Synthesis and Characterisation of Pt-alloy Oxygen Reduction Electrocatalysts for Low Temperature PEM Fuel Cells

by

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Dissertation submitted in partial fulfillment for the degree

Master of Science

In the Faculty of Science

at the Nelson Mandela Metropolitan University

August 2012

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Declaration

I declare that this dissertation is my own original work and that it has not been submitted before for any degree or examination in any other university.

Signature:  ..................  Date:  ..................

R. Mohamed
Abstract

In this dissertation the syntheses of Pt-based binary and ternary alloy electrocatalysts using the transition metals of Co and Ni are presented. These electrocatalysts were synthesised by an impregnation-reduction procedure at high temperature whereby Pt supported on carbon, (Pt/C (40%)), was impregnated with the various metal and mixtures thereof and reduced at high temperatures in a H₂ atmosphere.

The procedure was also designed in such a way so as to prevent the oxidation of the support material (carbon black) during the alloy formation. The resultant nanoparticles (9-12 nm) of Pt₃Co/C, Pt₃Ni/C and Pt₃Co₀.₅Ni₀.₅/C were also subjected to a post treatment procedure by acid washing (denoted AW) to produce electrocatalysts of Pt₃Co/C-AW, Pt₃Ni/C-AW and Pt₃Co₀.₅Ni₀.₅/C-AW to study the effect of acid treatment on these electrocatalysts. The synthesised electrocatalysts were then characterised by a number of physical and electrochemical techniques and compared to that of commercial Pt/C (Pt/C-JM, HiSpec 4000) as well as Pt/C catalysts (Pt/C-900 and Pt/C-900-AW) treated under the same conditions used for the alloy synthesis. The electrocatalysts were then used to fabricate MEAs that were loaded into commercial single test cells and characterised by means of polarisation curves and Electrochemical Impedance Spectroscopy (EIS).

The extensive physical characterisation included Powder X-Ray Diffraction (PXRD) analysis, Transmission Electron Microscopy (TEM), elemental analysis by Energy Dispersive Spectroscopy (EDS) and metal loading by Thermo-Gravimetric Analysis (TGA). These studies showed that Pt-based alloy electrocatalysts were successfully synthesised with particle sizes ranging from 9 - 12 nm, within their respective atomic ratios and whereby no significant loss of carbon support occurred. This indicated that significant sintering or electrocatalyst particles occurred when compared to that of the starting Pt/C catalyst (3 – 4 nm). From the combined results of the physical characterisation procedures, it was also shown that leaching as a result of acid washing was
catalyst dependent with Ni containing catalysts showing a significant degree of leaching compared to that of Co containing catalysts.

Electrochemical characterisation in terms of Electrochemical Active Surface Area (ECSA) by Cyclic Voltammetry (CV) and ORR activity by Rotating Disc Electrode (RDE) analysis revealed that a significant decrease in the ECSA resulted from the increase in particle size and this had a major influence on the ORR activity. Furthermore it was found that a significant improvement in the ORR activity was achieved by the synthesis of Pt-based alloys. It was also found that catalytic properties of the acid washed electrocatalysts were substantially different from that of non-acid washed electrocatalysts. The experimental data confirmed that it was possibly to achieve better catalytic performance as compared to that of Pt/C at a lower material cost when Pt is alloyed with base transition metals.

The trend observed from the ORR activity studies by RDE was successfully repeated in the in-situ fuel cell testing in terms of mass activity of the electrocatalysts. Of the electrocatalysts studied under ‘real’ fuel cell conditions Pt/C-JM had the best performance compared to the others, with the ternary Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C showing better catalytic performance compared to the Pt$_3$Co/C electrocatalyst. This was found to be due to a higher charge transfer resistance observed in Pt$_3$Co/C as compared to that of Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C which was similar than that of the commercial Pt/C-JM catalyst with both Pt$_3$Co/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW having similar but higher ohmic resistances than that of Pt/C-JM as determined by electrochemical impedance spectroscopy.

The results showed that a great potential exist to improve the catalytic performance of low temperature PEM fuel electrocatalysts at a reduced cost as compared to that of pure Pt provided a method of controlling the particle size was established.
Acknowledgements

I would like to express my deepest appreciation to my supervisors Dr. Shawn Gouws and Professor Ernst Ferg for their guidance, encouragement, continuous support and open door policy throughout the duration of this study.

Thanks also to the technical staff and fellow students at InnoVenton Research Laboratories for their assistance.

A special word of thanks is extended to the Director of HySA Catalysis, Dr. Olaf Conrad for his support and for allowing me the opportunity to conduct a large part of my research at the University of Cape Town (UCT). I would also like to thank all the members of UCT’s Centre of Catalysis Research for all their assistance and for creating a friendly working environment.

I wish to extend my sincerest appreciation to the members of HySA Catalysis without whom the completion of this project would not be possible. In particular: Dr. Pieter Levecque for his training, advice and willingness to assist with every aspect of this project, Mr. Nabeel Hussain for his training on MEA preparation and testing as well as guidance during the write up phase and Dr. Qiling Naidoo for her valuable assistance with analysis of the results.

Thank you also to Professor Günther G. Scherer of the Paul Scherrer Institute (PSI) for his valuable input into the project and words of encouragement.

I would also like to thank The Nelson Mandela Metropolitan University (NMMU), National Research Foundation (NRF) and HySA Catalysis for their financial support.

I would like to thank my beloved family and friends for their unconditional love and support throughout the years.

Last but most importantly, I wish to thank my God and Heavenly Father for His mercy and grace upon my life. Thanks be to God who gives me the victory through the Lord Jesus Christ.

“In every victory, let it be said of me, my source of strength, my source of hope is Christ alone” – Andrew Shawn Craig
Related Publications by the Author

A part of this work was presented at the 11th International Conference of Frontiers of Polymers and Advanced Materials conference, Presenters: Shawn Gouws, Rhiyaad Mohamed, and Ernst Ferg title PEM Fuel Cells and electrolysers: Characterization of metal catalysts with PGM metals at The University of Pretoria in 22 - 27 May 2011.

A part of this work was presented as posters CATSA 2010 (Bloemfontein 7 – 10 November 2010) and the 11th International Conference of Frontiers of Polymers and Advanced Materials (22-27 May 2011) by Authors: Rhiyaad Mohamed, Shawn Gouws and Ernst Ferg with the title: Physical and Electrochemical Characterization of Pt-based Catalysts for Low Temperature PEM Fuel Cells.

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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline Fuel Cell</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst Coated Membrane</td>
</tr>
<tr>
<td>CCS</td>
<td>Catalyst Coated Substrate</td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst Layer</td>
</tr>
<tr>
<td>CNF</td>
<td>Carbon Nanofibre</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct Methanol Fuel Cell</td>
</tr>
<tr>
<td>DST</td>
<td>Department of Science and Technology</td>
</tr>
<tr>
<td>ECSA</td>
<td>Electrochemical Active Surface Area</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray Analysis</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>X-ray Absorption Fine Structure Spectroscopy</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy Carbon</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas Diffusion Layer</td>
</tr>
<tr>
<td>GFC</td>
<td>Gas Flow Channel</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen Oxidation Reaction</td>
</tr>
<tr>
<td>HySA</td>
<td>Hydrogen South Africa</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten Carbonate Fuel Cell</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane Electrode Assembly</td>
</tr>
<tr>
<td>MPL</td>
<td>Microporous Layer</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric Acid Fuel Cell</td>
</tr>
<tr>
<td>PEFC</td>
<td>Polymer Electrolyte Fuel Cells</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton Exchange Membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum Group Metals</td>
</tr>
<tr>
<td>PSA</td>
<td>Perfluorocarbon-sulfonic Acid</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray Diffraction</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating Disc Electrode</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating Ring Disc Electrode</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>SPEFC</td>
<td>Solid Polymer Electrolyte Fuel Cell</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFE</td>
<td>Tetrafluoroethylene</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo-gravimetric Analysis</td>
</tr>
<tr>
<td>XANEX</td>
<td>X-Ray Absorption Near Edge Structure Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1    Introduction

1.1    Motivation

Energy forms the very basis of modern industrialised society. Our standard of living and our economic, social and physical wellbeing are highly dependent on the sufficient, uninterrupted supply of energy. Presently, global energy generation is predominantly based on the extensive utilisation of fossil fuels such as coal, oil and natural gas, which make up 85% of the primary world energy production. Although these energy fuels have been relatively easy to harness, it was shown that their final emissions contribute a considerable proportion to the greenhouse effect and thus impacts negatively on the global climate changes. Coupled with the fact that fossil fuels sources are ultimately limited, the growing gap between increasing demand for energy and a shrinking supply of fuel will have to be met with an increase from alternative primary energy sources without causing the collapse of the ecosystems upon which we depend.

This has become a major concern to governments, industries and individuals worldwide and has brought to light a need for a technological innovation or a combination thereof that will allow for a cleaner and cost effective supply of energy that would be available on demand on a large scale and at any location. The development of a range of alternative, renewable energy sources and climate friendly technologies such as solar, photovoltaic, hydrogen, wind and hydro-powered energies has thus accelerated over the past years. For most of these technologies however, costs still remain high when compared to fossil fuels and difficulties exist in efficiency and variable output as well as storage and availability.

A hydrogen-orientated energy based economy has emerged as a promising technology able to assist in reducing greenhouse gas emissions and improving the security of energy supply at a reduced cost. This energy economy uses hydrogen, as a relatively clean energy carrier and electrochemical devices such as fuel cells, that oxidises a hydrogen based fuel and reduces oxygen (usually from air) to generate water and electricity at the point of use.
A key component of low temperature fuel cell systems in particular are their Platinum Group Metal (PGM) based electrocatalysts. South Africa, the world’s largest PGM producer and holding more than 80% of all known platinum reserves, is in a highly favourable position in a market that is expected to grow to a multi-billion dollar international industry.\(^3\)

As a result, the South African Government and its Department of Science and Technology (DST) launched the Hydrogen and Fuel Cell Technologies Research, Development and Innovation Strategy, called Hydrogen South Africa (HySA.) The long term primary goal of HySA is to generate wealth for the country by developing value added manufacturing of PGM catalysts for the emerging fuel cell market. The strategy also aims to attain a deliverable whereby South Africa supplies some 25% of the global demand for the Proton Exchange Membrane fuel cell (PEMFC) catalysts by 2020.\(^4\)

With the additional mandate of HySA Catalysis to develop and produce a power system suitable for portable and small mobile applications (0.5 – 3 kW), the PEMFC (or simply referred to as the Polymer Electrolyte fuel cell, PEFC) is the preferred candidate. Its high power density (up to 15 W kg\(^{-1}\)) and ability to vary the power output requirements quickly to supply the power demand makes it ideal for use in light-duty vehicles as well as small portable appliances such as laptops and video cameras.\(^4\)

Two of the several major challenges that currently inhibit the large scale commercialisation of PEMFCs are the high cost and low durability of the platinum based electrocatalysts. Currently, only expensive PGM based catalysts are practical for driving the electrochemical reactions in the acidic environment of a PEMFC which is cost inhibitive. Therefore to enable the production of commercially viable PEMFCs both stability and activity need to be improved. As a result, significant advancements need to be made in the development of high-performance, cost-effective and durable electrocatalysts.\(^5\)

This study forms a part of the development of a fuel cell catalyst platform technology for the PEMFC at HySA Catalysis. It specifically focuses on the
synthesis, characterisation and testing of Pt-based binary and ternary alloy electrocatalysts for low temperature hydrogen PEM fuel cells.

1.2 General Aspects of Fuel Cells

1.2.1 A Brief History of Fuel Cells

The timeline of fuel cell development history is shown in Figure 1.1.

![Fuel cell history timeline](image)

The origin of the fuel cell is usually regarded as being discovered by Sir William Robert Grove in 1839, although a publication by Professor Christian Friedrich Schönbein was released a month earlier, which indicated that he may have independently discovered the very same effect. It is however possible that Grove’s interpretation of his own experimental observations were influenced by the discussions he had with Schönbein prior to his own publication of the work. Grove discovered that an electric current is produced when oxygen and hydrogen that are held in separate containers reacted in the presence of a dilute acid and
two electrically connected platinum rod. This principle was discovered by serendipity during an electrolysis experiment shown in Figure 1.2a, when he disconnected the battery from the electrolyser and connected the two electrodes together and observed a current flowing in the opposite direction, consuming the gases of hydrogen and oxygen. He named this device a ‘gaseous voltaic battery’. It consisted of platinum electrodes placed in test tubes of hydrogen and oxygen, immersed in a bath of dilute sulphuric acid as shown in Figure 1.2b. The voltage generated was about one volt (1V). Higher voltages were obtained by connecting cells in series to form a stack. Very little further research and development was carried out for many years to follow.

It was not until the 1950’s that the first practical fuel cell was produced when engineer Dr Francis T. Bacon produced an alkaline fuel cell at Cambridge University (UK), that used an alkaline electrolyte (potassium hydroxide) instead of dilute sulphuric acid. He demonstrated a five-kilowatt fuel cell system that was able to power a welding machine and named this the ‘Baco Cell’.

The fuel cell was then found to be useful for applications in the U.S. Space program in the early 1960’s when the first polymer membrane fuel cell was developed for the Gemini Program by the company General Electric. This was
followed by the Apollo Program that used fuel cells to produce electricity for life support systems, guidance and communications. Even today, the U.S. Space Program continues to use fuel cells successfully however for other ‘terrestrial' applications, fuel cells found little importance until the early 1990's when Ballard Power Systems demonstrated a number of fuel cell powered vehicles, in particular with Daimler Chrysler's, the NECAR 1 and NECAR 2 models. Together with Perry Energy Systems, Ballard also developed a polymer electrolyte membrane (PEM) fuel cell-powered submarine and then later fuel cell powered buses while Energy Partners, a successor of Perry Energy Systems, then also demonstrated the first passenger car running on PEM fuel cells in 1993.

This prompted various car manufacturers and the U.S. Department of Energy to fund and develop a new industry, where by the end of the century, almost every car manufacturer could demonstrate the feasibility of a fuel cell-powered vehicle.

Fuel cell technologies and systems has vastly improved with many universities and research institutions across the world being involved where there are already a number of commercial companies, such as Ballard and Plug Power, being established that can provide suitable systems from small scale portable power supply to home electrification and to large Megawatt power utilities. Fuel cells can offer a clean, efficient, reliable electrical power generation, provided an effective hydrogen infrastructure is available.

1.2.2 Basic Overview of Fuel Cells

A fuel cell is an electrochemical device that directly converts chemical energy into electrical energy without going through the heat exchange process of traditional mechanical heat engines. Fuel cells therefore are not limited by the ‘Carnot' efficiency and promise an efficiency improvement that could lead to considerable energy savings, when other loses such as fuel utilisation and parasitic loses are excluded. Fuel cells also have the advantage over conventional combustion-based technologies in that they produce little or no greenhouse gases.
If pure hydrogen is used as fuel, fuel cells only produce heat and water as by-products. Generally, such a fuel cell process is the reverse of electrolysis of water as hydrogen and oxygen are combined to form water. Unlike batteries that rely on the charging and discharging cycle, fuel cells provide a continuous discharge current to produce power and heat for as long as fuel and oxidant are supplied from external sources.\(^7\)

### 1.2.3 Types of Fuel Cells

Fuel cells may be classified on the basis of various parameters which include the operating temperature, the fuel and the type of electrolyte used. They are however most commonly classified by the type of electrolyte used in the cells. The five common fuel cell types are the Polymer Electrolyte Membrane Fuel Cell (PEMFC), Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell (SOFC). There is another kind of fuel cell known as Direct Methanol Fuel Cell (DMFC) which attracted much attention for its application in portable devices. It is a subcategory of the PEMFC since it is based on liquid fuel (methanol) instead of hydrogen and also capable of using a liquid electrolyte.\(^9\)

Generally, the choice of electrolyte determines the operating temperature of the fuel cell and this affects the physicochemical and thermomechanical properties of materials used in the cell components.\(^10\) The characteristics of these types of fuel cells are compiled in Table 1.1.
Table 1.1 Typical characteristics and essential features of fuel cell types

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrolyte used</th>
<th>Operating temperature (°C)</th>
<th>Cell Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>Polymer membrane</td>
<td>60-140</td>
<td>H₂ → 2H⁺ + 2e⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \frac{1}{2} ) O₂ + 2H⁺ + 2e⁻ → H₂O</td>
</tr>
<tr>
<td>DMFC</td>
<td>Polymer membrane</td>
<td>30-80</td>
<td>CH₃OH + H₂O → CO₂ + 6H⁺ + 6e⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \frac{3}{2} ) O₂ + 6H⁺ + 6e⁻ → 3H₂O</td>
</tr>
<tr>
<td>AFC</td>
<td>Potassium hydroxide</td>
<td>150-200</td>
<td>H₂ + 2 OH⁻→ H₂O + 2e⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \frac{1}{2} ) O₂ + H₂O + 2e⁻ → 2 OH⁻</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid</td>
<td>180-200</td>
<td>H₂ → 2H⁺ + 2e⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \frac{1}{2} ) O₂ + 2H⁺ + 2e⁻ → H₂O</td>
</tr>
<tr>
<td>MCFC</td>
<td>Lithium/Potassium Carbonate</td>
<td>650</td>
<td>H₂ + CO₃⁻→ H₂O + CO₂ + 2e⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \frac{1}{2} ) O₂ + CO₂ + 2e⁻ → CO₃²⁻</td>
</tr>
<tr>
<td>SOFC</td>
<td>Yttria stabilised Zirconia</td>
<td>1000</td>
<td>H₂ + O²⁻→ H₂O + 2e⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \frac{1}{2} ) O₂ + 2e⁻ → O²⁻</td>
</tr>
</tbody>
</table>

From the types of fuel cells listed the PEMFC, also known as the Solid Polymer Electrolyte Fuel Cell (SPEFC) has emerged to the forefront as the most promising power source. It offers the advantage of low weight and volume with using a solid proton conducting membrane as the electrolyte. It also has a relatively low operating temperature, typically around 80°C which gives the advantage of quick start up and coupled with the very high power density PEMFC’s generate (e.g. given at 1,400 W kg⁻¹ for an 80 kW PEMFC stack with a pure hydrogen source), it seems the most likely candidate as a power source for transportation, small-scale power generation and portable power.¹¹,¹²

However, lower operating temperatures results in the kinetic mechanism to be slower, a problem that is addressed by using specialised electrocatalysts and electrodes. These electrocatalysts are generally platinum based with high surface area, which increases the cost of the final power supply. Much research focuses into designing electrode structures that minimise the electrocatalyst loading while maximising its utilisation.¹³
1.3 The Polymer Electrolyte Membrane Fuel Cell (PEMFC)

1.3.1 Principle of PEM Fuel Cells

Typically the PEM fuel cell consists of a set of components that include the membrane electrode assembly (MEA) which is at the heart of the system. The components of the MEA include: 1) the proton exchange membrane (PEM); 2) catalyst layers (CL); 3) gas diffusion (backing) layers (GDL) and micro-porous layers (MPL) (together referred to as the diffusion media) through which gases are delivered via the gas flow channels (GFC’s) and the fluid flow field (bipolar) plate hardware (Fig 1.3).

