

**Optimisation of the hydrogen pressure control in a
regenerative proton exchange membrane fuel cell**

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Declaration

I, Melanie Burger, hereby declare that the following research information is solely my own work. This is submitted in the fulfillment of the requirements for the Magister Technologiae: Engineering: Electrical to the Department of Applied Electronics and Electronic Communication at the Vaal University of Technology, Vanderbijlpark. This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any other degree.

Signed.....

Date.....

Acknowledgements

I would like to thank the following individuals:

- Prof H.C.vZ Pienaar
- Telkom Centre of Excellence
- TFMC
- M-TEC
- THRIP

Dedication

Never accept failure, no matter how often it visits you.

Keep on going.

Never give up.

Never

- DR. MICHAEL SMUREŃ

I hereby dedicate this document to my heavenly Father, my family and Prof. H C vZ Pienaar.

Abstract

Industrial countries, such as South Africa, rely heavily on energy sources to function profitably in today's economy. Based on the 2008 fossil fuel CO₂ emissions South Africa was rated the 13th largest emitting country and also the largest emitting country on the continent of Africa, and is still increasing. It was found that fuel cells can be used to generate electricity and that hydrogen is a promising fuel source. A fuel cell is an energy generation device that uses pure hydrogen (99.999%) and oxygen as a fuel to produce electric power. A regenerative fuel cell is a fuel cell that runs in reverse mode, which consumes electricity and water to produce hydrogen.

This research was aimed at designing and constructing an optimised control system to control the hydrogen pressure in a proton exchange membrane regenerative fuel cell. The hydrogen generated by the fuel cell must be stored in order to be used at a later stage to produce electricity.

A control system has been designed and constructed to optimise the hydrogen pressure control in a regenerative proton exchange membrane fuel cell. An experiment that was done to optimise the hydrogen system included the effects that the cathode chamber pressure has on the production of hydrogen and the most effective method of supplying hydrogen to a storage tank. The experiment also included the effects of a hydrogen buffer tank on the output hydrogen pressure and if the system can accommodate different output pressures.

It was found that the cathode chamber pressure doesn't need to be controlled because it has no effect on the rate of hydrogen produced. The results also showed that the flow of hydrogen need not to be controlled to be stored in a hydrogen storage tank, the best method is to let the produced hydrogen flow freely into the tank. The hydrogen produced was also confirmed to be 99.999% pure. The system was also tested at different output pressures; the control system successfully regulated these different output pressures.

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Glossary or abbreviations and symbols

A, B

BP - Bipolar plate

C

CDIAC - Carbon Dioxide Information Analysis Centre

CHP - Combined heat & power cogeneration

D, E

E° - Standard electrode potential in V

E - Electrodes potential in V

F

F - Faraday's constant 96485 C.mol⁻¹

FC - Fuel cell

G, H, I

ΔG – Gibbs' free energy (kJ.mol⁻¹)

ΔG° – Gibbs' standard free energy (kJ.mol⁻¹)

GC - Gas Chromatography

GHG - Greenhouse gas

GDL - Gas diffusion layer

J, K, L

kg - Kilogram

kPa - Kilo Pascal

M

MEA - Membrane electrode assembly

N, O

n - Amount of electrical charges transferred in the reaction

P, Q

$P_M^m P_N^n$ - Pressure of reactants in kPa

$P_A^a P_B^b$ - Pressure of products in kPa

PEMFC - Proton exchange membrane fuel cell

PEM - Proton exchange membrane

PIC - Peripheral Interface Controller

Pt - Platinum

PLC - Programmable logic controller

R

R - Universal gas constant (8.314 J.mol.K⁻¹)

RFC - Regenerative fuel cell

S

STP - Standard temperature and pressure

T, U

T - Absolute temperature in Kelvin (K)

TCD - Thermal conductivity detector

V, W, X

w – Electrochemical work in Joules

W - Watt

Y, Z

Chapter 1 Introduction

Industrial countries, such as South Africa, rely heavily on energy sources to function profitably in today's economy. Sustainable development is therefore a strategic goal of modern society reflecting contemporary demand for economic, social, political and environmental development. Access to affordable and reliable energy drawn from an environmentally acceptable source of supply is an important feature of sustainable development (Grimes, Varghese & Ranjan, 2008:1).

1.1 Background

According to the 1987 Brundtland Report from the United Nations, sustainable development is defined as a process of developing land, cities, business, communities, etc. that "meets the needs of the present without compromising the ability of future generations to meet their own needs" (Grimes *et al.*, 2008:2). When a kilogram of fuel is burned, it produces 3.2 kg of carbon dioxide and 1.0 kg of water. The extraction and combustion of fossil fuels is a major threat to the environment because of land damage, smog, acid rain and changes in the composition of the atmosphere. Environmental damage and atmospheric changes may soon alter the weather and climate patterns of the earth resulting in grave problems for many of its inhabitants. Hydrocarbons have extraordinary value as the source of chemicals used to produce goods and other essentials for living beings (Grimes *et al.*, 2008:2).

It is noted that hydrogen appears to be a promising, useful candidate to replace hydrocarbon fuels. Hydrogen can be used as a fuel to generate electricity, through use of a proton exchange membrane fuel cell (PEMFC). It is also important to note that the sun delivers 3×10^{24} joules of energy per year to the earth, which is 10,000 times our present global energy consumption (Grimes *et al.*, 2008:10).

A carbon footprint of a country is a measure of the greenhouse gas (GHG) emission associated with an activity, group of activities or a product and also a reason for sustainable development. Human activities produce the most important GHG which is carbon dioxide. Examples of direct GHG emissions are burning of fossil fuels for electricity generation, heating and transport. Energy is required for production and transport of products and when disposed at the end of their useful lives GHG is also released (Abbott, 2008:4).

On the global level 72% of greenhouse gas emissions are related to household consumption (Hertwich & Peters, 2009:6414).

The data presented in Table 1 below corresponds to the emissions in 2008. The data was collected by the Carbon Dioxide Information Analysis Centre (CDIAC) for the United Nations. This data only considers carbon dioxide emissions from the burning of fossil fuels and cement manufacture, but not emissions from land use such as deforestation (United Nations Statistics Division, 2011).

Table 1 List of some counties by 2008 emission (United Nations Statistics Division, 2011)

Country	Annual CO₂ emissions (in thousands of metric tonnes)	Percentage of global total
China	7,031,916	23.33%
United States	5,461,014	18.11%
European Union	4,177,817.86	14.04%
India	1,742,698	5.78%
Russia	1,708,653	5.67%
Japan	1,208,163	4.01%
Germany	786,660	2.61%
Canada	544,091	1.80%
Iran	538,404	1.79%
United Kingdom	522,856	1.73%
South Korea	509,170	1.69%
Mexico	475,834	1.58%
Italy	445,119	1.48%
South Africa	435,878	1.45%
Saudi Arabia	433,557	1.44%
Indonesia	406,029	1.35%
Australia	399,219	1.32%

Based on the 2008 fossil fuel CO₂ emissions South Africa is the 13th largest emitting country and the largest emitting country on the continent of Africa. The fossil fuel emissions of South Africa are clearly shown in Table 2 and Figure 1 from the year 1884 to 2008 and 1875 to 2010 respectively (CDIAC, 2011).

Table 2 Total fossil fuel emissions of South Africa from 1884-2008 (CDIAC, 2011)

Year	Total Fossil Fuel Emissions	Year	Total fossil Fuel Emission
1884	6	1956	23819
1892	131	1964	32631
1900	636	1972	46830
1908	3550	1980	62300
1916	6026	1988	93552
1924	7700	1996	97802
1932	6695	2004	112944
1940	13043	2008	118865
1948	15585		

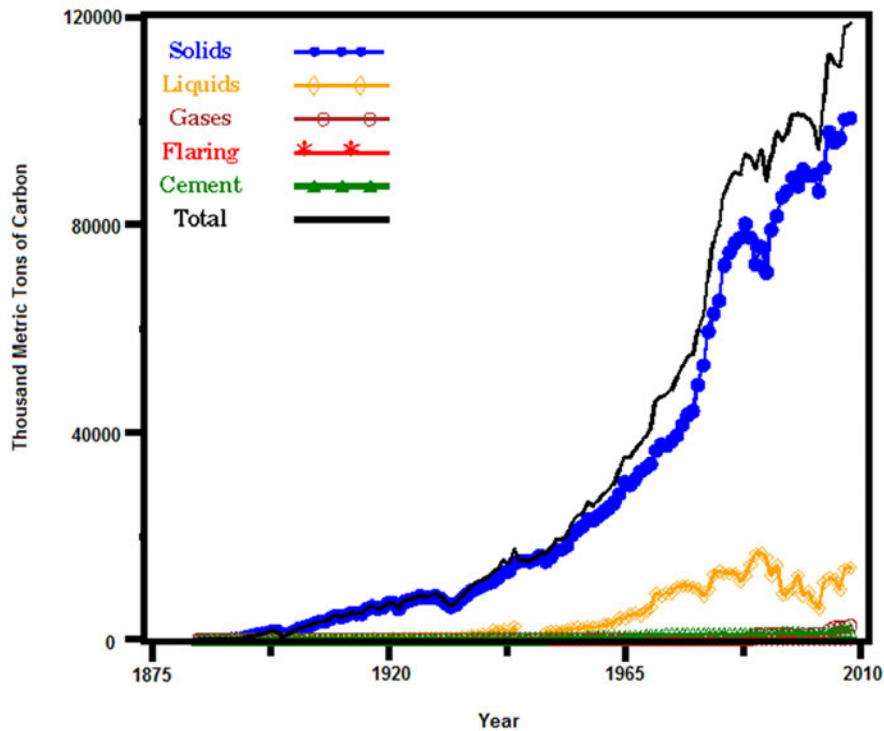


Figure 1 CO₂ emissions of South Africa from 1875-2010 (CDIAC, 2011)

For these years shown in the table and figure above it clearly indicates that the total CO₂ emissions for South Africa keep increasing.

Table 3 shows an example of the carbon footprint of a typical business with five offices (Abbott, 2008:9).

Table 3 Breakdown of company emissions by activity (Abbott, 2008:9)

Source of emissions	Equivalent emissions CO₂ (t/yr)	Proportion of total
Premises – electricity	2342.4	40%
Premises – gas	394.3	7%
Premises – heating oil	530.5	9%
Premises – backup generators	1.6	0%
Premises – refrigerant loss	0.0	0%
Company - owned vehicle – petrol cars	587.3	10%
Business travel – petrol cars	162.1	3%
Business travel – taxi hire	58.5	1%
Business travel – air travel	830.4	14%
Business travel – train travel	11.5	0%
Business travel – hotel stays	401.9	7%
Commuting – petrol car	206.9	4%
Commuting – motorcycle travel	7.3	0%
Commuting – train	37.6	1%
Commuting – bus	40.4	1%
Deliveries – van	3.7	0%
Premises – landfilled waste	191	3%
Total	5834	100%

The source of emissions that takes up the largest portion of the total is the electricity that is being used. This is a great concern and therefore sustainable development is considered as a solution to the electricity problem.

A fuel cell is an energy generation device that uses pure hydrogen (99.999%) and oxygen as a fuel to produce electric power (Züttel, Borgschulte & Schlapbach, 2005:60). A very interesting fact about the fuel cell is that it could also be used in the 'reverse' mode to produce hydrogen and oxygen if electrical power is applied to its terminals.

There are different types of fuel cells based on size, advantages and disadvantages, operating temperatures and efficiency. The most common types of fuel cells are shown in Table 4 (Chambers, 2004:176).

Unfortunately hydrogen for fuel cells is not readily available like other fuels (coal and oil). Hydrogen has to be generated.

Table 4 Types of fuel cells with important information (Chambers, 2004:176)

Type	Size	Temperature	Efficiency	Advantages	Disadvantages
Phosphoric acid	Up to 200 kW	190-210°C	37-45% 75-80% CHP	Commercially available, Proven reliability, Low CHP potential.	External reformer, Corrosive electrolyte, Large size and weight, Low cost cut potential, High operating cost, Expensive catalyst.
Molten carbonate	200 kW to 10 MW	650°C	50-60% 80-85% CHP	Strong CHP potential, Fuel flexibility, Internal reforming, No core materials, Nearing commercialisation.	Expensive, Long start-up cycle, Inflexible to load change, Heat shield needed, Efficiency affected by temperature.
Solid oxide	<1 kW to several MW	650-1000°C	45-55% 80-85% CHP	Top CHP potential, High efficiency, Fuel flexibility, Internal reforming, Scalable, Potential for load following.	High temperature speeds cell breakdown, Heat shield needed, High capital cost, Efficiency sensitive to temperature.
Proton exchange	50 W to 250 kW	80-100°C	30-40% 55-70% CHP	Fast start-up, High power density, Low temperature, Possible load following, Long cell and stack life, Potential cost cuts.	Lower efficiency and CHP potential, High material costs, External reformer, Sensitive to fuel impurities.

There are several methods that are currently being used for generating hydrogen. Some of them are:

- Steam reforming: uses thermal energy to separate hydrogen from the carbon components in methane and methanol, and involves the reaction of these fuels with steam on catalytic surfaces (Potter & Newell, 1992/1993:42-45);
- Electrolysis: separates the elements of water –H and oxygen –O by charging water with an electrical current (Potter & Newell, 1992/1993:42-45);
- Steam electrolysis: is a variation of the conventional electrolysis process. Some of the energy needed to split the water is added as heat instead of electricity, making the process more efficient than conventional electrolysis (Potter & Newell, 1992/1993:42-45);
- Thermochemical water splitting: uses chemicals such as bromine or iodine, assisted by heat (Potter & Newell, 1992/1993:42-45);

- Photoelectrochemical processes: use two types of electrochemical systems to produce hydrogen. One uses soluble metal complexes as a catalyst, while the other uses semiconductor surfaces. The other method uses semiconducting electrodes in a photochemical cell to convert optical energy into chemical energy (Potter & Newell, 1992/1993:42-45);
- Photosynthesis: produces hydrogen from sunlight (Potter & Newell, 1992/1993:42-45);
- Biological and photobiological processes: use algae and bacteria to produce hydrogen (Potter & Newell, 1992/1993:42-45);
- Algae: allowing the algae culture to grow under normal conditions it is then deprived of both sulphur and oxygen, causing it to switch to an alternate metabolism that generates hydrogen. After several days of generating hydrogen, the algae culture was returned to normal conditions for a few days, allowing it to store up more energy. The process can be repeated many times. Producing hydrogen from algae could eventually provide a cost-effective and practical means to convert sunlight into hydrogen (Potter & Newell, 1992/1993:42-45);
- Methane and ethanol: is another way of producing hydrogen through natural processes. Methane (CH_4) is a component of 'biogas' that is produced by anaerobic bacteria. Anaerobic bacteria occur widely throughout the environment. They break down organic material in the absence of oxygen and produce biogas as a waste product. Landfills, livestock waste and municipal sewage treatment facilities are all sources of biogas. Ethanol is produced by the fermentation of biomass (Potter & Newell, 1992/1993:42-45);
- Glucose: a sugar produced by many plants. This process occurs at relatively low temperatures and can produce fuel cell grade hydrogen in a single step. Glucose is manufactured in vast quantities from corn starch and can also be derived from sugar beets, low-cost waste streams or wood waste. (Potter & Newell, 1992/1993:42-45);
- Thermal water splitting: this process uses heat of up to 5,430°F (3,000°C) to split water molecules (Potter & Newell, 1992/1993:42-45); and
- Fuel cell electrolysis process. During this process the elements of water-hydrogen and oxygen are separated by charging water with an electrical current. The charge breaks the chemical bond between the hydrogen and oxygen and splits the atomic components apart, creating charged particles called ions (Potter & Newell, 1992/1993:42-45).

Of the fuel cell water electrolyzers the three most common types are:

- Alkaline: which is further classified into the monopolar (tank-type cells) and bipolar (filter-press type cells). In the monopolar design, the cells in a stack are connected externally in a series/parallel arrangement, while in the bipolar design, a bipolar plate serves as a current collector for the anode on one side and for the cathode on the other (Srinivasen, 2006:402);
- Proton-exchange membrane regenerative fuel cells (PEMRFC): This compact design with a thin PEM electrolyte layer (Nafion) in an electrode structure permits the escape of evolved gases through the electrodes to the flow channels in the bipolar plate (Srinivasen, 2006:405); and
- Solid-oxide (SORFC): the same as the proton-exchange membranes but it works at a much higher temperature and uses a different electrolyte (Srinivasen, 2006:407).

This research concentrated on the proton exchange membrane (PEM) method for the generation of hydrogen. As seen in Table 3 the percentage of electricity used by a typical company is as high as 40%. Hydrogen is used to produce electricity by means of a fuel cell. The process of generating electricity by means of hydrogen is a more cost-effective way and this process can reduce the percentage of electricity that is used. The reason for using the PEM-method are:

- it is environmental friendly;
- it operates at a much lower temperature; and
- it makes use of less complicated and hazardous material but is limited to relatively low power levels.

A short description of the operation of a PEM fuel cell and regenerative PEM fuel cell is given next.

