Hydrogen Economy: MEA Manufacturing for PEM electrolysers

By

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Baccalerus Technologiae Chemistry

A dissertation submitted for the fulfilment of the requirements

for the

Masters Degree in Technology: Chemistry

In the Faculty of Science at

Nelson Mandela Metropolitan University

January 2011

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Abstract

The electrolysis of water was evaluated as a potentially efficient, as a low cost means of hydrogen production. The theoretical energy, voltage, current, and energy efficiencies of water electrolysis were considered by using various catalyst materials used in the fabrication of membrane electrode assemblies used in low temperature water electrolysis systems.

Traditionally, iridium based catalysts have shown to be the most suitable material for its use on electrocatalysis of water to form hydrogen. This study showed that a combination of various elements as a binary and or ternary mixture in the base catalyst that was applied to the anode and cathode by using the Adam’s method had shown to give comparatively good results to that of using iridium oxide on its own. These catalysts were characterized by cyclic voltammetry, at different temperatures (30°C-80°C) with a range of catalyst loading of 0.2-0.5 mg.cm^{-2} noble metals.

The study showed that the Ir_{40}Co_{40} mixture as an anode catalyst was found to show highest hydrogen efficiency of 73% with a relatively low over potential of 0.925V at higher temperature of 80°C. The mixture also showed to give the best electrocatalytic activity with a low Tafel slope of 30.1mV.dec^{-1}. Whereas the Ir_{50}Pt_{50} showed a comparatively lower hydrogen efficiency of 65% with a lower over potential of 0.6V at 50°C.

Ternary mixed oxide of Ir_{20}Ru_{40}Co_{40} showed an even lower over potential of 0.5-0.6V over a large range of temperatures with a low hydrogen efficiency of 44%, but gave good electrocatalytic activity in terms of the Tafel slope analysis.
On the other hand, mixtures with relatively cheaper material such as Nickel in binary mixture systems such as Pt$_{50}$Ni$_{50}$ as cathode catalyst was found to show promising performance of a relatively low over potential that was less than 1.4 V with a low hydrogen efficiency of 62.1 %. Ternary cathode catalyst materials such as Pt$_{33}$Ni$_{33}$Co$_{33}$ exhibited good performance with higher hydrogen efficiency of 65.2 % at lower over potential of 1.2 V and a higher Tafel slope of 133.9 mV.dec$^{-1}$ at 80 $^\circ$C.
Acknowledgements

- To the Lord for his mercy
- My supervisor Dr. S. Gouws and co-supervisor Dr. E. Ferg for their support and guidance and showing great interest in my work.
- To my friends and family for their sacrifice, love and support.
- To Dr. P. Makgwane for advice and guidance.
- To HySA Catalyst for financial support.
- NMMU for financial support.
Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Technology at the Nelson Mandela Metropolitan University, Port Elizabeth. It has not been submitted before for any degree or examination in any other Institution.

Ntombekaya Gojela
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Chapter 1: Introduction

1. Introduction

1.1 Motivation
Air pollution and continuous global warming are environmental problems that can contribute to climate changes and damage to the environment. Pollutants such as carbon dioxide, sulphur dioxide and nitrogen oxide that result from transportation and industrial areas can contribute heavily to global warming. Carbon dioxide is considered as one of the main contributors to the greenhouse effect. In 2007 South Africa was listed 13th in the world with regards to carbon dioxide emissions that is roughly 433,527.00 metric ton per annum which contribute to about 1.48% of the global CO$_2$ emission.$^1$

While hydrogen production by water electrolysis is considered to be of small volume when compared to other processes such as steam reforming from methanol or other alcohols and direct thermal water-splitting, there is a general agreement that in the long term hydrogen generation through water electrolysis will be one of the main routes to produce hydrogen.$^2,3$ Current water electrolysis processes use high-voltage electrolytic cells with either a basic (KOH) or acidic (perfluorosulphonic acid) electrolytes.$^4$ These processes are significantly more expensive than steam reforming from methane, and use comparatively more energy as much as 65-82% for PEM electrolysis and 40-60% for steam electrolysis that is required in comparison to the stored energy in the hydrogen gas generated.$^5$ Steam reforming electrolysis uses a solid oxide as an electrolyte instead of an aqueous alkaline solution in water electrolysis. It operates at high temperatures that make the reaction become thermodynamically favoured.$^6,7$

In some applications, water electrolysis would be a preferred method for the production of hydrogen. For example, at an on-site remote energy station or when pure hydrogen is required for a laboratory application. Approximately 4% of today’s hydrogen use is produced by the electrolysis of water and typical applications include the food industry (hydrogenation of fatty acids),$^8-10$ semi conductors (furnace atmosphere),$^{11,12}$ chemical industry (petrochemical refining of
polyethylene, polypropylene), laboratory R & D and for standalone systems to refill hydrogen storage tanks for PEM fuel cells

The global energy crisis is not a direct problem of depleting resources such as coal for energy, but it is running out of cheaper crude oil and more importantly, the air pollutants as a result of burning the fossil fuels cannot be effectively absorbed and dissipated within the current environmental capacity. The present energy system is unsustainable in the long term, which means it will not be able to provide global continuous economic growth as it has done in the past. In order to alleviate the impact of the global energy crisis is to investigate the possibility of alternative energy sources and storing of renewable energies as hydrogen production, which can be used as an energy carrier for the future energy demands.

1.2 Hydrogen-Background
The effects of carbon dioxide emissions into the atmosphere on global climate change, together with a carbon-depleted world (such as fossil fuel and natural gas) it is for this reason that alternative energy sources will be required to supplement fossil fuel sources that currently power homes, business, and motor vehicles. Natural gas is available, but the supply will start to run out by 2026 shown in Figure 1.1 according to the statistics given by OPEC.

Hydrogen-rich materials such as coal, natural gas, biomass, or water can be used to manufacture hydrogen. Coal will continue to supply power for most of our electricity demand. Currently in literature, the primary means of manufacturing hydrogen is to strip it from natural gas such as methane via steam reforming. Other technologies to provide electricity from biomass, wind and solar does exist, and produce hydrogen that can create less carbon dioxide when compared to fossil fuel.

Another possible energy source is the use of advanced nuclear energy technologies to produce electricity, however nuclear waste will remain a concern where only a few new industries plants have been built in the last 30 years in countries such as the United States.
Figure 1.1 World crude oil supply\textsuperscript{21}

Hydrogen is the simplest, lightest, and in the universe is an abundant element. Hydrogen is a colourless, odourless gas, which becomes a solid with metallic properties when subjected to 500 K bars\textsuperscript{1,22}

Renewable energy can produce hydrogen as an energy carrier from water by electrolysis, which is commercially feasible. Hydrogen can be used as an energy storage medium that can be transported and used when required with limited environmental pollution. As a stored energy medium, it can be converted into electrical energy by a system using a fuel cell. This energy can be further converted, to motion by means of an electrical motor.\textsuperscript{23}

Some advantages of using hydrogen as energy source include:

- Hydrogen can be produced from renewable energy such as solar or wind.
- Hydrogen can be distributed and stored in a variety of ways such as in tanks or as a metal hydride.
- Hydrogen can replace the use of fossil fuels to provide electrification and transportation.
- National resources can be used to produce the hydrogen that allows a country to be energy independent.
1.2.1 Hydrogen as an energy carrier
Preferred route of making hydrogen with lower emission of greenhouse gases is by using water electrolysis. Water can be split into hydrogen and oxygen gas by the use of DC power in an electrolyser unit. The differences in electrolysers are the use of their electrolyte and type of electrodes.

At the anode side, the water is oxidized to form oxygen and protons. The protons migrate through the membrane that contains active sulfonic groups to the cathode, where they are reduced to hydrogen. Proton Exchange Membrane (PEM) electrolyzer offers a number of advantages when compared to the alkaline electrolyzer as it will be explained later, such as higher gas purity, the increased level of safety, and a possibility of producing compressed gas directly to application.

1.2.2 The economy of hydrogen production
Figure 1.3 shows the typical cost of producing hydrogen from a large-scale electrolysis system that is commercially available using industrial rates for comparison.\(^{24}\) Rand to liquid for hydrogen production could be used on a comparative basis to support the new technology. If a kilogram of hydrogen and the 4.5L of petroleum have the same cost and are used in a vehicle with the same efficiency, the resultant R/km could be similar.

There is an economic comparison between the cost of fuel for vehicles and cost for applying electricity for national use.\(^{25}\) As a result, to meet this target, the cost of hydrogen produced via industrial electrolysis should decrease to be between $1.00 to $2.00. In order to achieve this target it would be necessary to utilize alternative energies such as solar or wind energies obtain hydrogen via electrolysis.
1.3 Water electrolyser units

1.3.1 Alkaline electrolyser

Water is reduced to hydrogen and hydroxyl ions at the cathode. The hydrogen at the cathode in a gaseous form and the hydroxyl ions migrate under the influence of the electrical field through the separator to the anode, where they form oxygen and water.\textsuperscript{26} The following reactions would summarize the chemistry of an alkaline electrolyser (Eq.\textsuperscript{s} 1-3):

\begin{align*}
\text{Cathode:} & \quad (1) \\
& \quad (2) \\
& \quad (3)
\end{align*}

The reaction at the anode for an alkaline electrolyser:

Equations 4 – 6 explain the reactions taken place at the anode of an alkaline electrolyser cell.\textsuperscript{27-30}

\begin{align*}
\text{Anode:} & \quad (4) \\
& \quad (5) \\
& \quad (6)
\end{align*}
Some of the advantages of alkaline water electrolysers are the relatively cheap and available material used for their construction. The current densities to operate these systems are relative low and therefore economically feasible. However, these types of electrolysers have several disadvantages. They are limited in their ability to be constructed into multiple cell configurations that have typical low current densities with limited ability to reduce packing size. Another multiple cell configuration problem is that the alkaline electrolyser needs to be purged with nitrogen to prevent explosive limits between the oxygen and hydrogen that is produced in the single gas line configuration used in monopolar electrolysers. Alkaline water electrolysers also use corrosive electrolytes such as KOH that are corrosive for metal cell components at 60°C and higher operating temperatures.

1.3.2 PEM electrolyser

PEM water electrolyser technologies presented in the literature are an alternative to the more conventional alkaline water electrolysers PEM water electrolyser systems provide several advantages over the traditional technologies including energy efficiency, higher production rates, and compact design. A basic schematic of a PEM water electrolyser is shown in Figure 1.4.

