EXPERIMENTAL STUDY OF A REVERSIBLE POLYMER ELECTROLYTE MEMBRANE FUEL CELL (PEMFC) PERFORMANCE CHARACTERISTIC WITH RESPECT TO VARIABLE CATALYST LOADING

A

THESIS

Submitted in partial fulfilment of the requirements for the award of

Master of Engineering (M.E.)

In

Thermal Engineering

Submitted by

Tanvi Joshi

(ROLL NO. 801683028)

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

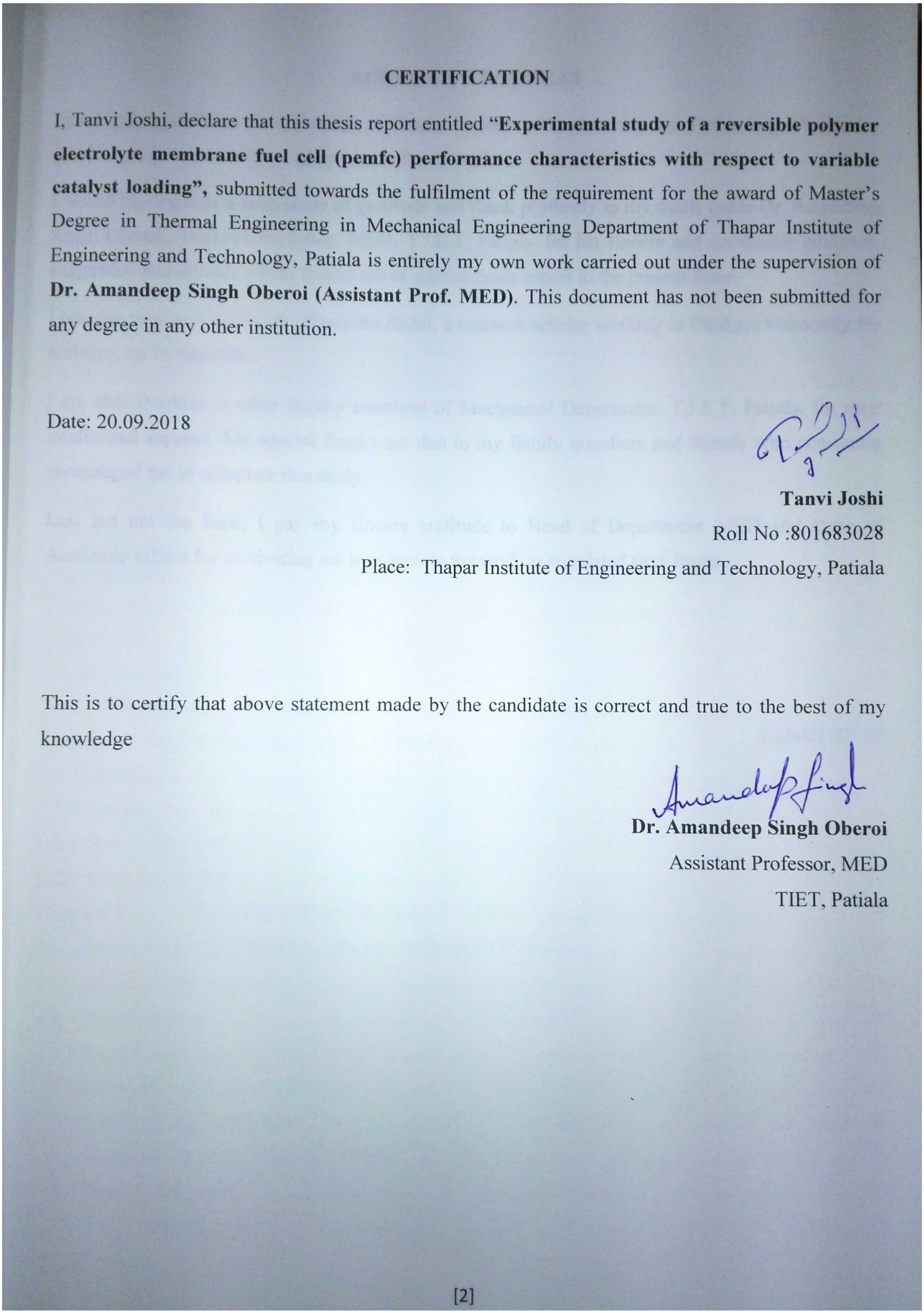
UNDER THE GUIDANCE OF

Dr.Amandeep Singh Oberoi
Assistant Professor (MED)

DEPARTMENT OF MECHANICAL ENGINEERING

THAPAR INSTITUTE OF ENGINEERING AND TECHNOLOGY, PATIALA-147004

SEPTEMBER, 2018



CERTIFICATION

I, Tanvi Joshi, declare that this thesis report entitled "**Experimental study of a reversible polymer electrolyte membrane fuel cell (pemfc) performance characteristics with respect to variable catalyst loading**", submitted towards the fulfilment of the requirement for the award of Master's Degree in Thermal Engineering in Mechanical Engineering Department of Thapar Institute of Engineering and Technology, Patiala is entirely my own work carried out under the supervision of **Dr. Amandeep Singh Oberoi (Assistant Prof. MED)**. This document has not been submitted for any degree in any other institution.

Date: 20.09.2018

Tanvi Joshi
Roll No :801683028
Place: Thapar Institute of Engineering and Technology, Patiala

This is to certify that above statement made by the candidate is correct and true to the best of my knowledge

Amandeep Singh
Dr. Amandeep Singh Oberoi
Assistant Professor, MED
TIET, Patiala

ACKNOWLWDGEMENT

I am highly grateful to the authorities of Thapar Institute of Engineering and Technology, Patiala for providing this opportunity to carry out the thesis work.

I would like express a deep sense of gratitude and thank profusely to my thesis guide Dr. Amandeep Singh Oberoi, Assistant Professor, MED, T.I.E.T, Patiala, for his sincere and invaluable guidance, suggestion and attitude which inspire me to submit thesis report in the present form.

I am also very grateful to Mr Himanshu Jindal, a research scholar working in Chitkara University for assisting me in this area.

I am also thankful to other faculty members of Mechanical Department, T.I.E.T, Patiala, for their intellectual support. My special thanks are due to my family members and friends who constantly encouraged me to complete this study.

Last but not the least, I pay my sincere gratitude to Head of Department MED and Dean of Academic affairs for motivating me to complete the work in stipulated time frame.

TANVI JOSHI

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ABBREVIATIONS

PEMFC	Proton exchange membrane fuel cell
URFC	Unitised Regenerative Fuel Cell
MCFC	Molten carbonate fuel cell
DMFC	Direct methanol fuel cell
RGF	Regenerative fuel cell
SOFC	Solid oxide fuel cell
AFC	Alkaline fuel cell
IEMFC	Ion exchange membrane fuel cells
PEM	Polymer Electrolyte Membrane
MEA	Membrane Electrode Assembly
ORR	Oxygen Reduction Reaction
GDL	Gas Diffusion Layer
PES	Poly Ether Sulphone
SPEEK	Sulphonated Polyether ether Ketone
PTFE	Poly Tetra FluroEthylene
GDE	Gas Diffusion Electrodes
OCV	Open circuit voltage
AC	Activated Carbon
PFB	Proton Flow Battery
Pt/C	Carbon Supported Platinum

ABSTRACT

Proton exchange membrane fuel cells (PEMFCs) run on pure hydrogen and oxygen (or air), producing electricity, water, and some heat. This makes PEMFCs an attractive option for clean power generation. PEMFCs also operate at low temperature which makes them quick to start up and easy to handle. PEMFCs have several important limitations which must be overcome before commercial viability can be achieved. This study discusses and shows the results obtained after an experimental investigation on the operational behaviour and characteristics of a single proton exchange membrane fuel cell (PEMFC) with the variation in the catalytic loading. The Platinum catalyst reserves are not adequate to fulfil its demands in automotive, industrial and stationary applications; hence the main focus of this study is on the platinum loading reductions (both on anode and cathode side) without any significant loss of voltage. For the experimental investigation a single reversible PEMFC with active area of 6.25 cm^2 and Nafion-117 membrane loaded with Platinum catalyst of 1 mg/cm^2 and 2 mg/cm^2 density is used.

Keywords-Catalytic loading, cell voltage, polarisation curve

INTRODUCTION AND OBJECTIVES

1.1 Introduction

The augmentation in energy demand in today's world is due to the ever growing technologies, population boom and largely developed societies. Although fossil fuels are produced repeatedly in nature they are non-renewable energy resources because the viable reserves can run out of fuel due to high demand of population. Fossil fuel with high carbon content causes a lot of pollution in the environment. Therefore, as the necessity of the situation guides we need an alternate energy resource. The renewable energy resources catch the eye of numerous researchers to develop ecosystem friendly or cleaning devices. Intensive research and development studies are being continuously made to enhance the quality of life without causing any harm to the nature.

Hydrogen is a very noticeable energy carrier, like electricity, as it is produced from a primary energy source such as solar energy, biomass, that are renewable energy sources. Hydrogen fuel is a zero-emission fuel when burned with oxygen. It can be used in electrochemical cells or internal combustion engines to power vehicles or electric devices. It has been started to be used in commercial fuel cell vehicles.

$$2H_2\,(g) + O_2(g) \rightarrow 2H_2O(g) + \text{energy}$$

Hence the gas has become an important energy carrier and fuel for fuel cells. Sir William Grove in 1839 made the first successful attempt to develop a fuel cell, and the research work has grown since then as the importance in the eye of many researchers is increasing. A fuel cell converts chemical energy of hydrogen into electrical energy, liable to be called as an electrochemical device. It has numerous advantages over other energy conversion devices like IC engines that work on carbon based fuels. They are additionally highly efficient, run on easily found fuel, produce zero emission, and are compact. They are therefore an excellent source of energy. Fuel cells require an additional external storage device for its fuel accommodation and batteries are already provided with the accommodation for its fuel inside the battery. Fuel cells can produce electricity unceasingly as long as fuel and oxygen are supplied to it.

A fuel cell comprises two electrodes with electrolyte in between them. The electro-catalyst fosters the reaction between fuel and oxidant to combine and generate electricity which is shown in Figure 1.1.

Generally, the hydrogen gas is supplied to anode (negatively charged electrode) and the molecule splits into proton and one electron. The oxidation by loss of electrons occurs in the anode side and the oxygen gas is supplied in the cathode side to produce water with hydrogen.

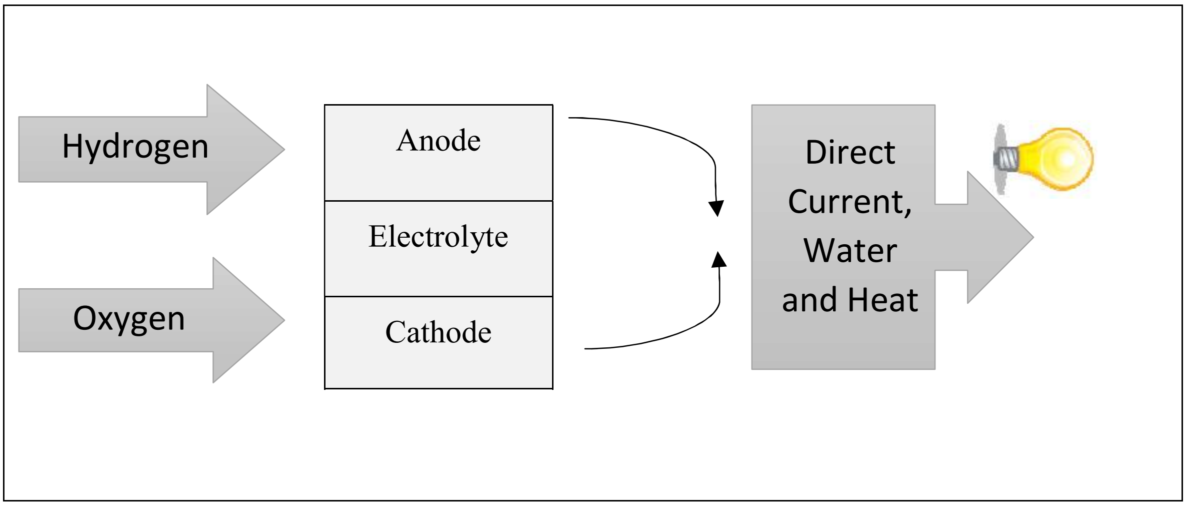


Figure 0.1: Block Diagram of fuel cell

The storage of the reactants fuel of the cell is external and fed into electrodes when electricity is required. When the cylinders for storing fuel are exhausted the fuel cell acts just like a empty storage tank, liable to be refuelled quickly. An unceasing supply of fuel is required for the cell to be running continuously.

1.2 Classifications

Fuel cells are categorized with respect to the electrolyte that is being used. The operating temperature of a fuel cell system is an important factor in its performance and reactions; therefore it is dependent on the material of the electrolyte to be used. Every fuel cell has its advantages and disadvantages.

Five types of fuel cells have been under active development, i.e. molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), solid oxide fuel cell (SOFC), proton exchange membrane fuel cell (PEMFC). In addition to the five primary fuel classes, there are two more classes of fuel cells that are not distinguished by their electrolyte. These are the direct methanol fuel cell (DMFC), distinguished by the type of fuel used, and the regenerative fuel cell (RGF) distinguished by its method of operation. The properties of the fuel cell are summarized in Table 1.1. The major differences among the cells is of the electrolyte used, the requirement of an external reformer the working temperature and the charge carrier.

Table no 0.1: Classifications of Fuel Cell

	PEMFC	**SOFC**	**AFC**	**PAFC**	**MCFC**
Electrolyte	Polymer electrolyte membrane	ceramic	Aqueous alkaline solution	Molten phosphoric acid	Molten alkaline carbonate
Operating Temperature	50°C- 100°C	850ºC - 1100ºC	80°C	150ºC-200ºC	600ºC-650ºC
Charge carrier	H+	O-	OH-	H+	CO3

Among all these cells PEMFCs are considered the most versatile, viable, pollution free, simpler, and quick starting fuel cells. It is very suitable for automotive applications.

The proton exchange membrane is made of Nafion. It is dependent on the moisturized membrane to enhance the proton transfer. Nafion had characteristic substance, warm and oxidative dependability up to temperatures 80°C. So it is worth investigating and expanding the power operation temperature above 100ºC. These focal points are; quick cathode energy, straightforward warm and water administration and warmth use. Another advantage is the diminished impetus harming by fuel debasements, for example, CO and CO2. This harming impact has been appeared to be exceptionally temperature-ward and it is less articulated with expanding temperature.

1.3Proton Exchange Membrane Fuel Cells

Proton exchange membrane fuel cells (PEMFCs) are also called Polymer electrolyte (membrane) fuel cells (PEMFCs). More and more institutes and industries are investigating on PEMFCs for their capability to stand as the most efficient simple device among all the other fuel cell types. Till date man efforts have been credited from the scientists to work for better performance in case of low platinum loading, thinner membranes and better bipolar plates. Till date many efforts have been credited from the scientists to work for better performance in case of lower catalytic loading, thinner membranes and better bipolar plates. Hence these typical PEMFCs are growingly gaining stron attention due to their compactness, flexibility and many applications. These low temperature fuel cells do not require higher start-up temperature too. Till date many efforts have been credited from the scientists to work for better performance in case of lower catalytic loading, thinner membranes and better bipolar plates.

1.4Principles of Proton Exchange Membrane Fuel Cells

Every fuel cell has an integral, most important part of it known as electrolyte that acts as a membrane for protons to pass through. The membrane is at the centre of the whole fuel cell system. Fuel cell has two electrodes, anode and cathode. Anode is made up of porous carbon with platinum as catalyst and on the cathode side the iridium oxide in the following experiment done. Both the electrodes with catalyst on the inside are pressed to the membrane to form an assembly. The gases hydrogen and oxygen are supplied to get a circuit formed by stimulating the disbursal of electrons from hydrogen molecules in the presence of catalyst. A schematic portrayal of a PEM energy unit is appeared in Figure1.2.

Fuel cell is much different from battery although they both are electrochemical devices, the supply of hydrogen and oxidant is ex-situ in the case of fuel cells in the form of cylinders. The fuel cell keeps on working until the amount of fuel in the cylinders is finished. Figure 1.2 shows that the intake of hydrogen from the anode side flowing through flow channel and passing on to the anode. On the other side of the fuel cell is cathode flow channel that let the oxygen gas to pass through it to the cathode electrode. At the anode the hydrogen gas is parted into the hydrogen proton and electrons. The protons travel through the electrolyte and the electrons under potential difference (since load is applied in the external circuit) travel to the other side of the cell. The electrons and protons meet at the cathode with oxygen molecules to form water as the product of the reaction. Water is directed out of the system.

The hydrogen atom part is for the most part basic using a platinum impetus. The more grounded oxygen atom is more troublesome, which causes critical actuation misfortune. Platinum has been looked up as the best for the lower reduction rate of oxygen. One important reason for execution misfortune is the hindrance of the polymer layer to proton stream, which is controlled by making it extremely optimized thin membrane, to work in normal light of the current situation. The protons travel through the electrolyte and the electrons under potential difference (since load is applied in the external circuit) travel to the other side of the cell. Regardless, the PEMFC is a sustainable stable system whose successful operation with a ground-breaking yield depends upon all the sub-structures; its execution depends upon parts, for instance, stream field example, catalyst, and film, and moreover on working parameters, for instance, temperature and dampness.

