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# Investigating the impact of operating conditions and applying empirical models suitable for evaluating fuel cell technology

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## Abstract

Fuel cells have been gaining significant attention owing to their high efficiency, their potential to combat climate change through reduction in fossil fuel use, fuel flexibility and so on. This experimental study represents an overview of polymer electrolyte membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC) as well as influence of various operating conditions such as cathode/anode inlet gas flow rate and gas pressure on the performance. An empirical model is also used to characterise the behaviour of the cell at various fuel flow rates. The work forms part of a larger study to investigate the impact of various gas diffusion layer (GDL) designs and membrane electrode assembly (MEA) combinations in the performance of PEMFC. This investigation focuses in detail on a single GDL MEA combination in order to provide a detailed understanding of the PEMFC performance under a broad range of fuel flow rates and pressures. The focus is particularly made on understanding the performance of low fuel flow rates. Then these experimental data was used in the analytical model and some of the kinetic parameters of the cell were calculated using a nonlinear regression analysis. The impact of various operating conditions on SOFC performance is also presented from the literature. Consequently, higher fuel flow rate increases the cell performance. This could be linked with the combined effect of humidification and fuel flow rate since fully humidified reactants were used. An increase in the cell performance with increasing pressure was also observed. It is found that the experimental data fits excellent with modelling data at high fuel flow rate. Conversely, there are some differences for low fuel flow rates where the effect of concentration losses becomes dominant. The parameters which have an impact on the concentration losses are observed. It is found that the parameter n has greater effect on the mass transport limitation than the parameter of m.

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## Nomenclature

| | |
|---|---|
| F | Faraday Constant |
| N | Avagodro's number |
| $\Delta\bar{g}_f$ | Gibbs free energy |
| E | Cell voltage |
| A | Electron transfer coefficient |
| I | Exchange current density |
| $E^0$ | Reversible open circuit voltage at standard pressure |
| R | Resistance |
| b | Tafel slope |
| α | Transfer coefficient |
| Er | Reversible cell potential |
| T | Temperature |
| P | Partial Pressure |
| $\sigma_{ion}$ | Ionic conductivity |
| $\eta_{act}$ | Activation overpotential |
| $\eta_{ohm}$ | Ohmic overpotential |
| $\eta_{conc}$ | Concentration overpotential |
| **Abbreviations** | |
| CHP | Combined heat power systems |
| FC | Fuel cell |
| PEMFC | Polymer electrolyte membrane fuel cell |
| SOFC | Solid oxide fuel cell |
| MEA | Membrane – electrode assembly |
| PTFE | Polytetrafluoroethylene |
| GDL | Gas diffusion layer |
| AFC | Alkaline fuel cell |
| DMFC | Direct methanol fuel cell |
| PAFC | Phosphoric acid fuel cell |
| MCFC | Molten carbonate fuel cell |
| SLM | Standard litter per minute |

# Chapter 1

## Introduction

Fuel cells have received a lot of attention recently due to their potential to mitigate global warming and reduce the consequences of the use of fossil fuels [1]. With increasing demand on energy, these clean and efficient energy systems have been under development.

The world's energy consumption comes from 80 % fossil fuel [2]. It is estimated that there will be petroleum and natural gas shortages after 2020. Another problem with fossil fuels is that they contribute to environmental issues such as climate change, ozone layer depletion and pollution [2]. All these concerns have encouraged the development of fuel cells.

Fuel cells have many advantages such as high efficiency, simplicity, low emissions and silent operation [3] .They will have a potential impact on hydrogen fuel economy [1]. The applications of fuel cells are numerous. In particular, vehicles and combined heat and power systems (CHP) are the main areas besides, mobile power systems, portable computers, mobile telephones, and military communications equipment [3] .Although these various applications and advantages, there are still problems with current fuel cells. The theoretical efficiency is higher than the actual efficiency due to limitations. Also high material costs are problem. Therefore, much research is required in this area to investigate cost and efficiency effective materials.

## 1.1 Fuel Cells

Fuel cells are electrochemical devices which can convert the chemical energy of a fuel directly into electrical energy. Therefore, FCs have the potential for high efficiency even in small scale systems. Besides, their high efficiency, FCs also produce waste heat which can be used. FCs can maintain their performance as long as fuel is supplied [4]. However, the life of the fuel cell and the losses limit the performance.

There are different kinds of fuel cells depending on the electrolyte type used, fuel types, or even efficiency and temperature in the literature such as Alkaline (AFC), Proton Exchange Membrane or Polymer Electrolyte Membrane Fuel Cell (PEMFC), Direct Methanol Fuel Cell

(DMFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC) etc. An overview of these six types of fuel cells is given in table 1.1 including applications and specifications. [1] [2] [4].

**Table 1.1 Data for different types of fuel cells [1] [3] [4]**

| **Fuel Cell Type** | **Mobile ion** | **Temperature** | **Fuel** | **Electrolyte** | **Applications** |
|---|---|---|---|---|---|
| Alkaline (AFC) | $OH^-$ | 50-200$^0$ C | $H_2$ | Aqueous KOH | Transport, i.e. London Taxi(Zevco), stationary, space (Apollo) |
| Proton Exchange Membrane (PEMFC) | $H^+$ | 70-110$^0$ C | $H_2$, $CH_3OH$ | Sulfonated polymers(Nafion$^{TM}$) | Transport, i.e. NECAR series, Ford P2000, stationary, portable,space. |
| Direct Methanol (DMFC) | $H^+$ | 80-110$^0$ C | Methanol | Nafion | Transport, portable. |
| Phosphoric acid (PAFC) | $H^+$ | 150-250 $^0$ C | $H_2$ | $H_3PO_4$ | Transport i.e. golf cart hybrid. |
| Molten carbonate (MCFC) | $CO_3^{2-}$ | 600-800$^0$ C | Hydrocarbons, CO | $(Na,K)_2CO_3$ | Stationary i.e. ERC (Santa Clara) |
| Solid Oxide (SOFC) | $O^{2-}$ | 800-1000$^0$ C 500-600$^0$ C possible | Hydrocarbons, CO | $(Zr,Y)O_{2-\delta}$ | Stationary, i.e. Siemens-Westinghouse |

### 1.1.1 Basic Principles of Fuel Cells

In a basic fuel cell, water is electrolysed into hydrogen and oxygen by passing an electric current through it. As a result of this, a small current is produced. The hydrogen and oxygen combine again due to the electrolysis process being reversible. The current is small because of low contact area between the gas, the electrode and the electrolyte and the distance between electrodes [3].

A simple fuel cell consists of a cathode, an anode and an ion conducting electrolyte as shown in Figure 1.1. [1]. The fuel such as hydrogen ionises and creates $H^+$ ions and electrons. The electrons pass through an external circuit to the cathode and create the current. The oxygen ions are released at the cathode due to reaction of oxygen and electrons. The oxygen ions pass through the electrolyte and forms water at the anode by combining hydrogen in SOFC. The hydrogen ions pass through the electrolyte and forms water at the cathode by combining oxygen in PEMFC. The electrolyte should only allow passing through the ions not electrons. The overall reaction and the schematic of a fuel cell are shown below [1].

$H_2 + ½\ O_2 \rightarrow H_2O$ (R1.1)

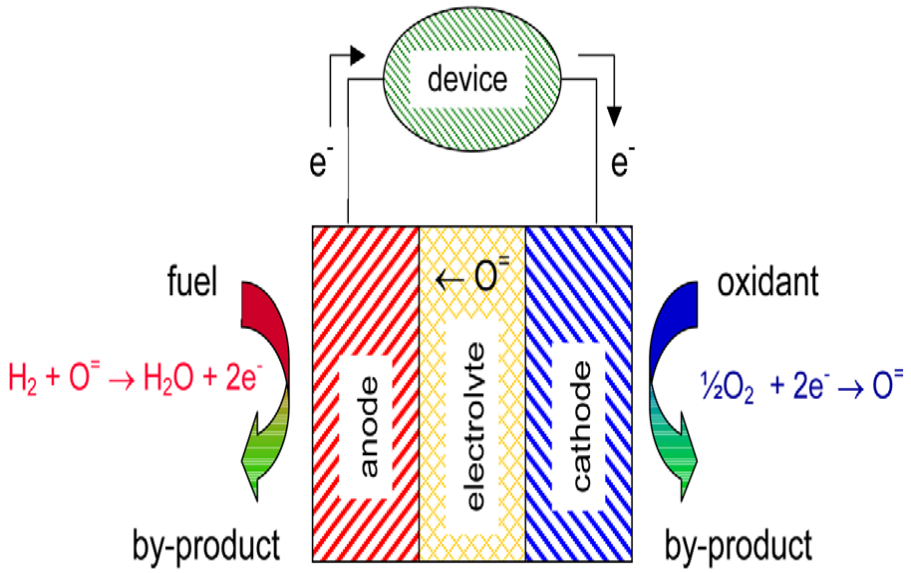



**Figure 1.1 Schematic of a fuel cell [1].**

### 1.1.2 History of Fuel Cells

The basic operation of a fuel cell was discovered by lawyer and scientist William Grove in 1839. He performed the experiment using two platinum electrodes and dilute acid electrolyte. He obtained a small current flowing through an external circuit [3].

Several kinds of fuel cell were investigated during the twentieth century. Firstly, a 6 kW fuel cell was developed by Francis T. Bacon in 1950s. The US Space Program included the first applications of fuel cells. The first polymer membrane fuel cells were developed by General Electric and were used in the program of Gemini in 1960s. In 1990s, PEMFCs were used to power submarine and produce cell-powered buses [2].