1.2 Operation of the fuel cell and regenerative fuel cell

Fuel cell mode:

The fuel cell uses oxygen and hydrogen as fuel to generate electricity with the only by-products being pure water and heat as shown in Figure 2, resulting in no air pollution. Hydrogen, the fuel, is introduced at the anode (negative) terminal of the FC and oxygen (the oxidant) is introduced at the cathode (positive) side of the cell. The fuel and oxidant undergo chemical reactions known as oxidation-reduction (redox) reaction at the electrodes, and electric current, water and heat are generated (Cook, 2001:17).

The hydrogen atoms (H) are oxidised (loss of electrons) under the effects of an electrocatalyst, such as Pt, which is coated onto the porous electrolyte. The positive ions (protons) that are released from the hydrogen bond form weak H-Pt bonds. The electrons released from the hydrogen atom travel through an external circuit in the form of electrical current and can be used to perform work. The electrolyte is non-conductive to electrons and only allows the H^+ -ions to pass through to the cathode side (Cook, 2001:19).

The H^+ -ions join up with H_2O molecules in the electrolyte to form hydronium ions (H_3O^+). These move through the electrolyte from the point of higher energy to a point of lower energy at the cathode. The removal of the H^+ from the catalyst site leaves the site free for the next hydrogen atom to react (Cook, 2001:18). The hydrogen not used in the reaction is either vented into the atmosphere or returned for storage or could be recycled and used again (Cook, 2001:19).

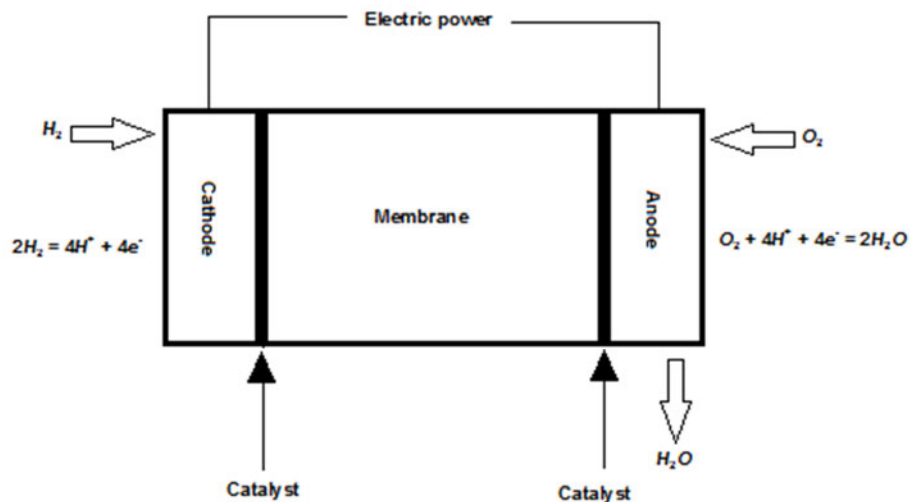


Figure 2 Fuel cell mode

At the cathode the oxygen from the air is introduced into the FC. An electrocatalyst normally in the form of a noble metal (i.e. Pt) allows the O_2 to break up and bond to the Pt sites in the form of weak O-Pt bonds. The oxygen atom accepts two electrons from the external circuit and two H^+ from the electrolyte, resulting in the formation of water and heat.

Upon the formation of the H_2O molecules the catalyst sites become free to accept more oxygen atoms and the process is repeated (Cook, 2001:19).

The chemical reactions are as follows:



As mentioned earlier a very useful fact about a fuel cell is that it is reversible. This means that if electric power is applied to the fuel cell, hydrogen and oxygen are produced if the fuel cell is supplied with pure water at the anode side.

Regenerative mode:

In the RFC, as shown in Figure 3, water is introduced at the anode electrode chamber. A potential is placed across the anode (positive) and cathode (negative) electrodes. This voltage usually must be greater than 1.23 V (equations will be given in Chapter 2) for the decomposition of H_2O to take place. At the anode a platinum (Pt) catalyst allows the H_2O molecule to split. The oxygen protons (O^+) and hydrogen protons (H^+) form weak O-Pt and H-Pt bonds at the respective catalyst sites. The electron (e^-) from the hydrogen atom is released into the external circuit. The O^+ does not lose its e^- to the external circuit but rather joins with another O^+ and its e^- to form O_2 gas (Proton Energy Systems, 2004).

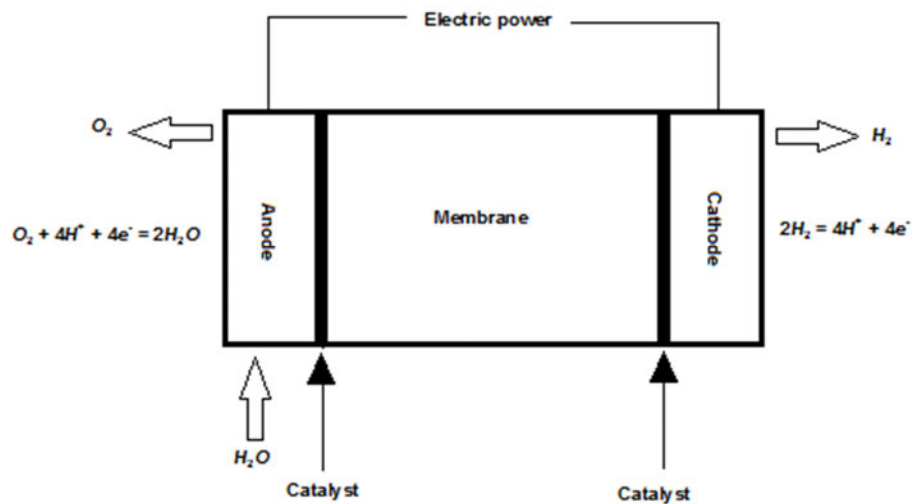
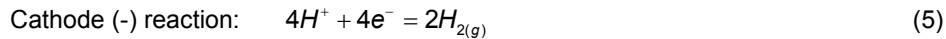
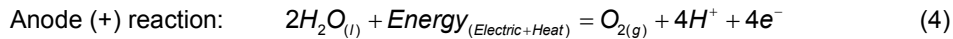


Figure 3 Regenerative fuel cell

The H^+ protons travel through the membrane from the anode side to the cathode side under the effects of the potential that was applied across the anode and cathode. The electrons

that were previously lost to the external circuit are attracted to the hydrogen at the weak H-Pt site and rejoins with them to form hydrogen atoms. Two of these atoms join to form an H_2 molecule. This effectively is the evolution of H_2 gas at the cathode electrode (Proton Energy Systems, 2004).

The chemical reactions in a PEM RFC, in electrolyser mode, can be summarized as follows:



When produced from renewable resources and technologies, such as hydro, solar, and wind energy, hydrogen becomes a renewable fuel without any carbon footprint.

This research concentrates on producing hydrogen at a controlled pressure from a reversible fuel cell.

1.3 Problem statement

When generating hydrogen from a regenerative fuel cell the following are problematic:

- Regulating the pressure of hydrogen in the fuel cell during the process,
- regulating the pressure of the generated hydrogen,
- the pressure at which the hydrogen must be stored,
- starting and stopping the production process, and
- optimisation of the abovementioned.

1.4 Delimitations

The research will not involve the construction of the membranes for the PEM RFC. However, the construction of the regenerative fuel cell was executed.

1.5 Importance of the research

The importance of the research is to find new, cleaner and better ways for the production of electrical energy.

Another important point of this research is to reduce the total fossil fuel emissions, mainly electricity, of South Africa.

1.6 Methodology

The design and development of the optimisation of the hydrogen pressure control in a regenerative proton exchange membrane fuel cell will be addressed in the following manner:

- There will be a theoretical side as well as practical side to this research.
- The first phase of the research is the theoretical part that will consist of in-depth research done on the PEM fuel cell as well as on the PEMRFC.
- The second phase will be the design and construction of the research.
- The third phase will be to perform experiments to get results for the research and to see where optimisation can take place. Following after the third phase will be the conclusions and recommendations based on the results that were found.

1.7 Overview of the report

In Chapter 1 a background is given on why to use fuel cells to produce electricity. The carbon footprint of South Africa is discussed. A table with some of the fuel cell types is given and some methods on the generation of hydrogen are discussed. The operation of the fuel cell as well as the regenerative fuel cell is mentioned and the reason for the importance of this research is given.

Chapter 2 discusses the components of the fuel cell and important calculations will be given. Two industrial regenerative fuel cell generators will be discussed.

In Chapter 3 the proposed flow diagram and block diagram of the hydrogen control system will be given and its operation will be discussed.

Chapter 4 will show the results from the experiments done for this research.

In Chapter 5 conclusions will be given and recommendations will be made.

1.8 Summary

In this chapter the reader was familiarised with the background of fuel cells and the regenerative fuel cells as well as some of the different hydrogen production processes. Carbon footprint was discussed and graphs and tables were given on South Africa's CO₂ emissions. The operation of both the FC and RFC was given. The problem was stated and delimitations were given. The importance of the research and the methodology that was used in this research were described and an overview of the report was given.

Chapter 2 Theoretical considerations

This chapter focuses on the literature studies of the FC and RFC required for this research. The components of a fuel cell stack will be discussed. It is important to know the role of each component to ensure that the stack is correctly assembled. Each RFC stack, in electrolyser mode, has its own specifications, for example the output pressure, number of membranes and the required potential across the anode and cathode. Equations will be given to calculate the minimum potential that must be used across the anode and cathode of one membrane in order for decomposing of water. The working of two commercial RFCs is discussed and a block diagram is given. The commercial RFCs are controlled by a PIC microcontroller. At the end of the chapter a summary is given.

2.1 A fuel cell

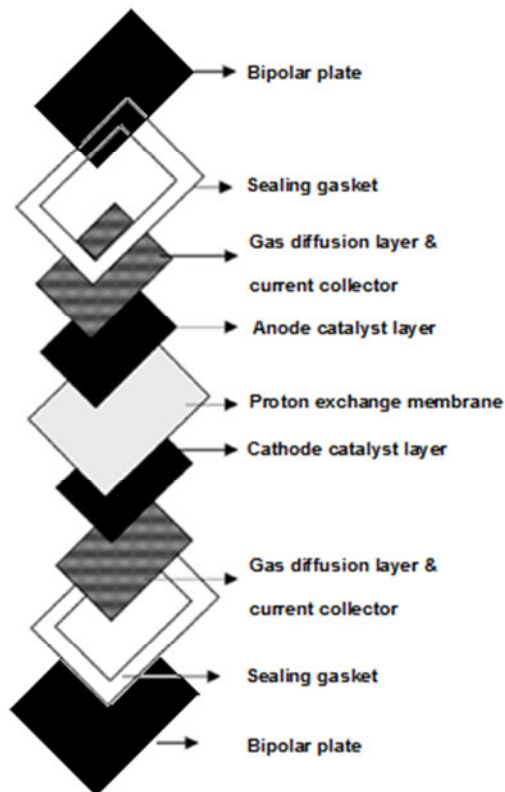


Figure 4 Components of a fuel cell

Components of a PEMFC as shown in Figure 4 on page 13 are:

- Proton exchange membrane
- Catalyst layers
- Gas diffusion layer (GDL)
- Sealing gaskets
- Bipolar plates (flow plates)

The bipolar plates are allocated after the sealing gasket. The proton exchange membrane and the catalyst layers are known as the membrane electrode assembly (MEA) and are thus usually a unit.

All of these components together are known as a single cell whereas a FC stack consists of a number of cells.

2.1.1 Membrane electrode assembly (MEA)

The MEA is the 'heart' of the fuel cell and consists of an anode catalyst layer, proton exchange membrane and a cathode catalyst layer as shown in Figure 5.

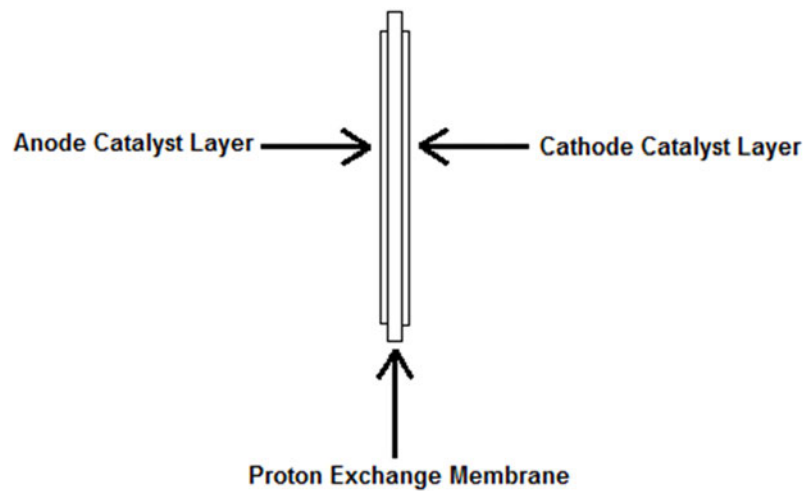


Figure 5 Schematic of a MEA

The anode and catalyst layers are not separate components but are manufactured onto the membrane.

2.1.2 Membrane

The material that is the most widely used in the manufacturing of MEAs is Nafion®, a sulphonated fluoro-polymer. The base material is a polymer called polyethylene with its structure shown in Figure 6. This basic polymer is modified by substituting fluorine for the hydrogen, creating polytetrafluoroethylene (or PTFE). The polytetrafluoroethylene (or PTFE) structure is shown in Figure 7. The final stage in making the electrolyte membrane is by sulphonating the PTFE by adding a side chain ending with sulphonic acid (HSO₃). The final structure is shown in Figure 8 (Larminie & Dicks, 2003:69).

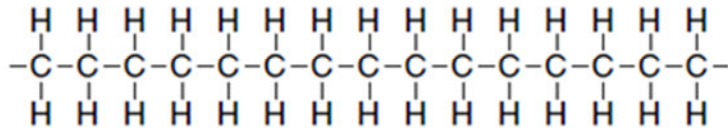


Figure 6 Polyethylene structure (Larminie & Dicks, 2003:70)

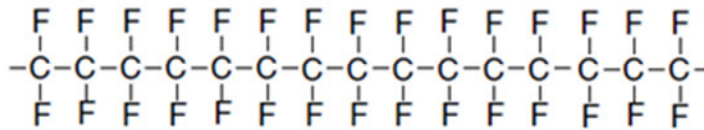


Figure 7 Polytetrafluoroethylene structure (Larminie & Dicks, 2003:70)

Larminie and Dicks (2003:71) give the following main features of Nafion®. They are:

- chemically highly resistant,
- strong (mechanically), and so can be made into very thin films, down to 50 µm,
- acidic
- can absorb large quantities of water,
- good proton conductors.

To provide satisfactory proton conductivity and fuel cell performance the membranes have to be hydrated.

It is possible to operate the fuel cell under dry conditions with the product water being the only source of hydration. This can simplify the whole system and offer cost savings (Vengatesan, Kim, Cho, Jeong, Ha, Oh, Hong & Lim, 2005:1).

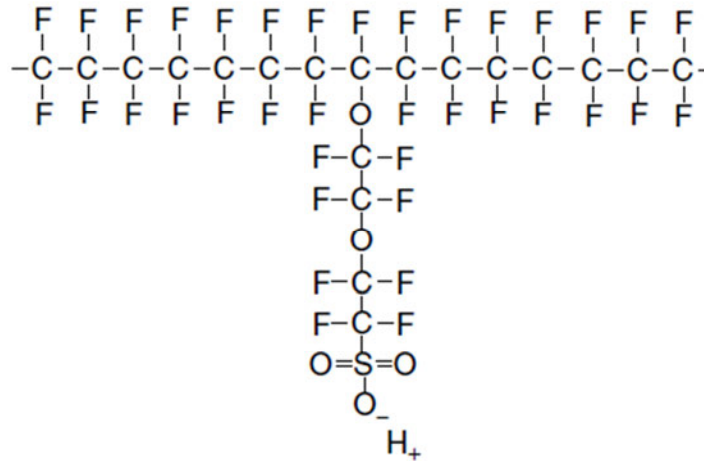


Figure 8 Structure of the electrolyte membrane (Larmine & Dicks, 2003:70)

Table 5 below shows some of the different types of Nafion® membranes as well as their thickness and application. The Nafion® datasheet can be viewed in Annexure B.

Table 5 Nafion® membrane types with their thickness and suited application (Swanepoel, 2005:28), (DuPont, 2011)

Nafion® Membrane Type	Thickness (microns)	Application
N-112	51	MEA for Reformate & H ₂ /Air FC
N-115	127	MEA for PEMWE/MEA for Reversible PEMFC
N-117	183	DMFC and MEA

Gentry (2004:3) found that the Nafion® N-117 has a thickness of 183 µm which is a considerable distance for the protons to travel across in the conduction phase and increase the mass transport resistance of the cell. The thinner membranes such as the N-112 decrease the problem of the membrane internal resistance and the associated mass transport problems. This is the reason why dedicated devices make use of the N-112 membrane (Refer to Table 5).

Lynntech Industries indicated that the Nafion® N-115 is the membrane to be used for a RFC. The reason for this is that its thickness allows a balance between the internal resistance and the strength of the membrane (Swanepoel, 2005).

Figure 9 shows a typical MEA using Nafion® N-115 which will be used in this research.