1.5 Components of Proton Exchange Membrane Fuel Cells

The components of polymer electrolyte membrane fuel cells are: (1) the proton exchange membrane; (2) the electrodes that are composed of catalyst and gas diffusion layers on both the sides (3) gaskets for preventing any leakage of fuel or oxidant and insulating the whole setup (4) bipolar plates that contain flow channels on the inside provide the gases into the system. The Figure1.2. below demonstrates the assembly:

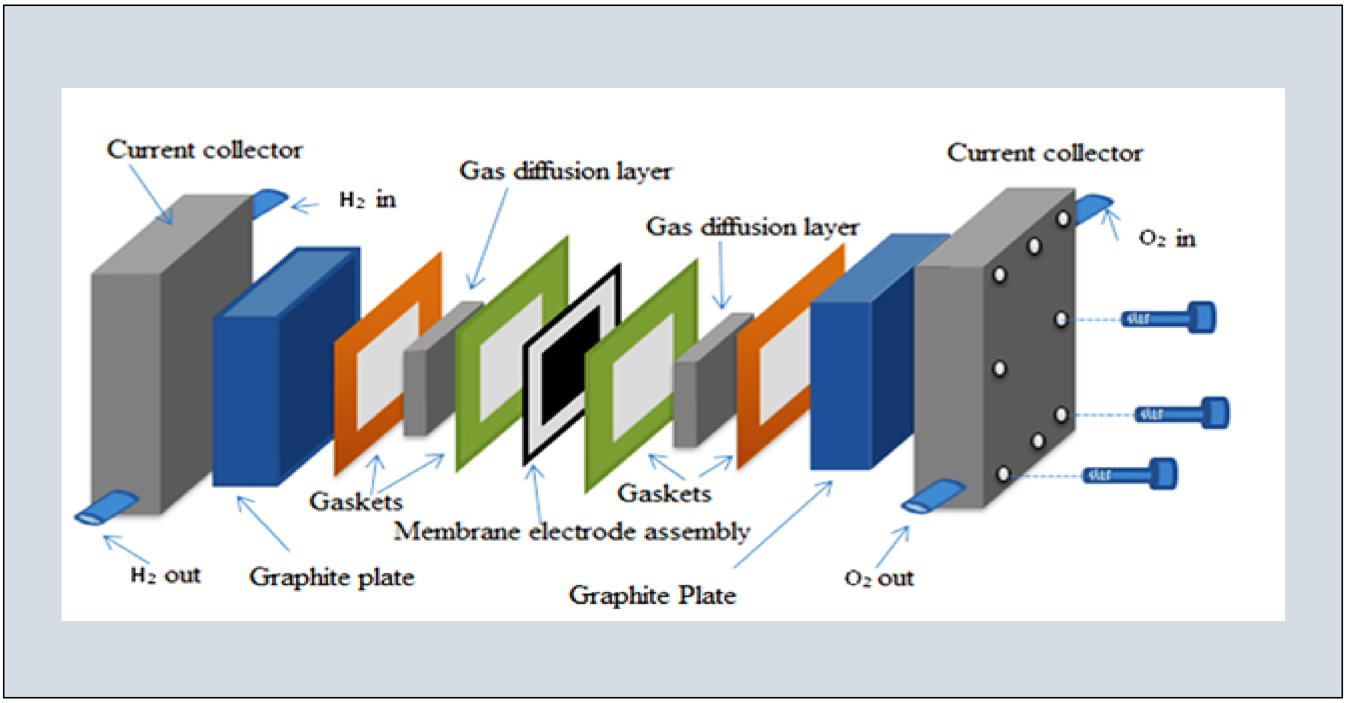


Figure 0.2: Components of PEMFC

1.6 Electrolyte Membrane

Polymer film electrolytes for the most part a solid state ionomer, usually perfluorosulphonic acid. Acid, for example, sulphuric acid, is connected onto this polymer arrange for particle trade, in this way layers are proton directing. In this sense the principal limit of the electrolyte is to let only protons pass through it from anode to cathode. Properties of the membrane such as thickness of the membrane equivalent weight and capacity to reduce the gas crossover work as very important features. The ideal polymer must have efficient proton conductivity, blend and warm security, quality, versatility, low gas vulnerability, low water drag, speedy vitality for cathode reactions, straightforwardness, and incredible availability. The films are typically polymers altered to incorporate particles, for example, sulfonic gatherings.

More thin layers increase execution capability and proton conductivity. Be that as it may, from the lifetime point of view; the thinner membranes have reduced severely the physical strength and higher gas vulnerability, allowing more gas crossover, which revives corrosion and short circuit. Properties of the membrane such as thickness of the membrane equivalent weight and capacity to reduce the gas crossover work as very important features. Acid, for example, sulphuric acid, is connected onto this polymer arrange for particle trade, in this way layers are proton directing.

A standout amongst the most generally utilized films is Nafion, a polymer made by the DuPont Company. Other business firms that produce the membrane are Dow layer (Dow Chemical), "C" layer (Chlorine Engineers), Flemion (Asahi Glass) and Aciplex (Asahi Chemical). Nafion has a per fluorinated spine with ether-connected side chains finishing off with sulfonate cation trade destination. It is made up of tetra-fluoroethylene and sulfonyl fluoride vinyl. At the point when the film assimilates water, the ionic spaces swell andform proton-leading channels over a basic water containing film. The conductivity increases with the water content to a limited degree. Nafion 112 was accounted for to achieve 10000 long stretches of task (43– 82°C).

1.7Electrodes and gas diffusion layer

A power gadget anode is the force layer arranged between the film moreover, gas diffusion layer . The chemical reactions occur on the surface inside seeing protons, electrons and gases. The force is in contact with ionomer to empower the development of protons through ionomer. Simply more unquestionably the anodes are penetrable to allow gases to development to the reaction areas (Barbir, 2005).

Carbon powder that has greater particles goes about as a supporter for them. An extensively used carbon-based powder is Vulcan XC72® (by Cobalt). Along these lines the platinum is profoundly isolated and spread out, so that a high extent of the surface region will be in contact with the reactant, bringing about an extraordinary decrease of the impetus stacking with an increment in control

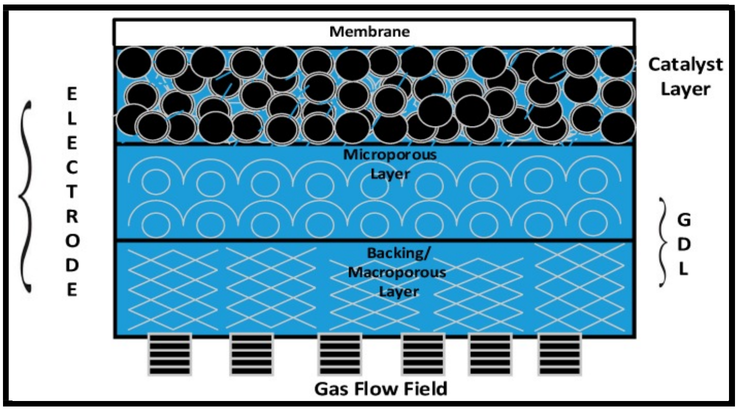


Figure 0.3: Electrodes and gas diffusion layer

Researchers are inventing new platinum based alloy catalysts to foster the response in the reaction. Platinum and platinum-ruthenium-constructed impetuses in light of various carbon bolsters have been made by supercritical carbon dioxide testimony and microwave illumination forms in Bayrakçeken's investigation. It was seen that the power misfortunes emerging from carbon dioxide in hydrogen feed can be diminished by using platinum-ruthenium based impetuses. Metal ophthalocyanines electro - synergist action was likewise seen as a substitute of oxygen decrease since their exceptionally conjugated structure and high synthetic security.

The impetus layer really contains an extensive segment of ionomer (up to ~30% by weight) to upgrade ionic transport to/from the electrolyte film. A few procedures were produced for readiness of MEA, for example, GDL Spraying, Membrane Spraying, and Decal techniques. GDLs are basic segments in PEMFCs. The essential work of the GDL is to diffuse the gas. The permeable propensity of the sponsorship material enhances the compelling dissemination of every reactant gas to the impetus on the MEA. The GDL is additionally an electrical travel between the carbon upheld impetus and the bipolar plate or other current gatherers. Aside from this, the GDL likewise helps in overseeing water in the framework as it diverts the item water from the electrolyte surfaceInitially, GDL is treated with a hydrophobic polymer like polytetrafluoroethylene (PTFE). PTFE upgrades: (1) gases contact to the impetus locales by keeping water from "pooling" in the pore volume of the sponsorship layer, (2) the resultant water to be expelled from the cathode site and (3) the humidification of the film by permitting the correct measure of water vapor to go through the GDL and achieve the MEA.

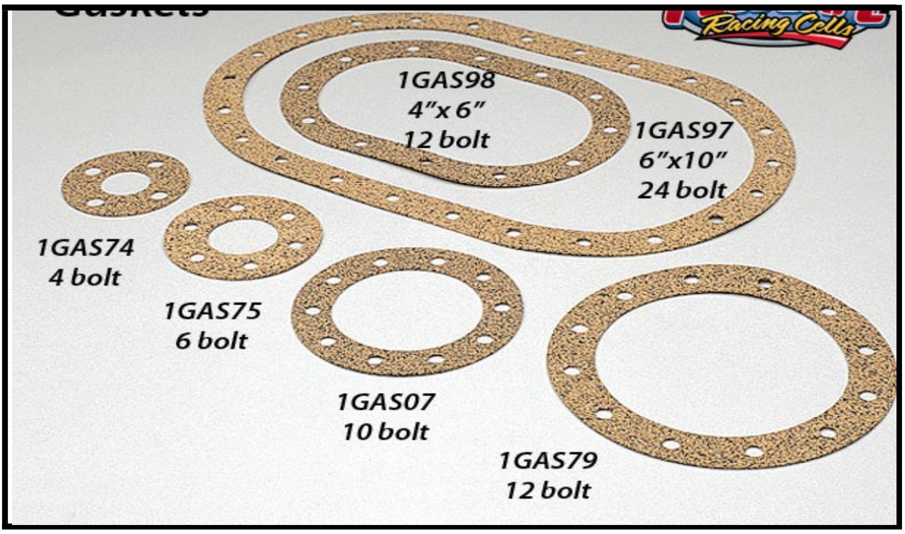
Furthermore, GDL gives mechanical help to MEA by protecting it from hanging into the stream field channels. It is likewise a flexible piece of the MEA to deal with the power expected to pack and set up a personal contact.

1.8 Bipolar plates

The two plates on each side of the MEA are called 'end plates' or 'flowfield plates'. The completely working bipolar plates are fundamental for multi-cell arrangements, by electrically associating the anode and cathode of the adjoining cell. The bipolar plate is for various purposes. Its most imperative job is to supply reactant gases to the gas dissemination terminals (GDEs) through stream channels. Bipolar plates give electrical associations between the individual cells. They definitely would need to expel water created at the cathode successfully. The most widely recognized material utilized for bipolar plates in PEMFC stacks is graphite. Graphite has great electronic conductivity, erosion opposition and furthermore low thickness. Composite materials and metals, for example, steel, copper and so forth are likewise utilized in creating as bipolar plates.

1.9 Gaskets

Moreover, to the expressed misfortunes there are likewise hybrid misfortunes that can be noteworthy for low temperature energy units. Despite the fact that the electrolyte is basically impermeable to reactant gases, little measure of hydrogen can diffuse from anode to the cathode. In any case, the rate of hydrogen saturation is a few requests of greatness lower than hydrogen utilization rate. In this way, these misfortunes are inconsequential in energy component activity. In any case, at open circuit voltage (OCV) these misfortunes can affect cell potential because of the high centralization of hydrogen on the layer surface. In this way, it might prompt a drop on OCV.



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1.10 Operation of PEM Fuel Cell

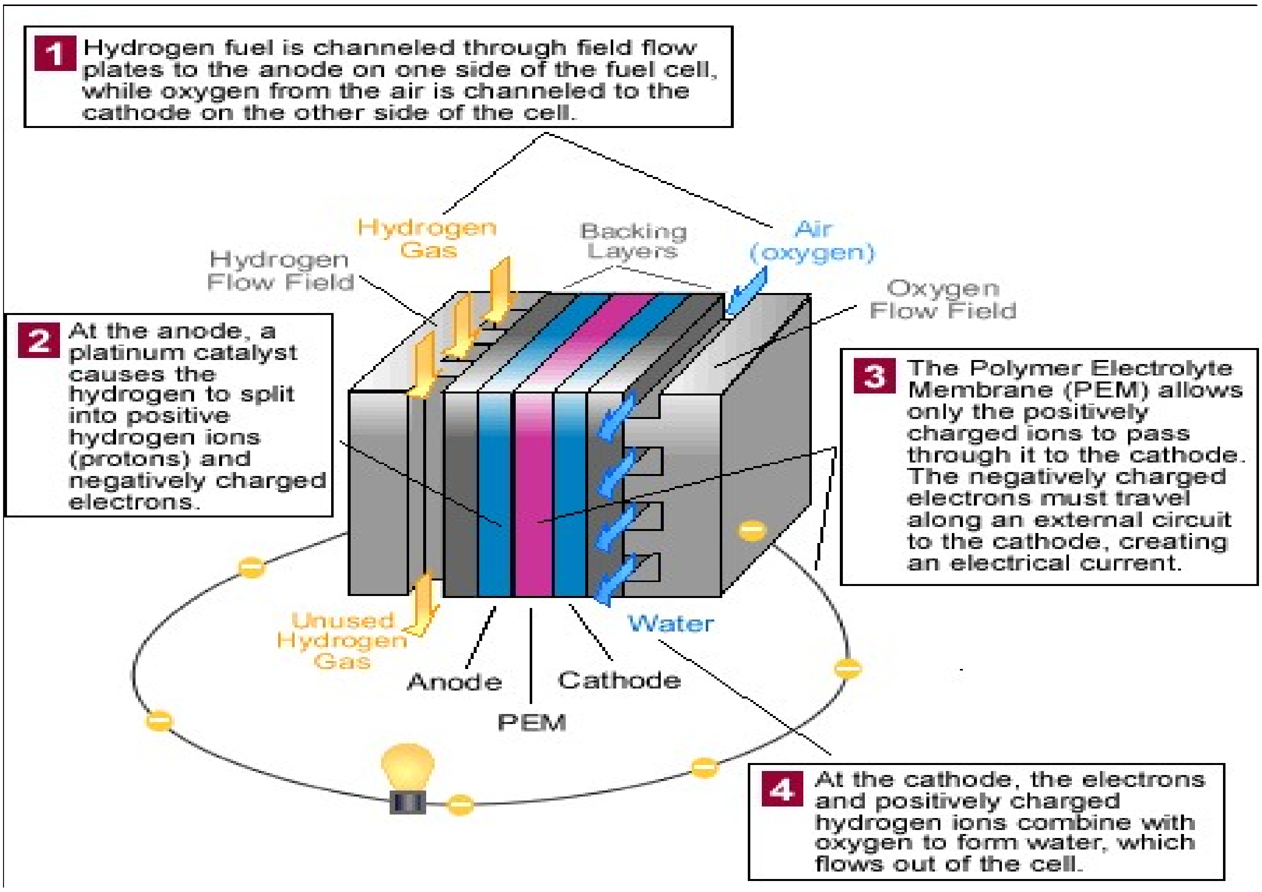


Figure0.4: Operation of PEMFC

High performance of a P

EM fuel cell requires maintaining optimal temperature, membrane hydration, and partial pressure of the reactants.

1.11 Fuel Cell Electrochemistry

The fuel cell reaction Eq. (1.1) is exactly same as the reaction of hydrogen combustion. Combustion is an exothermic process, which means that the energy released in the process:

$$H2 + ½O2 \rightarrow H2O + heat \qquad (1.1)$$

The difference between the heats of formation of products and reactants the heat (or enthalpy) of a

$$\Delta H = h_f, H_2O\ (l) - h_f, H_2\ (g) – ½\ h_f, O_2\ (g) = -286\ kJ/mol \qquad (1.2)$$

Due to the entropy generation, there are irreversible losses in energy transformation. Gibbs free energy, ΔG, is defined as the part of the reaction enthalpy that can be converted to electricity, as shown below.

$$G = H - T\ S \qquad (1.3)$$

The values of G, H and S at 25°C are given in Table 1.2.

Table 0.2: Enthalpies, entropies and Gibbs free energy for hydrogen oxidation process (at 25°C)

	ΔH(kJ/mol)	**ΔS(kJ/mol/K)**	**ΔG(kJmol-1)**
$H_2 + ½\ O_2 \rightarrow H_2O$ (l)	-286.02	-0.1633	-237.34
$H_2 + ½\ O_2 \rightarrow H_2O$ (g)	-241.98	-0.0444	-228.74

The work in this fuel system is produced by the transport of electrons across a potential difference. Electrical work (J/mol) is defined as the relation:

$$W = q\ E \qquad (1.4)$$

E stands for the cell voltage and q for the charge (coulombs/mol). The final whole charge transported per mole of hydrogen in the cell reaction consumed (q) is expressed as Eq. 1.5

$$q = n\ N_{avg} q_{el} = n\ F \qquad (1.5)$$

n stands for the number of electrons transferred which is equal to 2 for each hydrogen molecule in fuel cells, N_{avg} is the Avagadro's number (6.02 x 10^23), $q_{el,}$ the charge per electron (1.602 x 10^-19 coulombs/electron) and F is the Faraday's constant equal to 96485 coulombs/mol. electron.

Now the electrical work can be defined as (Eq.1.6):

$$W = n\,F\,E \qquad (1.6)$$

The work here is defined as Gibbs free energy due to the electro-chemical reaction:

$$W = -\Delta G \qquad (1.7)$$

So, the cell voltage of the system can be calculated as (Eq. 1.8) when pure hydrogen and oxygen gases are fed at standard conditions

$$E=-\Delta G/n\,F= 237.34\ (\text{kJ/mol})/\ (2\ \text{electrons} \times 96485\ (\text{C/mol electron}) =1.23\text{V} \qquad (1.8)$$

The efficiency that is defined generally for all energy conversion devices is the ratio between useful energy output and energy input. So, the energy that is liable to be utilized by the external work producing device is the energy output, and energy input is hydrogen's higher heating value. Assuming that all of the Gibbs free energy can be converted into electrical energy, the maximum possible(theoretical) efficiency of a fuel cell is

$$\eta = \Delta G/\Delta HLHV = 228.74/241.98 = 94.5\% \qquad (1.9)$$

The real energy component potential (Vcell) and the genuine productivity are lower than the hypothetical qualities inferable from different misfortunes (ΔVloss) with energy and elements of the procedures, reactants and the items. The genuine energy component potential is characterized as it is appeared in Eq. 1.10 where E is the reversible open circuit voltage (OCV):

$$V_{cell} =E - \Delta V_{loss} \qquad (1.10)$$

For the actual operation of a PEM fuel cell the potential is decreased from its ideal value because of several irreversible losses. These lossesare referred to as;

(i) Activation- related losses (ΔV_{act})

(ii)Ohmic losses and (ΔV_{ohm})

(iii) Mass transport related losses (ΔV_{conc})

Cell voltage can be interpreted in terms of these losses such as:

$$V_{cell} =E - (\Delta V_{act} + \Delta V_{ohm} + \Delta V_{conc}) \qquad (1.11)$$

Right off the bat, some voltage contrast is expected to get the electrochemical responses going. This is called initiation polarization. Its impact is seen at low current densities. These misfortunes rely upon responses, electro-impetus material and reactant exercises. ΔVact can be composed by the Butler-Volmer Equation 1.12

$$\Delta Vact= RT/F \ln(i/i_o) \qquad (1.12)$$

where R is the gas constant, T is temperature, α is transfer coefficient, i is current density and i_o is exchange current density. Activation losses can also be defined as Tafel Equation:

$$\Delta Vact = a + b \log (i) \qquad (1.13)$$

$$a=-2.3\, RT/F \log(i_o) \text{ and } b=2.3\, RT/F \qquad (1.14)$$

Term b is called the Tafel slope.

At middle of the road current densities the cell potential drops directly with present because of ohmic misfortunes. These misfortunes are the consequence of ionic opposition in electrolyte, electronic obstruction in terminals and furthermore in other electrically conductive energy unit parts. So obviously these misfortunes rely upon material determination. ΔVohm can be communicated by Ohm's law Equation 1.14

$$\Delta V_{ohm} = iR_c \qquad (1.14)$$

where R_c is the total internal resistance. The mass transport related losses are a result of mass transfer limitation rates of the reactants and depend on the current density, reactant activity and electrode structure. ΔV_{conc} can be written according to the Nernst Equation.

$$\Delta V_{conc}= RT/nF\ln(i_L/ i_L-i) \qquad (1.15)$$

where i_L is the limiting current density.