The solid oxide fuel cell (SOFC) research started in 1900s with the investigation of appreciable ionic conductivity which is also called Nernst mass- doped zirconia. However, the SOFC has gained a lot of attention since 1970s due to its high efficiency [5]. In 1970, Isenberg developed electrochemical vapour deposition (EVD). In 1978, this method was used by Westinghouse to close the pores in the electrolyte and interconnecting layers which resulted in designing long tubular cells. This design was used to produce a 5 kW SOFC generator and a 100 kW SOFC power system which were operated in the Netherlands in January 1998 [6].

Many new fuel cell technologies and ideas are under development currently. It created a new industry. The car companies are investigating and producing fuel cell vehicles. The world has shown a lot of interest in fuel cell technology especially the United States and Japan. Large scale hybrid SOFC gas turbine power plants and combined heat power systems (CHP) are also receiving a lot of attention by researchers and industry [5] [6].

### 1.1.3 PEMFC

PEMFCs are low temperature fuel cells. They operate at 70-110$^0$ C. PEMFC consists of a membrane- electrode assembly (MEA), two bipolar plates and two seals [7]. A proton conducting polymer membrane is used as an electrode in PEMFCs. It was first used as an auxiliary power source in the Gemini program. It also provided clean drinking water to the astronauts [8]. The biggest improvement was seen with using Nafion membranes (DuPont). Nafion membranes have higher acidity and conductivity and they are more stable than other

types of membranes. Usage of Nafion and some other PTFE based polymer membrane give three or four times higher current densities [8].

There has been intense investigation and development of a single PEMFC performance experimental work for a few decades. This part of PEMFC investigation considers mainly material properties, transport conditions, membrane electrode assembly (MEA) materials, bipolar plate design, MEA stability, contamination, water management and thermal management whereas other research focuses on macroscopic properties such as stack performance and stability, classification of stack behaviours, designing of stacks and so on [9].

The development of PEMFC has been continuing in different areas depending on applications. More specific discussion of materials, components and limitations will be detailed in the following chapter.

### 1.1.4 SOFC

Solid oxide fuel cells have existed for almost 100 years. The basic principles and materials were proposed by Nernst and his colleagues at 1930s. They can operate at 600-1000$^0$ C. Low temperature SOFC can operate at 500$^0$ C. They have the potential for residential combined heat and power, auxiliary power supplies, vehicles and stationary power supply from coal [6].

A single cell produces only a small voltage under normal operating conditions. Therefore, it requires stacking many fuel cells together in order to produce high voltage. This combined cell is called a 'stack'. It has been manufactured in various geometries. Tubular and planar designs have been most popular among these geometries. The tubular SOFC was developed by Siemens Westinghouse. It has no seals and the shape looks like a pipe. The length of tubular SOFC ranges from 30-150 cm and diameter is usually less than 15mm. There are also micro-tubular SOFC with the diameter of about 5mm and length of about 10 cm [5]. The problem with the tubular design is that it has low power density and high manufacturing costs. The long length of the cell and voids within the stack cause the lower power density. The high costs are owing to the technique of electrochemical vapour deposition (EVD) which deposits the electrolyte and requires vacuum equipment [3].

Unlike the tubular design, the planar design has a higher power density. The plate structure of the cells ensures a simple electrical connection between cells and does not require long current path which decreases ohmic losses. Another advantage of this design compared to the tubular design is that it has low manufacturing costs due to low cost production methods such as screen printing and tape casting. On the contrary, sealing is one of the drawbacks of the planar design. It requires gas tight sealing at the edges of structure. Glass ceramics have been used for sealing which needs high temperatures. This process results in thermal stresses at the interfaces between stacks which lead to mechanical degradation. Therefore, the production focuses on 5 x 5 cm size stacks [3].

Despite some of the disadvantages, these designs have been receiving abundant attention from several organisations. The market and research are investigating the materials and components in order to increase power density and efficiency.

### 1.1.5 Advantages and Applications

The advantages of PEMFC are; [2] [3]

- Operate at low temperature
- Quick start up
- The efficiency is relatively high
- Low emissions
- Silent
- The system is simple and have a relatively long life time

The advantages of SOFC are; [3] [6]

- Very high efficiency up to 60% (diesel engine has up to 50 % efficiency)
- Low emissions
- Fuel flexibility, methane and hydrocarbons can be used
- The SOFC can drive a gas turbine
- Can produce useful heat

Fuel cells can be used for vehicles, power plants, and portable applications. PEM fuel cells have been tested for vehicles due to their quick response and start up. Large scale power

plants use both high temperature and low temperature fuel cells. Batteries for small portable power applications such as laptops and mobile phones are under development [8].

### 1.1.6 Disadvantages and Limitations

Besides the advantages of fuel cells, there are disadvantages and limitations with operating and producing them. The technical problems are; slow reaction rate and issues around hydrogen for instance difficulties with producing hydrogen and hydrogen storage. In order to increase reaction rates, catalysts are required. Platinum (Pt) catalysts have been used in PEMFC so far which increases the cost of cell. Due to this problem most research focuses on MEA and membrane manufacturing processes so as to decrease the content of the Pt catalyst [10]. PEMFC also requires pure hydrogen and does not show tolerance to CO. Water management is also a difficult and complex issue for PEMFC. When it comes to the SOFCs, they have longer start up times, high operating temperatures and cracking problems [8]. Electrolyte's materials need to be improved and researched.

## 1.2 Aims, Objectives and Structure of this Dissertation

The aim of this dissertation is to develop an understanding of fuel cell technology currently available, to understand the operation of an inhouse PEM fuel cell test station and how it can be used to evaluate a new PEM fuel cells under a range of operating conditions and to investigate how the experimental data can be used to predict cell parameters with the aid of theoretical model. The model will be used to interpret the performance of the cell, kinetic parameters and voltage losses associated with the cell.

The objectives of this dissertation are;

- To develop an understanding of a fuel cell components and thermodynamics of the fuel cell.
- To be able to operate the inhouse the PEM fuel cell test station and to understand its behaviour and function of each component and operating parameters.
- To be able to perform experimental works which allows the performance of the PEM fuel cell to be evaluated over a range of operating conditions for example fuel flow rates based on producing polarisation curves.

- To design a series of experiments suitable for evaluating the performance of a given PEM fuel cell with a range of different MEA properties if time is sufficient.
- To compare the performance of the PEM fuel cell under a range of operating conditions.
- To use an analytical model and see how it fits with the experimental data.
- To calculate kinetic parameters of the cell and voltage losses in the cell using the model.
- To compare the effect of the parameters on the cell performance.

This dissertation consists of 5 main chapters;

- The first Chapter starts with the basic principles and the history of fuel cells both PEMFC and SOFC. Then it outlines the benefits and drawbacks of fuel cells.
- Chapter 2 discusses the operational principles and components of PEMFCs and SOFCs. Then electrochemistry, voltage losses and water management in PEMFCs are presented followed by the explanation of empirical model.
- Chapter 3 discusses the methodology of the experiments for PEMFC. First, the test station, the function of the test station components and MEA preparation are discussed. Then governing equations for a PEM fuel cell are outlined. Finally, experimental data are determined and presented to reach the aim of the experiments.
- Chapter 4 outlines the results of the experiments. The results are compared to the literature and interpreted in this chapter. The influences of parameters on cell performance are presented. The experimental data is used in the empirical model and some of the kinetic parameters of the cell are calculated. The model results compared to each other to evaluate over potential impacts on the cell performance.
- Chapter 5 concludes this work and suggests for future studies.

# Chapter 2 Literature Review

## 2.1 Operation Principles of PEMFC

A single PEM fuel cell is comprised of a membrane electrode assembly (MEA), two bipolar plates and two seals. The MEA composes of two catalyst layer, a membrane and two gas diffusion layers (GDLs) [7].

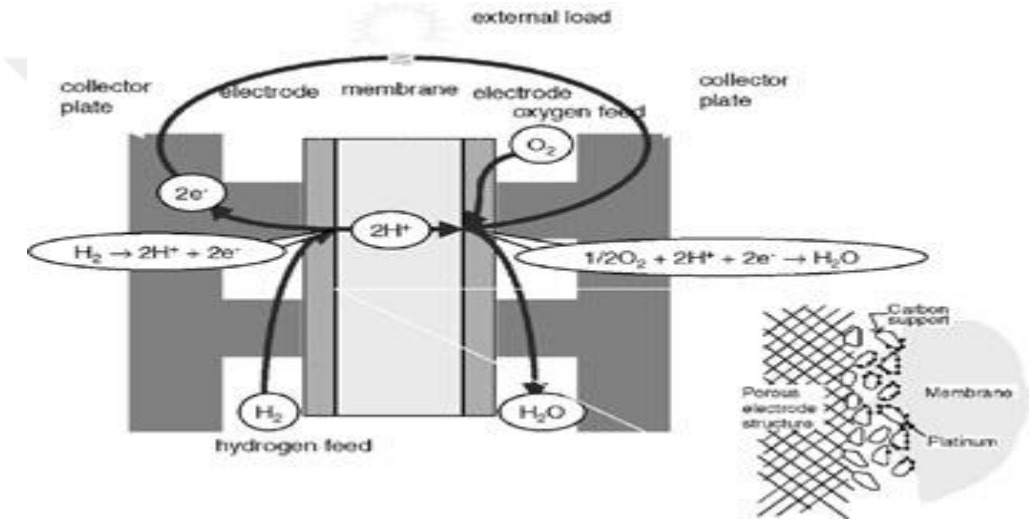



**Figure 2.1 Basic structure of a PEM fuel cell [11]**

Basic operation of a PEM fuel cell is simple as shown in Figure 2.1. Hydrogen oxidation reaction happens at the anode. Hydrogen ionises to release electrons and protons with the help of the Pt catalyst; the protons (hydrogen ions) pass through the membrane to the cathode [8].