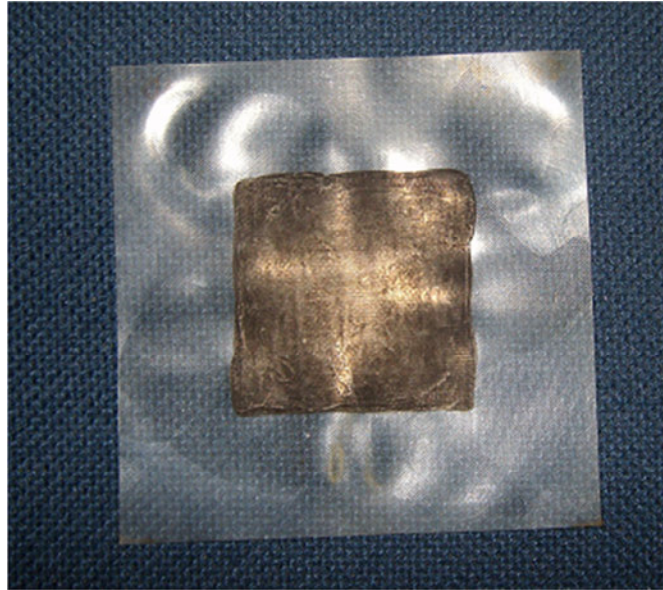


Figure 9 Nafion® N-115 membrane

2.1.3 Catalyst layers

The catalyst layers for a fuel cell and a regenerative fuel cell are different.

Fuel cell:

The catalyst layers on the anode and cathode are composite structures consisting of the proton conducting polymer (e.g., Nafion®) and a carbon supported metal catalyst. Depending on the catalyst loading levels, the thickness varies between 10 and 20 μm . Platinum is the best catalyst for the anode and the cathode. However, the fuel source also determines the type of anode catalyst and loading levels (Ralph & Hogarth, 2002).

The most popular fuel sources are pure hydrogen and methanol. The catalyst layer for both the anode and cathode side for pure hydrogen is platinum black (known as Pt black) and the loading level is 0.4 mg/cm^2 (Fuller, Gasteiger, Cleghorn, Ramani, Zhao, Nguyen, Haug, Bock Lamy & Ota, 2007:486).

As for methanol the anode and cathode catalyst is also Pt black but with a loading level of 0.3 mg/cm^2 . Pt black is a fine powder of platinum of which the colour is black (Nafion® Store Europe).

Regenerative fuel cell:

An anode electrode and cathode electrode are on each side of the co-polymer membrane. The porous electrode is only a layer of a fine compound painted or pressed onto the membrane. The fine compound is carbon cloth or Toray carbon fibre paper (Jiabin, Higier & Hongtan, 2006).

The electrodes are then doped with a noble metal catalyst such as platinum or platinum oxide. To make the electrodes more hydrophobic the back of the electrode layers are coated with a Teflon® type of compound. The electrodes allow the reactant and product gases to diffuse through to the catalyst sites (Hirshenhofer, Stauffer, Engleman & Klett, 2001:3-1).

The catalyst on the hydrogen side is platinum as Pt black and must be able to resist corrosion in the presence of water molecules. The catalyst on the oxygen side is more challenging. The Pt black is mixed with materials such as iridium, ruthenium, rhodium and titanium, or oxides such as iridium oxide and ruthenium oxide.

An important fact is that the catalyst must retain its structure in the presence of liquid water, and its constituent materials must not corrode or degrade in the presence of both water and oxygen.

2.1.4 Gas diffusion layer (GDL)

The gas diffusion layer (GDL) ensures the distribution of reactant gases over the entire membrane surface. 'Gas diffusion layer' is a slightly misleading name for this part of the electrode, as it does much more than diffuse the gas. It also forms an electrical connection between the carbon-supported catalyst and the bipolar plate, or other current collector. In addition, it carries the product water away from the electrolyte surface and also forms a protective layer over the very thin (typically ~30 m) layer of catalyst (Larminie & Dicks, 2003:73).

The GDL can be made from carbon paper or carbon cloth material. Carbon paper is chosen when it is required to make the cell in compact designs as thin as possible. Carbon cloths are thicker, and so will absorb a little more water, and also simplify mechanical assembly, since they will fill small gaps and irregularities in bipolar plate manufacture and assembly (Larminie & Dicks, 2003:73). Figure 10 shows how the gas diffusion layer works (Inoue, Matsukuma & Minemoto, 2005:3).

This information about the GDL applies only for the FC and not for the RFC as the RFC has no GDL. According to Lynntech (membrane manufacturers) the reasons for this are:

- A carbon based GDL on the O₂ side cannot be used during electrolysis because it will be consumed in the reaction,
- water management (in a FC the water must be away from the membrane and in the RFC the water must be in contact with the membrane).

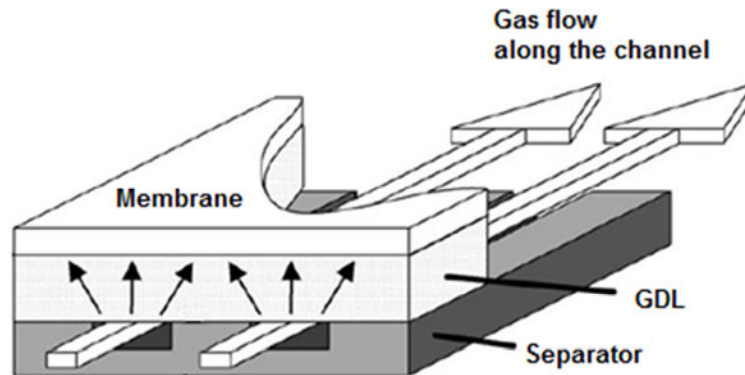


Figure 10 Explanation of the gas diffusion layer (Inoue et al. 2005:3)

2.1.5 Sealing gaskets

In a PEMFC and a RFC sealing is very important in order to separate the gas compartments from each other and to avoid mixing of hydrogen and oxygen respectively and also to prevent any reactant gas leakages out of the stack.

A mixture of hydrogen and oxygen of a certain ratio can explode. It is unlikely for an explosion to occur in a FC since the platinum catalyst stimulates the reaction of hydrogen and oxygen. But the heat of reaction of this catalytic combustion generates hot spots in the MEA which can destroy the membrane.

The resulting holes enhance mixing of the gases that finally may lead to an open fire. Typical sealing materials are fluorine caoutchouc, EPDM and silicon (Schulze, Knori, Schneider & Gulzow, 2004:223).

2.1.6 Bipolar plates (BPs)

Bipolar plates (BPs) are a key component of fuel cells with multifunctional character. The design of the bipolar plates is the same for the FC and RFC. They uniformly distribute fuel gas and air, conduct electrical current from cell to cell, remove heat from the active area, and prevent leakage of gases and coolant.

BPs also significantly contribute to the volume, weight and cost of PEM fuel cell stacks. Therefore, the plates must be of inexpensive, lightweight materials and must be easily manufactured. The main materials studied include graphite, coated and uncoated metals and graphite polymer composites (Hermann, Chaudhuri & Spagnol, 2005:1297).

Flow channels are machined, stamped or moulded (depending on the BP material) into the surface of both sides of a BP. These channels are used to distribute the gases over the membrane as well as to serve as path through which excess water can exit the cell. Different flow channels are shown in Figure 11.

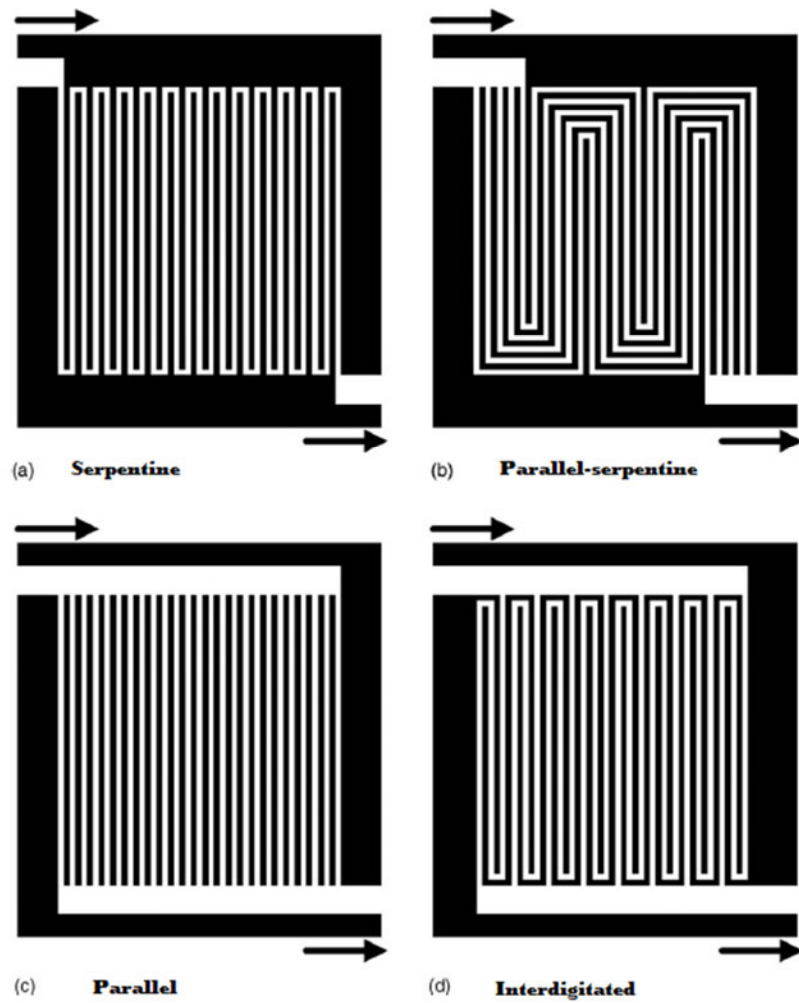


Figure 11 Designs of different flow fields (Hermann *et al.*, 2005:1297-1302)

According to Hermann *et al.* (2005:1298) the most commonly used BP material is graphite, both natural as well as synthetic, because it has excellent chemical stability to survive the fuel cell environment. It also has very low resistivity, resulting in the highest electrochemical power output. The flow fields that are being used in this study are a parallel-serpentine and are shown in Figure 12.

This specific plate has three continuous serpentine flow channels and was chosen to eliminate the problem of increased water removal (Swanepoel, 2005:53).

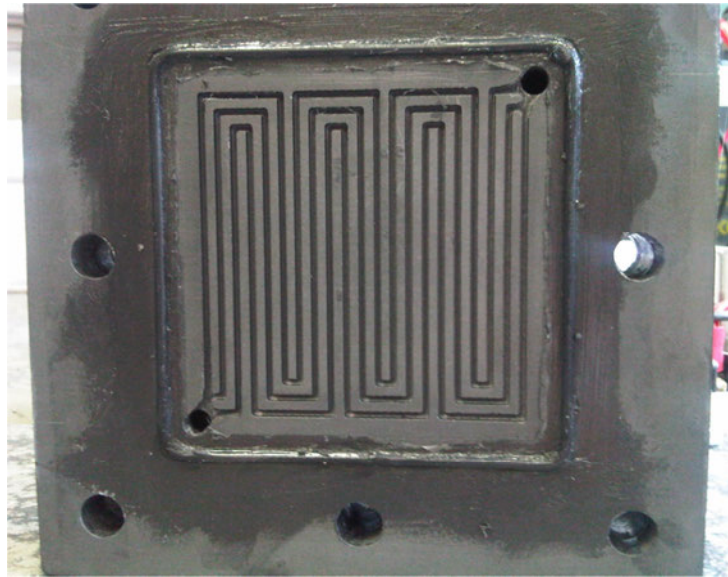


Figure 12 Flow field

2.2 Equations for potential across the anode and cathode of the RFC

The working of the RFC revolves around the chemical thermodynamics inside the cell. The reaction that takes place inside the RFC is:



Both of these reactions involve Gibbs' free energy or Gibbs' energy. Gibbs' free energy is a function of pressure and temperature and can be derived from the ideal law. If the chemical reactions occur under constant temperature and pressure the Gibbs' free energy can be calculated with the following equation (Lee, 2001):

$$\Delta G = \Delta G^0 + RT \ln \frac{P_M^m P_N^n}{P_A^a P_B^b} \quad (8)$$

Where:

$\Delta G \equiv$ Gibbs' free energy (kJ.mol⁻¹)

$\Delta G^0 \equiv$ Gibbs' standard free energy (kJ.mol⁻¹)

$R \equiv$ Universal gas constant (8.314 J.mol.K⁻¹)

$T \equiv$ Absolute temperature in Kelvin (K)

$P_M^m P_N^n \equiv$ Pressure of reactants in kPa

$P_A^a P_B^b \equiv$ Pressure of products in kPa

Equation 9 (Swanepoel, 2005) can be converted to electrochemical values using the work relationship

$$W = nFE \quad (9)$$

Where:

$W \equiv$ electrochemical work in J

$n \equiv$ amount of electrical charges transferred in the reaction

$F \equiv$ Faraday's constant, 96485 C.mol⁻¹

$E \equiv$ electrodes potential in V

According to Chen the change in Gibbs' energy is a negative electrochemical energy given off by the reaction and is given by the following equation (Swanepoel, 2005):

$$\Delta G^0 = -nFE^0 \quad (10)$$

Where:

$\Delta G^0 \equiv$ Gibbs' standard free energy (kJ.mol^{-1})

$n \equiv$ amount of electrical charges transferred in the reaction

$F \equiv$ Faraday's constant, 96485 C.mol^{-1}

$E^0 \equiv$ standard electrode potential in V

In the PEMRFC device two electrons are released into the external circuit by the H_2 molecule. Using the standard temperature and pressure (STP) the value of ΔG can be found on the list of thermodynamic properties of various substances found in Annexure A.

The voltage at which the RFC will start to decomposing the H_2O in the liquid form can be calculated using equation 11 (Swanepoel, 2005):

$$\begin{aligned} E^0 &= \frac{-\Delta G}{2F} \\ &= \frac{-(-237200)}{2(96485)} \\ &= 1.229\text{V} \end{aligned} \tag{11}$$

Where:

$E^0 \equiv$ Reversible voltage (V)

$\Delta G \equiv$ Gibbs' free energy (kJ.mol^{-1})

$F \equiv$ Faraday's constant, 96485 C.mol^{-1}

Due to the number of overvoltages' at each of the electrodes inside the RFC the current flow is opposed and will increase the voltage at which the RFC will start decomposing the water.

The decomposing voltage is increased to round about 1.5 V per cell. In order to calculate the potential across the anode and cathode for a RFC stack, the potential for one cell is multiplied by the number of cells in the stack (Swanepoel, 2005).

2.3 Commercial RFC hydrogen generators – how they work

Next two industrial regenerative fuel cell generators are discussed. The first one is the HOGEN® GC 300 and the second one is the Horizon hydrogen filling station.

2.3.1 HOGEN® GC 300



Figure 13 HOGEN® hydrogen generator

The HOGEN GC 300, as shown in Figure 13 above, is used in laboratories to generate hydrogen. The HOGEN® GC 300 ELECTROLYTE SYSTEM is a PEM solid electrolyte which is maintenance and caustic-free. It requires an electrical supply of 110 to 220 V AC, single phase, and a frequency of 50 or 60 Hz. In applications today the HOGEN® GC system is replacing cylinders where an ultra-high purity, medium pressure and electrolytic hydrogen gas supply makes processes safer, easier, more productive and more accurate. The typical application of the hydrogen generator is:

- Chromatograph carrier/ fuel gas
- Pharmaceutical hydrogenation
- Process instrument reactant gas
- Fuel cell development

The HOGEN® GC 300, used in this research, has an hydrogen purity of 99,999% at a rate of 300 ml/min and a delivery pressure that is adjustable up to 13.8 bar.

The HOGEN® GC 300 hydrogen generator uses a four cell stack. A DC voltage of 5.44 V and a current of 20 A (which was measured) is supplied to the stack, which can be seen in Figure 14. When the hydrogen generator is powered the filament of the Thermal Conductivity Detector (TCD) inside the generator must first be warmed up to a certain temperature before the hydrogen generation process can start. This startup time is approximately 7 minutes and 23 seconds.

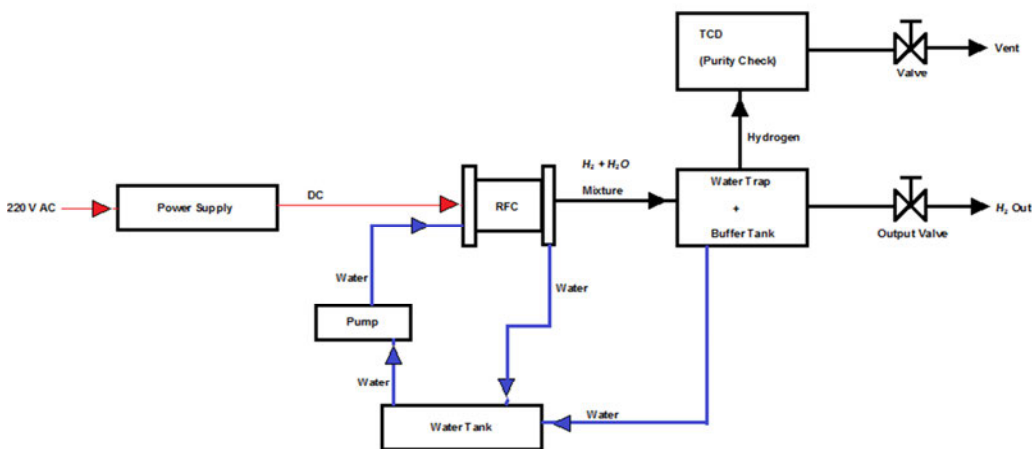


Figure 14 The HOGEN® GC 300 block diagram

The hydrogen that is generated by the RFC inside the HOGEN GC 300 is fed to the water trap that also serves as a buffer tank. The water inside the buffer tank is fed back to the water tank if it reaches a certain level. There are two hydrogen outputs in the system namely the hydrogen output and the TCD output (vent) as seen in Figure 14. The TCD is used to determine the purity of the hydrogen generated by the RFC. The TCD constantly tests the hydrogen in the buffer tank by venting the hydrogen every minute. Each time the TCD vents, new hydrogen enters in the TCD to be tested.