![Figure 1.3](image.png)

Figure 1.3 A schematic of the PEM fuel, showing the MEA and cell hardware, adopted from.

The MEA is designed in such a way that the reduction and oxidation half reactions are separated by the membrane, such that protons are able to migrate through the membrane and electrons are forced to travel along an external circuit to generate electricity. The catalyst layers facilitate each half reaction and the
GDL further improves the efficiency of the systems by allowing direct and uniform access of the hydrogen and oxygen to the respective catalyst layers. Typically, the catalyst layers can be cast as thin films that can be either transferred to the membrane via a decal or applied directly. The resulting three-layer structure is referred to as a catalyst coated membrane (CCM). Alternatively, the catalyst layers may be deposited onto the GDL in which case it is referred to as a catalyst coated substrate (CCS) or gas diffusion electrode (GDE). Finally, the CCM is sandwiched between two GDL, or two CCS are bonded on either side of a membrane. In both cases the resultant product is a five-layered structure called the membrane electrode assembly (MEA).\textsuperscript{15}

The GDL is not only responsible for heat/water removal but also ensures the direct and uniform access of hydrogen and oxygen to the anode and cathode catalyst layers respectively. The gases are fed (by forced convection) through their respective GFC’s and reach their respective CL’s via diffusion through the GDLs. The hydrogen is oxidised via the hydrogen oxidation reaction (HOR) at the anode CL producing protons and electrons as shown in equation (1.1):

\begin{equation}
\text{Anode Reaction: } \quad H_2 \rightarrow 2H^+ + 2e^- \quad (1.1)
\end{equation}

The protons released during oxidation of hydrogen are conducted through a proton exchange membrane to the cathode. Electrons move via the carbon support to the anode current collector and then to the cathode current collector via an external circuit with a resistive load.

Oxygen is reduced via the oxygen reduction reaction (ORR) with protons and electrons at the cathode CL to produce water as shown in Equation (1.2).

\begin{equation}
\text{Cathode reaction: } \quad \frac{1}{2}O_2 + 2H^+ + 2e^+ \rightarrow H_2O(l) \quad (1.2)
\end{equation}

The net result of these simultaneous reactions is a direct electric current resulting from the flow of electrons (caused by the potential difference at opposite ends) through the external circuit, given by Equation (1.3).
1.3.2 Main Components of the PEMFC

1.3.2.1 Polymer Electrolyte Membrane (PEM)

The membrane refers to a thin layer of a solid electrolyte (usually 10 – 100 µm thick), which allows protons to move from the anode to the cathode. Ideally the membrane material should exhibit high proton conductivity, while preventing electron transport and act as an adequate barrier against the cross-over of hydrogen fuel from the anode and oxygen reactant from the cathode. Membranes are also required to be chemically stable in the fuel cell environment where hydroxyl (HO⁻) and perhydroxyl (HOO⁻) radicals may be present, thermally stable throughout the operating temperature range and be mechanically robust.¹⁴⁻¹⁶

Typically most membranes are based on the perfluorocarbon-sulfonic acid (PSA) ionomer that is marketed under the trade name Nafion® (Fig 1.4). This was first developed by the DuPont Company in 1960’s.¹⁰ It is essentially a polymeric backbone of tetrafluoroethylene (TFE) and ether-linked side chains ending in a perfluorocarbonsulfonate moiety. The polytetrafluoroethylene (PTFE or Teflon) backbone provides the membrane with physical strength while the perfluorocarbonsulfonate functional groups provide charge sites for proton transfer.
transport.\textsuperscript{14} Other membranes for PEM fuel cells that differ in the length and flexibility of the side chain as well as the ion exchange capacity include Flemion\textsuperscript{®} (Asahi Glass), Aciplex\textsuperscript{®} (Asahi Chemicals), ‘C’ membrane (Chlorine Engineers), Aquivion\textsuperscript{®} (Solvay) and Gore-Select\textsuperscript{®} (G.L Gore and Associates Inc.).\textsuperscript{14}

On-going research is being conducted in the field of membranes to reduce costs and improve the water management properties or to eliminate the reliance on water completely for proton conduction which would enable operation at higher temperatures. This in turn would increase performance by increasing the specific rates of reactions.\textsuperscript{17-19}

\subsection{1.3.2.2 Catalyst and Catalyst Layer (CL)}

The catalyst layer is in direct contact on the one side to the membrane and with the backing layer on the other. It is here where the reactions of HOR and ORR occur. Although the reaction of oxygen and hydrogen to form water is a thermodynamically spontaneous reaction, the reaction rate is extremely slow under normal conditions, especially for the ORR. For this reason specialised electrocatalysts are used to accelerate the reactions by reducing the reaction activation barrier.\textsuperscript{14}

The type of catalyst used in PEMFCs depends on the fuel it uses. In the case of low temperature hydrogen PEMFCs, Platinum and platinum alloys are considered as the best electrocatalysts for both the HOR and the ORR\textsuperscript{15}, thus the CL contributes a significant portion of the cost of the fuel cell and one of the major barriers for commercialisation of PEM fuel cells. Generally the platinum is finely dispersed on the surface of a catalyst support, typically carbon powders (~40 nm) with high mesoporous area (> 75 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{16}

The catalyst surface area is of importance where particles in the range of 4 nm are used.\textsuperscript{16} The reaction zone is further enhanced by roughening the surface or incorporating the ionomer in the catalyst layer.\textsuperscript{14} The large surface area of both the carbon and the catalyst increases the three phase reaction zone which consists of the reactant gas phase, the electron supply to the catalyst particle and
the protons from the electrolyte that have to be in contact with each other to provide efficient current distribution. The three phase reaction zone is indicated in Figure 1.5.

![Figure 1.5 Schematic of three phase reaction zone](image1)

An ideal support material is required to have (i) high electrical conductivity, (ii) uniform and high degree of catalyst dispersion, (iii) a mesoporous structure to allow the ionomer and polymer electrolyte to bring the catalyst particles close to the reactants and (iv) to provide sufficient access of reactant gases to the catalyst surface, thereby maximising the triple phase boundary, the site at which the reaction occurs, while also (v) being highly corrosion resistant.

The most commonly used support materials are, highly conductive carbon blacks (CBs) of turbostratic structures with high surface areas, such as Vulcan XC-72R (Cabot Corp, 250 m² g⁻¹), Shawinigan (Chevron, 80 m² g⁻¹), Black Pearl 2000 (BP2000, Cabot Corp., 1500 m² g⁻¹), Ketjen Black (KB EC600JD & KB EC600J, Ketjen International, 1270 m² g⁻¹ and 800 m² g⁻¹, respectively) and Denka Black (DB, Denka, 65 m² g⁻¹). Other catalyst support materials include carbon nanotubes (CNT), carbon nanofibers (CNF) or they may also be non-carbonaceous materials such as suboxides of titanium or tungsten, indium or antimony doped tin oxides, alumina, silica and tungsten carbide as well as conducting polymers.
Research efforts have focussed around reducing the catalyst loading for cost reductions and to increase tolerance to contaminants. Most activities are focused on exploring new catalyst materials by alloying or otherwise nanostructuring Pt particles with less expensive transition metals. Alloys like Pt-Ru/C, Pt-Ir/C, Pt-V/C, Pt-Rh/C, Pt-Cr/C, Pt-Co/C, Pt-Ni/C, Pt-Fe/C, Pt-Mn/C, Pt-Pd/C and Pt-Mo/C are most commonly investigated as possible binary catalysts. Investigations into Pt-based ternary catalyst are also done where Pt is commonly combined with two of the first row transition metals.

1.3.2.3 Gas Diffusion Layer (GDL)

The GDL has the basic functions of transporting reactant gases from the gas flow channels to the catalyst layers effectively and draining liquid water from the catalyst layers to the flow channels. The layer has to also conduct electrons efficiently with low resistance and to keep the membrane wet under low humidity conditions.

An ‘ideal’ GDL should thus have good gas diffusion, with optimum bending stiffness, porosity, surface hydrophobicity, air permeability, water vapour diffusion, electrical/electronic conductivity, crack free surface morphology, high mechanical integrity and enhanced oxidative stability. In addition, it should display good ‘freeze-thaw’ cycling.

The above requirements are achieved by non-woven, porous carbon fiber paper or woven carbon cloth that is typically 100-300 µm thick. The GDL may also be divided into a low porous layer and consist of a highly porous layer that is in direct contact with the catalyst layer. This microporous layer is typically composed of fine carbon particles and a hydrophobic bonding agent. The microporous layer provides proper pore sizes to enhance the electronic contact between the catalyst layer and the macroporous carbon layer of the GDL.
1.3.2.4 Flow-Field (Bipolar) Plates

Flow-field plates constitute the backbone of a hydrogen fuel cell, conduct current between individual cells, facilitate water and thermal management through the cell and provide pathways for the reactant gases.\textsuperscript{27} When the flow channels are formed on both sides of the same plate, one side serves as the anode plate and the other side as the cathode plate to the adjacent cell, and the plate unit is called bipolar (separator) plate. When the reactant flow channels are formed on the anode and cathode plates as is the case with single fuel cells, the plates are normally referred to as fluid flow-field plates.\textsuperscript{28}

The requirements of the flow field plates are as follows\textsuperscript{28}:

- good electrical conductivity (> 100 S cm\(^{-1}\) bulk conductivity),
- high thermal conductivity (> 0.2 W m\(^{-1}\) K\(^{-1}\)),
- high chemical and corrosion resistance,
- mechanical stability toward compression forces,
- low permeability for hydrogen,
- low-cost and recyclable material
- low weight and volume
- low surface contact resistance

The plates are commonly made of graphite composites which are considered the standard material for PEM fuel cells. Graphite containing products are however brittle and permeable to gases and thus metals such as aluminium, stainless steel, nickel and titanium have also been used. Metals enjoy higher mechanical strength however they are susceptible to corrosion in the harsh acidic and humid environment inside the PEM fuel cell. Researchers are looking into the possibility to develop bipolar plates that have the combined properties of graphite and metals and thus would exhibit ideal characteristics of high corrosion resistance and low surface resistance with high mechanical strength, no brittleness and no permeability to reactant gases.\textsuperscript{28}
1.4 Thermodynamic Considerations of PEM Fuel Cells

1.4.1 Theoretical Cell Voltage

The fuel cell thermodynamics have been extensively described in literature and only the basic aspects will be discussed here. The overall fuel cell reaction operated with hydrogen and oxygen given by Eq. (1.3) is the same as the reaction of thermal hydrogen combustion which is exothermic releasing energy in the process. The theoretical heat (enthalpy) of the reaction, is \( \Delta H = -286 \text{ kJ mol}^{-1} \) (at 298.15 K). If the fuel cell is reversible all the Gibbs free energy \( (\Delta G) \) would be converted to electrical energy by the following equation:

\[
\Delta G = \Delta H - T \Delta S \tag{1.4}
\]

However some irreversible losses in the energy conversion occur due to the creation of entropy, \( \Delta S \). The theoretical or reversible potential of the fuel cell is given by the following equation:

\[
\Delta G_R = -nFE \tag{1.5.1}
\]

which is rearranged as follows:

\[
E_R = \frac{-\Delta G}{nF} \tag{1.5.2}
\]

Where \( \Delta G \) is the Gibbs free energy, \( n \) is the number of electrons involved in the fuel cell reaction is 2 per molecule of hydrogen, \( F \) is the Faraday constant \( (F = 960485 \text{ C mol}^{-1}) \) and \( E_R \) is the theoretical voltage. The theoretical fuel cell voltage is of 1.229 V at (under standard conditions) and decreases with an increase in temperature. At typical PEM fuel cell operating temperatures, of 60-80°C, this value decreases to between 1.20-1.18 V.\(^6\)

The cell potential for the fuel cell reactions is obtained from the following equation:
\[ E_R = E_0 + \frac{RT}{nF} \ln \left( \frac{\Pi_{H_2} \Pi_{O_2}^{0.5}}{\Pi_{H_2O}} \right) \]  

(1.6)

where \( \Pi \) is the partial pressure of the reactants relative to atmospheric pressure, when reactants and products are both in the gaseous state. When liquid water is produced in the fuel cell, \( \Pi_{H_2O} = 1 \).\textsuperscript{29}

The actual cell voltage and efficiency of a fuel cell are due to various losses associated with the kinetics and dynamics of the processes, reactants and products and can be expressed by Eq. (1.7).\textsuperscript{29}

\[ V_{cell} = E_R - \Delta V_{loss} \]  

(1.7)

The different phenomena that cause efficiency losses are discussed below.

### 1.4.2 The Open Cell Voltage (OCV)

Under conditions where no electrical load is applied to the cell i.e. the circuit is not closed, no current will be generated and the voltage provided is known as the open-circuit voltage (OCV). Under OCV conditions, true equilibrium potential is achieved and the measured voltage represents the thermodynamic voltage, \( E_R \), which in practice is always lower than the theoretical OCV\textsuperscript{30} as shown in Figure 1.6. This difference is mainly due to fuel cross over from the anode to cathode and can be caused by impurities or current leakage and is called the irreversible voltage loss.\textsuperscript{29}
1.4.3 Working Potential

When the circuit is closed with a load applied, the potential is expected to drop even further as a function of the current being generated and continue to decrease as the current density increases. This decrease is expressed by a polarisation curve which plots the cell voltage (V) versus the current density (mA cm\(^{-2}\)) and it provides information about the polarisation loses which include kinetic-related (activation) losses, cell resistance (ohmic) losses and mass transport (concentration) losses. Such a polarisation curve can be divided into three regions corresponding to the regions where activation, ohmic and mass transport voltage losses are dominating respectively.

1.4.3.1 Activation Losses

In the low current density region the working potential drops as a result of charge-transfer kinetics, i.e. the HOR and ORR rates at the electrode surfaces. These are dominated by the Butler-Volmer equation

\[
  i = i_0 \left[ \exp \left( \frac{\alpha n F \eta_{act}}{RT} \right) - \exp \left( - \frac{\beta n F \eta_{act}}{RT} \right) \right]
\]

(1.8)
where $\eta_{\text{act}}$ denotes the activation losses and represents the overpotential of the individual electrode reactions, i.e. how far to move away from $E_r$ to get the reaction going; $\alpha$ and $\beta$ are transfer coefficients and $\alpha + \beta = 1$; $n$ is the apparent electron number involved in the rate determining step and $i_0$ is the exchange current density.

