is summarized and the key findings are discussed.
2 The oxygen reduction reaction

The two main reactions in a hydrogen fuel cell are the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). The latter is of particular concern due to its comparable low reaction rate dominating the voltage losses in a fuel cell.

Even though the ORR in fuel cells is one of the most studied chemical reactions in the field of electrochemistry, our understanding of its mechanism is limited. This can be attributed to multiple possible reaction paths of which most intermediates would have a very short life and are attached to the solid catalyst. Secondly, the ORR is a heterogeneous reaction that takes place on the interface between a solid and a liquid/ionomer held at a certain electrochemical potential under a gas atmosphere and thus inaccessible by nearly all physical and chemical analyzing techniques. The reason is, that these techniques require either ultra high vacuum condition (XPS, TEM, etc.), a liquid-free sample surface (SAXS, IR, UV/Vis, etc.), a certain electric potential that differs from the applied potential (ECSTM) or a combination of these.

However, a summary of the current understanding of the ORR mechanism is provided in the following section.

2.1 Current understanding

2.1.1 Mechanism

The overall cathode reaction, equation 2.1, of converting one molecule of oxygen to water involves 4 protons and 4 electrons from the anode, supplied through the membrane and the GDL, respectively.
The oxygen reduction reaction

\[ \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \]  

(2.1)

This reaction involves surface adsorption, one splitting and the formation of four new bonds including the transfer of four electrons resulting in a complex network of possible reaction pathways. A simplified model of the reaction mechanism only involving isolatable intermediates is shown in 2.1.

Figure 2.1: Three oxygen reduction paths are shown: A 4e\(^-\) and the 2e\(^-\)+2e\(^-\) path both leading to the final product water and a 2e\(^-\) path resulting in hydrogen peroxide. Adapted from [15].

Figure 2.2 proposes the reaction mechanism including possible intermediates. After the oxygen has adsorbed on the catalyst surface the reaction pathway can proceed essentially via the dissociative or the associative path: In the first the oxygen-oxygen bond is split as the first step while in the latter the oxygen bond is split last [16]. The latter is also a path that can lead to the formation of hydrogen peroxide without a recombination of single oxygen species. Interestingly, computational calculations show that both the associative and the dissociative path take a role in the overall ORR reaction mechanism, with one dominating over the other depending on the catalyst surface [17].
2.1 Current understanding

Figure 2.2: The scheme showing the proposed dissociative (a) and associative (b) pathway of the ORR, interpreted from various sources: [18], [19], [17], [20], [16], [21]. The displayed steps combine the transfer of one electron and one proton (except for the adsorption and desorption steps), hence all displayed intermediates are neutral. Note that more intermediates within these steps are possible.

2.1.2 The scaling relationship

The Sabatier principle in catalysis suggests that intermediates may not bind too strong or too weak. If it binds too weakly, the intermediates do not bind and interact with the catalyst. If it binds too strongly the intermediates fail to dissociate or are too immobile to leave free adsorption sites [22].

A reaction pathway in which all intermediates are bound to the surface of the catalyst by an oxygen bond has significant consequences towards designing a good catalyst. However, the intermediate binding to the catalyst surface cannot be altered with complete freedom, its limits are understood by the scaling relationship:

The scaling relationship is a well established concept in catalyst theory. Its name arises from the observation that the binding energies of intermediates to a catalyst surface scale in the same manner among a wide variety of surfaces: Most catalytic reactions involve the binding of the various intermediates via the same atom as part of the adsorbents. In case of the ORR that is the binding of oxygen atom of the various intermediates to the surface. Since the binding energy contributes most to the overall energy of the intermediate, changing it by changing the catalyst will affect all intermediates in the reaction path equally. A schematic explanation can be found in figure 2.3 showing a simple three step...
2 The oxygen reduction reaction

mechanism.

\[ \text{Educt} \rightarrow *I_A \rightarrow *I_B \rightarrow \text{Product} \tag{2.2} \]

Figure 2.3: Top: Energy levels of the educts, products and intermediates of an arbitrary surface catalyzed chemical reaction, see the reaction equation 2.2. The red path depicts the path of minimized activation energies between the different steps and hence the highest kinetic rate. Bottom: Contour plot of the reaction kinetics depending on the intermediate-surface binding energies. Different binding energies correspond to different energy levels in the top energy diagram.

Typically the bond of the intermediate to the catalyst surface remains the same, e.g. all intermediates of the ORR bind via an oxygen atom to the catalyst. In order to obtain the optimal reaction path in terms of intermediate-catalyst binding energies it is necessary to change the O-catalyst bond energies independently, as sketched in figure 2.3. Tuning and optimizing catalysts are mostly limited to altering the electronic structure on the surface by alloying or support interactions. However, any change in the electronic structure will scale all oxy-
2.1 Current understanding

Gen binding energies by the same value - either strengthening or weakening them. Thus only a local activity maximum can be reached, which can still mean a significant improvement in catalytic activity.

Consequently, the multidimensional contour plot of the reaction activity can be reduced to a two dimensional graph by choosing an arbitrary intermediate energy state as the variable:

$$r(\Delta E_1, \Delta E_2, \ldots) \rightarrow r(\Delta E)$$

(2.3)

The resulting figure is called a volcano plot due to its characteristic shape - see figure 2.4 for the ORR case. Here the binding energy of the \( \cdot \) OH intermediate to the surface is chosen as the variable on the x-Axis, but in principle any other intermediate binding energy or for that matter intermediate energy state can be chosen.

Figure 2.4: The volcano plot for the ORR showing common and novel catalyst systems, adapted from [23].

In the presented volcano plot various catalyst systems are displayed. It has to
be noted that the ORR activities in this plot are actual measured values rather than based on calculations as it would be for the three dimensional energy diagram in figure 2.3. One can find that the ORR activity of a platinum surface can be enhanced by up to one order of magnitude by alloying platinum with another metal. How this effect is used towards enhancing the mass activity of platinum based catalysts is discussed in the sections 2.4 to 2.7.

2.2 Platinum on carbon

Platinum dispersed on high surface area carbon is the benchmark system in the development of new ORR catalysts for fuel cells. Platinum nanoparticles between 3 and 6 nm in diameter are dispersed on carbon black with a typical surface area of 10-100 $m^2/g$. The high surface area provides sufficient distance between the platinum nanoparticles to avoid agglomeration and coalescence forming bigger particles. Both effects would reduce the electrochemical active surface area from 50-100 $m^2/g$ and therefore the mass activity of the catalyst. The platinum loading of commercial Pt/C for applications in PEMFC ranges between 10 mass-% and 70 mass-% [24].

2.2.1 Preparation

The synthesis routes of Pt/C vary greatly depending on the objective of the final catalyst. For commercial applications the cost of the precursors, processing, environmental and safety aspects (disposal of solvents, hazardous chemicals, etc.) and throughput ($kg/day$) play a dominant role in choice of the synthesis path. On a research level one is much more concerned with obtaining a certain mean particle size, a narrow particle size distribution and shape control of the catalyst nanoparticles.

**Reduction of a platinum salt in solution** A very versatile method is to dissolve an anorganic platinum salt like H$_2$PtCl$_6$ together with dispersing carbon black (e.g. Vulcan XC72). If further size and shape control is desired, surfactants
2.3 Platinum free catalysts

are added that prevent agglomeration or the growth of certain facets. Eventually a reducing agent is added, such as hydrogen gas [25], citric acid [26], etc. The strength and the concentration of the reducing agent and temperature also play a significant role on the particle size distribution of the final product. Eventually the sample is washed and a heat treatment is sometimes applied.

**Solvothermal reduction**  Despite its high positive reduction potential, platinum can be reduced by many solvents themselves by raising their temperature. Common solvents for this synthesis route are ethyleneglycol [25] and DMF [27]. The solvent can also act as a surfactant, providing control over the particle shape and the size distribution.

**Impregnation Methods**  The platinum salt is dissolved in an appropriate solvent and high surface area carbon is added. The mixture is eventually filtered and the wet carbon is dried, allowing the remaining solvent in the carbon to evaporate and the platinum salt to precipitate highly dispersed within the support. If the pore volume is matched by the liquid volume no filtration step is needed. This so called incipient wetness method relies completely on the capillary forces of the porous carbon [28].

2.3 Platinum free catalysts

Due to its high price and limited availability many researchers have dedicated their work to finding alternatives to platinum. These catalysts are often referred to as platinum group metal (PGM) free catalysts.

Platinum based catalysts offer both the highest ORR activity and high stability under the highly acidic conditions in PEMFCs. In order to be a viable alternative PGM-free catalysts need to have an ORR activity and stability similar to that of platinum [29]. If the specific ORR activities are not met, the fuel cell stack would need to be scaled up increasing the overall system cost and dimensions which is not an option.

Two classes of PGM-free catalysts exist: Iron-nitrogen doped carbon and conductive metal oxides. All metal oxides in question can not be used under acidic conditions...
conditions, but show a lot of promise in alkaline fuel cells. The option to utilize PGM-free catalysts is actually the main advantage of this class of fuel cells over PEMFCs. However, despite great efforts alkaline polymer membranes have not reached the necessary stability and conductivity needed to allow alkaline based fuel cells to be an option [30].

Iron-Nitrogen doped Carbon promised to be another alternative PGM free catalyst in acidic media. These F/N/C catalysts have in common that transition metal atoms, mostly iron, stabilized by nitrogen-carbon groups act as the catalytic center for the ORR. However, the long-term stability has not been proven and the need for thicker electrode layers in fuel cell applications introduces mass transport challenges that need to be overcome before these catalysts can be a viable alternative to platinum based materials [29].

2.4 Platinum alloys of the late transition metals

Fuel cell catalysts for commercial applications are almost entirely platinum alloy nanoparticles in which the alloying element is either nickel or cobalt. Next to significantly enhanced ORR activity these catalysts are sufficiently stable and easy to prepare. Other late transition metals such as Pt$_3$Fe, Pt$_3$Cu and Pt$_x$Ru have also been investigated, the latter for its high CO tolerance [31], but do not match the performance of Pt$_3$Ni and Pt$_3$Co in terms of ORR activity.

2.4.1 Preparation

Characteristic for the most late transition metals are their rather high reduction potentials in the range of -0.5 V to 0.5 V, see table 2.1. Under certain conditions (pH, temperature, concentration, etc.) some of the late transition metals can be reduced in water and alcohols together with platinum by mild reducing agents - even though their standard reduction potential is lower than that of water (0 V). Typically a mild heat treatment, either in an autoclave as part of a one-pot synthesis or in a tube furnace is required to anneal in order to heal defects and obtain homogeneous platinum alloy nanoparticles.
2.5 Platinum alloys of the early transition metals

The platinum alloys of the early transition metals have not gained as much attention as the late transition metal alloys. Due to their significantly lower reduction potentials, see table 2.2, it is more challenging to synthesize them. Only little literature exists on these alloys in respect to their ORR activity. Their high alloying energy might lead to Pt alloy nanoparticles with superior stability compared to its Pt$_3$Ni and Pt$_3$Co counterparts [33].

Pt$_3$Cr has been successfully synthesized. Small Pt$_3$Cr nanoparticles on carbon are reported by Sakthivel et al. exhibiting a significant improvement of the ORR compared to Pt/C [34]. However their XRD data fails to demonstrate that their nanoparticles exhibit a Pt$_3$Cr crystal structure except few minor shift in platinum peak positions. Currently Pt$_3$Cr/C catalysts for fuel cells are commercially available.

Table 2.1: Reduction potentials of various late transition metals [32].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$ + 2e$^-$ ⇌ Fe</td>
<td>-0.44 V</td>
</tr>
<tr>
<td>Co$^{2+}$ + 2e$^-$ ⇌ Co</td>
<td>-0.28 V</td>
</tr>
<tr>
<td>Ni$^{2+}$ + 2e$^-$ ⇌ Ni</td>
<td>-0.25 V</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 3e$^-$ ⇌ Fe</td>
<td>-0.04 V</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2e$^-$ ⇌ Cu</td>
<td>+0.159 V</td>
</tr>
<tr>
<td>Cu$^+$ + e$^-$ ⇌ Cu</td>
<td>+0.52 V</td>
</tr>
<tr>
<td>Pt$^{2+}$ + 2e$^-$ ⇌ Pt</td>
<td>+1.188 V</td>
</tr>
</tbody>
</table>

Table 2.2: Reduction potentials of various early transition metals [32].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{2+}$ + 2e$^-$ ⇌ Ti</td>
<td>-1.63 V</td>
</tr>
<tr>
<td>Zr$^{4+}$ + 4e$^-$ ⇌ Zr</td>
<td>-1.45 V</td>
</tr>
<tr>
<td>Ti$^{3+}$ + 3e$^-$ ⇌ Ti</td>
<td>-1.37 V</td>
</tr>
<tr>
<td>Mn$^{2+}$ + 2e$^-$ ⇌ Mn</td>
<td>-1.185 V</td>
</tr>
<tr>
<td>V$^{2+}$ + 2e$^-$ ⇌ V</td>
<td>-1.13 V</td>
</tr>
<tr>
<td>Nb$^{3+}$ + 3e$^-$ ⇌ Nb</td>
<td>-1.099 V</td>
</tr>
<tr>
<td>Cr$^{3+}$ + 3e$^-$ ⇌ Cr</td>
<td>-0.74 V</td>
</tr>
<tr>
<td>Ta$^{3+}$ + 3e$^-$ ⇌ Ta</td>
<td>-0.6 V</td>
</tr>
<tr>
<td>Pt$^{2+}$ + 2e$^-$ ⇌ Pt</td>
<td>+1.188 V</td>
</tr>
</tbody>
</table>
2 The oxygen reduction reaction

Another obstacle in the synthesis and application of these alloys is that the early transition metals form very stable oxides. During the necessary annealing step remaining precursors may decompose into the metallic state and are readily oxidized by impurities to form the respective oxide. These oxides may be present on the surface of the platinum alloy nanoparticles and hinder its ability to catalyse the ORR. Moreover, these oxides eventually also form during operation due to metal leaching from the alloy nanoparticles [23]. It is suggested that the rather low ORR activity measured on bulk polycrystalline surfaces of Pt$_2$Zr and Pt$_3$Hf originates from a blocking oxide layer detected by XPS. The oxide layers of the early transition metals are very stable, as a simple overview on the respective bulk oxides in table 2.3 shows.

Table 2.3: Overview of the most common early transition metal oxides and the conditions they require to be dissolved. This list was compiled by data from [32] and has to be taken with care. Moreover, the oxides can exist in different modifications depending on the formation conditions which can greatly alter its acid stability.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_2$O$_3$</td>
<td>Maybe HF</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>Mineral acids</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>HF</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>HF</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>Mineral acids and strong bases</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Hot mineral acids</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>Mineral acids and strong bases</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>HF, hot H$_2$SO$_4$</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>Water</td>
</tr>
<tr>
<td>MoO$_2$</td>
<td>hot H$_2$SO$_4$</td>
</tr>
</tbody>
</table>

Other platinum early transition metal alloy nanoparticles have been reported to be synthesized, not necessarily as catalysts for the ORR: Among them are Pt$_x$Mo [35], Pt$_x$Mn [36], Pt$_x$W$_y$ [37], PtRh [38] and PtNb$_2$O$_5$ [39]. Some of the reports however have to be taken with a grain of salt: XRD data is some publications does not show the presence of the alloy phase by its characteristic peaks or even a peak shift.
2.6 Platinum alloys of the rare earth metals

The synthesis of platinum alloys of the rare earth metals, which covers yttrium, scandium and the lanthanides, is the main objective of this thesis. Therefore this section is a detailed discussion about the motivation and published results of synthesizing these alloys. The challenges regarding the synthesis are discussed in detail in chapter 4 on page 71.

2.6.1 Motivation

The screening of a number of platinum alloys in respect to the · O binding energy revealed that Pt$_3$Y is a promising candidate for novel alloy catalysts [33]. Eventually bulk polycrystalline samples were tested using the RDE technique and Pt$_3$Y showed a surface activity up to 10 times that of platinum. Moreover, the alloying energy between platinum and yttrium is among the highest under the bimetallic alloys promising a significant stability enhancement towards similarly active bimetallic alloys such as Pt$_3$Ni.

The investigations were expanded to other alloys of platinum and the early transition and rare earth metals: Pt$_5$La, behaves, similarly to Pt$_3$Y, as an exceptional ORR activity [40].

Escudero-Escribano et al. soon after published a study on Pt$_5$Gd, another platinum lathanide alloy, showing an exceptional ORR activity and stability similar to Pt$_3$Y [41]. From there on, a new class of alloy catalysts for a future application PEMFCs was established: The platinum alloys of the rare earth metals. These alloys with the exception of platinum scandium and promethium (not investigated due to its radioactivity) show all an exceptional and comparable ORR surface activity and have many other common chemical properties.

This class of alloys share the key feature of forming a platinum overlayer on top of the bulk alloy. The high alloying energy next to the rather large atomic radii of the rare earths prevents them from leaching out further than the first atomic layers [42]. The platinum crystal structure in the overlayer exhibits strain as has been discussed by a study on Pt(111)$_x$Y: The binding energy of *OH is about 0.1 eV smaller than in the case of unstrained platinum [43]. This value is
2 The oxygen reduction reaction

very close to the optimal binding energy for the highest possible ORR activity in respect of an unbroken scaling relationship. The overlayer after ORR testing was about to 1.5 nm thick, suggesting that the increase in ORR activity is entirely due to the strain and not the ligand effect. The latter requires the alloying metal to be sufficiently close to the surface which is not the case for these structures.

Additionally, the overlayer acts as a diffusion barrier preventing the yttrium atoms to leach out further from the bulk. This barrier, see figure 2.5, seems to be the greatest advantage in comparison to the commercial high performing Pt$_3$Ni based ORR catalysts. In their cases the alloying metal leaches out significantly leaving back an unstrained surface of platinum.

![Figure 2.5: Scheme of the bulk and surface structure of Pt$_3$La, representative for other platinum rare earth metal alloys, adapted from [23]. The Pt overlayer is thick enough to act as a diffusion barrier preventing further leaching of lanthanum while still being under compressive strain reducing the *OH binding energy sufficiently to increase the ORR activity substantially.](image)

So far only the surface activity had been investigated, while the mass activity remains unknown. All rare earth metals exhibit a reduction potential significantly more negative, see table 2.4, compared to the late and even the early transition metals for which most alloy nanoparticle synthesis routes with platinum had been designed up to this date.

Eventually Pt$_3$Y and Pt$_5$Gd as the most promising candidates were chosen to be synthesized in nanoparticulate form on high surface area carbon using a so called nanocluster source. This technique allows the production of mass...

---

1When the electronic surface structure of the host metal (platinum) is changed by the alloying metal the term ligand effect is used [44].
2.6 Platinum alloys of the rare earth metals

Table 2.4: Reduction potentials of various rare earth metals [32].

<table>
<thead>
<tr>
<th>Metal</th>
<th>Reduction Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y³⁺  + 3e⁻ ⇌ Y</td>
<td>-2.372 V</td>
</tr>
<tr>
<td>Sc³⁺ + 3e⁻ ⇌ Sc</td>
<td>-2.077 V</td>
</tr>
<tr>
<td>La³⁺ + 3e⁻ ⇌ La</td>
<td>-2.379 V</td>
</tr>
<tr>
<td>Ce³⁺ + 3e⁻ ⇌ Ce</td>
<td>-2.336 V</td>
</tr>
<tr>
<td>Pr³⁺ + 3e⁻ ⇌ Pr</td>
<td>-2.353 V</td>
</tr>
<tr>
<td>Nd³⁺ + 3e⁻ ⇌ Nd</td>
<td>-2.323 V</td>
</tr>
<tr>
<td>Sm³⁺ + 3e⁻ ⇌ Sm</td>
<td>-2.304 V</td>
</tr>
<tr>
<td>Eu³⁺ + 3e⁻ ⇌ Eu</td>
<td>-1.991 V</td>
</tr>
<tr>
<td>Gd³⁺ + 3e⁻ ⇌ Gd</td>
<td>-2.279 V</td>
</tr>
<tr>
<td>Dy³⁺ + 3e⁻ ⇌ Dy</td>
<td>-2.295 V</td>
</tr>
<tr>
<td>Ho³⁺ + 3e⁻ ⇌ Ho</td>
<td>-2.33 V</td>
</tr>
<tr>
<td>Er³⁺ + 3e⁻ ⇌ Er</td>
<td>-2.331 V</td>
</tr>
<tr>
<td>Tm³⁺ + 3e⁻ ⇌ Tm</td>
<td>-2.319 V</td>
</tr>
<tr>
<td>Yb³⁺ + 3e⁻ ⇌ Yb</td>
<td>-2.19 V</td>
</tr>
<tr>
<td>Lu³⁺ + 3e⁻ ⇌ Lu</td>
<td>-2.28 V</td>
</tr>
</tbody>
</table>

selected nanoparticles of nearly any composition in high vacuum, even though only on a very small nanogram scale. In summary: A target composed of the desired combination of metals is sputtered by argon ions in high vacuum. This results in the release of charged fragments of the target into a chamber where a mass spectrometer using their mass to charge ratio selects the fragments and deposits them onto high surface area carbon, see figure 2.6. The sample can then be analyzed by in-situ techniques, such as XPS, and eventually removed from the high vacuum chamber and transferred to an electrochemical cell to perform the necessary measurements to evaluate the ORR activities.

While the optimal particle size in terms of mass activity of Pt/C ORR catalysts ranges between 3-4 nm and for commercial platinum alloy catalysts is around 5-6 nm. The study interprets the data shown in figure 2.7 that the optimal particle size of the platinum rare earth metal alloys is > 8 nm. At this diameter, the initial ORR activity of these nanoparticles is about 4x of that of Pt nanoparticles and about 2x that of Pt₃Ni/C and Pt₃Co/C.

The rather high optimal particle size exhibits two benefits: First, the synthesis of these alloys is presumably simpler if larger particles are desired. Secondly,
2 The oxygen reduction reaction

Figure 2.6: Sketch of the nanocluster source used to create mass selected Pt₅Y and Pt₅Gd nanoparticles, adapted from [45].

the tendency for nanoparticles to grow in the application is disproportional to their size. Pt/C are observed to grow under normal operating conditions to about 7 nm and higher [46]. One can therefore expect that the platinum rare earth metal alloy nanoparticles of around 9 nm will be rather stable in terms of size distribution.