If impurities are detected in the hydrogen that is generated by the RFC the hydrogen output valve will close and the system will display an error code and will then power down. The hydrogen generator also uses a buffer tank to keep the output pressure of the hydrogen as constant as possible. The control of all the components of the hydrogen generator is done by a PIC microcontroller. Figure 14 shows the block diagram of the HOGEN® GC 300 hydrogen generator.

2.3.2 Horizon hydrogen filling station

This type of hydrogen generator is used for small scale use such as hobbies like the hydrogen cars and Figure 15 shows an example of a hydrogen car.



Figure 15 Picture of an example of a hydrogen car

Horizon fuel cell technologies such as the Hydrofill is a 'world-first' small-scale home hydrogen station that allows consumers or retailers/distributors to refill solid state canisters in a simple way by using only water and electricity as the input. By adding water, and plugging the Hydrofill system into an electrical wall-socket (220 V), or a solar panel, consumers can generate hydrogen and store it automatically in a solid form in the Hydrostik cartridges (known as refillable solid-state hydrogen cartridge) that is provided. Once the Hydrostik is full, the battery-like 'solid-state' Hydrostiks can be unplugged from the Hydrofill.

The Hydrostiks can then be used to supply hydrogen to a fuel cell in the hydrogen car. Figure 16 shows an example of a hydrogen filling station manufactured by Horizon Fuel Cell Technologies and Figure 17 shows the block diagram of the filling station. The small metal solid state Hydrostik, as shown in Figure 18, is inserted in the front of the filling station. It takes about 6 hours to fill one Hydrostik.

The method used to generate hydrogen by the Hydrofill is mostly the same as the method used by the HOGEN® hydrogen generator. The only difference is that the Hydrofill does not test the purity of the hydrogen produced. The basic operation of the filling station is as follows:

The water used by the fuel cell is not heated or cooled as the Hydrofill operates at room temperature. The water is pumped through the RFC by means of a water pump. The water

oxygen mixture that exits the RFC is fed back to the water tank. A voltage of 12V is applied across the RFC in order for the decomposition of the water to take place.



Figure 16 Horizon Hydrofill hydrogen filling station

The hydrogen is fed to a buffer tank which also serves as a water trap. The water trap traps the water that is formed in the hydrogen gas system. If the water inside the water trap reaches a certain level the valve opens and uses the pressure inside the system to feed the water into the water tank.

The hydrogen inside the hydrogen system is measured with two pressure sensors; the pressure inside the tank will be the same as the pressure in the hydrogen system. When the tank has reached its desired pressure the system will shut down. The operation of the Hydrofill system is controlled by a PIC microcontroller.

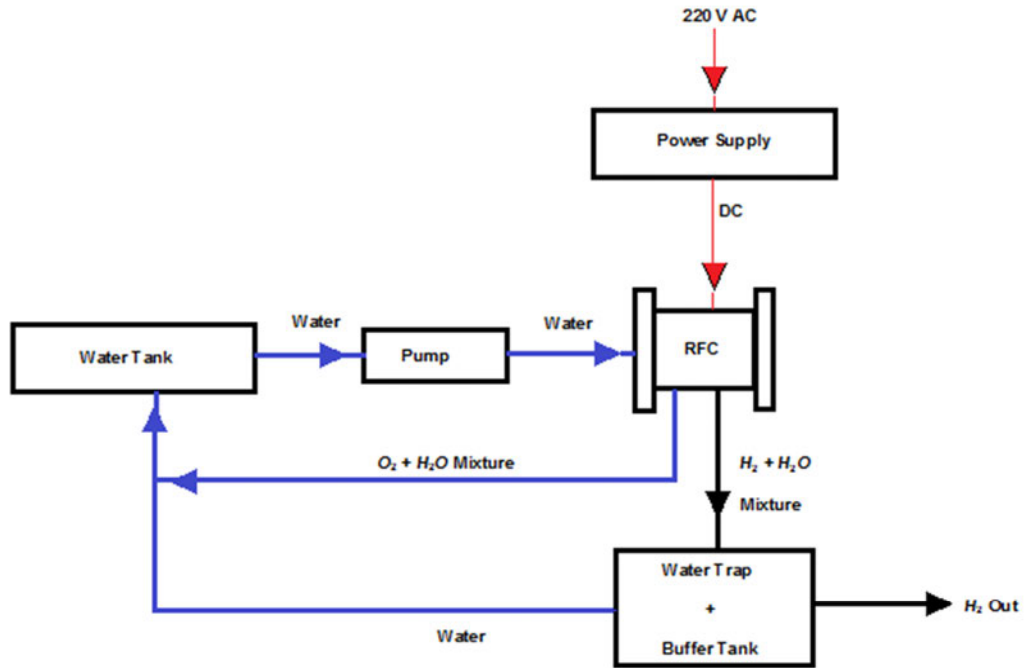


Figure 17 Block diagram of the Hydrofill hydrogen filling station



Figure 18 Example of the Hydrostik

2.4 Summary

In this chapter a more in-depth discussion was given on the components of a fuel cell and how they work. Equations are given to calculate the potential across the anode and cathode that must be used for each different case of fuel cell information. The working of two commercial RFC hydrogen generators was looked at and block diagrams were given. In Chapter 3, the proposed design of the control system will be given and discussed.

Chapter 3 Design of the control of a RFC

The previous chapter considered all the literature done for this research. This chapter focuses on the design of the control system that will be used for this research to optimise the hydrogen production. A flow diagram and block diagram of the control system will be given. The hydrogen control system and its design will be discussed in detail in this chapter and all the connections to the PLC will be given as well as the programs written for the PLC. Each component used in this control system and the part it plays in the system, will be discussed.

3.1 Control system flow diagram

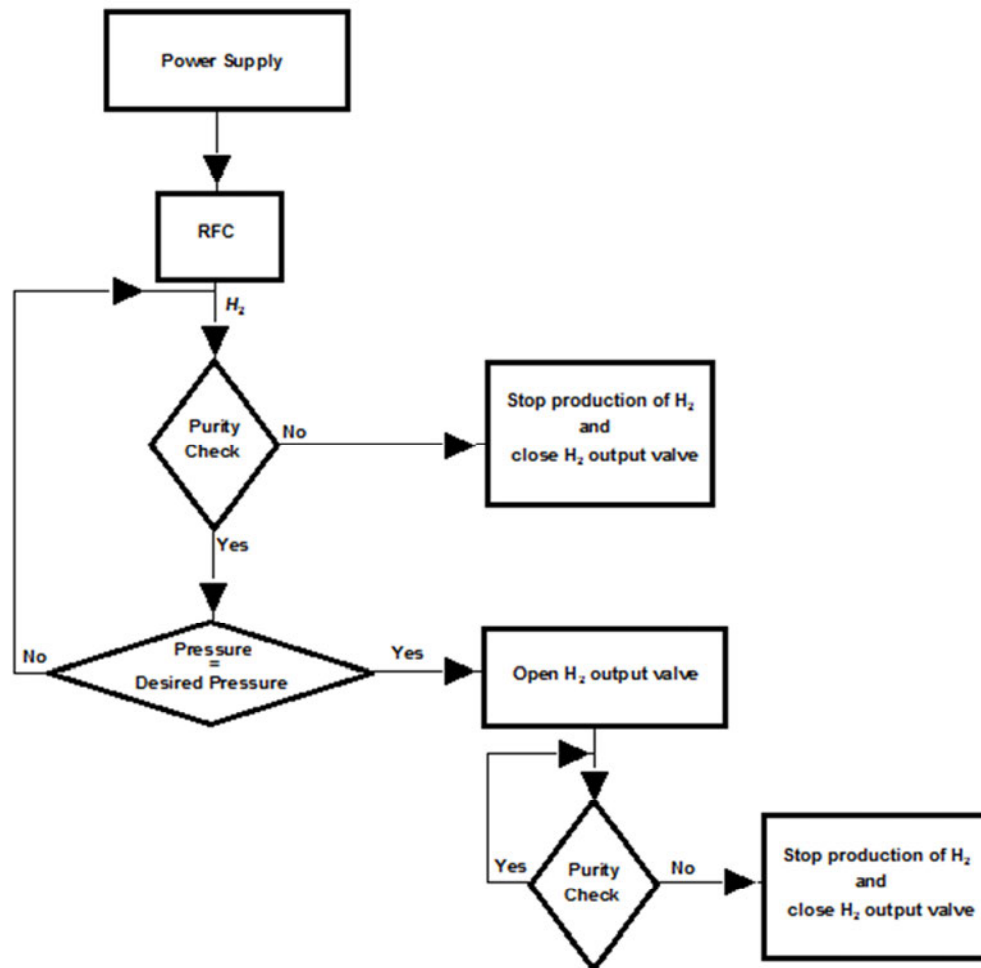


Figure 19 Flow diagram of the control system

The control system must control the following:

- Pressure
- Purity

A flow diagram is given in Figure 19 on page 30 to show how the control system will work.

3.2 Control system block diagram

Figure 20 shows the block diagram of the control system.

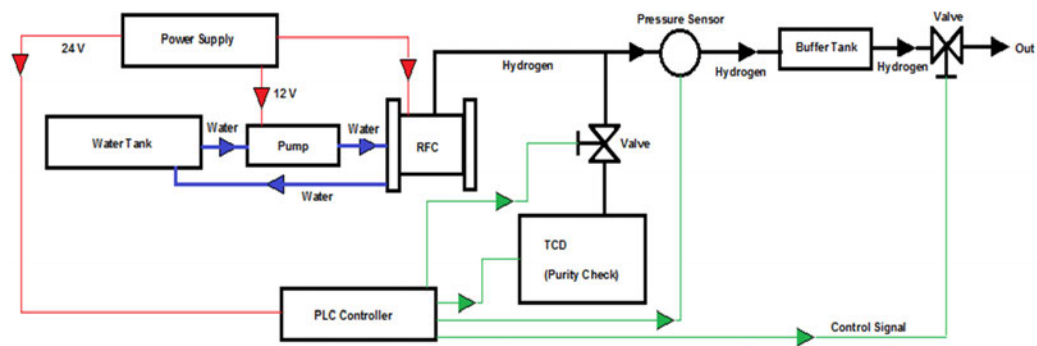


Figure 20 Block diagram of the control system

3.2.1 Control circuit

There are many types of controller that could be used for the control of the system. The most common types of controllers are:

- Computer (PC)
- PIC microcontroller
- PLC

The ABB PM554 PLC was chosen for this research. The ABB PM554 is an entry level PLC which means it was the cheapest and it was sufficient for the requirements of this research.

A PLC is used in this research and in Figure 21 the basic PLC system is given. The reason for using a PLC instead of a PIC microcontroller is that changes can be made much faster to the program, the PLC gives you a visual form where setting can be set instantly and that the

design of this research will be connected to an existing project at Vaal University of Technology which is already controlled by a PLC.

The basic operation of the PLC used is as follows:

The input devices in the system are connected to the PLC as they are monitored by the PLC. A sequence of instructions, a program, is entered into the memory of the PLC. The controller then, according to the program, monitors the inputs and outputs and carries out the control rule for which it has been programmed (Bolton, 2009:3).

The advantage that the PLC has is that the same basic controller can be used with a wide range of control systems. By making changes to the instructions or keying in different instructions the control system can be modified (Bolton, 2009:3).

The basic functional components of a typical PLC system are processor unit, memory, power supply unit, input/output interface section, communications interface and the programming device.

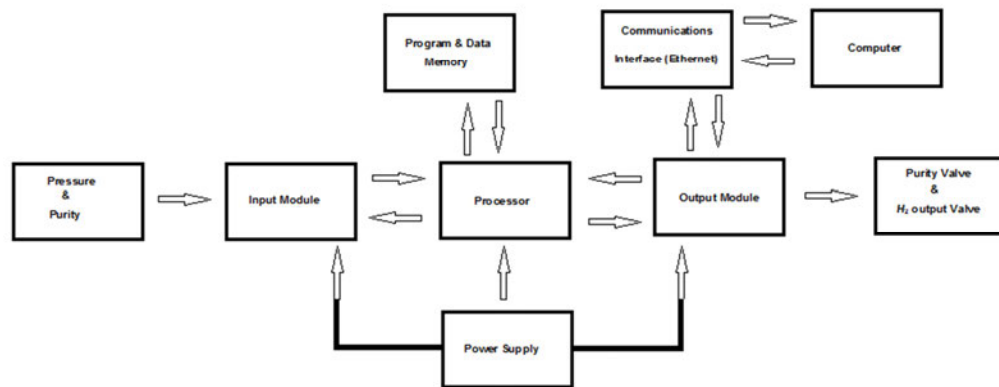


Figure 21 Basic PLC system of the research

3.2.2 Hydrogen control

Figure 20 on page 31 shows the block diagram for the design of the hydrogen control system that will be used to store the hydrogen generated by the RFC.

The design of the control system is based on the same principles as those of the HOGEN® GC 300 and the Horizon hydrogen filling station discussed in the previous chapter, except

that the control system of this research will be controlled by a PLC and not by a PIC microcontroller.

The control system was designed in such a way that the output pressure can be changed.

The PLC was used to control all the necessary aspects.

The PLC was programmed in codesys that enabled the user to see the data in a graphical format (hydrogen pressure, hydrogen pressure graphs, etc.). It also enabled the user to make changes to the pressure output and hydrogen purity check.

The system must be able to continuously test the hydrogen in order to make sure the hydrogen stored is pure. The graphical user interface of the system is shown in Figure 22.

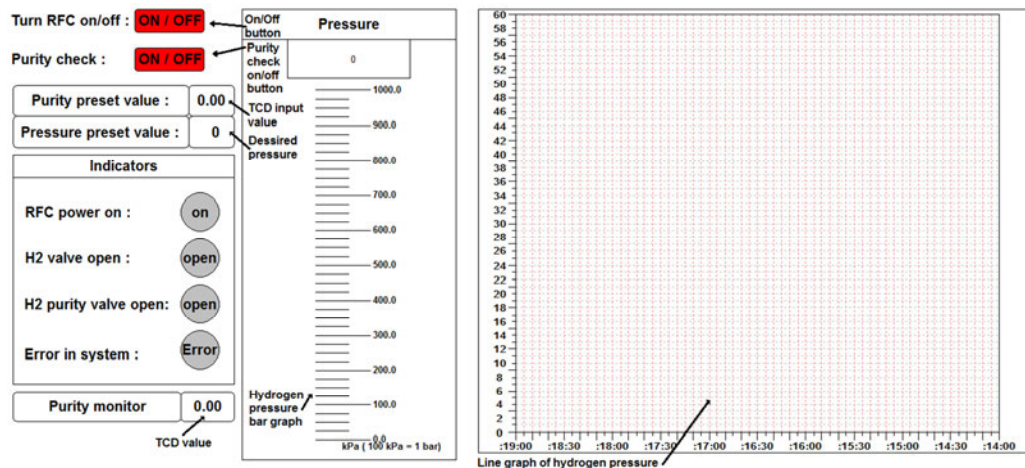


Figure 22 Graphical user interface

The system can be switched on or off by clicking on the 'turn RFC on/off button' when the system is on, the button color will change to green and red if it is off. When the output pressure must be changed the user can click on the pressure preset value.

When the user clicks on the pressure preset value a popup will appear on the screen seen in Figure 23 which enables one to enter the new output pressure.

The hydrogen pressure will be displayed on the graph as well as on the line graph. Initially when the system is switched on to produce hydrogen the hydrogen output valve will be closed that will result in an increase of pressure within the system.

When the system pressure is the same as the pressure preset value the hydrogen output valve will open. When the pressure is higher than the pressure preset value the power to the RFC will be switched off in order to stop producing hydrogen. However if pressure falls below the pressure preset value the power to the RFC will be restored to start producing hydrogen again.

When the purity of the hydrogen generated must be tested the purity check function must be enabled; that is done by clicking on the purity check button.

When the purity check function is enabled it will open the purity valve which enables the hydrogen to pass through the TCD which will produce an external voltage.