When $\eta_{\text{act}}$ is large enough such that the other factors become negligible, equation (1.8) is simplified and rearranged to give

$$\eta_{\text{act}} = a + b \log i$$  \hspace{1cm} (1.9)

where $a = -(2.303RT/\alpha nF)\log i_0$, and the slope $b = 2.303RT/\alpha nF$. This indicates that a linear relationship exists between the activation losses and the logarithmic of current density given by the so-called Tafel equation (1.9).\(^{29}\)

Under PEM fuel cell operating conditions, the electrode potentials of the anode and cathode deviate from equilibrium, and Eq. (1.8) applies to both sides. Thus for the anode, the overpotential $\eta_a$ for the HOR is given by equation (1.10),\(^*\)

$$i_a = i_0^H \left\{ \exp \left( \frac{\alpha_H n_H F \eta_a}{RT} \right) - \exp \left[ -\frac{\beta_H n_H F \eta_a}{RT} \right] \right\}$$  \hspace{1cm} (1.10)

where $i_0^H$ is the exchange current density of the HOR, $n_H$ is the electron number at the rate determining step, $\alpha_H$ and $\beta_H$ are the electron transfer coefficients. The overpotential $\eta_c$ for the ORR at the cathode can be similarly expressed. The working potential at low current densities due to polarisation losses is thus given by $\eta_{\text{act}} = \eta_a + \eta_c$.\(^{29}\)

1.4.3.2 Ohmic Losses

In the intermediate current density region of the polarisation curve, internal resistance losses dominate. These loses are as a result of the various components of the fuel cell including the electric contact resistance, the electrode
resistance, as well as the proton resistance of the electrolyte membrane. This internal resistance is referred to as the ohmic resistance, \( R_{\text{ohmic}} \). The drop in the working potential due to the ohmic resistance is denoted as ohmic losses, \( \eta_{\text{ohmic}} \), and defined as \( \eta_{\text{ohmic}} = iR_{\text{ohmic}} \).^{29}

### 1.4.3.3 Mass Transport Losses

In the high current density region, the working potential decreases drastically due to the transfer speed of the reactants and products being slower than the reaction rate. The transport of reactants and products which occurs by convection and diffusion in the fuel cell is called mass transport and it is due to the concentration gradient in the diffusion media. Concentration polarisation causes a concentration loss or concentration overpotential, which is caused by a drop in the concentration of the reactants as they are consumed in the reaction.\(^{30}\)

The theoretical voltage losses resulting from mass diffusion are called Nernst losses, \( \eta_{\text{conc}} \), and are calculated by:

\[
\eta_{\text{conc}}^{1} = E - E^{*} = \left( E^{0} - \frac{RT}{nF} \ln \frac{1}{c_{R}} \right) = \frac{RT}{nF} \ln \frac{c_{R}^{0}}{c_{R}^{*}} \quad (1.11)
\]

where \( E^{*} \) is the real potential, \( c_{R}^{0} \) is the bulk concentration of the reactant, \( c_{R}^{*} \) is the reactant concentration on the catalyst layer, and the build-up of product is ignored.\(^{29}\)

In the mass diffusion region \( c_{R}^{*} \) is very small compared to \( c_{R}^{0} \) resulting in high efficiency losses. When the Butler-Volmer equation is modified to account for concentration changes in the reactant and product, which also affects activation losses, it is given by

\[
i = i_{0}' \left\{ \frac{c_{R}^{*}}{c_{R}^{0}} \exp \left( \frac{\alpha nF \eta_{\text{act}}^{*}}{RT} \right) - \frac{c_{R}^{*}}{c_{R}^{0}} \exp \left( - \frac{\beta nF \eta_{\text{act}}^{*}}{RT} \right) \right\} \quad (1.12)
\]
where \( i_0 \) is the exchange current density obtained when the concentrations of the reactants and products are \( C_R' \) and \( C_P' \) respectively, and \( \eta_{act}^* \) is the overpotential corresponding to \( E^* \). Under high-current density, the second term in equation (1.12) is ignored and thus it is simplified and rearranged to

\[
\eta_{act}^* = \frac{RT}{anF} \ln \frac{iC_R'}{i_0C_R^0} \quad (1.13)
\]

The increase in activation losses resulting from the mass transport of reactants and products, \( \eta_{conc}^2 \) can be calculated by

\[
\eta_{conc}^2 = \eta_{act}^* - \eta_{act} = \left( \frac{RT}{anF} \ln \frac{iC_R'}{i_0C_R^0} \right) - \left( \frac{RT}{anF} \ln \frac{iC_R'}{i_0C_R^0} \right) = \frac{RT}{anF} \ln \frac{C_R^0}{C_R^0}
\]

\[
(1.14)
\]

The total voltage losses caused by mass diffusion are thus given by

\[
\eta_{conc} = \eta_{conc}^1 + \eta_{conc}^2 = \left( 1 + \frac{1}{\alpha} \frac{RT}{nF} \ln \frac{C_R^0}{C_R^0} \right)
\]

\[
(1.15)
\]

### 1.5 Kinetic Considerations of PEM Fuel Cells

The kinetics of an electrochemical reaction may also be described by the Butler-Volmer equation:

\[
i = i_0 \left[ \exp \left( \frac{-anF}{RT} \eta \right) - \exp \left( \frac{(1-\alpha)nF}{RT} \eta \right) \right]
\]

\[
(1.16)
\]

where \( i_0 \) is the exchange current density of the electrochemical reaction at its reversible potential on a certain surface, \( \alpha \) is the transfer coefficient at the rate determining step, \( n \) is the number of electrons transferred and \( \eta \) is the
overpotential (for the anode reaction $\eta_a = E_a - E_{eq} > 0$, for the cathode reaction $\eta_c = E_c - E_{eq} < 0$).\textsuperscript{30}

Applying the Butler-Volmer equation to the fuel cell anode and cathode reaction, the anodic and cathodic kinetic current densities can be expressed as eq. (1.18) and (1.19) respectively,

\begin{align*}
i_a &= i_{0,H_2} \left[ \exp \left( \frac{-\alpha_H n_{H} F \eta_a}{RT} \right) - \exp \left( \frac{(1-\alpha_H)n_{H}F\eta_a}{RT} \right) \right] \quad (1.18) \\
i_c &= i_{0,O_2} \left[ \exp \left( \frac{-\alpha_O n_{O} F \eta_c}{RT} \right) - \exp \left( \frac{(1-\alpha_O)n_{O}F\eta_c}{RT} \right) \right] \quad (1.19)
\end{align*}

where

\begin{align*}
i_c &= \text{the cathodic current} \\
i_a &= \text{the anodic current} \\
i_{0,O_2} &= \text{the apparent exchange current density for the ORR} \\
i_{0,H_2} &= \text{the apparent exchange current density for the HOR} \\
n_{\alpha,O} &= \text{the electron transfer number in the rate determining step for the ORR} \\
n_{\alpha,H} &= \text{the electron transfer number in the rate determining step for the HOR} \\
\alpha_O &= \text{the transfer coefficient in the rate determining step for the ORR} \\
\alpha_H &= \text{the transfer coefficient in the rate determining step for the HOR}
\end{align*}

and it can be seen from equations (1.18) and (1.19) that $i_c = -i_a$.\textsuperscript{32}
Since the parameters of $R$, $T$ and $F$ are defined constants the Butler-Volmer equation may be also be simplified to the following:

$$i = i_0 \left[ 10^\frac{\eta}{a} - 10^{-\frac{\eta}{b}} \right] \quad (1.20)$$

where $a$ and $b$ are referred to as Tafel slopes (TS) and equal to $\frac{2.303 \, RT}{\alpha n_{a,0} F}$ and $\frac{2.303 \, RT}{\beta n_{a,H} F}$ respectively. The first term in the brackets of Eq. (1.20) represents the kinetics of the forward reaction (oxidation) and the second term represents the kinetics of the backward reaction (reduction). The value of $n_{a,H}$ has been widely reported in literature to be 1.0\textsuperscript{32} while the value for $n_{a,0}$ has been reported as a value of 2.0 where the slope is approximately 60mV decade$^{-1}$ and a value of 1.0 where the slope is approximately 120mV decade$^{-1}$, corresponding to a low cathode potential where the electrode surface is that of pure Pt.$^{33}$

When the overpotential is large, the backward reaction becomes negligible and one term in the Butler-Volmer reaction may be ignored. For the ORR, where $n_c < 0$, the kinetics may then be described as

$$i_c = i_{0,O_2} \left[ \exp \left( \frac{-\alpha H \eta_{a,0} F \eta_a}{RT} \right) \right] \quad (1.21)$$

This may then be simplified as the well-known Tafel equation describing that at a certain current density, the overpotential is linearly dependant on the logarithm of current density which correlates back to Eq. (1.9) given by $\eta_{act} = a + b \log i$.

The exchange current density, which represents the net current density when the forward reaction equals that of the backward reaction, may be determined from the intercept at the current density axis, is indicated in Figure 1.7. The higher the Tafel slope, the faster the overpotential increases with the current density and thus the slower the reaction kinetics. On Pt and Pt alloys this exchange current density has been reported around $10^{-10}$ A cm$^{-2}$ at low overpotential and around $10^{-6}$ A cm$^{-2}$ at high overpotential and varies depending on the catalyst used.$^{33}$

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1.6 Electro catalysis in PEM Fuel Cells

In general, electrocatalysis can be considered as a specific type of heterogeneous catalysis whereby reactants and products adsorb on the electrocatalyst surface during the reaction process. In the process, the reactant is activated by the interaction with the electrocatalyst surface and rapidly and selectively converted to products. The products are then released from the catalyst surface by desorption, enabling the catalyst sites to be free for the next cycle of the reaction to continue.\(^\text{23}\)

The HOR (anode reaction) and the cathode reaction, the ORR can be described by both the mechanisms and the application of different electrocatalysts with respect to each reaction. These catalysts are either state of the art or in the state of development. The main focus is directed at the oxygen reduction reaction as this is one of the main topics of this dissertation.

It is well known that Pt supported on carbon is the most commonly used catalyst for both the anode and cathode reactions because of its high activity.\(^\text{35}\) However
due to its high cost it negatively impact the price of MEAs and therefore it is a barrier to the commercialisation and widespread usage of fuel cells.

1.6.1 The Hydrogen Oxidation Reaction (HOR)

The hydrogen oxidation reaction takes place at the anode by the reaction given by Eq. (1.1). The net reaction proceeds via two pathways, the Tafel-Volmer mechanism, Eq. (1.22) and the Heyrovsky-Volmer mechanism, Eq. (1.23).

Tafel-Volmer: \[ 2Pt + H_2 \rightarrow 2Pt + 2H^+ + 2e^- \] (1.22)

Heyrovsky-Volmer: \[ Pt + H_2 \rightarrow Pt - H_{ad} + e^- \rightarrow Pt + H^+ + e^- \] (1.23)

The favoured mechanism depends on both the catalyst used as well as the electrolyte medium. Although the reaction kinetics of the HOR are considerably faster relative to the ORR and this enables catalyst loading to be substantially lower at the anode. However a serious poisoning problem can occur when impure hydrogen is used. Typical Pt-loadings for the anode are in the region of 0.2-0.4 mgPt cm\(^{-2}\) with an aim to reduce this to 0.05 mgPt cm\(^{-2}\) being easily achievable due to the fast reaction kinetics.\(^{36}\) However, carbon monoxide present in hydrogen supplied from steam reformers adsorbs strongly and irreversibly on the pure Pt surface, blocking hydrogen adsorption. Efforts have thus focused alloying Pt with other base metals such as Ru, as well as using carbides and Raney nickel, in an attempt to find alternative HOR catalysts that are not susceptible to CO poisoning.\(^{30}\)

1.6.2 The Oxygen Reduction Reaction (ORR)

The ORR takes place at the cathode via the reaction given by Eq. (1.2). As mentioned the ORR kinetics is sluggish and much slower compared to the HOR and thus most of research attention has been directed at this reaction. The reaction pathway is quite complex, depending on the pH of the electrolyte and the nature of the catalyst, and involves a number of elementary steps with
different intermediates. A simplified version of the mechanism is shown in Figure 1.8 showing the products of hydrogen peroxide and water.

\[
\begin{align*}
O_2 & \xrightarrow{k_1} O_{2,\text{ad}} \xrightarrow{k_2} H_2O_{2,\text{ad}} \xrightarrow{k_3} H_2O \\
H_2O_2 & \xleftarrow{k_4} \xrightarrow{k_5} H_2O
\end{align*}
\]

**Figure 1.8** Simplified version of the ORR pathways.

In fuel cell processes, the 4-electron transfer process of \( O_2 \) reduced directly to \( H_2O \) given by the rate constant, \( k_1 \), is preferred. Although the interpretation of the reaction pathway of the ORR has not been completely resolved, studies show that the indirect reduction of \( O_2 \) via the \( H_2O_2 \) intermediate, given by the rate constants \( k_2, k_3 \) and \( k_4 \) is the most possible pathway, on Pt and Pt bimetallic catalysts, in a special case where \( k_1 = 0 \). This is unwanted as the peroxide radicals formed is detrimental to the membrane and electrode components.

The ORR has also been studied by theoretical calculations including Density Functional Theory (DFT) calculations and it was found that the ORR activity is structure dependent. Two mechanisms were proposed whereby the dissociative mechanism operates with low overpotential with the associative mechanism becoming favourable with increasingly high overpotential.

During the dissociative ORR pathway oxygen is split (O-O bond breakage) and is adsorbed on the Pt surface and where it consequently gains two electrons to form water. A match between the O=O bond length (1.3 Å) and the Pt-Pt nearest neighbour distance (~ 2.7 Å), is thus very significant for the oxygen dissociation from the Pt surface. In order to enhance the ORR dissociative pathway on the Pt surface, Pt particle size and composition needs to optimised, by methods such as alloying Pt with other metals. Theoretical calculations on the \( O_2 \) binding energy predict that Pt:M (M = Fe, Ni, Co, etc.) show a higher catalytic activity towards
the ORR as the Pt-Pt bond distance is reduced by lattice contraction, becoming more favourable towards the ORR dissociative adsorption.\textsuperscript{39}

Commonly used catalysts include Pt-based and other noble metal alloys, carbon materials, quinone and its derivatives and transition metal carbides, chalcogenides and macrocyclic compounds.\textsuperscript{24}

One of the key concepts of alloying Pt for fuel cells that are to be used in the automotive industry is to reduce the Pt loading in catalyst layers, which is currently at 0.4-0.6 mg\textsubscript{Pt} cm\textsuperscript{-2} for the cathode to approximately \textasciitilde0.15 mg\textsubscript{Pt} cm\textsuperscript{-2} for the anode.\textsuperscript{35} Alloying not only reduces the Pt content but also increases the catalytic activity and since the ORR kinetics is so sluggish, an activity benchmark has been set to increase its activity by a factor of 4 for commercialisation.\textsuperscript{39}

The ORR activity has been shown to be influenced by the size, shape and distribution of the metal particles.\textsuperscript{40} Thus the crystallite size and crystallographic structure of the catalyst particles are of importance, showing a maximum mass activity at a size of approximately 3-4nm.

Current state-of-the-art MEAs typically consist of highly dispersed Pt on carbon with a loading of approximately 0.4 mg\textsubscript{Pt} cm\textsuperscript{-2}. Such catalysts have a specific activity ($i_s$) at 80°C and a partial pressure of \textasciitilde100kPA at 0.9V of about 180-210\textmu A cm\textsuperscript{-2} and a mass activity ($i_m$) in the range of 0.11-0.16 A mg\textsuperscript{-1}Pt. In order to enable commercialisation of PEM fuel cells, it is required to reduce the Pt-loading to \textsuperscript{1}{/4} of the current state-of-the-art MEA catalyst layer, without any performance loss and at the same time maintaining low rates of degradation.\textsuperscript{39}

1.7 Catalyst Synthesis Methods

Several methods are currently employed to synthesise both state of the art Pt supported on carbon (Pt/C) and Pt-based alloy catalysts. Although no single method is superior to the others, one method may be preferred depending on the end application of the catalyst and the instrumentation available.\textsuperscript{41} Methods used
to synthesise these catalysts include low-temperature chemical precipitation, colloidal, sol-gel, impregnation-reduction using various reducing agent, microemulsion, electrochemical, spray pyrolysis, vapour deposition and high energy ball milling.\textsuperscript{41-48}

The key parameters in the preparation of carbon supported Pt alloys are 1) the Pt:M\textsubscript{1}:M\textsubscript{2} (M = other transition metal) ratio as this may differ from that expected from the concentrations of the initial starting materials used, 2) the amount of M\textsubscript{1} and M\textsubscript{2} alloyed as this may be lower than the total M content in the catalyst and 3) the metal particle size as this influences the metal surface area which has a direct influence on the electrocatalytic activity of the alloy.\textsuperscript{42}

The low-temperature chemical precipitation method may be used to prepare both supported and unsupported catalysts of Pt\textsuperscript{43} and Pt-based alloys.\textsuperscript{44} It has the advantage of using “mild conditions” of low temperature and fairly simple procedure of which involve the addition of a suitable reducing agent to a platinum-salt solution or solution of two metal precursors. Ideally the precursor salt is reduced to the metallic state and precipitates out of solution, forming unsupported catalysts that are then filtered and washed. Sodium borohydride and hydrazine hydrate are used as suitable reducing agents with the former being preferred. To prepare supported catalysts, carbon black is added prior to the reduction of the metal salts.\textsuperscript{41}

The colloidal method is similar to the chemical precipitation method but involved the added benefit of a capping agent that allows for size control of the catalysts and prevents agglomeration of the catalyst particles.\textsuperscript{41} Pt and Pt-based alloys have been prepared by this method that involved combining the metal source, reducing agent and capping agent together and simply mixing. This method has also been adapted to allow for size and composition control as well as shape control for Pt nanoparticles.\textsuperscript{41}

Carbon supported alloys are also commonly prepared by first preparing the carbon supported platinum (Pt/C) followed by impregnation of the second and third metal in the case of binary and ternary alloys respectively followed by
alloying at high temperatures. However, this thermal treatment at high temperatures gives (e.g. 900°C) rise to undesired metal particle growth by means of sintering and coalescence of the platinum particles.\textsuperscript{47} It has also been noted that a decrease occurs in the mass activity for the dispersed Pt electroactivity towards the ORR for particles larger than 3.5 nm, thus it is important to avoid excessive metal particle sintering.\textsuperscript{49, 50} However such catalysts as in the case of Pt\textsubscript{5}Co/C and Pt\textsubscript{5}Ni/C have been shown to have high catalytic activity and exhibit increased stability particularly an increased resistance towards sintering under fuel cell operations.\textsuperscript{51} Leaching of the non-Pt metal has also been performed (either chemically in acidic solutions or electrochemically) to form a skeletal-type catalyst. It should be noted that great care need to be taken to eliminate O\textsubscript{2} in the synthesis process as this will result in the corrosion of carbon at high temperatures.\textsuperscript{42}

1.8 Characterisation of Supported Platinum Catalysts

New catalysts prepared by any methods require to be compared to current commercially available catalysts or previous work done by other research groups. Characterisation of synthesised electrocatalysts may be done by both physical methods, usually ex-situ and electrochemical methods which may be both ex-situ and in-situ in the case of fuel cell testing. The most important aspects of the theory involved in the characterisation methods are outlined here. The practical aspects of will be covered in Chapter 2.

1.8.1 Physical characterisation techniques

These include measurements of particle size and size distribution of the active components. The surface area, the electrochemical active surface area, the phase and composition as well as morphology and crystal planes of the active components may also be determined. The active components in the case of supported electrocatalysts are the Pt and Pt-based alloys whereas the carbon on which they are supported provided good conductivity.\textsuperscript{30}
Powder X-Ray Diffraction (PXRD) and Transmission Electron Microscopy (TEM) are the most commonly used techniques for the identification of the particle size of the dispersed electrocatalyst crystallites. Information about the chemical composition and crystallographic structure may also be determined by XRD. Other techniques employing the use of X-rays such as X-Ray Photoelectron spectroscopy (XPS), X-Ray Absorption Fine Structure Spectroscopy (EXAFS) and X-Ray Absorption Near Edge Structure Spectroscopy (XANES) may be used to determine the degree of alloying, chemical states of metals and oxidation states of the metals of the electrocatalysts. Energy Dispersive X-Ray analysis (EDX) or otherwise known as Energy Dispersive Spectroscopy (EDS) provides information about the composition of a prepared alloy and is closely related to Scanning Electron Microscopy (SEM) and TEM analysis, while Thermo-Gravimetric Analysis (TGA) may provide information about the metal to carbon ratio with respect to supported electrocatalysts after preparation.