![Schematic of a PEM water electrolyser](image-url)

**Figure 1.4** Schematic of a PEM water electrolyser.
The cell consists primarily of a PEM on which the anode and cathode are bonded. This electrode cell membrane electrode assembly consists of electro catalytic particles and an electrolyte membrane. Cells that use a solid-polymer electrolyte are usually constructed on the filter press arrangement. These electrolysis cells do not require electrolyte circulation because the electrolyte is immobilized in the form of an ion exchange resin (PTFE). The electrode catalyst is embedded either on the membrane or on the gas diffuse layer. The advantages of the PEM cells are:

- a) The electrolyte membrane can be made very thin, allowing for good conductivity without the risk of gas crossover,
- b) The electrolyte is embedded into the membrane and cannot leach out of the cell,
- c) It is ecologically clean, since loss/leaching of electrolyte of large system is reduced when compared with the alkaline type cells
- d) A large volume can be exposed to a small sample of catalyst with a high surface area,
- e) Can produce a very pure gas if required, and
- f) Increased level of safety with respect to electrolyte being impregnated in a membrane form and not a caustic liquid\textsuperscript{32}

Some of the disadvantages of the PEM electrolysers are that the electrolyte membrane costs are high and significantly more than the conventional alkaline solutions.

Several types of catalysts can be used for the anodic and cathodic layer. In a PEM water electrolyser, oxygen is produced by passing water over the anode electrode and $H^+$ migrate through the membrane electrolyte to the cathode to form hydrogen according to (Eqn’s 7 – 9). The protons are transported through the proton conductive membrane such as the nafion membrane to the current collectors. The electrons exit the cell via the external circuit, which supplies the cell potential for the reaction. At the cathode, the electrons combine to give hydrogen gas (Eqn. 8).
Anode: \[2H_2O \rightarrow 4H^+ + O_2 + 4e^-\] \hspace{1cm} (7)

Cathode: \[4H^+ + 4e^- \rightarrow 2H_2\] \hspace{1cm} (8)

Cell: \[2H_2O \rightarrow 2H_2 + O_2\] \hspace{1cm} (9)

Only a few PEM electrolysis systems are commercially available.\textsuperscript{33-35} The limit of these systems are the high cost of the materials such as the electrolytic membrane and the electrode catalysts, as well as the relative complex system components to ensure safe and reliable gas transport.

1.4 Thermodynamics of PEM
Thermodynamic theory was used to calculate the hydrogen efficiency from the overall chemical reaction in Eqn 9 of the PEM water electrolysis by using Faraday’s law.\textsuperscript{35} At equilibrium, to split one mole of water, the amount of electricity (n.F.E) required is equal to the Gibbs free energy \(\Delta G_d\) (shown in Eqn. 10) of the water dissociation reaction (Eqn. 9):

\[
\Delta G_d - nFE = 0 \text{ and } \Delta G_d > 0 \hspace{1cm} (10)
\]

where \(n = 2\) (number of electrons exchanged during electrochemical splitting of water); \(F\) is the Faraday, \(E\) is the thermodynamic voltage associated with the water dissociation reaction (Eqn. 9). \(\Delta G_d\) is a function of both operating temperature and pressure (Eqn. 11) and thus:

\[
\Delta G_d(T; P) = \Delta H_d (T; P) - T\Delta S_d (T, P) > 0 \hspace{1cm} (11)
\]
$\Delta H_d (T; P)$ and $T\Delta S_d (T, P)$ are respectively the enthalpy change (J mol$^{-1}$) and entropy change (J mol$^{-1}$K$^{-1}$) associated with the water dissociation reaction (Eqn. 9). To split one mole of water, $\Delta G_d$ (J mol$^{-1}$) of electricity and $T\Delta S_d$ (J mol$^{-1}$) of heat are required. The thermodynamic potential $E$ in volt is defined in Eqn. 12.

$$E(T, P) = \frac{\Delta G_d(T, P)}{nF}$$

(12)

The thermo-neutral voltage $V$ is defined as:

$$V(T, P) = \frac{\Delta H_d(T, P)}{nF}$$

(13)

In STD conditions of temperature ($T^o = 298K$ and $P^o = 1$ bar) water is a liquid, and H$_2$ and O$_2$ are gaseous. Standard free energy, enthalpy and entropy changes for reaction (Eqn. 9) are;

$\Delta G^o$ (H$_2$O) = 237.22 KJ mol$^{-1}$ → $E^o = \Delta G_d^o$ (H$_2$O) / 2F = 1.229 V ≈ 1.23 V$^{36}$

$\Delta H_d^o$ (H$_2$O) = 285.84 KJ mol$^{-1}$ → $V^o = \Delta H_d^o$ (H$_2$O) / 2F = 1.481 V ≈ 1.48 V

The $\Delta G^o$ (H$_2$O) and $\Delta H_d^o$ (H$_2$O) these values shows the maximum possible potential that can be achieved through a single PEM water electrolyser cell.

The current efficiency impacted by gas-cross-permeation phenomena. Hydrogen formed at the cathode catalyst surface diffuses across the cell to the anode where it is oxidized to hydrogen protons. Also, the oxygen formed at the anode catalyst surface diffuses through the PEM membrane to the cathode where it is reduced back to water. As a result, the energy is given off as heat in the cell.
1.5 **Kinetic considerations**

Kinetic parameters can be obtained from the performance characteristic I-V curves in order to calculate the Tafel slope in the low current density (high load resistance) region, where the mass and ohmic transport effects do not interfere with the data.

Figure 1.5 illustrated the different kinetic regions in a PEM electrolyser I-V curve.

![Graph showing different kinetic regions in a PEM electrolyser I-V curve](image)

**Figure 1.5: Typical PEM electrolyser graph**

The required voltage for PEM electrolysis can be expressed in the following Eqn.14:

\[ V = E + \eta_{ohmic} + \eta_{act,a} + \eta_{act,c} \]  \( (14) \)

Where \( E \) is the equilibrium voltage; \( \eta_{ohmic} \) is the ohmic over potential across the proton exchange membrane, \( \eta_{act,a} \) and \( \eta_{act,c} \) are activation over potentials at the anode and cathode, respectively. The concentration over potential is neglected because the gas transport limitations in thin electrodes are insignificant for PEM water electrolysis.\(^{37} \)
Kinetic rates can be determined directly from the electrochemical devices by measuring the current. Assuming that no transport losses occurs, the Butler-Volmer expression (Eqn. 15) can be used for the overall electrochemical reaction at the anode of water electrolysis.\textsuperscript{39,40}

\[ J = J_{A0} \left[ \exp\left(\frac{\nu_e \Delta \eta_A}{RT}\right) - \exp\left(-\frac{(1-\alpha_A)\nu_e \Delta \eta_A}{RT}\right) \right] \] (15)

Where \( J_{A0} \) is the anode exchange current density [A/cm\(^2\)], \( \nu_e \) is the stoichiometric coefficient of electrons in the anode reaction, \( \alpha_A \) is the transfer coefficient, and \( \eta_A \) is the anode over potential. Alternatively, the anode over potential may be written in the following form, assuming the effective transfer coefficient \( \alpha_A = 0.5 \) and \( \eta_A = 2 \).\textsuperscript{41,42}

The current inputs are directly proportional to the kinetic rate of an electrochemical reaction. To analyze the kinetics and thermodynamics of electrochemical reactions by means of Tafel analysis, a simplified Butler Volmer equation can be used (Eqn. 16).

The Tafel slope equation described the current density –voltage polarization curve in the kinetic controlled region.

\[ n^{\text{act}} = \beta \log |i| - A \] (16)

\( n^{\text{act}} \) is the voltage loss (mV) due to slow kinetics, \( i \) is the current density (mA/cm\(^2\)), and \( A \) and \( \beta \) are the constant kinetics parameters where \( \beta \) (is called the Tafel slope) given by:\textsuperscript{43}

\[ \beta = 2.303RT/\alpha F \] (17)

\( \alpha \) is the transfer coefficient (with the value between 0 and 1, but assumed to be 0.5 on the cathode side). The Tafel slope should be plotted by \( n^{\text{act}} \) (E-V) vs log \( i \) and slope of the line can measured in the kinetically controlled portion of the plot (at low value of log \( i \)). If the measured Tafel slope is higher it is difficult to determine the exact reason for the difference as it could be mass transport or ohmic loss in the system.\textsuperscript{44}
1.6 Electrode reaction in PEM water electrolysis

1.6.1 The hydrogen evolution reaction (HER)

The hydrogen evolution reaction (HER) is the most studied electrochemical reactions.\textsuperscript{45} The mechanism and rate of HER depends on the bond strength between hydrogen atom and the metal. HER is described by a simple reaction where two protons and two electrons form hydrogen gas, the reaction is given by Eqn. 9 above.

It followed by two steps: discharged of protons to give adsorbed H atoms (Volmer step) followed by electrochemical H desorption (Heyrovsky)\textsuperscript{46} then the combination of two H atoms (Tafel step) which are the rate-determining step. The following steps are predicted in acidic medium. (Eqn’s 19-21):

\begin{align*}
Pt + H^+ + e^- &\rightarrow Pt-H \text{ (Volmer)} \quad (19) \\
Pt-H + H^+ + e^- &\rightarrow H_2 + Pt \text{ (Heyrovsky)} \quad (20) \\
Pt-H + Pt-H &\rightarrow 2Pt + H_2 \text{ (Tafel)} \quad (21)
\end{align*}

The plot of M-H bond strength and log $i_o$ exhibit a “volcano curve” that shows a Pt as the active catalyst for the combination with other metals, with high current and M-H bonding strength. Figure 1.6 shows the volcano curve.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{volcano_curve.png}
\caption{Volcano Curve for the M-H bond strength for the HER reaction}
\end{figure}
Volcano plot of Trasatti for log \( i_0 \) values for the HER as a function of M-H bond energy\(^4\).

In this heterogeneous catalyst process, there is an adsorption and desorption process. The Figure 1.6 can be distinguished into 4 groups as A, B, C, and D, where A and D demonstrate low electro catalytic activity with weak and strong hydrogen adsorption at D. The platinum group metals in the Volcano curve show the optimal binding energy for electro catalytic activity. The rate-determining discharge of H refers to low bond strength, whiles the rate-determining H desorption refers to higher binding energy\(^{47,48}\).