Then equation 1.11 is rewritten as equation 1.16

$$V_{cell}=E- RT/F \ln(i/i_o)-iR_c- RT/nF\ln(i_L/i_L-i) \qquad (1.16)$$

Moreover, to the expressed misfortunes there are likewise hybrid misfortunes that can be noteworthy for low temperature energy units. Despite the fact that the electrolyte is basically impermeable to reactant gases, little measure of hydrogen can diffuse from anode to the cathode. In any case, the rate of hydrogen saturation is a few requests of greatness lower than hydrogen utilization rate. In this way, these misfortunes are inconsequential in energy component activity. In any case, at open circuit voltage (OCV) these misfortunes can affect cell potential because of the high centralization of hydrogen on the layer surface. In this way, it might prompt a drop on OCV.

OBJECTIVES

- To fabricate the porous activated carbon electrode for electrochemical hydrogen storage within the electrode
- To fabricate an experimental Proton Flow Battery(PFB) with an integrated hydrogen storage electrode.
- To test the PFB for its feasible running.
- To study the behavior of the voltage output with respect to the change in catalytic loading in the URFC.
- To determine the relation between the two catalytic loading in the URFC.
- To determine the relation between the two catalytic loadings and performance characteristics of the proton flow battery.

Research Method

- To achieve the identified objectives the following methodology was employed.
- Conversion of natural wood into charcoal by burning it in an electric oven and obtaining the activated carbon in powder form.
- Activation of the carbon powder by conventional method of adding KOH (potassium hydroxide).
- Mixing of the activated carbon powder with a commercial binder-polytetrafluoroethylene(PTFE) to obtain a slurry mixture
- Casting the slurry mixture in a desired shape to obtain a solid porous activated carbon electrode.

- Fabrication of the PFB with an integrated activated carbon electrode.
- Testing and analysis of the characteristics curves of the PFB.

Chapter 2 : BACKGROUND AND LITERATURE SURVEY

2.1 Literature

Review of literature is one of the very important steps of any research work. The study of previous literature related to the research topic, directly or indirectly, provides the researcher with food-for-thought for various aspects of thesis writing. Review of literature on the related topic allows the researcher to understand

- The approach of previous researchers on the topic;
- The methods, tools and techniques deployed by previous researchers;
- Interpreting the results and findings of previous literature;
- Identification of research gaps of previous research works.

Understanding developed through review of previous literature related to the topic, allows the researcher to establish the framework of the research undertaken. The researcher is able to define the purpose of research work through the research gap created by previous researches. It further enables the researcher to adopt tools and techniques aptly suitable to conduct the research work.

2.2 Background

The famous company General Electric of USA developed first polymer electrolyte membrane fuel cell (PEMFC) also known as proton exchange membrane fuel cell, polymer electrolyte fuel cell (PEFC) and solid polymer fuel cell (SPFC) IN 1960 for use OF NASA. The electrolyte is an ion conducting polymer membrane and Anode and cathode are bonded to either side of the membrane. This assembly is normally called membrane electrode assembly (MEA) or EMA which is placed between the two flow field plates (bipolar plates) to form what is known as "stack". The basic operation of the PEMFC has been discussed in chapter one in detail.

The researcher is able to define the purpose of research work through the research gap created by previous researches. It further enables the researcher to adopt tools and techniques aptly suitable to conduct the research work.

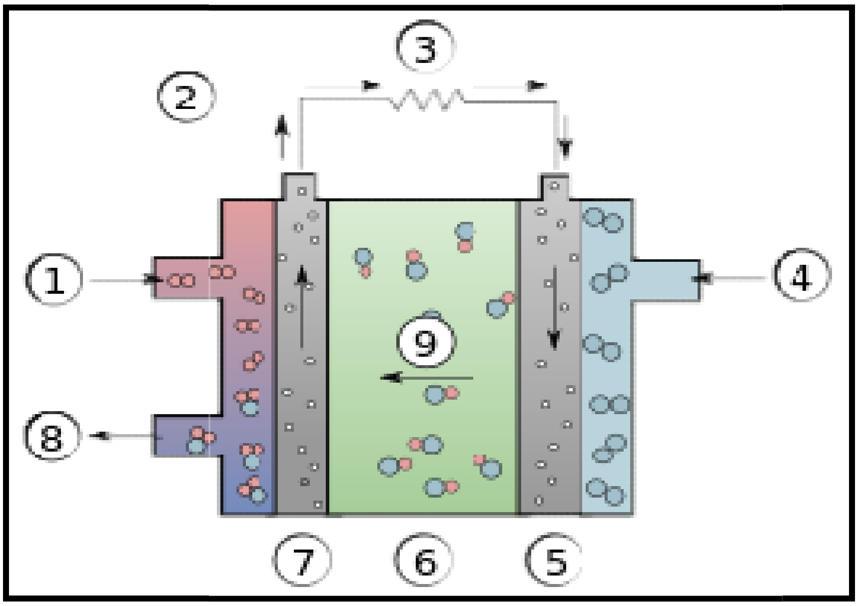


Figure 2.1: 1:Hydrogen 2: Electron flow 3: Load 4: Oxygen 5: Cathode 6: Electrolyte 7: Anode 8: Water 9: Hydroxyl Ions

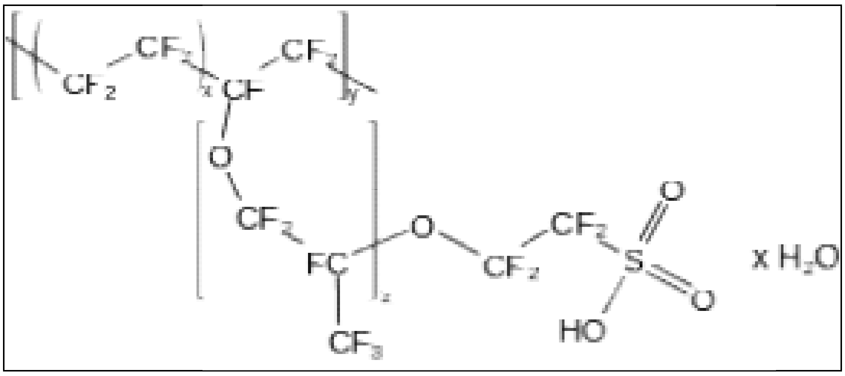


Figure 2.2: Structure of Nafion

The researcher is able to define the purpose of research work through the research gap created by previous researches. It further enables the researcher to adopt tools and techniques aptly suitable to conduct the research work. Fuel cell technology is going to play an important role in the future of the world. The increasing energy demand among the different standards of people in different countries, calls for the various renewable energy sources as an alternate to trap the energy.

I am highly motivated towards fuel cell technology and its advancements in recent years due to the many benefits that it offers like high efficiency, zero emission and compactness in size. Although some challenges invite the researchers to work on them.

A large number of global companies are taking interest in fuel cells, both as developers and strategic partners. Big supplier and manufacturer companies of PEMFC components such as DuPont, Gore, SGL, 3M and Johnson Matthey, are establishing themselves as a driver for zero emission vehicles leading to great technological strides in the development of PEMFC.

Various renowned automobile companies like GM, Daimler Chrysler, Ford, Toyota, Nissan, Hyundai and Honda have also initiated commercialization of automobile fuel cells with sustainability for less emission of greenhouse gases.

2.3 Rationale for study

Fuel cell technology is going to play an important role in the future of the world. The increasing energy demand among the different standards of people in different countries, calls for the various renewable energy sources as an alternate to trap the energy.

I am highly motivated towards fuel cell technology and its advancements in recent years due to the many benefits that it offers like high efficiency, zero emission and compactness in size. Although some challenges invite the researchers to work on them.

2.4 Literature Review

Niels *etal.* 2000 found that blend polymer solid electrolytes had low resistivity and higher mechanical strength. Fuel cell technology is going to play an important role in the future of the world. The increasing energy demand among the different standards of people in different countries, calls for the various renewable energy sources as an alternate to trap the energy. Highly motivated towards fuel cell technology and its advancements in recent years due to the many benefits that it offers like high efficiency, zero emission and compactness in size. Although some challenges invite the researchers to work on them.

The researcher is able to define the purpose of research work through the research gap created by previous researches. It further enables the researcher to adopt tools and techniques aptly suitable to conduct the research work.

.H.A. Gasteiger *etal.* 2004 mentioned that the works in the sustainability of the Pt/C cathodic catalysts in PEMFC, Platinum Carbon combination has been studied for prolonged duration. Various catalysts duration prospects are also being observed. Paper also describes the shortcomings which could not be removed and contemporary researches on the usability and applicability of PEMFC to various ongoing operations, for example automobiles, power generating systems and portable computers. , this paper also speaks and consolidates the future prospects and the comparison of market forces for PEMFCs in these areas.

Z R Ismagilov *et al.* 2005,investigated the MEA testing on Pt cathode catalysts on CNF show poor output than a catalyst on conventional carbon black support Pt/Vulcan XC-72R. The cathode catalyst prepared on ASC support exhibits reasonably higher output in MEA, compared with Pt/Vulcan XC-72R even at a lower Pt loading.

M Carmo *et al*. 2006, mentioned that in order to provide the best performance, platinum metallic is the most important electro-catalysts material employed and investigation results concerning electrochemical properties for electro-catalysts have resemblance with organisations such as Vulcan XC72; Vulcan XC72R and Carbon Pearl.

L Xiong*et al.2007,* illustrated that two electrolytes Nafion and sulfonated aromatic polymers used in PEMFC technologies have less strength above 100°C and need wetting, so porous inorganic solid acid membranes such as mesophoric phosphates may be one of the alternate.

G. Pollet*et al.* 2009,found that PEMFC electrodes prepared sono-electrochemically has better output then using galvano-static pulse and conventional methods. Maximum power densities of 98.5 mWcm^{-2} were found in comparison to 91.5 mWcm^{-2} (by galvanostatic pulse method alone) and 86 mWcm^{-2} (by conventional method) respectively.

Chuang Liu *et al*. 2010 2004 mentioned that the works in the sustainability of the Pt/C cathodic catalysts in PEMFC, Platinum Carbon combination has been studied for prolonged duration. Various catalysts duration prospects are also being observed. Paper also describes the shortcomings which could not be removed and contemporary researches on the usability and applicability of PEMFC to various ongoing operations, for example automobiles, power generating systems and portable computers. , this paper also speaks and consolidates the future prospects and the comparison of market forces for PEMFCs in these areas.

Yu Wang Ken *et al.2011,*in his study stated that in preceding two years hence his study fabrication of fuel cell had been economic by more than 35%.

HWRhee *et al.* 2012,while studying in “ Advances in Polymer Nano-composites” illustrated that PEMFCs operating at room temperature have issues like poisoning of catalyst and spilling over of fuel .Which can be mostly tackled using nano-composites of sulfonated polymer electrolyte membranes with inorganic compounds for example hygroscopic metal oxides and solid proton conductors.

R Sridhar *et al*. 2013,in study relating to mechanical properties like stress, strain and modulus depicted that due to delimitation decrease in modulus has been found. Study of mechanical properties of MEA can be used for causes of degradation.

Carral *et al*. 2014 investigated the mechanical state of (PEMFC) during its assembly which necessary for more output 2004 mentioned that the works in the sustainability of the Pt/C cathodic catalysts in PEMFC, Platinum Carbon combination has been studied for prolonged duration. Various catalysts duration prospects are also being observed. Paper also describes the shortcomings which could not be removed and contemporary researches on the usability and applicability of PEMFC to various ongoing operations, for example automobiles, power generating systems and portable computers. , this paper also speaks and consolidates the future prospects and the comparison of market forces for PEMFCs in these areass.

Q Jhang *et al.* 2016,studied performance in stability and homogeneity under variable operating parameters. He 2004 mentioned that the works in the sustainability of the Pt/C cathodic catalysts in PEMFC, Platinum Carbon combination has been studied for prolonged duration. Various catalysts duration prospects are also being observed. Paper also describes the shortcomings which could not be removed and contemporary researches on the usability and applicability of PEMFC to various ongoing operations, for example automobiles, power generating systems and portable computers. , this paper also speaks and consolidates the future prospects and the comparison of market forces for PEMFCs in these areass.

H Ren *et al*.2017, in his study relating to Wireless MEMS Networks and Applications mentioned that due to cheaper catalysts and refined cell configurations the amount of platinum used in PEMFC has been decreased by nearly 10–100 times and the power density of these cells has shooted to 0.5–0.7 W cm^{-2}. The ideal conditions reflect number of cells on the stack properties whereas the end-plates deflection and deformations can inform us about the compression ratio distribution of the active layer of the cell (MEA) under real assembly conditions.

Q Jhang *et al.* 2016,studied performance in stability and homogeneity under variable operating parameters. He used Polarization curves and Electrochemical Impedance Spectroscopy (EIS) to show the overall performance and resistance losses of PEMFC. Under higher air stoichiometry the fuel cell shows better overall and local performance, current distribution homogeneity and local stability. It is also noticed that in all cases the output in the vicinity of the outlet parts are very low due to weak water management and poor gas concentration.

Chapter 3 : FABRICATION OF ELECTRODE

This includes fabrication of activated carbon electrode using PTFE binder, the wood from a tree was used as the precursor for carbon. The wood of the tree was cut in pieces and heated in an electric oven (shown in Figure 3.1) at 110 degree Celsius until the smoke was obsolete leaving the charcoal behind. The specifications of the used oven are shown in Table 3.1.

Figure 3.1: A laboratory electric oven.

Table 3.1: Specifications on a laboratory electric oven

Sr. No.	**Description**
1	Name: Laboratory oven
2	Capacity: 104 L
3	Amperage: 14A

4	Dimensions Interior (D x W x H): 58.9 x 46.4 x 60.8 cm
5	Dimensions Exterior (D x W x H): 56.5 x 64 x 82 cm
6	Hertz: 60 Hz
7	Shelves – 2 Nos.
8	Temperature range: 50 °C to 250 °C
9	Temperature Control: Microprocessor control
10	Temperature stability: ±0.3°C

The charcoal was crushed into powder in a laboratory ball-mill (shown in Figure 3.2) and segregated according to particle size using a Sieve Shaking Machine (shown in Figure 3.3). The specifications for the used ball mill and sieve shaker machine are given in Table 3.2 respectively.

Figure 3.2: A laboratory ball mill

The catalyst layer is made of 30% of ionomer of the membrane to stimulate the ion transfer via the membrane. Numerous methods have been developed to produce MEA such as GDL Spraying, Decal methods, Membrane Spraying. GDLs are the main components in PEMFCs. The main work of the GDL is to let the gas diffuse through it. The property of the backing material is to let the gas to diffuse effectively to the catalyst layer. GDL works as a transit between the current collectors, bipolar plates and the catalyst layer. Apart from this, the GDL is responsible of getting the water produced in the reaction transported away from the electrolyte. The porous tendency of the backing material improves the effective diffusion of each reactant gas to the catalyst on the MEA. GDLs are the main components in PEMFCs. The main work of the GDL is to let the gas diffuse through it. The property of the backing material is to let the gas to diffuse effectively to the catalyst layer. GDL works as a transit between the current collectors, bipolar plates and the catalyst layer. Apart from this, the GDL is responsible of getting the water produced in the reaction transported away from the electrolyte. GDL works as a transit between the current collectors, bipolar plates and the catalyst layer. The catalyst has the ionomer composition so as to increase the rate of transfer of ions.

Figure 3.3: A laboratory sieve shaker machine

Table 3.2: Specification of a laboratory steel ball mill

Model	**BST/BM-1**
Capacity	1 KG
Housing	Stainless Steel / MS Powder Coated
Jar Construction	Aluminum / Stainless Steel
Speed	80 rpm
Motor	FHP Geared Motor
Material feed size	< 10 mm
Final fineness	< 10 µm, for colloidal grinding < 1 µm
Grinding stations	1
Power Supply	220 / 230 Volts, 50Hz

Table 3.3: Specification of a laboratory sieve shaker machine

Model	**BST/ESS-8**
Sieve Capacity	- 8 sieves (200 mm Dia x 50 mm H)
Wet Sieving	Optional Kit
Vibration Source	Electromagnetic vibrator
Construction	Cast Iron, Painted Mild steel
Display	LCD Display
Sieving Timer	Digital / Analog
Set Time	0 ~ 99 min
Vibration Frequency	3000 times / min
Noise Level	> 61 db w/o sieves at max. power level
Vibration Mode	- Fine Vibration - Intermittent Vibration - Continued Vibration
Test Sieves	Brass or Stainless Steel
Accessories	- Two supporting SS Rods - Sieve retaining assembly - Rubber pad
Power Supply	220 Volts

The fine charcoal powder was then activated by adding KOH (Potassium Hydroxide) in the weight ratio of 1:1. As soon as the activated carbon powder was produced, a commercial PTFE (Polytetrafluoroethylene) was added as to bind the mixture to obtain a slurry mixture. The commercially available PTFE solution bottle is shown in Figure 3.4. the obtained slurry was poured down in the mould, shown in Figure 3.5, and was baked in an electric oven at 110 degree Celsius for 2 hours dry it out and then the electrode formed will be dry solid. the obtained slurry was poured down in the mould, shown in Figure 3.5, and was baked in an electric oven at 110 degree Celsius for 2 hours dry it out and then the electrode formed will be dry solid. The fine charcoal powder was then activated by adding KOH (Potassium Hydroxide) in the weight ratio of 1:1. As soon as the activated carbon powder was produced, a commercial PTFE (Polytetrafluoroethylene) was added as to bind the mixture to obtain a slurry mixture. The commercially available PTFE solution bottle was used. As soon as the activated carbon powder was produced, a commercial PTFE (Polytetrafluoroethylene) was added as to bind the mixture to obtain a slurry mixture.

Figure 3.4:A bottle of commercially available liquid PTFE

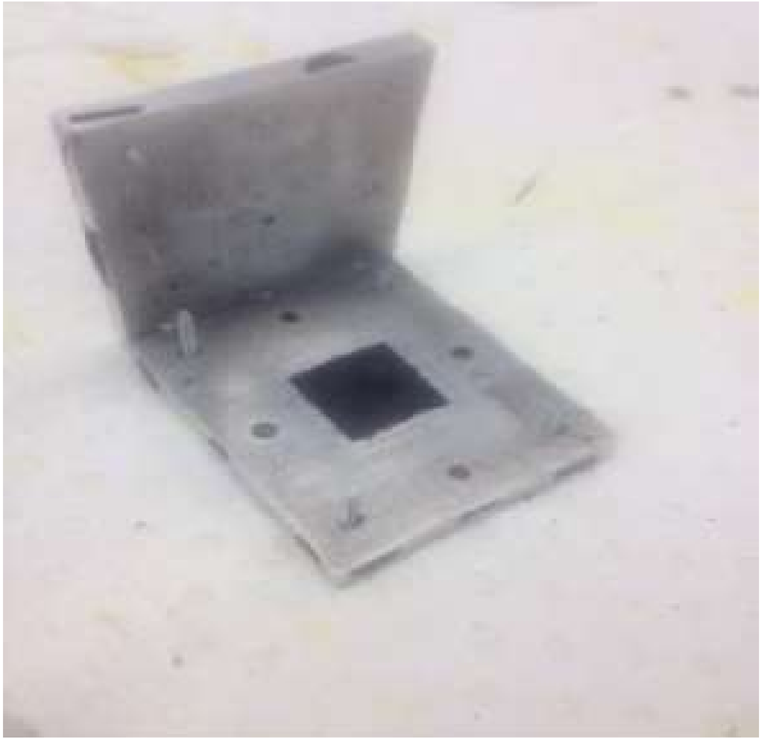


Figure3.5: Mould with cavity filled with slurry mixture to obtain desired shape

This solid electrode was soaked in a dilute 1 mol. sulphuric acid and used in the proton battery. The following are the specifications for PTFE used.