1.8.2 Electrochemical characterisation techniques

The reactions occurring at the anode and cathode both involve the transport of electrons as well as reactants and products and only the catalyst surfaces at the catalyst-ionomer-reactant three phase regions are electrochemically active. This area, referred to as the electrochemical active surface area (ECSA). Cyclic voltammetry (CV) is a well-established technique used to measure the ECSA of the catalyst. It makes use of either the adsorption/desorption of atomic hydrogen or the oxidative stripping of adsorbed carbon monoxide. The ECSA may be compared to the total surface area measurements of the catalyst particles obtained from physical characterisation methods to reveal the actual catalyst surface utilisation.

Rotating Disc Electrode (RDE) and Rotating Ring Disc Electrode (RDDE) techniques can be used to probe reaction mechanisms as well as evaluating the performance/stability of the prepared catalysts. The measurements are used to give an indication of the catalytic activity of a specific catalyst. It also allows for the electrode kinetics of the relevant fuel cells reactions to be evaluated without the use of mathematical modelling.
1.8.3 Fuel Cell Testing

Once the catalysts have been screened by the various ex-situ methods it is essential to determine the catalytic activity in a working fuel cell. This involves the preparation of an MEA with the catalyst layer present on either side which is then inserted into a single cell where the operating conditions may be modified using a fuel cell test station. The major purpose of such an evaluation is to understand the relationship between the fuel cell performance and the MEA components such as the catalyst itself and the catalyst layer. This then enables the optimisation of the catalyst layer and MEA in terms of composition and fabrication parameters. Fuel cell testing mainly involves the analysis of polarisation curves (yields information about performance loses in the cell under operating conditions), CV and electrochemical impedance spectroscopy (EIS) and also degradation and durability studies of the MEA.

Electrochemical kinetic parameters are more complex that what can be obtained from a fuel cell polarisation data because of difficulty in delineating the ohmic and mass transport losses however the kinetics can be obtained from analysis of the iR-free (ohmic loss compensated) plots of potential versus logarithm of current (i.e. the Tafel plot) for the oxygen reduction reaction.
1.9 Focus of Research

The primary objective of this study is the development and characterisation of Pt-based/C binary and ternary alloy electrocatalysts for the ORR that still have comparably high electrochemical activity. This would in effect reduce the cost of the commercial Pt/C. This aim will be achieved through the following objectives:

a) To develop a range of Pt-based/C binary and ternary electrocatalysts using Co, Ni 3:1 with respect to Pt and a combination of both Co and Ni with a ratio of 3:0.5:0.5 for the ORR that competes with material cost, durability and performance criteria of currently commercialised technology.

b) Characterise the physical and structural properties of the prepared catalysts using different techniques.

c) Evaluate whether acid treatment conditions used in preparing catalysts yield catalysts with similar or different characteristics.

d) Study the electrochemical properties and intrinsic kinetics of the prepared catalysts so as to evaluate the best catalyst to be used in an MEA to be analysed in a unit fuel cell.

e) Evaluate the MEA performance and catalytic properties of synthesised electrocatalysts selected from d) and compare that to the performance of a commercial Pt/C catalyst.
Chapter 2 Experimental Methods

The catalyst synthesis procedure as well as the techniques used for both the physical and electrochemical characterisation of each synthesised catalyst is described. The procedure for the MEA preparation and characterisation in a fuel cell test station is also given. A summary of the instrumentation used in all of the experimental procedures has also been included. An overview of the experimental procedure is illustrated in Figure 2.1.

2.1 Synthesis of catalysts

Pt-based alloy catalysts supported on carbon were prepared using an impregnation method whereby Pt/C (40%) as well as Co- and Ni nitrate salts were used precursors. Binary alloys of Pt₃Co/C and Pt₃Ni/C as well as a ternary alloy of Pt₃Co₀.₅Ni₀.₅/C were obtained via a heat treatment-reduction process carried out under a H₂/Ar atmosphere at 900°C.

2.1.1 Materials for Catalyst Synthesis

A list of the chemicals used in the catalyst synthesis procedure is given in Table 2.1.

Table 2.1 Chemicals used for catalyst synthesis

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Specifications</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C (HiSpec 4000)</td>
<td>40 wt. %</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Co(NO₃)₂.6H₂O</td>
<td>Analytical grade</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ni(NO₃)₂.6H₂O</td>
<td>Analytical grade</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>98 % AR</td>
<td>KIMIX</td>
</tr>
<tr>
<td>dNH₄OH</td>
<td>25%</td>
<td>KIMIX</td>
</tr>
</tbody>
</table>
Figure 2.1 Outline of experimental work contained within this dissertation
2.1.2 Impregnation procedure for Pt$_3$Co/C

Pt/C (40%) (3.0g) and H$_2$O (18 MΩ.cm) (100 mL) was added to a beaker followed by sonication of the suspension in an ultrasonic bath at 30°C for 15 minutes to obtain a homogenous mixture. Co(NO$_3$)$_2$.6H$_2$O (0.5964g, 0.2049 moles) was added to the mixture while stirring. The pH was adjusted to 9 with dilute ammonium hydroxide (25%). Stirring was sustained during and after pH adjustment and continued overnight. The sample was then filtered under vacuum, washed with water and dried at 60°C overnight to remove any water still present. Once completely dry, the solid was sieved through 850µm, 425µm and 250µm sieves to obtain a fine powder.

2.1.3 Impregnation procedure for Pt$_3$Ni/C

The synthesis procedure was similar to the previous (Section 2.1.2) where the Co(NO$_3$)$_2$.6H$_2$O was replaced with Ni(NO$_3$)$_2$.6H$_2$O (0.5959g, 0.2049 moles) to produce impregnated Pt$_3$Ni/C particles.

2.1.4 Impregnation procedure for Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C

This followed the synthesis procedure as specified in Section 2.1.2 and where Co(NO$_3$)$_2$.6H$_2$O (0.2982g, 0.1025 moles) and Ni(NO$_3$)$_2$.6H$_2$O (0.2980g, 0.1025 moles) were added simultaneously to produce impregnated Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C particles.

2.1.5 Heat treatment-Reduction and Passivation of impregnated catalysts

Nanoparticles of Pt$_3$Co/C, Pt$_3$Ni/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C were then obtained through a heat treatment-reduction process at 900°C under a H$_2$/Ar of each impregnated sample. The temperature profile of the heat treatment-reduction procedure is given by Figure 2.2. A passivation procedure whereby O$_2$ was systematically fed into the gas stream was also performed upon cooling of the reduced catalyst samples to prevent the oxidation of carbon black and this is shown by Figure 2.2.
as well. This reduction-heat treatment and passivation procedure was done using a Micrometrics Autochem 2910 and 2950 HP, where gases could be carefully controlled.

During the passivation procedure the carbon monoxide level was visually monitored using a mass spectrometer and levels were found to be sufficiently negligible to rule out carbon oxidation during the passivation procedure.

Once reduced, a portion of each catalyst sample was treated with an acid wash by stirring in 20 mL 0.5 M sulphuric acid for 2 hours at 70°C. This was done to obtain an acid washed sample which could then be compared to the non-acid washed catalyst to assess the impact of the possibility of the Co and Ni to leach from the catalyst structure and morphology thereby affecting its catalytic activity.

![Heat treatment-reduction and passivation profile for catalyst synthesis](image)

Figure 2.2  Heat treatment-reduction and passivation profile for catalyst synthesis
2.2 Ex-Situ Characterisation Methods

This consisted of both physical and electrochemical methods of characterisation.

2.2.1 Physical Characterisation

2.2.1.1 Powder X-Ray Diffraction Analysis (PXRD)

Powder X-ray diffraction (PXRD) is one of the most commonly used techniques employed for catalyst characterisation. It is a powerful tool used to identify crystalline phases within catalysts by means of lattice structural parameters as well as to obtain an indication of the particle size. In this study XRD analysis was used to determine the average crystallite size and structure, of the commercial Pt/C as well as each prepared alloy catalyst, before and after being subjected to fuel cell operation. This gives an indication of the chemical composition, degree of alloying as well as the catalyst stability.\(^{54}\)

Rietveld refinement was done on samples to obtain crystallographic information about each catalyst in terms of phase composition, crystal structure, lattice parameters and crystallite size. This method uses known crystal information for phases in a sample to calculate a theoretical line profile from which the locations of each atom in a structure could be found by an iterative process of refinement of instrumental and structural parameters.\(^{55}\)

Average crystallite size was also determined from the spectral line broadening, whereby the size of the crystallite decreases with an increase in the width of the diffraction beam. The size obtained from XRD analysis is a measure of the effective length, in the direction of a diffracting vector, along which diffraction is coherent. This phenomenon is described by the ‘Scherrer equation’:

\[
t = \frac{K \lambda}{B \cos \theta}
\]  

(2.1)
where \( t \) is the crystallite size (nm), \( \lambda \) is the wavelength of the x-rays (Co-K\( \alpha \) = 0.1789 Å), \( \theta \) is the ‘Bragg angle’ and \( B \) is the full width at half-maximum (FWHM) of the peak located at 2\( \theta \) in radians.\(^{54}\) Furthermore the lattice parameter (\( \alpha \)) can be calculated from the following equation:

\[
\alpha_{fcc} = \frac{\frac{1}{2} \lambda_{K}}{\sin \theta_{max}}
\]

(2.2)

The XRD analysis was done on a Siemens Bruker D8 Advance XRD unit for which the operation parameters are provided in Table 2.2. Rietveld refinement was done using Bruker’s Topas 4.1 software.\(^{56}\)

Table 2.2 Operative parameters for Siemens D8 Advance XRD

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray detector</td>
<td>Cobalt tube with Co – K( \alpha )</td>
</tr>
<tr>
<td>Generator voltage</td>
<td>35 kV</td>
</tr>
<tr>
<td>Generator current</td>
<td>40 mA</td>
</tr>
<tr>
<td>Scanning range (2( \theta ))</td>
<td>10-130</td>
</tr>
<tr>
<td>Scan type</td>
<td>2( \theta )/( \theta ) locked</td>
</tr>
<tr>
<td>Scan speed</td>
<td>103 s step(^{-1})</td>
</tr>
<tr>
<td>Scan time</td>
<td>45 minutes</td>
</tr>
<tr>
<td>Step size</td>
<td>0.012 °</td>
</tr>
<tr>
<td>Synchronous rotation</td>
<td>No</td>
</tr>
</tbody>
</table>

2.2.1.2 Transmission Electron Microscopy (TEM)

TEM was exclusively used to determine the average particle size, particle shape and particle size distribution of electrocatalysts. In this study TEM was used to obtain the aggregate morphology, particle size and particle size distribution of the catalysts. All samples were viewed and photographed using a Technai T20 electron microscope operated at 200 kV. The samples were prepared by carefully suspending the catalyst powders ultrasonically in methanol solution and depositing a drop of the suspension on a copper grid covered with carbon. This was mounted in the sample holder which goes directly into the microscope shaft.
2.2.1.3 Energy Dispersive Spectroscopy (EDS)

The elemental composition of each catalyst was analysed using energy dispersive spectroscopy (EDS) emission analysis with a FEI Nova NANOSEM 260 equipped with an Oxford Xmax 20 mm$^2$ detector. INCA software was used to obtain the elemental composition. Each sample was scanned three times to obtain an average wt. % of the elements.

2.2.1.4 Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) is used to study the weight loss of a sample as a function of temperature. In this study TGA was used to determine the total percentage metal loading on carbon black by finding the difference in weight of the sample before and after carbon black decomposition in air atmosphere as the temperature increases. Analysis was done using a Mettler Toldedo TGA/SDTA 851e with a heating rate of 5 ºC min$^{-1}$ up to a temperature of 850 ºC.

2.2.2 Electrochemical Characterisation Methods

The chemical properties of the catalysts were investigated using a Metrohm Autolab Potentiostat/Galvanostat and are described in this section. Catalysts were analysed to obtain the chemical properties in terms of electrochemical active surface area (ECSA) as well as activity towards the ORR. Cyclic voltammetry and rotating disc electrode techniques were used for these investigations.

2.2.2.1 Electrode Preparation

For ex-situ electrochemical characterisation techniques an electrode containing the prepared catalysts was prepared whereby a certain amount of catalyst was deposited as an ink on a Glassy Carbon (GC) disc and subsequently dried in an oven at 60 ºC for 30 minutes.
The GC disc electrode (5 mm) was first polished to a mirror like finish with 0.05 µm alumina suspension before each experiment and acted as the substrate for the catalyst layer. The catalyst ink was prepared as follows: 10mg catalyst was weighed into a 25 mL volumetric flask to which 3.24 mL isopropanol, 10.27 mL H₂O (Millipore) and 54.05 µL Nafion® (5%) was added and the solution was placed in an ice bath and subjected to ultrasonication for 30 minutes at 30 ºC. Once an evenly distributed solution was obtained, 10µl was carefully spread on the surface of the glassy carbon disc which was then dried at 60 ºC for 30 minutes or until completely dry. A metal loading of 2.96 µg cm⁻² was obtained from this. This electrode acted as the working electrode for CV and RDE experiments as described below.

2.2.2.2 Cyclic Voltammetry (CV)

CV was one of the most commonly used electrochemical techniques. The basis of the technique is a linear potential waveform that applies a potential change between chosen high and low points with a linear change in time and the rate of change of potential with time was defined as the scan rate. The current in the potential cycling region is recorded and the resulting potential versus current plot is known as a voltammogram. The analysis is usually carried out in a conventional three electrode cell which consists of a working electrode (usually the entity being characterised, i.e. catalyst), a reference electrode and counter electrode. The potential or current of the working electrode is changed and resulting in electrons being transferred between the electrode and the molecules of the electrolyte, which is usually an aqueous acidic or alkaline solution. The working electrode and counter electrode form a circuit through which a current flows, that causes a reaction at the counter electrode as well. However the current at the counter electrode is not of interest except that it should not interfere with the working electrode. To minimise the impact of the electrolyte resistance on the working electrode, a reference electrode such as a standard hydrogen electrode is used.

A typical voltammogram for a reversible single electrode transfer reaction is given by Figure 2.3 In this figure, iₚc and iₚa are cathodic and anodic peak currents
respectively. $E_{pc}$ and $E_{pa}$ are cathodic and anodic peak potentials respectively. The position of the peak maxima shifts with a change in scan rate.\textsuperscript{57, 58}

![Figure 2.3](image.png)  
**Figure 2.3** Typical cyclic potential sweep (A) and resulting voltammogram (B) showing cathodic and anodic parameters, adapted from.\textsuperscript{59}

The electrochemical active surface area (ECSA) of Pt can generally be measured using CV and two different methods are commonly used to determine the ECSA quantitatively. The first method uses the hydrogen adsorption/desorption peak areas and the second uses the oxidative stripping peak area of carbon monoxide (CO). These techniques are discussed below, however for the purposes of this dissertation only the method of hydrogen underpotential adsorption/desorption was used.

### 2.2.2.2.1 Hydrogen underpotential adsorption/deposition ($H_{upd}$)

This method uses the area under the adsorption/desorption peaks of atomic hydrogen as shown in Figure 2.4. A larger area under the peak indicates a greater surface area of active Pt particles (per mass of Pt). A fully covered monolayer corresponds to a charge of 210 $\mu$C cm$^{-2}$ for a polycrystalline Pt surface. This value is established based on the polycrystalline surface of Pt having a Pt atom surface density of $1.3 \times 10^{15}$ per cm$^2$ and each Pt allows one hydrogen atom to adsorb.\textsuperscript{59}

The CV scan is divided into three regions and the hydrogen underpotential deposition ($H_{upd}$) region is of interest in this investigation as the adsorption/desorption of hydrogen occurs here. The $H_{upd}$ region from +0.05 to
+0.4 V is shown in Figure 2.3, from which the hydrogen adsorption and desorption peaks are visible. The area of the hydrogen adsorption peak is used to calculate the ECSA of each Pt by the following equation:

\[
ECSA \ (m^2 \ g^{-1}) = \frac{\text{Charge area} \ (\mu C \ cm^{-2})}{10 \times 210 \ (\mu C \ cm^{-2} \times \text{Catalyst loading} \ (mg \ cm^{-2}))}
\] (2.3)

CV analysis was performed in N₂ purged 0.5 M H₂SO₄ by cycling the potential between 0.2 V and 1.1 V vs. Standard Hydrogen Electrode (SHE) at 50 mV s⁻¹, ambient pressure and 25 °C. The potential cycling to clean and activate the electrode surface was carried out at 100 mV s⁻¹ until reproducible results were obtained (20 cycles) and the voltammograms obtained at 50 mV s⁻¹ after a steady state has been achieved are presented in this study. A three electrode cell was used with a glassy carbon rod as a counter electrode and Ag|AgCl (0.1 M KCl) as the reference electrode and the prepared disc electrode as the working electrode. The charge of atomic hydrogen adsorption was determined by integrating between the straight baseline drawn from the double layer capacitance region (\(E \approx 0.4V\)) and the final minimum in the cathodic curve (\(\varphi_{min}\)), as shown in Figure 2.4.

![Figure 2.4](image-url)  
**Figure 2.4** Typical voltammogram for Pt electrode in acidic medium.⁵⁷
2.2.2.2 Carbon Monoxide (CO) Stripping

The ECSA was also determined by a technique known as carbon monoxide (CO) stripping voltammetry. CO stripping makes use of the oxidative peak area of CO (potential range between +0.4 V and +1.0 V), which strongly adsorbs on the surface of Pt to form a monolayer that is completely removed at a high enough potential by oxidation of CO to CO$_2$. This results in a sharp well-defined peak during the anodic potential scan and no corresponding reduction current exists during the cathodic potential scan. The corresponding monolayer charge area for CO oxidation is 420 µC cm$^{-2}$ adsorbed on polycrystalline Pt which is replaced in equation 2.3 to obtain the ECSA of Pt in each alloy.