Figure 2.7: Plots a) and b) on the left show the dependency of the ORR specific and mass activity respectively on the nanoparticle size. The right figure shows how stable the nanoparticles are under cycling in terms of mass activity. All graphs are adapted from [47].
2.6 Platinum alloys of the rare earth metals

2.6.2 Synthesis

Molten Salt

Alkali metal triethylborohydrides (MEt$_3$BH) are strong reducing agents. Typically their lithium, sodium and potassium salts are the most applied and are produced in situ in THF using triethylborane and the respective alkali metal hydride as starting compounds. Kanady et al. separated these compounds from and made use of the low melting points of 30°C and 80°C of the sodium and potassium forms, respectively [48]. Then platinum and rare earth metal salts were mixed with MEt$_3$BH and subsequently melted under an inert gas atmosphere at 200°C for 1 h. Eventually the sample was THF and hexane washed and a matrix of the used alkali metal chloride embedded with platinum and rare earth metal hydride species was obtained. The matrix was then heated for 2 h at 650°C under vacuum. The sample was then dispersed together with carbon in THF, filtered, water and finally acid washed.

![XRD diagram of Pt$_3$Y/C nanoparticles](image)

Figure 2.8: The XRD diagram of the Pt$_3$Y/C nanoparticles obtained by the synthesis involving molten salts, adapted from [48]. Besides the peak at 30 all peaks correspond to the Pt$_3$Y phase, however they are shifted at higher angels which might originate from strain within the nanoparticles. The rather sharp peaks indicate large crystallites.

Unfortunately the mean particle size of the obtained samples are in a wide range of 5-20 nm and the lack of electrochemical measurements on the samples in the publication suggest an underwhelming performance. The salt matrix seems not to be sufficient in preventing the particle growth during the annealing step. Nevertheless, the provided XPS and XRD data showed clearly that these alloys can be produced in a scalable chemical manner even though the control of particle size is lacking.
2 The oxygen reduction reaction

Ultrapure hydrogen reduction

Another approach is the utilization of ultra pure hydrogen as reducing agent. Roy et al. used this method to reduce rare earth metal chlorides dryly mixed with Pt/C at temperatures above 700°C [49]. At these temperatures the reduction of the chlorides with hydrogen becomes thermodynamically feasible when the produced hydrogen chloride gas is removed fast from the sample, e.g. by a sufficiently high gas flow.

Figure 2.9: Adapted from [49]. XRD diagram of Pt₃Y/C catalyst obtained by the reduction by ultra high purity hydrogen.

The high temperatures however in pair with the strong reducing environment by the hydrogen gas can lead to significant particle growth [50]. In the present publication this was partly avoided by using Pt/C that already exhibited a mean diameter of 7 nm with the objective to obtain particle of a mean diameter of 9 nm. The heat treatment however lead to a significant broadening of the particle size distribution resulting in a rather poor mass activity compared to commercial platinum catalysts and in terms of the expected activity
2.6 Platinum alloys of the rare earth metals

gain.

**Very high temperature annealing of yttrium and platinum salts mixed with carbon**

Schwämmlein et al. reported the synthesis of Pt$_x$Y/C nanoparticles [51]. They mixed carbon, a platinum salt and yttrium nitrate under an inert atmosphere and annealed the sample at temperatures higher than 1000°C in an 5% H$_2$/Ar atmosphere. The XRD of the resulting catalysts is shown in figure 2.10.

![XRD diagram of Pt$_x$Y/C catalyst obtained by the reduction at very high temperatures.](image)

The resulting particles are still mostly consisting of platinum with a minor fraction being composed of Pt$_2$Y and Pt$_3$Y. The authors measured an increase in specific activity but a decrease in mass activity in ORR activity in RDE measurements.
2 The oxygen reduction reaction

Author’s remarks to the synthesis attempts in literature

The synthesis attempts of platinum rare earth metal catalyst share the necessity of high to very high annealing temperatures. This leads to uncontrolled particle growth and a poor phase control of the final nanoparticles. The uncontrolled particle growth not only leads to an increase in average particle size but also to a very broad particle size distribution, which is unfavorable in order to achieve high mass activities. Despite some increase in specific activity this has not matched the predicted OR-R activities, presumably due to the lacking phase control.

Therefore, a successful platinum rare earth metal nanoparticle synthesis must circumvent the use of high temperatures or take measures to somehow inhibit the nanoparticles from the dominant particle growth modes (Ostwald ripening, coalescence).

2.7 Platinum alloys of other metals

2.7.1 PtPb

Bu et al. showed in their 2016 paper the synthesis of so-called PtPb nanoflakes [52]. Using a simple and scalable but well-tuned wet chemistry approach they report an ORR activity of about 20 times that of commercial Pt/C which is retained to about 90% even after 50,000 potential cycles.

Figure 2.11: Adapted from [52]. Pictures (A) and (B) display the shape and size of the PtPb nanoflakes and (D) shows their stability after cycling in terms of mass and specific activity initially.
2.7 Platinum alloys of other metals

Even though the results are very encouraging, shape controlled nanoparticles have yet not show their stability in an actual fuel cell set-up.

2.7.2 Shape controlled metal doped platinum alloy nanoparticles

Shape controlled platinum and platinum alloy nanoparticles have been investigated as a potential ORR catalyst. Among them, octahedral Pt$_3$Ni nanoparticles show extraordinary ORR activities [53] due to the presence of extended {111} facets. However, as most metal alloy nanoparticles these catalysts suffer from the dissolution of the alloying metal and in case of shape controlled particles; the tendency to become spherical to reduce surface energy [54].

It can be shown that doping these nanoparticles with another metal tremendously increases their stability and enhances their activity even further [55].

Figure 2.12: Adapted from [55]: a) Initial ORR activity data of commercial Pt/C, octahedral Pt$_3$Ni and Gallium doped octahedral Pt$_3$Ni nanoparticles. b) and c) show the particle dimensions (STEM) and composition (STEM + EDS) after 30000 potential cycles.

Figure 2.12 shows that gallium doped octahedral Pt$_3$Ni nanoparticles both exhibit outstanding ORR performance and great stability in RDE. Lim et al. also showed for the first time that these catalysts perform equally well in a PEMFC setup.
3 Techniques

The development of catalysts for the oxygen reduction reaction (ORR) is rather complex and requires a set of characterization and testing techniques to optimize the employed synthesis method. Characterization techniques are used to obtain information the following parameters about the desired nanoparticles:

- Particle size and shape
- Crystalite size
- Elemental composition
- Crystal phase
- Their surface composition
- Dispersion on the support
- Their loading on the support

Using testing techniques the catalytic performance can be investigated. These techniques mainly differ in its ability to mimic the conditions of the aimed application. Moreover other factors such as their time and laboratory resource consumption play a major role at which developing stage a certain technique will be employed.

In figure 3.1 a simplified scheme is presented on how the novel ORR catalyst in this thesis was developed. After on synthesis attempt an XRD diagram was measured to obtain information about the particle size and phase composition of the catalyst. In many cases the results were not satisfactory and another synthesis attempt was made. In case of promising results or the need for more
3 Techniques

Figure 3.1: Scheme of the aimed catalyst development procedure.

information about how the synthesis process should be altered XPS, TEM, TGA and/or EDS measurements were performed. A new sample was synthesized restarting the feedback loop or the sample’s ORR activity was tested using the RDE technique. The details of the mentioned techniques will be discussed in the following sections.

3.1 Characterization

A diverse set of characterization techniques are available for a material scientist. Figure 3.2 provides an overview over typical methods and its applications.

- Secondary electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Low energy electron diffraction (LEED)
- X-Ray diffraction spectroscopy (XRD)
- Electron diffraction spectroscopy (EDS)
- Electron energy loss spectroscopy (EELS)
3.1 Characterization

Figure 3.2: Characterization techniques in Material Science ordered by application and properties probed.

- X-ray absorption near-edge structure spectroscopy (XANES)
- X-Ray photon spectroscopy (XPS)

All techniques rely on the interaction of the probed sample with photons or electrons. The energy level of the photons is typically in the X-ray level which results in a considerable penetration depth, reaching millimeters. Electrons at the same energy interact much stronger with matter and its energy is very decisive if just the surface or the bulk phase of the sample is probed. The relationship between penetration depth, (inelastic) mean free path (IMFP), and electron energy is displayed in figure 3.3.

This characterization techniques carried out for this thesis were XRD, EDS, TEM, XPS and TGA and are discussed in the following sections.

3.1.1 XRD

In X-ray Diffraction Spectroscopy (XRD) the scattering of x-rays on crystalline samples is used to gain information about their crystallite size and phase composition. In fact multiple forms of XRD techniques exists, however, in this thesis
3 Techniques

Figure 3.3: The universal curve reproduced from [56]. The highlighted areas of the XPS, SEM, EDS and TEM techniques aim to give a broad overview over the involved electron energies and its typical penetration depth into matter.

XRD refers to X-ray Powder Diffraction Spectroscopy since it is the only one used in this project.

A beam of monochromatic and coherent x-rays is generated by exciting K-shell electrons of a target metal by thermoelectrons from a heated filament. The x-ray beam is focused on the sample under the angle $\Theta$. The x-rays are scattered on the crystal planes of the sample and leave the sample in all directions, as displayed in figure 3.4. A detector positioned on the opposite side by the same angle $\Theta$ collects the x-rays that were scattered by $2\Theta$. A monochromator assures that only scattered x-rays with the same wavelength as the source enter the detector to prevent signals from lower energy secondary x-rays.

Depending on the angle $\Theta$ of the incident beam to the crystal planes the scattered x-rays either interfere constructive or destructive as illustrated in figure 3.5 on the facing page. In case of constructive interference of x-rays scattered to the detector by $2\Theta$ a signal is recorded, while in case of destructive interference only noise is recorded.

The angle at which constructive interference and hence a signal is detected
3.1 Characterization

Figure 3.4: A simplified sketch of the main components in an XRD apparatus is shown. Note that the sample and detector angles are altered to scan over the desired angle range. The construction of XRD devices limits range of $\Theta$ between ca. 5° and 175°.

![XRD apparatus diagram](image)

Figure 3.5: The scheme shows two incoming monochromatic x-rays at two different angels respectively. Note that only the outgoing X-rays that reach the detector under the specified angle are shown, while actually x-rays are reflected homogeneously in all three spatial dimensions. In the left case the outgoing x-rays towards the detector are in phase and interfere constructively. In the right case the x-rays interfere destructively and annihilate.

![X-ray interference diagram](image)

depends on the distance between the lattice $d$ planes that are perpendicular aligned to the symmetry line between x-ray source and the detector, or just $\Theta$. The relationship between $\Theta$ and $d$ is mathematically express by Bragg’s Law, equation (3.1) on the next page.
3 Techniques

\[ 2 \cdot d \cdot \sin(\Theta) = n \cdot \lambda \]  \hspace{1cm} (3.1)

\( \lambda \) is the wavelength of the x-rays and \( n \) denotes any positive integer greater than 0. Every set of \( \Theta \) and \( d \) that fulfill Bragg’s Law will show constructive interference. In some less trivial crystal structures scattered x-rays from another family of lattice planes can interfere deconstructively.

Figure 3.6: Illustration of Bragg’s law, compare to figure 3.5. Description of the symbols in the text.

Since in a powder sample the crystallites are oriented randomly and always a significant amount are oriented in a way that positive interference for the angle attributed to a family of lattice plane with the distance \( d \) can be detected. A lattice plane of a crystal is denoted in miller indices of the form \((h \ k \ l)\) for cubic or \((h \ k \ l \ m)\) for hexagonal systems. Any integer multiple of \((h \ k \ l)\) corresponds to one specific \(d\) and is a member of this family of lattice planes. Figure 3.7 shows the peak positions and intensities of metallic platinum. The different peak intensities arise from different packing densities and the specific cross section of atoms on the corresponding lattice planes among other factors.

The XRD pattern is characteristic for a certain crystal structure and hence is used to identify the composition, stoichometry and symmetry of the analyzed crystalline material. When powders are analyzed the crystallites are randomly distributes, however a sufficient quantity will fulfill the Bragg-condition and show an interference pattern similar to single crystal. The smaller the crystallites however, the more the reflected beams interact with each other. This and other reasons lead to the broadening of the obtained interference peaks which
3.1 Characterization

Figure 3.7: Idealized XRD diagram of an infinitely large platinum crystal.

The Scherrer Equation can be taken advantage of to determine the mean crystal size:

$$\tau = \frac{K \lambda}{\beta \cos \theta}$$  \hspace{1cm} (3.2)

where $K$ is a shape factor, typically 0.9 - 1.0, $\lambda$ is the x-ray wavelength, $\beta$ is the peak width at half peak maximum intensity (FWHM) and $\theta$ is the angle associated with the peak. The FWHM has to be reduced by the instrumental peak broadening that before it can be used as value for $\beta$.

Conclusively the XRD diagram allows the extraction of two important pieces of information early on in the characterization process: The sample composition and approximate particle size. For this purpose a Rigaku MiniFlex 600 benchtop X-ray diffractometer with a Cu-K\(_\alpha\) X-Ray source ($\lambda = 0.154$ nm) and an operating voltage of 40 kV and 15 mA was used.

3.1.2 EDS

Energy dispersive X-ray spectroscopy (EDS or EDX) is a technique to identify the chemical composition of materials. It is often used in combination with transmission electron microscopy (TEM) or secondary electron microscope (SEM). Since the used electrons possess rather high energies (10 keV) and X-rays travel well through matter, EDS is rather a bulk not a surface sensitive tech-
3 Techniques

The electron beam used in TEM and SEM interacts with matter so that electrons are removed from their current orbitals\(^1\). Orbitals with the same angular momentum can be grouped as shells, the term that will be used from now on. When an electron is removed from its shell, a hole is created that will be filled by an electron from a higher shell. The energy of this transition is released as a photon. Since the binding energy is different from each shell and chemical element, the photon energy is characteristic for each chemical element. However, these energies can lie closely to each other thus requiring the knowledge of multiple transition energies to safely identifying the elemental composition of the sample.

![Diagram of a silicon atom and its K, L and M shell](image)

**Figure 3.8**: Scheme of a silicon atom and its K, L and M shell. (1) The K-shell is excited by an incoming electron or photon, releasing an electron and leaving a vacancy. (2) The vacancy is filled by an electron from an M-shell which releases a specific energy in form of a photon.

In figure 3.8 silicon is probed as an example: Silicon has three shells, denotes as K, L and M. If an electron is removed from the innermost shell the created electron vacancy can be filled by L or M electrons. Each transition is denoted by the shell where the vacancy is filled and how distant the shell is where the electron originates from:

\(^1\)X-Rays of sufficient energy can remove electrons form their orbitals as well
3.1 Characterization

- K-shell electron-vacancy filled by a L-shell electron: $K_{\alpha}$ transition
- K-shell electron-vacancy filled by a M-shell electron: $K_{\beta}$ transition
- L-shell electron-vacancy filled by a M-shell electron: $L_{\alpha}$ transition

Thus, in case of silicon, three different possible electron transitions are possible, each is associated with a different amount of energy released and intensity. The electron vacancy of the M-shell is filled by electron conduction through the sample which releases an insignificant amount of energy.

3.1.3 TEM

Transmission electron microscopy (TEM) allows the imaging of objects by a focused electron beam allowing a spatial resolution down to 0.05 nm (Platinum by comparison: Atomic radius: 0.139 nm, lattice parameter: 0.39 nm). The main objective in using TEM in this work was obtaining the particle size distribution of the catalyst particles dispersed on the carbon support. Moreover, agglomeration of the particles and the homogeneity was of interest. A scheme and a picture of a TEM microscope is shown in figure 3.9.

The specimen is prepared by dispersing a minuscule amount of the sample in an appropriate solvent. A tiny amount of the dispersion is then dried on a carbon matrix that is fixed on a copper grid and the solvent is removed by drying. The copper grid with the sample particles is then fixed on a sample holder and transferred into the microscope and its chambers are sufficiently vacuумed. The electron gun accelerates electrons to 200 V forming a beam that is condensed and focused on the specimen using the condensor and the objective aperture. The electrons pass through the specimen depending on the thickness of its structures and its atomic density (z-contrast). The transmitted electrons can be viewed on a fluorescent screen or are recorded by a charge-coupled device (CCD) camera. The thicker the structure or the higher the atomic number of the elementd the structure is comprised of, the darker the structure appears. The carbon matrix and the carbon support from the catalyst sample appear light, while the catalyst nanoparticles appear dark. Moreover, the reso-
3 Techniques

Figure 3.9: Scheme obtained from wikipedia.org, Picture of the FEI Tecnai T20 G2 instrument from cen.dtu.dk.

...olution of a TEM allows the observation of single atomic rows of the crystalline material and directly observe their lattice spacing.

The electron beam in a TEM microscope can be used for other techniques as well, complementing the sample analysis:

- **LEED**: Under the right conditions, the Bragg-condition of the crystalline nanoparticles is fulfilled and a diffraction pattern can be recorded. This pattern in its form and its dimension is characteristic for a crystalline phase and can be directly related to XRD measurements.

- **EDS/EELS**: The electrons that do not pass the specimen lead to energy transitions within the shell of the atoms of the specimen ways. When states of higher energy relay back to their lower energy states a spectrum of x-rays characteristic to its elemental composition is released and can be
3.1 Characterization

3.1.4 XPS

Through X-Ray Photoelectron Spectroscopy (XPS) one gains insights into the surface of solids. The main information that can be obtained is the elemental composition of the first few atomic layers of a solid surface and the chemical state of the respective elements.

![Figure 3.10: Simplified sketch of the XPS measurement principle.](image)

XPS relies on the photoelectric effect: Electromagnetic radiation, or simply photons, interacts with the atomic orbitals and excite electrons. When the photon energy exceeds the binding energy of an electron it can be emitted from its respective orbital, hence the emitted electron is called a photoelectron. If the photoelectron originates from an inner orbital, the formed hole is filled by an outer orbital that transfers the released energy to another outer orbital electron and leads to its emission - a so called auger electron. Photo- and auger electrons carry the information of their origin as kinetic energy. The binding energy of atomic orbitals differs significantly between the elements and slightly depending on the chemical state of its atom. For instance, the higher the oxidation state of an atom, the higher binding energy of its electrons in its orbitals is.
3 Techniques

Therefor, the principle of XPS is the generation of photo- and auger electrons by radiating a sample surface with sufficiently high-energetic X-rays and to detect the energy spectra of the emitted electrons. Since the energy of the X-ray source is known, the binding energy of the detected electrons can be calculated via equation 3.3.

\[ E_{\text{binding}} = E_{\text{source}} - E_{\text{kinetic}} \]  

The intensity of detected electrons is then plotted against the binding or kinetic energy. Since the majority of electrons do not hit the detector directly, they interact within the sample or the apparatus’ surface and lose energy. Hence these electrons are detected at a lower kinetic energy which leads to a background. A typical XPS survey spectrum is shown in 3.11.

![Figure 3.11: Idealized XPS spectrum.](image)

The survey spectrum allows to identify which elements are present on the surface of the sample based on the peak positions. A detailed assessment of every peak is needed to accurately identify the surface composition and chemical state of the elements present, see figure 3.12. Every singlet or doublet, depending of the orbital origin of the photoelectrons, corresponds to a specific element. After subtracting the background using the Shirley method the peak area can be analyzed by correcting its value using tabulated parameters. The corrected peak area can then be used to calculate the elemental composition on the sur-
3.1 Characterization

face. Secondly, the exact peak position is examined to identify a shift in binding energy typical in the order of $\pm 2$ eV to identify the nature of the chemical binding of the respective element.

![Figure 3.12: Sketch of how the Shirley method is used to correct for background signals. The obtained peak area is an accurate measure of the fraction the species associated binding energy occurs in the sample surface.](image)

To identify the chemical composition and binding state of the catalyst surface a ThermoScientific K-alpha XPS instrument was utilized.

3.1.5 TGA

In a Thermogravimetric analysis (TGA) the sample is heated under a controlled atmosphere while its mass change is recorded. This technique is valuable if the components of the sample have different boiling points or gasification temperatures. Heating for instance a metal on carbon sample in an oxygen atmosphere will result in the removal of the the carbon support in the form of CO$_2$ leaving only behind the metal or its oxide. This allows to determine the original loading of the metal in the sample.
3 Techniques

In this work, the TGA on catalyst samples was performed on a Netzsch STA409 PC instrument.

3.2 Electrochemical testing

The assessment of the synthesized and characterized catalyst in respect of the Oxygen Reduction Reaction (ORR) is crucial for its further development. While the final performance of a catalyst only shows in an actual fuel cell, preparing such a measurement required significant amount of catalyst material and time. Hence, the ORR performance is first measured using a Rotating (Ring) disc electrode (RRDE) setup which results roughly transfer to the fuel cell case, but require significantly less sample material and can be performed and analyzed comparably quick. Moreover, an RRDE measurement requires less parameters to be optimized and taken into account, that make a proper catalyst testing in a fuel cell more challenging.

3.2.1 RDE

The rotating disc electrode is a common tool in the analysis of the kinetics of electrochemical reactions. In order to understand this technique and the common section will discuss the model of an electrochemical reaction in terms of its thermodynamic, kinetic and mass transport.

3.2.2 The electrochemical reaction

The main difference between a chemical and an electrochemical reaction is the involvement of electrons as "educts" or "products". For this very reason, electrochemistry belongs to the field of heterogeneous catalysis, since electrons must be transported through a conductive surface while the other reactants have to be in a certain contact at any point during the reaction.

In the next sections the temperature and pressure remain constant and the most simple and general electrochemical reaction scheme is used, which is written as a reduction:
3.2 Electrochemical testing

Figure 3.13: General scheme of processes occurring on an electrode during a chemical reaction [57].

\[ \nu_{O} O + z e^{-} \rightleftharpoons \nu_{R} R \]  

(3.4)

\( O \) and \( R \) denote the reactants accepting (oxidant) and releasing (reductant) electrons respectively in stoichiometries of \( \nu_{O} \) and \( \nu_{R} \). \( z \) is the number of electrons \( e^{-} \) transferred through the electrode surface in one elementary step. It has to be noted that equation 3.4 can be part of an extended reaction system, but has to represent the rate determining step in order to be analyzed as to be discussed.