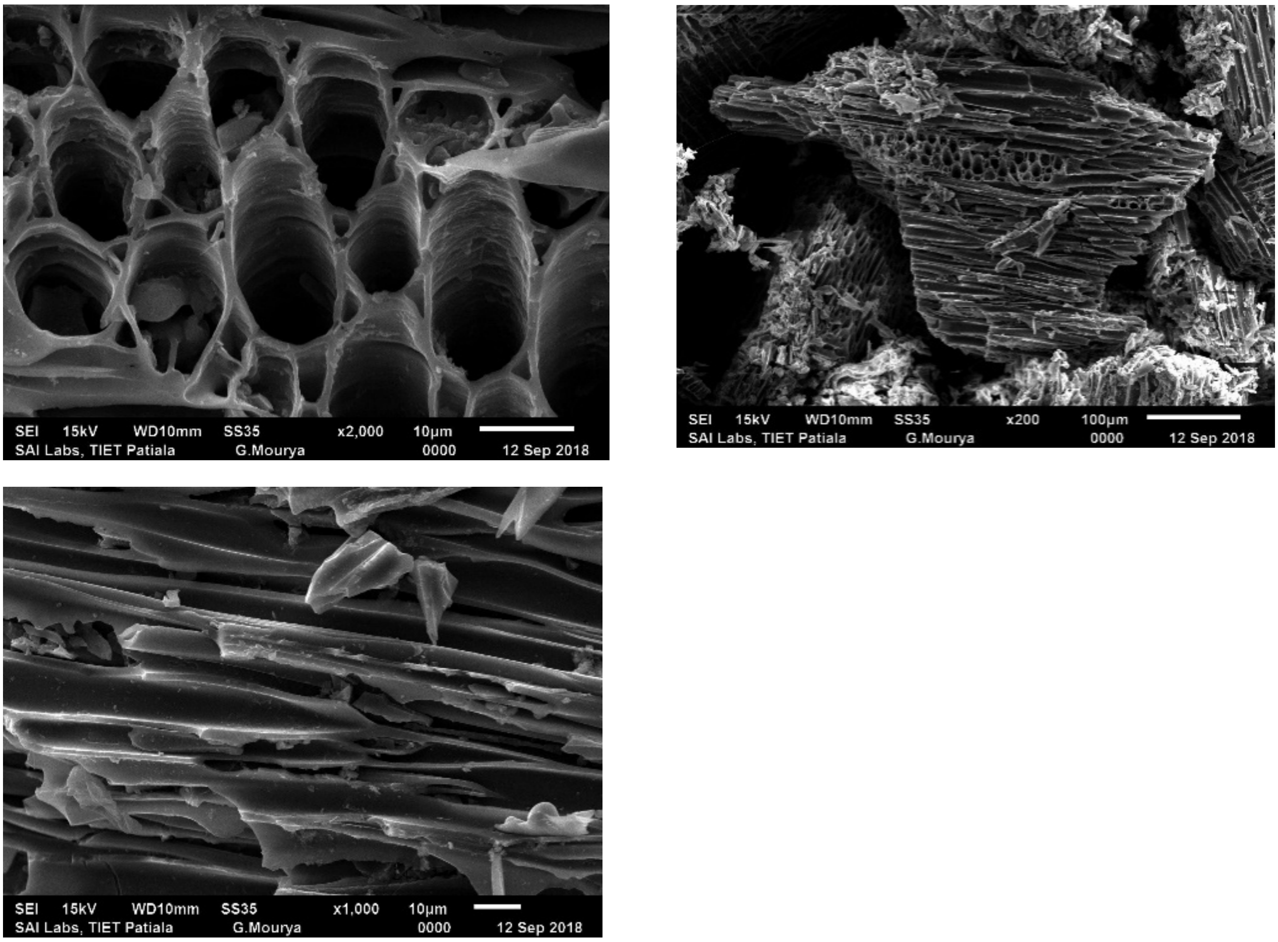


Figure 3.6:SEM image at a different resolution of electrode

Scanning electrode microscopy as the name signifies is the method to scan a substance to a certain depth of its composition and magnification is really important up to which the true changes are seen in the material after the experiment is shown.

Chapter 4 : EXPERIMENTAL SETUP AND TESTING

The setup used in the experiment is a modified form of PEMFC or as it is said generally the proton flow battery. We are using the activated carbon electrode for storing hydrogen. The PEMFC we use here is reversible in nature meaning that the call acts as an electrolyzer and fuel cell both. We can even call it as a Unitized Regenerative Fuel cell. In the E-mode the water hydrolysis on one side of the cell causes hydrogen ions to come from the membrane and , The stored protons come out of the storage material under the influence of an opposite electric potential in the case of fuel cell. The stored protons then are released under potential difference to react with oxygen and electrons to form water. It is a very new concept of storing hydrogen in the electrode and producing no gaseous form. Thus, this makes the system safer than other types of storage. This is the way electricity is produced back from he stored fuel. It is to be noted that the experimentation was carried out in the energy lab.

4.1 Material of the End Plates

One very important component that holds the system upright is bipolar plates. These plates need to be resistant to any corrosion or physical, chemical hindrance. thus, these plates are preferred in the material titanium plates or of stainless steel. In this case we have used SS316. Stainless steel contains high electrical and thermal conductivity. Hence, here we used SS316 stainless steel.

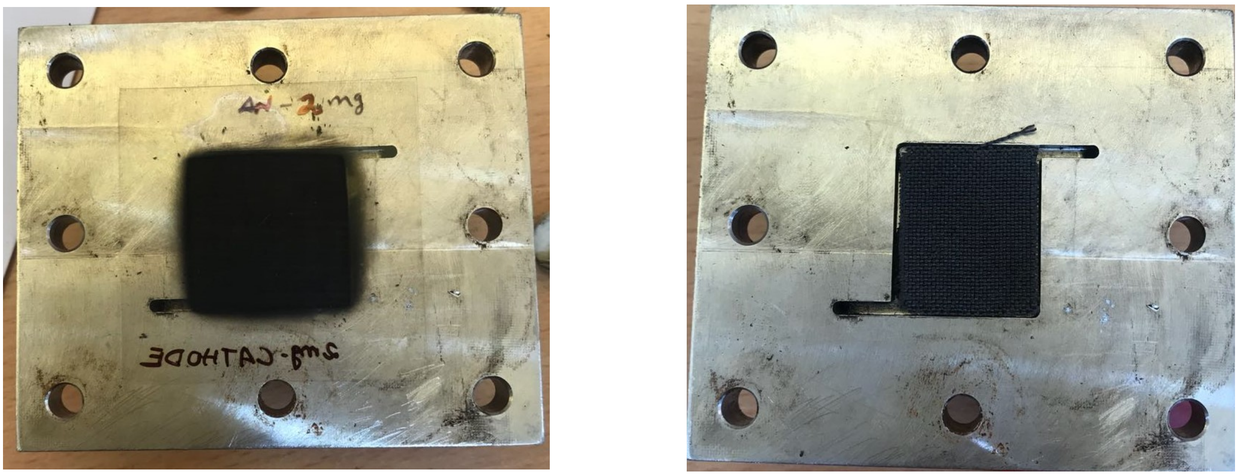


Figure 4.1: MEA 2 end plates

These plates need to be resistant to any corrosion or physical, chemical hindrance. thus, these plates are preferred in the material titanium plates or of stainless steel. these plates are preferred in the material titanium plates or of stainless steel. In this case we have used SS316. Stainless steel contains high electrical and thermal conductivity. Hence, here we used SS316 stainless steel.

4.2 Flow Channels

Flow channels are built to perform a very important role in fuel cell. Flow channels are made extruded in the bipolar plates at the centre which is equal to active area of the cell. The appropriate circulation distribution of the reactant gases over the electrode to increase the rate of reaction and uniform stable operation. There are many patterns for designing the flow channels. Although the most efficient flow channel has been the parallel channels. Researchers have worked on tdifferent patterns for this purpose.

4.3 Gas diffusion layer

The gas diffusion layer, as the name signifies gas diffusion through the GDL is important to remove all the unnecessary molecules and dust. The gas is diffused to the electrode side. The GDL is made porous material which is also electrically conductive to transfer the current from the catalyst to the end plates.

As we have already discussed in this proton battery the E-mode is responsible to get the hydrogen ions into the electrode. Further is the storage of the hydrogen is needed (more than the capacity of the electrode to store) then gas cylinders are appointed enough to store the additional gas. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. There effectiveness to diffuse gives current to flow in the circuit a greater boost.

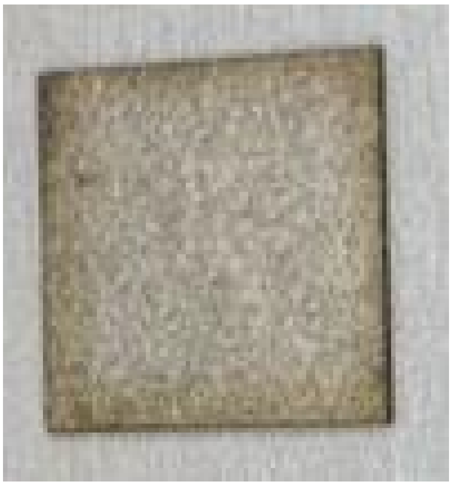


Figure 4.2: Sintered Titanium Fuel

The gas diffusion layer, as the name signifies gas diffusion through the GDL is important to remove all the unnecessary molecules and dust. The gas is diffused to the electrode side. The GDL is made porous material which is also electrically conductive to transfer the current from the catalyst to the end plates. Further is the storage of the hydrogen is needed (more than the capacity of the electrode to store) then gas cylinders are appointed enough to store the additional gas. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst.

Table 4.1: Specifications of the GDL

Sr no.	Description	Value
1	production	Bekaert Germany
2	product	Sintered titanium felt
3	thickness	1mm
4	size	27 × 27mm
5	porosity	50% - 65%
6	Fibre diameter	20µm

Further is the storage of the hydrogen is needed (more than the capacity of the electrode to store) then gas cylinders are appointed enough to store the additional gas. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion layer, as the name signifies gas diffusion through the GDL is important to remove all the unnecessary molecules and dust. The gas is diffused to the electrode side. The GDL is made porous material which is also electrically conductive to transfer the current from the catalyst to the end plates. . The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion layer, as the name signifies gas diffusion through the GDL is important to remove all the unnecessary molecules and dust. The gas is diffused to the electrode side. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion layer, as the name signifies gas diffusion through the GDL is important to remove all the unnecessary molecules and dust. The gas is diffused to the electrode side.

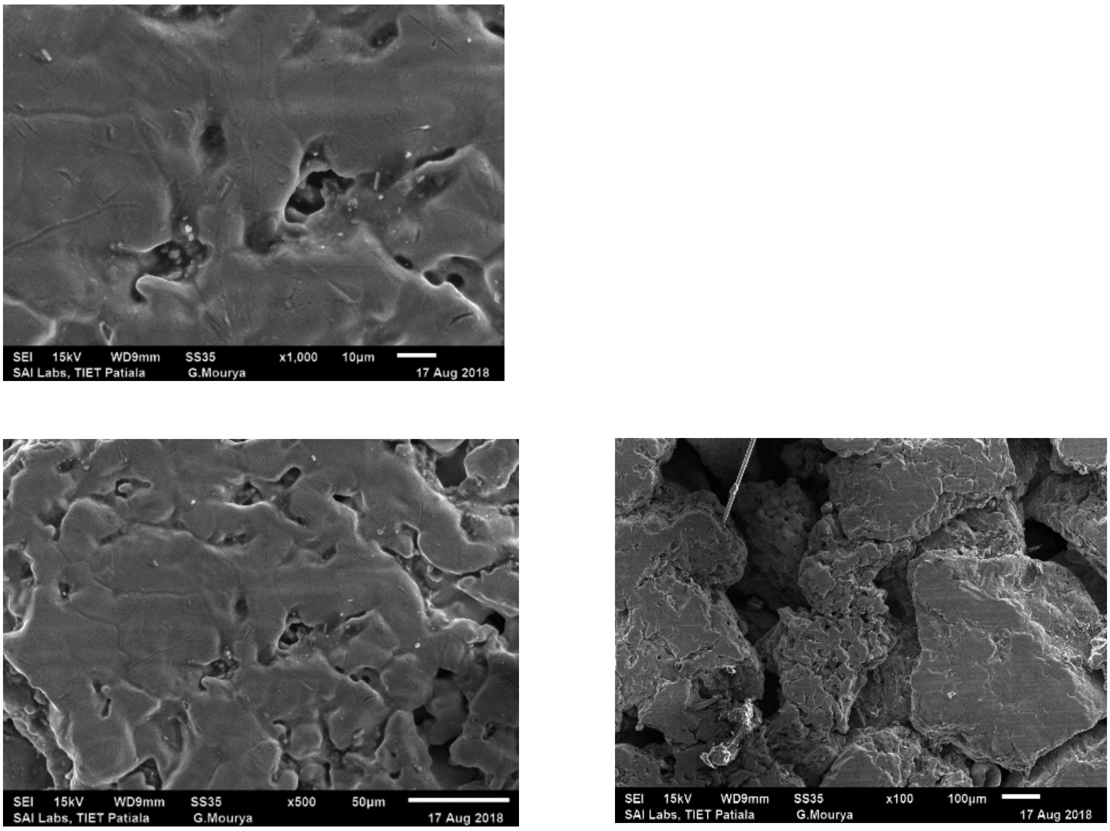


Figure 4.3:SEM images of GDL surface at different resolutions

Proton flow battery although similar to the traditional set-up of the URFC but the different components included in the set-up are given below

- Hydrogen side end plate (modified by machining flow channels and headers in plate)
- Storage electrode – activated carbon electrode in this project
- Gas diffusion layer – sintered titanium felt in this project

The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion layer, as the name signifies gas diffusion through the GDL is important to remove all the unnecessary molecules and dust. The gas is diffused to the electrode side. The GDL is made porous material which is also electrically conductive to transfer the current from the catalyst to the end plates. . The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion layer, as the name signifies gas diffusion through the GDL is important to remove all the unnecessary molecules and dust. The gas is diffused to the electrode side. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst. The gas diffusion as the name tells is a pathway between the bipolar plates and the catalyst.

The exact sandwich of the MEA is shown below which made up of the new components highlighted in the diagram and clearly shown :

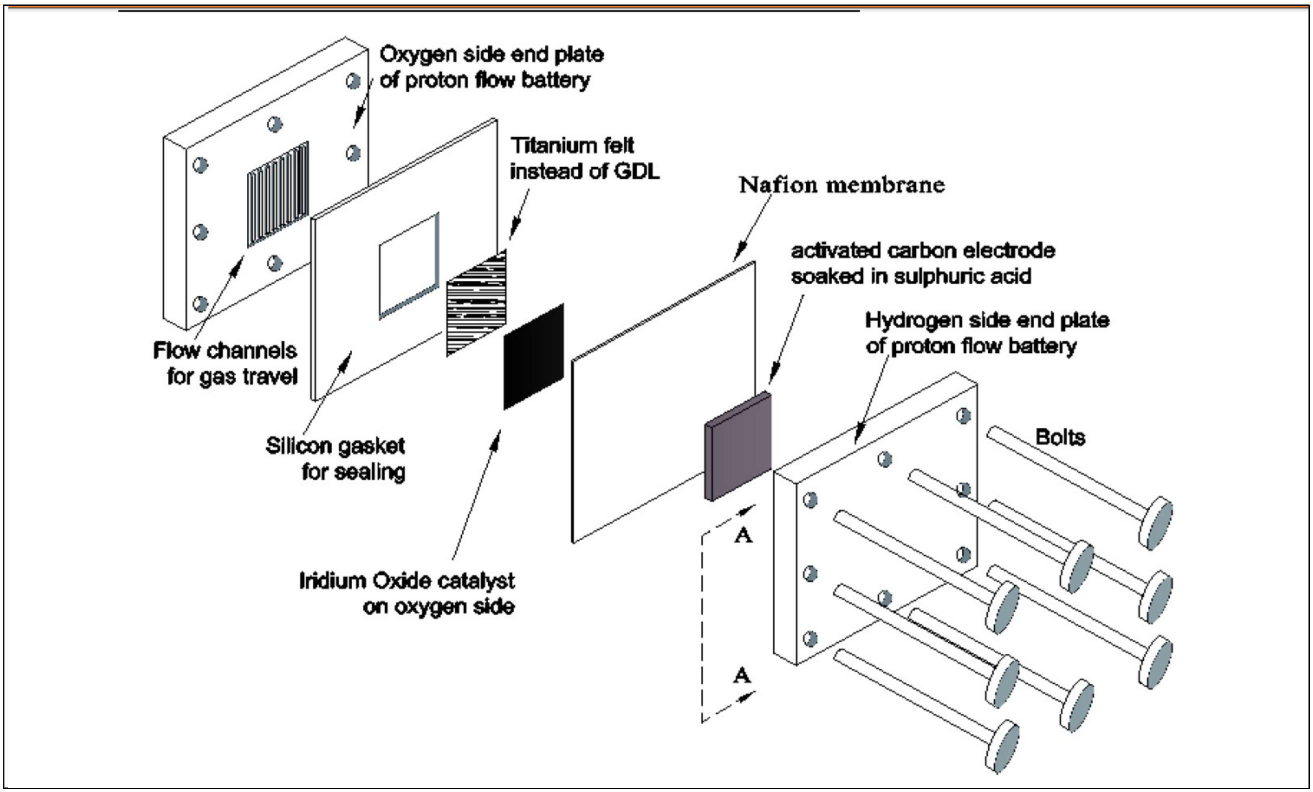


Figure 4.4: Exploded view of the PFB showing all the components of the cell

4.4 Membrane electrode assembly

Acid, for example, sulphuric acid, is connected onto this polymer arrange for particle trade, in this way layers are proton directing. In this sense the principal limit of the electrolyte is to let only protons pass through it from anode to cathode. Properties of the membrane such as thickness of the membrane equivalent weight and capacity to reduce the gas crossover work as very important features. The ideal polymer must have efficient proton conductivity, blend and warm security, quality, versatility, low gas vulnerability, low water drag, speedy vitality for cathode reactions, straightforwardness, and incredible availability. The films are typically polymers altered to incorporate particles, for example, sulfonic gatherings. More thin layers increase execution capability and proton conductivity. Be that as it may, from the lifetime point of view; the thinner membranes have reduced severely the physical strength and higher gas vulnerability, allowing more gas crossover, which revives corrosion and short circuit. Properties of the membrane such as thickness of the membrane equivalent weight and capacity to reduce the gas crossover work as very important features. Acid, for example, sulphuric acid, is connected onto this polymer arrange for particle trade, in this way layers are proton directing.