Anode:

$\frac{1}{2} H_2 \rightarrow H^+ + e^-$ (R2.1)

The electron migrates through an external circuit to the cathode, and creates electric current. The reduction reaction happens at the cathode. Oxygen is reduced and reacts with protons to form water.

Cathode:

$½ O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (R2.2)

### 2.1.1 PEMFC Components

The components of PEMFC are membrane, catalyst layer, gas diffusion layer and bipolar plates. Each component has a specific role. The properties of components and duties of them are outlined.

**Membrane:** The membrane is a polymer electrolyte which should depict high conductivity for transporting protons, should show a good barrier property to mix fuel and reactant gases and should have small temperature range in which it is chemically and mechanically stable. The membrane assembly (MEA) is the heart of the PEM fuel cell which membrane is a part of it. Membrane also should be hydrophilic to ensure enough humidity for the reactions in the cell. The most common and well know membrane is Nafion (sulphonated fluoropolymers) [2].

One technique of producing membrane is as follows. The first point is changing hydrogen with fluorine in the polymer-polyethylene structure. The composite compound is called polytetrafluoroethylene or PTFE is shown in Figure 2.2. [3].

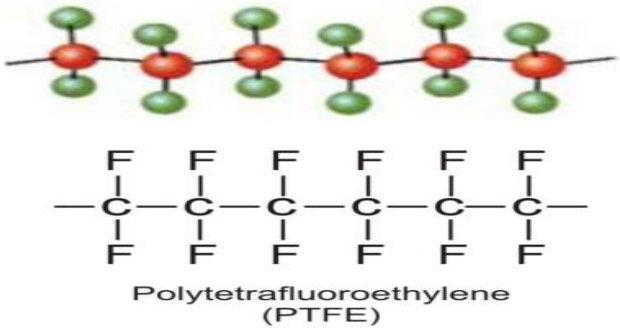



**Figure 2.2 Structure of PTFE [12]**

The PTFE has strong bonds between carbon and fluorine which increases its resistance and stability and this makes it significantly important for fuel cells. It is also important in terms of water management. Owing to its hydrophobic property, the product water is driven out of the

electrode which prevents the fuel cell from flooding. The PTFE is sulphonated. The $HSO_3$ group is added ionically which creates a side chain. Due to the presence of $SO_3^-$ end of the chain, an attraction between $SO_3^-$ and $H^4$ is formed. This results in a cluster of side chain molecules. Because of the fact that sulphonic acid is hydrophyllic, a hydrophyllic region is created in Nafion which is a hydrophobic substance is shown in Figure 2.3 [3].

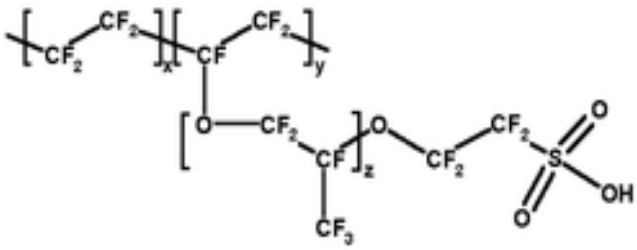


**Figure 2.3 Structure of Nafion. [13]**

The water absorption by hydrophyllic region can increase the weight of the material by up to 50%. In a good material the hydrated region should be as large as possible to increase the conductivity. The advantages of Nafion are, its resistance to chemical attacks is high, they are mechanically strong which allows making thin films, they are acidic, they absorb water which makes them a good proton conductor, and its permeability of reactant gases is low [3].

There are other techniques to prepare membranes such as plasma polymerisation or radiation grafting. First technique is mostly used for preparing thin ion exchange films which decreases the ohmic losses and prevents the membrane from drying. Second technique is most promising for PEM fuel cells that the membranes are very stable mechanically and electrochemically. They have higher diffusion than Nafion and less oxygen solubility [8].

**Catalyst layer:** A thin catalyst layer which is electrically conductive pressed between the ionomer membrane and the porous gas diffusion layers. Due to gases, electrons and protons have access to the catalyst surface, the electrochemical reactions happen on the catalyst surface [2].

The best and most common catalyst to use for both anode and cathode, is platinum this is a reason for the high cost of PEM fuel cells. The platinum catalyst is formed into small particles on the surface and bounded to a carbon support in order to increase electronic

conductivity. The particles should contact with an electronic conductor directly to ensure the electrons are provided and removed from the reaction area [8].

The choice of catalyst is very important in terms of tolerance to carbon monoxide (CO). It is proven that even only very little concentration of CO decreases the performance of PEMFCs because of strong chemical force of CO onto the catalyst [7]. In order to overcome this problem two methods have been used; fuel reforming or catalyst alloys. Pt-C, Pt- Ni, Pt-Ru catalysts have been under investigation and used so far [9]. The CO level can be decreased by fuel reforming in the fuel. By using onboard fuel reforming and the PEM fuel cell's tolerance to CO concentration (at least 100 ppm), the reformer size can be reduced. CO is one of poisons in low temperature fuel cells owing to adsorption of the species to reaction area of catalyst surface which causes reduction of available reaction area for $H_2$ [8]. The reforming can be done by selective oxidation or hydrogen peroxide bleeding. In the selective oxidation method, the reformed fuel is mixed with air or oxygen. In the second method, the hydrogen peroxide ($H_2O_2$) is used in an anode humidifier to combat CO concentration. A result of this an unintended $O_2$ bleed produced [7].

Another study [9] shows that catalyst degradation causes the failure of the cell. The oxygen reduction potential of the catalysts can reduce the cell voltage. Better catalysts have been investigated by research groups to improve CO tolerance.

**Gas Diffusion Layer (GDL):** The GDL is the layer between the catalyst layer and bipolar plates which allows the reactant gases to reach the reaction area on the catalyst surface. It also ensures electron delivery between catalyst and bipolar plates. The product water is transported from catalyst layer to the flow field channels by GDL. Moreover, this layer removes generated heat and enables mechanical support to the MEA [2].

The GDL is usually made of a porous carbon paper or carbon cloth and generally between 100-300 µ thick. Porous GDL enables an effective diffusion of gases to the catalyst on the membrane/electrode surface. The gas is also spread out to the reaction area of the catalyst membrane easily due to its porous structure. The GDL plays a role in the water management as well. It allows the adequate water vapour to access the membrane/electrode assembly which helps to keep the membrane humidified and increases the cell efficiency. PTFE is used for carbon based PEM GDL owing to its wet-proofed property. The wet- proofed GDL ensures that the pores are always open in order to prevent from slow gas diffusion. Slow gas diffusion reduces the reaction rate and decreases the cell performance [7].

Despite the fact that carbon cloth provides a good performance for GDLs, other properties of the GDL such as density, thickness, pore-size distribution, and electrical conductivity are still under investigation. The MPL (micro porous layer) can also be used to coat the interface with catalyst layer in order to have better electrical contacts and good water management. The MPL is composing of carbon graphite particles mixed with the PTFE material [14]. Since the GDL has a great impact on the cell efficiency, there has been increasing interest to investigate the impact of PTFE loading and permeability of the GDL. Different properties of GDM (gas diffusion media which consists of GDL coated with MPL) have been under investigation. The electronic performance of GDM under different air humidity level was studied Stampino et al. It was found that ohmic resistance has higher detrimental impact on the cell efficiency in the high current density region when air relative humidity is kept over 80%. However, this impact is not big when compared to the cell resistance (contact, bulk...) [15]. Another study was done by Shahraeeni et al [16] to investigate the impact of GDL properties on the time of breakthrough. The time was measured for water to penetrate and travel through the GDL with different thicknesses. The different PTFE loading (0% and 40wt %) was used for each thickness. It was found that the thickness of GDL does not increase the time of breakthrough. However, the PTFE loading increases the time of breakthrough significantly. It was observed that this PTFE loading impact on the time of breakthrough can be negligible when high flow rate is used.

**Bipolar Plates:** Bipolar plates have a number of duties within the PEM fuel cell. They supply fuel and oxidant in the cell, spate the individual cells, current collection, water removal, humidify gases, and help to cool the cell [7]. Bipolar plates contribute nearly 60% of weight and 30 % of the cost to the cell stack. Figure 2.4 shows the place of the bipolar plates in the fuel cell stack.

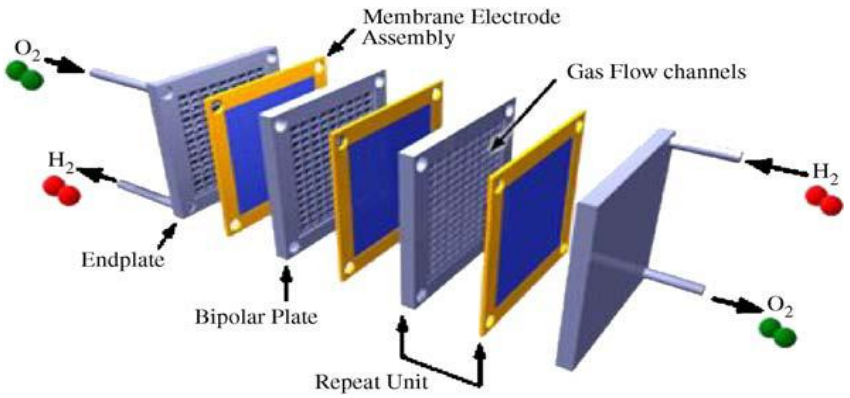



**Figure 2.4 Stack components of fuel cell [17].**

Topologies include different flow field design in bipolar plates; straight, serpentine, or inter digitated flow fields, internal manifolding, internal humidification, and internal cooling [17].