**Thermodynamics**

The change in the Gibbs free energy \( \Delta G \) of this reaction can be written using chemical potentials \( \mu \) as:

\[ \Delta G = \nu_{R} \mu_{R} - (\nu_{O} \mu_{O} + z \mu_{e^{-}}) \]  

(3.5)

The chemical potential can be calculated using the standard state denoted by \( \circ \), \( \Delta G_{i} \) using the the activities \( a \) of the components \( i \):

\[ \mu_{i} = \mu_{i}^{\circ} + RT \ln(a_{i}) \]  

(3.6)
3 Techniques

$\mu_{e^-}$ can be replaced by $\mu_{e^-} = -FE$ where $F$ is the Faraday constant and $E$ is the electrode potential. At equilibrium it holds:

$$\Delta G = 0 = \nu_R \mu_R^0 - \nu_O \mu_O^0 + RT \left( \frac{a_R^{\nu_R}}{a_O^{\nu_O}} \right) + zFE \Rightarrow E = \frac{\nu_O \mu_O^0 - \nu_R \mu_R^0}{zF} + RT \ln \left( \frac{a_O^{\nu_O}}{a_R^{\nu_R}} \right)$$

Replacing $\mu_O^0 - \mu_R^0/zF$ with the standard (reduction) electrode potential $E_{O/R}^o$ for the reaction leads to the Nernst-Equation:

$$E = E_{O/R}^o + RT \ln \left( \frac{a_O^{\nu_O}}{a_R^{\nu_R}} \right)$$

(3.7)

Since the concentration $c$ of a species is more accessible, this common form of the Nernst-Equation is used from here on\(^2\):

$$E = E_{O/R}^o + RT \ln \left( \frac{c_O^{\nu_O}}{c_R^{\nu_R}} \right)$$

(3.8)

3.2.3 Kinetics

Current

A deviation of the system from its equilibrium leads to a net current, arising from the transfer of electrons through the electrode boundary. This quantity of the current follows Butler-Volmer kinetics; Without derivation:

$$i = Fk^0 \left[ a_R^{\nu_R} \exp \left( \alpha_R \frac{zF}{RT} (E - E^o) \right) - a_O^{\nu_O} \exp \left( -\alpha_O \frac{zF}{RT} (E - E^o) \right) \right]$$

(3.9)

The kinetic parameters are $k^0$, $\alpha_R$, and $\alpha_O$\(^3\).

At equilibrium potential $E = E_{eq}$ no current, $i = 0$\(^4\), is observed and equation 3.9 can be rewritten to a form commonly known as the Butler-Volmer-Equation.

\(^2\) $E^{o'} - E^o = \frac{RT}{zF} \ln \left( \frac{\gamma_O^{\nu_O}}{\gamma_R^{\nu_R}} \right)$ with the activity coefficients $\gamma_i$

\(^3\) Called the symmetry factor. In simple cases: $\alpha = \alpha_O = 1 - \alpha_R \approx 0.5$

\(^4\) Under this condition the Nernst-Equation applies: $E_{eq} = E_{O/R}^{o'} + RT \ln \left( \frac{c_O^{\nu_O,e}}{c_R^{\nu_R,e}} \right)$

56
3.2 Electrochemical testing

\[ i = i_0 \left[ \left( \frac{c_R}{c_{R,eq}} \right)^{\nu_R} \exp \left( \alpha_R \frac{zF}{RT} \eta \right) - \left( \frac{c_O}{c_{O,eq}} \right)^{\nu_O} \exp \left( -\alpha_O \frac{zF}{RT} \eta \right) \right] \]  

(3.10)

\( \eta \) is used as the reaction overpotential \( \eta = E - E_{O/R} \) that corresponds to its driving force. \( E \) is the potential in the electrode, whereas \( E_{O/R} \) corresponds to the electrochemical potential in the electrode interface. \( E_{O/R} \) can change during the course of reaction since it is controlled by the Nernst-Equation, that is by itself governed by the concentration of involved species that may form or deplete. Thus, the overpotential measured on the disc, \( \eta_D = E - E_{eq} \), differs from the relevant overpotential \( \eta \). \( k^o \) is replaced by \( i_0 \) called the exchange current density which quantifies how much positive and negative current is flowing simultaneously through the electrode boundary at equilibrium.

![Figure 3.14: Potentials at the electrode surface. Symbols defined in the text.](image)

Equation 3.10 has three limiting cases. The first was used in deriving it - when \( \eta \) is zero it approaches the Nernst-Equation. To simplify the following cases further, the concentration of reactants at the electrode does not change \( c_i = c_{i,eq} \) and the so called Tafel slope is introduced \( z \ln(10) \frac{RT}{zF_{O/R}} = b_{O/R} \).

The second case arises when \( |\eta| \) is small\(^5\) and equation 3.10 can be linearised using the first two terms of the Taylor series of the Euler function:

\(^5\)For errors less than 1%: \( |\eta| < |b|/10 \)
3 Techniques

\[ i = \ln(10)i_0\eta \left(\frac{1}{b_O} + \frac{1}{b_R}\right) \]  

(3.11)

The third case, when \(|\eta|\) becomes sufficiently large\(^6\) leads to the Tafel-Equation:

\[ i = i_010^{\eta/b_R} \quad \vee \quad i = -i_010^{-\eta/b_O} \]  

(3.12)

Oxidant and reductant

At the electrode surface the consumption/formation of the O and R species is related to the current:

\[-\nu_O\hat{n}_O = \frac{i}{zF} = \nu_R\hat{n}_R\]  

(3.13)

\(\hat{n}\) denotes the flux of species imposed by the reaction, that results in concentration gradients in respect to the bulk of the solution leading to mass transport.

Mass transport

Two cases of mass transport can be distinguished:

1. The concentration of reactants in the electrolyte is solely controlled by diffusion, following the Cotrell-Equation.

2. Some kind of convection is applied to the electrolyte, dividing the electrode interface into a section with one governed by diffusion and the other by convection.

When performing a kinetic analysis, the changes of the reactant concentration by mass transport has to be accounted for. The second case is much simpler to include in a kinetic analysis than the first case. By using convection, a stationary and well defined mass transport can be achieved.

Based on this principle, two common systems have been established in electrochemistry to analyze the kinetics of electrochemical reactions. The flow cell method and the RDE method, the latter is used in this work to test the synthesized catalyst and will be discussed in detail later on.

\(^6\)For errors less then 1%: \(|\eta| > |b|\)
3.2.4 How to measure kinetics

Starting in section 3.2.2 a model for one electrode was developed. In reality, the potential of an electrode can only be measured, and a current drawn, against another electrode. Luckily the same model applies on all electrodes. The common three electrode set-up (in a liquid electrolyte) allows the independent determination of the electrode potential drop, which is called reaction overpotential.

The reaction to be analyzed occurs on the working electrode (WE). At the counter electrode (CE) the opposite current flows, closing the circuit. Since an electric potential is required to draw a current at the CE and an ion transport through the electrolyte, one needs a third electrode, the reference electrode (RE), to distinguish between these electric potential drops/overpotentials, figure 3.15 illustrates that.

![Figure 3.15: Current voltage curves showing the necessity of a reference electrode.](image)

In this example the overpotential of the ORR is to be measured: Case 1 and 2 do not use a reference electrode and the cell potential is measured between
3 Techniques

the WE and the CE. In case 1 the balancing reaction on the CE is the oxygen evolution reaction (OER) and the measured cell potential without a reference electrode is $\Delta E_{\text{case1}}$. It is obvious that in this mode no kinetic information can be extracted. In case 2 the counter electrode is supplied with hydrogen, allowing the hydrogen oxidation reaction to proceed: Due to its fast kinetics the measured cell potential subtracted by the reversible cell potential $E_{\text{rev}}$ of $\text{O}_2/\text{H}_2\text{O}$ gives a better approximation of the ORR overpotential $^7$. Contrary to case 1 and 2, a reference electrode has a fixed and known potential at all currents and therefore allows to calculate $\eta_{\text{ORR}}$ accurately. However, both the counter and reference electrodes have to be chosen with care.

The counter electrode

The surface area of the counter electrode should be as high as possible, i.e. by using a metal mesh, hence the current density is minimised as is the needed overpotential to balance the WE on this electrode. The electrode material should be inert and if possible equal in order for the WE. Both properties avoid any contamination by products of the countering electrochemical reactions or due to dissolution. In addition the CE can be separated by a frit from the WE compartment to reduce mass transport of dissolved electrode material and reaction products.

The reference electrode

The reference electrode senses the potential difference between the WE and a fixed potential point. Theoretically, no current must flow over this electrode but in practice the instrument needs to apply a minuscule current to sense any potential. To reduce any overpotential induced by the sensing current, the RE should be non-polarisable. The mass transport between RE and WE compartment should be minimized as well. Any changes of the electrode-electrolyte interface on the RE caused by reaction products of the WE would change the RE potential and invalidate the measurement.

$^7$Since in fuel cells, the anode is supplied hydrogen and no reference electrode is used, case 2 is actually valid representation of their potential and current characteristics.
3.2 Electrochemical testing

Special reference electrodes

The standard hydrogen electrode The standard hydrogen electrode (SHE) can be understood more as theoretical electrode, even though experimental versions exist. Its potential is zero in an ideal solution in which the activity of H\(^+\) is unity (and no interactions with any other ions) and the hydrogen pressure is 1 bar. The electrode material is platinum. If not indicated otherwise, potential values are in respect to the SHE.

The normal hydrogen electrode The normal hydrogen electrode (NHE) comes closest to SHE, since it acknowledges that H\(^+\) do interact with other ions. It can be constructed by immersing platinum wires in a strong acid (pH = 0) and bubbling hydrogen gas at atmospheric pressure in water. The potential difference between an SHE and an NHE is minuscule, hence the terms NHE and SHE are often used interchangeable.

The reversible hydrogen electrode The reversible hydrogen electrode (RHE) is a NHE which potential does not change with pH. Thus any water based electrolyte saturated with hydrogen can be used. Its potential in strong acids (pH = 0) is 0 \(V_{\text{NHE}}\) and in strong bases (pH = 14) is -0.826 \(V_{\text{NHE}}\). The RHE is the most common electrode in the ORR catalyst research.

Saturated calomel electrode The saturated calomel electrode (SCE) uses Hg\(_2\)Cl\(_2\) and a saturated solution of KCl in water. Its potential is -0.244 \(V_{\text{NHE}}\). Without getting further into the details: Its main benefit is, compared to the RHE, that it does not require a gas to be present.

Other special reference electrodes are necessary if the electrochemical processes on the working electrode are too fast (A palladium hydride electrode if the HOR/HER kinetics are to be measured) or an electrolyte is used that is not based on water.
3 Techniques

3.2.5 The ORR case

This section develops the specific equations needed for the determination of the Oxygen Reduction Reaction Kinetics and additional corrections due to experimental limits.

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \] (3.14)

Considering the ORR on platinum one sees that only oxygen is mass transport limited, since in an acidic media the depletion and formation of protons and water can be omitted. The limiting current is written as \( i_{\text{lim}} \). The sluggish ORR kinetics give need to apply a large overpotential to get reasonable currents which allow the use of the Tafel-Equation. For these reasons, the model developed in the previous sections can be applied.

The potential on the electrode \( E \) needs to be corrected for (a) the electrolyte and wiring contact resistance between the WE and the RE and (b) for the change of the (equilibrium) potential due to the depletion of oxygen at higher currents. The subscript \( D \) denotes the current measured on the electrode, in RDE terminology also called disk.

(a) The so called iR-Correction is widely used and straightforward to measure with impedance spectroscopy:

\[ \Delta E_\Omega = i_D R_\Omega \]

(b) The Butler-Volmer-Equation applies for the overpotential \( \eta \) as drawn in figure 3.14, but the RE senses the overpotential \( \eta_D \) at the disc for which it has to be correct:

\[ \Delta E_{\text{diff}} = \frac{RT}{4F} \ln \left( 1 - \frac{i}{i_{\text{lim}}} \right) \]

This correction is rarely used in literature, but becomes significant at higher currents and is therefore included in this analysis.

(c) The reference electrode potential is supposed to be constant, but changes
3.2 Electrochemical testing

from its ideal value can not be excluded and have to be encountered by a calibration measurement. The correction is usually done during the experiment but is shown for complicity:

$$\Delta E_{RE} = E_{D, measured} - E_{D, ideal}$$

The corrected potential is:

$$E = E_D - i_D(E_D) \cdot R_{\Omega} - \frac{RT}{4F} \ln \left( 1 - \frac{i(E_D)}{i_{lim}} \right) - \Delta E_{RE} \quad (3.15)$$

Besides the mass transport correction developed in the previous section, the current needs to be corrected for pseudo-capacitive reactions and their resulting currents $i_{psc}$ occurring in parallel to the ORR reaction as well. The source of these currents will be discussed later. When normalising the currents, it has to be incorporated that real surfaces are not ideally flat and two kinds of areas exist. The first is the geometric area, in some cases denoted by an index "geo" at the unit, that is just the projected area parallel to the surface. The second, is the area of the surface on which the actual reactions take place that can consist of steps, terraces and edges arranged at different angles, denoted by "Pt" for platinum at the unit. This area is referred to as electrochemical surface area (ECSA) since it is the actual area at which the chemical reactions occur. Both areas are connected by the roughness factor $r_f$.

Besides $i_{kin}$ and $i_{psc}$ that are normalised to the platinum area, all other quantities are normalised to the projected area.

$$r_f = \frac{A_{Pt}}{A_{geo}} \quad (3.16)$$

In cyclic voltammograms on surfaces that exhibit significant roughness or consist of dispersed nanoparticles on a support, the current density is commonly given per platinum area.

It follows the final corrected current with stoichiometries of $\nu_{O_2} = 1$:

$$i_{kin}(E) = \frac{1}{r_f} \cdot \frac{i_{lim}(i_D(E) - i_{psc}(E))}{i_{lim} - (i_D(E) - i_{psc}(E))} \quad (3.17)$$

Equation 3.26 shows how $i_{lim}$ can be calculated, nevertheless it is straight-
3 Techniques

Figure 3.16: A rough electrode surface: The different current densities are referred to either the platinum or the geometric surface area, as discussed in the text.

forward to read its value from experimental data, which is simply the most negative current that can be drawn after the correction of the pseudocapacitive background.

Comparing catalyst activities

The used equilibrium potential in the Tafel equation can only be determined with great uncertainties. Therefore, \( i_0 \) can not be used for comparing catalytic activities. Benchmark currents at certain potentials are used instead. For low surface area and high active catalysts, literature agrees upon using 0.9 V\(_{\text{RHE}}\). Depending on the purpose, the chosen potential(s) may differ. The Tafel equation can still be used to calculate the Tafel slope \( b \):

\[
\log (|i_{\text{kin}}|) = \log (i_0) + \frac{|E_{eq} - E|}{b} \rightarrow b = \left| \frac{dE}{d \log (|i_{\text{kin}}|)} \right| \tag{3.18}
\]

\[
i_{\text{kin,0.9V}} = i_{\text{kin}}(E = 0.9V) \tag{3.19}
\]

Mass transport and RDE

As the name implies, a rotating disc that serves as the electrode generates a convective flow due to radial forces in the electrolyte. Along the axis of the
3.2 Electrochemical testing

rotator, the electrolyte flow is towards the electrode that subsequently will be
deflected, resulting in a flow along the disc, respectively the electrode surface.

In case of a laminar flow along the surface of the electrode, a constant diffusion boundary layer of the thickness $\delta$ is established. On the electrode surface concentrations and the bulk concentrations of the species are found on the limits of the boundary layer\(^8\). $\delta$ can be directly controlled by the velocity of the electrolyte flow on the surface and consequently by the rotation of the disc:

$$\delta_i = 5 \frac{\sqrt{D_i \nu}}{\sqrt{\omega}} \quad \omega \text{ in [rpm]} \quad (3.20)$$

In the stationary case, the transport towards and from the electrode surface into the bulk solution follows the Nernst-Plack-Equation:

$$\dot{n}_i = -D_i \frac{\partial c_i}{\partial x} - D_i c_i \frac{zF}{RT} \frac{\partial \Psi}{\partial x} \quad (3.21)$$

The contributions of the electric field $\frac{\partial \Psi}{\partial x}$ are omitted leading to Fick’s laws of diffusion:

$$\dot{n}_i = -D_i \frac{\partial c_i}{\partial x} \quad (3.22)$$

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} = 0 \quad \Rightarrow \quad \dot{n}_i = -D_i \frac{\Delta c_i}{\Delta x} \quad (3.23)$$

In case of only one species, $O$, depleting significantly on the electrode, applying Faraday’s law, $\dot{n} = \frac{i}{zF}$ and assuming that the bulk concentration does not change with respect to the equilibrium state, it follows:

$$i = -zF D_i \frac{c_{O,eq} - c_O}{\delta} \quad (3.24)$$

At sufficiently negative overpotentials, the anodic term of equation 3.10 can be omitted, called Tafel simplification, and its combination with equation 3.24 results in the following relation:

\[^8\text{The thickness of the diffusion boundary may vary depending on the nature of the diffusive species.}\]
3 Techniques

\[
\frac{i_D}{i_{\text{kin}}} = \left( 1 + \frac{i}{i_{\text{lim}}} \right)^{\nu_O}
\] (3.25)

\[i_{\text{lim}} = 0.2 c_{O, eq} \sqrt[\frac{1}{5}]{D_i} \sqrt[\frac{1}{2}]{\nu} \sqrt{\omega}
\] (3.26)

\(i_D\) is the observed current on the disc electrode. It is partly controlled by mass transport, whose part is called limiting current \(i_{\text{lim}}\). \(i_{\text{kin}}\) is the pure kinetic part of \(i_D\) and contains all kinetic parameters of the presented reaction:

\[i_{\text{kin}} = -i_0 10^{-\eta/b}
\] (3.27)

The usage of the Tafel slope \(b\) over \(\alpha_O\) and \(z\) is preferred, since both can be uncertain.

**ECSA determination**

In order to access the actual platinum area \(A_{Pt}\) or ECSA, introduced in section 3.2.5, the specific adsorption is particularly useful. If the coverage of a species at a certain point and the area or surface atoms covered by an adsorbate is known, one can extract \(A_{Pt}\) from electrochemical measurements.

This is the case for hydrogen underpotentially depositing on H-upd metals\(^9\). It is well established that for all platinum, low index planes \(\gamma = +1\) at any potential, \(\theta\) can approach unity at sufficient negative potentials and that one hydrogen binds per platinum surface atom. The presented equation calculates \(rf\) if \(Q_{H-\text{upd}}\) is referred to the geometric area, otherwise it calculates \(A_{Pt}\):

\[A_{Pt} \text{ or } rf = \frac{\text{upd hydrogen atoms}}{\rho_{\text{Plane,Pt}} \cdot e}
\] (3.28)

\(Q_{H-\text{upd}}\) denotes the measured absolute/specific charge assigned to H-upd and \(e\) the elementary charge. For Pt(pc) the charge associated to the H-upd is averaged over the three low single crystal planes to \(Q_{H-\text{upd},Pt(pc)} = 210 \mu C/cm^2\):

\(^9\)“Underpotentially” deposition, hence hydrogen is reduced before its reversible reduction potential at 0.0 V\(_{RHE}\)
3.2 Electrochemical testing

\[ A_{Pt} \text{ or } rf = \frac{Q_{H-upd}}{Q_{H-upd, Pt(pc)}} \]  

(3.29)

In figure 3.17, a schematic cyclic voltammogram is shown, used to calculate the ECSA of a Pt(pc) surface. Either the positive scan, the negative scan or both can be used to determine the ECSA. In this work, only the negative scan is used, guaranteeing the independence of the ECSA of the vertex potential\(^{10}\). If the sweep rate is higher than 20 mV/s and it is swept through higher potentials at which oxide is formed, some remain on the surface due to their sluggish dissolution kinetics. This leads to a comparably small underestimation (overestimation of the non-faradaic charging of the EDL) of the ECSA. This can be avoided by setting the upper vertex potential in the double layer region.

Since HER currents and the (uncompleted) hydrogen adsorption overlap, this kind of ECSA determination has to be interpreted carefully, dealt by consistent measurements. Another ECSA determination concept is the CO-displacement method, which is not discussed in this work.

The H-upd charge can be calculated using the following equation, which incorporates that the charge under the current-potential curve consists of two parts: The H-upd charging and the assumed to be constant charging of the non-faradaic part of the EDL, commonly referred to simply as double layer, \(Q_{DL}\):

\[
Q_{H-upd} = \frac{1}{v} \left( \int_{\Delta E} i \, dE - i(E = E_{DL}) \cdot \Delta E \right) = \int_{\Delta E} C \, dE - C(E = E_{DL}) \cdot \Delta E
\]  

(3.30)

3.2.6 Typical experiment protocol

All water used in the measurements is milli-Q water with an ohmic resistance of 18 MΩ

\(^{10}\)The lower the vertex potential is chosen, the more hydrogen will be developed in the negative scan during HER, that remains in the boundary layer of the electrode. This hydrogen will be oxidised in addition to the adsorbed hydrogen in the subsequent positive scan, which results in ECSA values varying with the chosen vertex potential.
3 Techniques

Figure 3.17: Schematic cyclic voltammogram on a polycrystalline surface. The area marked is used in this work to calculate the ECSA. The ideal ECSA determination would make use of the CV in the dotted line. Instead, the CV of the solid line is used. $Q_{DL}$ is displayed as striped area. Using the CV, displayed by the dashed line, explains why the cathodic/negative scan is used, see text.

Electrode preparation

Ink preparation  A small amount of catalyst, typically around 4 mg of the catalyst is dispersed in half the nominal amount in ml of N,N-Dimethylformamide (DMF). Adjusted to the carbon content a 5% solution of Nafion in ethanol is added to achieve an ionomer to carbon ratio of 1.5. The solution is then horn sonicated (30%, 200 W, 1 second pulse, 1 second break, Branson 250) for 1 min of total pulse time.

Film preparation  7 μl of ink is pipetted on an ethanol and water washed on multiple glassy carbon electrodes and left to dry under a 400 ml glass beaker. When the films had been dried, they were examined for film quality and the electrode with the apparent best film was selected for the measurement.
3.2 Electrochemical testing

Cell preparation

A typical three electrode cell setup was used: The cell, its side lit and the platinum counter electrode were kept under water and boiled in fresh milli-Q water before use. 0.1 M HClO₄ as the electrolyte was prepared by mixing 70% with water in a boiled beaker and filled into a PTFE flask only used for this purpose.

Reference Electrode An RHE was prepared fresh before the experiment and calibrating during the measurements. The holder for the reference electrode was filled with the electrolyte together with the reference electrode itself. The electrode was placed in its holder that contained a platinum wire acting as counter and reference electrode for filling the actual reference electrode with hydrogen. The platinum wire in the electrode was connected as the working electrode to the potentiostate (Biologic VSP) and a negative current of -3 V for 10 min was applied to fill the upper half of its inner compartment with electrolytical hydrogen.

Figure 3.18: Pictures of the RDE cell (a) and the reference electrode and its holder (b) used in this work

The three electrode cell setup was filled with electrolyte and the counter and reference electrodes were placed in their respective compartments. The electrode was connected to the Pine MSR rotator placed on top of the three electrode
3 Techniques

cell which then is connected to the potentiostate and the gas line, see figure 3.19.

Figure 3.19: Picture of the RDE set-up.