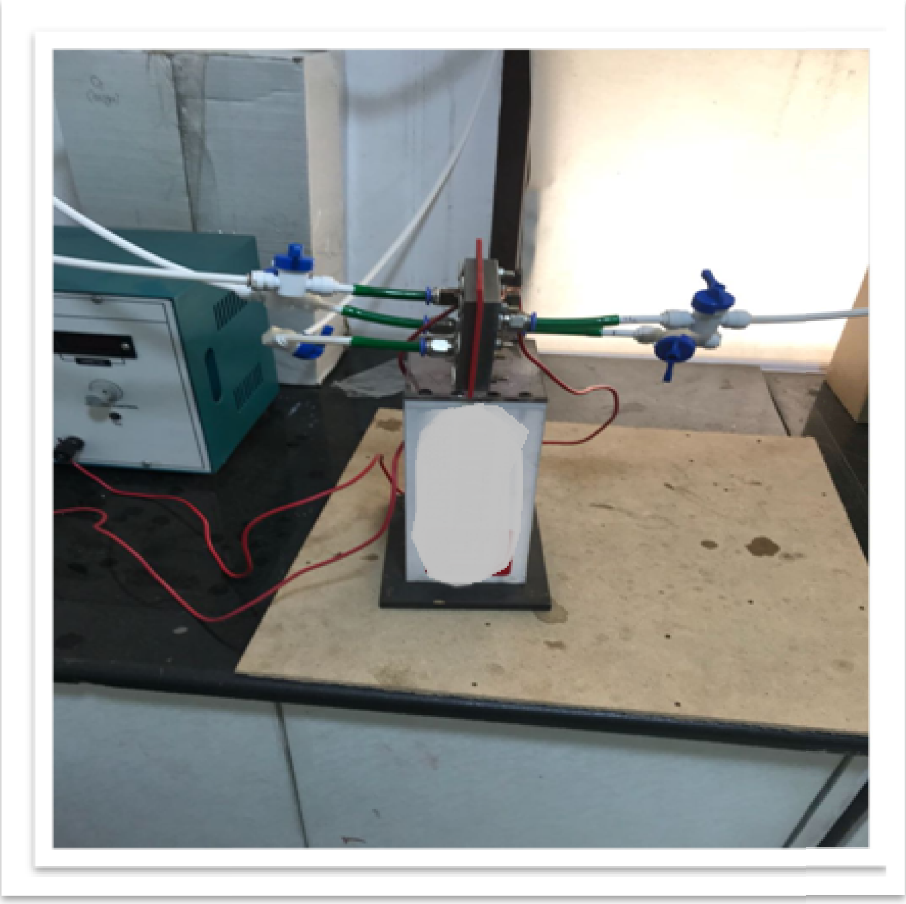


Figure 4.5: MEA in working in the energy lab at CUPB

4.5 Activated carbon electrode

This includes fabrication of activated carbon electrode using PTFE binder 'Prosopis Julifora' tree was used as the precursor for carbon. The wood of the named tree was cut in pieces and heated in an electric oven (shown in Figure 3.1) at 110 degree Celsius until the smoke was obsolete leaving the charcoal behind.

The catalyst layer is made of 30% of ionomer of the membrane to stimulate the ion transfer via the membrane. Numerous methods have been developed to produce MEA such as GDL Spraying, Decal methods, Membrane Spraying. GDLs are the main components in PEMFCs. The main work of the GDL is to let the gas diffuse through it. The property of the backing material is to let the gas to diffuse effectively to the catalyst layer. GDL works as a transit between the current collectors, bipolar plates and the catalyst layer. Apart from this, the GDL is responsible of getting the water produced in the reaction transported away from the electrolyte. The porous tendency of the backing material improves the effective diffusion of each reactant gas to the catalyst on the MEA. GDLs are the main components in PEMFCs.

4.5.1 The end-plates and the flow channel

The two plates on each side of the MEA are called 'end plates' or 'flowfield plates'. The completely working bipolar plates are fundamental for multi-cell arrangements, by electrically associating the anode and cathode of the adjoining cell. The bipolar plate is for various purposes. Its most imperative job is to supply reactant gases to the gas dissemination terminals (GDEs) through stream channels. Bipolar plates give electrical associations between the individual cells. They definitely would need to expel water created at the cathode successfully. The most widely recognized material utilized for bipolar plates in PEMFC stacks is graphite. Graphite has great electronic conductivity, erosion opposition and furthermore low thickness. Composite materials and metals, for example, steel, copper and so forth are likewise utilized in creating as bipolar plates.

4.6 Experimental Setup

4.6.1 DC power supply

Instek DC power supply was given to the fuel cell system. It works on Dc supply plainly. This is shown in order to demonstrate the E mode of the fuel cell where splitting of water takes place.

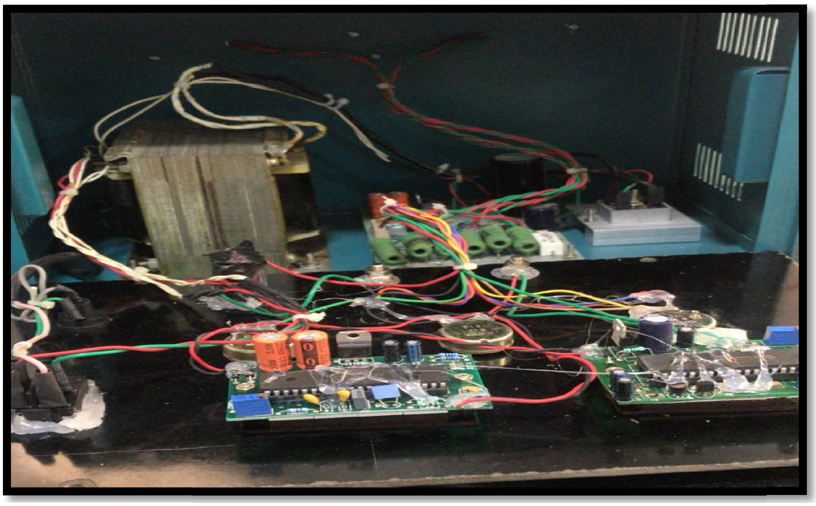


Figure 4.6: The DC power supply

4.6.2 Gas collection cylinders

There two gas cylinders appointed where it is graduated to measure the volume of the gas collected. The gas collectors are properly sealed to avoid any leakage. Oxygen and hydrogen both the cylinders have been appointed as the electrolysis of the water takes place. There two gas cylinders appointed where it is graduated to measure the volume of the gas collected. The gas collectors are properly sealed to avoid any leakage.

Figure 4.7: Oxygen Gas Cylinder

4.6.3 Setting-up of the apparatus

Two multimetres and the variable resistor in the circuit for current flow were established due to the completion of the circuit. Thus the accommodation of the electrode made y us was done by horizontally placing the entire setup where hydrogen side is down.

4.7 Experiment Procedure

The bipolar plate is for various purposes. Its most imperative job is to supply reactant gases to the gas dissemination terminals (GDEs) through stream channels. Bipolar plates give electrical associations between the individual cells. They definitely would need to expel water created at the cathode successfully. The most widely recognized material utilized for bipolar plates in PEMFC stacks is graphite. Graphite has great electronic conductivity, erosion opposition and furthermore low thickness. The ideal polymer must have efficient proton conductivity, blend and warm security, quality, versatility, low gas vulnerability, low water drag, speedy vitality for cathode reactions, straightforwardness, and incredible availability. The films are typically polymers altered to incorporate particles, for example, sulfonic gatherings. More thin layers increase execution capability and proton conductivity. Be that as it may, from the lifetime point of view; the thinner membranes have reduced severely the physical strength and higher gas vulnerability, allowing more gas crossover, which revives corrosion and short circuit. Properties of the membrane such as thickness of the membrane equivalent weight and capacity to reduce the gas crossover work as very important features.

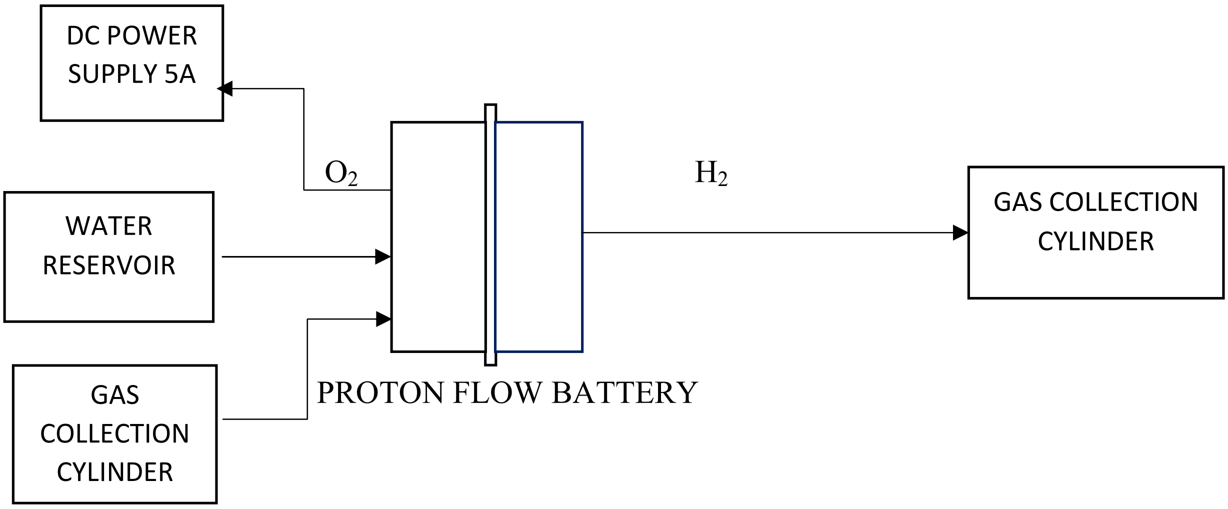


Figure 4.8: Flow diagram for E mode

The first circuit shows the PFB acting as an electrolyzer for splitting of the hydrogen molecule and taking in the activated carbon as gas collecting part. The fuel cell mode was given in the second setup and now we are able to differentiate which part is playing its role. The fuel cell setup is in regarding the gas utilization to form water and electricity. Electrolyzer is working in its own way. The oxygen-side electrode was then fed with oxygen gas previously produced in E-mode and collected in the storage cylinder. The external load or resistor that is variable in its way is employed in the fuel cell mode only. The fuel cell mode was given in the second setup and now we are able to differentiate which part is playing its role. The fuel cell setup is in regarding the gas utilization to form water and electricity. The films are typically polymers altered to incorporate particles, for example, sulfonic gatherings. More thin layers increase execution capability and proton conductivity. Its most imperative job is to supply reactant gases to the gas dissemination terminals (GDEs) through stream channels. Bipolar plates give electrical associations between the individual cells. The external load or resistor that is variable in its way is employed in the fuel cell mode only. The fuel cell mode was given in the second setup and now we are able to differentiate which part is playing its role.

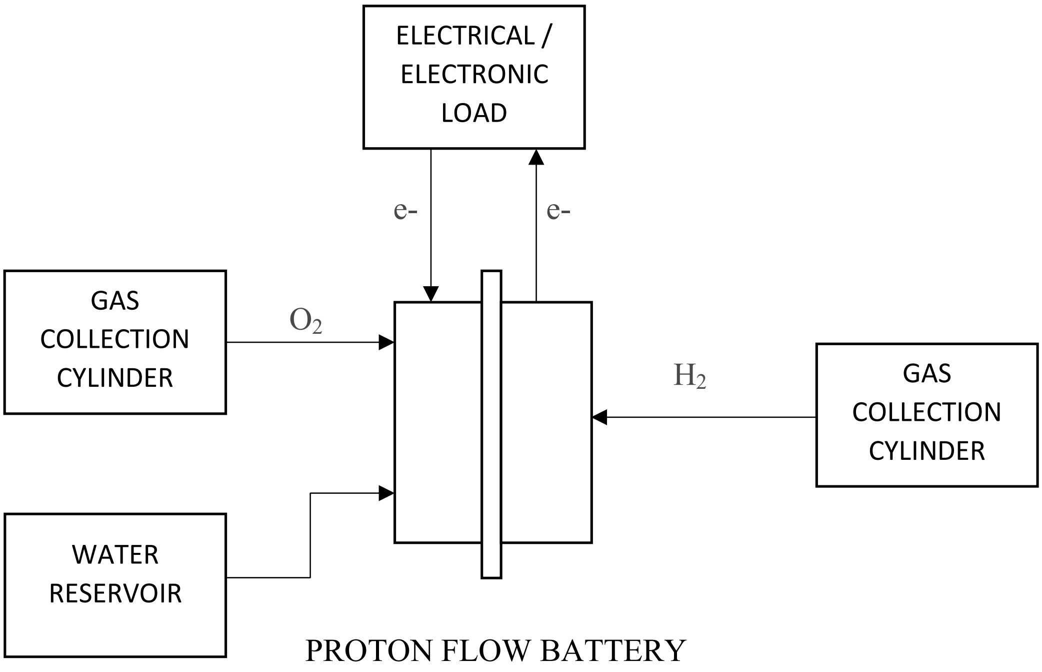


Figure 4.9: Fuel cell mode

Chapter 5 : RESULTS AND DISCUSSIONS

To test the feasibility of the fabricated reversible PEMFC, the single cell was made to run in electrolyser mode (E-mode) and fuel cell mode (FC-mode) using two different membrane-electrode-assembly (MEA) named as MEA-1 ND MEA-2. Both the MEAs contained catalyst loading of different loading densities viz. 1 mg/cm^2 and 2 mg/cm^2, respectively. The cell was supplied with water and electric potential was applied across the cell that splits water in oxygen and hydrogen. In the present work, electrolyser mode is also referred to as charging and FC-mode as discharging.

5.1 Charging results

The following results were obtained when the fabricated reversible PEMFC, what we are naming as a proton flow battery (PFB), was charged by the applying the electrical potential across the cell in the voltage range between from 0-3.5 V. The cut-in voltage, where the water disassociation was observed to be started, was found to be1.5 V. The produced oxygen during charging was allowed to move out of the cell through the provided flow channel in the end-plates and collected in a cylinder. The hydrogen further got split into ions viz. H^+ and e^- under the influence of the catalyst loaded on the membrane-electrode-assembly (MEA).

The PFB was charged for 4 hours, until a rapid production of hydrogen gas was observed in the gas collection cylinder. The cell was initially at a low voltage to increase the probability of hydrogen entering the activated carbon electrode and discourage the formation of H_2. Figure 5.1 shows the voltage vs current graph of the PFB in E-mode or during charging. It could be seen from the figure that the V-I curve showed a fairly linear behavior. It is to be noted that he plateauformed in the curve indicates the adsorption of hydrogen in the storage electrode either chemically or physically.Figures 5.1 and 5.2 represents the MEA-1 and MEA-2 in the system, respectively. The operation was ceased when the rapid generation of gas bubbles was observed in the gas collection cylinders indicating that the storage is full and all the produced H ions are combining with electrons to form hydrogen gas instead of electrochemical adsorption.