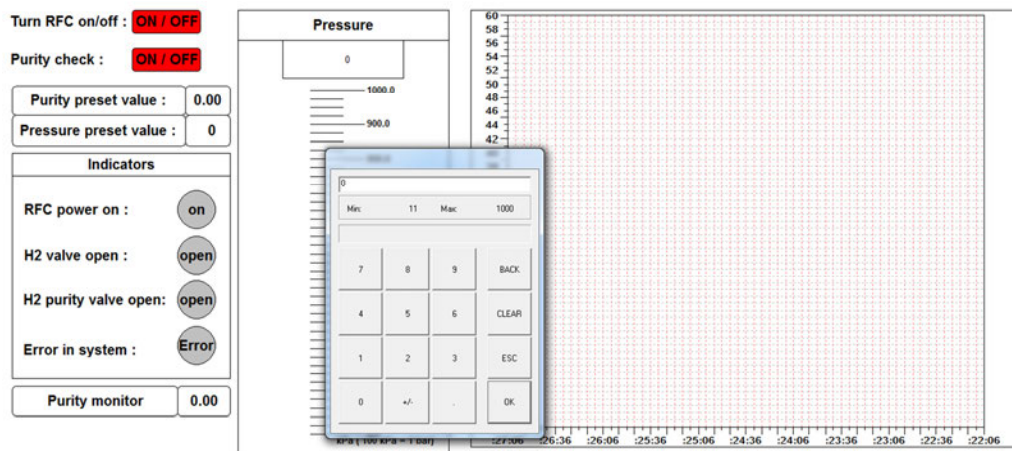


Figure 23 Changing the pressure preset value

The output voltage of the purity TCD will be converted to a value and will be displayed in the purity monitor number block. The TCD value must be entered in the purity preset value by clicking on the purity preset value. When clicked on the purity preset value a popup will also appear which enables the user to insert the desired value.

If the purity of the hydrogen changes the voltage output of the TCD will change as will the TCD value in the visual user interface.

When the TCD value is not the same as the purity preset value initially entered the system will generate an error that will close the output valve as well as switch off the system so that no more hydrogen will be produced. Figure 24 shows the readings and plots the graph when the system is on.

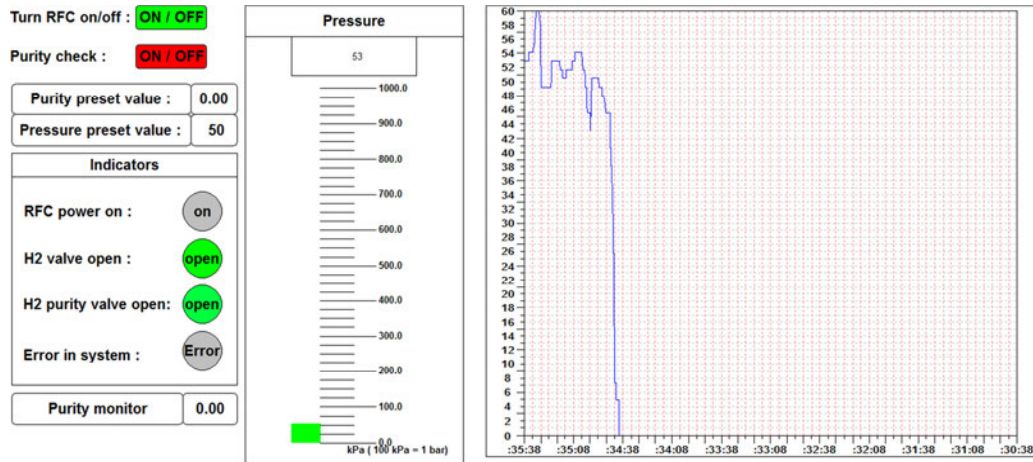


Figure 24 Graphical user interface when system is on

3.2.3 Pressure control

The PLC control system must be able to regulate the output hydrogen at certain pressures (from 0 kPa to 1000 kPa). This pressure can be adjusted through a computer that is connected to the PLC. The circuit diagram of the pressure control is shown in Figure 25 below.

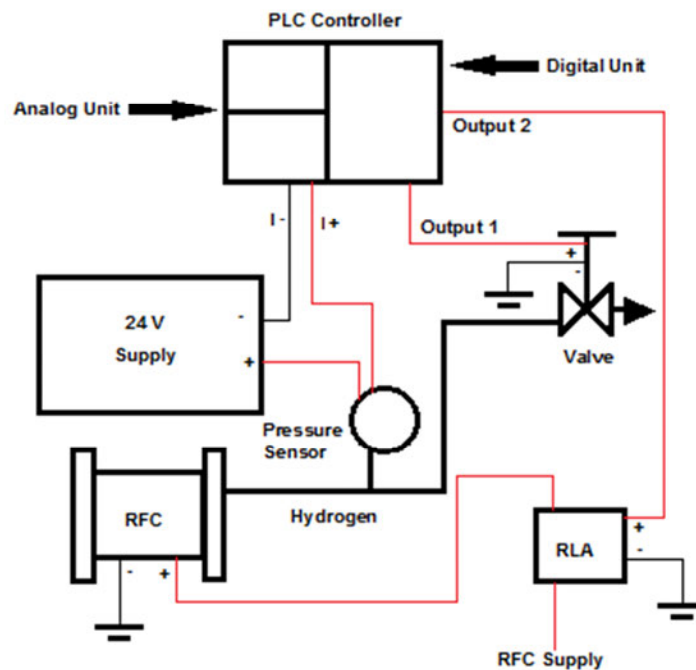


Figure 25 Pressure circuit

The pressure sensor used has a 4 - 20 mA output that is connected to the PLC analog in channel. The valve and relay is switched by the PLC digital output channels. A logic 1 represents + 24V and a logic 0 represents 0V.

The analog pressure signal is converted to a digital integer that can be between 1 (0 kPa) and 27648 (1000 kPa).

The Pressure_lin block performs a linear transformation on the initial integer value to convert it into the pressure, which is a real value. The real value is then converted to an integer pressure value which can be displayed on the visual form. The pressure value is then compared to a low and a high value seen in the Pressure_test block.

The program written in codesys can be seen in Figure 26 and works as follows:

The low value is defined as 0 and the high value can be changed in the visual program (desired pressure). If the pressure is higher than the high input (desired pressure) the output will be 1. If the pressure is lower than the high input (desired pressure) the output will be 0. If the output is 1 the SR latch will latch and the output of the SR latch will remain 1.

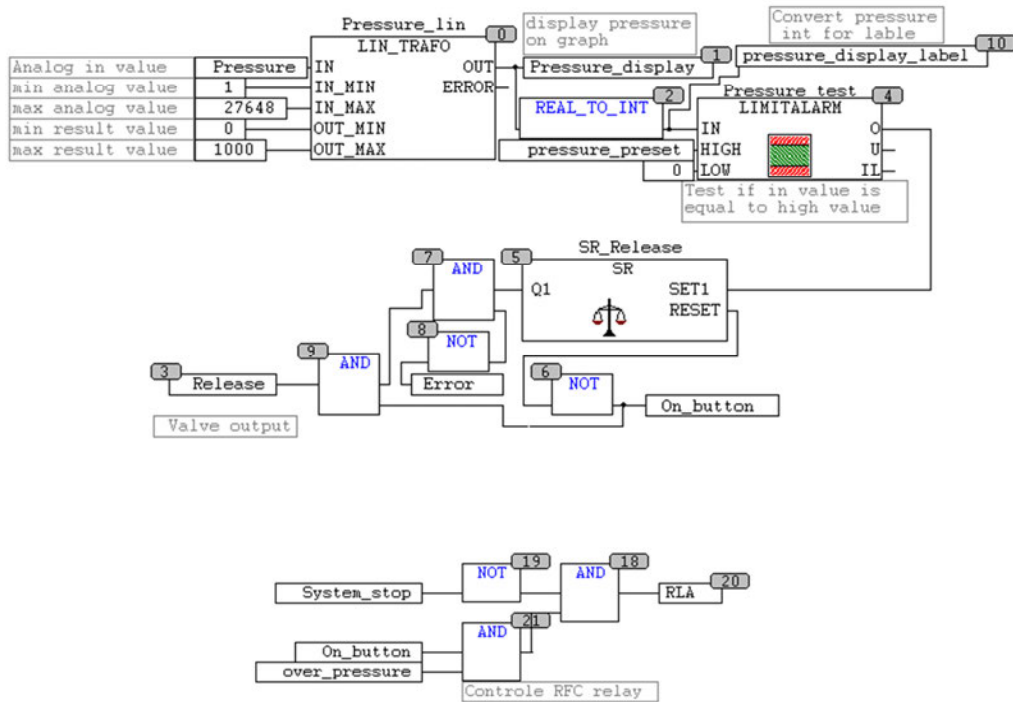


Figure 26 Codesys program for the pressure

The On_button variable and Error variable must have a value of 1 and 0 respectively otherwise the release output will be 0 even if the SR latch output is 1; this is done with gates 6, 7, 8 and 9.

3.2.4 Purity testing

As shown in Figure 20 on page 31 the purity of the produced hydrogen is measured by the Thermal Conductivity Detector (TCD). A photo of the TCD is shown in Figure 27. The operation is based on changes in the thermal conductivity of the gas that passes across the detector filament as components elute from the column.



Figure 27 Thermal conductivity detector

Heat is lost by the filament through the carrier gas to the cell wall of the detector. To maintain a constant filament the required current must be measured, a voltage that corresponds to the gas crossing the filament will be displayed on the TCD screen.

The TCD model used in this study is the TCD2 and is a stand-alone system.

The system consists of a detector which includes two separate filaments that are capable of independent or referenced operation, and a control module which incorporates the

electrometer and temperature controls.

The circuit diagram for the purity check is given in Figure 28 and the program written in codesys is given in Figure 29. The TCD has a 0 – 10 V output that is connected to the PLC analog channel to monitor the purity of the hydrogen produced by the RFC. The purity valve is connected to the digital output channel. If the error variable is true the system_stop variable will also be true which will switch off the relay shown in Figure 29.

The purity check program works as follows:

The analog signal from the TCD is converted to a digital real number. The real value of the TCD is converted to an integer number. The integer number is compared against the high and low value by the purity_check block. The high value is the purity preset value (defined in the visual form) plus one.

The low value is the purity preset value (defined in the visual form) minus one.

If the value of the TCD is higher than the high value the O output will be high. If the TCD value is lower than the low value the U output will be high. When the TCD value is between the high value and the low value, the IL output will be high.

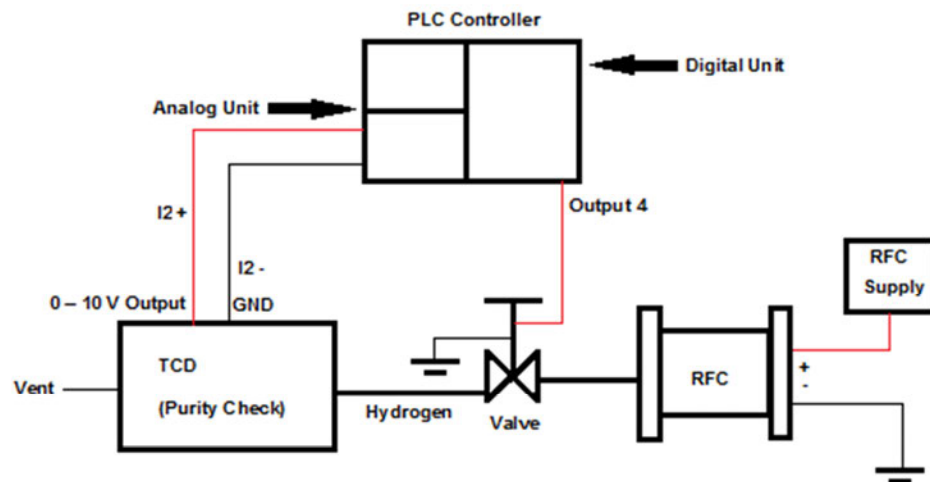


Figure 28 Purity check circuit

When the IL output is high the Error_timer block will monitor the input for one second. If the input stays high for one second, the output of the Error_timer will also be high. If the

Error_timer output is high and the purity_button variable is high, the error variable will be set and will signal an error state.

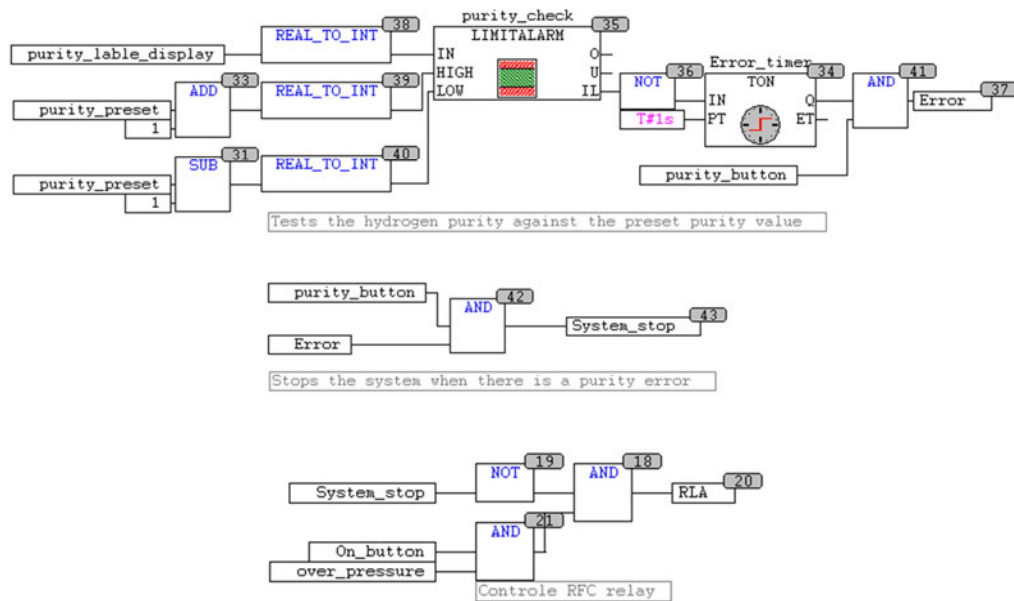


Figure 29 Purity check program written in codesys

The AND block will monitor if the purity_button and error variable are high. When this is the case, the System_stop variable will be high (done by AND gate 42). When the System_stop variable is high and the On_button and over_pressure variable is also high the RLA variable will be low and this will close the H_2 out valve.

3.3 Summary

A flow diagram and a block diagram of the control system were given. The control in the HOGEN® GC as well as the hydrogen filling station and the control system in this research operate on more or less the same manner. A PLC is used as the controller to control the operation of the control system used in this research to be able to store 99,999% pure hydrogen. The hydrogen control as well as the pressure control and the purity testing is also discussed.

Chapter 4 Results

The previous chapter presented the design of the control system in order to store the hydrogen. This chapter will show and discuss the experiments that have been done for the study. A small three membrane RFC stack was set up to perform a number of experiments regarding the pressure control inside the RFC in order to store the hydrogen being produced by the RFC.

4.1 Current versus pressure

Figure 30 shows the block diagram for the test setup. The first experiment that was done, as shown in Figure 31 and Table 6, was to see if the pressure inside the cathode chamber has any effect on the current drawn by the RFC. The current drawn by the RFC is directly proportional to the amount of hydrogen produced by the RFC (van Tonder, 2011:33-36). The voltage for this experiment was kept constant at 5.05 V which is the optimal voltage for the three cell RFC, and the temperature was 24.4°C (room temperature at that stage); these two factors can influence the results obtained. The current drawn by the RFC was measured by an Amp meter seen in Figure 30.