Rasten et al.\(^4\) reported reaction step and Tafel slope of HER as 120mV/dec for lower and higher over potential in Volmer,\(^4\) 40mV/dec for lower over potential and 120mV/dec for higher over potential in Heyrovsky\(^4\) and 30mV/dec for lower over potential in Tafel slope with no higher over potential due to the ohmic loss and diffusion. Pt is plotted on the top of the volcano curve that shows the corresponding of the standard Gibbs energy as being zero\(^5\).

In the hydrogen region of H atom in cyclic voltammogram, the hydrogen evolution reaction (HER) occurred on Pt, at a less negative potential region than that of hydrogen evolution, platinum surface is fully covered by under potential adsorbed H atom.

In acid medium, platinum is the more active catalyst when compared to other metals for HER (Figure 1.6). In this study, the use of lower cost metal oxides in interaction with Pt will be studied.

1.6.2 The oxygen evolution reaction (OER)
Iridium and ruthenium oxides are the more active catalyst for OER in acid medium, since these catalysts do not undergo corrosion in comparison to other transition
metals. On the active oxide electrode, the mechanism for oxygen evolution in acid medium was proposed as follows (Eqn’s 22-24):

\[ S + H_2O \rightarrow S-OH_{ads} + H^+ + e^- \] (22)

\[ S-OH_{ads} \rightarrow S-O_{ads} + H^+ + e^- \] (23)

\[ S-O_{ads} + S-O_{ads} \rightarrow 2S + O_2 \] (24)

Where S stands for metal oxide, and OH\textsubscript{ads} and O\textsubscript{ads} represents adsorption intermediates (Figure 1.7). J.H. Hu et al\textsuperscript{52} reported the Tafel slope of OER in the above reactions as 120 mV/dec for the reaction 1, and 40 mV/dec for reaction 2 and 30mV/dec for the reaction 3. The mixtures of IrO\textsubscript{2}, RuO\textsubscript{2} and Ta\textsubscript{2}O\textsubscript{5} are used as anode coating for the oxygen evolution.\textsuperscript{53}

For oxygen evolution to occur, an oxide layer has to be formed on the surface of the metal oxide, which needs a high potential to be stable. IrO\textsubscript{2} and RuO\textsubscript{2} are the most active oxides. For the ruthenium to be stable in oxygen evolution, it needs another metal oxide such as Ir-oxide and Ta-oxide. The mixture of IrO\textsubscript{2}-Ta\textsubscript{2}O\textsubscript{5} shows the best electro catalytic activity and high corrosion-resistant in sulphate system for oxygen evolution.\textsuperscript{54} The volcano curve for the OER reaction catalysts is shown in Figure 1.7.
In this study, the effect of interaction of these low cost metal oxides with the PGM group metal will be studied.

1.7 The polymer membrane
The proton exchange membrane (PEM) also referred to as solid polymer electrolyte (SPE) is popular for both PEM electrolizer and fuel cell applications. This is mainly due to its high conductivity, low permeability to hydrogen and oxygen gasses, thermal stability, chemical and mechanical durability are attracted as electrolyte for water electrolysis and fuel cell.

The perfluorosulfonic membrane was developed in 1962 by DuPont de Nemours, and is commercially referred to as, Nafion®. The perfluorosulfonic membrane consists of a perfluoronated pendant side chain terminated by a sulfonate ionic group that is responsible for ionic conductivity (Fig 1.8). The poly tetrafluoroethylene backbone gives the membrane its thermal and mechanical
stability. Due to its chemical resistance and excellent ionic conductivity, it was used extensively as a separator in the chlor-alkali production. Typical membrane thicknesses used are between 200 µm and 400µm.

Figure 1.8: Structure of the Nafion membrane monomer unit.

1.8 Focus of Research
There are several potential benefits of using electrolysis as an integral part of the electrical power generation especially in standalone system for the development of alternative fuel for the transportation industry. Hydrogen-based generation via electrolyser can provide this opportunity. The objective of this research was to investigate the feasibility of the electro catalysis needed for both cathode and anode side in order to achieve maximize efficiency of the gas produced. In order to reduce costs of the PEM electrolyser, the possibilities of reducing the use for base metal catalysts that are typically platinum group metals such as Pt and Ru were investigated. In order to study this property, various combinations of the catalysts were prepared and characterized by a cyclic voltammetry in order to establish its hydrogen desorption capabilities.

During these experiments, the coated catalyst on the membrane was characterized for its physical properties, its chemical composition by XRF and the membrane stability by comparative SEM imaging before and after electrolysis. The electrochemical performances of the systems were studied by comparing the Tafel slopes from the electrolyser I-V curves.
Chapter 2: Experimental details

2.1 Experimental

2.1.1 Chemicals and apparatus
Chemicals used for the preparation of the metal oxides and MEA are given in Table 2.1 below

Table 2.1: Chemicals, membrane and catalysts for electrolyser

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Manufacturing</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt black</td>
<td>Aldrich</td>
<td>40% Pt on carbon</td>
</tr>
<tr>
<td>Nickel cobalt oxide</td>
<td>Aldrich</td>
<td>99.99%</td>
</tr>
<tr>
<td>Cobalt oxide</td>
<td>Fluka</td>
<td>AR Grade</td>
</tr>
<tr>
<td>Iridium (II) chloride hydrated</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>Merck</td>
<td>99%</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>Alfa Aesar</td>
<td>95%</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>Merck</td>
<td>98%</td>
</tr>
<tr>
<td>Nafion ® membrane (N-117)</td>
<td>Fuel cell store USA</td>
<td>N/A</td>
</tr>
<tr>
<td>Nafion solution 5 wt%</td>
<td>Alfa Aesar</td>
<td>5 w/t%</td>
</tr>
<tr>
<td>Carbon paper</td>
<td>Fuel cell store USA</td>
<td>N/A</td>
</tr>
<tr>
<td>Charcoal</td>
<td>Aldrich</td>
<td>99</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Alfa Aesar</td>
<td>99.9%</td>
</tr>
</tbody>
</table>

2.2 Electrolyzer assembly
PEM electrolysis uses a solid polymer electrolyte instead of liquid electrolyte and platinum electrode metal at cathode and iridium electrode metal at the anode. Cell current and potential are typically at 0-1000 mA and at a cell voltage of 1.4-1.9V.

The electrolyser was made of two inlet tubes, the hydrogen and the oxygen. In between the two tubes, a polymer electrolyte membrane (PEM) (Fig 2.1a) which consists of electrode plates was made of stainless steel and a gasket (Teflon) after the electrode. Inside the MEA, there was Pt on carbon nanoparticles and the
electrolyte that was the conducting medium. Figure 2.1B shows a photo of the PEM electrolyser.

Figure 2.1 A) Example of a MEA, B) PEM Electrolyser

Figure 2.2 shows a schematic outline of the PEM electrolyser test rig that were utilized to gather the information such as the characterized I-V curves, volume versus time studies and the current density versus time studies. The latter two studies were used in calculating by means of Faraday’s first principles the hydrogen efficiencies produce on a monolayer PEM electrolyser setup.

Figure 2.2: Schematic outline for the PEM electrolyser measurements
Potentiostat was utilized to supply energy to the electrolyzer cell unit, where the water splits into hydrogen and oxygen gas. The hydrogen gas then goes through a flow meter into a storage tank through gas pipeline to the fuel cell while the oxygen goes to the air. Both the current and potential were measured. The electrons that have been produce from the fuel cell, carried to an electric motor/fan or to a light bulb. Figure 2.3 shows a photo of the experimental test station.

The activated Nafion membrane was dried on a stainless steel vacuum plate in order to get rid of the wrinkles in the membrane. The two treated GDE was placed facing each other with the activated membrane in between and covered with a metal foil to avoid sticking of the MEA with hot plate after pressing. The hot press (CARVER Catalog #4120.4010 (Model 12-10H) Hydraulic Laboratory Press) which is shown as a photo in Figure 2.4 was preheated to 150°C. The MEA in the aluminium foil was placed onto the bottom hot plate without applying pressure for 1 min. This helps to soften the Nafion membrane before pressing to a pressure of 2500psi. This is to ensure complete curing of the membrane and gas diffuse layer interface. The pressure valve was release and the MEA removed, stored for latter testing.
2.3 Analytical instrumentation

2.3.1 Epsilon Cyclic Voltammetry system

Cyclic voltammetry (CV) is the most effective and versatile electro analytical technique for the mechanistic study of redox system. The potential of a redox reaction system can be determined through sweeping at a specific potential range versus a reference electrode. From the sweep rate, dependence coupled homogeneous reactions and complications such as the absorption and desorption of gases. In cyclic voltammetry a sweep is performed on the electrode potential range between $E_1$ (initial) and $E_2$ (final) at a known sweep rate and stopped after reaching the initial potential. This time profile was shown in Figure 2.
Figure 2.5: Potential-time profiles for sweep voltammetry.

The cell current was recorded as a function of the applied potential. The sweep rate can vary from a few mV s\(^{-1}\) to thousands mV s\(^{-1}\), but at these high values, the technique becomes restricted to the double layer charging and the large \(iR_u\) drop (uncompensated resistance) effects. Generally for very fast sweep rates a microcomputer interfaced with a potentiostat-galvanostat is required to capture all the information during the sweep.\(^{57}\) Under steady state conditions the concentration of the substance are kept constant by natural convection. Within the region adjacent to the electrodes centre. The concentration gradients are linear and the ratio of oxidized to reduced species for a reversible reaction is given by the Nerst equation. (Eqn. 2.1)

\[
E_e = E_e^0 + \frac{RT}{nF} \ln \frac{C_o}{C_R} \tag{2.1}
\]

Where \(E_e\) is the equilibrium potential (V), \(E_e^0\) is the standard potential (V), \(R, T, n\) and \(F\) are constants and \(C_o\) and \(C_R\) the surface concentrations of oxidized and reduced species. When the scan rates are increase, this shortens the time scale of the CV redox cycle and the concentration gradient has time to relax. Therefore, at fast sweep rates, one will develop high concentration gradients that will lead to large current densities. The relationship between the peak current density and scan rate is mathematically shown by the Randles-Sevčík equation (Eqn 2.2)
\[ I_p = -0.4463 \text{nF (nF/RT)}^{1/2} C_\infty^{1/2} v^{1/2} \]  

(2.2)

Where \( I_p \) is the peak current density (mA cm\(^{-2}\)), \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( v \) is the sweep rate (V s\(^{-1}\)) and \( C_\infty \) is the concentration of electro active species (mol cm\(^{-3}\)).