Protocol

First, the electrolyte in the cell was saturated with 99.999 % pure argon gas and the electrode with the catalyst film was cycled 200 times between 50 mV and 1200 mV at 200 mV/s to clean and activate the surface. Then a CV in the same voltage window was performed at 50 mV/s, the third and last cycle was used as the signature CV and for the background correction in the ORR measurements. While the cell was saturated with 99.99 % pure hydrogen gas, an impedance spectrum was recorded to obtain the high frequency resistance, typically around 21 Ω. Eventually the open circuit voltage (OCV) was recorded to calibrate the reference electrode. Subsequently the electrolyte was discarded, replaced and saturated with 99.999 % pure oxygen gas. Th rotation was set to 1600 rpm and three linear cycles between 1200 mV and 50 mV where collected at 50 mV/s and 20 mV/s respectively. Finally the electrolyte was saturated with hydrogen gas and the OCV was recorded once again, this time with the rotation turned on.
4 Synthesis strategies

The synthesis of platinum rare earth metal alloys is a challenging field as has been briefly discussed already in section 2.6 on page 31. When developing new synthesis routes, often inspired by literature, one has to be aware of all aspects of these challenges. Prior to discussing the synthesis routes that were employed, one must discuss the limitations and conditions in designing the experiments and that governed the thinking process.

4.1 Challenges in the synthesis of platinum rare earth metal alloy nanoparticles

Figure 4.1: Overview of the approximate location of relevant reduction potentials.

4.1.1 Reducing agents

An overview over reduction potentials of different ions in their most common oxidation state is given in figure 4.1. It also shows the location of the reduction potentials of common reducing agents and the lower stability bound of a class of solvents.
The reduction potential is a measure of the stability of the oxidized state with respect to the reduced state. Electrons are always transferred from the components of lower reduction potentials to the component of higher reduction potentials.

The reduction potential of rare earth metals is more negative than -2 V and requires, therefore, rather strong reducing agents in order to transfer the oxidized rare earth metal from their respective component into the metallic state.

Unfortunately, the strong reducing agents necessary and the reduced rare earth metals itself limit the choice of the environment they can be handled to oxygen free and water free environments.

### 4.1.2 Solvents

Solvents whose reduction potentials are higher than that of the reducing agent of the rare earth metal cannot be used. This excludes water, all alcohols, primary and secondary amines and many other organic solvents.

Alkanes, ethers, ternary amines, acetonitrile and other special solvents are stable - they have a wide electrochemical window extending below -3 V<sub>SHE</sub>.

The second factor in choosing the right solvent is their solubility for the necessary components: They need to dissolve or complex the reducing agents, the rare earth metal compound and the platinum salts. However, in certain synthesis routes not all of these compounds need to be dissolved, a dispersion may be sufficient.

### Dissolving rare earth metal salts

In the carried out synthesis routes, the source of the rare earth metal were the respective halogenites: [RE]Cl₃, [RE]Br₃ and [RE]I₃. Relevant solubilities are shown in table 4.1.

The anhydrous forms are known to dissolve very well in many different polar solvents, but always by forming a complex with the respective solvent molecules [62].

When using the rare earth metal in excess, it is not trivial to remove them from the solution before the annealing step since any washing step might cont-
4.1 Challenges in the synthesis of platinum rare earth metal alloy nanoparticles

Table 4.1: List of the solubilities of relevant rare earth metals in water and THF.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Water</th>
<th>THF</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>[g/l]</td>
<td>[g/l]</td>
<td>-</td>
</tr>
<tr>
<td>GdCl₃</td>
<td>soluble</td>
<td>19.1</td>
<td>[32], [58]</td>
</tr>
<tr>
<td>GdBr₃</td>
<td>soluble</td>
<td>3.8</td>
<td>[32], [59]</td>
</tr>
<tr>
<td>GdI₃</td>
<td>soluble</td>
<td>2.7</td>
<td>[32], [60]</td>
</tr>
<tr>
<td>YCl₃</td>
<td>820</td>
<td>9.3</td>
<td>[61], [58]</td>
</tr>
<tr>
<td>YBr₃</td>
<td>833</td>
<td>1.6</td>
<td>[61], [59]</td>
</tr>
<tr>
<td>YI₃</td>
<td>soluble</td>
<td>1.5</td>
<td>[32], [62]</td>
</tr>
<tr>
<td>TbCl₃</td>
<td>soluble</td>
<td>-</td>
<td>[32]</td>
</tr>
<tr>
<td>TbBr₃</td>
<td>soluble</td>
<td>2.9</td>
<td>[32], [59]</td>
</tr>
<tr>
<td>TbI₃</td>
<td>soluble</td>
<td>8.6</td>
<td>[32], [62]</td>
</tr>
</tbody>
</table>

taminate the sample. Upon heating however, the ligands can either evaporate or decompose. The latter might contaminate the surface of the forming alloy nanoparticles. The RE salt ligand interaction appears to be very strong and only for a few cases, e.g. LaCl₃·6H₂O [63] it has been reported that careful and well controlled heating under vacuum can remove the ligands by means of evaporation. In the case of the hydrated RE metal salts the typical result of a heat treatment is the formation of the respective oxyhalogenide (X represents the halides of F, Cl, Br or I):

\[
[\text{RE}]X_{3} \cdot 6\text{H}_2\text{O} \rightarrow [\text{RE}]\text{OX} + 2\text{HX} + 5\text{H}_2\text{O} \tag{4.1}
\]

If other ligands are present, especially when containing carbon-carbon bond such in the case of THF, the ligands will decompose to carbon rather then evaporate at their boiling temperature.

The ligands apparently can be exchanged according to the spectrochemical series [64]. At least in case of YCl₃ dissolved in THF giving YCl₃·3.59THF [58], it could be observed that once stoichiometric amounts of water were added, YCl₃·6H₂O precipitates. The solvent choice appears to be critical towards a successful synthesis of any REM alloys by wet chemistry - moreover it may be the determining factor in deciding if a synthesis attempt is even worthwhile.
4 Synthesis strategies

4.1.3 The ammonia route

The ligand replacement can be made use of by adding an overstoichoimetric amount of ammonium chloride NH₄Cl to the hydrated rare earth metal salt:

\[ [\text{RE}]\text{Cl}_3 \cdot 6\text{H}_2\text{O} + 2\text{NH}_4\text{Cl} \rightarrow (\text{NH}_4)_2[[\text{RE}]\text{Cl}_5] + 6\text{H}_2\text{O} \]  (4.2)

The formed \((\text{NH}_4)_2[[\text{RE}]\text{Cl}_5]\) can then be completely dried and heated to decompose to ammonia, hydrochloric acid and the respective anhydrous rare earth metal chloride [65]. This process, the so called ammonia route, is used to commercially obtain the anhydrous rare earth metal halides.

4.1.4 Difference in reducing potentials

The aim is to synthesize homogeneous platinum rare earth metal alloy nanoparticles on a carbon support: The simultaneous reduction of a platinum salt and the rare earth metal salt in the solvent directly on the support is therefore favored. The difference in reducing potentials of platinum and the rare earth metals suggests however that this may not be possible: Platinum will always be reduced first, even if metallic rare earth metal agglomerates form - they will act as a strong reducing agent towards platinum ions. Formed particles therefore might not be homogeneous and an annealing step is very likely to be necessary to homogenize the particle structure and form the alloy phase.

The necessity of an annealing step introduces a couple of challenges: The precursor needs to be dried and may be cleaned from side products before the annealing. Additionally phase and size distribution will be altered depending on the annealing conditions.

4.1.5 Phase and particle size control

Platinum rare earth metal alloys exist in different phases. The platinum rich phases are desired since they will be more stable towards leaching in the application. This potentially limits the use of an annealing step since the thermodynamically most stable phase might not be the desired phase. Moreover, any
4.1 Challenges in the synthesis of platinum rare earth metal alloy nanoparticles

annealing alters the particle size distribution.

4.1.6 Water and oxygen impurities

As mentioned when discussing reduction potentials, water and oxygen must be avoided in the synthesis process. This extends to the fact that even trace amounts are expected to rapidly oxidize and interfere with the synthesis process. It is therefore required to work in an inert gas atmosphere and limits the necessary washing steps after any wet synthesis prior to an annealing step.

4.1.7 Experimental outline

In the next chapters paths towards an applicable synthesis method of platinum rare earth metal alloy nanoparticles on a carbon are described. Every synthesis technique is based on a combination of literature, experiences from our previous attempts and own ideas.

Consequently, the order of the following chapters represents a try and error process rather than throughout planning. The interpretation and discussion that will be given at each experiment moreover represents our current understanding at this point in time and has to be seen in the context of previous experiments.

- The discussion starts by describing the use liquid ammonia as the solvent. The reducing agent in the form of solvated electrons (sourced from metallic sodium) and platinum and rare earth metal salts can easily be dissolved in liquid ammonia. In addition with the capability to disperse high surface area carbon easily in liquid ammonia it presented a promising synthesis approach towards the formation of the aimed Pt_x[RE]/C catalyst.

- Next up it was attempted to use the liquid eutectic alloy of sodium and potassium (NaK) complexed by crown ether or naphthalene in Tetrahydrofuran (THF) as the reducing agent. Similar to liquid ammonia, THF shows the formation of solvated electrons and has a high solubility of platinum and rare earth metal salts. Carbon can be well dispersed in THF
4 Synthesis strategies

and its high surface area promises the synthesis of small well dispersed nanoparticles.

- Rieke metals were briefly considered as an option to synthesize Pt₃[RE]/C. Rieke metals are finally dispersed metals in polar aprotic solvents.

- Finally the means of potassium vapor to reduce the rare earth metal salt while annealing it together with platinum or a platinum salt on carbon is discussed.

The experiments and measurements in the ammonia chapter was carried out by the bachelor student Thomas Carpenter under my supervision. The work in the subsequent chapters has been conducted by myself.
5 Synthesis using sodium in liquid ammonia as reducing agent

5.1 Introduction

Ammonia (NH$_3$) is pungent smelling gas at ambient conditions but can be liquefied by pressurizing it over 10 bar or cooling it below -35°C. The latter is the common method to obtain liquid ammonia. The high dipole moment of the ammonia molecule allows liquid ammonia to be a versatile solvent, similar to water. Most interestingly, alkali metals (commonly sodium) can be dissolved in liquid ammonia providing sovated free electrons that exhibit a very negative reduction potential [66] [67] [68]:

\[
\text{Na} \xrightarrow{\text{Liquid Ammonia}} \text{Na}^+ + e^-_{\text{ammonia}}
\]  

(5.1)

These solutions appear blue, characteristically for solvated electrons which at higher alkali metal concentrations change to a golden copper color. These solutions are fairly stable, however in the presence of some transition metal ions ammonolysis is greatly accelerated [69] [70]:

\[
\text{Na} + \text{NH}_3 \rightarrow \text{Na}^+\text{NH}_2^- + \frac{1}{2}\text{H}_2
\]

(5.2)

The reduction potential of the solvated electrons depends on the alkali metal that is used in their formation. Calculations indicate that smaller atoms, including the alkaline earth metals lead to stronger reduction potentials of the solvated electrons [71]. To our knowledge it has not been agreed on the exact values. An example of suggested potentials can be found in table 5.1.

It must be noted that the reduction potentials of the alkali metals ammonia
5 Synthesis using sodium in liquid ammonia as reducing agent

Table 5.1: Reduction potentials of various alkali metals in water (calculated [32]) and ammonia (experimental [72]).

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>-3.04 V</td>
<td>-2.64 V</td>
</tr>
<tr>
<td>Na</td>
<td>-2.71 V</td>
<td>-2.38 V</td>
</tr>
<tr>
<td>K</td>
<td>-2.93 V</td>
<td>-2.25 V</td>
</tr>
</tbody>
</table>

solutions are somewhat lower than the respective metals in aqueous solutions.

Liquid ammonia has both an electronic and ionic conductivity together with being rather inert appears to be an excellent choice in the synthesis of nanoparticles of metals with low reduction potentials:

\[
y \text{Na}^+ + y e^-_{\text{ammonia}} + MX_y \rightarrow M^0 + y \text{NaX} \quad MX_y = \text{Metal (M) halide (X)} \quad (5.3)
\]

Zhu et al. managed to synthesize tantalum nanoparticles with a mean diameter of 10 nm [73]. In the same publication the synthesis of intermetallic Nb₃Al nanoparticles was also reported promising that various alloy nanoparticles can be synthesized using liquid ammonia. The synthesis of tungsten [74], bismuth, rhenium [75] nanoparticles in liquid ammonia has been reported as well. However in the case of cobalt and gallium, nitrides (CoN, and GaN) instead of metallic nanoparticles were obtained [75]. Another application of dissolved alkali metals in liquid ammonia is the formation of Zintl phases [76] [77] [78]. This occurs when elements of the fourth main group or higher are used, but it also has been reported for thallium and indium [79]. This illustrates that the formation of metal nanoparticles using liquid ammonia is not as straightforward as one would hope. It has to be considered that instead of the desired metallic (alloy) nanoparticles, the respective nitrides or Zintl phases may form and that the used precursors materials catalyze ammonolysis.
5.2 Concept

The objective of this chapter is utilizing liquid ammonia in the synthesis of platinum alloy nanoparticles. The lanthanide gadolinium and the early transition metals chromium and zirconium were center of this approach. Only the respective metal halide salts were used as precursors. This excludes yttrium from the analysis, since its halides do not dissolve sufficiently well in liquid ammonia.

The general approach was to dissolve the metal halite salt and sodium independently in liquid ammonia and subsequently mixing the two liquids to facilitate the reduction.

5.3 Experimental

5.3.1 Chemicals

Water free ammonia gas was provided by Linde AG, Pullach, Germany. \( \text{PtCl}_2 \), \( \text{K}_2\text{PtCl}_6 \) and anhydrous \( \text{GdI}_3 \), \( \text{CrCl}_3 \), \( \text{ZrCl}_4 \) were supplied by Sigma Aldrich. \( \text{Pt/C} \) 20 % and \( \text{Pt/C} \) 40 % were obtained from Johnson Matthey (HiSPEC 3000 and HiSpec 4000, respectively).

5.3.2 Method

Since any traces of water might spoil the reduction of the rare earth metal salt the handling of the liquid ammonia needs to be carried out in a closed system. The experimental setup of the nanoparticle synthesis was designed to exclude traces of moisture in the reactor, allow a controlled condensation of the ammonia gas to the liquid and include safety measures in case ammonia boils unexpectedly, pressurizing the system which would eventually lead to its rupture. A picture and a sketch of the utilized system can be found in figure 5.1.

The overall procedure was to condense ammonia over sodium to remove any traces of moisture. Then to distill the purified ammonia to other compartments with metal salts and another portion of sodium, respectively. Finally the solutions of metal salts and of sodium are mixed and the metal salts are reduced.
Every experiment started with preparing the two chamber reactor in an inert gas environment (Glove box) by loading it with sodium, carbon black and a Pt salt or platinum on carbon (Pt/C) and rare earth metal or early transition metal salts. The sodium metal and carbon or Pt/C are loaded in compartment 2a and the metal salts are loaded compartment 2b. The two chamber reactor is then connected to the experimental setup and all lines are vacuumed for an hour before supplying the system with liquid ammonia: V2, V4, V5, V7 together with the supply valves Vn, Va and Vv remain closed while V1 and V3 are open.
Subsequently the valve Vv to the vacuum pump is opened.

Liquid ammonia is stored under its vapor pressure of ca. 10 bar, depending on the ambient temperature. When the lines have been sufficiently evacuated, the vacuum valve is closed and the NH$_3$ valve Va opened. The flow is controlled by a needle valve (F). Once the pressure indicator (P) indicates a pressure 0.5 bar above ambient conditions V4 is opened and from now on the washing bottles on the outlet have to be monitored to ensure that the gas is continuously flowing out from the setup.

The ammonia gas is condensed in the sodium washing bottle (1) immersed in a ethanol/dry ice coolant mixture (3) (ca. -70°C) in presence of sodium metal. Any water traces in the ammonia gas stream should solidify and react with the sodium to form solid sodium hydroxide and tolerable hydrogen gas. While the ammonia gas is liquefying in both chambers in the reactor, its flow has to be controlled and adjusted to prevent any formation of negative pressure and thus back flow from the outlet washing bottles (4). In an equilibrium state as much ammonia is condensing as is evaporating.

Now V7 and V5 can be opened and V1 can be closed. V3 remains open and V2 remains closed. Ammonia gas is now flowing through the reactor (V6 is at position b) and the reactor (2) can be immersed in the same ethanol/dry ice coolant mixture (3) as the sodium washing bottle. The ammonia gas started to condense up to a volume of ca. 50 ml in both compartments. Magnetic stirring and violent bubbling from the gas fed through V6 helped dissolving the metal salts in compartment 2a.

Eventually the flow of ammonia gas through the reactor was reversed by first opening V1 and V2 and then closing V3 and V4. The metal salts in ammonia solution was rapidly pressed through V6 into the blue ammonia sodium solution. The excess of solvated electrons facilitates the reduction of the metal salts and the formed nanoparticles are immediately dispersed on the carbon.

Once the reduction has been finished, all valves were opened towards the outlet and the coolant was removed to allow the liquid ammonia to evaporate. Additional argon gas was flushed through the reactor to prevent any back-flow once the ammonia has been boiled off. Eventually a mixture of a fine black and white powders and unreacted sodium was left behind. Except in the case
5 Synthesis using sodium in liquid ammonia as reducing agent

of sample E (details in the next section), left over sodium was neutralized by dropping water or ethanol in the reactor under a strong argon flow. The argon diluted and carried away the forming hydrogen gas and displaced any oxygen to minimize explosion hazards.

The powders were then dispersed in the very high pH liquid by placing the reactor in an ultrasound bath. The liquid was centrifuged off and the samples went under further heat treatment and were acid or water washed. Sample E was not washed and collected from the two chamber reactor in the glove-box. While transferring it to the annealing set-up, air exposure was avoided to a minimum: The samples were placed in an alumina boat inside a tubular furnace connected to an argon flow with a flow a rate of at least 50 ml/min. The aimed temperature was reached by heating the sample by 15 °C/min to the desired temperature and held for 3h. Subsequently the sample was allowed to cool down to room temperature by natural convection. When indicated, the sample was subjected to an acid wash. The characterization of all samples was carried out by using EDS and XRD measurements.

5.4 Results

The precursor and synthesis conditions of the samples discussed in this section can be found in table 5.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal Salt</th>
<th>Pt Source</th>
<th>Pt:Pt</th>
<th>Carbon</th>
<th>Annealing</th>
<th>Acid Wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>110 mg GdI₃</td>
<td>4 mg PtCl₂</td>
<td>1:14</td>
<td>12.5 mg</td>
<td>800 °C</td>
<td>0.1 M H₂SO₄</td>
</tr>
<tr>
<td>B</td>
<td>61 mg CrCl₂</td>
<td>61 mg K₂PtCl₆</td>
<td>1:1</td>
<td>-</td>
<td>800 °C</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>79 mg CrCl₃</td>
<td>79 mg K₂PtCl₆</td>
<td>1:1</td>
<td>-</td>
<td>800 °C</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>31 mg CrCl₂</td>
<td>27 mg K₂PtCl₆</td>
<td>1:3</td>
<td>50 mg</td>
<td>800 °C</td>
<td>3 M H₂SO₄</td>
</tr>
<tr>
<td>E</td>
<td>12 mg CrCl₃</td>
<td>30 mg Pt/C 20 %</td>
<td>1:2.5</td>
<td>-</td>
<td>800 °C</td>
<td>2 M HCl</td>
</tr>
<tr>
<td>F</td>
<td>47 mg ZrCl₄</td>
<td>27 mg K₂PtCl₆</td>
<td>1:3</td>
<td>50 mg</td>
<td>800 °C</td>
<td>2 M H₂SO₄, 0.1 M HF</td>
</tr>
<tr>
<td>G1</td>
<td>13 mg CrCl₃</td>
<td>20 mg Pt/C 40 %</td>
<td>1:3</td>
<td>-</td>
<td>600 °C</td>
<td>-</td>
</tr>
<tr>
<td>G2</td>
<td>13 mg CrCl₃</td>
<td>20 mg Pt/C 40 %</td>
<td>1:3</td>
<td>-</td>
<td>700 °C</td>
<td>0.1 M HF</td>
</tr>
<tr>
<td>G3</td>
<td>13 mg CrCl₃</td>
<td>20 mg Pt/C 40 %</td>
<td>1:2</td>
<td>-</td>
<td>800 °C</td>
<td>-</td>
</tr>
</tbody>
</table>
5.4 Results

5.4.1 Precursor solubility in liquid ammonia

Over the course of the experiments it was observed that the platinum salts were reasonable soluble in contrast to the rare earth metals. Among the gadolinium halides, the respective iodide dissolved better than the bromide and the chloride (in that order). Yttrium and terbium salts were tested regardless of their lower solubilities and the same pattern was observed. While ZrCl$_4$ dissolved easily, CrCl$_3$ was soluble initially but in later experiments only minuscule amounts could be dissolved. CrCl$_2$ exhibited a significant higher solubility in liquid ammonia than CrCl$_3$ but was instantaneously oxidized to CrCl$_3$ by the platinum salt when dissolved together.

Despite increased efforts in working moisture and oxygen free a newly obtained batch of CrCl$_3$ did not dissolve better.

5.4.2 Synthesis of platinum rare earth metal alloys

The synthesis of platinum rare earth metal alloys using liquid ammonia showed to be particularly difficult. Next to their insufficient dissolution in liquid ammonia no apparent reduction was observed.

Using the procedure described in the experimental section, a platinum solution (no carbon support) was brought into contact with an overstoichometric sodium solution: The transparent solutions turned instantaneously dark and a black precipitate formed. A dark black dispersion is a typical indication of metal nanoparticles. Various rare earth metal solutions (YI$_3$, TbI$_3$, GdI$_3$, GdBr$_3$, GdCl$_3$) were mixed with the sodium solution in the same manner: In every case, the transparent solutions became cloudy and a white precipitate could be observed. The bromides and chlorides were not fully dissolved and some undissolved salt was mixed in the white precipitate. The XRD diagrams of the washed samples identified the powders as the respective oxides.

The very high ratio between gadolinium and platinum was chosen to reduce the particle size and increasing the chances of alloying.

In order to analyze the precipitate without a washing step to neutralize the excess sodium a understoichometric sodium solution was prepared. This solution was then mixed with a GdI$_3$ solution and the precipitate collected without
5 Synthesis using sodium in liquid ammonia as reducing agent

Further washing. The dried white powder was analyzed by XRD, but no specific phase could be identified.

In subsequent experiments, GdI$_3$ in great excess was dissolved together with PtCl$_2$ and reduced understoichiometrically to eventually form the respective alloy nanoparticles. A grey dispersion was formed upon mixing.

Figure 5.2: XRD diagram of the simultaneous reduction of platinum and gadolinium. In case of a successful reduction of gadolinium sodium iodide had to be formed and any subsequent oxidization should be revealed by the presence of gadolinium oxide.

In figure 5.2 the result of the simultaneous reduction of platinum and the GdI$_3$ is displayed. The platinum phase has no visible peak shift indicating that no alloy phase was formed. The second phase(s) could not be identified and are the same that have been observed without the presence of platinum.