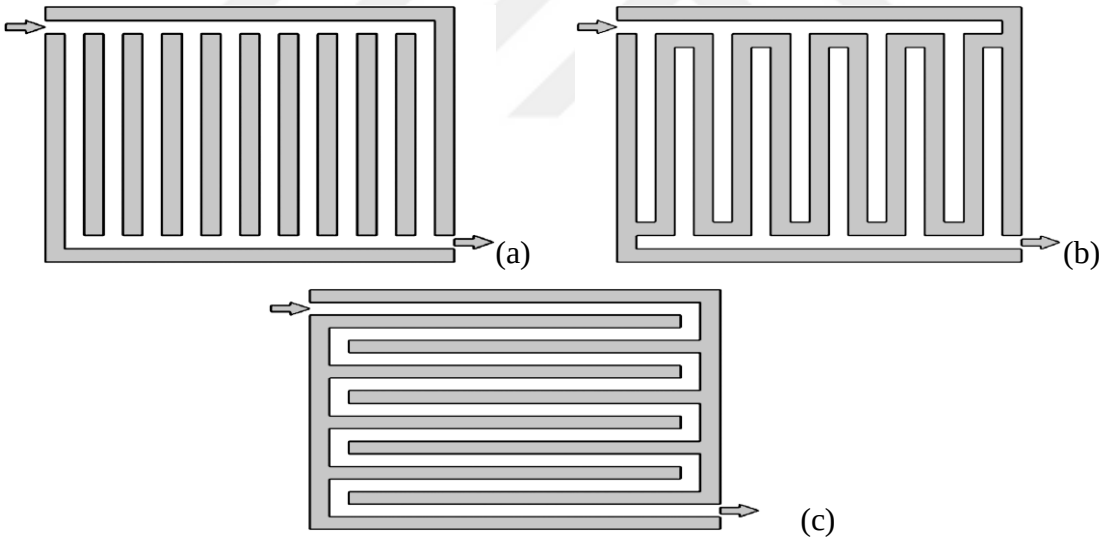



**Figure 2.5 Schematic drawing of (a) parallel channel flow field, (b) interdigitated flow field, (c) serpentine flow field [18].**

One side of the bipolar plates behaves as anode plate; the side serves as cathode plate. Cooling is performed by adding a separate a cooling plate after a few cells within the stack.

Reactant gases move on one side of the plate while cooling fluid moves on the other side of the plate so as to remove waste heat [17].

Different kinds of materials have been used in bipolar plates so far such as metallic and graphitic. The most common material is graphite due to its chemical stability and high conductivity. Non-porous graphite plates, coated plates, composite plates are the main types of bipolar plates. Aluminium, stainless steel, titanium and nickel are used as alternative materials for bipolar plates in PEM fuel cells [7]. The important parameters for bipolar plates are; a good distribution of reactant gases on the electrode surface, high electronic conductivity, high mechanical and chemical stability, a good resistance to corrosion, long lifetime, cheap and easy fabrication [17].

## 2.2 Operation Principles of SOFC

Figure 2.6 shows basic operational principles of solid oxide fuel cell. A single solid oxide fuel cell (SOFC) is composed of an anode, a cathode and an electrolyte between them.

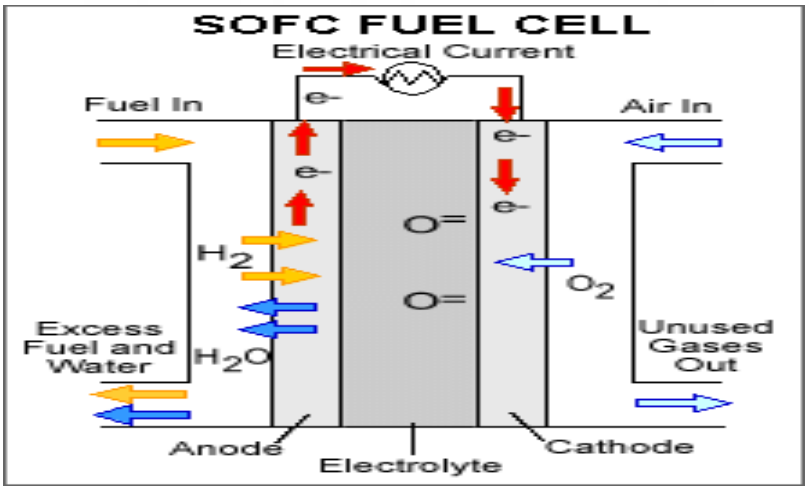



**Figure 2.6 Schematic of the basic operational principle of a SOFC [19].**

Oxygen ions are formed at the cathode and migrate to the anode. If the fuel is hydrogen and the oxidant is air, the reaction at the cathode is;

$O_2 + 4e^- \rightarrow 2O^{2-}$ (R2.3)

The electrolyte within the cell has high electrical resistivity and ionic conductivity; therefore only ions can pass through the electrolyte and flow to the anode. The overall reaction at the anode is;

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ (R2.4)

Since CO poisoning is not a problem for the anode material in SOFC, hydrocarbons can be used as fuels [20].

### 2.2.1 SOFC Components

The components of SOFC are outlined in terms of chemical and physical properties for different types of materials.

**Electrolyte:** The electrolyte presents one of the components of the SOFC which ions flow through from one electrode to the other electrode. The electrolyte is the reason for voltage differences between anode and cathode, and electric current through the external circuit. Electrolytes must have some requirements such as; high ionic conductivity, high electrical resistivity, thermal and chemical stability, a good resistance to thermal cycling and low cost [20].

The most common electrolytes are yttria-stabilised zirconia and fluorite- structured electrolytes [6]. Yttria- stabilised zirconia (YSZ) is preferred in most cases due to its high ionic conductivity at reduced temperatures. Although some compounds such as $CeO_2$ and $Bi_2O_3$ have higher oxygen conductivity, it is found at the anode that they have less stability at low oxygen partial pressures [3].

The reason for voltage losses within SOFC is ohmic polarisation due to interfacial resistance between anode and electrolyte. In order to solve this problem, nickel particles are dispersed to adhesion of the anode to YSZ electrolyte. 100 mol % nickel anode has high electrical conductivity which makes its thermal expansion greater than YSZ electrolyte. This creates thermal mismatch problem. This problem is solved by mixing ceramic powders with Ni or NiO. The ideal mixing value is Ni/YSZ: 30/70 , by volume [21].

Other electrolyte materials are still under investigation. Partially stabilised $ZrO_2$ and adding $Al_2O_3$ to the fully stabilised YSZ are currently taking more attention.

**Anode:** The anode is made of a mixture of Ni and a small percentage of YSZ. The YSZ is used owing to decrease the anode sinter ability and make the anode's and the electrolyte's thermal expansion close [20]. The role of the anode within the cell is to supply the reaction area for fuel gas and oxygen ions and to provide charge neutralisation [6]. The anode must have high electronic and ionic conductivity, high catalytic activity, high chemical and mechanical stability and porous structure to allow mass transport of the gases. Recent research focuses on ceramic anodes in order to increase direct oxidation of methane [3].

**Cathode:** The cathode is a porous material which should allow mass transport of reactant and product gases. The cathode must possess high electrical conductivity and high catalytic activity similar to the anode. Pt was used as cathode in early times; however Pt is an expensive material less cost effective materials have been investigated [6]. Nowadays, strontium-doped lanthanum manganite $(La_{0.84}Sr_{0.16})MnO_3$ (LSM) which is a p-type semiconductor is widely used. Besides this material, perovskite structures have been taking great attention due to its mixed ionic and electronic conductivity. It is very important for low temperature SOFC owing to the polarisation of the cathode increases [2]. One of advantages of low operating temperature is it does not require expensive current collector such as ceramic. Stainless steel can be used as current collector. However, this may reduce cathode activity due to stainless steel contains Cr which may react LSM [20].

In the case of intermediate temperature SOFC, a composite cathode is composed of strontium-doped lanthanum manganite and YSZ which exhibits good performance [6].

**Interconnects:** Interconnect is responsible for electrical connection between cells and gas separation within the cell. Interconnect must have high electronic and thermal conductivity, low ionic conductivity, chemical stability, high mechanical strength and thermal mismatch with other components of the cell [6].

At operating temperature of about $1000^0$C, the interconnect material should be ceramic. [20] Below this temperature, it can be less cheap material such as stainless steel. However, stainless steel has a thermal mismatch problem with the YSZ electrolyte. In order to solve this problem, alloys such as Cr-5Fe-$1Y_2O_3$ have been developed. Unfortunately, Cr may poison the cathode. For low temperature SOFC, this is not problem due to austenitic steel can be used as interconnect. Austenitic steel does not include Cr. Usage of other metal interconnects may cause oxide coating which may decrease electrical conductivity [3].

## 2.3 Electrochemistry

A fuel cell converts the chemical energy of a fuel into electrical energy. The chemical reactions are happening simultaneously on the anode and cathode side. Thus, the calculation of electrical work is required to predict the cell performance.

In a hydrogen fuel cell, n electrons pass through an external circuit, water is produced and hydrogen is used. The charge passes through the circuit is,

-nNe= -nF (Coulombs) (Eq 2.1)

F is the Faraday's constant, N is Avogadro's number, e is the charge of one electron. The work is done by this movement is [2],

Electrical work done= -nFE (Eq 2.2)

E is the voltage of the cell. If there is no losses in the system, the electrical work corresponds to the Gibbs free energy released $\Delta\bar{g}_f$ [2].

$\Delta\bar{g}_f$ = -nFE (Eq 2.3)

E= - $\Delta\bar{g}_f$ / nF (Eq 2.4)

This equation presents reversible open circuit voltage of the hydrogen fuel cell [3].