There should be a linear relationship between peak current density and square root of the scan rate, deviation from this relationship can be related to a quasi reversibility or completely irreversibility system.

In search of redox couples, the electrode potential sweep rapidly (meaning moving back and forth). The characteristics of the reversible electrochemical reaction on CV record are as followed.

- \( \Delta E = E_p^a - E_p^c = 59/n \text{ mV} \)  
- \( |i_p^a / i_p^c| = 1 \)
- \( I_p \propto V \)

Another related test is the separation between oxidative peak potential \( (E_a) \) and the reduction peak potential \( (E_c) \) given in Eqn 2.3 above.

Cyclic voltammetry of both anode and cathode catalysts was measured against a Ag/AgCl reference electrode at different scan rates that ranged from 100 – 400 mV s\(^{-1}\) at room temperature. The potential limits of hydrogen and oxygen evolution reaction were 1.48V.

2.3.2 XRF

In X-ray fluorescence (XRF) an electron can be ejected from its orbital by the absorption of a photon of sufficient energy. The energy of the photon \( (h\nu) \) must be greater than the energy with which the electron is attached to the nucleus of the atom. When an inner orbital electron is ejected from an atom, an electron of a higher energy orbital level will be transferred to the lower energy orbital level. During this transition a photon maybe emitted from the atom. This fluorescent light is called the characteristic X-ray of the element. Because the energy difference between two specific orbital shells, in a given element, is always the same (i.e.
characteristic of a particular element), the photon emitted when an electron moves between these two levels, will always have the same energy. Therefore, by determining the energy (wavelength) of the X-ray light (photon) emitted by a particular element, it is possible to determine the identity of that element.

For a particular energy (wavelength) of fluorescent light emitted by an element, the number of photons per unit time (generally referred to as peak intensity or count rate) is related to the amount of that analyte in the sample.

The counting rates for all detectable elements within a sample are usually calculated by counting, for a set amount of time, the number of photons that are detected for the various analytes characteristic X-ray energy lines. It is important to note that these fluorescent lines are actually observed as peaks with a semi-Gaussian distribution because of the imperfect resolution of modern detector technology. Therefore, by determining the energy of the X-ray peaks in a sample's spectrum, and by calculating the count rate of the various elemental peaks, it is possible to qualitatively establish the elemental composition of the samples and to quantitatively measure the concentration of these elements.

XRF Spectrometer was used to confirm the catalyst content and was analyzed on a portable Innov-X Analyzer.

2.3.3 SEM

The particle morphology of the catalysts is observed by scanning electron microscopy (SEM) using a JEOL 6380 SEM operated at 15 kV, specifically, this analysis involves the evaluation of surface structure and morphology. The distribution and chemical composition of catalysts are some of the data, which can be obtained. Analysis includes sample preparation, high-quality digital images at various magnifications, positions, and image descriptions. A SEM may be equipped with an Energy Dispersive X-ray analysis (EDX) system to enable and to perform compositional analysis on specimen, as well as estimating the relative concentrations for selected components at the surface of the specimen.
SEM image analysis was done on a Joel SEM 6380. EDAX analysis were done on certain section to confirm the catalytic elemental composition and sample before and after use in the PEM electrolyzer were analysed.

2.4 Experimental details

2.4.1 Preparation of metal oxide by Adams method

Iridium oxide prepared by iridium precursor and sodium nitrate by Adams fusion.\(^{55,60}\) Iridium oxide was precipitated and nitrogen dioxide was evolved during fusion process. The reaction process was carried out in the temperature of 340°C. The reaction was as follows:

\[
6\text{NaNO}_3 + \text{H}_2\text{IrCl}_6 \rightarrow 6\text{NaCl} + \text{Ir(NO}_3)_4 + 2\text{HNO}_3
\]

\[
\text{Ir(NO}_3)_4 \rightarrow \text{IrO}_2 + 4\text{NO}_2 + \text{O}_2
\]

For the anode catalyst, IrCl\(_3\) was used as precursor for the formation of IrO\(_2\).\(^{60}\) Metal oxide precursor (0.1g) was mixed with 5g of NaNO\(_3\) and dissolved in 20mL of water (tap water). The mixture was evaporated to remove water and the salt mixture was pre-heated in an oven at 340°C for 30 minutes. The salt mixture was then cooled at 25°C, and washed with water to eliminate traces of chlorine from the IrCl\(_3\) precursor. The IrO\(_2\) salt was dried and stored for later use.\(^{58}\)

2.4.2 Preparation of MEA’s

The membrane (Figure 2.6) was cleaned according to the procedure described by Shukla et al (2001).\(^{61}\) The Nafion 117 membrane was first preheated in 5 wt% H\(_2\)O\(_2\) at about 92-98 °C for 1 hour to remove any organic residue. The membrane was then kept in pure water for 10 minutes at 80 – 90 °C and further treated in 1M H\(_2\)SO\(_4\) at 92 – 98 °C for 1 hour to protonate the membrane completely with protons. Then lastly, the membrane was boiled in water for 1 hour to remove acid, then cooled and rinsed. The membrane was kept hydrated in water until ready for use.
The oxygen electrode and hydrogen electrode was hot-pressed on aluminium plate with pretreated Nafion membrane in-between the electrodes and with charcoal sprinkled on the plate at 80°C for 3hrs in vacuum oven.\textsuperscript{61}

![Figure: 2.6 Membrane Electrode Assemble (MEA)](image)

2.4.3 Preparation of gas diffusion layer (GDL)

The catalyst ink was prepared by weighing out a known amount for the active catalyst and added to the noble metals. The catalyst solutions prepared contained Pt black mixture of Ni for PtNi and NiCo for PtNiCo as binary mixtures for the cathode catalyst according to a ratio of 0.2-0.5 mg/cm\textsuperscript{2}, while IrO\textsubscript{2} was used as an anode metal at a ratio of 0.25-0.3 mg/cm\textsuperscript{2}. A Nafion solution (0.3 mL, 5% w/t; DuPont) and ethanol aqueous solution of 20 ml was added to the metal, sonicated for 1 minute, and stirred with a magnetic stirrer to form an ink. The carbon paper was then soaked with the ink until all the catalyst was embedded onto it.\textsuperscript{61}
Chapter 3: Results and Discussion

3.1 Introduction
This Chapter will discuss the anodic and cathodic behaviour of PGM with other metals in a membrane electrode assembly. The anodic catalyst characterization was based on iridium oxide (IrO) compounds together with platinum, ruthenium and cobalt. These oxides form either a binary or a ternary catalyst mixture on the membrane electrode assembly. The cathode catalyst Pt / Ni oxide mixture was kept the same for all these experiments.

Similar studies were performed on the cathodic catalyst compartment of the membrane electrode assembly. On the cathodic side in the study, the Pt black was used and the Pt content was reduced by means of introducing Ni, Co, and ruthenium. The anode catalyst was Ir oxide for all these type of experiments.

Characterizations of these catalysts were first tested on a cyclic voltammetry to investigate the absorption and desorption charge of hydrogen in a sulphuric acid medium. The scan rate versus current density will be used to explain the electrochemically adherence of these catalysts on the gas diffuse layer. XRF and SEM imaging will be used to provide scientific evidence of these metal particles that adheres onto the gas diffuse layer.

3.2 Anodic catalyst characterization
3.2.1 Characterization of Ir_{50}Pt_{50} binary oxide as anode catalyst.
In the hydrogen reduction region between 1.250-0.863 V, a peak was observed that increased as scan rate increased. In between 0.088-(-0.300), there was also a sharp peak on the cathode side, it was stable for all scan rate and was evident of hydrogen reduction (Figure 3.1).
Figure: 3.1. Voltammogram of Ir$_{50}$Pt$_{50}$ catalyst in H$_2$SO$_4$ (0.05M) measured at scan rate from 100-500 mV/s. Reference electrode was a Ag/AgCl (0.01M) Insert: A linear relationship between the current density and scan rate.

In Figure 3.2 the current density varied with temperature, as the potential was not stable for all temperatures. At 80 °C the potential was 0.6 V while at 30 °C and 50 °C the potential achieved was close to 1.26 V.
Figure: 3.2. Polarization curves of Ir$_{50}$Pt$_{50}$ in PEM water electrolyser cell at different temperatures.

Figure: 3.4. Tafel plot for Ir$_{50}$Pt$_{50}$ at different temperatures

The Tafel slope parameters of the catalyst above that show a discrepancy as the temperature increases, at 30 °C the Tafel slope was 113.6 mV.dec$^{-1}$ and 50°C was 100.4 mV.dec$^{-1}$ while 80°C was 192.1 mV.dec$^{-1}$, that shows an exponential curve in Figure 3.4, as was discussed in Chapter 1.
Figure 3.5 show a broken well-adhered thin layer of catalyst, which covers the carbon paper, the EDAX graph showed the other elements that were not expected.

**Figure: 3.5. SEM image of Ir$_{50}$Pt$_{50}$**

Figure 3.6 showed the elements that were brushed on the gas diffusion layer, Pt showed the sharp peak while the Ir was not appeared.

**Figure: 3.6. EDAX graph showing elements on Ir$_{50}$Pt$_{50}$**
Figure: 3.6. XRF image of Ir$_{50}$Pt$_{50}$

3.2.2 Characterization of Ir$_{20}$Ru$_{80}$ binary oxide as anode catalyst  
As the scan rate increased, the catalytic activity was slightly decreasing which means no sharp peaks at the anode side while at the cathode side on the hydrogen region the catalytic activity increases in Figure 3.7 below. The numbers below the graph was the differences of scan rates.
Figure: 3.7. Voltammogram of Ir$_{20}$Ru$_{80}$ catalyst in H$_2$SO$_4$ measured at scan rate from 100-500mV/s. Reference electrode was a Ag/AgCl (0.01M). Insert: A linear relationship between the current density and scan rate.

At 30 °C the potential was 1.48 V, at 50 °C was 1.52 V and at 80 °C, it was 1.55 V. For all the catalyst, the hydrogen gas evolution was observed at approximately the slightly the same potentials.