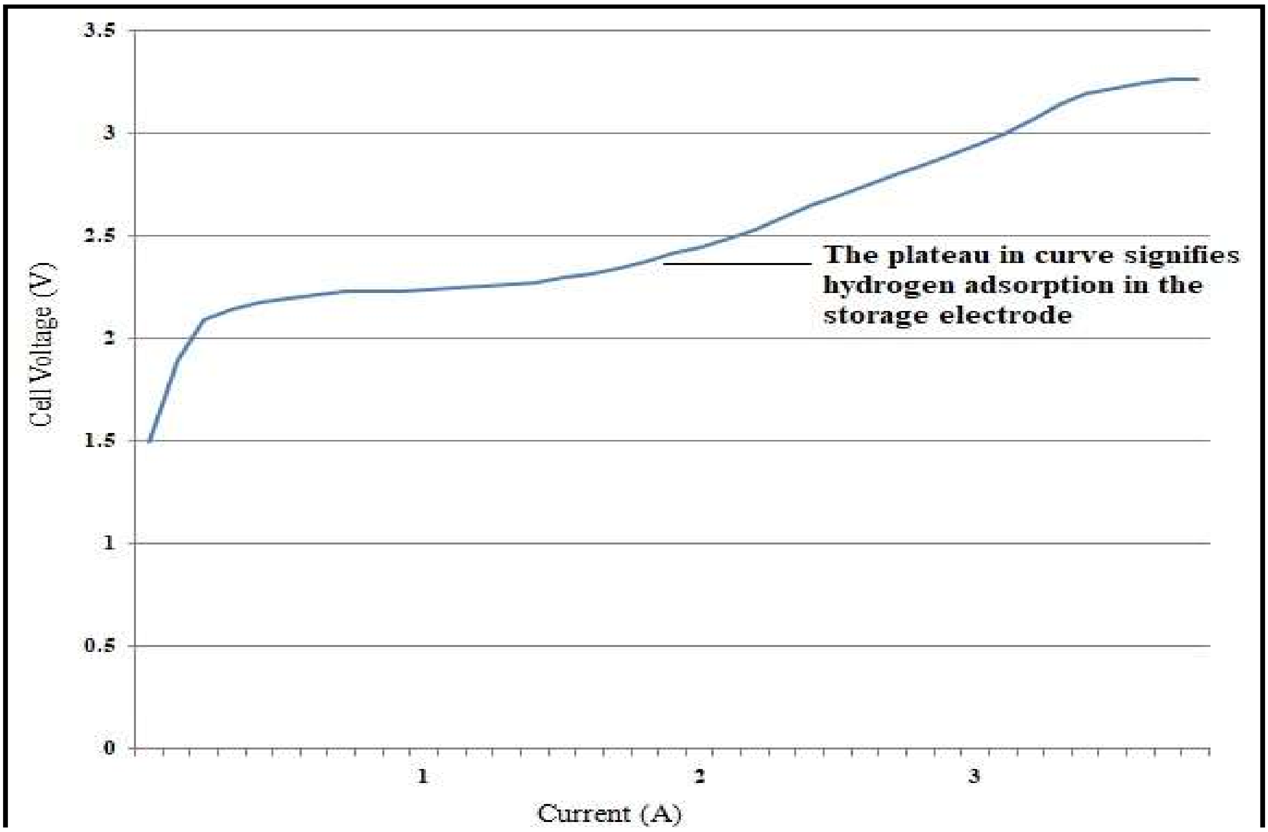


Figure 5.1:V-I curve for the E mode operation of PFB containing MEA-1

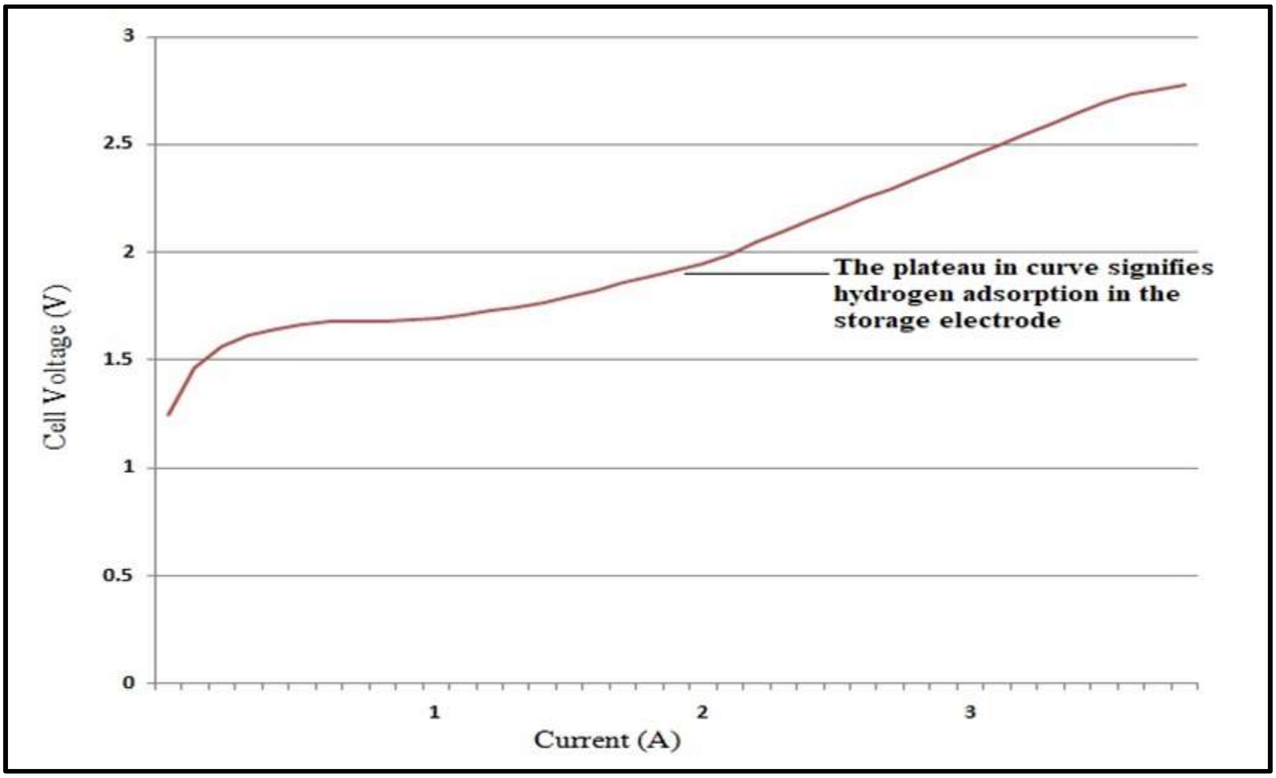


Figure 5.2:V-I curve for the E-mode operation of PFB containing MEA-2

In the case of MEA-2, as shown in Figure 5.2,due comparatively higher catalytic loading of 2 mg/cm^{2}an earlier cut in voltage of 1.25 V was observed. Due to higher Platinum (Pt) catalyst, an early water disassociation reaction was observed thereby, liberating oxygen gas.Similar to Figure 18, plateau in Figure 19 signifies the adsorption of hydrogen in the electrode. The graphshows a higher gradient in VI curve than the first case and theduration of the dissociation is the same herei.e., 4 hours.

In E-mode, the water was continuously supplied to the cell and hydrogen protons (H-protons) were emerged on the membrane. The water consumption was recorded and shown in the form of graph in Figure 5.3.

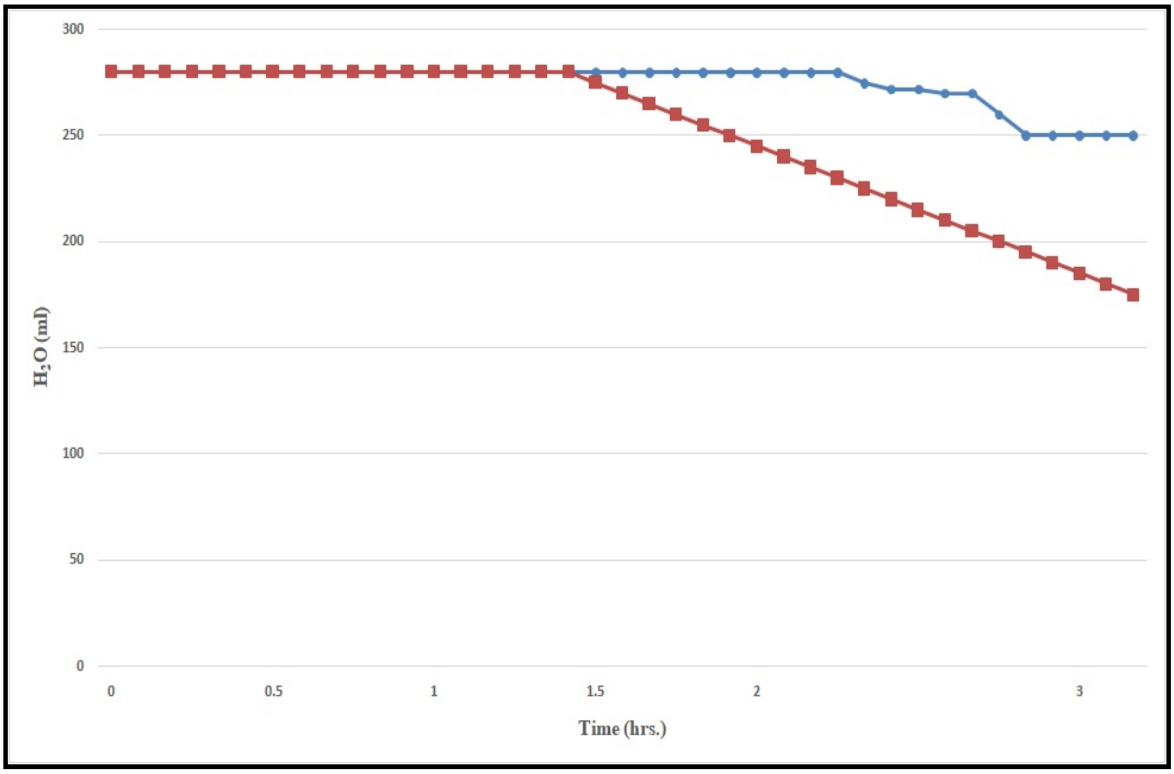


Figure 5.3: Comparative graph of water consumption with time when PFB was run in E-mode with MEA-1 and MEA-2

Both the MEAs are under clear observation here and it shows that for MEA 1 the water level is decreasing slightly from its source. But the MEA 2 graph represents sharper and much earlier fall in the readings, Pt here being 2 mg Pt/cm^2. The water level decrease is obvious due to the dissociation. This sharp downfall is in correspondence with the sudden increase in the hydrogen gas formation.

This is due to the fact that MEA 1 carries 1mg Pt/cm^2 which means the catalytic activity is normal in this case. But the MEA 2 graph represents sharper fall, Pt here being 2 mg/cm^2.Therefore, the catalytic activity is more due to larger amount ofPlatinum in the second case.

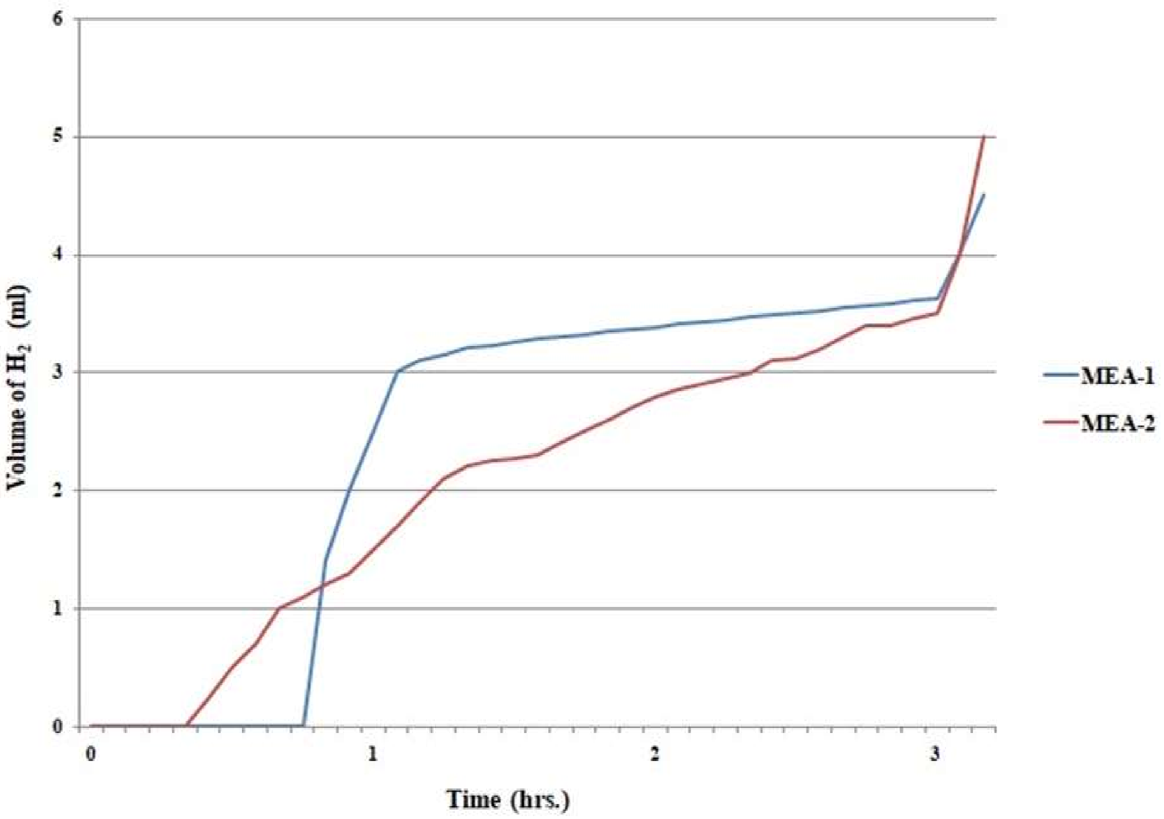


Figure 5.4: Comparative graph of hydrogen gas production in E-mode of the PFB equipped with MEA-1 and MEA-2

Here, in this graph the result demonstrates that both the MEAs have similarity in trend. The content of hydrogen gives a sharp increase after some time, this is due to the saturation with hydrogen ions in the storage electrode. Showing these both membranes' graph in one is important as it shows the volume adsorption in case of MEA-2 far more considerable than in the case of MEA-1.The content of hydrogen gives a sharp increase after some time, this is due to the saturation with hydrogen ions in the storage electrode. Showing these both membranes' graph in one is important as it shows the volume adsorption in case of MEA-2 far more considerable than in the case of MEA-1. The content of Hydrogen release in the system is much earlier for the MEA-2 (as shown in Figure 21).The reason to this is the higher catalytic loading in the MEA-2 that increases the reaction rate and hence, the release of hydrogen. The content of hydrogen gives a sharp increase after some time, this is due to the saturation with hydrogen ions in the storage electrode. The content of hydrogen gives a sharp increase after some time, this is due to the saturation with hydrogen ions in the storage electrode. Showing these both membranes' graph in one is important as it shows the volume adsorption in case of MEA-2 far more considerable than in the case of MEA-1. The content of hydrogen gives a sharp increase after some time, this is due to the saturation with hydrogen ions in the storage electrode.

Showing these both membranes' graph in one is important as it shows the volume adsorption in case of MEA-2 far more considerable than in the case of MEA-1.

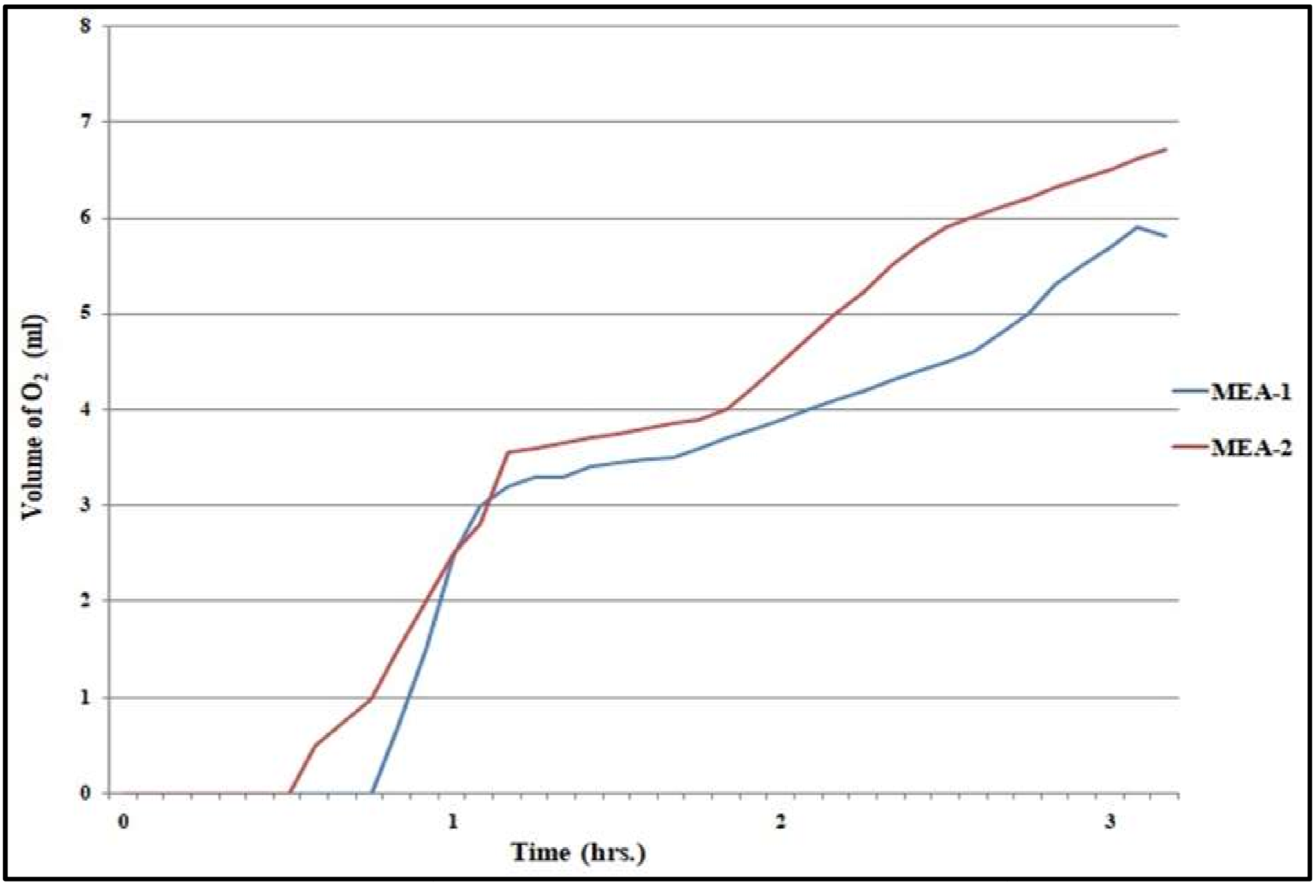


Figure 5.5: Comparative graph of oxygen gas evolution in E-mode of the PFB equipped with MEA-1 and MEA-2

Oxygen is released earlier in the case of MEA-2 than MEA-1 and this is due to the higher catalytic loading of the MEA-2, as shown in Figure 22. Although both the cases are overlapping in trend but MEA-2 has more liberationof oxygen in its case due to higher amount of Platinum enhancing the water dissociation reaction. This is the main reason why the cumulative volume of the gas generated is higher in case of MEA-2. Oxygen is released earlier in the case of MEA-2 than MEA-1 and this is due to the higher catalytic loading of the MEA-2, as shown in Figure 22. Although both the cases are overlapping in trend but MEA-2 has more liberation of oxygen in its case due to higher amount of Platinum enhancing the water dissociation reaction. This is the main reason why the cumulative volume of the gas generated is higher in case of MEA-2. Oxygen is released earlier in the case of MEA-2 than MEA-1 and this is due to the higher catalytic loading of the MEA-2, as shown in Figure 22. Although both the cases are overlapping in trend but MEA-2 has more liberation of oxygen in its case due to higher amount of Platinum enhancing the water dissociation reaction. This is the main reason why the cumulative volume of the gas generated is higher in case of MEA-2.

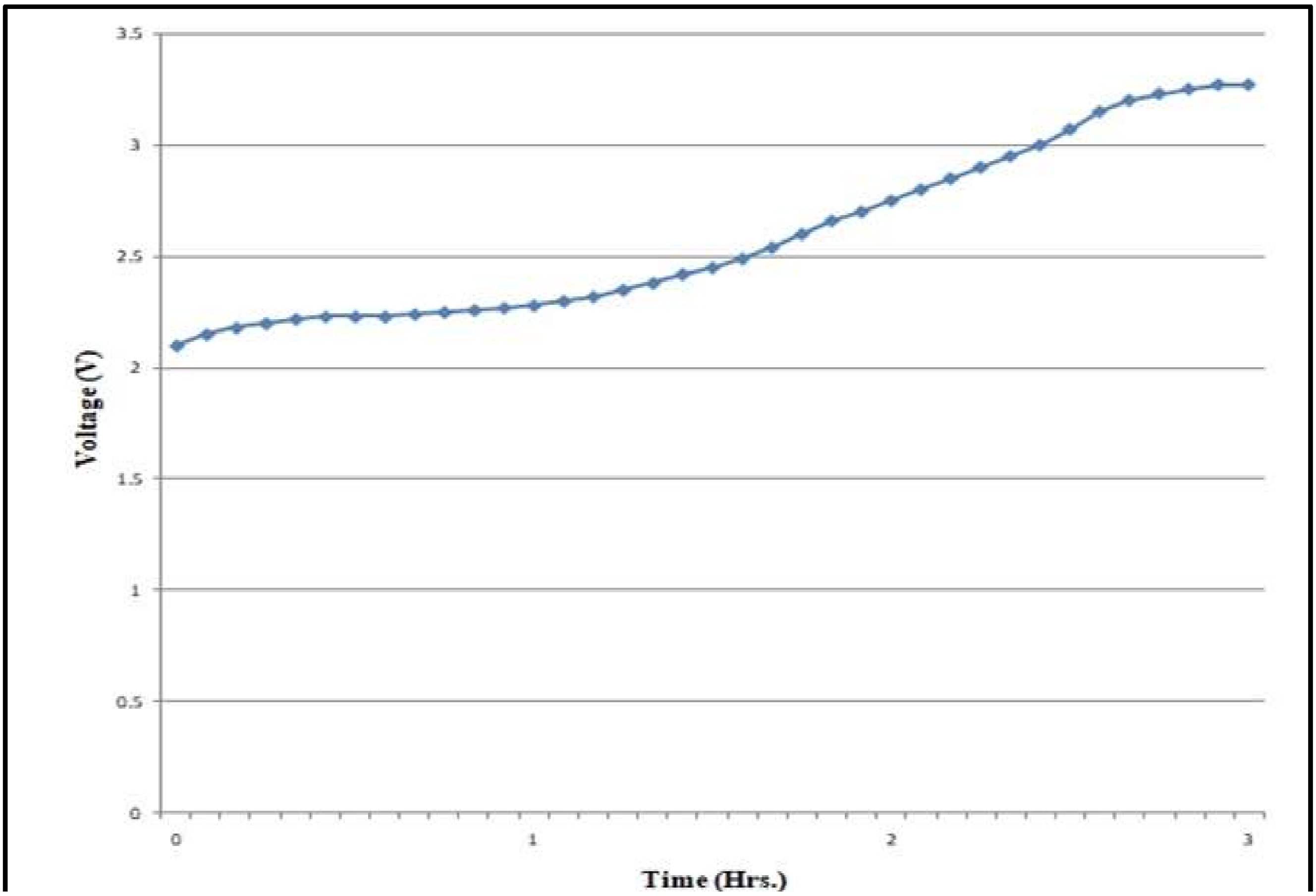


Figure 5.6: Graph showing voltage (V) behavior over time during charging of the PFB with MEA-1

Figure 5.8 and 5.9 shows the voltage vs time graph for MEA-1 and MEA-2, respectively during charging of the PFB.In the case of MEA-1 (as shown in Figure 23),voltage increased gradually for 3 hours before getting stable and dropping down thereafter. There is a desirable stagnancy in the graph at 30 minutes from the start due to the hydrogen ions getting trapped in the electrodes. The graph is representing the MEA 1 in the system. The bend signifies a slowdown in the reading of voltage. This is because the proton battery is getting charged by storing hydrogen in the storage electrode by the process of adsorption. The dip in the reading comes until the storage electrode is filled with the gas and adsorption is to the maximum limit.There is a desirable stagnancy in the graph at 30 minutes from the start due to the hydrogen ions getting trapped in the electrodes. The graph is representing the MEA 1 in the system. The bend signifies a slowdown in the reading of voltage. This is because the proton battery is getting charged by storing hydrogen in the storage electrode by the process of adsorption. The dip in the reading comes until the storage electrode is filled with the gas and adsorption is to the maximum limit.