### 2.3.1 Losses

The ideal voltage of the cell is always lower than the theoretical voltage of the cell due to 3 main voltage losses. The ideal characteristic of a single PEM fuel cell is shown in Figure 2.7 [22]. These three losses are which affect the cell performance; activation losses, ohmic losses and concentration losses as shown in Figure 2.8 [21].

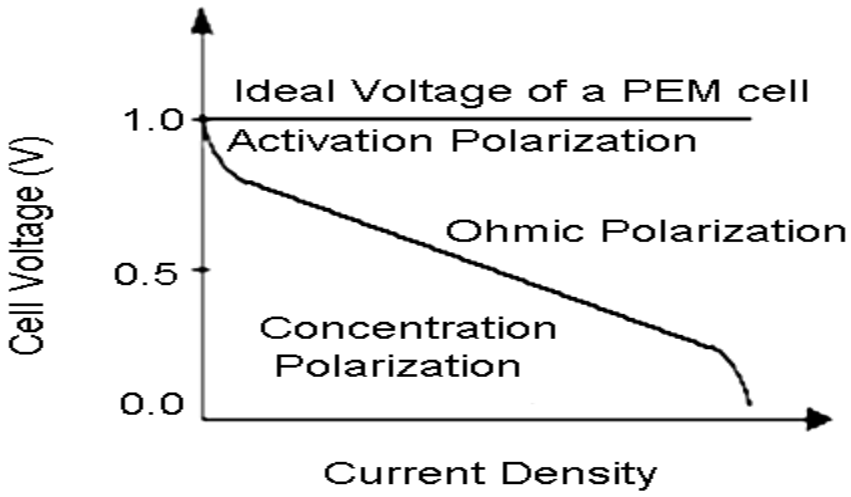



**Figure 2.7: Ideal characteristic of a single PEMFC [22].**

As shown in Figure 2.7 the activation over potential becomes dominant at the low current density area whereas ohmic over potential and concentration over potential become dominant in the medium and high current density region, respectively.

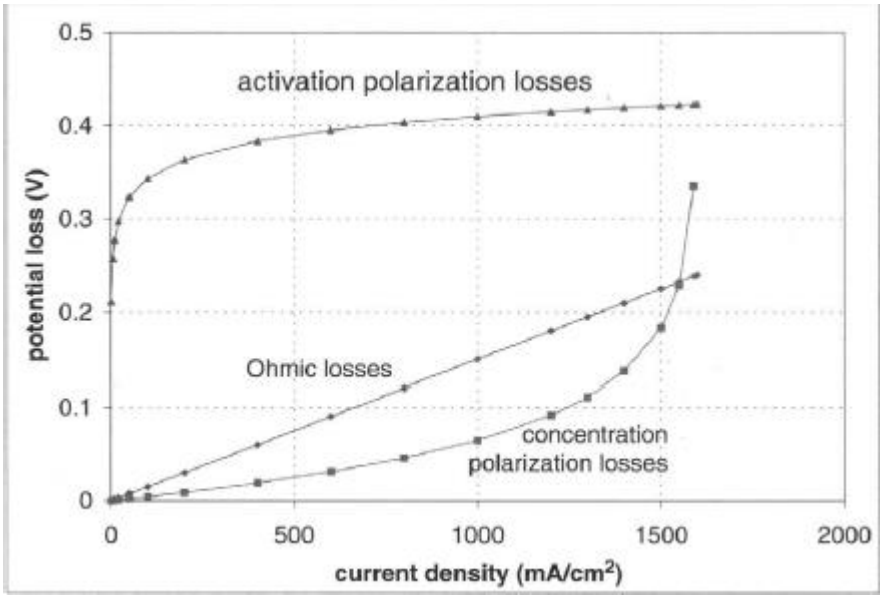



**Figure 2.8: Voltage Losses in the fuel cell [2].**

### 1- Activation Losses

Activation losses are due to slow reaction rate at the anode and cathode sides. It is expressed by a semi-empirical Tafel Equation.

$$\eta_{act} = \frac{RT}{\alpha nF}\ ln\ i/i_0 \quad \text{(Eq 2.5)}$$

α electron transfer coefficient, $i_0$ is the exchange current density [21]. High temperature SOFCs have less activation losses than low temperature SOFCs due to the fact that high temperatures increase the reaction rate at the anode and cathode.

### 2- Ohmic Losses

Ohmic losses are as a result of the resistance to the electrons through the electrodes and interconnects and to the ions through the electrolyte [3]. The total ohmic resistance of the cell is caused by electronic, ionic and contact resistance of the cell. It is expressed by Ohms Law.

$$\eta_{ohm} = iR \quad \text{(Eq 2.6)}$$

Ohmic losses are mostly higher at the electrolytes than the other components of the cell. Since ionic resistance of the electrolyte contributes to the total ohmic resistance of the cell higher than electronic and contact resistance. There are some possible ways to reduce ohmic losses; using high conductive electrodes, designing good bipolar plates and interconnects, using appropriate materials, making electrolytes thin [3].

### 3- Concentration Losses

Concentration losses occur owing to the change in mass transport to the surface of the electrodes. The failure of enough reactant mass transport to the electrode surface causes the reduction. This is explained by Nernst equation. [3]

$$\eta_{cont} = \frac{RT}{nF}\ ln\ (1 - \frac{i}{i_L}) \qquad \text{(Eq 2.6)}$$

Activation losses are negligible compared to concentration losses for high temperature SOFCs [21].

### 2.3.2 Water Management in the PEMFC

In the PEM fuel cell proton conductivity through the membrane depends on the water content. Therefore, water management of the membrane is one of the important issues for PEMFCs. The problem can be defined in two parts. First part is flooding in GDLs and flow channels and second part is drying of the membrane. Flooding occurs due to the condensation progress. Flooding causes blockage of the supplied gases which causes a decrease in the cell voltage and reduces electricity generation. The drying happens as a result of water molecules movement from anode to cathode with the proton conduction. The water content reduces near the anode and ionic resistance increases which results in voltage decreases [20].

One of the ways in order to solve drying problem is to humidify the gases which flow through into the cell. Polysulfonic membranes have good water permeability that they can perform a better internal humidification than Nafion 115. Another way is direct hydration of the membrane. Porous fibre wicks can be mounted to the membrane which provides water directly from the humidifiers or product water from the cathode by taking the advantage of pressure difference. In some cases, self humidified membranes are used in the fuel cells. These are made of Nafion and a small percentage of $SiO_2$ or $TiO_2$ [8].

## 2.4 Empirical Model

There has been a lot of research into modelling model PEMFC since a better understanding of the parameters which affect the cell efficiency is required for reducing the cost and time. There have been proposed two models; mechanistic and semi-empirical PEMFC models so far [23]. Mechanistic models involve a great knowledge of parameters such as transfer coefficient, electrochemical, thermodynamic and fluid dynamic equations which are difficult to obtain. However, semi-empirical model is easier to obtain. This study will mainly focus on semi-empirical model.

The performance of fuel cell is characterised by polarisation curves. The voltage of the cell is usually lower than the ideal voltage of the cell due to irreversible losses as mentioned section 2.3.1. The potential of the cell can be expressed as follows [24]:

$$V = E_0 - \eta_{act} - \eta_{ohm} - \eta_{con} \quad \text{(Eq. 2.7)}$$

The activation losses are caused by voltage drops in chemical reaction which transfers the electrons from or to the electrodes [31]. The activation voltage loss can be expressed as follows [24]:

$\eta_{act} = a + b \ln(i)$ (Eq. 2.8)

where a is $-RT/\alpha nF\ln(i_0)$ and $b= RT/\alpha nF$. $i_0$ is the exchange current density which is the indication of reaction at the equilibrium, F Faraday constant, $\alpha$ is the transfer coefficient which depends on the electrode kinetics.

The ohmic losses obey Ohms Law. Thus, $\eta_{ohm}$ is expressed as follows [23]:

$\eta_{ohm}=-Ri$ (eq.2.9)

The concentration losses are as a result of mass transport limitations. The concentration of reactant at the electrode surface changes and the concentration of product water increases which leads to voltage drops at the high current density region. The voltage drop is expressed as follows [23]:

$\eta_{con}= -m \exp(ni)$ (Eq. 2.10)

where m and n are constant. The impact of these parameters will be discussed in Section 4.

# Chapter 3 Research Methodology

## 3.1 Methodology

An empirical study is being undertaken in this study using the 10BC GDL in the MEA. The 10BC GDL is a one type of commercial GDLs. The properties of the 10BC GDL will be presented in section 3.1.3. The cell performance will be evaluated for different fuel flow rates and operating pressure. The catalyst's cost increases the MEA and PEMFC cost. Therefore, different MEA designs are under investigation. The experiments are being undertaken using the test station suitable for PEMFC in order to determine the effects of varying fuel flow rate at the anode and cathode on the cell performance. It is clear that increasing the gas flow rate more than enough might waste the fuel for the cell. The polarisation curves (potential versus current density) will be obtained. The impact of varying gas pressure is also observed. In order to see the impact of high inlet pressure on the cell performance, the cathode and anode inlet gases pressure can be increased. Firstly, the experiments are performed to test the influences of high and low fuel flow rates on the cell performance using the 10BC GDL in the MAE. The GDL was supplied by the company, namely, the SGL Technologies GmbH, Meitingen, Germany. There are several kinds of GLD available commercially. In this study GDL BC will be used which has 5 wt% PTFE loading with MPL (microporous layer) on one side [24]. This MEA is used to prepare the PEM fuel cell which is tested in the laboratory using the test station. In the flow rate testing experiments, the temperature of inlet gases and humidifiers as well as the pressure of the inlet gases and the cell will be kept constant. On the other hand, for the pressure tests, the flow rate of fuel, the temperature of humidifiers and inlet fuel gases and inlet pressure of fuel gases will be kept constant. After these experiments, the polarisation curves will be obtained and compared to each other in order to interpret these parameters impacts on the power output as well as observing and predicting the different voltage losses in the cell. The results then will be used to evaluate the performance of the PEM fuel cell and to develop a potential approach to increase the fuel cell efficiency including SOFC. Finally, an analytical modelling of PEMFC performance is characterised using the models which outlined in the literature.