Figure: 3.8. Polarization curves of Ir$_{20}$Ru$_{80}$ in PEM water electrolyser cell at different temperature
Figure: 3.10. Tafel plot for Ir$_{20}$Ru$_{80}$ at different temperatures

The Tafel plot in Figure 3.10 shows that the slope at 30°C was 16 mV.dec$^{-1}$ and at 50°C was 9.0 mV.dec$^{-1}$ while 80°C was 80.2 mV.dec$^{-1}$ with a linear graph.

Figure 3.11 shows the distribution of Ir$_{20}$Ru$_{80}$ catalyst that was dispersed on the surface of the carbon paper. The graph 3.11 below shows the elementary contents that are in the surface of the carbon paper.
Figure: 3.11. SEM image of Ir$_{20}$Ru$_{80}$

Figure 3.12 show the entire elements on the gas diffusion layer, where Ir was appeared between 9.18-10.7 mV while Ru appeared between 19.28-21.66 mV of energy.

Figure: 3.12. XRF image of Ir$_{20}$Ru$_{80}$
3.2.3 Characterization of Ir₅₀Ru₅₀ binary oxide as anode catalyst

Figure 3.13 show no distinctive sharp peaks in the oxidation region but was increasing in the final oxidation current, while the cathode side showed a decrease in current. As the loading of the Ir metal was the same with the Ru metal, the catalysts showed no activity in the voltammogram and instead showed an increase as scan rate increased.

![Test Overlay files](image)

Figure: 3.13. Voltammogram of Ir₅₀Ru₅₀ catalyst in H₂SO₄ measured at scan rate from 100-500mV/s.

Figure 3.14 showed slight differences in the onset potential for the three temperatures, at 30°C the potential was 1.4 V and 50°C was 1.45 V while 80°C was 1.45 V. The onset potential is where the release of hydrogen gas starts.
Figure: 3.14. Polarization curves of Ir$_{50}$Ru$_{50}$ in PEM water electrolyser cell at different temperature

Figure: 3.16: Tafel plot for Ir$_{50}$Ru$_{50}$ at different temperatures

The Tafel slope showed an increase as the temperature increased, this gave a linear increase over this temperature range. At 30 $^\circ$C the electrical power was 81.9 mV.dec$^{-1}$, 50 $^\circ$C the Tafel slope was 91.1 mV.dec$^{-1}$ while 80 $^\circ$C was 198 mV.dec$^{-1}$ from Figure 3.16.
Figure 3.17 shows a distribution of a catalyst on a carbon paper that was dispersed on a surface, with a graph that shows the elementary contents that are on the catalyst.

**Base(1041)**

![SEM image of Ir50Ru50](image1)

**Full scale counts: 365**  **Base(1041)_pt3**

![Graph showing elemental contents](image2)

**Figure: 3.17. SEM image of Ir50Ru50**

Figure 3.18 shows the elements that are on the surface of the gas diffusion layer; it appears that the Ir metal did not show on this specific area scanned on the XRF.
Figure: 3.18. XRF image of Ir$_{50}$Ru$_{50}$

3.2.4 Characterization of Ir$_{40}$Co$_{60}$ binary oxide as anode catalyst

Figure 3.19 show no electrocatalytic activity on the oxidation region on anode and cathode side, but a small peak between 0.863-0.475 V in the hydrogen region on the anode side. Due to the mixture of Ir metal with Ru metal, the voltammogram showed no activity on the catalyst with an increase as scan rate increasing.
Figure: 3.19. Voltammogram of Ir₄₀Co₆₀ catalyst in H₂SO₄ measured at scan rate from 100-500mV/s. Insert: A linear relationship between the current density and scan rate.

As the temperature increases, there was a slight change in current density and the potential. At 50°C was 1.325 V while 80°C was 0.925 V potentials. The higher potential was observed at 30°C in Figure 3.20 below, where the hydrogen gas was released more.
Figure: 3.20. Polarization curves of Ir$_{40}$Co$_{60}$ in PEM water electrolyser cell at different temperature

As the temperature increased, the Tafel slope varies due to gas diffusion in the reaction causes a low Tafel slope at higher degree. At 50 °C was 24.8mV.dec$^{-1}$ while at 80 °C was 30.1mV.dec$^{-1}$.

Figure: 3.22. Tafel plot for Ir$_{40}$Co$_{60}$ at different temperatures
A reason for this could be the gas diffuse where the slope decreases while become the rds (rate determining step) for all the reaction when combined. This could be due to the interaction effect of the Co on the Ir catalysts.

Figure 3.23 show a distribution of a catalyst that was dispersed on the surface of the carbon paper, where we observed the Ir and Co on EDXS with other element (such as Ni, C and O) that might be on the carbon paper.

![Base(1044)](image)

**Figure: 3.23. SEM image of Ir\textsubscript{40}Co\textsubscript{60}**

Figure 3.24 show the elementary components that are on the gas diffusion layer, where the Co metal at about 6.92-6.93 mV and Ir metal was not clearly seen.
3.2.5 Characterization of Ir$_{20}$Ru$_{40}$Co$_{40}$ ternary oxide as anode catalyst.

The ternary catalyst of Ir$_{20}$Ru$_{40}$Co$_{40}$ mixed oxide was studied at different scan rate from 100-500 mV.s$^{-1}$ at H$_2$SO$_4$ medium and 100mA sensitivity.

Figure 3.25 shows the cyclic voltammogram of Ir$_{20}$Ru$_{40}$Co$_{40}$ measured at different scan rate from 100 to 500 mV.s$^{-1}$. There was a sharp peak present in the hydrogen region, which increases as scan rate increases. Secondly, in the oxidation region, there was an anodic peak at 0.465V, then after potential cyclic there was another anodic peak. These two anodic peaks are reversible with cathodic peaks at the same potential values. The second part of cathodic peak was reduced to the more positive value up to zero, where oxide was reduced with hydrogen deposition.

It appears that the ternary catalyst show the best activity on the gas diffusion layer where the base metals (such as Ru and Co) was at the same loading with decrease in Ir metal.
The current density increased as the temperature decreased at the same cell potentials. At 30°C there was a potential of 0.975 V and 50°C of 0.975 V while at 80°C there was 0.95 V. This lower potential at higher temperatures of 80°C shows the best performance in the single cell of PEM water electrolysis in figure 3.26 below.
Figure: 3.26. Polarization curves of Ir$_{20}$Ru$_{40}$Co$_{40}$ in PEM water electrolyser cell at different temperature.

Figure: 3.28. Tafel plot for Ir$_{20}$Ru$_{40}$Co$_{40}$ at different temperatures

The Tafel slope for the 30 °C was 83.5 mV.dec$^{-1}$ while for the 50 °C was 53.5 mV.dec$^{-1}$ and for the 80 °C was 33.5 mV.dec$^{-1}$. That shows as the temperature increases the Tafel slope decrease that causes an increased linear slope.
The SEM image shows the distribution of the $\text{Ir}_{20}\text{Ru}_{40}\text{Co}_{40}$ on the carbon in figure 3.29 below. This represents the surface structure of the catalyst ink on the carbon paper, where Ir metal and Co metal appeared on EDXS without Ru metal observed.

Figure: 3.29. The SEM photo of $\text{Ir}_{20}\text{Ru}_{40}\text{Co}_{40}$ catalyst layer on a carbon paper.

Figure 3.30 show all the elementary components that are on the gas diffusion layer, Co metal was observed between 6.92-6.93 mV and Ir metal between 9.18-10.71 mV while Ru between 19.28-21.66 mV.
Figure: 3.30 XRF image of Ir$_{20}$Ru$_{40}$Co$_{40}$

3.2.6 Characterization of Ir$_{20}$Ru$_{20}$Co$_{60}$ ternary oxide as anode catalyst.

As the scan rate increases, there were anodic peaks increase at 0.088-(-0.300) V potential value, but with no sharp peaks. The reason for not having clear sharp peaks might be due to the decrease of the Ru metal but increase the Co metal according to the 1:3 ratios.

Another reason was due to the different ratio that was added in metals, as the cobalt has an effect on the mixture.
At high temperature ($80^\circ C$), gave a potential of 0.6 V where hydrogen gas started to be produced while at $50^\circ C$ gave a potential of 0.575 V and at $30^\circ C$ gave a potential of 0.525 V. The best performance was observed at low temperature. Siracusano et al\textsuperscript{62} reported that the observed fluctuation of voltage and ohmic drop increased was caused by the membrane dehydration effect at high temperature.

**Figure: 3.31. Voltammogram of Ir$_{20}$Ru$_{20}$Co$_{60}$ catalyst in H$_2$SO$_4$ measured at scan rate from 100-500mV/s.**
Figure: 3.32. Polarization curves of Ir$_{20}$Ru$_{20}$Co$_{60}$ in PEM water electrolyser cell at different temperature.

The Tafel slope for the catalyst in Figure 3.34 above increased as the temperature increased, where for 30 °C was 40.0 mV.dec$^{-1}$ and 50 °C was 38.7 mV.dec$^{-1}$ while 80 °C was 31.8 mV.dec$^{-1}$ these results showed a negative linear slope.

Figure 3.35 show a distribution of a catalyst that was dispersed on the surface of the carbon paper, where Ru metal was not observed on EDXS while Ir metal and Co metal observed with other elements that was maybe on carbon paper.
Figure 3.35. SEM image of Ir$_{20}$Ru$_{20}$Co$_{60}$

Figure 3.36 show the entire elementary components that were on the gas diffusion layer, where Co metal was observed between 6.92-6.93 mV and Ir metal between 9.18-10.71 mV while Ru between 19.28-21.66 mV.
3.2.7 Summary

Ir$_{50}$Pt$_{50}$ show the best performance at 50°C of low potential than other binary catalysts. Best performance was obtained from the ternary catalyst of Ir$_{20}$Ru$_{40}$Co$_{40}$ at 80°C, which gave a lower potential, but lower efficiency at higher temperature than other ternary catalyst of Ir$_{20}$Ru$_{20}$Co$_{60}$. Addition of Co metal to Ir oxide according to the mole ratio (1:3) has found to give higher catalytic activity on the GDL and higher efficiency.