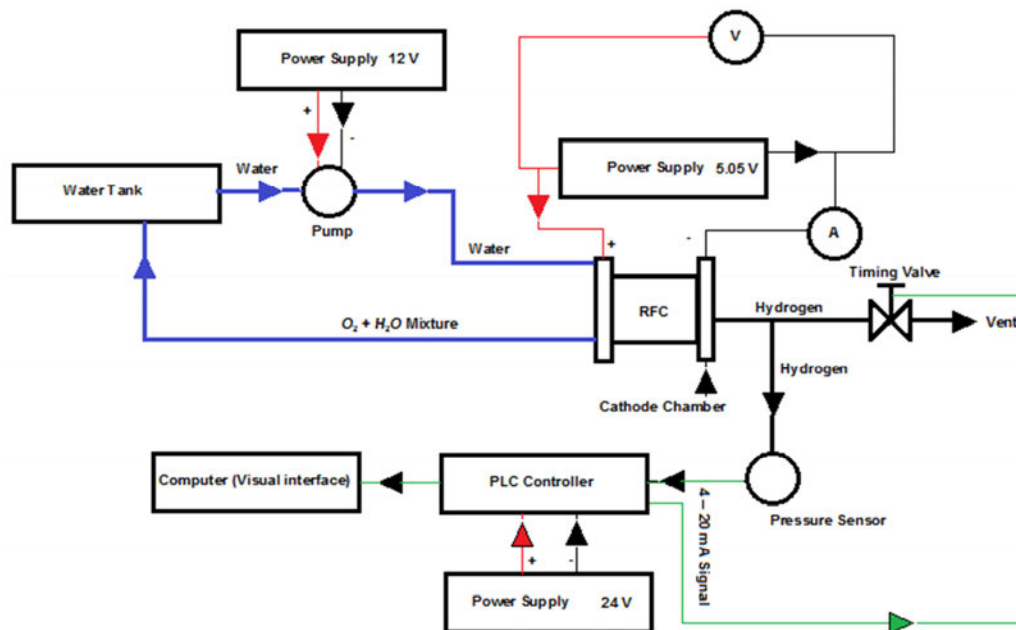


Figure 30 Test setup for current vs. pressure

Table 6 Results for current versus pressure

Temperature (°C)	Voltage (V)	Pressure (kPa)	Current (A)
24.4	5.05	10	5.1
24.4	5.05	20	5.1
24.4	5.05	30	5.1
24.4	5.05	40	5.1
24.4	5.05	50	5.1
24.4	5.05	60	5.1
24.4	5.05	70	5.1
24.4	5.05	80	5.1
24.4	5.05	90	5.1
24.4	5.05	100	5.1

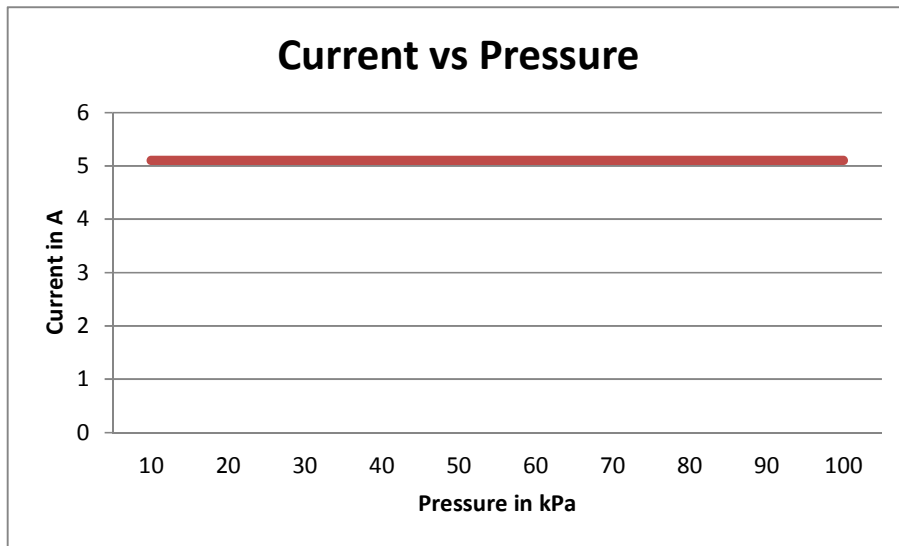


Figure 31 Current versus pressure

The hydrogen output of the RFC was connected to a pressure valve that can regulate the pressure inside the cathode chamber. The pressure inside the cathode chamber, measured by a pressure meter, was increased by 10 kPa increments then the measurements were taken. Table 6 above shows the results obtained.

It was noticed that the pressure inside the cathode chamber had no effect on the current drawn by the RFC. Thus there is no need to control the pressure inside the cathode chamber to increase the RFC's efficiency.

4.2 Time versus pressure

The hydrogen that is generated by the RFC must be stored in external tanks so that the stored hydrogen can be used again to produce electricity. The block diagram for the experimental setup is shown in Figure 32. The following experiment was done to determine whether it is best to let the hydrogen flow freely into the storage tanks or wait until it reaches a certain pressure threshold before releasing it into the external tank.

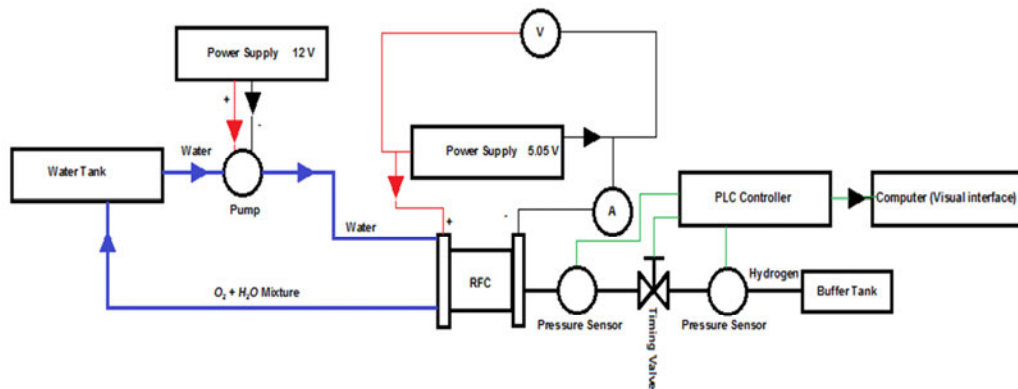


Figure 32 Test setup for time vs. pressure

The pressure threshold inside the RFC was made the same as the desired pressure of the hydrogen storage tank (being 15 kPa) and the pressure was released with the help of a pressure valve. The results are shown in Figure 33 and Table 7. It was timed how long it takes to fill the tank from 0 kPa to 5kPa, 10kPa and 15 kPa.

It was noticed that the time it took for the hydrogen bottle to fill to a pressure of 15kPa with a pressure valve was very close to the time it took to fill the hydrogen bottle without a pressure valve. The conclusion can be made that there is no need for a pressure valve to regulate the pressure because of the small difference in time.

A stop watch was used to monitor the time taken. The pressure inside the tank was measured with a pressure meter

Table 7 Results for time versus pressure with and without a pressure valve

Pressure (kPa)	Time (s) without pressure valve	Time (s) with pressure valve
0	0	0
5	10	8
10	21	21
15	33	34

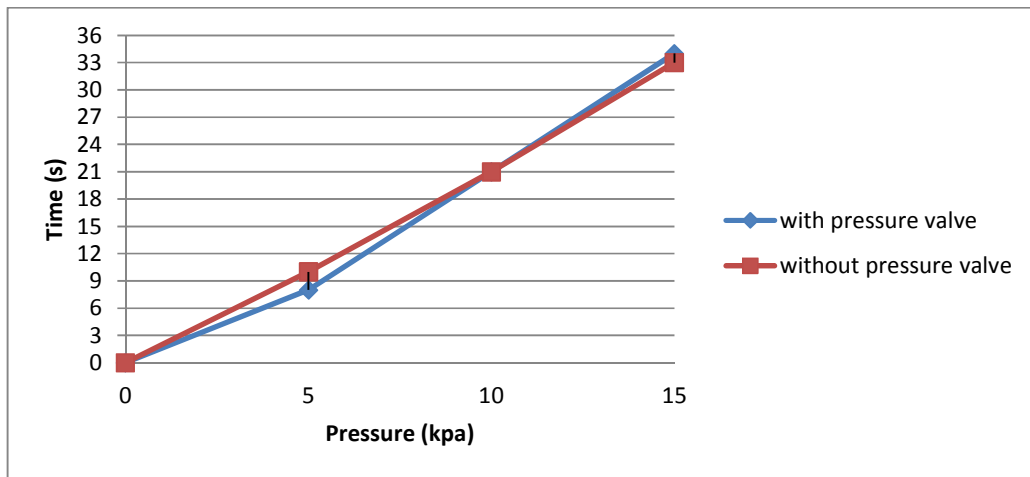


Figure 33 Time versus pressure

4.3 Effects of a hydrogen buffer tank

In the following experiment an H-200 PEMFC from Horizon was connected to the RFC in order to determine what role the hydrogen buffer tank would play in the hydrogen system. The temperature of the RFC was kept constant at 22°C and the supply voltage to the RFC was set to 5.05 V. A block diagram is given in Figure 34. Near the fuel exhaust outlet, impurities gradually accumulate, and are needing to be well managed.

The H-200 PEMFC will purge the hydrogen inside the FC on startup and during its operation in order to release the water, impurities and redundant air gas generated inside the fuel cell. The pressure meter inside the RFC pressure system was connected to the PLC in order to record the pressure over a certain time period. The system was set to regulate the pressure at 50 kPa. The overshoot seen in Figures 35 and 36 is due to the control system.

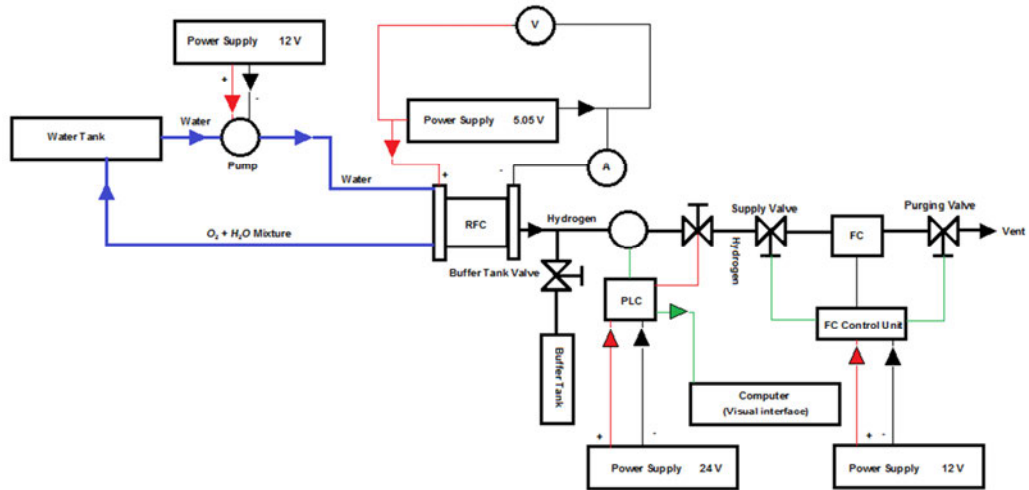


Figure 34 Test setup for the hydrogen buffer tank

The PLC was programmed to wait 5 seconds before it switched off the RFC power in order to stop generating hydrogen when the pressure inside the hydrogen system is more than the preset pressure.

As seen in Figure 35 each time the FC purges the pressure drops significantly; a pressure drop of 7 kPa was recorded each time the FC purged.

A buffer tank was connected into the system to try to keep the pressure more stable. The buffer tank in the hydrogen system can be seen in Figure 14 on page 25. The buffer tank has a capacity of 275 ml. The temperature and voltage supply to the RFC were the same as the test without the hydrogen buffer tank.

As in the first test the system was set to regulate the pressure at 50 kPa. The results can be seen in Figure 35. If the graph with the hydrogen buffer tank in Figure 36 is compared to the graph with no hydrogen buffer tank in Figure 35, it is seen that the graph with the hydrogen buffer tank is more stable. The pressure drop inside the RFC hydrogen system fell an average of 4 kPa when the FC purged.

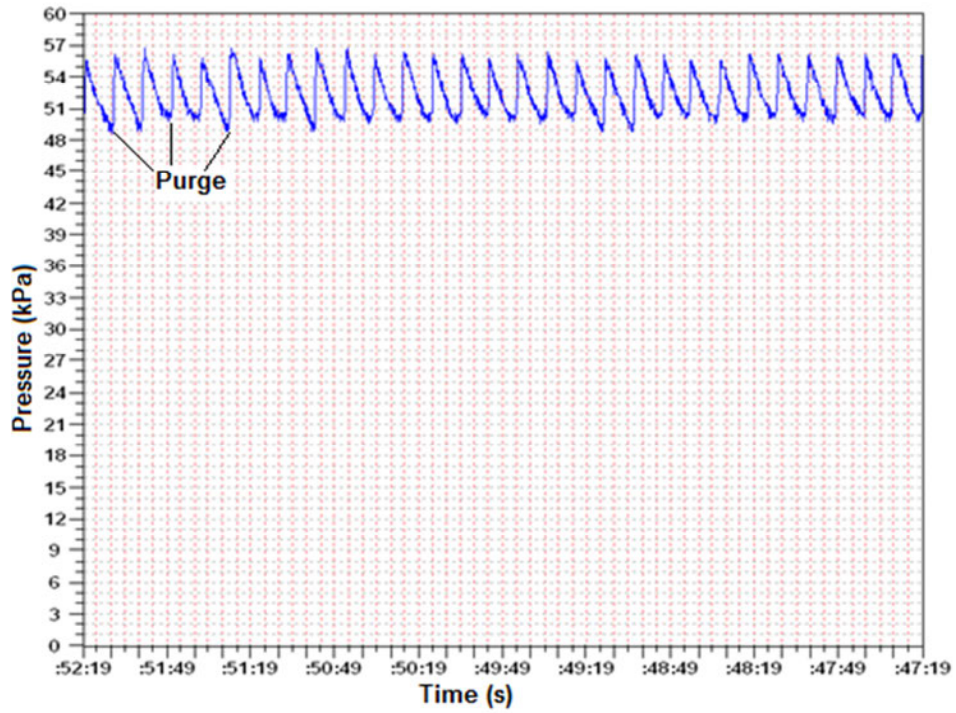


Figure 35 Hydrogen supply without a buffer tank

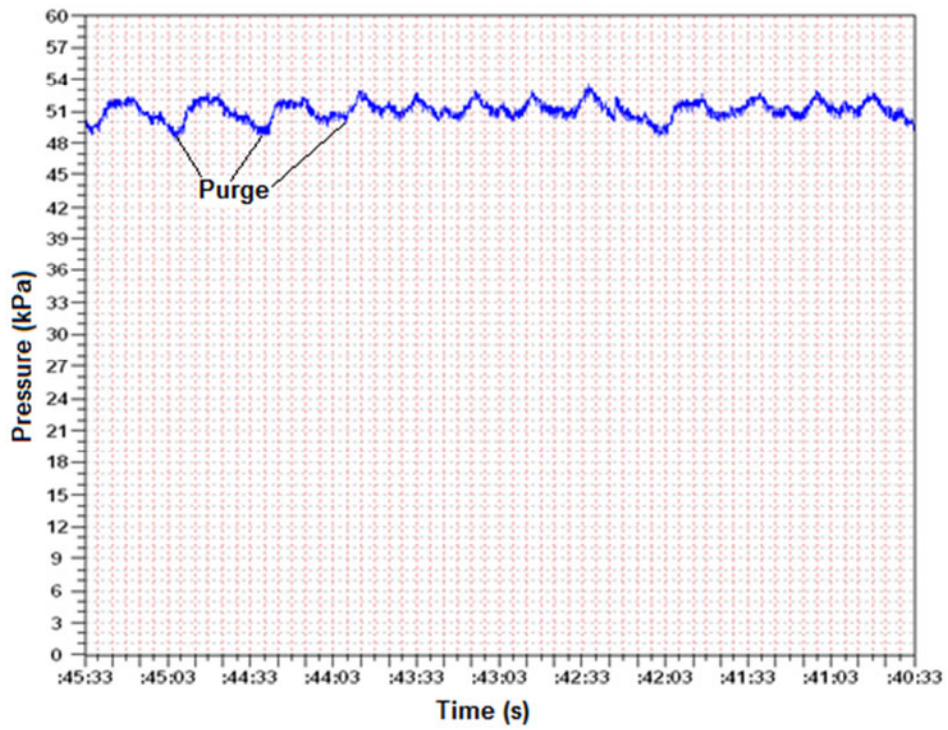


Figure 36 Hydrogen supply with a buffer tank

It was concluded that the hydrogen supply was more stable when a hydrogen buffer tank was used. It was noted that the HOGEN® GC hydrogen generator also uses a hydrogen buffer tank; this can be seen in Figure 14 on page 25.

4.4 Hydrogen purity

The following experiment was done to determine if the hydrogen generated by the regenerative PEM fuel cell is the required 99,999% pure. If the hydrogen is impure it cannot be stored for further use for it will damage the fuel cell membrane.

Samples were taken from the hydrogen generated by the RFC and also from the hydrogen purchased from Afrox. A small amount of hydrogen was extracted into a bag called a sample bomb and is shown in Figure 37. The tests were done in an external laboratory by Mr Nkazi Diakanua from the University of Witwatersrand on their calibrated Gas Chromatography system (GC) and the results are shown below. Figure 38 shows the result for the purchase hydrogen.

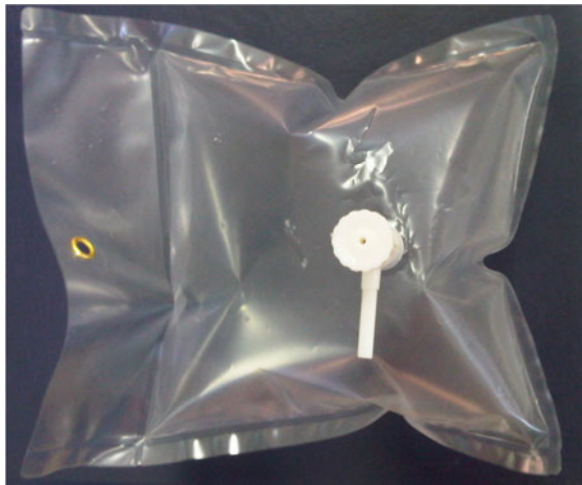


Figure 37 Picture of the sample bomb

Figure 39 shows results for the hydrogen generated by the regenerative PEM fuel cell.

Chromatography is the ability to separate components based upon their affinities for two separate phases known as stationary and mobile. The mobile phase is the carrier gas (usually helium) and the stationary phase is the chromatography column.