Interestingly, the formation of Pt$_2$Gd alloy nanoparticles after an annealing treatment was observed when the temperature was at least 800 $^\circ$C, see the XRD diagrams in figure 5.3, sample A. These results were obtained independently
of a washing step and the ratio between GdI$_3$ and the platinum precursor for ratios greater than 10:1.

Figure 5.3: XRD diagram of Pt$_2$Gd alloy nanoparticles after annealing from sample A.

The Rietveld refinement suggested a mean particle diameter of ca 17 nm which is too high for expecting a good catalyst. The experimental conditions were varied in terms of increased Gd:Pt ratio, different platinum sources, such as Pt/C 20% and K$_2$PtCl$_4$ or lower temperatures and annealing times.

K$_2$PtCl$_4$ was chosen as the platinum salt since the platinum anion PtCl$_4^{2-}$ has a lower reduction potential than Pt$^{2+}$, 0.758 V vs 1.118 V. As discussed in 4.1.4, a smaller difference in reduction potentials between the platinum and alloying metal salt enhances the chance of a simultaneous reduction and consequently a formation of an alloy. A low platinum loading was aimed in case of the supported catalysts to reduce particle growth during annealing.

Unfortunately, the particle size did not decrease by any of these measures and the focus was turned to other platinum alloys to be synthesized in liquid
5 Synthesis using sodium in liquid ammonia as reducing agent

ammonia.

5.4.3 Synthesis of platinum early transition metal alloys

In our attempts to synthesize novel platinum alloys apart from the rare earth metals, focus was laid on early transition metals such as chromium and zirconium. Preliminary experiments indicate that both chromium and zirconium chlorides can be reduced in the present setup to nanoparticles by the black dispersions that had been formed. Nevertheless any post treatment in order to neutralize the excess sodium leads to their partial oxidation. When chromium and zirconium were reduced in the presence of platinum salts and analyzed in XRD however, no indication of alloy formation was found: Since Pt, Pt$_3$Cr and Pt$_3$Zr all crystallize in the fcc structure, incorporating chromium and zirconium, even understoichometrically, would result in a peak shift to higher angels. However, no peak shift in XRD was observed.

However, when the washed samples were annealed Pt$_3$Cr and Pt$_3$Zr nanoparticles were formed. In the next section the influence of the precursor stoichoimetry is investigated.

Precursor stoichiometry

During the annealing at 800 °C the XRD diagrams from sample B and C showed complete alloying of the platinum with the chromium forming Pr$_3$Cr. The peaks are rather narrow and amean particle diameter of at least 30 nm was calculated.

The molar ratio of chromium to platinum was significantly increased to about 3 in sample D. The same treatment as for the samples B and C was employed, leading to a reduction of particle diameter to about 9 nm. It is assumed that the Cr$_2$O$_3$ that forms during the neutralization acting as a spacer, preventing the platinum growth to below 10 nm. A further increase of Cr$_2$O$_3$ did however not lead to a further decrease the in particle size. The presence of Cr$_2$O$_3$ is suggested by EDS measurements in which the atomic ratio of Cr:Pt was typically around 2:1 instead of the expected ratio from the alloy composition of 1:3. The atomic ratio of Cr:O was typically around 1:2, suggesting Cr$_2$O$_3$ as the dominant
5.4 Results

present oxide with extra oxygen attributed to the carbon support. Interestingly no chromium oxide phase could be observed in XRD.

After reaching a lower minimum in the particle size, it was switched to commercial Pt/C instead of using a platinum salt and carbon in the synthesis, sample E. The predispersed platinum nanoparticles of around 4 nm in mean diameter allowed the usage of a lower chromium to platinum ratio, which is desirable considering the poor solubility of Pt₃Cr. However, the particle size could not be further decreased than the sample using the in-situ formation of Cr₂O₃ as a spacer.

One sample, sample E, interestingly showed the presence of metallic chromium after the annealing step and before the acid washing, see figure 5.5.
5 Synthesis using sodium in liquid ammonia as reducing agent

After the acid wash, the peaks associated to metallic chromium have vanished together with the peak at $32^\circ$ which could not be identified.

This suggests that sodium in liquid ammonia is indeed capable of reducing chromium chloride to the metallic state. The formed compounds of metallic chromium might be protected by a layer of $\text{Cr}_2\text{O}_3$.

$\text{Pt}_3\text{Zr}$ (sample F) was successfully synthesized in the same manner as $\text{Pt}_3\text{Cr}$, see figure 5.6.
5.4 Results

Effect of annealing temperature

To reduce the particle size, the annealing temperature in the synthesis of Pt$_3$Cr was altered between 600°C and 800°C, samples G1 to G3. The resulting XRD diagrams can be found in figure 5.7.

It is evident that the crystallite size increases with annealing temperature and consequently one favors lower temperatures to obtain a higher specific surface area of the platinum alloy catalyst. However, at temperatures of 700°C platinum does only incompletely alloy with chromium as can be seen by the peak separation at higher angles. At 600°C a small peak shift towards the platinum chromium phase can be observed. At 700°C the XRD diagram matches that of Pt$_3$Cr indicating a complete alloying has been achieved. Interestingly, the peak shift continue at 800°C further than expected for Pr$_3$Cr suggesting the existence of a solid solution where the atomic ratios between platinum and chromium are not fixed. This behavior can be expected from the platinum chromium phase di-
5 Synthesis using sodium in liquid ammonia as reducing agent

Figure 5.7: XRD diagrams regarding the effect of annealing temperature on Pt$_3$Cr.

agram in figure 5.8 which does not show a stoichometric Pt$_3$Cr compound.

**Oxide persistence**

Of each sample EDS measurements were performed to obtain information about the bulk chemical composition. Every sample as hinted earlier showed an excess of chromium or zirconium in comparison to the expected atomic amount from the alloy composition.

It is well known that chromium and zirconium exhibit an extraordinary stability against dissolution, especially after a heat treatment. Any attempts to remove excess chromium and zirconium for that matter by multiple strong acid washes on top of the standard wash by solutions of 1 M H$_2$SO$_4$, 0.1 M HCl and 0.1 M HF failed.

The catalytic activity was tested in RDE of both the Pt$_3$Cr (sample G2) and Pt$_3$Zr (sample F). It was already clear from the cyclic voltammograms that the
5.5 General discussion and conclusion

The ammonia synthesis proved that the platinum alloys of zirconium, chromium and gadolinium despite their low reduction potentials can be synthesized. While chromium and zirconium salt can be reduced by solvated electrons in liquid ammonia, it appears not to be possible for gadolinium. However, a undefined compound formed in the case of gadolinium that in the later annealing step indeed lead to the formation of Pt$_2$Gd alloy nanoparticles. Generally, alloy formation was only observed after an annealing step.

The particle size could somewhat be influenced by oxide formation of zirconium and chromium. A higher content of oxide leads to a lower particle size which can be attributed to the strength of the early transition metal oxides in general and the fine dispersion of the reduced salts during the rapid reduction.

Figure 5.8: The phase diagram of platinum chromium [80] and zirconium [81] binary alloys.

surface was blocked since little to no H-upd could be detected and the measurements were discontinued.
6 Synthesis using sodium potassium alloy in THF as reducing agent

The alkali metals are among the strongest reduction agents known. It would be desired to bring them in close contact to dissolved ions of rare earth metal salts and platinum to facilitate their reduction and eventually forming alloy nanoparticles.

As discussed in the previous chapter in the case of ammonia it is possible to transfer the electron of the alkali metals to the solvent and obtain a solvated electron as one of the strongest reducing agents known. If the solvent is not capable of stabilizing the alkali metal cation together with the solvated electron, compatible complexing agents can be used to obtain solvated electrons similarly to these in ammonia.

The solvent used in the synthesis has to be sufficiently inert against reduction by the alkali metal and dissolve the alkali metal complex and metal precursors to an acceptable extend. Ethers as a solvent class fulfill these requirements well, such as diethylether, dioxane and tetrahydrofuran (THF). Due to their relatively high dipole momenta in comparison to other organic solvents, they can dissolve many inorganic salts and provides a water free environment at the same time. Therefore ethers are the chosen solvent in many organometallic synthesis applications, most famous is the Grignard-Reaction.

THF is especially suited due to its higher boiling points than other ethers and the procedures to dry it sufficiently are well established.

The eutectic alloy of potassium, (80 atom-%), and sodium, (80 atom-%), has been chosen as the source of alkali metals. Since this alloy is liquid at room
6 Synthesis using sodium potassium alloy in THF as reducing agent

Temperature, see figure 6.1, it is much easier to handle than the respective solids and maintains a metallic surface since any oxides that may form cannot form a stable surface layer.

![Phase Diagram](image)

Figure 6.1: The binary phase diagram of the sodium potassium system, adapted from [82]. The eutectic point sits at 67 at. % (ca. 80 mass %) potassium and a mixture of sodium and potassium metals (NaK) of this composition will be liquid at room temperature.

6.1 Crown ether as complexing agent

Crown ethers are ring structures that contain periodical ether groups hence their name, see figure 6.2. The ring structure creates a pocket in which depending on its size only certain ions fit comfortably. The ether groups point inwards to the center of the ring, thus stabilizing electrophilic species within the pocket by donating electron density from the oxygen atoms. Due to their ether groups these components dissolve well in a range of organic solvents including THF.

Generally, crown ethers follow a notion of X-Crown-Y-Ether in which X represents the number of atoms that form the ring and Y is the number of ether groups.
6.2 Naphthalene as complexing agent

15-Crown-5 and 18-Crown-6 are known to be selective for Na\(^+\) and K\(^+\) ions, respectively. Hence it was suggested to utilize them to form so called alkalides [83]: Species that contain alkaline metals (sodium or potassium) in the form of K\(^+[15\text{-Crown-5}]_{2}\)Na\(^-\) [84]. It has to be noted that the exact structure of these alkalides and especially the charge distribution of the alkali metals has yet to be understood. However, it is evident that the reduction strength of the metallic alkali metals is maintained to a great degree, which makes it possible to use them in the reduction of rare earth metal cations to their metallic state in solution of THF.

It is possible to isolate the alkalides from the THF solution, however it is advisable to prepare them fresh.

6.2 Naphthalene as complexing agent

Naphthalene reacts with metallic alkali metals to form the corresponding alkali metal naphthalenide, see figure 6.3. In a similar manner as for the preparation of alkalides by crown ethers, the alkali metal (commonly lithium, sodium or potassium) is stirred in an inert solvent such as ethers or alkanes.

Figure 6.3: The structure of sodium naphthalenide.
6 Synthesis using sodium potassium alloy in THF as reducing agent

The resulting liquid is of dark, blue-green color and is supposed to have a similar reduction power as in the case of NaK complexed by 15-Crown-5 and can be used interchangeable.

6.3 General experimental procedures

6.3.1 Preparation of ultra dry THF

The reduction of rare earth metals is very sensitive towards oxidation. Therefore it is believed that the absence of water and oxygen in THF is the key of a successful synthesis. Common procedures are drying THF over molecular sieves with a right average pore diameter for water absorption (< 6 Å) and a subsequent distillation step. THF is stirred over the molecular sieves until an indicator shows the absence of water up to a certain level.

The synthesis attempt discussed in this section is entirely carried out under an inert atmosphere and most work was performed in an argon filled glove box. The transfer of THF into the glove box adds additional sources of contamination. Consequently, it was decided to add another drying step inside the glove box before the distillation: THF was predried over a molecular sieve and then pumped into the glove box by a pressure differential. The second drying step and the distillation are then performed inside the glove box in the apparatus shown in figure 6.4.

The scheme in figure 6.5 shows the different components of the apparatus. Initially all valves V1 to V5 are closed. The 500 ml drying flask is filled with a stirring bar and about 3 ml NaK. V1 is opened and the flask is set under vacuum for 15 minutes before V2 is opened. The pressure differential rapidly sucks predried THF from a storage flask outside of the glovebox into the drying flask. When the flask is half filled first V1 is closed and when the lines attached to V2 are emptied, V2 is closed. The stirring is turned on leading to the dispersion of the NaK alloy into smaller bubbles floating around the flask.

It was observed that it took 24 h to 48 h before the color of the THF turned from colorless to pale blue, indicating complete absence of water, oxygen and other oxidizing species. No indicator was added to the THF and that water free
6.3 General experimental procedures

Figure 6.4: THF in the drying flask after an extended amount of time stirred together with liquid NaK alloy, noticeable by silver bubbles on the right picture. The blue color is an indicator of the absence of any moisture, oxygen and other oxidants in the solvent.

Figure 6.5: Sketch of the THF drying, distillation and dispensing equipment. A detailed description of its function can be found in the text.

THF is able to solvate sodium and/or potassium in a similar manner as ammonia to form similar species as the solvated free electrons as suggested by the blue color. This phenomenon has been reported before and the concentra-
6 Synthesis using sodium potassium alloy in THF as reducing agent

tion of dissolved potassium to be around 0.1 mmol/l [85] [86].

The final dried THF was always distilled right before its usage. Ethanol as the coolant outside of the glovebox is cooled down to -70°C using an ethanol/dry ice coolant mixture and refluxed through the jacket of the distillation flask. The ethanol from the coolant mixture could not be used directly due to the dissolution of CO₂ and its release in the jacket distillation flask thus hindering heat transfer.

V3 and V4 are opened and the vacuum distillation is started. The distillation is stopped once a sufficient amount of THF is collected in the distillation flask or the rate of evaporation of the THF in the drying flask has been declined to a minimum due to the cooling effect of evaporating THF. V3 and V4 are closed and the connection between V3 and the distillation flask is carefully opened to equalize the pressure with the glove box interior and closed again.

A flask or another container used for the synthesis is placed underneath V5 and the valve is opened to drain the desired amount of ultra dry THF. The THF was used for two different synthesis attempts which will be discussed in the following sections.

6.3.2 Reducing agents

15-Crown-5 was dissolved in a sufficient amount of THF in a THF rinsed glass flask. A stoichiometric in respect to the crown ether amount of NaK is added under vigorous stirring 0.5 ml 15-Crown-5 ether. The crown ether was kept in slight excess to ensure that all NaK was complexed and the exact reducing power of the solution was known. A solution of increased viscosity with a dark blue color was obtained, proving the presence of solvated electrons. Since solvated electrons are only stable in the absence of reducible compounds, especially water and oxygen, the THF is completely dry.

Dissolved alkali metal naphthaleneide was prepared by dissolving an over-stoichiometric amount of naphthalene in THF or toluene together with NaK.
6.3.3 Annealing and acid wash

The annealing procedure started by loading the sample into an alumina boat that was placed in quartz tube seated in a tubular furnace. The tube was flushed with 5% H\textsubscript{2}/Ar with a minimum flow rate of 50 ml/min. The temperature was raised by 15°C/min until the desired temperature was reached and held there for a standard time of 6 h until the sample was allowed to cool down to room temperature.

The sample was then dispersed in 0.1 M H\textsubscript{2}SO\textsubscript{4} and ultrasonicated for 10 min before the liquid phase was centrifuged and discarded. Two washing steps using distilled water followed before the sample was air dried at 110°C in an oven.

6.3.4 Chemicals

Anhydrous GdCl\textsubscript{3}, Pt(acac\textsubscript{2}), sodium and potassium (chunks and cubes in mineral oil), anhydrous toluene and anhydrous heptane were supplied by Sigma Aldrich. THF was sourced predried in-house and commercial Pt/C 40% (HiSPEC 4000) was obtained from Johnson Matthey.

6.4 Synthesis

Multiple routes of combining the reducing agent (Complexed NaK), carbon and the platinum salt or Pt/C and the rare earth metal salt are possible. The investigated paths are schematically displayed in figure 6.6. All experimental work in the coming sections have been performed in an argon filled glovebox that was only left for accessing the centrifuge (without opening the centrifuge tube) and transferring the samples into to the annealing setup.
6 Synthesis using sodium potassium alloy in THF as reducing agent

Figure 6.6: Scheme of different synthesis routes which were carried out and are discussed in this section.

6.4.1 Verification of the reduction of rare earth metal salts by NaK complexed in THF

First it has to be verified that the proposed synthesis route can indeed lead to the reduction from the rare earth metal salts to metallic nanoparticles. Gadolinium was chosen as the rare earth metal that would be investigated for several reasons: (i) [41] shows that Pt₅Gd is one of the most ORR active platinum alloy material and also had been produced, characterized and tested in nanoparticle form using a nanocluster source [47]; (ii) the chloride salt of gadolinium is the most soluble salt of any rare earth metal in THF, see table 4.1; (iii) metallic gadolinium nanoparticles are claimed to have been synthesized before.

200 mg GdCl₃ (0.76 mmol) were dissolved in 30 ml of freshly distilled THF from an ultra-pure batch. Subsequently, 2 ml (10 mmol) 15-Crown-5 and 200 mg of NaK (5.13 mmol) are mixed in 10 ml THF under vigorous stirring forming a dark blue solution. Once all metallic NaK droplets have disappeared the solution of GdCl₃ is added dropwise under stirring. The clear dark blue solution quickly became a dark brown dispersion, indicating the formation of both metallic gadolinium and insoluble potassium chloride, see equations 6.1 and
6.4 Synthesis

6.2.

\[
\begin{align*}
\text{Gd}^{3+} + 3e^- & \rightarrow \text{Gd}^0 \downarrow \quad (6.1) \\
\text{Cl}^- + \text{K}^+ & \rightarrow \text{KCl} \downarrow \quad (6.2)
\end{align*}
\]

After letting it stir for 30 min the mixture was filled into a THF-washed centrifuge tube, sealed and transferred out of the glovebox to a centrifuge. The solid fraction separated from the liquid fraction under 9000 rpm for 10 min and the sealed centrifuge tube was transferred back to the glovebox. The liquid fraction was disposed and fresh distilled THF was added. This procedure was repeated two more times until the liquid fraction did not show a blue color anymore and the solid fraction was vacuum dried.

The solid fraction was taken out of the glove box. One part was brought into contact with water and ignited, suggesting that either metallic sodium, potassium or gadolinium was present in the powder. The XRD diagrams of the other part of the sample showed the presence of sodium chloride, potassium chloride and gadolinium oxide.

The same experiment was repeated with Gd$_2$O$_3$ instead of GdCl$_3$ and neither any ignition when contacted with water or any other XRD feature of sodium chloride or potassium chloride could be observed verifying that the present method can indeed reduce GdCl$_3$. The formed metallic Gd nanoparticles are presumably just too reactive to be analyzed further and can therefore only indirectly confirmed.

The procedure was repeated with naphthalene as a reducing agent, by replacing 2 ml (10 mmol) 15-Crown-5 for 1.5 g naphthalene (11.7 mmol). The experimental procedure remained and the same results were obtained. A minor difference is the formation of a dark green solution in contrast to the deep blue solution obtained when using 15-Crown-5 ether.
Simultaneous reduction (A)

Concept

The most straightforward synthesis route is the simultaneous reduction of platinum and the rare earth metal salt. The simultaneous reduction of the metal salts can either lead to nanoparticles consisting of both of platinum and rare earth metal or nanoparticles only consisting of either platinum or the rare earth metal. Due to the difference in reduction potentials between platinum and the rare earth elements of more than 3 V the latter is more likely: Any formed metallic rare earth species will act as a reducing agent of present platinum ions until they are depleted.

The carbon support material was present in the beginning (Route A1) or was added after the reduction of the metal salts to nanoparticles (Route A2). In principle it is desired to reduce the metals while the carbon support is present to avoid agglomeration and increase the interactions of the nanoparticles and the support [87], see the scheme in figure 6.7.

![Figure 6.7: Synthesis route A, carbon support added with the reducing agent. Either homogeneous Pt₆, Gd nanoparticles or nanoparticles both of platinum and gadolinium form.](image)

Figure 6.8 shows the synthesis scheme if the carbon is added after the nanoparticles have been formed. This procedure might lead to agglomerates of platinum and rare earth metal nanoparticles in contrast to a homogeneous distribution. The agglomeration of nanoparticles of different kind may enhance the chances of alloying in the annealing step due to a greater proximity of platinum and the rare earth metal nanoparticles. However, no difference in the results have been observed. Therefore the description and discussion focuses on adding the carbon prior to the reduction of the metal salts.
6.4 Synthesis

Figure 6.8: Synthesis route A, carbon support added after the formation of Gd\textsuperscript{0} nanoparticles. Either homogeneous Pt\textsubscript{x}Gd nanoparticles or nanoparticles both of platinum and gadolinium form.

**Procedure**

A typical experiment started with dissolving 200 mg GdCl\textsubscript{3} (0.76 mmol) and 100 mg Pt(acac)\textsubscript{2} (0.25 mmol) in 30 ml THF. 75 mg of vacuum dried Vulcan XC-72R carbon is stirred together with 2 ml (10 mmol) 15-Crown-5 and 200 mg of NaK (5.13 mmol) in 10 ml THF until all NaK alloy has vanished and a black-bluish dispersion has been obtained. The platinum gadolinium solution is added drop-wisely to the vigorously stirred reducing carbon dispersion. The dispersion was then transferred into centrifuge tubes, centrifuged and the liquid, blue colored solution discarded, the solid washed with fresh THF and centrifuged a second time.

After the powder had been vacuum dried, it was split into two parts. Part one was analyzed by XRD and subsequently acid washed by 0.1 M sulfuric acid, rinsed with an excess of distilled water, air dried at 110° and also analyzed by XRD. Part two is annealed in a quartz tube in a tube furnace at 800 °C before
6 Synthesis using sodium potassium alloy in THF as reducing agent

the same acid washing protocol as for part one is followed). The obtained XRD diagrams are presented in figure 6.9.

Results

Figure 6.9: The XRD results of the experimental route A1. From bottom to top: As synthesized, acid washed, annealed and annealed plus acid washed.

It can be concluded that only Pt nanoparticles and Gd$_2$O$_3$ but no Pt$_x$Gd
nanoparticles have been formed prior to the annealing step. Moreover, the acid wash also seemed to have reduced the amount of Pt nanoparticles, indicating that a significant amount of Pt nanoparticles were supported on the Gd$_2$O$_3$ instead of the carbon. When the Gd$_2$O$_3$ was dissolved in the acid washing step, they seem to be mobilized as well and washed out.

The annealing step, however, leads to the partial formation of Pt$_x$Gd nanoparticles where $x$ can be assumed to be 2, even though the XRD feature of Pt$_2$Gd are shifted. A pure platinum peak can be excluded since its dominant peaks at 46° and 67° are not visible or greatly reduced. This alloy phase is unstable against acids and its contribution is significantly reduced after the acid wash. The majority of nanoparticles apparently consists of platinum.

The particle size is rather large of about 30 nm based on the Scherrer equation of the largest peaks at around 40°. EDS measurements confirmed the presence of gadolinium in all samples except the not annealed, acid washed sample.