### 3.1.1 Description of the Test Station and Experimental Setup

The physical system used in the experiments is shown in Figure 3.1. It is a fuel cell test system available at the University of Leeds. The test system consists of a gas supply system, a flow control system, a humidification system, an electronic load system and a computer software package to monitor and control aspects of the system. The reactant gases are hydrogen with 99.99 % purity and air which are supplied by compressed cylinders. Helium and nitrogen are also used to check reactant gases leakage and to purge unused gases from cathode and anode sides. The humidifiers are employed to humidify reactant gases which are bubbler-type humidifiers (HygroFlex, rotronic).

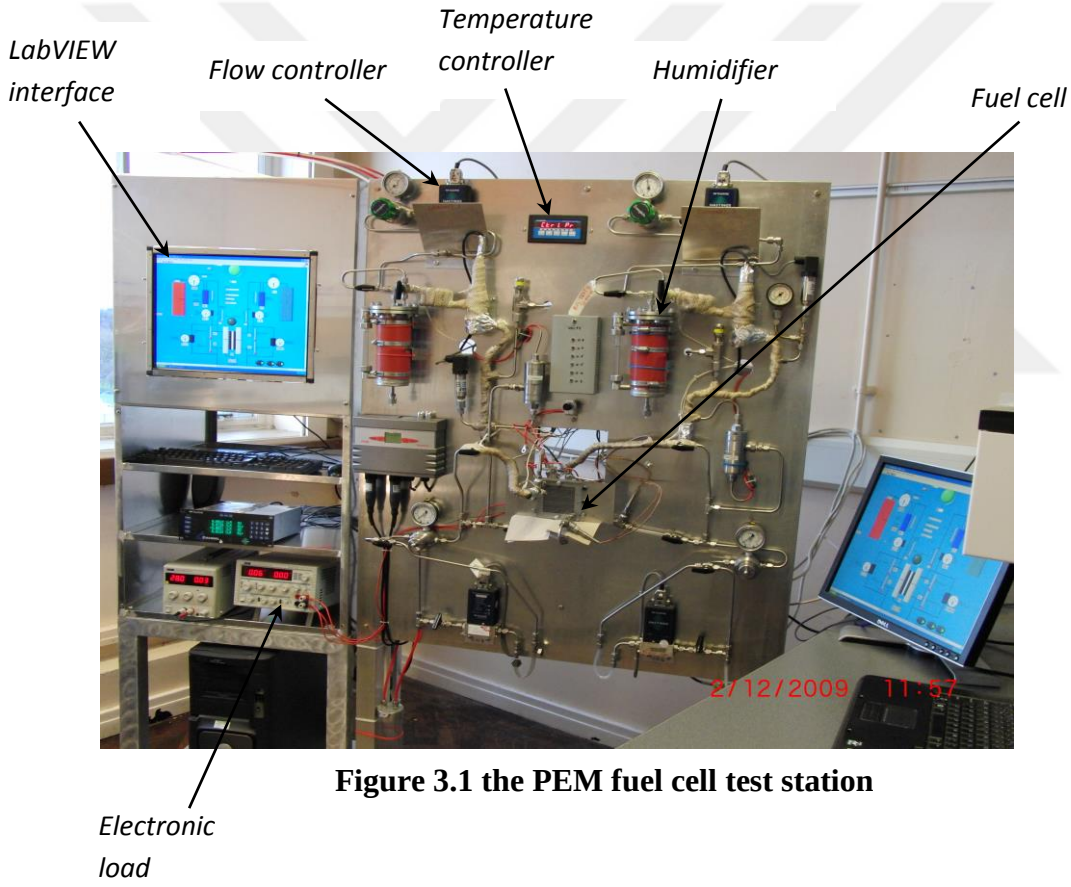



**Figure 3.1 the PEM fuel cell test station**

**Humidification of inlet gases:** The hydrogen should be humidified due to avoid drying in the anode side; air should be humidified due to ensure that water is not consumed much than produced in the electrochemical reaction. The membrane should be humidified adequately in order to obtain best performance from the cell. In the type of bubbler humidifier, air is

distributed through tube immersed using heated liquid water. This ensures enough contact area between gas and liquid water. The humidification is adjusted by controlling the water temperature. The temperature of gases is controlled by a multi-zone temperature controller (Omega, CN1500).

The pressure of the inlet and outlet gases is controlled thanks to 10 psi pressure regulators (Swagelok). However, the actual pressures of inlet gases are controlled via flow controllers. The operating voltage of the cell is adjusted and monitored between 0 and 1 V thanks to an electronic load, LD300 DC. This digital electronic load automatically increases the load in order to maintain a particular voltage. The voltage is adjusted using this electronic load and kept constant across the cell.

The parameters (fuel flow rate, pressure) which are controlled and monitored in order to observe cell performance are measured and monitored by a data acquisition system with LabVIEW (National Instruments) as a monitor-and-control system.

The system allows for varying the temperatures of inlet gases and humidifiers, the pressures of inlet gases and the outlet gases and flow rates of inlet gases.

Figure 3.2 shows a schematic of the experimental setup. The various sensors, heaters and other transducers are outlined.

In the first step nitrogen and helium will be used as inert gases to purge the system before and after running the experiments in order to achieve a safe run and same homogeneous conditions. The 99.99 % pure hydrogen and air come to the fuel flow rate controller through pipes with the stoichiometric ratio of 2.

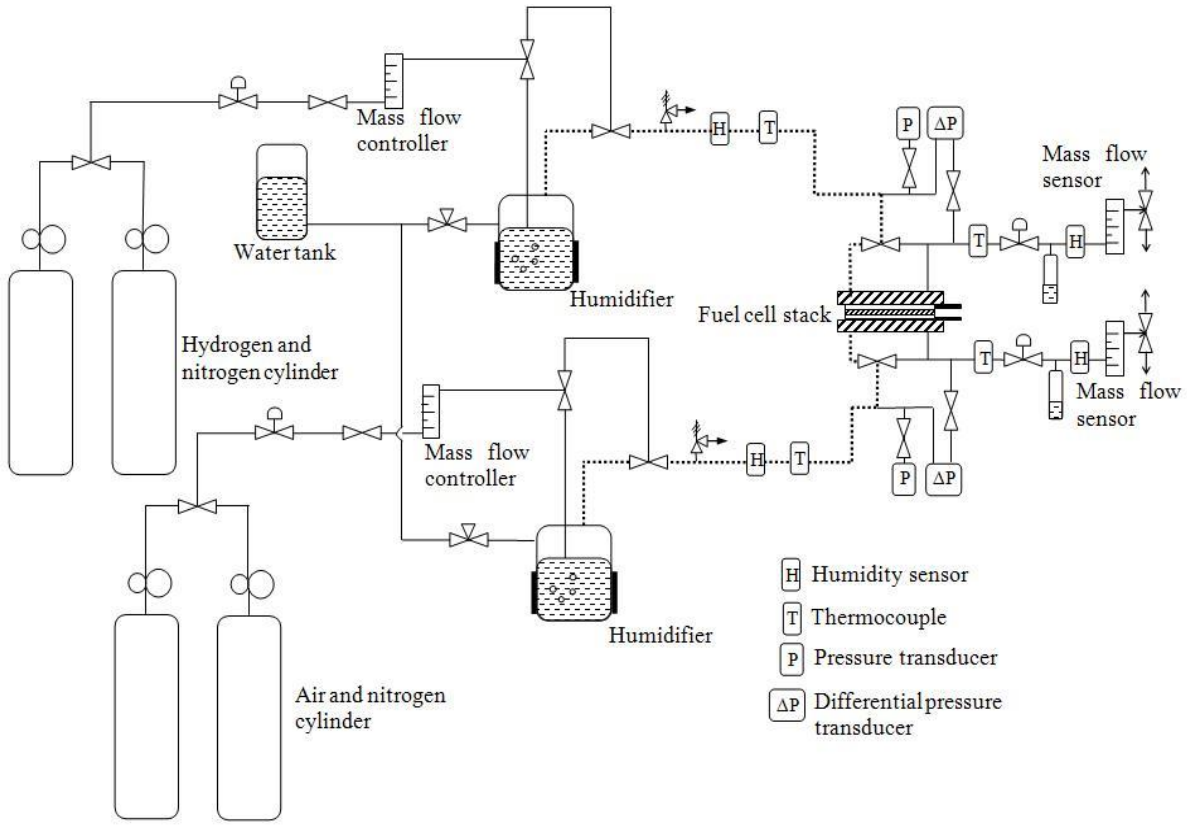



**Figure 3.2 Schematic representation of the experimental set up**

**The stoichiometric ratio:** The stoichiometric ratio shows the ratio of fuel flow rate of cathode and anode. This is kept at 2 in these experiments. The stoichiometric ratio of 2 is chosen to supply adequate oxidant to the cathode. The volume flow rate of oxygen has a great effect on the cell performance. However, the stoichiometric ratio lying beyond 2 has a little effect on the cell performance [26]. Therefore, the stoichiometric ratio of 2 will be used in these experiments. The effect of different stoichiometric ratio for this cell can be studied further. Once the reactant gases arrive at the mass flow controller, fuel flow rate is adjusted according to given fuel flow rate conditions which are specified (connected to LABVIEW).