2.2.2.3 Rotating Disc Electrode (RDE)

The RDE technique was used to quantitatively evaluate the ORR electroactivity of the prepared electrocatalysts. In this hydrodynamic technique the working electrode is rotated to induce forced convection as shown in Figure 2.5 and obtain diffusion limited current ($i_d$). The overall current density ($i$) is related to the diffusion limited current density ($i_d$) and the true kinetic current density ($i_k$) which is the current in the absence of any mass transfer effects, determined by the mass-transport properties of the RDE (the Koutecky–Levich equation):

$$\frac{1}{i} = \frac{1}{i_d} + \frac{1}{i_k}$$

(2.4)

where $i_d = 0.62nFAD^{2/3} Cu^{-1/6} \omega^{1/2}$ (Levich equation), $n$ is the total number of electrons transferred, $F$ is the Faraday constant (96485 C mol$^{-1}$), $A$ is the area of the electrode, $D$ is the diffusion coefficient of oxygen in cm$^2$ s$^{-1}$, $C$ is the concentration of oxygen in mol cm$^{-3}$, $\nu$ is the kinematic viscosity in cm$^2$ s$^{-1}$, and $\omega$ is the rotation rate in rad s$^{-1}$. Along with the kinetic activity, the number of electrons transferred during the ORR can also be calculated from the Koutecky–Levich equation and the measured slope of $1/\omega^{1/2} - 1/i$ plot. Unfortunately there was not access to an RRDE set up and thus only RDE experiments were possible.
In this study RDE experiments were conducted to obtain both the mass activity and specific activity of each catalyst. The experimental set-up consisted of the catalyst coated glassy carbon disc electrode mounted onto an interchangeable RDE holder in O₂ saturated 0.5 M H₂SO₄. The polarisation curves were recorded at 400, 800, 1200 and 1600 rpm from +0 to +1.1 V vs. SHE at a scan rate of 10 mV s⁻¹.
2.3 In-Situ MEA Characterisation

Once catalysts have been screened experimentally in RDE type setup, it was of interest to determine the activity of catalyst in a working fuel cell in order to evaluate its performance.

2.3.1 MEA Preparation

This involved preparation of one catalyst coated substrate (CCS) containing Pt/C-JM catalyst (HiSpec 4000) or the alloy electrocatalyst for the cathode. This CCS was then hot pressed to a Nafion® 212 membrane together with a GDL containing Pt/C-JM, for the anode. The various components used in the MEA preparation were obtained from commercial suppliers and are described in detail below. Two MEA for each catalyst were prepared and experimental procedure for this was according to the procedure outlined in a previous study.60

2.3.1.1 Description of MEA components

Table 2.3 lists the various components used in the MEA preparation.

Table 2.3 List of MEA components

<table>
<thead>
<tr>
<th>Component</th>
<th>Supplier</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Electrochem Inc.</td>
<td>Nafion® 212 (50.8 µm think)</td>
</tr>
<tr>
<td>GDL</td>
<td>Freudeberg FCCT</td>
<td>H2315 I3 C1 Carbon paper</td>
</tr>
<tr>
<td>Nafion ionomer solution</td>
<td>Ion Power</td>
<td>15% Nafion solution (1100 EW)</td>
</tr>
</tbody>
</table>

Nafion® 212 has a thickness of 50.8 µm and a specific mass of 100 g m⁻² at 23 ºC and 50% relative humidity. The membrane was used as received i.e. no membrane preconditioning was done prior to hot pressing. The GDL has a thickness of approximately 260 µm, has an average wet proofing of 10% PTFE and contains a microporous layer.
2.3.1.2 Catalyst ink Preparation

The catalyst ink consisted of Pt/C-JM or the synthesised alloy electrocatalyst, Nafion® ionomer solution, organic solvent (isopropanol) and de-ionised water. The catalyst ink was prepared as follows: de-ionised water (0.65 mL) was added dropwise to a sample vial containing the catalyst powder (200.7 mg), organic solvent (1.7 mL) Nafion® ionomer (0.68 mL) solution was then added quickly and the resultant mixture was dispersed for 1 minute using a Bandelin ultrasonic homogeniser with a frequency of 35 kHz. The resultant catalyst ink was then immediately applied onto the GDL as described in section 2.3.1.3 below.

2.3.1.3 Application of Catalyst Layer to GDL

Application of the catalyst ink to the GDL was done via a technique known as doctor blade spreading. For this technique a 25 by 8 cm GDL piece was cut and weighed.

The doctor blade spreading equipment as shown in Figure 2.6 was obtained from the company Erichsen and consisting of a doctor blade device driven by a mobile control box with a keypad and LCD display. Once prepared, the catalyst ink was immediately placed in the doctor blade positioned above the GDL sheet and then activated via the controller to drive the blade through the whole GDL sheet. The thickness of the coated catalyst layer and, therefore, the final catalyst loading is dependent on the blade speed, blade height and the catalyst ink viscosity. For target loadings of approximately 0.4 mg\text{Pt} cm^{-2}\text{GDL} the blade speed and height were 7.5 mm s^{-1} and 100 μm respectively. The final loading was calculated from the difference between the coated and uncoated GDL and was found to be close to 0.4 mg\text{Pt} cm^{-2}\text{GDL} for each MEA.

Following coating, the resultant CCS was dried overnight in an oven at 60 °C. Once the catalyst loading and approximate catalyst layer thicknesses were calculated, two 5 X 5 cm CCS pieces were cut in preparation for the hot pressing step.
2.3.1.4 Hot Pressing

Hot pressing was used to laminate the prepared CCS for the anode and cathode onto the membrane. The procedure was carried out using a Carver twelve ton, manual, four-column hydraulic press as shown by Figure 2.7 below.

Before placement into the press, the two CCS and a 8 X 8 cm membrane sheet were manually aligned and placed between two surface ground 15 cm X 15 cm X 1 cm stainless steel plates. In order to prevent the membrane from sticking to the plates during hot pressing, the two CCS and membrane were sandwiched between 100 μm NOWOFLON PFA sheets which were in turn then placed
between the stainless steel plates. The plates were left in the press for at least 30 minutes prior to pressing to allow the hot pressing temperature to be reached. Hot pressing was then carried out at 130 °C at a pressure of 5000 kPa for 180 seconds.

Following hot pressing, the plates were immediately removed and left to cool at ambient conditions for at least 2 - 3 hours. The complete MEA was then removed and stored as described in Section 2.3.2.5.

2.3.1.5 MEA Storage

The fabricated MEAs were stored in a sealed plastic sleeve away from direct sunlight. Prior to conditioning and testing, a die cutting tool was used to punch holes on the outer edges of the membrane for purposes of placing the MEA in the test cell.

2.3.2 MEA Characterisation

Once the MEA was prepared it was ready to be placed in a unit fuel cell to investigate the performance of the prepared catalyst under fuel cell operating conditions. The MEA was placed into a 25 cm² single test cell fixture that was operated with a commercial fuel cell test station. The experimental conditions of operation, as well as the analysis carried out are described here.

2.3.2.1 Description of Cell Components

The fuel cell hardware used for this analysis was obtained from Baltic Fuel Cells. This consisted of the main test cell (25 cm² active area) and a support frame pressure unit used to provide compression during operation. The test cell houses the flow fields, heating and current collector plates. The support frame pressure unit consists of a pneumatic actuator and an attached frame in which the test cell is mounted. The hardware therefore uses a pneumatic principle to provide cell compression allowing for a continuously adjustable contact pressure on the
active area of the MEA under test. Table 2.4 provides a summary of the technical
data for the fuel cell test unit.

Table 2.4 Technical data for the fuel cell test unit

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Baltic Fuel Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>cF 25/100 LT V1.1</td>
</tr>
<tr>
<td>Active area</td>
<td>25 cm²</td>
</tr>
<tr>
<td>Flow Field Parameters</td>
<td></td>
</tr>
<tr>
<td>(anode and cathode)</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>graphite compound</td>
</tr>
<tr>
<td>Geometry</td>
<td>5-fold mixed serpentine</td>
</tr>
<tr>
<td>Channel configuration</td>
<td>Parallel</td>
</tr>
<tr>
<td>Channel width</td>
<td>1 mm</td>
</tr>
<tr>
<td>Channel depth</td>
<td>1 mm</td>
</tr>
<tr>
<td>Cell clamping pressure</td>
<td>2 bar</td>
</tr>
</tbody>
</table>

2.3.2.2 Cell Assembly

Prior to assembly of the cell for testing the flow fields and heating plates were cleaned with iso-propanol and lint-free cloth. The MEA was then carefully mounted into the fuel cell fixture while ensuring that the active area of the MEA was properly aligned with the geometric area of the flow field plate. The cell was then closed to complete the assembly. Baltic test cell uses an O-ring seal to prevent reactant gas leaks and, as a result, no additional gasket material was used during cell assembly. The assembled test cell was subsequently placed into the support frame pressure unit which in turn was placed into the test station described below.

2.3.2.3 Test Station Experimental Set Up

Fuel cell test stations from FuelCon (evaluator C50-LT) equipped with TrueDATA- EIS® impedance spectroscopy analyser shown in Figure 2.8 were used for testing of all MEA for both polarisation curves and EIS data. The primary components of the test stations include: electronic mass flow controllers, heated and insulated gas feed lines, electrical heating system, temperature control
systems, an external humidification system, an electronic load (TrueData-LOAD®), a pressure control system consisting of back pressure regulators and a computerised data acquisition system.

![Fuel cell test station](image)

**Figure 2.8** Fuel cell test station

Pure hydrogen (99.999% purity) was used as the anode reactant and pure oxygen (99.999% purity) for the cathode and the gases were provided from a set of pressurised gas cylinders for the polarisation curve and impedance measurements. Reactant humidification was achieved by saturators built into the test stations. All the settings of the test station and fuel cell were monitored and controlled through a data acquisition system connected to a computer running Windows XP Professional SP2 and FuelWork® software. The software allows measurement of voltage-current data in either potentiostatic or galvanostatic mode.
2.3.2.4 Polarisation Curves

The polarisation curve is a plot of cell potential versus current density under a set of constant operating condition, and is the standard investigative tools for characterising the performance of fuel cells. The current density, in mA cm$^{-2}_{\text{MEA}}$, allows comparison between fuel cells at the same voltage and MEA of different size and a good fuel cell should display a high current density at a high voltage indicating a high power output.

All polarisation curve measurements were performed under varied loads at fixed operating conditions. The current density was stepped up in increments from 0 mA cm$^{-2}_{\text{MEA}}$ to the maximum test current density (corresponding to a cell voltage of 0.35 V). Operation of the fuel cell at cell voltages of less than 0.35 V can lead to irreversible damage to the fuel cell components. At each current density, a 75 second stabilisation period was allowed before the cell voltage was recorded. Following each step increase in current density, a 20 second waiting period was allowed for the reactant flow rates to increase before the current density increased. The test sequence is outlined in Table 2.5.

Table 2.5 Polarisation curve test sequence

<table>
<thead>
<tr>
<th>Sequence step</th>
<th>I (A)</th>
<th>$i$ (mA cm$^{-2}_{\text{MEA}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (OCV)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>20.08</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>40.12</td>
</tr>
<tr>
<td>4</td>
<td>1.50</td>
<td>59.92</td>
</tr>
<tr>
<td>5</td>
<td>2.00</td>
<td>80.04</td>
</tr>
<tr>
<td>6</td>
<td>2.50</td>
<td>99.92</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>15</td>
<td>11.00</td>
<td>440.0</td>
</tr>
<tr>
<td>16</td>
<td>12.00</td>
<td>480.2</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Final</td>
<td>35.00</td>
<td>1400</td>
</tr>
</tbody>
</table>
After each polarisation curve measurement, the fuel cell was left to operate at OCV for 10 minutes before repeating the measurement. When changing between operating conditions for polarisation curves and impedance measurements as described in Section 2.3.2.5, the fuel cell was left to operate at 0.6 V for at least 30 minutes in order to allow stabilisation at the new conditions.

2.3.2.5 Electrochemical Impedance Spectroscopy (EIS)

EIS also known as AC impedance spectroscopy involves applying a low-level alternative current (AC) waveform to the electrochemical system (in this case fuel cell test unit) and measuring the response of the cell to the stimulus, i.e. the AC voltage across the cell and the AC current through the cell. The impedance is obtained by taking the ration of the AC voltage/AC current.

Electrochemical reactions consist of electron transfer at an electrode surface and these reactions may involve electrolyte resistance, adsorption of electroactive species, charge transfer at the electrode surface and mass transfer from the bulk solution to the electrode surface. EIS is able to provide detailed insight into the fuel cell losses resulting from individual processes that include kinetics, mass transfer resistances and the various ohmic losses such as membrane, GDL and contact resistances. EIS is also commonly used to study the ORR, characterise diffusion losses and evaluate catalyst layer properties such as charge transfer resistance \( R_{ct} \) and double layer capacitance \( C_{dl} \).64

The analysis of EIS data may be done by an equivalent circuit approach as each process of the electrochemical reaction may be considered as an electrical component or a simple electric circuit. The whole reaction process can be thus be represented by an electric circuit composed of resistance, capacitors, or constant phase elements combined in parallel or in series.

The most popular electric circuit for a simple electrochemical reaction is the Randles–Ershler electric equivalent circuit model (Fig 2.9), which includes electrolyte resistance, charge-transfer resistance at the electrode/electrolyte interface, double-layer capacitance, and mass transfer resistance. The values of
these circuit elements (e.g. capacitance) are obtained from fitting the effective impedance of the circuit elements to experimental data. This method provides a quick visualisation of the system properties under steady state conditions.\textsuperscript{64}

![Diagram of equivalent circuit model for PEM fuel cell](image)

The impedance of a fuel cell electrode is a combination of the impedances of three circuit elements. The double layer capacitance ($C_{dl}$) is used to account for the charge stored in the interfacial capacitance which arises from the contact of the electrode materials and the electrolyte. The charge transfer resistance ($R_{ct}$), which is parallel to the double layer capacitance, represents the electronic resistance in the electrode while the impedance of diffusion of the reactants and the reaction products is represented by a finite length Warburg impedance ($Z_w$). These circuit elements occur at both the anode and cathode. However in hydrogen-oxygen (air) fuel cells, the anode reaction is assumed to have fast reaction kinetics compared to the cathode and thus the anode can generally be neglected.\textsuperscript{64} The values of $C_{dl}$, $R_{ct}$, $R_m$ and $Z_w$ are obtained from fitting the equivalent circuit to the experimental data.

The most common representations of electrochemical impedance spectra are the Bode plots, where the logarithm of impedance magnitude $|Z|$ and the phase-shift ($\theta$) are plotted versus the logarithm of the frequency ($f$) and the Nyquist plots, where the imaginary part of the impedance is plotted versus the real part of the impedance.\textsuperscript{63} A typical Nyquist plot for a PEM fuel cell is shown in Figure 2.10.
The plot shows each of the circuit elements used in the equivalent circuit diagram. The Nyquist plot also shows regions (arcs or semi-circles) for the anode activation kinetics ($R_{ct, \text{anode}}$), cathode activation kinetics ($R_{ct, \text{cathode}}$) at high frequencies and mass transfer at low frequencies represented by the Warburg element ($Z_w$). It must be noted that the mass transfer region in the case of porous gas diffusion electrodes gives an impedance arc rather than a straight line as observed for planar electrodes. For real fuel cells the cathode loses are significantly larger than the anode loses thus gives rise to a much larger arc observed for the cathode activation kinetics.

![Nyquist plot](image)

**Figure 2.10** A typical Nyquist plot for PEM fuel cell

In this study, in-situ EIS was done using a two electrode set up in galvanostatic mode to provide diagnostic information about the various losses that occur during fuel cell information and how it related to the synthesised electrocatalyst. The cell was held at different dc current densities with the ac varied to a maximum of 5 % of the dc current density. The anode hydrogen reaction was also used as the reference electrode and the impedance with respect to the cathode across the frequency range from 0.1 Hz to 20 kHz was studied accordingly.
Chapter 3  Results and Discussions

The study of the fuel cell assembly was performed by firstly characterising the electrode material using ex-situ techniques in terms of structure, morphology, particle size and size distribution as well as elemental composition and metal loading. This was followed by their ex-situ electrochemical characterisation in terms of electrochemical surface area and ORR activity. Finally, the fabricated MEA’s assembled in a unit fuel cell was studied by polarisation curves and electrochemical impedance in-situ to obtain the performance of the synthesised electrocatalysts under real fuel cell operating conditions.

3.1  Physical Characterisation

3.1.1  Structure, Morphology, Particle Size and Size Distribution

3.1.1.1  Powder X-Ray Diffraction Analysis (PXRD)

- Overview

PXRD analysis and Rietveld refinement was used to characterise the structure and approximate active metal crystallite size distribution (Table 3.1). The lattice parameter values obtained from the Scherrer equation were based on the 2-theta position of the Pt (220) diffraction line and the average crystallite size estimates were based upon peak broadening of the Pt (111) and Pt (220) lines respectively (Fig 3.1). Lattice parameter and average crystallite size values were also obtained using least squares Rietveld refinement method which considers the entire diffraction pattern for each electrocatalyst respectively. The software used for this was Topas 4.2.

In general a good fit between the observed and calculated patterns for Rietveld refinement is represented by the discrepancy index, the Rietveld weighted pattern value (Rwp) where a value of below 15 is considered as a reasonable fit. As an example, Pt/C-JM is discussed. The Rietveld refinement graph in Appendix A showed a good fit with an Rwp value of 7.4 between the observed and calculated
patterns. Rietveld refinement graphs for Pt/C-900 and Pt/C-900-AW, Pt$_3$Co/C and Pt$_3$Ni/C and Pt$_3$Ni/C-AW as well as Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW are presented in Appendix A, and their results summarised in Table 3.1. Each group of electrocatalysts are discussed individually below.