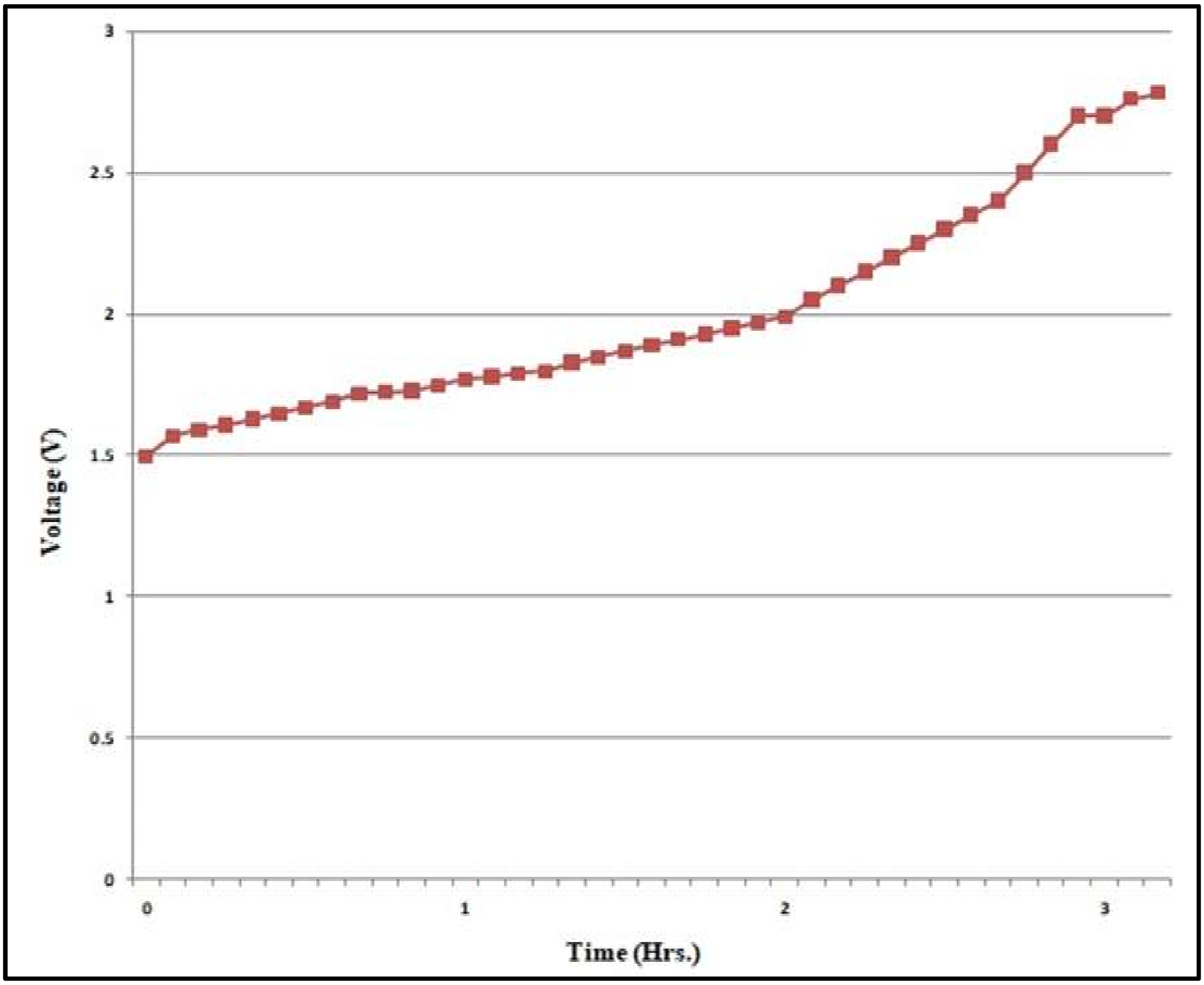


Figure 5.7: Graph showing voltage (V) behavior over time during charging of the PFB with MEA-1

The graph shows MEA-2receiving voltage for 3 hours and is very similar to the MEA 1 case. The gradual increase of voltage starts at 1.5 V to the maximum of 2.25 V. The bend signifies a slowdown in the reading of voltage. This is because the proton battery is getting charged by storing hydrogen in the storage electrode by the process of adsorption. The dip in the reading comes until the storage electrode is filled with the gas and adsorption is to the maximum limit.The bend signifies a slowdown in the reading of voltage. This is because the proton battery is getting charged by storing hydrogen in the storage electrode by the process of adsorption. The dip in the reading comes until the storage electrode is filled with the gas and adsorption is to the maximum limit..The bend signifies a slowdown in the reading of voltage. This is because the proton battery is getting charged by storing hydrogen in the storage electrode by the process of adsorption..The bend signifies a slowdown in the reading of voltage. This is because the proton battery is getting charged by storing hydrogen in the storage electrode by the process of adsorption..The bend signifies a slowdown in the reading of voltage. This is because the proton battery is getting charged by storing hydrogen in the storage electrode by the process of adsorption.

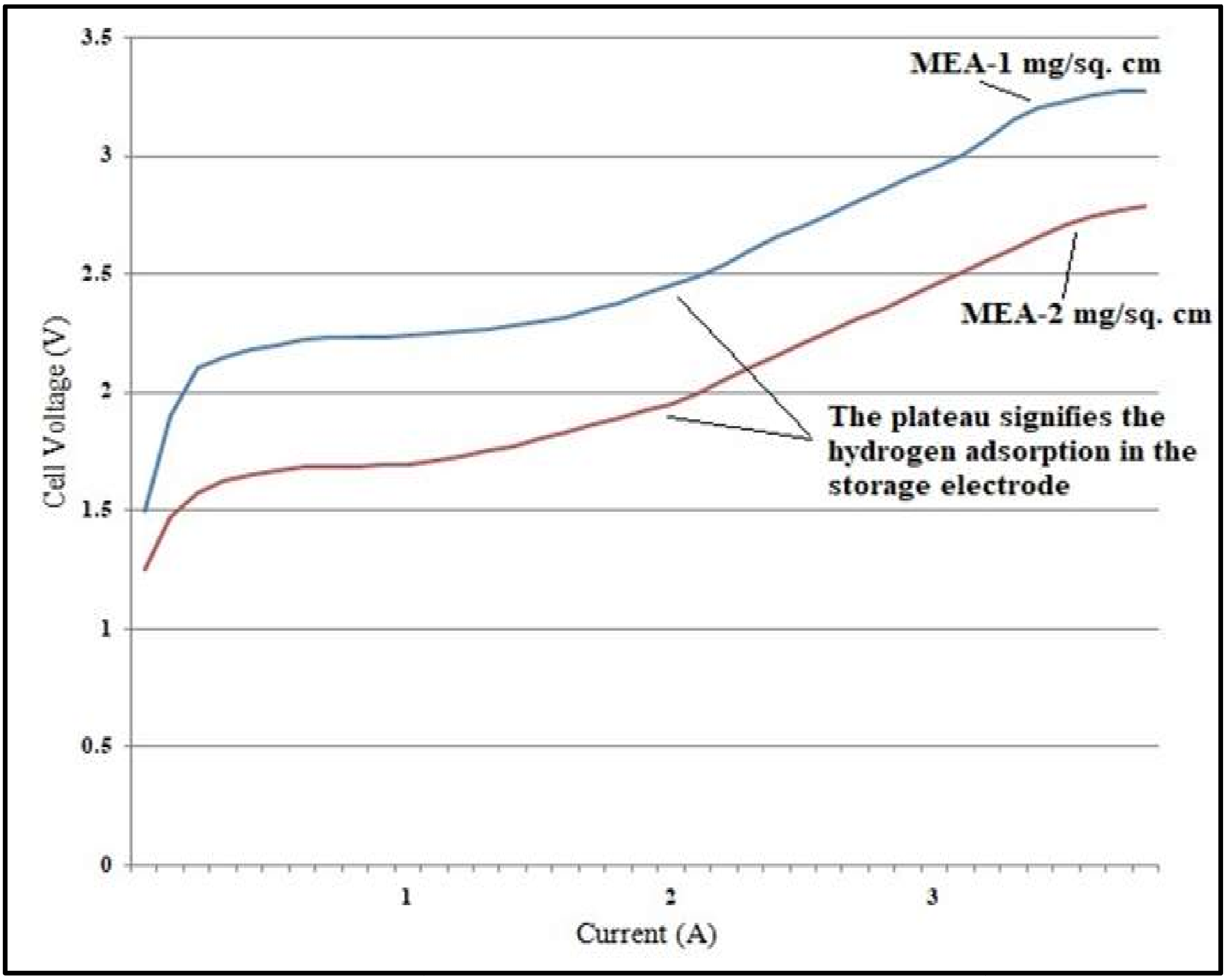


Figure 5.8: Comparative graph of PFB with MEA-1 And MEA-2 showing the cell voltage vs current behavior during charging

The graph demonstrates the important readings and comparison in the charging as the voltage vs current. The MEA 1 and MEA 2 has different electrolyzer modes. This shows that plateau for the hydrogen adsorption in the storage electrode. Storage electrode contains porous surface where the hydrogen H+ ionsare stored to be used in the future for fuel cell mode. Now as it is clearly visible the MEA 2 started showing results earlier than MEA 1. This is because of the higher catalytic loading in MEA 2 that enhances the processof the dissociation.Now as it is clearly visible the MEA 2 started showing results earlier than MEA 1. This is because of the higher catalytic loading in MEA 2 that enhances the process of the dissociation.

5.2 Discharging results

In the FC-mode or during discharging, the cell was connected to an electric load. The time of discharge was recorded and the consumption of oxygen gas from the collection cylinder was noticed. The characteristics of the voltage and current over time are given below. It is to be noted that there is no other hydrogen source of power generation but, the hydrogen stored electrochemically in the activated carbon electrode.

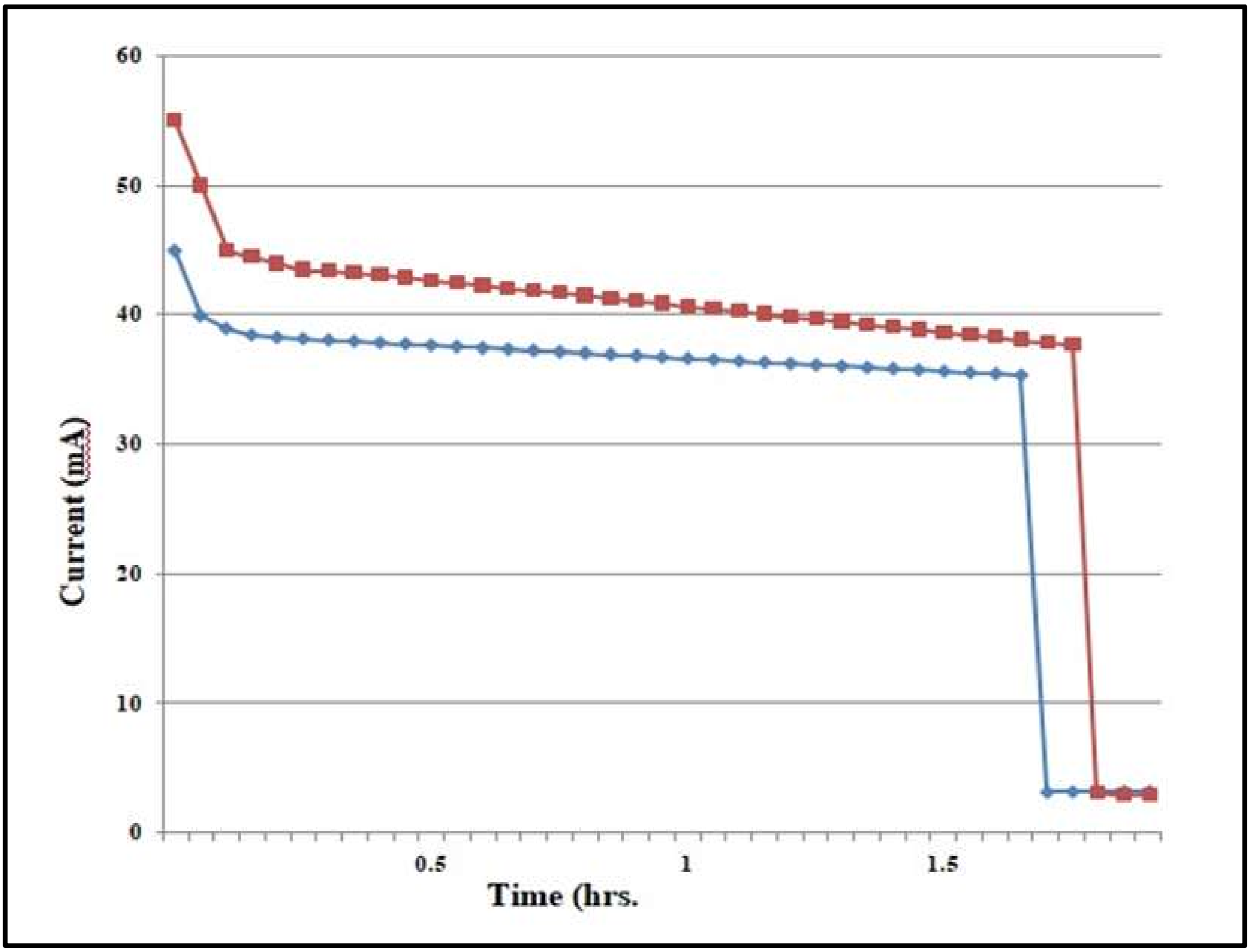


Figure 5.9: Comparative current vs time graph of the PFB with MEA-1 and MEA-2 during discharging

It is clear from Figure 5.10 that MEA-2 showed the current generation earlier than MEA- 1. Overall output from MEA-2 is observed to be better than MEA-1. Thus, we can say that higher catalytic loading per active surface area is more beneficial to us than with the lower loading. Also, after 1.75 hours we observe sudden decrease in the reading. This is due to the decrease in the supply of hydrogen ions from AC electrode after some time.

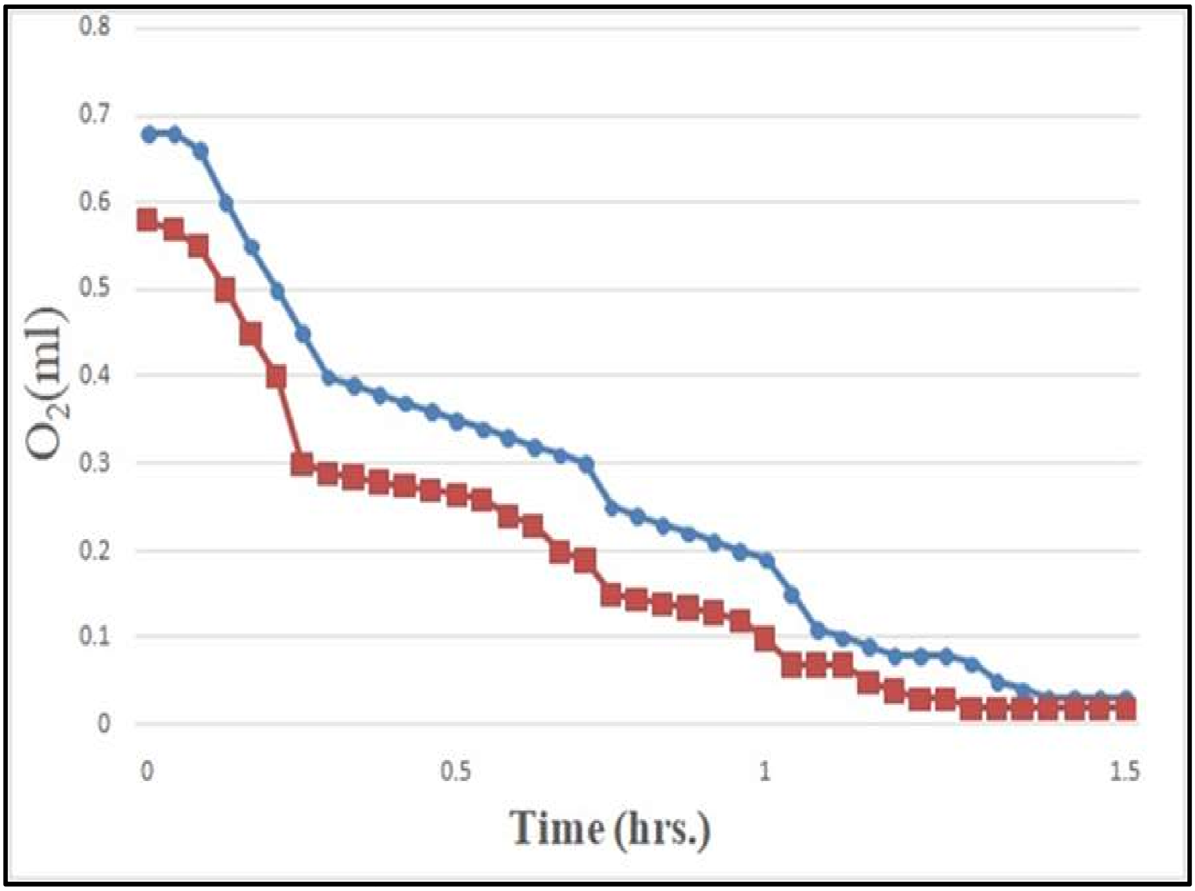


Figure 5.10: Graph showing O_2 consumption over time during discharging of the PFB equipped MEA-1 and MEA-2, respectively

It is clearly visible in Figure 5.11 that represents the MEA 1 and 2 during discharging overtime that in the case of MEA-2 with higher density of catalyst loading the oxygen consumption was at higher rate during high reaction rate. Here the decreasing graph is the consumption of the oxygen required in the fuel cell mode. Hence the required oxygen consumption in MEA 2 is lower than MEA 1. The figures below show the scanning electron microscopic (SEM) images of both the used MEAs after the charge-discharge cycle. The sign of distortion of catalyst on both sides of the MEA was observed in both the cases. This distortion signifies the consumption of the catalyst during the water disassociation reaction, oxygen reduction reaction (ORR) and hydrogen reduction reaction (HRR in charging and discharging cycles of the PFB.The figures below show the scanning electron microscopic (SEM) images of both the used MEAs after the charge-discharge cycle. The sign of distortion of catalyst on both sides of the MEA was observed in both the cases. This distortion signifies the consumption of the catalyst during the water disassociation reaction, oxygen reduction reaction (ORR) and hydrogen reduction reaction (HRR in charging and discharging cycles of the PFB.