**Temperature of the system:** After the mass fuel flow rate controller, the dry gas passes through the channels which are used to elevate the temperature of the inlet gases. The anode inlet temperature is set to $35^0$ C and the cathode inlet temperature is set to $50^0$ C. The saturated inlet gas with the temperature of $50^0$ C gives an increase in the cell performance due to the fact that it helps to increase ionic conductivity of membrane for protons and ions [27]. It also balances the water inlet and water production since higher water production causes

flooding at the high current density region. The anode temperature is set to $35^0$ C due to fact that the test facility does not allow to increase anode inlet temperature. The heater is then changed, but the temperature of $35^0$ C will not be changed in order to compare the results as further research with the results of Ismail et al [28]. Then the inlet gases with elevated temperature reach to humidifiers.

Humidifiers are employed to achieve the humidification of reactant gases. The temperature of humidifiers is set to $80^0$ C since the adequate humidification can be managed at this temperature [3]. The humidifications of inlet gases are very significant for the fuel cell in terms of performance. Since transport of protons is assured by the membrane and the Nafion membrane has low ionic conductivity in dry condition which deteriorates the cell performance.

As it can be seen from the Figure 3.1 at the top the system a temperature controller is set. The temperature controller is calibrated to control the humidifiers and reactant gases temperatures. The humidifiers ensure that the reactant gases are 100% humidified. The fully humidified reactants then arrive to the cell through the connection. After the humidifiers the connection is insulated with the heater tapes to ensure that the water does not condense or cool through the connection and the temperature of inlet gases is kept at a constant value. The temperature and the humidity level of the inlet gases are measured by sensors before entering the cell and monitored by LABVIEW and digital humidity sensor. The pressure of the cell is controlled using a backpressure regulator. This allows the pressure at the outlet of the cell to be controlled. The pressure at the inlet is controlled by the pressure regulator which is set to before the mass fuel flow controller in the system.

### 3.1.2 Limitations and Restrictions of the Test System

It can be seen from both Figure 3.1 and 3.2 that there is no temperature controller in the system in order to control the cell's temperature. This might affect the performance of the cell due to the fact that the cell temperature changes with the ambient temperature. However, the inlet gas temperature is controlled as the gases arriving at the cell which has a significant impact on the regulating the cell temperature.

The mass flow rate controller at the anode side control gas flows up to 1 L /min and the mass flow rate controller at the cathode side controls gas flows up to 5 L/min range. This

means that the mass flow controllers cannot control the gas flows below 0.01 L/min at the anode side and below 0.05 L/min at the cathode side. This requires a chance in the stoichiometric ratio for low flow rate operating. The testing experiments of low fuel flow rate have also big fluctuations in terms of current which deteriorates the accuracy of the results. Since, it could not be possible to record the data at the steady stage. The results are recorded every 10 minutes manually. This might result in an increase in the error of measurements. Besides these points, the experiments require significant time to get reasonable results about more than 12 hours each day to complete one experiment. The experiments are run about 11 hours for each run. Since the data which is used to plot the polarisation curve is obtained in the steady state. This means the results have very little fluctuation in the current density. Reaching the less fluctuation region for the low fuel rate requires much time than high fuel flow rate, especially for low voltages.

Another restriction of the test system is the accuracy of the electronic load. The electronic load measures the voltage and current in the range of 0.01 and 99.99. Therefore, it is not be possible to take readings for the current below 0.01 in the activation area. In addition to this, the LABVIEW software does not currently record and print the results. This was not undertaken during the experiments due to time limitations. Therefore, data was recorded manually every 10 minutes which might affect the accuracy of results. The LABVIEW software can be updated digitally to capture this information for future work.

The test facility includes mass flow controller at the bottom of the system. This allows the hydrogen consumption of the cell to be measured. However, the mass flow controller is not used in these experiments since the addition apparatus are required. Before the mass flow controller, the product water which comes from the cell needs to be removed. This could be done cooling the water and removing it from the system. Then the only gas which will reach the mass flow controller will be hydrogen. This can give a great opportunity to determine the amount of hydrogen consumed in the cell. This might help to save the fuel and run the cell efficiently.

### 3.1.3 Description of MEA to be used in this work

The MEA is the heart of the PEM fuel cell as the components of it have been discussed in Section 2.1.1. There are different methods to prepare the MEA. New methods use electrode

position and vacuum deposition to make the electrodes. They ensure thin layer and low loading of a catalyst. The most common used method is the thin film method. This method requires preparation of an ink with the catalyst. The ink is the mixture of 20% wt Pt/C support with 5% solution of Nafion. Ultrasound is used to homogenise ink until reaching adequate texture for coating. In another approach the catalyst layer is mounted to a PTFE blank using a transfer printing model. Using Nafion in the process of preparation ink ensures a good intimate interface between the catalyst and membrane [10].

There are different manufacturing techniques to prepare an MEA assembly. The catalyst layer application to GDL includes spreading method, thin film method, spray method, catalyst powder deposition, ionomer impregnation method, electrode position method, sputtering where as catalyst application to membrane is composed of impregnation reduction, dry spraying, novel fabrication method, catalyst decaling, painting, and sputtering [7].

The MEA tests with different GDLs are a part of large study area. This study looks for one kind of MEAs which was prepared by using SGL 10BC GDL. The properties of GDL are shown in table 3.1.

**Table 3.1 Properties of GDL [28]**

| **GDL** | **Thickness, µm** | **PTFE Loading[a], wt%** | **Areal Weight, g/m$^2$** |
|---|---|---|---|
| SGL 10BC | 415 | 23[b] | 135 |

[a] Provided by the supplier

[b] Values for PTFE loading in the MPLs. The PTFE loading in the corresponding carbon substrates is 5 %.

This SGL GDL is designed for transporting to reactant gases into the electro catalyst layer and product water out of the electro catalyst layer. It has open pore structure, high electrical conductivity and good mechanical strength. It suits best for stationary and portable power systems. The PTFE loading are available up to 30 wt%, but 5 wt% is standard [25].

### 3.1.4 Method for Preparation of the MEA

In this study the ink was prepared using 5 % Nafion, 50 % ethanol and water. The first step was to calculate the amount of the catalyst, 60% Pt/C (Alfa Aesar, UK). It was calculated using 0.4 mg/cm$^2$ platinum loading and 11.56 cm$^2$ active areas. The amount of catalyst was mixed with a few drops of deionised water to obtain a good dispersion of platinum. The second step is to add ethanol and water to the ink. The solution was mixed ultrasonically. This mix was stirred onto the surface of the GDL, mounted on a heated-to-75°C PTFE-plate by using a spray gun (BADGER 100, USA). In the third step, a mix of 5 wt% Nafion solution was sprayed onto the surface of the catalysed GDL so as to obtain better proton mobility and a good swell. The same procedure was applied for the anode side apart from the amount of Pt and loading, 0.20 and 0.25 mg/cm$^2$ for the platinum and Nafion loadings were applied for the anode [28].

After preparing the GDL and membrane the last step is to assembly the MEA which plays an important role on improving the cell performance and determining the operation characteristics. In order to manufacture the MEA, the catalyst GDL was bonded to the membrane by using hot- pressed (hydraulic press) at 130$^0$ C and 50 kg/cm$^2$ for 3 minutes. Before this process, the MEAs were boiled at 80$^0$ C in 2 % hydrogen peroxide solution for one hour, washed with deionised water and then boiled in 1M sulphuric acid at 80$^0$ C for one hour and washed again with deionised water. Then the MEA was stored in deionised water at the room temperature [28].

### 3.1.5 The PEMFC used in the experimental work

The PEM fuel cell was prepared by bonding the MEA and two composite bipolar plates (Bac2, UK) together. Since composite bipolar plates show better initial and long term performance than graphite bipolar plates [29]. Figure 3.2 shows the bipolar plate which has and 11-turn and single pass serpentine flow channel of depth 2mm and width 2 mm and a rib of width 0.8 mm [28].

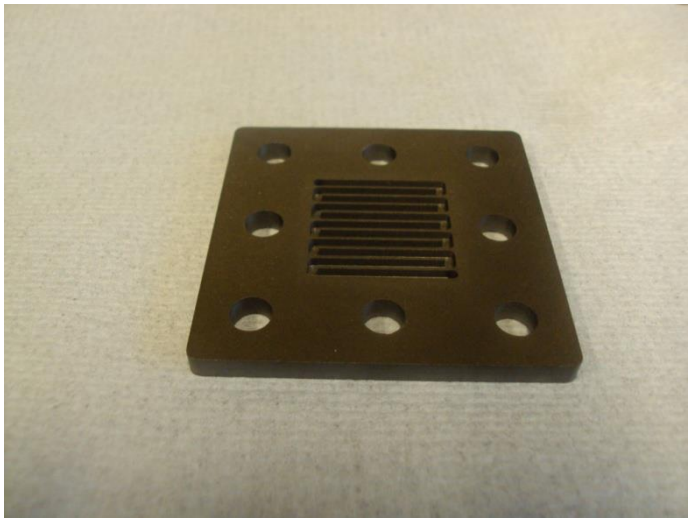


**Figure 3.3 bipolar plate (Bac2)**

The MEA and bipolar plates were placed between two copper as shown in Figure 3.3. The copper is used to support the cell mechanically. The current is measured directly from the bipolar plates and monitored by electronic load. The fuel cell is connected to the test station as shown in Figure 3.1. The hydrogen and air are supplied through the cylinders.