**Discussion**

The results show that the simultaneous reduction of platinum and gadolinium in THF does not directly lead to homogeneous nanoparticles. One reason can be the large difference between the reduction potentials of more than 3 V. Any cluster of metallic gadolinium would act as a reducing agent in respect to the platinum ions until all platinum has been reduced to metal nanoparticles. Eventually, gadolinium gets reduced but precipitates on the surface of the platinum or on the carbon unprotected from oxidation in the following steps.

**6.4.2 Core shell reduction (B)**

**Concept**

Using a concept similarly to the one applied by [84] the synthesis routes B1 and B2 aim to produce core shell particles where the gadolinium core is protected by a platinum overlayer. In the synthesis route B1, see figure 6.10, the platinum

---

1 Using the Scherrer equation at a peak that is merged with another peak is inaccurate. However, the peak is narrow enough to conclude that particle size is outside of the desired range.
6 Synthesis using sodium potassium alloy in THF as reducing agent

shell is formed by the reduction of platinum in solution by surface gadolinium atoms of the prior formed nanoparticles, see equation 6.3. In a second step the remaining dissolved gadolinium is reduced by solvated electrons.

$$2\text{Gd}^0 + 3\text{Pt}^{2+} \rightarrow 2\text{Gd}^{3+} + 3\text{Pt}^0$$  \hspace{1cm} (6.3)

Figure 6.10: Synthesis route B1; Gadolinium is reduced by a mixture of the reducing agent is with the carbon support. In a second step platinum is reduced by the surface Gd atoms and finally, remaining Pt and Gd are reduced by adding the rest of the reducing agent.

The same result, gadolinium core and platinum shell nanoparticles, is aimed by route B2: Here, the reduction occurs step-wise: First, gadolinium nanoparticles are formed and secondly platinum is reduced on the gadolinium particles that act as crystallization seeds. Both reduction would be facilitated by solvated electrons in contrast to route B1.

Figure 6.11: Synthesis route B2; Same as synthesis route B1 except that the carbon is added in the final step with the reducing agent.

Procedure

Synthesis route B1  In synthesis route B1, 200 mg GdCl$_3$ (0.76 mmol) were dissolved in 20 ml THF (flask 1) and in another flask (flask 2) 200 mg Pt(acac)$_2$ (0.51 mmol were dissolved in 10 ml THF. The reducing solution was prepared by
6.4 Synthesis

mixing 2 ml (10 mmol) 15-Crown-5 and 200 mg of NaK (5.13 mmol) in 10 ml THF (flask 3). 150 mg vacuum dried carbon 5 ml from the reducing solution in flask 3 and then dropwise added to the gadolinium solution in flask 1 under vigorous stirring. Then the platinum solution was added to flask 1. After waiting for 5 min, the rest of the reducing solution from flask 3 was added to flask 1.

**Synthesis route B2**  The original concept described in reference [84] was used in synthesis route B2: 20 mg GdCl₃ (0.076 mmol were dissolved in 20 ml THF (flask 1) and in another flask (flask 2) 140 mg Pt(acac)₂ (0.36 mmol were dissolved in 10 ml THF. The reducing solution was prepared by mixing 2 ml (10 mmol) 15-Crown-5 and 200 mg of NaK (5.13 mmol) in 10 ml THF (flask 3). The gadolinium solution from flask 1 was then added dropwise to the reducing solution in flask 3 under vigorous stirring. Subsequently the platinum solution from flask 2 was added in the same manner to flask 3.

Both synthesis routes finished by the dispersion being centrifuged, the solid part washed with THF and centrifuged a second time and then vacuum dried. Finally all samples were annealed for 3 h at 600°C, acid washed (except one sample, see the results) and eventually analyzed by XRD and EDS. Moreover, the synthesis route B2 was varied by using carbon that has been additionally reduced (removing adsorbed water and reducing oxygen containing surface groups) instead of just vacuum dried. This was done by mixing the carbon in a crown ether, NaK and THF solution and eventually centrifuging and drying it. Another sample was washed by dried heptane instead of THF. A third synthesis alteration was reducing loading to effectively 10 % from 40 % Pt/C by using 900 mg of carbon. The final alteration was using 150 mg Gd₂O₃ as a support material instead of carbon.

Samples synthesized using the reduced carbon were subjected to different annealing treatments. The temperatures were decreased to 500°C and 550°C at 3 h and the annealing time was decreased to 30 min at 600°C.
6 Synthesis using sodium potassium alloy in THF as reducing agent

Results

The resulting XRD diagrams of annealed samples can be found in figure 6.12, all after an acid wash, except in case of the reduced carbon. The samples using the reduced carbon showed the formation of Pt$_x$Gd, presumably Pt$_2$Gd, similar to the simultaneous reduction route. Samples prepared by only vacuum dried carbon or the heptane wash both showed alloying but somewhat greater crystallite sizes. Changing the annealing conditions only let to incomplete alloying and interestingly no detectable crystallite size change in XRD.

When the carbon content was increased in case for the reduced loading sample or when Gd$_2$O$_3$ was used as a support material, a very minor or no allowing occurred.

Unannealed samples only showed platinum and no signs of alloying and are therefore not further discussed.

EDS was obtained from all but the Gd$_2$O$_3$ sample. A ratio between Pt:Gd of about 2 to 1 was found consistently.

Discussion

The different outcome may be explained by different moisture levels during the synthesis route. Not dried high surface area carbon contains about 2% water that might not completely be removed by only vacuum drying. The dry heptane was used without any purification and might also lead to some introduction of moisture. Increasing the carbon content might introduced enough moisture to fully oxidize the gadolinium nanoparticles after their formation.

The results indicate that the a complete protection of the gadolinium core was not achieved, the findings moreover resemble the results found for the homogeneous reduction of Pt and Gd discussed previously. The EDS spectra suggest that non-alloyed gadolinium was not removed by the acid washing or that alloy phases with a greater Gd content were formed. However, not much attention was paid on getting deeper insights into this phenomenon.

In conclusion, using the core shell approach a complete alloying of platinum and gadolinium to form Pt$_2$Gd was achieved, but the particle size could not be reduced.
6.4 Synthesis

6.4.3 Deposition on Pt/C (C)

In the previous experiments it became evident that Pt-Gd alloy nanoparticles can be synthesized by the reduction of GdCl$_3$ in THF and a subsequent annealing step. However, the particle size could not be decreased by changes of experimental parameters so far.
6 Synthesis using sodium potassium alloy in THF as reducing agent

Concept

Agglomeration during the synthesis of the nanoparticles prior to their deposition and dispersion on the high surface area carbon could be the cause of the unacceptable particle size. Therefore, in-situ produced Pt nanoparticles or commercial Pt/C on carbon are chosen as a starting material. Gadolinium nanoparticles would be synthesized in close vicinity to them in the hope that an annealing step will result to well dispersed, small Pt$_x$Gd nanoparticles dispersed on carbon. All three synthesis routes would end with an annealing step.

Three different synthesis routes are investigated:

Synthesis of platinum on carbon and subsequent deposition of gadolinium nanoparticles (C1) In this route, platinum nanoparticles are first synthesized by the reduction of platinum in solution with carbon and the reducing agent in great excess. Subsequently, the gadolinium salt is added and reduced on to the just formed Pt/C, see figure 6.13.

![Figure 6.13: Scheme of the synthesis of platinum on carbon and subsequent deposition of gadolinium nanoparticles (C1).](image)

Deposition of gadolinium nanoparticles on commercial Pt/C (C2) In synthesis route C2 the reducing agent in great excess is mixed with commercial Pt/C, removing residual moisture. Subsequently the gadolinium solution is added to reduce and deposit gadolinium nanoparticles on the carbon in close proximity to well dispersed platinum nanoparticles as displayed in figure 6.14.

Formation of gadolinium nanoparticles in solution and their subsequent deposition on commercial Pt/C (C3) Another route is to synthesize the gadolinium nanoparticles first in solution and later add commercial Pt/C.
6.4 Synthesis

Figure 6.14: Scheme of the deposition of gadolinium nanoparticles on commercial Pt/C (C2).

Ideally the Gd nanoparticles would deposit next to the Pt nanoparticles on carbon, see figure 6.15.

Figure 6.15: Scheme of the formation of gadolinium nanoparticles in solution and their subsequent deposition on commercial Pt/C (C3).

Procedure

**Synthesis route C1** 100 mg Pt(acac)$_2$ 0.25 mmol were dissolved in 10 ml of THF (flask 1) and 100 mg GdCl$_3$ in 30 ml THF (flask 2). 75 mg dried carbon together with 2 ml 15-Crown-5 and 200 mg NaK (5.13 mmol) were mixed in 10 ml THF and the content of flask 1 slowly added. Subsequently the content of flask 2 was added in the same manner.

**Synthesis route C2** 200 mg GdCl$_3$ were dissolved in 30 ml THF. 50 mg of Pt/C 40 % together with 2 ml 15-Crown-5 and 200 mg NaK (5.13 mmol) were mixed in 10 ml THF and the gadolinium solution dropwise added.
Synthesis using sodium potassium alloy in THF as reducing agent

**Synthesis route C3** 200 mg GdCl$_3$ were dissolved in 30 ml THF and then added dropwise to a solution of 2 ml 15-Crown-5 and 200 mg NaK (5.13 mmol) in 10 ml THF. Subsequently 50 mg of Pt/C were dispersed in the solution. All synthesis routes were continued by removing the liquid phase by centrifugation with one THF wash step in between. Finally the solid was vacuum dried and then annealed at 600 °C for 3 h, acid washed and dried.

**Results**

Figure 6.16: XRD diagrams of samples from the synthesis routes C1, C2 and C3.

When the platinum and gadolinium nanoparticles were synthesized sequentially (C1) no alloying during annealing could be observed. However, if the
Gd nanoparticles were formed in the presence of commercial Pt/C (C2) Pt$_2$Gd was formed - but with no reduction in particle size. When the Pt/C powder was added after the formation of Gd nanoparticles (C3) a very broad signal of Pt$_2$Gd or Pt in XRD is observed, suggesting very small crystallites (< 2 nm).

**Discussion**

It appears that the rather fast reduction of platinum by the solvated electrons does not lead to well dispersed nanoparticles, as examined by TEM. The synthesized Gd nanoparticles do not seem to be in close vicinity, so neither protecting the Pt particles from growth nor alloying with the Pt particles.

The best results were obtained when using route C2. The Gd nanoparticles alloyed well with well dispersed Pt nanoparticles from the commercial Pt/C sample. The sample from C3 shows a phenomenon that will further discussed in 7.

### 6.4.4 Optimized deposition of gadolinium nanoparticles on commercial Pt/C

So far, synthesis route C2 gave the best and consistent results. Since different annealing protocols did not lead to significant reductions of the particle size, other changes to the synthesis protocol were attempted.

**Concepts**

**Filling the annealing tube inside the glovebox** A quartz tube was manufactured that can be taken inside the glovebox, filled with the sample and sealed by closing the inlet and outlet valved prior taking it out of the glovebox. At the annealing setup, the connecting lines would be evacuated before the annealing tube is flushed with argon gas. All samples from that point onward would use the air-free transfer to the annealing setup.

**Sodium/potassium naphthalenide as a reducing agent** Naphthalene can replace the crown ether to allow sodium and potassium to act as reducing
6 Synthesis using sodium potassium alloy in THF as reducing agent

agents.

**Toluene and triethylamine**  It was observed in some instances, that despite the centrifuge steps, not all Gd nanoparticles could be deposited on the carbon support and remained in solution. In order to decrease their stability in solution a mixture between toluene and THF is used instead of pure THF. Another extreme is the usage of the polar solvent triethylamine (TEA) instead of THF. This solvent might need to stabilize the Gd NPs stronger than THF and lead to less agglomeration. However, more Gd might be lost in the centrifugation step.

**Experimental**

**Filling the annealing tube inside the glovebox**  A quartz tube was manufactured that can be taken inside the glovebox, filled with the sample and sealed by closing the inlet and outlet valved prior taking it out of the glovebox. At the annealing setup, the connecting lines would be evacuated before the annealing tube is flushed with argon gas. All samples from that point onward would use the air-free transfer to the annealing setup.

**Sodium/potassium naphthalenide as a reducing agent**  The experimental procedure is the same as for the synthesis route C2, except that 2 ml crown ether were replaced by 0.4 g naphthalene.

**Toluene**  100 mg GdCl$_3$ (0.38 mmol) were dissolved in 20 ml THF. 25 mg of Pt/C 40% together with 0.4 g naphthalene (3.1 mmol) and 100 mg NaK (2.6 mmol) were mixed in 5 ml THF and 25 ml toluene and the gadolinium solution was added dropwise.

**Triethylamine**  100 mg GdCl$_3$ (0.38 mmol) were dissolved in 20 ml TEA. 25 mg of Pt/C 40% together with 0.4 g ((3.1 mmol) naphthalene and 100 mg NaK (2.6 mmol) were mixed in 10 ml TEA and the gadolinium solution was added dropwise.

All samples were then, as in C2, centrifuged, dried and annealed at 600 °C.
Results

The XRD diagrams of the three responding samples can be found in figure 6.17.

![XRD diagrams](image)

Figure 6.17: XRD diagrams of samples synthesized by using THF, THF/Toluene and TEA as the solvent using the procedure C2.

The extend of alloying follows THF > TEA > Toluene/THF. The THF sample showed complete alloying and the smallest crystallite size.

Discussion

The use of THF still resulted in the best outcome in terms of crystallite size and agglomeration. The switch from the crown ether to naphthalene and the use of
6 Synthesis using sodium potassium alloy in THF as reducing agent

the air-free transfer to the annealing chamber seem to have positive effects as well.

6.4.5 Effect of annealing temperature on the THF/naphthalene/air-free transfer samples

Experimental

Another sample was prepared in the same manner as in the previous section. The effect of the annealing procedure using different temperatures was tested at 500 °C, 600 °C and 700 °C with the same dwell time of 3 h.

Results

The optimum temperature appears to be 600 °C where the platinum rich Pt-Gd alloy phase is formed. As discussed in section 2.6 on page 31, the platinum rich phases are desired due to stability reasons. Consequently the ORR activity was tested for that catalyst using the RDE technique, following outlined in section 3.2.6 on page 67. Due to the large particle size however, the ORR mass activity was minuscule and the small H-upd area compared to the background carbon signal did not allow a sensible evaluation of the ECSA to even obtain the specific ORR activity.

Discussion

Interestingly, the underpotentially deposition of hydrogen (H-upd) is entirely suppressed. The ORR activity is also lower than from the commercial catalyst which was used as the starting material. The same observation was made for other synthesized catalysts and the H-upd also could not recovered after cycling in a window of 50 mV to 1200 mV for 2000 cycles at 200 mV/s.

A TGA measurement revealed, see figure 6.19 that the carbon content in the samples increased after annealing. It was therefore concluded that carbon must have formed a layer on the Pt-alloy nanoparticles during annealing. This layer then prevents mass transport to the surface and interacts with the active sites.
6.4 Synthesis

Figure 6.18: XRD diagrams of samples annealed at different temperatures.

to suppress the formation of H-upd and greatly reducing the ORR activity. The origins of this extra carbon lie very likely in the way rare earth metal halides dissolve in solvents, by a complex with the solvent molecules as ligands rather than dissolve directly. One can argue that these components are in fact insoluble but there respective solvent complex. It was seen that a sample of anhydrous GdCl$_3$ after being dissolved in THF, centrifuged and vacuum dried, doubled in mass corresponding to 3 mol-2.5 mol THF ligands per mol of GdCl$_3$, which is agreement with literature (GdCl$_3$ · 2.07 THF) [58].

The THF ligands decompose to carbon rather than evaporating during annealing - leading to the proposed a carbon overlayer on the metal nanoparticles. It is expected that this is also a problem for the complexing agents 15-Crown-
6 Synthesis using sodium potassium alloy in THF as reducing agent

Figure 6.19: TGA diagram of sample annealed at 600 °C. The initial mass drop originates from the evaporation of adsorbed water, thus setting an effective 100 % mass level. Two plateaus are visible, both indicating that the metal content is lower than that of the precursor material. Why two plateaus are visible is not further discussed.

5 ether and Naphthalene, consequently greatly reducing the prospects of any approach using any of these chemicals.

6.4.6 General observations and interpretation

The data presented in the previous sections is highly selective. Many experiments despite great efforts to maintain constant conditions varied in the observations during the experiments and their outcome:

1. While adding the metal salts to the over stoichiometric (> 2) reducing agent the blue color should not vanish. In many instances it did. However, during washing and after the centrifuge step it returned, verifying that it was indeed present in excess.

2. The formation of NPs when no carbon was present led to cloudy solutions of brown, violet, black and grey - even when the conditions were the same between different runs.
3. In many cases no alloying, even after annealing did happen. All data presented here are the best runs with the greatest extent of alloying.

4. Different annealing temperatures (800°, 700°, 600°, 500°) showed no improvement in particle size. When the annealing temperature was further dropped no alloy nanoparticles were formed.

5. The washing step is necessary to remove the crown ether from the sample prior to annealing. Since the metallic Gd is very sensitive to be oxidized, this step may also introduce the oxidation of the surface by water and oxygen traces and harm the formation of the following annealing step.

6.4.7 Conclusion

Overall, Pt-Gd nanoparticles were synthesized by the reduction of gadolinium chloride in THF by solvated electrons and a subsequent annealing step. Nevertheless, the desired particle sizes were not achieved and a synthesis control was lacking and further understanding of would be needed. The spectroscopic methods to evaluate the current state of the materials between the different synthesis steps is very limited due to the sensitivity of the intermediates towards moisture and oxygen contamination.

A second look into this method might finally evaluate if the method using NaK in THF as a reducing agent can be a meaningful contribution to the field of rare earth metal platinum alloy nanoparticle synthesis.
7 Synthesis involving Rieke metals

The term Rieke metals originates from the work by Reuben D. Rieke: Rieke metals are finely dispersed metal powders in organic solvents. Their surface is free from oxides leading to their high reactivity, hence also called activated metals.

Typically, an anhydrous metal chloride is dispersed in a solvent (that is inert to the reduction of alkali metals) together with an alkali metal. The alkali metal is dispersed using a complexing agent such as naphtalene under stirring or sonication for hours up to days. Simultaneously with the dispersion, the metal chloride is reduced to the metal and forms nanoparticles and the respective alkali chloride. These nanoparticles can be stabilized and held in suspension by the right solvent (e.g. THF) or other surfactants. A extensive review of Rieke metals can be found in [88], [89].

7.1 Concept

NaK alloy is used as the reducing agent and is dispersed into the solvent by sonication together with an insoluble gadolinium salt, see the scheme in figure 7.1.

Even though the gadolinium salt is insoluble, the finely dispersed NaK will lead to the formation of metallic gadolinium. The gadolinium nanoparticles are deposited on Pt/C that are added to the dispersion. A subsequent alloying step will lead to the formation of the respective alloy.
7 Synthesis involving Rieke metals

Figure 7.1: The scheme of the concept of how to produce Gd nanoparticles:
First, NaK is finely dispersed supported by naphthalene and subsequently GdCl₃ is reduced.

7.2 Procedure

All chemicals were added inside a glovebox in a bottle that was capped and transferred to an ultrasound bath and sonicated for 4 h. The following samples were prepared:

**Sample A** 100 mg NaK (2.6 mmol) in 30 ml toluene. Discarded after sonication.

**Sample B** 100 mg NaK (2.6 mmol) and naphthalene (3.1 mmol) in 30 ml toluene. Discarded after sonication.

**Sample C** 100 mg NaK (2.6 mmol), naphthalene (3.1 mmol) and 200 mg GdCl₃ (0.76 mmol) in 30 ml toluene. Discarded after sonication.

**Sample D** 100 mg NaK (2.6 mmol), naphthalene (3.1 mmol), 200 mg GdCl₃ (0.76 mmol) and 50 mg Pt/C in 30 ml toluene. Eventually the sample was centrifuged and vacuum dried in a glovebox. It was split into two parts and separately filled in an alumina boat and transferred under inert gas to a tube furnace for the annealing treatment at 600 °C (D600) and 800 °C (D800), respectively. Finally the samples were acid washed using the standard procedure.
7.3 Results and discussion

Sample A showed no signs of the formation of a black dispersion, while the liquid in sample B and C quickly turned black. Visibly there was no difference between samples B and C and the formation of Gd nanoparticles in sample C could not be confirmed. The results of the annealed and acid washed samples D600 and D800 can be found in figure 7.2.

Figure 7.2: XRD diagrams of the Pt/C treated with finely dispersed NaK.

One can observe that the main platinum peak at 39.6° has broadened and all other platinum features vanished. The explanation of this observation can be the formation of very small crystallites. EDS confirmed the presence of gadolinium in the sample. Looking at the XRD on can not conclude if the nanoparticles
7 Synthesis involving Rieke metals

are in the form of Pt₂Gd or pure platinum. TGA measurement suggested a formation of a carbon overlayer since the metal content dropped from nominally 40% to about 30%, similarly to previous experiments.

7.4 Conclusion

the investigations into this method were rather soon stopped due to the ongoing formation of a carbon overlayer, similar to when THF is used as discussed in the previous section. In this case naphthalene seems to remain in the sample before the annealing step and decomposing. When no naphthalene was used, NaK was not mobilized and GdCl₃ could not be reduced to metallic gadolinium.

It was not investigated if the same results in terms of platinum peak broadening would have occurred when no GdCl₃ would be present in the dispersion. The results shown in section 8.4 on page 135 would suggest that the peak broadening originates from the interaction of the platinum nanoparticles and dispersed NaK within the carbon support evaporating during the heat treatment.
8 Synthesis using potassium vapor as reducing agent

Employing vaporized potassium as reducing agent in the synthesis of nanoparticles has, to our knowledge, never been reported in literature. While hydrogen gas is a common reducing gas used at elevated temperatures the use of alkali metal vapors seem to be the logical as the next step since a stronger reducing environment is needed. Conveniently, alkali metals exhibit fairly high vapor pressures, especially sodium and potassium, as can be seen in figure 8.1. Potassium shows the highest vapor pressures of all common alkali and alkali earth metals (excluding rubidium and cesium due to their scarcity and reactivity). Applicable vapor pressures range from 1 mbar to 100 mbar, consequently suggesting a temperature window of ca. 300°C to ca. 600°C.

The concept is to heat the potassium metal in close vicinity to the precursor which needs to consist of a rare earth metal salt and platinum on carbon or carbon and a platinum salt. When the temperature is raised the potassium will vaporize and metallic potassium atoms will diffuse into the the precursor reducing the rare earth metal salt and the platinum salt if present. The high temperature allows now the rare earth metal to alloy with platinum to form platinum rare earth alloy nanoparticles.

The following parameters can be altered in this synthesis route:

1. Precursor competition: Platinum on carbon or a platinum salt dispersed on carbon; Dispersion of the rare earth metal salt; Used solvent/liquid and method (stirring, ultrasound, etc.) to facilitate the dispersion.