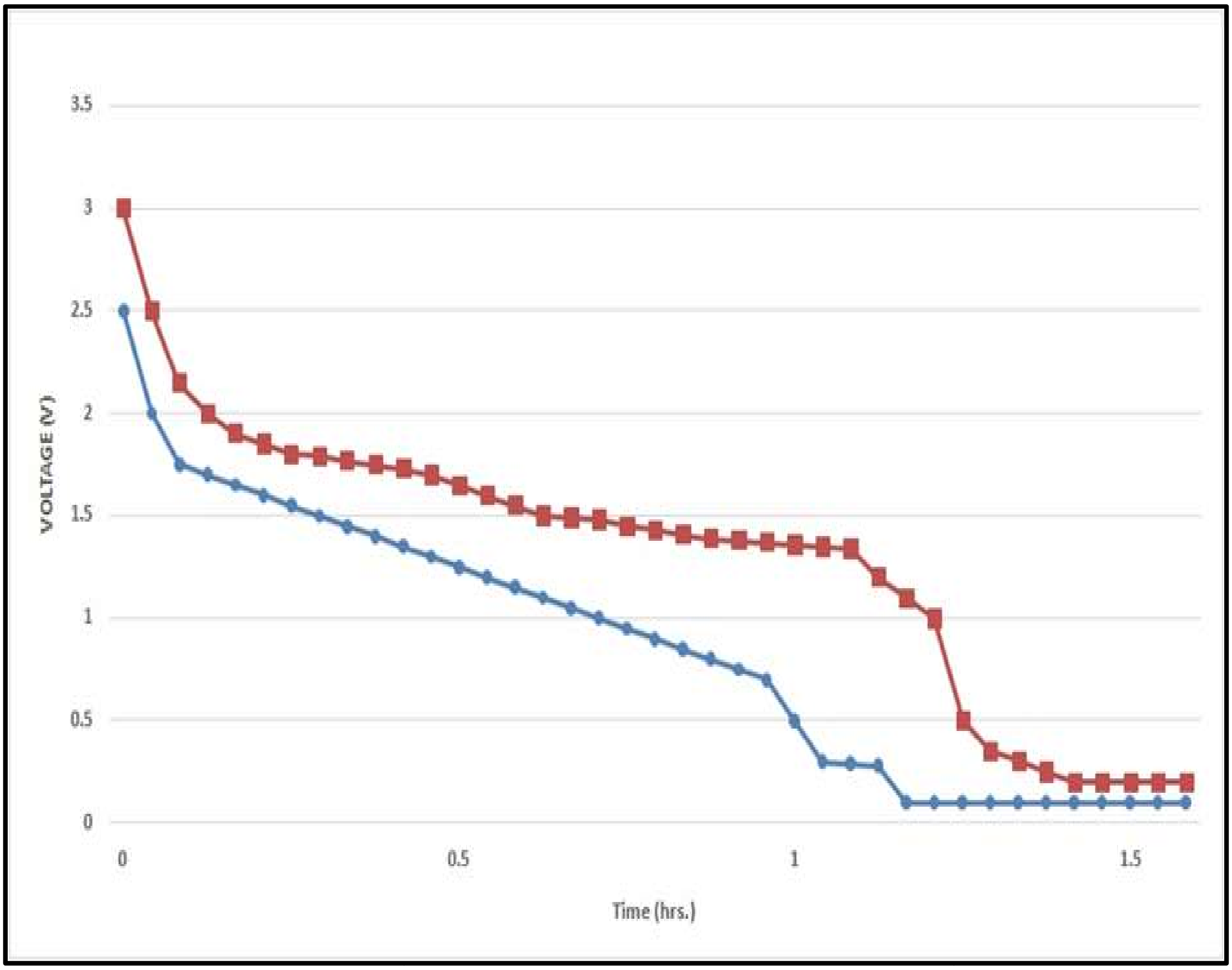


Figure 5.11: The voltage time graph for both the MEAs

Figure5.12 Graph showing Voltage behavior over Time during discharging of the PFB equipped with MEA-1 and MEA-2, respectively.The graph represents the discharging time voltage in progress. The MEA 2 is observed to start from a higher voltage reading than MEA 1. Voltage output in the case of MEA 2 is higher than the MEA 1. It was observed that MEA-2 was able to meet the load demand for longer duration than MEA-1 and exhibit high voltage than the latter. One probable reason for such behavior is high hydrogen reducing reaction (HRR) rate due to higher catalyst loading density compared to MEA

The figures below show the scanning electron microscopic (SEM) images of both the used MEAs after the charge-discharge cycle. The sign of distortion of catalyst on both sides of the MEA was observed in both the cases. This distortion signifies the consumption of the catalyst during the water disassociation reaction, oxygen reduction reaction (ORR) and hydrogen reduction reaction (HRR in charging and discharging cycles of the PFB. The amount of distortion of the catalyst layer or in other words, the consumption of the catalyst in MEA-2 was found to be higher than MEA-1. This is an obvious behavior due to higher loading density of the catalyst.

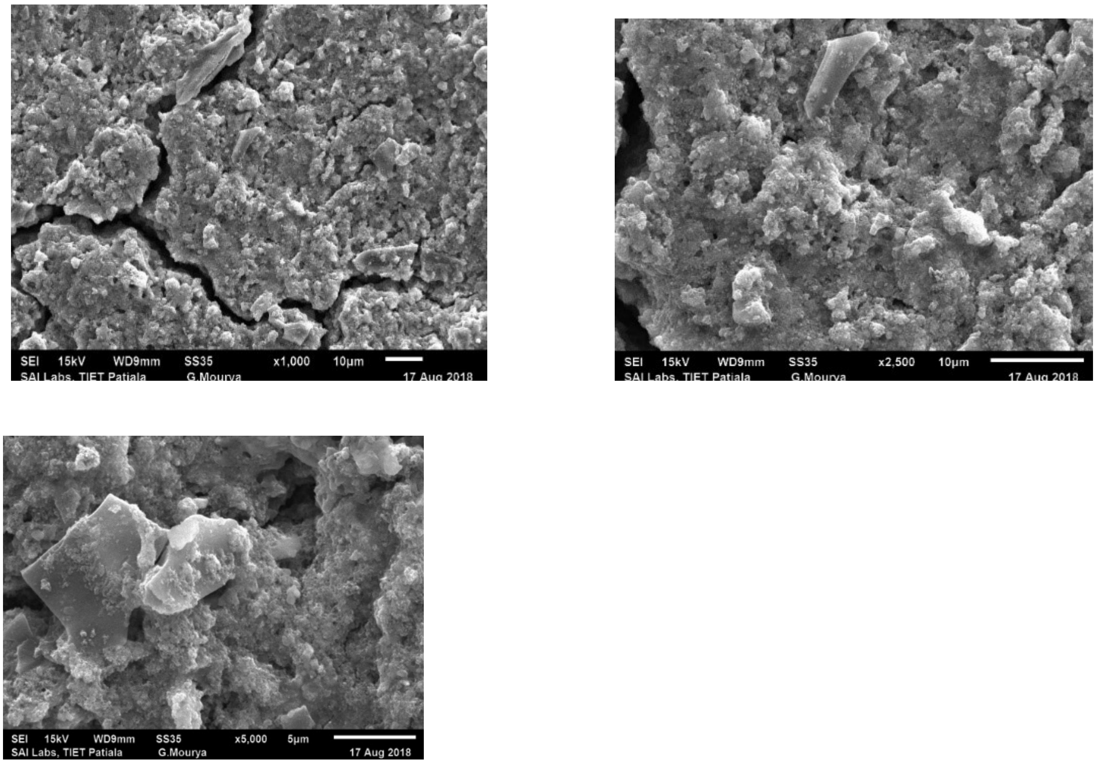
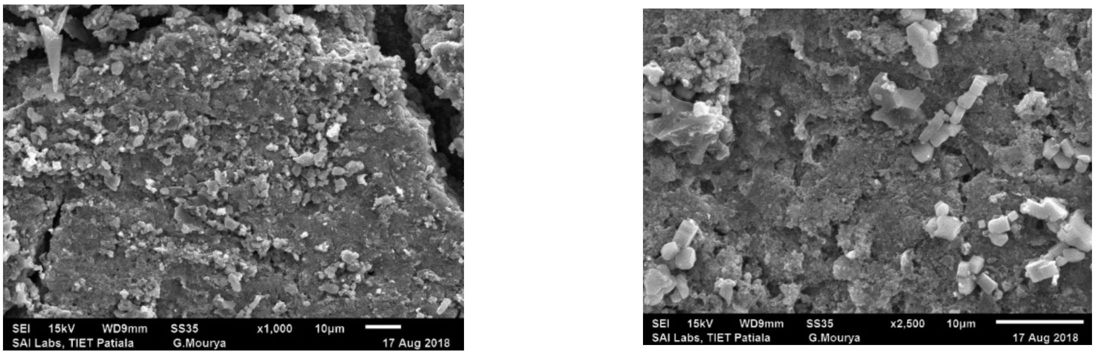


Figure 5.12:SEM image of MEA 1



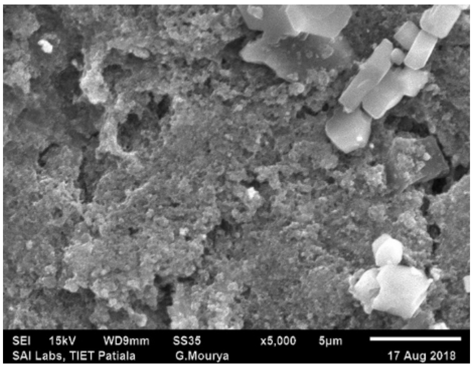


Figure 5.13:SEM image of MEA 2

Figures below show the Electron Dispersive Spectroscopy (EDS) results of both the MEAs which gives the constituents of the layers.

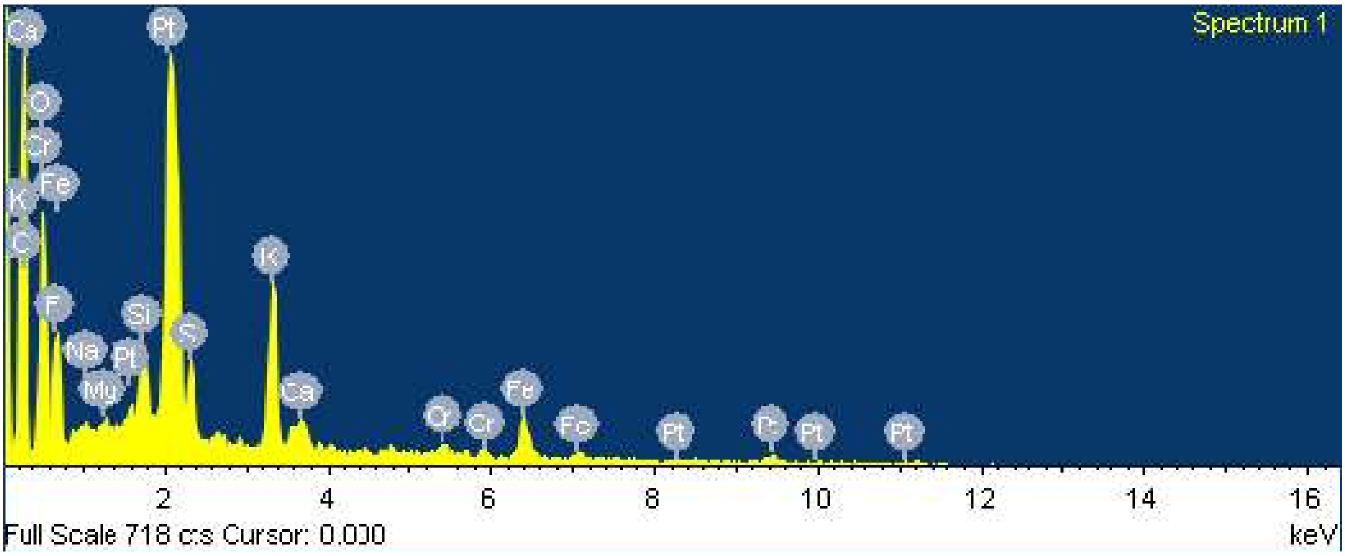


Figure 5.14: EDS analysis of MEA 1

Table 5.1: Components of MEA 1

Element	Weight%	Atomic%
C K	25.93	48.17
O K	20.21	28.19
F K	8.56	10.05
Na K	0.23	0.23
Mg K	0.29	0.27
Si K	1.50	1.19
S K	2.03	1.41
K K	6.85	3.91
Ca K	1.23	0.69
Cr K	1.14	0.49
Fe K	6.12	2.44
Pt M	25.91	2.96

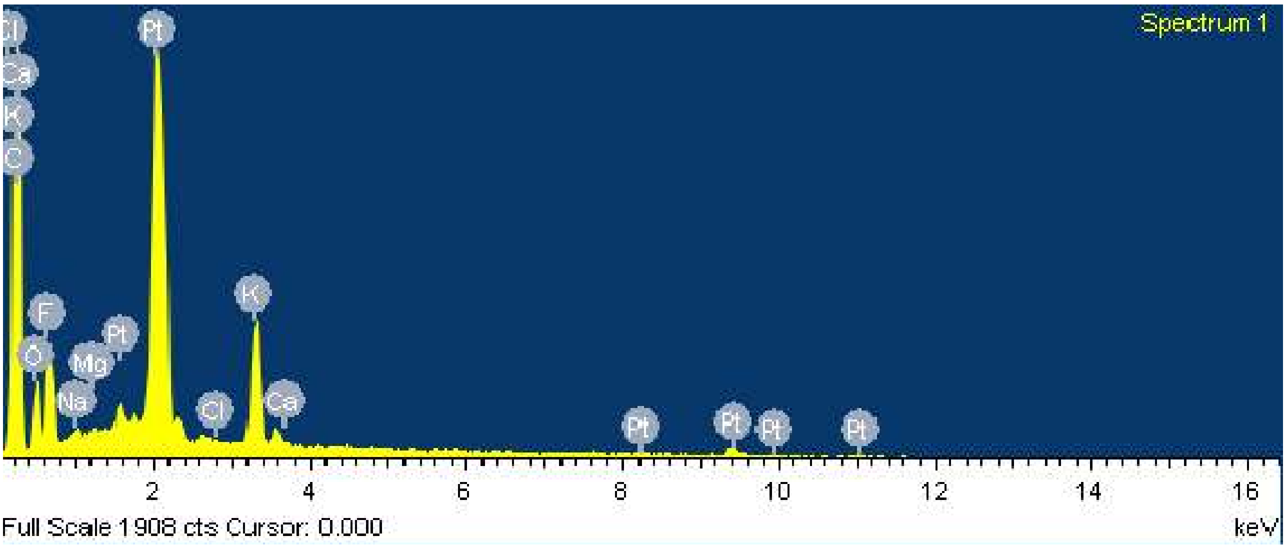


Figure 5.15: EDS analysis of MEA 2

Energy-dispersive X-ray spectroscopy, usually known as energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical method for an elemental analysis or chemical characterization of a sample. It depends on an interaction of a source of X-ray excitation and a sample. Its characterization features are due to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum(which is the main principle of spectroscopy).

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being considered. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus

Table 5.2: Components of ME-2

Element	Weight%	Atomic%
C K	32.12	62.25
O K	9.15	13.32
F K	11.79	14.45
Na K	0.30	0.31
Mg K	0.07	0.07
Cl K	0.31	0.20
K K	8.11	4.83
Ca K	0.05	0.03
Pt M	38.09	4.55

. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured.

Chapter 6 : CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

From the above results we concluded that

- The presented work has proved the technical feasibility of aa novel proton flow battery with an integrated carbon-based hydrogen storage electrode thereby, testing the effect of varied catalyst loading on its performance.
- Higher platinum loading shows better results in terms of reaction rate and hydrogen adsorption (both chemical and physical) under normal temperature and pressure conditions.Thus, higher catalyst loading shall be preferred over the lower one wherever higher reaction rates are required depending upon the user end conditions.
- It was shown that hydrogen could be stored electrochemically in a porous activated carbon electrode that is safer than storing hydrogen in liquid or gaseous form.
- The developed experimental reversible PEMFC or a proton flow battery was able to complete the charging and discharging cycles thereby, fulfilling the load demand of the applied electrical load.
- The experimental work showed the hydrogen ions moving in and out of the designated storage, activated carbon electrode in this case.
- The stagnancy in the obtained VI curve is desirable and proton flow battery that signifies that signifies the chemical or physical adsorption of hydrogen in the E-mode or charging of the PFB.
- The presented work contributed toward development of a novel concept capable of replace the commercially available lithium-based batteries that could meet the continuous energy demand with potential application in remote area power supplies.

6.2 Recommendations

The following recommendations are made on the basis of the thesis.

- Cyclic charging and discharging of the developed novel PFB is suggested to estimate the life-cycle of the battery.
- It would be worth calculating the gravimetric and volumetric energy storage densities along with round-the-trip efficiency of the PFB to compare it with the commercially available batteries.
- Since the experiments that were conducted in this thesis have indicated the likely attractive potential of higher catalytic loading in the MEA and AC electrodes in a PFB to act as reversible

hydrogen stores, the anomalies in the results obtained for oxygen production and consumption need to be explained by additional experiments before it can be stated with confidence that the higher catalytic loading tested here does work effectively for the output of voltage. Unfortunately, these further experiments have been beyond the scope, resources and timelines of the present thesis.

- There are many topics in fuel cells and proton flow battery that require further research to achieve higher energy densities and to rectify the problems encountered in the present project (as still there are many improvements going on water management flow channels). The use of other proton conductors such as protic ionic liquids and proton conducting gels, the problem of bisulphate ions reacting with platinum catalyst and titanium GDL could be avoided. Further, the use of air-tight fittings for connections could fix the gas leakages if any.

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