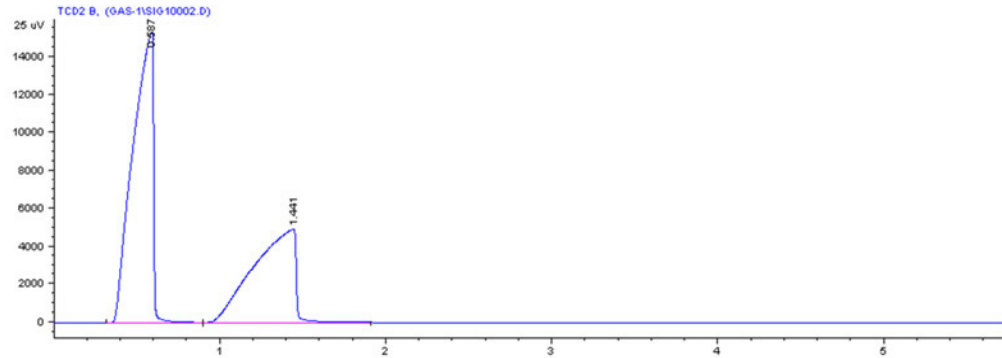


Figure 38 GC spectra of the purchased hydrogen

According to the GC spectra shown in Figures 38 and 39 there is no trace of any other gas. There are two peaks shown in the spectra; this is only because the GC uses two columns for the testing.

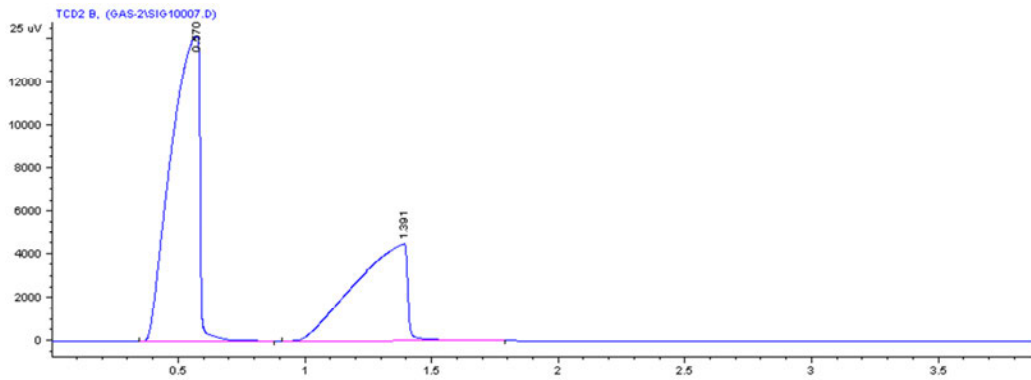


Figure 39 GC spectra of the generated hydrogen

The first peak of the purchased hydrogen was at 0.587 and the generated hydrogen was at 0.570 and the second peaks were at 1.441 and 1.391 respectively.

According to Mr Nkazi Diakanua from the University of Witwatersrand (mentioned earlier) the detector detected that the hydrogen generated by the RFC is 99,999% pure.

4.5 Controlling the output pressure

The following experiment was done to see if the hydrogen control system can regulate the hydrogen pressure at different pressures given to the control system by the PLC.

Figure 40 shows the block diagram for this experiment.

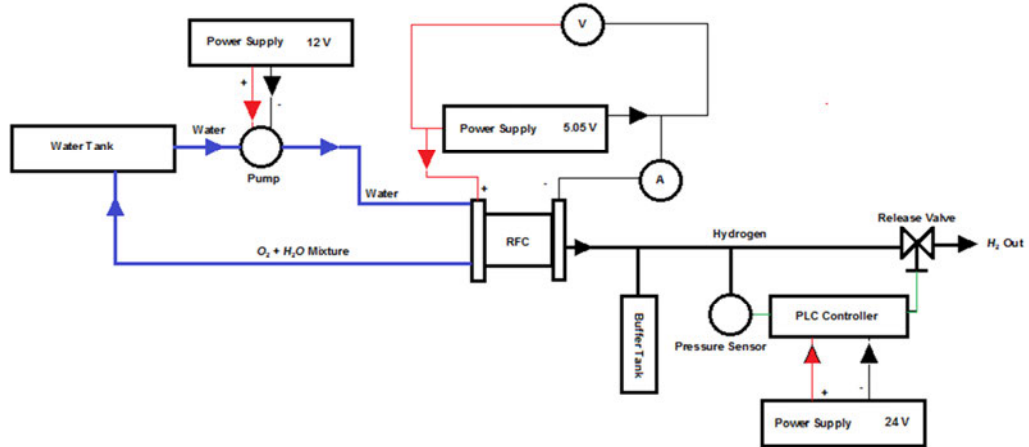


Figure 40 Test setup for different pressures

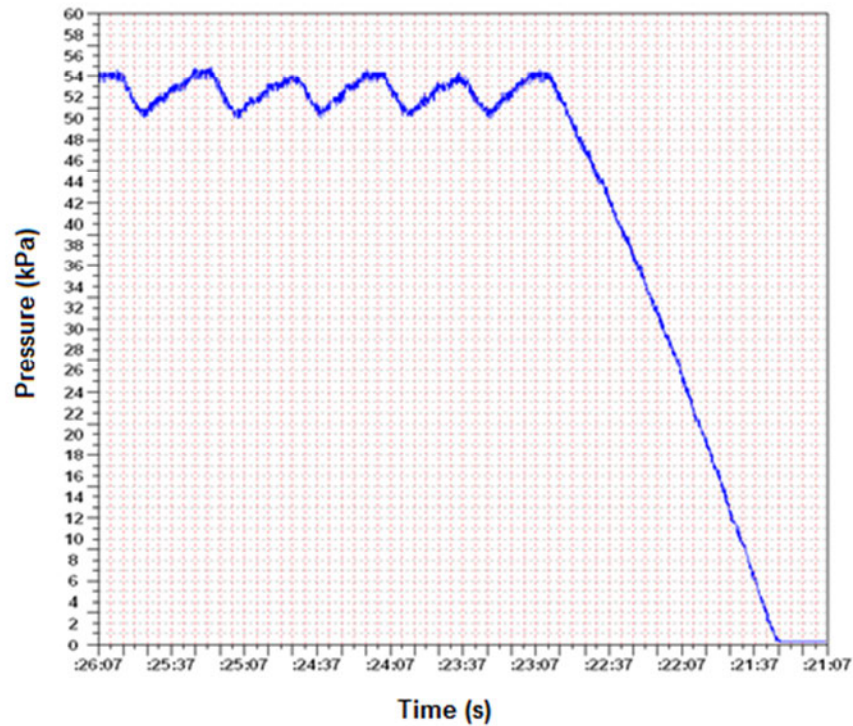


Figure 41 Pressure at 50 kPa

It is clearly seen in the three graphs that the system can supply different output pressures. The output pressure was only tested up to 150 kPa because the RFC used began to leak at higher pressures. There is a slight overshoot in the system pressure vs. the pressure preset valued the overshoot is 4 kPa.

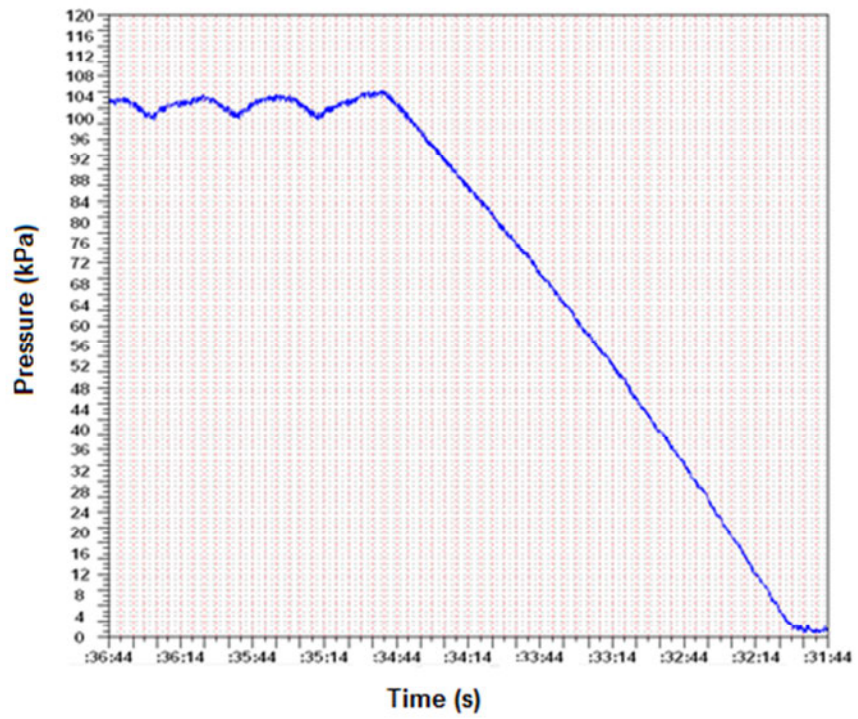


Figure 42 Pressure at 100 kPa

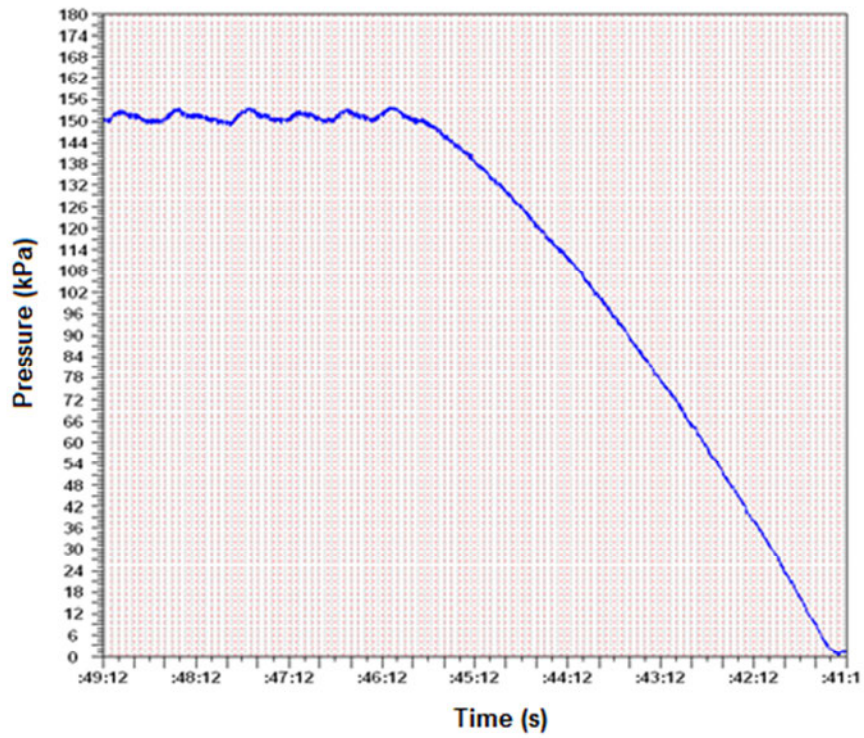


Figure 43 Pressure at 150 kPa

As discussed in Chapter 3 any pressure up to 1000 kPa can be programmed into the PLC.

The pressures 50, 100 and 150 kPa were used to get the results and were plotted versus time on graphs as shown in Figures 41, 42 and 43 above.

4.6 Summary

Block diagrams of the experiments were given and also discussed. The results that were found after completion of the experiments were plotted into graphs and were drawn up into tables and also discussed. It is also found that any pressure can be assigned to the hydrogen control system.

Chapter 5 Conclusions and recommendations

5.1 Introduction

In this chapter the research results on optimising the hydrogen pressure control in a regenerative proton exchange membrane fuel cell will be discussed. The conclusions are given. All of the intended objectives were achieved. Finally recommendations regarding future research and possible alternatives to the proposed design, are made.

5.2 Conclusions

In order to optimise the hydrogen pressure control for a regenerative proton exchange membrane fuel cell a three cell RFC was used. The three cell stack was chosen for practical reasons. It was decided to use the ABB PM554 PLC as the controller because it is an entry level PLC and sufficient for the requirements of this research. The reason for using a PLC instead of a PIC microcontroller is the ease with which program changes could be made. The PLC gives a visual interface on a computer on which the input data and output data could be displayed and captured. The components used in the control circuit included an analog pressure sensor, electrical valves and a thermal conductivity detector.

It was found if that the pressure in the cathode chamber of the RFC had no effect on the hydrogen production rate. The pressure inside the cathode chamber was increased to see if there is a change in current drawn by the RFC. The current drawn by the RFC is directly proportional to the flow rate of hydrogen produced. Thus, there is no need to control the pressure inside the cathode chamber of the RFC as it has no effect on the rate of the hydrogen production of the RFC.

The research showed that two methods could be used to supply hydrogen to a storage tank. The first method was to let the hydrogen flow freely into the tank. The second method is to wait for the pressure inside the cathode chamber of the RFC to reach the desired storage pressure and then release the hydrogen into the tank. The time it took for the two methods to fill the tank to the desired pressure were compared and the first method filled the tank significantly faster. Thus there is no reason to control the hydrogen produced to be stored in the tank.

Results showed that when a FC was connected to the RFC system the pressure of the output pressure was not stable. The output pressure of the RFC system was set at 50 kPa. The FC purges automatically on startup, as well as during its operation in order to release the water, impurities and redundant air gas generated inside the fuel cell. It was noted that a pressure drop of 7 kPa occurred each time the FC purged. A buffer tank was connected in the output line and a decrease in pressure drop to 4 kPa was obtained. Thus the buffer tank increased the stability of the hydrogen supply.

In order to ensure that the RFC produces 99.999% pure hydrogen a sample of the produced hydrogen was taken and analysed for purity at the University of Witwatersrand. The result showed that the hydrogen produced by the RFC is 99.999% pure. There is thus no need for hydrogen purification in the system.

One of the objectives was also to design an adjustable pressure control. The PLC was used again to be able to adjust the hydrogen pressure. The desired pressure could be set by using the computer that sends the information to the PLC controller. The results showed that the system regulated the output pressure exactly according to the desired set pressure. The results also showed that there was an overshoot of 4 kPa but this was due to the control method used.

5.3 Recommendations

From the research the following recommendations are given:

- The control system must be tested on a larger stack because the three cell RFC has limited maximum pressure and flow of hydrogen.
- The effects of a larger buffer tank can be investigated to stabilise the hydrogen output.
- Research into replacing the PLC with a PIC must be done because this will make the design much smaller and cheaper and could also decrease the reaction time of the system.
- The use of digital sensors such as the pressure sensor and the TCD can be investigated. The digital sensors can have an influence on the response of the system.
- The analogue meters used for the research could be replaced by digital readouts. For commercial applications and to make the product competitive research should be done on the cosmetic aspect of the RFC.

Bibliography

- ABBOTT, J. 2008. *What is a carbon footprint?*. Edinburgh: Midlothian, 3-23.
- AMOO, A.O. 2011. *Solar driven hydrogen generation for a fuel cell power plant*. Vanderbijlpark: Vaal University of Technology.
- BOLTON, W. 2009. *Programmable logic controllers*. 5th ed. London: Newnes : Oxford, 3-4.
- CHAMBERS, A. 2004. *Renewable energy in nontechnical language*. 1st ed. Tulsa, Oklahoma: PennWell Corporation, 176.
- CHO, E.A, JEON,U.S., HA, H.Y., HONG, S.A. & OH, I.H. 2004. Characteristics of composite bipolar plates for polymer electrolyte membrane fuel cell. *Journal of Power Sources*, 125:178-182.
- CHU, H., YE, C. and CHEN, F. 2003. Effects of porosity change of gas diffuser on performance of proton exchange membrane fuel cell. *Journal of Power Sources*, 123:1-9.
- COOK, B. 2001. An introduction to fuel cells and hydrogen technology. [Online]. Available at:<www.fuelcellstore.com/products/heliocentris/INTRO.pdf>. Accessed: 12/04/2010.
- DIAKANUA, N. (Diakanua.Nkazi@students.wits.ac.za). 2011. Vaal University / Wits contact form. [Email to:] Burger, M. (mburger9@gmail.com). 19 October 2011.
- DODDATHIMMAIAH, A.K. 2006. *The use of PEM unitized regenerative fuel cells in solar-hydrogen systems for remote area power supply*. School of Aerospace, Mechanical and Manufacturing: RMIT University.
- DUPONT. 2011. DuPont™ Nafion® PFSA Membranes. [Online]. Available at:<http://www.google.co.za/url?sa=t&rct=j&q=Nafion%2Bmembrane%2Bthickness&source=web&cd=6&ved=0CF4QFjAF&url=http%3A%2F%2Fwww.fuelcellmarkets.com%2Fcontent%2Fimages%2Farticles%2Fnae101.pdf&ei=Es-nTvqoDe7ImQW3862dCA&usg=AFQjCNEJ1PkPcWPwJOD24TaRUf4XS4X9_g>. Accessed: 19/10/2011.

FULLER, T., GASTEIGER, H.A., CLEGHORN, S. RAMANI, V., ZHAO, T., NGUYEN, T.V., HAUG, A., BOCK, C., LAMY, C. & OTA, K. 2007. *Proton exchange membrane fuel cells 7*. New Jersey: The Electrochemical Society, 11(1):486.

GENTRY, M. 2004. A review of some developments in regenerative fuel cells. [Online]. Available at: <www.lib.duke.edu/chem/chem110/papers/Micheal%20Gentry.htm>. Accessed: 5/04/2011.

GRIMES, C.A., VARGHESE, O.K., & RANJAN, S. 2008. *Light, water, hydrogen*. New York: Springer, 1-10.

HERMANN, A., CHAUDHURI, T. & SPAGNOL, P. 2005. Bipolar plates for PEM fuel cell: A review. *International Journal of Hydrogen Energy*, 30:1297-1302.