Table 3.1 Data from the PXRD and Rietveld Refinement analysis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average crystallite size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Rietveld weighted pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scherrer Equation</td>
<td>Rietveld Refinement</td>
<td>Scherrer Equation</td>
</tr>
<tr>
<td>Pt/C-JM</td>
<td>2θ = 46</td>
<td>2θ = 80</td>
<td>Complete spectrum</td>
</tr>
<tr>
<td>Pt/C-900</td>
<td>4.1</td>
<td>10.7</td>
<td>3.8</td>
</tr>
<tr>
<td>Pt/C-900-AW</td>
<td>11.0</td>
<td>10.9</td>
<td>10.8</td>
</tr>
<tr>
<td>Pt$_3$Co/C</td>
<td>6.1</td>
<td>4.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Pt$_3$Co/C-AW</td>
<td>6.2</td>
<td>4.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Pt$_3$Ni/C</td>
<td>10.6</td>
<td>9.4</td>
<td>14.0</td>
</tr>
<tr>
<td>Pt$_3$Ni/C-AW</td>
<td>11.1</td>
<td>10.0</td>
<td>13.4</td>
</tr>
<tr>
<td>Pt$<em>3$Co$</em>{0.5}$Ni$_{0.5}$/C</td>
<td>9.2</td>
<td>8.5</td>
<td>11.6</td>
</tr>
<tr>
<td>Pt$<em>3$Co$</em>{0.5}$Ni$_{0.5}$/C-AW</td>
<td>9.6</td>
<td>9.0</td>
<td>11.7</td>
</tr>
</tbody>
</table>

- **Pt/C-JM, Pt/C-900 and Pt/C-900-AW**

The unit cell lattice parameter calculated from the Scherrer equation (Equation 2.2) for pure Platinum used as catalyst that was prepared under different conditions (Pt/C-JM, Pt/C-900 and Pt/C-900-AW) was found to be very similar with an average of 3.915 Å. The lattice parameter from the Rietveld refinement was on average slightly lower at 3.906 Å where both values were in agreement to literature values that are reported to be 3.920 Å.$^{65}$ The results showed that the average crystallite size for Pt/C-JM which was the commercial Pt/C (40%) catalyst
used as the starting material for synthesis of the alloys at 3.8 nm was considerably smaller when compared to that of the heat-treated catalysts of Pt/C-900 and Pt/C-900-AW as well as the alloyed catalysts. This indicated that the particle size increased due to the high thermal treatment during the reduction and alloying process resulting in possible sintering of the Pt particles.

Figure 3.1 PXRD patterns for Pt/C-JM, Pt/C-900 and Pt/C-900-AW

- **Pt$_3$Co/C and Pt$_3$Co/C-AW**

The Pt$_3$Co/C and Pt$_3$Co/C-AW showed that the lattice parameters determined from the Scherrer and Rietveld were found to be in good agreement with an average of 3.867 Å for Pt$_3$Co/C and 3.873 Å for Pt$_3$Co/C-AW. These values were slightly higher yet still in good agreement with the value of 3.854 Å reported in literature for a primitive cubic (Pm3m) single phase alloy. As with Pt/C, particle growth occurred due to sintering of the metal particles when the material was exposed to high temperature during the reduction and alloying process. It is however noted that particle growth was not as severe as with Pt-Co samples as compared to Pt/C and other alloyed catalysts (Pt-Ni and Pt-Co-Ni), with average crystallite sizes of
6.2 for Pt₃Co/C and Pt₃Co/C-AW as compared to 10.7 and 10.9 for Pt/C-900 and Pt/C-900-AW respectively. A possible reason for this may be the formation of ordered structures for Pt-Co catalysts as outlined below.

For comparison purposes, the PXRD patterns for Pt₃Co/C and Pt₃Co/C-AW are plotted with that of Pt/C-JM. The slightly broad halo observed at 2θ = 30° was due to the (002) peak of the carbon black support. The shift in the (111) and (200) peaks to higher 2θ values would correspond to a decrease in the lattice parameter caused by lattice contraction when Pt is alloyed with transition metals of smaller ionic radius, in this case Co. Superlattice reflections indicative of the formation of an ordered primitive cubic Pt₃Co/C Li₂ alloy structure (space group: Pm3m) were observed at 2θ = 38°, 62° and 69°. This structure was also obtained from the Rietveld refinement for which there is also a superlative peak at 2θ = 27°, observed in the Rietveld refinement calculated pattern (Appendix A) and is in this case masked by the (002) carbon peak in the observed pattern. The formation of a single phase Pt₃Co alloy was expected but had been rarely reported until recently. Literature also reported a disordered face centered cubic, FCC (Fm3m)
phase similar to that of pure Pt which did not fit the current data well. The refinement yielded a poor fit for the diffraction pattern showing crystal imperfections with a broad peak at \(2\theta = 100^\circ\) and an additional peak near \(2\theta = 40^\circ\) (Fig 3.2). In addition, there were no well-defined diffraction peaks that could suggest the presence of any metallic Co or oxide phases. This is most likely due to the Co loading being very low and any metal or oxide Co species present would be highly dispersed and in very small concentrations and thus would not be detected. For the \(\text{Pt}_3\text{Co/C}\) and \(\text{Pt}_3\text{Co/C-AW}\) a primitive cubic structure (Pm3m) was assigned with the (011) peak clearly present at around \(40^\circ\), and the Rietveld refinement showed the Co atoms to occupy positions at the eight edges of the unit cells and Pt atoms occupy the six face center positions of the unit cells.\(^{68}\)

- **\(\text{Pt}_3\text{Ni/C}\) and \(\text{Pt}_3\text{Ni/C-AW}\)**

Figure 3.3 shows the PXRD pattern of \(\text{Pt}_3\text{Ni/C}\) and \(\text{Pt}_3\text{Ni/C-AW}\) compared to that of \(\text{Pt/C-JM}\). As previously discussed the broad halo observed at \(2\theta = 30^\circ\) was once again due to the (002) peak of the carbon black support. The rest of the pattern can be indexed to (111), (200), (220), (311) and (222) diffractions of a typical FCC (Fm3m) structure implying that it was isostructural to the \(\text{Pt/C-JM}\) catalyst. In this case some of the Pt atomic positions are replaced with smaller Ni atoms. The shift to higher \(2\theta\) values of the (111) and (200) peaks likewise indicated the formation of an alloy whereby Ni was incorporated into the crystal lattice resulting in a smaller unit cell. The lattice parameter obtained from Rietveld refinement (Appendix A) was found to be in good agreement with the value reported in literature of 3.841 Å.\(^2\) The average crystallite size (Table 3.1) was found to be larger than that of \(\text{Pt/C}\) due to particle sintering during the alloy formation process. The absence of any superlattice reflections or any well-defined Ni or Ni-oxide peaks in the pattern indicated that no additional phases were present in the sample. This indicted that in the \(\text{Pt}_3\text{Ni/C}\) samples the Pt and Ni atoms are disordered and distributed randomly across the Pt positions.\(^69\)
Figure 3.3  PXRD patterns for Pt\(_3\)Ni/C and Pt\(_3\)Ni/C-AW

- \(\text{Pt}_3\text{Co}_{0.5}\text{Ni}_{0.5}/\text{C} \) and \(\text{Pt}_3\text{Co}_{0.5}\text{Ni}_{0.5}/\text{C-AW}\)

Figure 3.4 shows the PXRD pattern of the alloy mixtures of \(\text{Pt}_3\text{Co}_{0.5}\text{Ni}_{0.5}/\text{C-AW}\) compared to that of Pt/C-JM. Again, the broad halo observed at 2\(\theta\) = 30° was due to the (002) peak of the carbon black support. The rest of the pattern can be indexed to (111), (200), (220), (311) and (222) diffractions of a FCC (Fm3m) similar to that of Pt. The shift to higher 2\(\theta\) values of the (111) and (200) peaks indicate the formation of an alloy where the atomic positions of the inserted metal are shared between the Co and Ni resulting in a smaller lattice parameter to that of pure Pt (Appendix A). As with Pt\(_3\)Ni/C no superlattice reflections or any well-defined oxide peaks in the pattern were observed. Within the Topas software, allowance was made for the refinement of the atomic site occupancy of the Ni, Co and Pt atoms respectively. This however did not improve the Rwp considerably and sometimes gave erroneous results, implying that the refinable parameters had to be constrained. At this stage, it would not be possible to quantitatively take the solid solution effect into consideration from purely the PXRD data. It was more
appropriate to keep the site occupancy of the atoms at the theoretical values and rely on other techniques such as EDS to verify the quantity of the elemental composition of the mixed alloy samples.

Figure 3.4  PXRD patterns for Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW

3.1.1.2. Transmission Electron Microscopy (TEM)

- **Overview**

The following TEM study of starting pure Pt material (Pt/C-JM), heat-treated, acid washed Pt catalysts (Pt/C-900 and Pt/C-900-AW) as well as the alloyed samples (Pt$_3$Co/C, Pt$_3$Co/C-AW, Pt$_3$Ni/C, Pt$_3$Ni/C-AW, Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW) was done in order to determine the particle size distribution of each electrocatalyst. This was done by measuring the diameter of 200 particles using ImageJ software. In general the TEM images showed the carbon support with the metal particles well identified. Particle agglomeration was observed but the metal particles were well distributed over the much large carbon black material. Due to limited resolution of the electron microscope, detailed study of the particle surface morphology was not done. The particles did however show a roughly spherical
shape. Notably, the sample size used in the TEM study is considerably smaller to the sample size in PXRD analysis which may be based on the particular method of calculation used.

- **Pt/C-JM, Pt/C-900 and Pt/C-900-AW**

The histograms of the particle size distributions and corresponding TEM images of Pt/C-JM, Pt/C-900 and Pt/C-900-AW catalyst samples are shown in Figure 3.5 respectively. An average size distribution for the unheated catalyst (Pt/C-JM) was 4.1 nm while larger particles were observed for the heat treated samples (8 nm). The particle sizes obtained from TEM analysis were slightly smaller but similar in the order of magnitude to those obtained from PXRD analysis (Table 3.1).

![Histograms of particle size distributions and corresponding TEM images for Pt/C-JM, Pt/C-900 and Pt/C-900-AW](image)

**Figure 3.5** Histograms of particle size distributions and corresponding TEM images for Pt/C-JM, Pt/C-900 and Pt/C-900-AW
- **Pt$_3$Co/C and Pt$_3$Co/C-AW**

Figure 3.6 show the histograms of the particle size distributions and corresponding TEM images of Pt$_3$Co/C and Pt$_3$Co/C-AW catalysts. Larger particles were clearly observed for both samples with the alloy particles well distributed over the carbon support. The particles showed a roughly spherical shape and the size distribution showed an average of 9 nm for the two samples. Similarly, the particle sizes obtained from TEM analysis were slightly smaller but comparable to those obtained from PXRD analysis.

- **Pt$_3$Ni/C and Pt$_3$Ni/C-AW**

Figure 3.7 show the histograms of the particle size distributions and corresponding TEM images of Pt$_3$Ni/C and Pt$_3$Ni/C-AW catalysts. Similarly, larger particles were clearly observed for both samples. The size distribution was comparatively wider to the previous samples, with an average particle size of 7.7 nm for both samples. The particle sizes obtained from TEM analysis were slightly smaller but again comparable to those obtained from PXRD analysis.
Figure 3.7  Histograms of particle size distributions and corresponding TEM images for Pt$_3$Ni/C and Pt$_3$Ni/C-AW

- **Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW**

Figure 3.8 show the histograms of the particle size distributions and corresponding TEM images of Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW catalysts. Particle agglomeration was observed with the alloy particles being well distributed over the carbon support. The particles were spherical in shape with a wide size distribution and an average particle size of 8.5 nm. This again supports the fact that significant particle growth occurred when compared to the starting material, Pt/C-JM. The particle sizes obtained from TEM analysis are again slightly smaller than those obtained from PXRD analysis but within the order of magnitude acceptable.
Figure 3.8  Histograms of particle size distributions and corresponding TEM images for Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW

The average particle size for each electrocatalyst obtained from the TEM study is summarised in Table 3.2. By comparing the results obtained from both PXRD and TEM, the acid washed alloys and non-acid washed alloys showed that the acid washing step had very little or no effect on the crystallite sizes of the electrocatalysts. Hence, due to the similar crystallite sizes between heat-treated electrocatalysts used in the study (acid washed and non-acid washed), a size dependant activity would have a limited effect on the performance of these catalyst. It is well known however that electrocatalytic activity is highly dependent on the particle size and therefore it would be expected that these electrocatalysts (heat-treated) with relatively larger particles sizes than that of the starting material (Pt/C-JM) would have different activities from that of the Pt/C-JM (HiSpec 4000).
Table 3.2  Average particle size from TEM

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C-JM (HiSpec 4000)</td>
<td>4.1 ± 1.0</td>
</tr>
<tr>
<td>Pt/C-900</td>
<td>8.2 ± 2.3</td>
</tr>
<tr>
<td>Pt/C-900-AW</td>
<td>7.6 ± 2.1</td>
</tr>
<tr>
<td>Pt$_3$Co/C</td>
<td>8.5 ± 2.4</td>
</tr>
<tr>
<td>Pt$_3$Co/C-AW</td>
<td>9.2 ± 2.2</td>
</tr>
<tr>
<td>Pt$_3$Ni/C</td>
<td>7.7 ± 2.1</td>
</tr>
<tr>
<td>Pt$_3$Ni/C-AW</td>
<td>7.7 ± 2.1</td>
</tr>
<tr>
<td>Pt$<em>3$Co$</em>{0.5}$Ni$_{0.5}$/C</td>
<td>9.6 ± 3.4</td>
</tr>
<tr>
<td>Pt$<em>3$Co$</em>{0.5}$Ni$_{0.5}$/C-AW</td>
<td>8.3 ± 2.6</td>
</tr>
</tbody>
</table>

3.1.2 Elemental Composition

3.1.2.1 Energy Dispersive Spectroscopy (EDS)

The elemental composition of the metal particles of each catalyst was analysed by EDS analysis and compared to the theoretical atomic composition calculated from the number of moles of starting materials (Table 3.3).

The results showed that there was good agreement between the measured and weighed molar composition of the various catalysts. The EDS spectra for each sample are in Appendix B, also showing that no other contaminants from the synthesis were present from the acid washing procedure. The comparison between acid washed and non-acid washed alloy samples showed that the acid washing caused leaching to occur on the Pt$_3$Ni and Pt$_3$Co$_{0.5}$Ni$_{0.5}$ samples whereby the amount of Ni and Co decreased in these samples. It must be noted that EDS does not provide an accurate evaluation of the bulk sample, but primarily gives a surface composition and thus these values may vary.
Table 3.3 Elemental composition for each alloy obtained from EDS

<table>
<thead>
<tr>
<th>Electro catalyst</th>
<th>Theoretical Pt:Co:Ni Atomic ratio (atomic percentage in brackets)</th>
<th>Experimental Atomic Ratio (atomic percentage in brackets)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>Pt/C-JM (HiSpec 4000)</td>
<td>1:0:0 (100:0:0)</td>
<td>1 (100)</td>
</tr>
<tr>
<td>Pt/C-900</td>
<td>1:0:0 (100:0:0)</td>
<td>1 (100)</td>
</tr>
<tr>
<td>Pt/C-900-AW</td>
<td>1:0:0 (100:0:0)</td>
<td>1 (100)</td>
</tr>
<tr>
<td>Pt₃Co/C</td>
<td>3:1:0 (75:25:0)</td>
<td>2.66 (75.4)</td>
</tr>
<tr>
<td>Pt₃Co/C-AW</td>
<td>3:1:0 (75:25:0)</td>
<td>3.57 (69.2)</td>
</tr>
<tr>
<td>Pt₃Ni/C</td>
<td>3:0:1 (75:0:25)</td>
<td>3.09 (75.8)</td>
</tr>
<tr>
<td>Pt₃Ni/C-AW</td>
<td>3:0:1 (75:0:25)</td>
<td>2.45 (80.1)</td>
</tr>
<tr>
<td>Pt₃Co₀.₅Ni₀.₅/C</td>
<td>3:0.5:0.5 (75:12.5:12.5)</td>
<td>3.12 (75.4)</td>
</tr>
<tr>
<td>Pt₃Co₀.₅Ni₀.₅/C-AW</td>
<td>3:0.5:0.5 (75:12.5:12.5)</td>
<td>346 (76.1)</td>
</tr>
</tbody>
</table>

3.1.3 Metal Loading

3.1.3.1 Thermo-gravimetric Analysis (TGA)

The thermo-gravimetric analyses of the carbon supported electrocatalysts are shown in Figures 3.9 to 3.12 respectively. The analysis was done in order to show that the metal loading was consistent with that of the starting material and that no significant carbon oxidation occurred during the reduction process.
Figure 3.9  TGA data of Pt/C (JM), Pt/C-900 and Pt/C-900-AW in air; heating rate 5°C min\(^{-1}\)

Figure 3.10  TGA data of Pt\(_3\)Co/C and Pt\(_3\)Co/C-AW in air; heating rate 5°C min\(^{-1}\)
Figure 3.11  TGA data of Pt\textsubscript{3}Ni/C and Pt\textsubscript{3}Ni/C-AW in air; heating rate 5°C min\textsuperscript{-1}

Figure 3.12  TGA data of Pt\textsubscript{3}Co\textsubscript{0.5}Ni\textsubscript{0.5}/C and Pt\textsubscript{3}Co\textsubscript{0.5}Ni\textsubscript{0.5}/C-AW in air; heating rate 5°C min\textsuperscript{-1}
The results for all the samples showed four distinct regions. Between 25 and 200 °C there was little or no mass loss observed, besides a very small mass loss phenomenon that occurred at the beginning of each experiment that was attributed to the initiation of the instrumental air flow. Oxidation of the samples occurred gradually between in the region from 200 to 400 °C at which point an abrupt precipitous mass loss occurred as the temperature further increased. This region extended to higher temperature depending on the composition of the catalyst. For Pt/C catalysts the oxidation of carbon was complete at about 450 °C upon which no further mass loss occurs in the fourth region up to 850 °C. For the alloyed catalysts carbon oxidation was only completed between 500 and 600 °C.