Figure: 3.36 XRF image of Ir$_{20}$Ru$_{20}$Co$_{60}$
3.3 Cathode in PEM electrolysis

Figure 3.37 shows the voltammogram of Pt in sulphuric acid, the sharp peak of hydrogen desorption on anodic side were observed, while in the cathode side there were two adsorption peaks. The second peak for the anodic formation on oxygen formed at 500 V.

\[ y = 0.3569x - 3.25 \]

\[ R^2 = 0.9996 \]

\[ \begin{array}{c|c|c|c|c|c|c|c|c}
    & 0.00 & 20.00 & 40.00 & 60.00 & 80.00 & 100.00 & 120.00 & 140.00 & 160.00 \\
\hline
    Scan rate / mV s \quadVs Ag/AgCl reference electrode & 100 & 150 & 200 & 250 & 300 & 350 & 400 & \quad & \\
\hline
    Current density / uA cm\(^{-1} \) & \quad & \quad & \quad & \quad & \quad & \quad & \quad & \quad & \quad
\end{array} \]

**Figure 3.37.** Voltammogram of Pt catalyst in H\(_2\)SO\(_4\) measured at scan rate from 100-300mV/s Vs Ag/AgCl reference electrode. Insert a linear relationship between the current density and scan rate

\[ E = +51.3 \text{mV} \quad i = -5.512 \times 10^{-5} \text{A} \]

Figure 3.38 below shows the distribution of Pt catalyst on the carbon paper, clusters between the Pt particles can be seen from the image below.
Figure: 3.38. SEM image of Pt catalyst

The investigation of Pt loading was to choose the better loading for manufacturing of MEA and decreasing the Pt loading while increasing Pt utilization in water electrolysis.

In Figure 3.39 below, the loading of Pt in the cathodes were changed from 0.2 and 0.3mg.cm\(^{-2}\) while the Ir in the anode was kept at 2 mg.cm\(^{-2}\). It showed that as the loading increases the current density increases. The best performance was obtained at 0.3 mg.cm\(^{-2}\).

Figure: 3.39. The effect of Pt loading in PEM performance at different temperature
3.3.1 Characterization of Pt$_{50}$Ni$_{50}$ binary oxide as cathode catalyst.

In this section, other metal will be introduced with the platinum catalyst either as a binary or as ternary mixtures in order to reduce platinum loading but still maintaining efficiency at low potential.

In Figure 3.41 below, the potential region for hydrogen adsorption and desorption are not well defined for Pt$_{50}$Ni$_{50}$ compared to the bare Pt. The starting potential for oxygen reduction was shifted to the more positive potential.

![Voltammogram](image)

**Figure: 3.41. Voltammogram of Pt$_{50}$Ni$_{50}$ catalyst in H$_2$SO$_4$ measured at scan rate from 100-400mV.s$^{-1}$**

In Figure 3.42, shows the potential of all the temperatures, at 30$^0$C the potential was 0.725 V, and 50$^0$C was 0.7 V while at 80$^0$C was 0.925 V. It shows that as the
temperature increases the current density increases at different potentials. The best performance is at 50°C with lower potential.

Figure: 3.42. Polarization curves of Pt$_{50}$Ni$_{50}$ in PEM water electrolyser cell at different temperature

Figure: 3.44. Tafel plot of Pt$_{50}$Ni$_{50}$ at different temperatures.
At 30 °C the Tafel slope gave a corrosion rate of 0.49 mV.dec⁻¹ while at 50 °C was 0.60 mV.dec⁻¹ and at 80 °C was 0.93 mV.dec⁻¹. Figure 3.44 shows that as the temperature increased that there was a linear increase of Tafel slope.

Figure 3.45 shows the distribution of Pt₅₀Ni₅₀ on the surface of the carbon paper.

![SEM image of Pt₅₀Ni₅₀ catalyst](image)

**Figure: 3.45. SEM image of Pt₅₀Ni₅₀ catalyst**

### 3.3.2 Characterization of Pt₃₃Ni₃₃Co₃₃ ternary oxide as cathode catalyst.

In Figure 3.46, the increase in scan rates from 100 to 400 mV s⁻¹ had shown a good adherence of catalyst to the membrane surface. Pt₃₃Ni₃₃Co₃₃ catalyst did not show well-defined hydrogen adsorption and desorption behaviour as compared with pure Pt black catalyst was used as the electrode catalyst. Due to charge associated to the hydrogen adsorption / desorption decreases with lowering of the Pt loading, which indicates a decrease in Pt active area, as was observed by Paulus et al.⁶³
Figure: 3.46. Voltammogram of Pt$_{33}$Ni$_{33}$Co$_{33}$ catalyst in H$_2$SO$_4$ measured at scan rate from 100-400mV/s. Insert: A linear relationship between the current density and scan rate.

At 30 °C the potential of 0.69 V was observed while at 50 °C the potential was 0.76 V and 80 °C the potential was 1.18 V with different current density. Figure 3.47 shows that as the temperature increases the potential increases as well as current density increases. The best performance was observed at the lower temperature.
The results in Figure 3.49 show the Tafel slope at different temperatures. At 30°C the Tafel slope was 86.8 mV.dec⁻¹ while at 50°C the Tafel slope was 85.7 mV.dec⁻¹ and at 80°C was 133.9 mV.dec⁻¹. The Tafel slopes shown an increased
Linear graph, the point at 50°C was lower due to experimental error in this experiment.

3.3.3 Summary
The results of cyclic voltammetry showed that a higher electrocatalytic activity for both binary and ternary catalysts on the surface of gas diffusion layer for HER. At 50°C the potential for Pt₅₀Ni₅₀, was 0.7 V for the release of hydrogen gas compared to other temperatures with higher potentials while at 30°C of Pt₃₃Ni₃₃Co₃₃ the potential of 0.69 V show the best hydrogen release than other temperatures.

Pt₅₀Ni₅₀ at 80°C gave an electrical power of 125 mW, compared to the ternary catalyst of Pt₃₃Ni₃₃Co₃₃ at 80°C, which gave a higher electrical power of 138 mW. A Tafel slope of 0.93 mV.dec⁻¹ was observed for Pt₅₀Ni₅₀ that show higher value compared to other temperatures, for Pt₃₃Ni₃₃Co₃₃ a higher Tafel slope of 133.9 mV.dec⁻¹ was observed at 80°C. This might be due to larger over potentials and slower diffusion currents.

3.4 Comparison of anode catalysts at 80°C

Figure 3.50 shows the summary of all the catalyst at 80°C for the anodic catalyst combination, where it was found that the ternary elements of Ir₂₀Ru₂₀Co₆₀ was the decrease in potential of 0.6 V compared to the Ir₂₀Ru₄₀Co₄₀ with potential of 0.95 V. This means as the cobalt metal increases with a decrease in ruthenium metal there was a change in potential, while for the binary elements, Ir₅₀Pt₅₀ show a potential of 0.6 V followed by Ir₄₀Co₆₀ with a potential of 0.925 V then Ir₅₀Ru₅₀ with a potential of 1.45 V finally the Ir₂₀Ru₈₀ with potential of 1.55 V. In binary element, Ir₅₀Pt₅₀ shows the best performance at higher temperature of 80°C compared to other catalysts, while the Ir₂₀Ru₂₀Co₆₀ in ternary catalyst was the best.
The results showed that the Ir$_{50}$Ru$_{50}$ gave a Tafel slope of 198 mV.dec$^{-1}$ followed by Ir$_{50}$Pt$_{50}$ with a Tafel slope of 192.1 mV.dec$^{-1}$. However, these catalysts gave a hydrogen efficiency of 37% and 44% respectively. Ir$_{40}$Co$_{60}$ gave a higher hydrogen efficiency of 73% with a lower Tafel slope of 30.1 mV.dec$^{-1}$ followed by Ir$_{20}$Ru$_{80}$ with a hydrogen efficiency of 65%. The Tafel slope of 80.2 mV.dec$^{-1}$ was observed for this sample studied. For the ternary elements, Ir$_{20}$Ru$_{20}$Co$_{60}$ a higher hydrogen efficiency of 58% than Ir$_{20}$Ru$_{40}$Co$_{40}$ with a hydrogen efficiency of 44% was observed, with a Tafel slope of 31.8mV.dec$^{-1}$ and 33.6 mV.dec$^{-1}$ respectively.

3.4.1 Hydrogen efficiency at anode catalyst

Thermodynamic measurements

The results in Figure 3.52 showed the characterization of electrolyser where in [X] show the volume of hydrogen released was proportional to time at constant current, at [Y] was the proportionality between the volumes of hydrogen released at various current with constant time.
Literature reported that the accepted range for hydrogen efficiency was between 50-90% and at 70% was the best possible hydrogen efficiency observed for PEM electrolyser systems.\textsuperscript{64} In Figure 5.53 below, show the different supports on the anode side with Pt on cathode side, except for the graphite there was a Pt\textsubscript{50}Ni\textsubscript{50} at cathode.

In Figure 3.53 A where the metal support for the IrO\textsubscript{2} catalyst was supported on Ti metal, the results showed a better hydrogen efficiency 50 °C compared to the 80 °C or 30 °C followed by Ir\textsubscript{50}Pt\textsubscript{50} at 80 °C then 50 °C compared with other catalysts that some are on the range. It showed that IrO\textsubscript{2} was the better with titanium support. In Figure 5.53 B where the metal support for the IrO\textsubscript{2} catalyst was on stainless steel 318 metal, Ir\textsubscript{20}Ru\textsubscript{40}Co\textsubscript{40} at 50 °C showed the better hydrogen efficiency at 80 °C compared to Ir\textsubscript{50}Ru\textsubscript{50} at 50 °C. In Figure 5.53 C where the metal support for the IrO\textsubscript{2} catalyst was supported on Ni metal, the Ir\textsubscript{50}Ru\textsubscript{50} at 30 °C was the highest at 80 °C followed by Ir\textsubscript{20}Ru\textsubscript{20}Co\textsubscript{60} at 80 °C and the Ir\textsubscript{50}Pt\textsubscript{50} at 50 °C. In Figure 3.53 D where the support for the IrO\textsubscript{2} catalyst was supported on graphite; the best efficiency was at 80 °C of Ir\textsubscript{40}Co\textsubscript{60} then 50°C followed by Ir\textsubscript{20}Ru\textsubscript{20}Co\textsubscript{60} at 50 °C and Ir\textsubscript{50}Pt\textsubscript{50} at 50°C.