2. Annealing temperature and time: The temperature sets the vapor pressure of potassium and therefore the reducing strength of the environment.
8 Synthesis using potassium vapor as reducing agent

Figure 8.1: Vapor pressure of potassium and sodium depending on the temperature. The experiments can be carried out reasonably at a potassium vapor pressure between 1 mbar and 100 mbar. At higher temperatures the potassium would evaporate too quickly and at lower temperature too slowly.

The temperature and time control particle growth and the alloy forming phases.

3. Positioning of the potassium source: When the potassium source is placed next to the precursor during the annealing, the vapor pressure and annealing temperature are bound together. If the potassium source is located upstream in the gas flow, its temperature can be controlled separately hence varying its vapor pressure and the potassium partial pressure at the precursor position. This allows the reducing strength to be controlled and can decouple the reduction of the rare earth metal and the alloying without opening the furnace and removing the potassium or relocating the sample.

The precursor preparation has been found to be crucial in order to successfully synthesize small platinum alloy nanoparticles. Interestingly, the simple dissolution of the rare earth metal salts in water and an impregnation in Pt/C or carbon was found to be the most effective route. Nevertheless the work with
8.1 Precursor preparation using THF

8.1.1 Experimental

The fact that potassium vapor can be used as a reducing agent was discovered by accident: 200 mg anhydrous YCl$_3$ and 50 mg Pt/C 40% was mixed in 30 ml THF in a glovebox, sealed in a glass bottle and transferred to an ultrasound bath. It was heated under sonication (ca. 50 °C) to completely dissolve the YCl$_3$. The beaker was then placed in an ethanol dry ice bath and the solution was magnetically stirred to precipitate the YCl$_3$ homogeneously onto the Pt/C. Subsequently the beaker was taken back to the glovebox, the THF discarded by centrifugation resulting in a wet powder, sample A.

Half of sample A was then added slowly to a solution of 30 ml Toluene, 0.4 mg naphthalene and 100 mg NaK. The dispersion was transferred to an ultrasound-bath and sonicated for 2h before being centrifuged and dried under vacuum, resulting in sample B. The other half of sample A was vacuum dried in the mean time. Both samples were placed into the quartz tube for individual annealing treatments. The quartz tube was not regularly cleaned as it was only transferred between the annealing sample and the glovebox and developed a brownish colored layer on inside wall.

8.1.2 Results

Both samples showed the formation of platinum yttrium alloy nanoparticles, as shown by the recorded XRD diagram in figure 8.2. However, when the tube was cleaned before the experiment, no alloying could be observed using precursor A.

---

1It was known from previous experiments at which temperature the YCl$_3$ completely dissolves.
8 Synthesis using potassium vapor as reducing agent

After more experimental work, it could be shown without doubt that the potassium that had been evaporating from the samples condensed on the tube walls and re-evaporation was responsible for the reduction of YCl$_3$.

![XRD diagram of the synthesized Pt$_x$Y/C nanoparticles. The dominant phase is Pt$_3$Y with a crystallite size of around 6 nm.](image)

This implies that in all prior experiments, where the presence of potassium and sodium in the precursor cannot be completely excluded, the significant reduction step did not happen in solution but during the annealing itself. This explains the wide variation of experimental results that were observed and falsely attributed to alternating levels of oxygen and moisture contamination.

Carbon formation could be confirmed by TGA, as had been observed previously when using THF as a solvent for the rare earth metal salt: The platinum loading decreased from 40% to about 27%.
8.2 Precursor preparation using hexane

8.2.1 Concept

Due to the carbon layer formation by the decomposing THF during annealing, hexane was chosen as the liquid to disperse the Pt/C and the yttrium salt.

8.2.2 Procedure

Varying amounts of YCl$_3$ (20 mg - 500 mg) and Pt/C 40% (20 mg - 100 mg) were dispersed in 45 ml anhydrous hexane in a beaker in a glovebox. The beaker was transferred to an ultrasound bath and the dispersion sonicated for minimum 10 h. The beaker was transferred back to the glovebox and after one centrifuge run the hexane discarded and the remaining wet powder vacuum dried.

The black powder, or precursor, was then placed in the glovebox in a transferable quartztube next to a boat containing ca. 100 mg freshly cut metallic potassium. The position of the boats was varied too, either in parallel or in series with the potassium boat located upstream. The tube was transferred from the glovebox to the tube furnace and the annealing protocol was started.

The standard acid wash was performed prior analyzing the samples in XRD. RDE measurement were performed by the standard procedure described in section 3.2.6 on page 67.

8.2.3 Results

Achieving the formation of Pt$_3$Y nanoparticles comparable to the experiment when THF is used was challenging. We attribute this to problems in the dispersion of the rather large crystals of the supplied YCl$_3$ when using THF. Moreover, the results were not very reproducible which can originate from the not completely understood mechanism behind the potassium vapor reduction.

Nevertheless, Pt$_3$Y nanoparticles were synthesized while having some Pt$_2$Y phase present, see figure 8.3. The small shift of the Pt$_3$Y associated peaks to lower angles suggests that the crystal structure is strained (higher lattice parameters). The contribution of platinum to the XRD diagram must come from
8 Synthesis using potassium vapor as reducing agent

unalloyed platinum nanoparticles which do are not strained by the treatment, confirming that the observed Pt$_3$Y peak shift is not a measurement artifact.

![XRD diagram](image)

Figure 8.3: XRD diagram of the acid washed Pt$_3$Y/C synthesized by using hexane to disperse the precursors.

TGA confirmed a platinum loading of about 40\% by heating the sample to 600°C in oxygen, transforming the carbon support to CO$_2$, see figure 8.4. The conclusion is that no carbon layer has been formed during annealing and the surface state of the nanoparticles can be analyzed by XPS. The XPS diagram in figure 8.5 confirms the presence of yttrium present on the surface in a lower binding energy state than its oxidized counterpart. This suggests that alloyed Pt$_3$Y or Pt$_2$Y for that matter is present within the detection depth of XPS of about 8 nm - 10 nm in the synthesized nanoparticles, possibly resulting in the anticipated strain effect in the thin platinum overlayer (supposedly around 1.5 nm, see section 2.6 on page 31) that has been formed during the acid leaching.

TEM images were recorded from the sample and exemplary micrographs and the particle size distribution are shown in figure 8.6. The mean diameter is
8.2 Precursor preparation using hexane

Figure 8.4: TGA diagram of Pt$_3$Y/C synthesized by using hexane to disperse the precursors.

about 5 nm, however the present broadening of the particle size distribution suggest a significant loss in overall surface area.

The RDE results shown in figure 8.7 confirm the loss in surface area: The ECSA has been reduced to about a third (21.5 m$^2$/g) from the original 58 m$^2$/g of the Pt/C starting material. While the surface activity remained the same as the Pt$_3$Y sample (1 mA/cm$^2$) as to the Pt/C catalyst (1.2 mA/cm$^2$), the mass activity significantly decreased significantly from 0.58 A/mg to 0.21 A/mg.

8.2.4 Discussion

The sonication assisted dispersion of yttrium chloride and Pt/C in hexane seem to be a viable alternative to using THF. Hexane has the advantage of not forming a complex with the yttrium salt and can be removed easily by a centrifuge and a vacuum drying step due to its high vapor pressure. Two main challenges remain: First, while the prefered mean particle diameter is 6-9 nm, the particle size distribution is too broad. Secondly, the formation of Pt$_2$Y needs to be avoided. The yttrium rich phase is not stable and even less active than pure platinum [40] and together with the presence of particles grown higher than
8 Synthesis using potassium vapor as reducing agent

Figure 8.5: XPS analysis of the surface yttrium in \( \text{Pt}_x \text{Y} \) particles (a) obtained from a nanocluster source, adapted from [45] and (b) the synthesized nanoparticles.

10 nm the sluggish ORR performance is to be expected.

8.3 Precursor preparation using water and ammonium chloride

All synthesis approaches taken to this point had a strong focus on avoiding contamination by moisture and air during the experimental procedures. However, dispersing the rare earth metal salt and Pt/C in water has become an option, if any crystal water can be removed before the reduction step during the annealing process.

8.3.1 Concept

In section 4.1.2 on page 72 the ammonia route of preparing anhydrous \( \text{YCl}_3 \) is introduced. This method can be utilized by first preparing a solution of the rare
8.3 Precursor preparation using water and ammonium chloride

Figure 8.6: On the left side a TEM micrograph shows a representative image of the Pt\(_x\)Y nanoparticle dispersion on the support. On the right the respective particle size distribution is shown based on this image.

Figure 8.7: The RDE results of the Pt\(_3\)Y synthesis using hexane. The CV (left) and the LSVs (right, absolute current, background corrected) compare the catalyst performance to the commercial Pt/C starting material. Potentials are given against RHE.

Earth metal salt and ammonium chloride. Pt/C is subsequently dispersed into the solution and, sonicated and slowly dried. The obtained powder will contain the very fine dispersed rare earth metal ammonium chloride complex. Before reaching the temperatures where potassium vapor evaporates, the complex decomposes leaving behind anhydrous, well dispersed the rare earth salt, similar
to the using hexane. The reaction equations in the case of YCl₃ are:

\[
\begin{align*}
\text{YCl}_3 \cdot 6\text{H}_2\text{O} + 2\text{NH}_4\text{Cl} & \rightarrow (\text{NH}_4)_2[\text{YCl}_5] + 6\text{H}_2\text{O} \\
(N\text{H}_4)_2[\text{YCl}_5] & \rightarrow \text{YCl}_3 + 2\text{NH}_3 + 2\text{HCl}
\end{align*}
\]

The benefits of this synthesis route are that no preparation inside a glovebox is required, no organic solvent is involved and hydrated rare earth metal salts can be used for preparing the precursor.

### 8.3.2 Procedures

The experiments were carried out during a research stay at the Korean Advanced Institute of Science and Technology (KAIST) in Daejeon, South Korea. (3 g of YCl₃ · 6 H₂O (10 mmol), (5 mg of NH₄Cl (90 mmol), 0.5 g of Pt/C 40% and 17.5 ml Water were mixed to a slurry and sonicated for 1 h. The slurry was then evaporated in a drying oven at 80 °C under occasional stirring. The powder was then filled into an alumina boat and placed in a multi-heating zone furnace. At the heating zone closest to the gas inlet freshly cut potassium was placed. The sample was placed at the heating zone closest to the outlet. 4.0 argon gas at a flow rate of 50 ml/min was used during the annealing experiments. First, the sample was heated to 150 °C for 0.5 h to evaporate residual water followed by the decomposition of the ammonium chloride complex at 400 °C. Eventually the potassium was heated to 500 °C while the sample was heated to 600 °C for 2 h to facilitate the reduction of YCl₃ to the metal and allow its alloying with platinum to occur. Finally the potassium was cooled down while the sample was further annealed at 600 °C for 1 h until it was allowed to cool down to room temperature. The sample was acid washed, dried and analyzed by XRD.

### 8.3.3 Results

In none of the carried out experiments a significant alloying between platinum and yttrium could be observed. Instead, the platinum particle size grew signif-
8.4 Potassium vapor induced platinum growth

icantly in some experiments.

8.3.4 Discussion

The ammonium chloride route appears to need a lot of optimization before it could be viable option to the other routes. The placement of the potassium, flow rates, temperature and precursor preparation all seem to have had great influence on the outcome. Unfortunately, no decisive conclusions could be drawn from the experiments except that the phenomenon of potassium vapor induced platinum particle growth needed to be further investigated.

8.4 Potassium vapor induced platinum growth

Previous experiments suggest that the strong reducing environment or another interaction between potassium and platinum increases its mobility at some what lower temperatures at which particle growth is commonly observed. This phenomenon has not been described previously and a separate experiment was carried out to provide better insight.

8.4.1 Concept

Commercial Pt/C is heated in close vicinity to metallic potassium at different temperatures. The effect on the strongly reducing potassium vapors on the particle growth of Pt nanoparticles is then analyzed by XRD.

8.4.2 Procedure

Two series of experiments were preformed: One without a source of potassium vapor and one with. In each experiment a sample of 20 mg of Pt/C 40 % was filled into an alumina boat and placed into an alumina tube inside a tube furnace. When potassium vapor was required, 200 mg of potassium pieces kept under heptane were placed into another alumina boat and moved in series upstream to the boat with the Pt/C sample inside the alumina tube.
8 Synthesis using potassium vapor as reducing agent

Subsequently the alumina tube was purged with 5.0 argon at a flow rate of 50 ml/min\(^2\) and the annealing program was started, consisting of a ramp at a rate of 15°C/min to the desired annealing temperature and kept there for 30 min before it convectively cooled down to room temperature.

8.4.3 Results

Since pure platinum nanoparticles supported on amorphous carbon were used one can safely use Rietveld refinement to determine the particle sizes in the XRD diagrams obtained from the annealed samples. Under inert gas conditions Pt particle growth could not be observed at temperatures lower than 700°C, as displayed in figure 8.8. It has to be noted that even mild annealing temperatures appear to increase the particles, from 3-4 nm to 4-6 nm. In the presence of potassium vapor however, platinum growth is triggered at temperatures as low as 500°C.

8.4.4 Discussion

A slight platinum particle growth (indicated by the slightly tilted horizontal lines) at increasing temperatures is observed and expected. However, above a threshold, 700°C and 500°C for no potassium and potassium vapor, the particle growth increases significantly. This growth is highly depended on the present amount of potassium vapor.

The result above 475°C have to be taken with care, since all the potassium has been evaporated before the 30 min ended and that the platinum sample was exposed to significant less potassium for the rest of the annealing treatment. For that reason the actual growth of the platinum particles might be underestimated from these temperatures on.

Since the annealing temperature and the potassium vapor pressure are intrinsically coupled in the present experimental set-up, one cannot draw any conclusion if either the temperature or/and the potassium partial pressure is the determining factor in the potassium induced particle growth of platinum.

\(^2\)Corresponding to a space velocity of ca. 0.3 cm/s
8.5 Precursor preparation using water and optimized potassium source

Figure 8.8: The particle size measured by XRD of Pt/C 40% subjected to potassium vapor at different temperatures compared to a sample without the potassium vapor.

These findings suggest that if potassium vapor is used as a reducing agent the annealing step must not be conducted at temperatures above 500°C.

8.5 Precursor preparation using water and optimized potassium source

8.5.1 Concept

A further simplification is achieved compared to ammonia route from section 8.3 on page 132. The significant change is wet impregnating the yttrium
8 Synthesis using potassium vapor as reducing agent

carbonate into the porous carbon to achieve a sufficient dispersion, see figure 8.9.

Figure 8.9: Preparation of the precursor for the potassium vapor reduction treatment.

The loading of the catalyst is determined by concentration of rare earth metal and platinum salts in the water and by the amount of the solution that can be impregnated in the carbon or Pt/C. The carbon used in the present Pt/C catalysts (HiSpec 3000 and HiSpec 4000) is of type vulcan XC-72 and has a pore volume ranging from 1.8 cm$^3$/g to 1 cm$^3$/g. The solubility of rare earth metal salts is sufficient to obtain rare earth metal to platinum ratios between 1 and 10, depending on the Pt loading and solubility of the rare earth metal salt.

The source of the potassium vapor is optimized based on the prior experiments: Instead of using metallic solid potassium, the eutectic alloy of sodium and potassium is used, see figure 6.1 on page 94. The vapor pressure in the applied temperature range of sodium compared to potassium is one order of magnitude lower than that of potassium therefore potassium will always dominate the alkali metal vapor according to figure 8.1 on page 126. This is somewhat important since sodium forms alloys with platinum [90] that might contribute to unwanted morphology changes after washing.

Potassium readily forms an oxide overlayer, even in when cut in the glovebox or stored already cut under heptane. The NaK alloy on contrast can be pipetted as a liquid and maintains its metallic surface. Other considerations and benefits:

- No inert gas environment such as a glovebox needed.
- Rare earth metal precursors can be hydrated and do not have to be supplied as anhydrous.
8.5 Precursor preparation using water and optimized potassium source

- Water is used as a solvent, providing a cheap and environment friendly alternative to organic solvents.

- Previous experiments and literature conduct the annealing temperature at temperatures higher than 600 °C, leading to significant broadening of the particle size distribution. The reduction by potassium vapor allows lower annealing temperatures low, thus decreasing the tendency of particle growth.

8.5.2 Procedure

A typical synthesis of Pt$_x$Y nanoparticles on carbon was performed as follows:

8 g YCl$_3$·6H$_2$O was dissolved in 10 ml water. 200 mg of Pt/C was dispersed in a vial filled with 5 ml of the YCl$_3$ solution using 1 h of ultrasound. The slurry was then vacuum filtered and the veil washed using the remaining YCl$_3$ solution and added to the filter. The filter and the filtercake were dried in an oven under air at 110 °C until dryness. The weight gain of the filter was recorded to estimate the amount of YCl$_3$ added to the Pt/C. The carbon was found to take about about 2 cm$^3$/g, resulting in final molar ratios between platinum and yttrium of about 1.5 to 1 for Pt/C 40 % and about 4:1 for Pt/C 20 %.

An alumina boat is placed on the edge of the alumina tube and NaK was pipetted into the boat under a strong argon flow (> 500 ml/min). A boat with the weighed precursor was placed next to it and then moved together within the alumina tube by a steal rod to the heating zone of the tube furnace.

The standard annealing procedure was heating the sample to 400 °C by a rate of 15 °C/min and holding it at this temperature for 6 h under a flow of 20 ml/min$^3$ 5.0 argon gas. After the sample has cooled down it was removed, acid washed by the standard 0.1 M sulfuric acid and dried.

The experimental procedure was varied over the course of the investigations. The deviations from the standard procedure will be clarified in the respective sections.

$^3$Corresponding to a space velocity of ca. 0.1 cm/s
8 Synthesis using potassium vapor as reducing agent

8.5.3 Results

A typical XRD diagram can be found in figure 8.10. In comparison to the unalloyed Pt/C, the characteristic platinum peaks are significantly weakened and broadened. Clearly identifiable are the peaks characteristic for Pt$_3$Y phase. A Rietveld analysis\(^4\) suggests a crystallite size of around 6 nm. However, the overlap of peaks of the low index planes of Pt, Pt$_3$Y and Pt$_2$Y between 38° and 40° increases the uncertainty in the crystallite size analysis.

![XRD diagram](image)

Figure 8.10: XRD diagram of the Pt$_3$Y ample synthesized as described. A XRD diagram of the Pt/C material used as the precursor is added for comparison.

\(^4\)A more complex yet comparable method to the Scherrer equation to determine the crystallite sizes corresponding to different phases.
8.5 Precursor preparation using water and optimized potassium source

8.5.4 Detailed results and discussion

ORR activity measurement results

The ORR activity was measured on various samples: The sample as prepared by the general procedure described earlier with a loading of 40 %, a sample where the Pt/C material was exchanged by 20 % Pt/C (same platinum mass), a sample where the yttrium chloride was replaced by gadolinium chloride (same molar solution concentration) and the responding untreated Pt/C 40 % and Pt/C 20 % catalysts. The electrochemical results can be found in figure 8.11.

Figure 8.11: Cyclic voltammograms (left) and ORR linear sweep voltammograms (right, absolute currents, background corrected) of different samples: The sample as prepared by the general procedure described earlier with a loading of 40 %, a sample where the Pt/C material was exchanged by 20 % Pt/C (same platinum mass), a sample where the yttrium chloride was replaced by gadolinium chloride (same molar solution concentration) and the responding untreated Pt/C 40 % and Pt/C 20 % catalysts. Experimental conditions as defined by the standard procedure in section 3.2.6 on page 67. Potentials are given against RHE.

The main observation is the reduced ECSA of the treated samples, indicating a significant particle growth. The H-upd features at low potentials and the platinum surface oxide features at high potentials appear mostly unchanged, apart
from being less pronounced. The ECSA values and ORR activities can be found in figure 8.12.

Figure 8.12: Electrochemical performance of Pt\textsubscript{x}Y and Pt\textsubscript{x}Gd nanocatalysts in comparison to the respective Pt/C precursors.

When comparing the mass activities between the samples of 40\% one finds that the platinum alloy catalyst are comparably active, even though their ECSA has decreased by 50\% (Pt\textsubscript{x}Y/C 40\%) to 30\% (Pt\textsubscript{x}Y/C 40\%). The increased specific activity has compensated the loss in ECSA, in case of Pt\textsubscript{x}Y/C even doubled, suggesting that the platinum overlayer has been succesfuly strained by the alloyed yttrium and gadolinium. On the contrary, the specific and mass activity of the 20\% Pt\textsubscript{x}Y/C sample did not enhance in comparison to the 20\% Pt/C precursor. This result can be attributed to the acid wash, discussed in detail in section 8.5.4 on page 144.

**Mechanism of alloy formation**

Understanding how the platinum alloys are formed during the annealing process in the presence of potassium vapor is obligatory in controlling the synthesis process. The main aim is to control the alloy phase formed, in the present case
8.5 Precursor preparation using water and optimized potassium source

Pt$_3$Y over Pt$_2$Y with as little unalloyed platinum as possible and a narrow particle size distribution around a mean diameter of about 8 nm.

To understand the mechanism of the alloy formation the annealing time was varied, see figure 8.13.

![XRD diagrams](image)

Figure 8.13: XRD diagrams of Pt$_3$Y synthesized by different annealing times and the respective untreated XRD diagram of Pt/C.

A shorter annealing time leads to minor alloying, while the platinum particles already grow significantly. When the sample has been annealing longer, alloying completes and almost no features of unalloyed platinum remain.

This indicates that the growth of platinum particles is occurring at a significant faster rate than the alloying with the rare earth metal. Assuming that the reduction of the rare earth metal salt is almost instantaneous, considering the
8 Synthesis using potassium vapor as reducing agent

strong reducing power of potassium the scheme in figure 8.14 is proposed.

Interestingly, YOCI was never observed in the XRD diagrams, neither with or without a acid wash: Since YOCI must form during the course of the experiment since hydrated YCl$_3$ is used, two conclusions can be drawn: First, the potassium vapor can reduce YOCI to metallic yttrium that turns into Y$_2$O$_3$ once in contact with air. Second, the potassium vapor must be able to access the sample homogeneously, otherwise YOCI should be observable after the annealing has been finished.

Effect of acid washing

Leaching the topmost layer is crucial to obtain the desired core-shell structure of most platinum alloy nanoparticles. However, many alloy phases are susceptible to dissolution by different extend. Generally, the higher the content of the non-precious metal and the stronger the acid the more severe is the leaching of that phase. Furthermore, the non-precious metal can leach out from smaller particles completely, while the platinum overlayer acting as a diffusion barrier prevents bigger particles from being completely de-alloyed.

The standard mild acid leach that was used in all of the experiments serves mainly to remove surface oxides formed by the non-precious and rare earth metal. When reducing the particle size as displayed over the course of the past
sections however, the acid wash seems to attack the alloy phase significantly, especially the rare earth metal rich Pt\(_2\)Y phase, see figure 8.15.