The final value provided an indication of the metal loading for each catalyst. The results are summarised in Table 3.4 and it was found to be in good agreement with the theoretical mass loading of the metal calculated from the amount of the starting materials used. From the analysis of the Pt/C-JM, Pt/C-900 and Pt/C-900-AW catalysts it was found that about 1.4% of the initial carbon was oxidised during the passivation procedure once the alloys had been formed.

Table 3.4  Metal loading from TGA

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Theoretical metal loading (%)</th>
<th>Metal + Carbon (mg)</th>
<th>Metal only (mg)</th>
<th>Loading (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C (JM)</td>
<td>40.0</td>
<td>3.248</td>
<td>1.302</td>
<td>40.07</td>
</tr>
<tr>
<td>Pt/C-900</td>
<td>40.0</td>
<td>2.93</td>
<td>1.21</td>
<td>41.41</td>
</tr>
<tr>
<td>Pt/C-900-AW</td>
<td>40.0</td>
<td>4.52</td>
<td>1.89</td>
<td>41.49</td>
</tr>
<tr>
<td>Pt$_3$Co/C</td>
<td>44.43</td>
<td>5.541</td>
<td>2.486</td>
<td>44.86</td>
</tr>
<tr>
<td>Pt$_3$Co/C-AW</td>
<td>44.43</td>
<td>3.816</td>
<td>1.683</td>
<td>44.10</td>
</tr>
<tr>
<td>Pt$_3$Ni/C</td>
<td>44.09</td>
<td>4.367</td>
<td>1.939</td>
<td>44.35</td>
</tr>
<tr>
<td>Pt$_3$Ni/C-AW</td>
<td>44.09</td>
<td>5.268</td>
<td>2.230</td>
<td>43.66</td>
</tr>
<tr>
<td>Pt$<em>3$Co$</em>{0.5}$Ni$_{0.5}$/C</td>
<td>44.10</td>
<td>4.386</td>
<td>1.967</td>
<td>44.84</td>
</tr>
<tr>
<td>Pt$<em>3$Co$</em>{0.5}$Ni$_{0.5}$/C-AW</td>
<td>44.10</td>
<td>5.207</td>
<td>2.282</td>
<td>43.82</td>
</tr>
</tbody>
</table>
3.1.4 Summary of Physical Characterisations

The PXRD results showed that Pt-based alloy electrocatalysts were successfully synthesised by a method whereby Pt/C was impregnated with Co or Ni or a combination of both to produce the respective alloys. From TEM and PXRD it was found that the particle size was substantially larger for the alloys that for the Pt/C-JM starting material due to particle sintering caused by the high thermal treatment under a H₂ atmosphere for the reduction process. This was also verified by the observed increase in Pt particle size when Pt/C was subjected to the same thermal temperature regime used for the reduction and alloying process. It was also found that Pt-based alloys were formed in all cases where Pt was combined with smaller transition metals. This was confirmed by both the lattice contraction observed for alloyed samples indicated by the decrease in lattice parameters as well as a shift in the XRD peaks to higher 2θ values.

From EDS and TGA data it was found that the respective alloys were synthesised in their respective atomic ratios and that the total metal loading was not significantly affected by the synthesis process or acid washing procedure.
3.2 Electrochemical Characterisations

3.2.1 Electrochemical Surface Area (ECSA)

3.2.1.1 Cyclic Voltammetry (CV)

- **Overview**

Cyclic voltammetry was performed to obtain the electrochemical surface area (ECSA) of the electrode coated with each respective catalyst. CV was also used to detect the presence of any contaminants that may have been introduced during the synthesis procedure as well as detect any changes in the structural or intrinsic properties of the catalysts. The resultant voltammograms are discussed below and Table 3.5 sums up the Pt ECSA for each catalyst.

- **Pt/C-JM, Pt/C-900 and Pt/C-900-AW**

![Cyclic voltammogram for Pt/C-JM, Pt/C-900 and Pt/C-900-AW catalysts in N₂ purged 0.5M H₂SO₄ at 50 mV s⁻¹](image)

*Figure 3.13 Cyclic voltammogram for Pt/C-JM, Pt/C-900 and Pt-900-AW catalysts in N₂ purged 0.5M H₂SO₄ at 50 mV s⁻¹*
Figure 3.13 shows the cyclic voltammograms of Pt/C-JM, Pt/C-900 and Pt/C-900-AW in 0.5M H₂SO₄. While Figures 3.14 – 3.16 provide the cyclic voltammograms for the alloyed electrocatalysts. From Figure 3.13 and given that the particle size obtained from TEM for Pt/C-JM was smaller than that of Pt/C-900 and Pt/C-900-AW, it can be seen the peak resolution decreased with increasing particle size. The area in the hydrogen underpotential deposition (H_{upd}) region, i.e. the adsorption pseudo capacitance decreases with increasing particle size because of the decrease in the ECSA when moving to larger particles. The base voltammetry still remains the same however with all catalysts showing hydrogen adsorption/desorption peaks in the region between +0 and +0.25 V vs. SHE and Pt-oxide formation/reduction peaks in the region between +0.5 and +0.9 V vs. SHE.

**Pt₃M/C and Pt₃M/-AW (M = Co, Ni or Co +Ni)**

![Cyclic voltammogram of Pt₃Co/C and Pt₃Co/C-AW catalysts in N₂ purged 0.5M H₂SO₄ at 50 mV s⁻¹](image.png)

Figure 3.14  Cyclic voltammogram of Pt₃Co/C and Pt₃Co/C-AW catalysts in N₂ purged 0.5M H₂SO₄ at 50 mV s⁻¹
Figure 3.15  Cyclic voltammogram of Pt$_3$Ni/C and Pt$_3$Ni/C-AW catalysts in N$_2$ purged 0.5M H$_2$SO$_4$ at 50mV/s

Figure 3.16  Cyclic voltammogram of Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW catalysts in N$_2$ purged 0.5M H$_2$SO$_4$ at 50 mV s$^{-1}$
In the case of Pt-Co, Pt-Ni and Pt-Co-Ni electrocatalyst systems, a cathodic potential shift in the onset of the oxide formation indicates the creation of a weakly adsorbed oxide layer on the Pt surface, which would be easier to reduce and thus would imply that the electrocatalyst would have an increased ORR activity.\textsuperscript{71} This phenomenon is only very slightly observed for all the alloys with the order being Pt\textsubscript{3}Co < Pt\textsubscript{3}Ni < Pt\textsubscript{3}Co\textsubscript{0.5}Ni\textsubscript{0.5}. This may indicate that the effect of alloying Pt with Co and Ni changed the way the Pt interacts with H\textsubscript{2}O and possibly O\textsubscript{2} which may affect the ORR kinetics. It is noted however that the oxide peaks for all heat treated electrocatalysts are substantially suppressed as compared to that of Pt/C-JM and this inhibition is attributed to the larger particle size of the heat treated electrocatalysts rather than the alloying effects.

Table 3.5 provides the Pt ECSA for each catalyst obtained from the integration of the hydrogen underpotential adsorption regime with respect to the Pt mass. The ECSA is a measure of the entire surface available from all catalyst in contact electronically to the carbon support and the glassy carbon electrode whilst also in contact with protons from the electrolyte solution. It can be seen that the ECSA significantly decreased upon alloying due particle growth as a result of sintering, as indicated from the TEM and XRD results. The electrochemical surface area is known to be inversely proportional to the particle size therefore this phenomenon is to be expected.\textsuperscript{72}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt loading (µg)</th>
<th>Integrated Peak Area (µC)</th>
<th>ECSA (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C-JM</td>
<td>3.05</td>
<td>395.6</td>
<td>61.77</td>
</tr>
<tr>
<td>Pt/C-900</td>
<td>3.02</td>
<td>151.0</td>
<td>23.81</td>
</tr>
<tr>
<td>Pt/C-900-AW</td>
<td>3.02</td>
<td>151.5</td>
<td>23.88</td>
</tr>
<tr>
<td>Pt\textsubscript{3}Co/C</td>
<td>2.42</td>
<td>124.0</td>
<td>24.40</td>
</tr>
<tr>
<td>Pt\textsubscript{3}Co/C-AW</td>
<td>2.35</td>
<td>107.7</td>
<td>21.79</td>
</tr>
<tr>
<td>Pt\textsubscript{3}Ni/C</td>
<td>2.29</td>
<td>78.2</td>
<td>16.28</td>
</tr>
<tr>
<td>Pt\textsubscript{3}Ni/C-AW</td>
<td>2.35</td>
<td>84.7</td>
<td>17.13</td>
</tr>
<tr>
<td>Pt\textsubscript{3}Co\textsubscript{0.5}Ni\textsubscript{0.5}/C</td>
<td>2.24</td>
<td>133.1</td>
<td>28.27</td>
</tr>
<tr>
<td>Pt\textsubscript{3}Co\textsubscript{0.5}Ni\textsubscript{0.5}/C-AW</td>
<td>2.20</td>
<td>119.9</td>
<td>25.96</td>
</tr>
</tbody>
</table>
3.2.2 Oxygen Reduction Reaction (ORR) Polarisation

3.2.2.1 Rotating Disc Electrode (RDE) Analysis

The ORR activity of each electrocatalyst was established by RDE in oxygen saturated H\textsubscript{2}SO\textsubscript{4} (0.5 M) at room temperature. It must be noted that the cathodic scans were done in these experiments and would be significantly different to the anodic scans for various reasons. These reasons include double layer charging and the formation of Pt-O in the anodic scans or its reduction in the cathodic scans. Thus the kinetic controlled region extends to about +0.8 V vs. SHE in these scans and a value of +0.77 V vs. SHE was selected for comparison with literature values taking the anodic scan, at a value of +0.9 V vs. SHE.\superscript{73}

![Polarisation curves of Pt/C-JM, Pt/C-900 and Pt/C-900-AW in oxygen-saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} at 1600 rpm and 10 mV s\textsuperscript{-1}

Figure 3.17]
Figure 3.18  Polarisation curves for Pt$_3$Co/C, Pt$_3$Co/C-AW, Pt$_3$Ni/C, Pt$_3$Ni/C-AW, Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW compared with Pt/C-JM in oxygen-saturated 0.5 M H$_2$SO$_4$ at 1600 rpm and 10 mV s$^{-1}$.

Figure 3.17 shows the polarisation curves for Pt/C-JM, Pt/C-900 and Pt/C-900-AW. While Figure 3.18 shows the polarisation curves for the synthesised alloy electrocatalysts compared to that of Pt/C-JM, it is noted that for all the catalysts the diffusion-limited current density, $I_{\text{lim}}$, reaches a maximum at about +0.2 V vs. SHE at which point the oxygen diffusion to the catalyst surface becomes the rate limiting step. Generally a plateau is reached at about +0.2 V - +0.7 V whereby the system reaches a diffusion limited regime much faster however this regime is not reached until 0.2 V which may indicate that the Pt loading on the GC electrode is too low and that the oxygen at the surface is not being reduced as quickly as it arrives at the electrode surface.$^{73}$ The diffusion-limited current density is in the range between $\pm 2.5$ and $\pm 4.5$ mA cm$^{-2}$$_{\text{geo}}$. There is an obvious difference in the diffusion-limited current density between catalysts and this is partially attributed to the different morphologies of the catalyst material, differences in Pt loading when preparing the electrodes as well as being caused by the unequal coverage of the electrode surface with catalyst due to the low loading, regarded as an
experimental artifact. Between the potential of about 0.2 V to 0.7 V vs. SHE the reaction regime exhibits one that is dominated by mixed kinetic and diffusion control. Beyond 0.7 V vs. SHE the reaction is strictly dominated by kinetic control, where the catalytic surface is the slowest component in the overall reaction process, relative to the mass transport which is considerably faster. Beyond +0.9 V the open cell potential (OCP) is reached whereby no electrocatalytic conversion of oxygen occurs.

3.2.2.2 Catalytic Activity

In order to extract the intrinsic catalytic activity, $I_{\text{kinetic}}$ of each catalyst, the Koutechy-Levich equation (Eq. 3.1) was used. This enabled the measured ORR current density, $I$, to be corrected for the mass transport accordingly:

$$I_{\text{kinetic}} = \frac{I_{\text{lim}} \times I}{I_{\text{lim}} - I}$$

(3.1)

Where $I_{\text{kinetic}}$ is the kinetic current and $I_{\text{lim}}$ is the measured diffusion limited current density. The Pt surface area specific ($I_s$) and mass specific ($I_m$) activities were then estimated by corrected for the electrochemical surface area and the mass of the Pt loaded onto the electrode and the ECSA or each catalyst respectively. Figures 3.19 and 3.20 show the Tafel plots obtained using Eq. 3.1 for the surface area normalised and mass normalised current density for Pt respectively. Similar Tafel plots are shown for the prepared Pt-alloy electrocatalysts in Figures 3.21 and 3.22.

The Tafel plots show that all the catalysts have similar Tafel slopes around 60 – 90 mV/decade: which are in good agreement with the value reported in literature for Pt/C of about 80mV/decade for the low current density region. It can clearly be seen that when corrected for surface area and mass of catalyst, the activities of the catalysts differ with respect to one another. From Figure 3.19 it can be seen that the specific activity increases as the Pt particle size increases, in the order Pt/C-JM < Pt/C-900 < Pt/C-900-AW. However when comparing mass activities, the order is reversed and Pt/C-JM still remains the most active catalyst.
When comparing the activities of the alloys to that of Pt/C-JM, Figure 3.21, it can be seen that the specific activity is higher for all the alloys except Pt$_3$Ni/C with a crossover occurring at about 0.74V when Pt$_3$Ni/C also becomes more active, with Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW having the highest specific activity. When looking at Figure 3.22, it can be seen that only Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW has a higher mass activity as compared to Pt/C-JM.

![Tafel Plot](image.png)

**Figure 3.19** Tafel Plot for the Pt surface area normalised current density (specific activity, $I_s$) for the ORR at 25°C on Pt/C-JM, Pt/C-900 and Pt/C-900-AW
Figure 3.20  Tafel Plot for the Pt mass normalised current density (mass activities, $I_m$) for the ORR at 25°C on Pt/C-JM, Pt/C-900 and Pt/C-900-AW

Figure 3.21  Tafel Plot for the Pt surface area normalised current density (specific activity, $I_s$) for the ORR at 25°C on Pt$_3$Co/C, Pt$_3$Co/C-AW, Pt$_3$Ni/C, Pt$_3$Ni/C-AW, Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW compared to that of Pt/C-JM
Table 3.6 compares the absolute activities at +0.77 V vs. SHE for each catalyst along with the respective low current density region Tafel slopes. It can be seen that the ternary electrocatalyst showed the highest activity with Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW having the highest specific activity of 430.8 μA cm$^{-2}$Pt and an improvement factor of 2.4 compared to that of Pt/C-JM, followed by Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C which had a specific activity of 340.6 μA cm$^{-2}$Pt and an improvement factor of 1.9. In terms of mass activity, only Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C exhibited a higher value with a slight improvement of about 15% with the rest all showing a decrease in mass activity.
Table 3.6  Summary of absolute activities and Tafel slopes at 0.77 V for each electrocatalyst. Improvement factor as compared to Pt/C-JM is shown in brackets.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific activity (μA cm⁻²)</th>
<th>Mass activity (A mg⁻¹)</th>
<th>Tafel slope (mV decade⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C-JM (HiSPec 4000)</td>
<td>179.3</td>
<td>0.1111</td>
<td>74.8</td>
</tr>
<tr>
<td>Pt/C-900</td>
<td>237.5 (1.33)</td>
<td>0.0597 (0.54)</td>
<td>91.3</td>
</tr>
<tr>
<td>PtCo/C</td>
<td>189.0 (1.05)</td>
<td>0.0535 (0.48)</td>
<td>74.6</td>
</tr>
<tr>
<td>PtCo/C-AW</td>
<td>245.0 (1.37)</td>
<td>0.0531 (0.48)</td>
<td>68.2</td>
</tr>
<tr>
<td>PtNi/C</td>
<td>153.8 (0.85)</td>
<td>0.0258 (0.23)</td>
<td>63.7</td>
</tr>
<tr>
<td>PtNi/C-AW</td>
<td>217.4 (1.21)</td>
<td>0.0362 (0.33)</td>
<td>68.2</td>
</tr>
<tr>
<td>Pt₀.₅Co₀.₅Ni₀.₅/C</td>
<td>340.6 (1.90)</td>
<td>0.1277 (1.15)</td>
<td>70.1</td>
</tr>
<tr>
<td>Pt₀.₅Co₀.₅Ni₀.₅/C-AW</td>
<td>430.8 (2.40)</td>
<td>0.0999 (0.90)</td>
<td>79.7</td>
</tr>
</tbody>
</table>

Since there is a vast difference in the particle size between the prepared alloy electrocatalysts and that of Pt/C-JM, a study of the absolute activity normalised for electrochemical surface area and mass does not sufficiently described the true alloying effect. A better understanding is obtainable from the activity decay which was not done in this study. Nevertheless an indication of the catalytic activity is observed from the RDE analysis which was found to be dependent on particle size and composition. It must be said that there is not a single value for these activity values that is accepted as being the convention but an activity increase by a factor of 4 have been reported in literature for both PtCo and PtNi prepared under similar conditions which has not been replicated here. This is once again largely described by the increase in the particle size observed in this study.
3.3 In-situ Fuel Cell testing

In-situ fuel cell testing was done in order to obtain a real evaluation of the catalytic performance under fuel cell operating conditions and how that compared to that of the carbon supported Pt catalyst (Pt/C-JM). MEA’s were fabricated with each catalyst as the cathode by the same procedure as described in Chapter 2 Section 2.3. This provides a direct comparison of the catalytic activity of each catalyst. A measure of the power output, which is the product of the current density and its corresponding cell voltage, was also obtained.