The stainless steel plate was scrubbed with hardbrush to get rid of impurities, then apply the catalyst ink and heat it, while the Ti and Ni support, the catalyst was brushed on them. As the temperature increases, the behaviour according to different metal supports varies as seen in figure 3.53.
3.4.2 Summary

The Ir_{50}Pt_{50} show the best hydrogen release at 0.6V when compared to Ir_{40}Co_{60} at 0.925V and other catalysts while the best performance at 0.15 A.cm\(^{-2}\) was found for the ternary catalyst of Ir_{20}Ru_{20}Co_{60} at low potential of 0.6 V when compared to Ir_{20}Ru_{40}Co_{40}. The electrical power for the binary catalyst of Ir_{40}Co_{60} had a higher power compared to Ir_{50}Pt_{50} and other catalysts while the ternary catalyst of Ir_{20}R_{20}Co_{60} also gave a higher power of 0.288mW.

Ir_{50}Ru_{50} show the higher Tafel slope at low hydrogen efficiency compared to other catalysts while Ir_{40}Co_{60} give higher hydrogen efficiency with low Tafel slope. In ternary catalysts, Ir_{20}Ru_{20}Co_{60} gave higher hydrogen efficiency with low Tafel slope compared to Ir_{20}Ru_{40}Co_{40}.
3.5 Comparison of cathode catalysts at 80°C

In Figure 3.54 below, show the binary and ternary mixture of cathode catalyst in gas diffusion layer, as the potential increased the current density increased for both catalysts. For the binary mixture the potential was at 0.925 V and for ternary mixture, the potential was at 1.18 V. On both catalysts, the hydrogen gas started to released at the more or less the same potential, but binary show the best performance.

Figure: 3.54. Polarization curves for cathode catalysts at 80°C
Figure 3.56: Tafel plot for cathode catalysts at 80°C
3.5.1 Summary
Pt$_{50}$Ni$_{50}$ as catalyst showed the best hydrogen release at low potential of 0.925 V when compared to Pt$_{33}$Ni$_{33}$Co$_{33}$. The electrical power for both Pt$_{50}$Ni$_{50}$ and Pt$_{33}$Ni$_{33}$Co$_{33}$ catalysts were the same of 125.0 mW and 124.6 mW respectively at the same potential. The ternary catalyst gave a higher Tafel slope in Figure 3.56 and higher hydrogen efficiency when compared to binary catalyst (Table 3.1).

Table 3.1. Summary of catalysts

<table>
<thead>
<tr>
<th>Catalysts at 80°C</th>
<th>Tafel slope (mV.dec$^{-1}$)</th>
<th>Hydrogen efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$<em>{50}$Ni$</em>{50}$</td>
<td>0.93</td>
<td>62.1</td>
</tr>
<tr>
<td>Pt$<em>{33}$Ni$</em>{33}$Co$_{33}$</td>
<td>133.9</td>
<td>65.7</td>
</tr>
</tbody>
</table>
Chapter 4

Conclusion
Preparation of the catalysts for electrodes in PEM water electrolysis were carried out using the Adam’s methods, at a current of 1 A.cm\(^{-2}\) and cell voltage of between 1.5-1.9 V and 30\(^{\circ}\)C-80\(^{\circ}\)C. Noble metals loading of 0.2-0.5 mg.cm\(^{-2}\) were used and application was done by using the brush technique.

The results showed that Ir\(_{40}\)Co\(_{60}\) gave the best electrocatalytic activity on the surface of gas diffuse layer, which gave the lowest potential at 80\(^{\circ}\)C. This resulted in a low Tafel slope with high hydrogen efficiency. This also resulted in the system to require to produce more electricity at 50\(^{\circ}\)C than other binary catalyst. For the Ir\(_{50}\)Pt\(_{50}\) catalyst system good electrocatalytic activity was observed at lower potential at 50\(^{\circ}\)C with relatively high Tafel slopes.

The systems with the Ir\(_{20}\)Ru\(_{80}\) and Ir\(_{50}\)Ru\(_{50}\) were found to show no promising performance as anode catalysts due to their low electrocatalytic activity, with low electrical power needed. Ir\(_{20}\)Ru\(_{80}\) showed to be promising in terms of the hydrogen efficiency at 65% at 80\(^{\circ}\)C, while Ir\(_{50}\)Ru\(_{50}\) showed acceptable Tafel slopes over a wide temperature range with low hydrogen efficiency. Further work need to be done on regarding various metal supports to prevent corrosion on the anode side.

Ternary mixed oxides of Ir\(_{20}\)Ru\(_{40}\)Co\(_{40}\) showed very good catalytic activity when compared to the Ir\(_{20}\)Ru\(_{20}\)Co\(_{60}\) catalyst system. The catalyst showed good performance at very low potentials of 0.5V-0.6 V at 30\(^{\circ}\)C-80\(^{\circ}\)C with and a promising electrical power output. Low Tafel slopes were observed with good hydrogen efficiency.

Pt\(_{50}\)Ni\(_{50}\) as binary cathode catalyst showed good electrocatalytic activity with a promising performance that required a potential of 1.4 V and with a 0.6 mW power output. By comparison, the ternary catalyst of Pt\(_{33}\)Ni\(_{33}\)Co\(_{33}\) showed to give good
performance with promising electrical power requirements and hydrogen efficiency.

The results of this study showed that by adding Co oxide to the noble metals mixture, the overall positive effect on the hydrogen electrolysis of the anode and cathode catalyst due to its catalytic property. Binary anode catalyst of Ir_{40}Co_{60} gave good hydrogen efficiency results with a low potential and high electrical power output at 80°C. This implied that it would be a better binary catalyst for anode side of the electrolysis cell. The Ir_{20}Ru_{20}Co_{60} catalyst showed to be a promising catalyst that gave higher electrical power output at lower over potential and at higher temperatures.

Pt_{33}Ni_{33}Co_{33} gave a better performance as a cathode catalyst that achieved higher hydrogen efficiencies at lower over potentials of less than 1.2V. The catalyst loading were relatively low that can work at higher temperatures. This catalyst proved to be a suitable candidate for electrolysis applications where further work would be required to optimize its application in binary anode and cathode systems.

Future work would include:

- To investigate the catalysts application on different supports such as Ti or stainless steel
- To simulate the distributed energy system in the laboratory from an electrolyser to the fuel cell and to build suitable stack systems in order to investigate the anode and cathode catalysts loading,
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Appendix: Research outputs

Appendix 1: Article accepted in Analytical letters

Characterization of base metal catalysts with platinum to reduce PGM content in a PEM electrolyser cell

Special Issue: KAC-10

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Abstract

The electrolysis of water is evaluated as a potentially efficient, low cost means of hydrogen production. The theoretical energy and voltage, current, and energy efficiencies of water electrolysis are considered. Various catalyst materials used in the fabrication of membrane electrode assemblies will be evaluated for this study.

Ternary element mixtures such as Pt-Ni-Co were introduced at the cathode side to reduce Pt loading, but keeping the electrolyzer performance the same as with a pure Pt catalyst loading. The catalysts were applied to a membrane electrode assembly (MEA) and characterized by cyclic voltammetry (CV). The Tafel slope
for the Pt-Ni-Co mixtures gave a Tafel slope of 86 mV dec$^{-1}$ at lower temperatures and 134 mV dec$^{-1}$ at higher temperatures of 80°C. The cyclic voltammetry results show a higher electrocatalytic activity for the oxidation formation of hydrogen on ternary catalysts mixtures compared to the platinum catalyst.

Keywords: Polymer electrode membrane, electrolyzer, platinum, hydrogen production, nickel cobalt catalyst
1. Introduction

Numerous attempts to investigate an electrochemical cell which could operate an alternative as a water electrolyzer has been reported in recent years (J Ahn et al 1992, Ghatak et al 2008, Millet et al 1990). The electrode materials used for the hydrogen evolution by water are mostly based on noble metals such as RuO$_2$, or PtO$_2$, (Song et al 2008, Trasatti 1991, Marshall 2007, Benedetti et al 1994); consequently it is important to reduce the noble metal loading of the electrocatalyst in the electrode due to their expense. This could be achieved by the introduction of base metals such as nickel or cobalt which is what will be investigated in this study.


At the anode side, the water splits into oxygen and hydrogen. The protons migrate through the membrane that has the active sulfonic groups, to the cathode, where they are reduced to hydrogen (Kreuter et al 1998). PEM electrolyzer offers a number of advantages compared to the alkaline electrolyzer, such as a higher gas purity, the increased level of safety, and a possibility of producing compressed gas directly in the installation (Grigoriev et al 2006, Millet et al 2009, Grigoriev et al 2009). Electrolyzers can be distinguished by the type of electrolyte, the type of
electrodes used which typically operate between 0-1000 mA and at a cell voltage between 1.4-1.9V.

Pt is the most well known catalyst for water electrolyzers, both for hydrogen oxidation and oxygen reduction. At high anodic potentials and in acidic medium Pt is stable. A better electrical conductivity and better voltage efficiency was obtained by using Pt black as a suitable cathode catalyst in water electrolysis.

Ternary catalysts for the electrodes in water electrolysis system using a polymer membrane as electrolyte was characterized and electrical power outputs calculated to determine which catalyst system could be a suitable candidate. In this investigation the IrO$_2$ was used as the preferred choice of anode catalyst for the electrode and the cathode catalyst was Pt mixed with one or more base metals such as Ni/Co mixtures.

2. Experimental

2.1 Chemicals and reagents

All chemicals were analytical grade. Platinum black (grade, purity), iridium oxide (grade, purity), nickel cobalt chloride (grade, purity) were obtained from Aldrich (Germany). The carbon cloth and Nafion 117 membrane were purchase from Fuelcell Store (USA).