![XRD diagrams of Pt\(_x\)Y](image)

Figure 8.15: XRD diagrams of Pt\(_x\)Y synthesized by the use of Pt/C 20%.

First, a standard synthesis of Pt\(_x\)Y nanoparticles was performed showing broad overlapping peaks in XRD indicating rather small particles. Secondly, a synthesis with the same parameters was conducted and without exposing the sample to air, the potassium vapor source removed. Then the sample was annealed further at 600 °C to induce particle growth so that the different alloy
phases can be better distinguished in XRD. Phases of Pt$_2$Y and Pt$_3$Y in figure 8.15 are clearly visible without any signs of an unalloyed platinum phase. So far, the samples were only water washed leaving a significant portion of Y$_2$O$_3$ in the sample.

After the standard acid wash of the further annealed sample the Pt$_2$Y phase has completely vanished and a rather broad platinum phase appears again. This leads us to the conclusion that small Pt$_2$Y-phase nanoparticles (< 5 nm) are unstable in an acidic environment and that any broad platinum phase observed so far is in fact a dealloyed Pt$_2$[RE]-phase, which can explain the phenomenon observed in chapter 7 on page 121.

The smaller the nanoparticles are, the more strongly the acid leaching will affect them. It is very likely that this is the case for the sluggish ORR performance of the Pt$_x$Y nanoparticles when synthesized by the use of Pt/C 20 % which leads to less particle growth compared to Pt/C 40 % under the same conditions.

**Phase control**

Principally two ways of phase control are possible: Annealing temperature, time and precursor composition. At higher annealing temperatures the formation of the rare earth metal rich phase is favored, in the present case this is the Pt$_2$Y. Since the annealing temperature in the synthesis route also determines the potassium vapor pressure and particle size, the temperature can not be used easily to control the alloy phases. Using a two zone furnace would allow the control of the potassium vapor pressure independently from the annealing temperature. However, transporting the potassium vapor uniformly to the sample might not be as trivial as the experience at KAIST, see section 8.3 on page 132, suggests.

In order to gain any control over the formed alloy phase, the ratio between yttrium and platinum was altered by changing the amounts of YCl$_3$·6H$_2$O dissolved in water together with the dispersed 20 % Pt/C: Instead of the standard 0.8 gml YCl$_3$·6H$_2$O it was reduced for one sample to 0.08 gml.

The XRD diagrams of the acid washed samples are shown in figure 8.16. Due to the rather small particles, the majority of the formed Pt$_2$Y has been leached.
8.5 Precursor preparation using water and optimized potassium source

Figure 8.16: XRD diagrams of Pt\textsubscript{2}Y synthesized by different yttrium to platinum molar ratios using Pt/C 20 % in the precursor.

out leaving behind platinum. The presence of very broad platinum peaks in the sample with the higher ratio between yttrium and platinum indicates that more of the Pt\textsubscript{2}Y was formed compared to the sample with the lower ratio of platinum to yttrium. Additionally, the particle size appears to be smaller which can be attributed to YCl\textsubscript{3} · 6H\textsubscript{2}O and its intermediates acting as a spacer hindering platinum particle growth.
9 Discussion and conclusion

In the last chapters four different, yet related attempts to synthesize platinum early transition and rare earth metal alloy catalysts were described and discussed. Based on the concept, a synthesis in liquid ammonia is most similar to conventional catalyst synthesis routes. In this work however, the desired alloy nanoparticles could only be obtained after an annealing step. The same is true for the synthesis routes involving organic solvents and the final route using a wet impregnation technique and potassium vapor. The latter is the most promising among the investigated synthesis techniques. In contrast to the other techniques the precursor is prepared under ambient conditions and the annealing step requires lower temperatures. The use of potassium vapor comes with challenges, which can be overcome with engineering solutions.

Overall, every investigated technique provided insights into the aspects of the synthesis of early transition metal and rare earth platinum alloy nanoparticles.

9.1 Early transition metal platinum alloy nanoparticles

Chromium and zirconium could be successfully reduced in liquid ammonia and formed the respective platinum alloy after annealing. The strong oxide layer formed by the early transition metals seems to protect the metallic core allowing it to subsequently alloy with platinum. Additionally, the oxide also appears to prevent particle sintering somewhat at the required temperatures. However, the final removal of the oxide showed to be unsuccessful. The high annealing temperatures necessary to form the alloys, increase the strength of the oxide phase and lead to particle growth (up to 10 nm) despite the oxide layer.
9 Discussion and conclusion

9.2 Rare earth metal platinum alloy nanoparticles

In retrospect, the final method, using K vapor, is rather simple and could have been discovered earlier in the process. However, each step and synthesis route gave deeper insights into the challenges and factors that determine a successful synthesis route.

Temperature

A general characteristic was the need of high temperatures to facilitate the alloying process. The minimum temperature required at which alloy formation could be observed was 350°C using potassium vapor as the reducing agent. The stronger the reducing agent and the better the rare earth metal salt is distributed over the support material the lower the minimum required annealing temperature.

Rare earth metal salt distribution

A well dispersed rare earth metal salt over the support allows short diffusion distances to platinum that eventually leads to the alloy formation. Precursor preparations where the dissolved rare earth metal salt precipitated from the solution on to the support (THF, water) showed consistently better results in terms of alloying extent, particle size and required temperatures compared to simple dispersion methods (hexane).

Pt/C as a starting material

Generally, commercial Pt/C with its well dispersed platinum nanoparticles resulted in a less broad particle size distribution in the product compared to when the platinum nanoparticles were synthesized in-situ. It did not seem to have a negative impact on the extent of alloying when it was made sure that the rare earth metal salt was well dispersed.
Particle size distribution

The particle size distribution is a major concern in the synthesis of these nanoparticles, not only during this work but also in the reported synthesis attempts in literature, see section 2.6 on page 31. The high annealing temperatures required to facilitate the alloying are the main reason for the particle size broadening.

The potassium vapor reduction route provides a method to reduce the required annealing temperatures substantially. However, the effect of the potassium vapor on the platinum nanoparticles has yet to be understood as it can lead particle growth, mitigating the benefit of lower annealing temperatures. On possible explanation can be a temporary formation of a platinum potassium alloy of an eutectic stoichiometry leading to an increased platinum mobility and hence increased rate of ripening.

Another approach to control the particle size distribution is the introduction of a spacer compound. The effect of a higher rare earth metal content in the precursor before annealing leading to smaller particles sizes was observed in the ammonia route of the synthesis of Pt$_x$Gd.

Phase control

Next to optimizing particle size distribution, controlling the phase of the obtained nanoparticles is crucial. The stoichiometry and the phase of the catalyst decides if the catalyst can meet its activity expectations and is stable enough to maintain its ORR activity level during operation. Generally, the lower the content of the alloying (and more oxophilic) metal the more stable is the compound. Especially the Pt$_2$[RE] phases seem to be easily attacked during acid leaching. Besides this phenomenon, these phases supposedly do not provide the right platinum surface strain to perform as exceptional as measurements on the respective Pt$_3$[RE] and Pt$_5$[RE] suggest.

The correlation of precursor and alloy stoichiometry (Pt/[RE] ratio) was very weak. When the precursor content was lowered, rather than forming phase pure Pt$_3$[RE] or Pt$_5$[RE], the Pt$_2$[RE] phase and pure platinum were formed, or a mixture thereof. However, Pt$_x$Y could be optimized to contain mostly Pt$_3$Y and
Discussion and conclusion

only little Pt$_2$Y.

It is entirely possible that most Pt$_5$[RM] are not accessible by means of chemical methods. This led to the hypothesis of a correlation which will be discussed in the next section.

Correlation between the preferred nanoparticle phase and its melting point

Examining the phase diagram of the relevant platinum alloys and our observation in their respective nanoparticle synthesis one can correlate the phase with the highest melting point to the formed nanoparticle composition:

Pt$_x$Zr  The phase with the highest melting point in the platinum zirconium system is Pt$_3$Zr, see figure 5.8 on page 91. This is not surprising, since most platinum transition metal alloys form Pt$_3$M nanoparticles.

Pt$_x$Cr  The platinum chromium system does not exhibit a defined stoichioime-try at its highest melting point composition, see figure 5.8 on page 91. However, this point would correspond to Pt$_5$Cr. When the annealing temperature was varied in the synthesis of Pt$_x$Cr nanoparticles, the change in peak position and therefor lattice parameters suggests that the alloy got more chromium rich. The correlation between the phase of highest melting point and nanoparticle composition seems to only hold to intermetallics and not to alloy phases without a defined stoicoimetry in the platinum rich area.

Pt$_x$Gd  Pt$_2$Gd has the highest melting point of all platinum gadolinium phases, see figure 9.1. This is in agreement with the exclusive formation of Pt$_2$Gd throughout all nanoparticle synthesis attempts.

Pt$_x$Y  In contrast to the platinum gadolinium system, the highest melting platinum yttrium phase is Pt$_3$Y, see figure 9.1. And indeed, while the formation of Pt$_5$Gd was observed only in one experiment to a insignificant extent, see 6.17, Pt$_3$Y is the dominant phase that forms in the synthesis of Pt$_x$Y nanoparticles.
9.2 Rare earth metal platinum alloy nanoparticles

The correlation seems to hold for the arguably few cases examined in this work. The logic behind this proposed correlation is, that the melting point of most substances corresponds to the strength of the bonds in the solid state: A stronger bound solid state empirically leads to a higher melting point. Since stronger atomic bonds also imply a lower energy state compared to other phases, the respective phase might form preferably since the systems energy can be minimized. A plot of the phase stoicoimetry and its respective melting point of various metals (If a fixed stoicoimetry exists) can be found in figure 9.2.

However, since the nanoparticles are formed at high temperatures - diffusion, crystal phase compatibility and other properties would be expected to govern the formation of specific phases.

Nevertheless, the proposed correlation might indicate which phase can be expected from a nanoparticle synthesis that involves an annealing step. In case of the platinum rare earth metals, a potassium vapor reduction of platinum with a lanthanum salt promises to lead to the desired Pt$_5$La nanoparticles.

Figure 9.1: Phase diagrams of the platinum binary alloys with gadolinium [91] and yttrium [92].


9 Discussion and conclusion

Figure 9.2: Stoicoimetry of the highest melting phases of various binary platinum metal phases and their melting point. Values researched from [93].

9.3 Final remarks

This thesis has shown that solvated electrons in liquid ammonia do not reduce rare earth metal salts. While solvated electrons in organic solvents do reduce rare earth metal salts the interactions with the solvent and the difference in reduction potentials to platinum prevent the formation of the respective alloy. Under sufficient annealing temperatures however, large platinum alloy nanoparticles can be obtained using either technique.

Finally, the application of potassium vapor as a powerful reducing agent was found. Small, nearly phase pure yttrium and gadolinium nanoparticles with an enhanced specific ORR activity were synthesized. This method has been described here for the first time by our best knowledge. Eventually, variations of this synthesis route can be utilized to obtain various currently inaccessible alloy nanoparticles for a multitude of applications.
List of Figures

1.1 Primary and electrical energy sources ........................................ 2
1.2 Energy consumption and wealth ............................................... 3
1.3 Affordability of oil .............................................................. 5
1.4 CO₂ and temperature ............................................................. 7
1.5 Greenhouse gas emissions ....................................................... 8
1.6 Storage technologies ............................................................. 12
1.7 Hydrogen economy ............................................................... 13
1.8 Types of hydrogen fuel cells ................................................... 15
1.9 Fuel cell components ............................................................. 16
1.10 Cost breakdown of a fuel cell system ....................................... 17
1.11 Typical fuel cell polarization curve ......................................... 19

2.1 ORR reaction path ................................................................. 22
2.2 ORR reaction mechanism ....................................................... 23
2.3 The scaling relationship ......................................................... 24
2.4 ORR volcano plot ................................................................. 25
2.5 Structure of Pt₅La ................................................................. 32
2.6 Nanocluster source sketch ...................................................... 34
2.7 ORR activity of PtₓY and PtₓGd ................................................ 34
2.8 XRD diagram of PtₓY by reduction in molten salt ....................... 35
2.9 PtₓY XRD diagram by ultra high purity hydrogen reduction .......... 36
2.10 PtₓY XRD diagram of a very high temperature annealing synthesis 37
2.11 PtPb nanoflakes ................................................................. 38
2.12 Gallium doped octahedral Pt₃Ni ............................................. 39

3.1 Catalyst development procedure ............................................. 42
3.2 Characterization techniques .................................................. 43
List of Figures

<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>Universal curve</td>
<td>44</td>
</tr>
<tr>
<td>3.4</td>
<td>Sketch of an XRD apparatus</td>
<td>45</td>
</tr>
<tr>
<td>3.5</td>
<td>XRD con- and destructive interference</td>
<td>45</td>
</tr>
<tr>
<td>3.6</td>
<td>Bragg’s law</td>
<td>46</td>
</tr>
<tr>
<td>3.7</td>
<td>Idealized XRD diagram</td>
<td>47</td>
</tr>
<tr>
<td>3.8</td>
<td>Electron transitions detected by EDS</td>
<td>48</td>
</tr>
<tr>
<td>3.9</td>
<td>TEM scheme and picture</td>
<td>50</td>
</tr>
<tr>
<td>3.10</td>
<td>XPS measurement principle</td>
<td>51</td>
</tr>
<tr>
<td>3.11</td>
<td>Idealized XPS spectrum</td>
<td>52</td>
</tr>
<tr>
<td>3.12</td>
<td>XPS background correction</td>
<td>53</td>
</tr>
<tr>
<td>3.13</td>
<td>Processes in the vicinity of an electrode</td>
<td>55</td>
</tr>
<tr>
<td>3.14</td>
<td>Potentials close to an electrode</td>
<td>57</td>
</tr>
<tr>
<td>3.15</td>
<td>Current voltage curves showing the necessity of a reference electrode</td>
<td>59</td>
</tr>
<tr>
<td>3.16</td>
<td>Electrode surface roughness</td>
<td>64</td>
</tr>
<tr>
<td>3.17</td>
<td>Cyclic voltammogram to obtain the ECSA</td>
<td>68</td>
</tr>
<tr>
<td>3.18</td>
<td>Pictures of the RDE cell and reference electrode</td>
<td>69</td>
</tr>
<tr>
<td>3.19</td>
<td>Picture of the RDE set-up</td>
<td>70</td>
</tr>
<tr>
<td>4.1</td>
<td>Overview of the approximate location of relevant reduction potentials</td>
<td>71</td>
</tr>
<tr>
<td>5.1</td>
<td>Liquid ammonia experimental setup</td>
<td>80</td>
</tr>
<tr>
<td>5.2</td>
<td>XRD diagram of the simultaneous reduction of Pt and Gd</td>
<td>84</td>
</tr>
<tr>
<td>5.3</td>
<td>XRD diagram of Pt$_2$Gd alloy nanoparticles</td>
<td>85</td>
</tr>
<tr>
<td>5.4</td>
<td>XRD diagrams of Pt$_3$Cr samples</td>
<td>87</td>
</tr>
<tr>
<td>5.5</td>
<td>XRD diagrams showing metallic Chromium</td>
<td>88</td>
</tr>
<tr>
<td>5.6</td>
<td>XRD diagram of Pt$_3$Zr</td>
<td>89</td>
</tr>
<tr>
<td>5.7</td>
<td>XRD diagrams regarding the effect of annealing temperature on Pt$_3$Cr</td>
<td>90</td>
</tr>
<tr>
<td>5.8</td>
<td>Phase diagram of platinum chromium and zirconium binary alloys</td>
<td>91</td>
</tr>
<tr>
<td>6.1</td>
<td>Na-K phase diagram</td>
<td>94</td>
</tr>
<tr>
<td>6.2</td>
<td>Crown ether structure</td>
<td>95</td>
</tr>
</tbody>
</table>
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>Sodium naphthalenide structure</td>
<td>95</td>
</tr>
<tr>
<td>6.4</td>
<td>Picture of the THF while being dried using NaK</td>
<td>97</td>
</tr>
<tr>
<td>6.5</td>
<td>Sketch of the THF drying, distillation and dispensing equipment</td>
<td>97</td>
</tr>
<tr>
<td>6.6</td>
<td>Possible synthesis routes</td>
<td>100</td>
</tr>
<tr>
<td>6.7</td>
<td>Synthesis route A</td>
<td>102</td>
</tr>
<tr>
<td>6.8</td>
<td>Concept for synthesis route A</td>
<td>103</td>
</tr>
<tr>
<td>6.9</td>
<td>XRD diagrams from samples of the synthesis route A1</td>
<td>104</td>
</tr>
<tr>
<td>6.10</td>
<td>Concept for synthesis route B1</td>
<td>106</td>
</tr>
<tr>
<td>6.11</td>
<td>Concept for synthesis route B2</td>
<td>106</td>
</tr>
<tr>
<td>6.12</td>
<td>XRD diagrams from samples of the synthesis route B1</td>
<td>109</td>
</tr>
<tr>
<td>6.13</td>
<td>Concept for synthesis route C1</td>
<td>110</td>
</tr>
<tr>
<td>6.14</td>
<td>Concept for synthesis route C2</td>
<td>111</td>
</tr>
<tr>
<td>6.15</td>
<td>Concept for synthesis route C3</td>
<td>111</td>
</tr>
<tr>
<td>6.16</td>
<td>XRD diagrams of samples synthesized by the routes C1, C2 and C3112</td>
<td></td>
</tr>
<tr>
<td>6.17</td>
<td>XRD diagrams of samples synthesized by the use of different solvents</td>
<td></td>
</tr>
<tr>
<td>6.18</td>
<td>XRD diagrams of samples annealed at different temperatures</td>
<td></td>
</tr>
<tr>
<td>6.19</td>
<td>TGA diagram of samples with a carbon overlayer</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Concept for the synthesis of Pt&lt;sub&gt;x&lt;/sub&gt;Gd nanoparticles using Rieke metals</td>
<td>122</td>
</tr>
<tr>
<td>7.2</td>
<td>XRD diagrams using the Rieke metal approach</td>
<td>123</td>
</tr>
<tr>
<td>8.1</td>
<td>Temperature window of operating with potassium vapor</td>
<td>126</td>
</tr>
<tr>
<td>8.2</td>
<td>XRD diagram of Pt&lt;sub&gt;x&lt;/sub&gt;Y using THF as the solvent</td>
<td>128</td>
</tr>
<tr>
<td>8.3</td>
<td>XRD diagram of Pt&lt;sub&gt;x&lt;/sub&gt;Y/C synthesized by using hexane to disperse the precursors</td>
<td>130</td>
</tr>
<tr>
<td>8.4</td>
<td>TGA diagram of Pt&lt;sub&gt;x&lt;/sub&gt;Y/C synthesized by using hexane to disperse the precursors</td>
<td>131</td>
</tr>
<tr>
<td>8.5</td>
<td>XPS analysis of the Pt&lt;sub&gt;x&lt;/sub&gt;Y synthesis using hexane</td>
<td>132</td>
</tr>
<tr>
<td>8.6</td>
<td>Particle size distribution of the Pt&lt;sub&gt;x&lt;/sub&gt;Y synthesis using hexane</td>
<td>133</td>
</tr>
<tr>
<td>8.7</td>
<td>RDE results of the Pt&lt;sub&gt;x&lt;/sub&gt;Y synthesis using hexane</td>
<td>133</td>
</tr>
<tr>
<td>8.8</td>
<td>Potassium vapor induced Pt/C particle growth</td>
<td>137</td>
</tr>
<tr>
<td>8.9</td>
<td>Precursor preparation for the potassium vapor reduction</td>
<td>138</td>
</tr>
</tbody>
</table>

157
### List of Figures

8.10 XRD diagrams of Pt₃Y synthesized by wet impregnation and Pt nanoparticles ........................................... 140
8.11 RDE results of the Pt₃Y synthesis using water ................................................................. 141
8.12 Electrochemical performance of Pt₃Y and Pt₃Gd nanocatalysts ........................................... 142
8.13 XRD diagrams of Pt₃Y synthesized by different annealing times ........................................ 143
8.14 Proposed alloy formation mechanism during annealing ...................................................... 144
8.15 XRD diagrams of Pt₃Y regarding the effect of the acid wash ........................................... 145
8.16 XRD diagrams of Pt₃Y synthesized by different yttrium to platinum molar ratios .......... 147

9.1 Phase diagrams of the platinum binary alloys with gadolinium and yttrium ................. 153
9.2 Stoicoimetry of the highest melting phases of various binary platinum metal phases ............ 154
List of Tables

1.1 Top producers of oil, natural gas and coal . . . . . . . . . . . . . . 6
1.2 Fatalities of different energy sources . . . . . . . . . . . . . . . . 10
1.3 Overpotentials in fuel cell . . . . . . . . . . . . . . . . . . . . . . . 17
1.4 DOE targets . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 18

2.1 Reduction potentials of various late transition metals . . . . . . 29
2.2 Reduction potentials of various early transition metals . . . . . . 29
2.3 Most common early transition metal oxides . . . . . . . . . . . . . 30
2.4 Reduction potentials of various rare earth metals . . . . . . . . . 33

4.1 List of the solubilities of relevant rare earth metals in water and
THF. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 73

5.1 Reduction potentials of various alkali metals . . . . . . . . . . . . 78
5.2 Noteworthy samples in the liquid ammonia reduction route . . . 82
References


References


References


References


References


References


[59] K Rossmanith. “Herstellung von Tetrahydrofuranverbindungen der Sel-
tenerdbromide”. In: Monatshefte für Chemie 97.5 (1966), pp. 1357–1364.
DOI: 10.1007/BF00902585.

Ceriterdiodide”. In: Monatshefte für Chemie Chemical Monthly 126.8-9

[61] David R. Lide. CRC handbook of chemistry and physics. 86th ed. CRC Press,

CHEMISTRY ANALYTICAL CHEMISTRY DIVISION COMMISSION ON
SOLUBILITY.

[63] Wesley W. Wendlandt. “The thermal decomposition of yttrium, scan-
dium, and some rare-earth chloride hydrates”. In: Journal of Inorganic
and Nuclear Chemistry 5.2 (1957), pp. 118–122. DOI: 10.1016/0022-
1902(57)80052-9.

DOI: 10.1246/bcsj.13.388.

Chloride Route to Anhydrous Rare Earth Chlorides-The Example of Ycl

[66] Edward Curtis Franklin. “Reactions in Liquid Ammonia”. In: 836.1898

[67] G. W. A. Fowles and D. Nicholls. “Inorganic reactions in liquid am-
References


[71] Vitaly V. Chaban and Oleg V. Prezhdo. “Electron Solvation in Liquid Ammonia: Lithium, Sodium, Magnesium, and Calcium as Electron Sources”. In: Journal of Physical Chemistry B 120.9 (2016), pp. 2500–2506. DOI: 10.1021/acs.jpcb.6b00412.


References


References