HERTWICH, E.G. & PETERS, G.P. 2009. Carbon footprint of nations: A global, trade-linked analysis. *Environmental Science & Technology*, 43(16):6414-6420.

HIRSCHENHOFER, J.H., STAUFFER, D.B., ENGLEMAN, R.R & KLETT, M.G. 2001. *Fuel cell handbook*. 6th ed. Morgantown: Federal Energy Technology Centre.

HOOGERS, G. 2003. *Fuel cell technology handbook*. Florida: CRC Press.

INOUE, G., MATSUKUMA, Y. & MINEMOTO, M. 2005. Effects of gas channel depth on current density distribution of polymer electrolyte fuel cell by numerical analysis including gas flow through gas diffusion layer. *Journal of Power Sources*, Article in press.

JIABIN, G.E., HIGIER, A. & HONGTAN, L. 2006. Effect of gas diffusion layer compression on PEM fuel cell performance. *Journal of Power Sources*, 159(2):922-927.

JORDAN, L.R., SHUKLA, A.K., BEHRING, T., AVERY, N.R., MUDDLE, B.C. & FORSYTH, M. 2000. Diffusion layer parameters influencing optimal fuel cell performance. *Journal of Power Sources*, 86:250-254.

LARMINE, J. & DICKS, A. 2003. *Fuel cell systems explained*. Sussex. John Wiley and Sons.

LEE, C. 2001. Enthalpy of formation and enthalpy of combustion. [Online]. Available at: <web.me.unr.edu/me372/Spring2001/Enthalpy.pdf>. Accessed: 10/06/2010.

LYNNTECH INDUSTRIES. 2011. Membrane and electrode assemblies. [Online]. Available at: <<http://www.lynntech.com/energy.htm>>. Accessed: 15/09/2010.

MURPHY, O., CISAR, A. & CLARK, E. 1998. Low-cost lightweight high power density PEM fuel cell stack. *Electrochimica Acta*, 43(24):3829-3840.

Nafion® Store Europe. 2011. [Online]. Available at: <<http://www.nafionstore.de/N117-25cm-Catalyst-Coated-Membrane>>. Accessed: 16/11/2011.

O'HAYRE, R., BRAITHWAITE, D., HERMAN, W., LEE, S., FABIAN, T., CHA, S., SAITO, Y. & PRINZ, F.B. 2003. Development of portable fuel cell arrays with printed-circuit technology. *Journal of Power Sources*, 124(2):459-472.

POTTER, A. & NEWELL, M. 12/1992-1/1993. *Hydrogen basics*, 32:42-45.

PRASANNA, M., HA, H.Y., CHO, E.A., HONG, S.A. & OH, I.H. 2004. Influences of cathode gas diffusion media on the performance of PEMFCs. *Journal of Power Sources*, 131:147-154.

PROTON ENERGY SYSTEMS. 2004. How PEM fuel cells work. Available at: <www.protonenergy.com/index.php/html/gasproducts/technology/howpemworks/>. Accessed: 12/04/2010.

RABIH, S., RALLIERES, O., TURPIN, C. & ASTIER, S. *Experimental study of a PEM reversible fuel cell*. University of Toulouse-Laboratory LAPLACE, France. Available at: <<http://www.icrepq.com/icrepq-08/268-rabih.pdf>>. Accessed 18/03/2010.

RALPH, T.R. & HOGARTH, M.P. 2002. *Platinum Metals Review*, 46(3):117.

SCHMITZ, A., TRANITZ, M., WAGNER, S., HAHN, R. & HEBLING, C. 2003. Planar self-breathing fuel cells. *Journal of Power Sources*, 118:162-171.

SCHULZE, M., KNORI, T., SCHNEIDER, A. & GULZOW, E. 2004. Degradation of sealings for PEFC test cells during fuel cell operation. *Journal of Power Sources*, 127:222-229.

SRINIVASEN, S. 2006. *Fuel cells from fundamental to applications*. New York: Springer, 402-407.

SWANEPOEL, F.K. 2005. *Design of a unitised regenerative fuel cell system for remote telecommunications applications*, 28-29, 53, 73-75.

United Nations Statistics Division. 2011. *Millennium development goals indicators*. Available at: <<http://mdgs.un.org/unsd/mdg/SeriesDetail.aspx?srid=749&crd=>>>. Accessed: 25/10/2011.

VAN TONDER, P.J.M. 2011. *Optimisation of water, temperature and voltage management on a regenerative fuel cell*. Vanderbijlpark: Vaal University of Technology, 12, 33-36.

VENGATESAN, S., KIM, H.J., CHO, E.A., JEONG, S.U., HA, H. Y., OH, I.H., HONG, S.A. & LIM, T.H. Operation of a proton exchange membrane fuel cell under non-humidified conditions using thin cast Nafion membranes with different gas diffusion media. *Journal of Power Sources*, Article in press.

WEIDNER, J.W., SETHURAMAN, V.A. & ZEE, J.W. 2003. Engineering a membrane electrode assembly. *The Electrochemical Society Interface*, 40.

WIND, J., SPÄH, R., KAISER, W. & BÖHM, G. 2002. Metallic bipolar plates for PEM fuel cells. *Journal of Power Sources*, 105(2):256-260.

YOON, Y.G., LEE, W.Y., PARK, G.G., YANG, T.H. & KIM, C.S. Effects of channel and rib widths of flow field plates on the performances of a PEMFC. *International Journal of Hydrogen Energy*, 30:1363-1366.

ZÜTTEL, A., BORGSCHULTE, A. & SCHLAPBACH, L. 2008. *Hydrogen as a future energy carrier*. Weinheim: Wiley-VCH, 60.

ANNEXURE A Standard electrode potentials

Substance (form)	Enthalpy ΔH (kJ.mol ⁻¹)	Gibbs ΔG (kJ.mol ⁻¹)	Entropy (J.K ⁻¹)	Specific heat C_p (J.K ⁻¹)	Volume V(cm ³)
Al (s)	0	0	28.33	24.35	9.99
Al ₂ SiO ₅ (kyanite)	-2594.29	-2443.88	83.81	121.71	44.09
Al ₂ SiO ₅ (andalusite)	-2590.27	-2442.66	93.22	122.72	51.53
Al ₂ SiO ₅ (sillimanite)	-2587.76	-2440.99	96.11	124.52	49.90
Ar (g)	0	0	154.84	20.79	...
C (graphite)	0	0	5.74	8.53	5.30
C (diamond)	1.895	2.900	2.38	6.11	3.42
CH ₄ (g)	-74.81	-50.72	186.26	35.31	...
C ₂ H ₆ (g)	-84.68	-32.82	229.60	52.63	...
C ₃ H ₈ (g)	-103.85	-23.49	269.91	73.5	...
C ₂ H ₅ OH (l)	-277.69	-174.78	160.7	111.46	58.4
C ₆ H ₁₂ O ₆ (glucose)	-1268	-910	212	115	...
CO (g)	-110.53	-137.17	197.67	29.14	...
CO ₂ (g)	-393.51	-394.36	213.74	37.11	...
H ₂ CO ₃ (aq)	-699.65	-623.08	187.4
HCO ₃ ⁻ (aq)	-691.99	-586.77	91.2
Ca ²⁺ (aq)	-542.83	-553.58	-53.1
CaCO ₃ (calcite)	-1206.9	-1128.8	92.9	81.88	36.93
CaCO ₃ (aragonite)	-1207.1	-1127.8	88.7	81.25	34.15
CaCl ₂ (s)	-795.8	-748.1	104.6	72.59	51.6
Cl ₂ (g)	0	0	223.07	33.91	...
Cl ⁻ (aq)	-167.16	-131.23	56.5	-136.4	17.3
Cu (s)	0	0	33.150	24.44	7.12
Fe (s)	0	0	27.28	25.10	7.11
H ₂ (g)	0	0	130.68	28.82	...
H (g)	217.97	203.25	114.71	20.78	...
H ⁺ (aq)	0	0	0	0	...
H ₂ O (l)	-285.83	-237.2	69.91	75.29	18.068
H ₂ O (g)	-241.82	-228.2	188.83	33.58	...
He (g)	0	0	126.15	20.79	...
Hg (l)	0	0	76.02	27.98	14.81
N ₂ (g)	0	0	191.61	29.12	...
NH ₃ (g)	-46.11	-16.45	192.45	35.06	...
Na ⁺ (aq)	-240.12	-261.91	59.0	46.4	-1.2
NaCl (s)	-411.15	-384.14	72.13	50.50	27.01
NaAlSi ₃ O ₈ (albite)	-3935.1	-3711.5	207.40	205.10	100.07
NaAlSi ₂ O ₆ (jadeite)	-3030.9	-2852.1	133.5	160.0	60.40
Ne (g)	0	0	146.33	20.79	...
O ₂ (g)	0	0	205.14	29.38	...
O ₂ (aq)	-11.7	16.4	110.9
OH ⁻ (aq)	-229.99	-157.24	-10.75	-148.5	...
Pb (s)	0	0	64.81	26.44	18.3
PbO ₂ (s)	-277.4	-217.33	68.6	64.64	...
PbSO ₄ (s)	-920.0	-813.0	148.5	103.2	...
SO ₄ ²⁻ (aq)	-909.27	-744.53	20.1	-293	...
HSO ₄ ⁻ (aq)	-887.34	-755.91	131.8	-84	...
SiO ₂ (a quartz)	-910.94	-856.64	41.84	44.43	22.69
H ₄ SiO ₄ (aq)	-1449.36	-1307.67	215.13	468.98	...

ANNEXURE B Nafion® datasheet for PFSA membranes

Product Information

DuPont™
Nafion® PFSA Membranes
N-112, NE-1135, N-115, N-117, NE-1110
perfluorosulfonic acid polymer

Membranes

Description

DuPont™ Nafion® PFSA membranes are non-reinforced films based on Nafion® PFSA polymer, a perfluorosulfonic acid/PTFE copolymer in the acid (H⁺) form. Nafion® PFSA membranes are widely used for Proton Exchange Membrane (PEM) fuel cells and water electrolyzers. The membrane performs as a separator and solid electrolyte in a variety of electrochemical cells that require the membrane to selectively transport cations across the cell junction. The polymer is chemically resistant and durable.

Order and Packaging Information

Membrane dimensions are based on dry product conditioned at 23 °C and 50% Relative Humidity before cutting. The membrane's water content will affect its dimensions, and the change may not be symmetrical in the length, width, and thickness directions. In addition, certain conditioning steps performed by the customer also may affect the dimensions. Customers may wish to review their membrane treatment steps and dimensional requirements with a Nafion® Technical Representative before establishing membrane shipping dimensions.

Standard dry product dimensions for individual pieces include:

- Width: 0.30 m (min.) to 1.22 m (max.)
- Length: 0.30 m (min.) to 1.22 m (max.)

The membrane delivery package for cut pieces will depend on the size and quantity of the membrane order. Smaller-sized membranes are shipped flat, while longer lengths of individual pieces are shipped on a roll. The membranes are protected with a polyethylene wrap and inner packaging, then placed in shipping containers.

Standard dry product dimensions for roll goods include:

- Width: 12-in (0.305-m) and 24-in (0.610-m) standard roll widths, and roll widths from 0.20-m (min.) up to 1.22-m (max.) on special order. Intermediate widths available in increments of 0.125-in.
- Length: 50-meter standard roll length

There is a 100 m² minimum order requirement for non-standard roll widths and lengths. Membrane pieces or rolls can be cut to custom sizes, and special packaging provided at additional cost and/or delivery time. Please contact Nafion® Customer Service for details.



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Properties of Nafion® PFSA Membrane

A. Thickness and Basis Weight Properties¹

Membrane Type	Typical Thickness (microns)	Basis Weight (g/m ²)
N-112	51	100
NE-1135	89	190
N-115	127	250
N-117	183	360
NE-1110	254	500

B. Physical and Other Properties

Property ²	Typical Value	Test Method
Physical Properties		
Tensile Modulus, MPa (kpsi)		
50% RH, 23 °C	249 (36)	ASTM D 882
water soaked, 23 °C	114 (16)	ASTM D 882
water soaked, 100 °C	64 (9.4)	ASTM D 882
Tensile Strength, maximum, MPa (kpsi)		
50% RH, 23 °C	43 (6.2) in MD, 32 (4.6) in TD	ASTM D 882
water soaked, 23 °C	34 (4.9) in MD, 26 (3.8) in TD	ASTM D 882
water soaked, 100 °C	25 (3.6) in MD, 24 (3.5) in TD	ASTM D 882
Elongation at Break, %		
50% RH, 23 °C	225 in MD, 310 in TD	ASTM D 882
water soaked, 23 °C	200 in MD, 275 in TD	ASTM D 882
water soaked, 100 °C	180 in MD, 240 in TD	ASTM D 882
Tear Resistance - Initial, g/mm		
50% RH, 23 °C	6000 in MD, TD	ASTM D 1004
water soaked, 23 °C	3500 in MD, TD	ASTM D 1004
water soaked, 100 °C	3000 in MD, TD	ASTM D 1004
Tear Resistance ³ - Propagating, g/mm		
50% RH, 23 °C	>100 in MD, >150 in TD	ASTM D 1922
water soaked, 23 °C	92 in MD, 104 in TD	ASTM D 1922
water soaked, 100 °C	74 in MD, 85 in TD	ASTM D 1922
Specific Gravity	1.98	—
Other Properties		
Conductivity, S/cm	0.083	see footnote ⁴
Acid Capacity, meq/g	0.89	see footnote ⁵

¹Measurements taken with membrane conditioned to 23 °C, 50% relative humidity (RH).

²Where specified, MD - machine direction, TD - transverse direction. Conditioning state of membrane given. Measurements taken at 23 °C, 50% RH.

³Tear resistance (g/mm) of dry membrane increases with thickness. Values given are typical for 0.05 mm membrane.

⁴Conductivity measurement as described by Zawodzinski, et.al, *J. Phys. Chem.*, 95 (15), 6040 (1991). Membrane conditioned in 100 °C water for 1 hour. Measurement cell submersed in 25 °C D.I. water during experiment. Membrane impedance (real) taken at zero imaginary impedance.

⁵A base titration procedure measures the equivalents of sulfonic acid in the polymer, and uses the measurement to calculate the acid capacity or equivalent weight of the membrane.

Properties of Nafion® PFSA Membrane

C. Hydrolytic Properties

Property	Typical Value	Test Method
Hydrolytic Properties		
Water content, % water ¹	5	ASTM D 570
Water uptake, % water ²	38	ASTM D 570
Thickness change, % increase		
from 50% RH, 23 °C to water soaked, 23 °C	10	ASTM D 756
from 50% RH, 23 °C to water soaked, 100 °C	14	ASTM D 756
Linear expansion, % increase ³		
from 50% RH, 23 °C to water soaked, 23 °C	10	ASTM D 756
from 50% RH, 23 °C to water soaked, 100 °C	15	ASTM D 756

¹Water content of membrane conditioned to 23 °C, 50% relative humidity (RH), compared to dry weight basis.

²Water uptake from dry membrane to water soaked at 100 °C for 1 hour (dry weight basis).

³Typical MD and TD values. MD expansion is slightly less than TD.

Recommended Roll Storage Conditions

Unopened roll packages of Nafion® PFSA membrane should be stored in the original shipping box, out of direct sunlight, and in a climate-controlled environment, maintained at 10 to 30°C, and 30 to 70% relative humidity. Before opening the package, pre-condition the membrane roll to the processing area temperature for 24 hours.

Once opened and exposed to the environment, the membrane will equilibrate to the ambient relative humidity, and change in dimensions accordingly. Membrane order dimensions are specified and measured at 23°C and 50% Relative Humidity.

Handling Practices

Ventilation should be provided for safe handling and processing of Nafion® PFSA membrane. The amount of local exhaust necessary for processing Nafion® PFSA membrane at elevated temperatures will depend on the combined factors of membrane quantity, temperature, and exposure time.

Scrap Disposal

Preferred disposal options are (1) recycling and (2) landfill. Incinerate only if incinerator is capable of scrubbing-out hydrogen fluoride and other acidic combustion products. Treatment, storage, transportation, and disposal must be in accordance with applicable federal, state/provincial and local regulations.

Safe Handling and Use of Nafion® PFSA Membranes

The following information should be reviewed before handling and processing Nafion® PFSA Membranes:

- DuPont Material Safety Data Sheet for Nafion® PFSA Membranes N-112, NE-1135, N-115, N-117 and N-1110
- Nafion® Technical Information "Safe Handling and Use"
- "Guide to Safe Handling of Fluoropolymer Resins", Third Edition, June 1998, Published by the Fluoropolymers Division of the Society of the Plastics Industry, Inc.

For more information about Nafion® contact:

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The data listed here fall within the normal range of product properties, but they should not be used to establish specification limits nor used alone as the basis of design. This information is based on technical data that DuPont believes to be reliable. It is intended for use by persons having technical skill and at their own discretion and risk. This information is given with the understanding that those using it will satisfy themselves that their particular conditions of use present no health or safety hazards. Because conditions of product use are outside our control, DuPont makes no warranties, express or implied, and assumes no obligation or liability in connection with any use of this information or for results obtained in reliance thereon. The disclosure of the information is not a license to operate under or a recommendation to infringe any patent of DuPont or others.

Caution: Do not use in medical applications involving permanent implantation in the human body. For other medical applications, see "DuPont Medical Caution Statement", H-50102.



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