2.2 Preparation of metal oxide
The cathodes were prepared by using nickel (Judex Lab Reagent) and nickel cobalt (Aldrich) on Pt black (Aldrich; 99.9%; FC Grade) as noble metals. For the anode catalyst, IrCl$_3$ (Aldrich) was used as precursor for the formation of IrO$_2$. 0.1g of metal oxide precursor was mixed with 5g of NaNO$_3$ and dissolved in 20mL of water (pure tap water). The mixture was evaporated to remove water and the salt mixture was pre-heated in an oven at 340$^\circ$C for 30 minutes. The salt mixture was then cooled to 25$^\circ$C, and washed with water to eliminate traces of chlorine. The IrO$_2$ salt was dried and stored for later use. (Rasten et al 2003)

2.3 Preparation of membrane electrode assemble (MEA)

The membrane was cleaned according to the procedure described by Shukla et al (2001). The Nafion 117 membrane was first preheated in 5 wt% H$_2$O$_2$ at about 92-98 $^\circ$C for 1 hour to remove the organic materials. The membrane was then kept in pure water for 10 minutes at 80 – 90 $^\circ$C and further treated in 1M H$_2$SO$_4$ at 92 – 98 $^\circ$C for 1 hour to protonate the membrane completely with protons and remove metallic impurities. Then lastly the membrane was boiled in water for 1 hour, cooled and rinsed. The membrane was then stored in water until ready for use. (Shukla et al 2001)

The oxygen electrode and hydrogen electrode was hot-pressed on aluminum plate with pretreated Nafion membrane in-between the electrodes and with charcoal sprinkled on the plate at 80$^\circ$C for 3hrs in vacuum oven. (Shukla et al 2001)

2.4 Preparation of gas diffusion layer (GDL)
Catalyst solutions were prepared using Pt black (Alfa Aesar), PtNi, PtNiCo as the cathode while IrO₂ was used as an anode metal. A Nafion solution (0.3 mL, 5% w/t; Dupont) and ethanol aqueous solution (20 mL) were ultra sonicated for 1 minute and stirred with a magnetic stirrer to form an ink. The carbon paper (Fuel Cell, USA) was then soaked with the ink until all the catalyst was embedded onto the carbon paper. The electrocatalyst loading of metal was approximately 0.3mg/cm². (Shukla et al 2001)

2.5 Electrochemical measurements

Cyclic voltammetry of both anode and cathode catalysts was measured against a Ag/Ag⁺ reference electrode at different scan rates from 100 – 400 mV s⁻¹, between the potential limits of hydrogen and oxygen evolution reaction. All voltammograms were measured at room temperature by a CV50w Bio Analytical System.

Steady state polarization curves were obtained under galvanostatic control at cds up to 2 A cm⁻². All potentials were determined by three digital multimeters and the data logged by a computer.

2.6 Scanning electron microscopy

SEM measurements were performed using a Joel SEM 6380. Catalysts were brushed on stainless steel strips and dried at 125°C before scanning.
3. Results and discussion.

3.1 Effect of catalyst loading

In this investigation, various cathode catalyst loadings were prepared to study the effect on the power characterization curves. In this study the anode catalyst was kept at 2 mg cm\(^{-2}\) IrO\(_2\) coated on the membrane and the Pt content on the cathodic side were varied between 0.2 and 0.3 mg cm\(^{-2}\). Figure 1A shows a typical polarization curve obtained for the electrolysis of water. When these catalyst material where used to make up the membrane electrode assembly.

![Polarization curve](image)

**Figure 1**: A) Polarization curves for the different Pt catalyst loading on the cathode electrode at different temperatures. B) Electrical power curves obtained for the Pt catalyst (0.2 mg cm\(^{-2}\)) at 40 and 60°C

On close inspection the cell potential becomes less when the temperatures increases from 40 °C to 60 °C and a further drop was observed at 80 °C with a 0.2
With higher platinum loading a further drop was observed in the cell potential from 1.1 V to 0.9V.

Figure 1B shows the electrical power curves when a Pt (0.2 mg cm^-2) // IrO_2 (2 mg cm^-2) were used at two temperatures of 40 and 60 °C respectively. At 40 °C an electrical power of 1.2W was observed while at slightly higher temperature of 60 °C an electrical power of 1.6W was observed. This indicates that temperature plays an important role in the electrolysis of water using lower temperature PEM electrolysis devices.

Based on the cell polarization data shown in Figure 1A, kinetic parameter can deduced from the linear part of the curve at each temperature and can be obtained from the empirical Tafel equation [1] and are summarized in Table 1.

\[
E = E_o - \log (i) - Ri
\]  \hspace{1cm} (1)

where

\[
E_o = E_r + \log(i_o)
\]  \hspace{1cm} (2)

b and \(i_o\) are Tafel slope and exchange current density for the hydrogen evolution reaction (HER), respectively. \(R\) the slope of the linear region of \(E\) versus \(i\) plot, which represents the resistance including the predominant membrane ohmic resistance, contact resistance and charge transfer of the hydrogen electrode. \(E_r\) is the reversible potential of HER.
Figure 2 shows the $iR$-corrected Tafel plots for the cathode electrode Pt (0.2mg cm$^{-2}$) at various temperatures of 30, 50 and 80$^\circ$C respectively.

![Tafel plots for the Pt catalysts loading (0.2 mg cm$^{-2}$) on a GDL surface at different temperatures](image)

**Figure 2:** Tafel plots for the Pt catalysts loading (0.2 mg cm$^{-2}$) on a GDL surface at different temperatures

It was observed that the Tafel slope at low temperatures, 30 $^\circ$C, for a Pt // IrO$_2$ was 100 mV dec$^{-1}$ compared to the higher temperature of 80$^\circ$C which gave a Tafel slope of 51 mV dec$^{-1}$. Literature suggests that a Pt // Pt system gives a Tafel slope of 130 mV dec$^{-1}$. (Ann et al, 1992). This deviation is attributed to ohmic and mass transport losses in the system.
Table 1: Summary of the Tafel slope obtained for Pt catalyst loading (0.2 mg cm$^{-2}$) at different temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>100.18</td>
</tr>
<tr>
<td>50°C</td>
<td>60.94</td>
</tr>
<tr>
<td>80°C</td>
<td>51.74</td>
</tr>
</tbody>
</table>

An improvement of the catalyst-membrane unit with respect to an improved membrane electrode assembly could reduce transport hindrance that will provide further information on the relative activity of the material studied.

3.2 Effect of base metals with PGM metals

By reducing the PGM content and in particular the Pt content, base metals were introduced. Ternary mixtures such as Pt-Ni-Co were investigated using cyclic voltammetry as a tool to characterize the hydrogen evolution reactions (Shukla et
al 2001). After the initial investigations, the catalyst was brushed on a gas diffuse layer and hot pressed to make the membrane electrode assembly. The MEA was then placed in an electrolysis device and the polarization curves were then studied. Figure 4 shows the cyclic voltammetry curves obtained for Pt$_{33}$Ni$_{33}$Co$_{33}$ catalyst in a sulfuric acid electrolyte medium. The increase in scan rates from 100 to 400 mV s$^{-1}$ has shown a good adherence of catalyst to the membrane surface. The SEM image shows a good distribution of the catalyst mixture on the surface of the gas diffuse layer.

**Figure 3:** Cyclic voltammogram of PtNiCo in saturated 1M H$_2$SO$_4$ at 25°C vs Ag/Ag$^+$ reference electrode. SEM imaging of the PtNiCo catalyst distribution on the gas diffuse layer. Anodic charging current measured at 1.2 V$_{Ag/Ag^+}$ scan rate.
Pt$_{33}$Ni$_{33}$Co$_{33}$ catalyst did not show well defined hydrogen adsorption and desorption behavior as was the case when pure Pt black catalyst was used as the electrode catalyst. Due to charge associated to the hydrogen adsorption/desorption decreases with lowering of the Pt loading, which indicates a decrease in Pt active area. This was also observed by Paulus et al (2002).

Figure 4 A and B shows the polarization curves and electrical output curves for the Pt$_{33}$Ni$_{33}$Co$_{33}$ catalyst.
**Figure 4:** A) Polarization curves for the different Pt-Ni-Co catalyst loading on the cathode electrode at different temperatures. B) Electrical power curves obtained for the Pt-Ni-Co catalyst at 30 50 and 80°C

The cell potential of 1.2V was observed at 80 °C with a Pt-Ni-Co loading.

Figure 4B shows the electrical power curves for the Pt-Ni-Co catalyst at various temperatures of 30, 50 and 80°C. The power obtained at 80 °C gave an electrical power output of 1.4W at 0.8 A.

The overall activity of the ternary Pt-Ni-Co catalyst has shown good comparisons with the Pt black catalyst. Figure 5 shows the $iR$-corrected Tafel plots for the cathode electrode Pt-Ni-Co at various temperatures of 30, 50 and 80°C respectively.

**Figure 5:** Tafel plots for the Pt-Ni-Co catalysts loading on a GDL surface at different temperatures
Table 2 gave the Tafel slope summary for the Pt-Ni-Co mixtures with a Tafel slope of 86 mV dec^{-1} at lower temperatures and 134 mV dec^{-1} at higher temperatures of 80°C. These values compares well with literature values (Ann et al, 1992).

Table 2: Summary of the Tafel slope obtained for Pt_{33}Ni_{33}Co_{33} catalyst loading (0.2 mg cm^{-2}) at different temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Tafel slope (mV dec^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>86.8</td>
</tr>
<tr>
<td>50°C</td>
<td>85.76</td>
</tr>
<tr>
<td>80°C</td>
<td>133.98</td>
</tr>
</tbody>
</table>

Conclusion

Various aspects of electrocatalysis have been studied in this paper and it was found that ternary mixtures of base metals can reduce PGM content in the electrolyzer. These catalysts have given similar or better performance to achieve higher efficiencies at lower over potentials of less than 1.2V on a 0.3mg cm^{-2} catalyst loading.
Various Pt loadings were investigated as a catalyst as a function of temperature. It was observed that higher temperatures of 80 °C gave considerable better results compared to lower temperatures of 30 °C. The cell potential had dropped and better electrical power was observed. The cell potentials were even dropped further when base metals were introduced but corrosion starts to occur at the oxygen electrode reaction side.

Ternary element mixtures were introduced at the cathode side to reduce Pt loading but keeping the electrolyzer performance the same as with a pure Pt catalyst loading. The catalysts were applied to a membrane electrode assembly (MEA) and characterized by cyclic voltammetry (CV). The cyclic results show a higher electrocatalytic activity for the oxidation formation of hydrogen on ternary catalysts compared to the platinum catalyst.

Acknowledgement

This work was financially supported by Hydrogen South Africa, Innoventon/DSTC Institute of Chemical Technology, NRF and Nelson Mandela Metropolitan University.

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Appendix 2: Conference paper


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