3.3.1 Polarisation curve analysis

Figure 3.23 shows the polarisation curves of MEA’s where Pt/C-JM was used for the anode (0.4 mg cm\(^{-2}\)) and Pt/C-JM, Pt\(_3\)Co/C and Pt\(_3\)Co\(_{0.5}\)Ni\(_{0.5}\)/C-AW (0.4 mg cm\(^{-2}\)) was used for the cathode in tested under the same fuel cell operating conditions. The curves show that the performance of Pt/C-JM was
superior at all current densities, with lower polarisation losses and higher power densities. At a typical cell voltage of +0.6 V the Pt/C-JM MEA produces a power density of 544 mW cm$^{-2}$ which is almost twice that of the power density for Pt$_3$Co/C of 227 mW cm$^{-2}$ with Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW producing a power output of about 355 mW cm$^{-2}$. It is also noted that the power density for the Pt/C-JM and Pt$_3$Co/C increase with a decrease in cell voltage, but peaks at about +0.4 V for Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW. At these lower cell voltages however, the fuel cell energy conversion efficiency decreases to below 50 % and therefore it would not be feasible to operate the fuel cell at these voltages.$^{76}$ Since MEA's were fabricated by the same procedure this provides a direct comparison of the catalytic activity of each catalyst. This result follows the same trend as the mass activity obtained from RDE studies, where the order is Pt/C-JM > Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW > Pt$_3$Co/C.

### 3.3.2 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were performed in order to obtain an indication of the various losses associated with electrocatalyst. A simplified equivalent circuit model accounting only for the cathode activation kinetics was required for this since the anode kinetics is significantly slower and no mass transfer resistance is observed as pure oxygen was used at the cathode. This model (Fig 3.24) consists of an electrolyte resistance ($R_m$), which is modelled by an ohmic resistance with the infinite Warburg impedance element ($Z_w$) excluded. As the influence of the anode was considered to be negligible and no mass transfer was observed, both electrodes were thus described together via a parallel arrangement of a double layer capacitance ($C_{dl}$) and a charge transfer resistance ($R_{ct}$). The impedance represents the charge transfer resistance in the ORR, which provides an indication of the properties of the cathode, such as the catalyst surface area, catalyst loading and catalyst utilisation.$^{77}$
Figure 3.25, 3.26 and 3.27 show the impedance spectra in the form of Nyquist plots at 100 mA cm$^{-2}$, 200 mA cm$^{-2}$ and 400 mA cm$^{-2}$ in the frequency range from 0.1 Hz to 20 kHz depicting a single impedance semi-circular arc referred to as the kinetic loop for each electrocatalyst. Under the operating conditions used only one loop is expected since with the high concentration of O$_2$ used mass transfer limitations become negligible, particularly at the low current density region of 100 mA cm$^{-2}$.

The results in Figure 3.25 show that the charge transfer resistance given by the diameter of the kinetic loop was smaller for the cells with the Pt/C-JM and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C catalysts at the cathode and larger for Pt$_3$Co/C. This corresponds to the drastic performance drop for Pt$_3$Co/C compared to Pt/C-JM. This trend was observed at all current densities studied.
Figure 3.25  Nyquist plot at a current density of 100mA cm\(^{-2}\) for cells with three different cathode electrocatalysts analysed under the operating conditions of \(T = 80\, ^\circ\)C, \(P = 2/2\) bar, \(s_{\text{hydrogen}} = 1.5\), \(s_{\text{oxygen}} = 10\), \(\text{RH}_{\text{anode}} = 50\%\), \(\text{RH}_{\text{cathode}} = 25\%\), \(\text{Cell compression} = 4.8\, \text{N mm}^{-2}\).

Figure 3.26  Nyquist plot at a current density of 200mA cm\(^{-2}\) for cells with three different cathode electrocatalysts analysed under the operating conditions of \(T = 80\, ^\circ\)C, \(P = 2/2\) bar, \(s_{\text{hydrogen}} = 1.5\), \(s_{\text{oxygen}} = 10\), \(\text{RH}_{\text{anode}} = 50\%\), \(\text{RH}_{\text{cathode}} = 25\%\), \(\text{Cell compression} = 4.8\, \text{N mm}^{-2}\).
Figure 3.27 Nyquist plot at a current density of 400 mA cm$^{-2}$ for cells with three different cathode electrocatalysts analysed under the operating conditions of $T = 80^\circ$C, $P = 2/2$ bar, $s_{\text{hydrogen}} = 1.5$, $s_{\text{oxygen}} = 10$, $\text{RH}_{\text{anode}} = 50\%$, $\text{RH}_{\text{cathode}} = 25\%$, Cell compression = 4.8 N mm$^{-2}$.

All the EIS data were modelled with the equivalent circuit shown in Figure 3.24. As an example for this is given in Fig. 3.28 for Pt/C-JM at 100 mA cm$^{-2}$ from which the values for respective resistances were obtained. It must be noted that a simple model was used to illustrate the variations between the different electrocatalysts at different current densities and may vary from the experimental data due to the complexity of the real system. The EIS analysis thus only served as supportive information for the discussion of the performance of the MEAs indicating the performance of the cathode catalyst used. More complex models include the replacement of a capacitance element with a constant phase element and to consider the deviation from ideal capacitance behaviour, these models are described by various authors$^{77}$. Since different circuits can describe the same set of data with increasing complexity the possibility of interpretational errors may increase.
Figure 3.28 The EIS fit of modelled and experimental data for Pt/C-JM at 100 mA cm$^{-2}$

The results for the ohmic resistance ($R_m$), charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$) extracted from the EIS fitting analysis and these are shown in Fig. 3.29, Fig. 3.30 and Fig. 3.31 for each current density respectively.
Figure 3.29 A plot of the ohmic resistance vs. current density for Pt/C-JM, Pt\textsubscript{3}Co/C and Pt\textsubscript{3}Co\textsubscript{0.5}Ni\textsubscript{0.5}/C-AW

Figure 3.30 A plot of the charge transfer resistance vs. current density for Pt/C-JM, Pt\textsubscript{3}Co/C and Pt\textsubscript{3}Co\textsubscript{0.5}Ni\textsubscript{0.5}/C-AW
The results in Fig 3.29 and Fig 3.30 showed that a general trend occurred where the ohmic resistance and charge transfer resistance decreases as the current density increased for each catalyst. The decrease in the ohmic resistance was attributed to the possible change in the humidity of the membrane.

At a current density of 100 mA cm\(^{-2}\) the ohmic resistance for Pt\(_3\)Co\(_0.5\)Ni\(_0.5\)/C (16.99 Ω) was similar to that of Pt\(_3\)Co/C (15.57 Ω) but was higher than that of Pt/C-JM (11.98 Ω) and this trend was observed at higher current densities. It was also noticed that the change in \(R_m\) was almost identical for all catalysts studied. As identical materials for the membrane, gas diffusion layer and bipolar plates as well as the same MEA fabrication procedure were used this difference between alloyed samples and that of Pt/C-JM this was expected. However reasons for the difference between the values for the Pt/C-JM compared to the alloys may be due to the some intrinsic properties of the Pt/C-JM catalyst that may change the
Comparing the charge transfer resistances for each catalyst it was found that the Pt/C-JM and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW had very similar values of 36.72 $\Omega$ and 36.71 $\Omega$ respectively, with Pt$_3$Co/C having a higher value of 56.25 $\Omega$ at 100 mA cm$^{-2}$. A similar change in the $R_{ct}$ values across the current density range was observed for the catalysts studied. The decrease in the charge transfer resistance with the increase in current density is attributed to the increase in the electrochemical kinetics of the ORR as the reaction proceeds.$^{77}$

The double layer capacitance ($C_{dl}$) values increased with an increase in the current density for all catalysts, with Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C showing higher $C_{dl}$ values at all current densities. This indicated that the surface capacitance of the ternary alloy was higher at all current densities. Possible reasons for the difference in the double layer capacitance may be the changes of various experimental parameters when fabricating the MEA used for the in-situ analysis. These may include a difference in the thickness of the catalyst layers produced by doctor blade spreading, slight variation in the membrane hot pressing conditions as well as differences in the humidity of the cell during operation which may affect proton conductivity. These parameters were not analysed in this study and thus difference in the double layer capacitance may not be adequately accounted for.

By the comparison of the EIS measurement and the polarisation curves it was found that the Pt/C-JM had a better fuel cell performance as this catalyst had the lowest ohmic and charge transfer resistances compared to Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW which had an identical charge transfer resistance but higher ohmic resistance. Pt$_3$Co/C was found to have both higher ohmic and charge transfer resistances and thus the performance of this catalyst was lower to that of Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW and Pt/C-JM.
3.3.3 Summary of Chemical Characterisation and Fuel Cell Testing

This increase in the particle size dramatically decreased both the ECSA, and the catalytic activity. Nevertheless RDE analysis showed that even with the decreased electrocatalytic surface area, the ORR activity improved with Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C showing a higher specific activity and mass activity than that of the Pt/C catalyst. The activity measurements combined with the physical characterisation clearly indicated that the lower than expected ORR activity observed for the Pt-based alloys was largely due to the increased particle sizes of the alloys.

This trend carried through to the fuel cell testing where the in-situ performance of the MEA made with cathodes containing the synthesised electrocatalyst showed the same trends as the ORR mass activity values obtained from ex-situ RDE studies.

Pt-ternary electrocatalysts containing both Co and Ni were shown to be the best alloys synthesised in terms of specific activity, mass activity and had the best MEA performance for the sampled analysed. This was followed by Co only containing alloys which were both better than that of Ni only containing alloys which showed the worst performance of the catalysts studied. However Pt/C was found to be better than these especially while tested under real fuel cell operating conditions. This was due to Pt/C-JM having lowered ohmic and charge transfer resistances as determined by EIS measurements.
Chapter 4  Conclusions

This study focused on the synthesis and detailed physical and electrochemical characterisation of Pt-based alloy electrocatalysts supported on carbon black. Pt was alloyed with Co, Ni and a combination of Co and Ni to for binary electrocatalysts of Pt$_3$Co/C, Pt$_3$Ni/C and ternary Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C.

Each catalyst synthesised was also subjected to an acid washing procedure to yield their respective acid washed counterparts of Pt$_3$Co/C-AW, Pt$_3$Ni/C-AW and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW. The physical and electrochemical properties of the prepared electrocatalysts were compared to that of the starting material (Pt/C-JM) as well as the Pt/C catalysts (Pt/C-900 and Pt/C-900-AW) subjected to the same thermal and acidic treatments used for the synthesis of the alloyed electrocatalysts.

The electrocatalysts were characterised in terms of its structural and morphological properties by PXRD and TEM as well as its elemental composition by EDS and the metal loading was also determined by TGA. In terms of electrochemical analysis CV was used to determine the electrochemical surface area or the respective electrocatalysts while RDE analysis was done to obtain the activity of the electrocatalysts towards the ORR as well as the intrinsic kinetics associated with the ORR. Finally membrane electrode assemblies (MEA) were fabricated using selected synthesised alloy electrocatalysts and its performance under ‘real’ fuel cell conditions were evaluated by means of polarisation curve analysis and electrochemical impedance spectroscopy and compared to that of Pt/C.

The physical and electrochemical analysis showed that it was possible to synthesis Pt-based alloy electrocatalysts with comparable ORR activity to that or commercial Pt/C. The PXRD results confirmed the formation of alloys by the shift in the Pt peaks to higher 2θ. This was as a result of lattice contraction due to Pt particles being replaced with the smaller metals of Co and Ni in the crystal lattice of the starting material, namely Pt/C. This lattice contraction was attributed solely to the formation of Pt-based alloys as no lattice contraction was observed when Pt only was subjected to conditions of the alloying procedure. It was also found that
ordered single phase alloys were formed when Pt was alloyed with Co to produce
the primitive cubic structure or Pt$_3$Co/C where the Co atoms to occupied positions
at the eight edges of the unit cells and Pt atoms occupied the six face center
positions of the unit cells. A result that until recently was not often reported in
literature. Disordered single phase alloys of Pt$_3$Ni and Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C were also
formed that were isostructural to that of the starting Pt/C catalyst. Finally it was
found that the crystallite size observed for heat-treated catalysts were greater than
that of the starting material and this was ascribed to possible sintering of the Pt
particles when subjected to the high thermal conditions coupled with the presence
of H$_2$ during the reduction process. It is also possible that this sintering process
may be allowed to proceed at a significantly slower rate when the crystal structure
is altered as in the case of the Pt-Co system that showed smaller crystallite sizes
(4.6 – 7.8 nm) than that of heat-treated Pt (Pt/C-900 and Pt/C-900-AW) (10.5 – 11
nm) yet still larger than that of the starting material (Pt/C-JM, 3.8 -4.1 nm).

Larger particles were also observed from the TEM studies for all heat treated
catalysts compared to that of the Pt/C starting material (4.1 ± 1.0 nm) which
confirmed the sintering of Pt particles. It was also found that the acid washing
procedure had very little or no effect on the particle sizes of the catalysts. Elementa
analysis by EDS confirmed the formation of alloys in these respective
atomic ratios and that acid washing has a significant influence on the atomic ratios
of the electrocatalysts. It was found that Ni was significantly leached from Ni
containing alloys (Pt-Ni and Pt-Co-Ni systems) while Co was only leached in the
ternary Pt-Co-Ni system and not for the Pt-Co system. This result was surprising
in that Co was not significantly leached in the Pt-Co system but may once again
be attributed the high ordering within Pt-Co catalyst structures. It was found that
no significant carbon oxidation occurred during the reduction-passivation
procedure and that the metal loading was close to that of their respective
theoretical loadings using Pt/C (40%) as the starting material. The combined
outcome of the PXRD, TEM, EDS and TGA results lead to a conclusion that the
alloying procedure was a success. The procedure was designed in such a way
that Pt was alloyed with Co, Ni or a combination of Co and Ni in a Pt 3:1 M ratio
without any significant carbon oxidation when using Pt/C (40%) and this was
found to be the case in this study.
The electrochemical analysis showed that the ECSA significantly decreased from 61.77 m² g⁻¹ for Pt/C-JM to ~ 17 – 28 m² g⁻¹ due to the formation of larger catalyst particles caused by the metal sintering upon the heat treatment procedure. This in turn was found to affect the catalytic performance of the catalysts in that the performance found in this study was not as substantially improved to that of similar catalysts performances reported in literature with respect to Pt/C. Nevertheless an improvement in the catalytic activity toward the ORR was observed by RDE analysis for Pt₃Co₀.₅Ni₀.₅/C in terms of both mass and specific activity with values of 0.1277 A mg⁻¹Pt and 340.6 μA cm⁻²Pt respectively.

The in-situ fuel cell performance analysis confirmed the result of the ex-situ RDE activity for the ORR with regard to the mass activity analysis. Pt/C-JM was found to have a better catalytic performance than the Pt₃Co₀.₅Ni₀.₅/C-AW catalyst which in turn performed better that Pt₃Co/C. This was indicated by the analysis the polarisation curves and power output as well as the EIS measurements for the ohmic and charge transfer resistance as was found to be largely due to the increase in the particle sizes during the heat treatment procedure.

Careful analysis of the ORR activity measurements did however reveal that the intrinsic activity of Pt was improved by alloying with less costly transition metals and that promising improvement of the performance of fuel cell catalysts are possible while lowering the material costs of the catalytic material, provided an increase in the particle size is controlled

Further improvement in the catalytic activity may be achieved by a number steps which should be regarded as future work. A thorough understanding of the particle surface properties is needed. These properties include wettability, surface energies, defect density, and crystal structure. A method of controlling the size of alloy catalysts during formation is also required. This may be achieved by evaluating alloy formation at lower temperatures; however this may lead to the formation of mixed phase alloys which may also negatively affect the catalytic activity of the electrocatalysts. Other methods of forming alloys may also studies
such as mechanical alloying by ball milling where a more uniform particle size distribution may be obtained.

Future work may also be focused on the use Ring Rotating Disc Electrode (RRDE) studies to evaluate the formation of peroxide species and therefore obtain a better understanding of the oxygen reduction reaction mechanisms. A better understanding of the catalyst performance may also be done by an in depth EIS study using an ex-situ three electrode system where loses due to issues such flooding, fuel cell components and MEA fabrication may be excluded.
References


56. AXS, B., TOPAS V4: General profile and structure analysis software for powder diffraction data, 2008, Bruker AXS: Karlsruhe, Germany.


Appendix

Appendix A: Rietveld Refinement Patterns

Figure A.1  Rietveld refinement of the commercial Pt/C-JM catalyst PXRD pattern

Figure A.2  Rietveld refinement of Pt/C-900 PXRD pattern
Figure A.3  Rietveld refinement of Pt-900-AW PXRD pattern

Figure A.4  Rietveld refinement of Pt$_3$Co/C PXRD pattern

Figure A.5  Rietveld refinement of Pt$_3$Co/C-AW PXRD pattern
Figure A.6  Rietveld refinement of Pt$_3$Ni/C PXRD pattern

Figure A.7  Rietveld refinement of Pt$_3$Ni/C-AW PXRD pattern

Figure A.8  Rietveld refinement of Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C PXRD pattern
Figure A.9  Rietveld refinement of Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW PXRD pattern
Figure B.1  EDS image of a) commercial Pt/C (JM), b) Pt-900 and c) Pt-900-AW catalysts
Figure B.2  EDS image of a) Pt$_3$Co/C and b) Pt$_3$Co/C-AW

Figure B.3  EDS image of a) Pt$_3$Ni/C and b) Pt$_3$Ni/C-AW
Figure B.4  EDS image of a) Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C and b) Pt$_3$Co$_{0.5}$Ni$_{0.5}$/C-AW
## Table B.1  Elemental composition for each alloy obtained from EDS

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