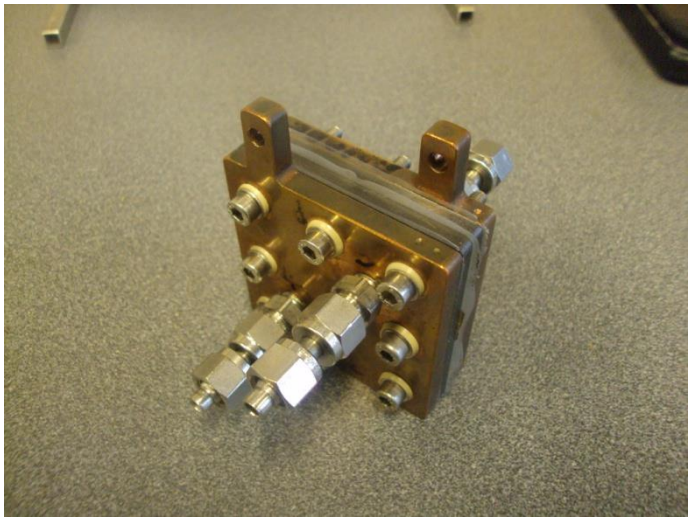


**Figure 3.4 the PEM fuel cell**

### 3.2 Operating Conditions for Experimental Work

The aim of these experiments is to investigate the impact of various fuel flow rate and pressures on the cell performance. The experiments were done using different operating conditions. The table 3.1 shows the experiments which were conducted. The experiments were started with testing various fuel flow rates. Then the experiments were done for various operating cell pressures.

**Table 3.2 Experiments plan.**

| | **Various fuel flow rate** | **Various pressure** |
|---|---|---|
| **Temp of humidifiers** | $80^0$ C | $80^0$ C |
| **Temp of anode inlet gas** | $35^0$ C | $35^0$ C |
| **Temp of cathode inlet gas** | $50^0$ C | $50^0$ C |
| **Stoichiometric ratio** | 2 | 2 |
| **Pressure of inlet gases** | 44.1 psi | 44.1 psi |
| **Pressure of anode outlet** | 21 psi | Ambient- 10psi- 21 psi |
| **Pressure of cathode outlet** | 34 psi | Ambient- 15psi- 34 psi |
| **Fuel flow rate** | 0.1-0.2-0.3-0.4-0.02-0.05 SLM | 0.1 SLM |

#### 3.2.1 Operating Condition Parameters for Various Flow rates

In all experiments, the humidifier's temperature is fixed at $80^0$ C to get the adequate humidification. The water content has an important effect on membrane conductivity. The Nafion membrane which is used in these experiments has low ionic conductivity in dry condition. This deteriorates the fuel cell performance. Therefore, it is significant to humidify the membrane adequately. Above $80^0$ C, it is very difficult to get adequate humidification with lower back pressure of 2 bar (29.4 psi) [3]. Since the temperature of humidifiers set to $80^0$ C. The reactant gases are humidified during the operation of the cell, at the higher temperature of the cell. The cathode inlet gas temperature is fixed to $50^0$ C and the anode inlet gas temperature is fixed to $35^0$ C thanks to temperature controller. The saturated gas with the temperature of $50^0$ C gives better fuel cell efficiency [27]. Therefore, the temperature of inlet

gases is chosen as $50^0$ C. The anode inlet gas heater could not manage to increase the inlet gas temperature to $50^0$ C at the beginning. Thus, the anode inlet gas temperature is used as $35^0$C which allows comparing the results with Ismail et al [28] as further research. The cathode higher temperature also helps to increase the electron transport and cell performance.

In the test system, hydrogen and air are kept at a constant stoichiometry of 2. The hydrogen and air inlet pressure are adjusted 3 bar (44.1 psi) since the pressure differential is needed between inlet and outlet pressure to continue inlet gases flux. This pressure has not have a significant impact on the system. It only needs to be enough pressure for flow controllers. Since the inlet pressures of gases are mainly controlled by flow controller. The outlet pressure for the anode is 21 psi and for the cathode is 34 psi. It is proven that the pressurised cathode side has better effect on the cell performance than pressurised anode side [30].

The effects of flow rates are observed and polarisation curves are obtained over the using 10BC GDL for the MEA in the cell. Nitrogen and Helium are supplied to purge the residual gases in the cell before and after the each test due to avoiding residual gases which might affect the experiment as well as being sure that opening the rig is safe.

The beginning fuel flow rates are 0.1, 0.2, 0.3, 0.4 SLM for the higher flow rate and 0.05, 0.02 for the lower flow rates. The experiments are needed to repeat at least once for each run in order to obtain comparable results. The lower fuel flow rate tests are run in order to obtain whole polarisation curve for the cell and interpret the behaviour of the cell in terms of voltage losses (activation, ohmic and concentration). The higher flow rate tests are run so as to observe the cell performance with flow rate and suggest the best fuel flow rate for the cell.

### 3.2.2 Operating Condition Parameters for Various Pressure

In order to observe the impact of cell pressure on the cell performance, a number of tests will be conducted. In these tests, the reactants will be humidified to $80^0$ C using the humidifiers. The cathode and anode inlet reactant's temperature are fixed $50^0$ C and $35^0$ C, respectively. The reactant inlet pressure is kept at 3 bar. The flow rates of reactants are set to 0.1 SLM with a stoichiometric ratio 2. The test will be conducted firstly at ambient pressure, then for later experiments the pressure adjusted to 10 psi for the anode and 15 psi for the cathode. Finally, the third test was run at 21 psi for the anode and 34 psi for the cathode.

Increasing the cell pressure raises the partial pressure of inlet gases. This might help to improve the diffusivity of reactants as well as the efficiency of the cell. The aim of these experiments is to obtain polarisation curves in order to see the effect of pressure and determine how the elevated pressure affects the performance of the cell.

# Chapter 4 Results and Discussion

## 4.1 Effect of Fuel Flow Rate on the PEMFC Performance

The purpose of these experiments is to investigate the influence of flow rate on the cell performance using the prepared MEA in the PEM fuel cell. Adequate gas and water management is significantly important to obtain high efficiency as discussed in section 2. Therefore, the fuel cell is humidified at $80^0$ C to get adequate humidification. Above $80^0$ C, it is very difficult to get adequate humidification unless high pressure above 2 bar is employed [3]. The anode flow rate and cathode flow rate influences on the cell performance can also be studied separately. In this study, this has not been done.

Table 4.1 shows the total runs of the cell with date performed. The numbers of runs and date have an effect on the cell performance since it affects the humidification of membrane. The performance of fuel cell increases with the humidification level of membrane [27]. The membrane could dry and that might influence the accuracy of the results. The experiments are stated with humidification of the membrane for a week. Then the tests are run beginning with the flow rate of 0.1, 0.2, 0.3, and 0.4 SLM. After these tests the low fuel flow rates of 0.02 and 0.05 tests are run. Repetitions of tests are also done after these tests.

**4.1 .Table of date fuel cell operated**

| June | | July | August |
|---|---|---|---|
| 7 (humidification) | 21 (0.3 SLM) | 4 (0.05 SLM) | 1 (pressure tests) |
| 8 (humidification) | 22 (0.4 SLM) | 5 (0.02 SLM) | 2 (pressure tests) |
| 9 (humidification) | 23 (0.05 SLM) | 8 (0.02 SLM) | 18 (pressure tests) |
| 10 (humidification) | 24 (0.05 SLM) | 12 (0.05 SLM) | 19 (pressure tests) |
| 14 (humidification) | 29 (0.4 SLM) | 19 (0.02 SLM) | |
| 15 (0.2 SLM ) | 30 (0.3 SLM) | 20 (0.4 SLM) | |
| 20 (0.3 SLM ) | | | |

The flow rates of gases are measured in standard litres per minute (SLM). In order to achieve high efficiency, the flow rates of gases should be equal to the gases which react in the

cell. In most cases, a higher flow rate for inlet gases is preferred especially at the cathode side due to the fact that excess flow rate is required to remove product water. However, there are limits for flow rates. If the flow rate is too high, the cell efficiency can be low and hydrogen is wasted or if the flow rate is too low, the cell can suffer owing to luck of enough hydrogen for the reaction [2]. If the mass fuel controller can be used at the bottom of test facility, the needed amount of hydrogen and air would be calculated for the cell. This might be done as a further research.

Amirinejad et al (2006) pointed out that the most important factors which affect the performance of PEMFC is mass transport limitations such as transportation of fuel gases and reactant in the catalyst layer, transport of hydrogen ions to the cathode and produced water transport from cathode to anode side [30]. In these experiments, the impact of flow rates and pressure on the cell performance considering mass transport are under investigation. Before running the experiments, the fuel cell is run in order to get adequate humidification. The tests are run for a week. The flow rate of reactants is increased with the stoichiometric ratio of 2. The experiments are started with the preliminary experiments in March. Each test is repeated for every pattern of fuel flow rate and results are presented with date performed. The results show perfect suitability in repeats as shown in Figures 4.1 and 4.2. The suitability of results shows that adequate humidification of membrane is achieved.

Figure 4.1 displays the experimental results for a flow rate of 0.2 SLM of $H_{2.}$ The experiments are performed in different two days. Before doing the second experiment, the fuel cell is run to solve membrane dry-out problem, and perfectly similar results are obtained. However, this graph does not show the whole characteristic of polarisation curve. The low and medium current density regions are obtained with this polarisation curve. The high current density region could not be obtained since the electronic load does not allow going low voltages. However, the activation and ohmic region behaviour can be seen clearly. The activation over potential seems similar for the all flow rates. The activation over potential is a function of exchange current density and temperature [27]. The exchange current density is also functions of temperature, electrode catalyst loading and catalyst specific surface area [2]. The behaviour of polarisation curves is similar since the parameters that affect the activation over potential are similar.

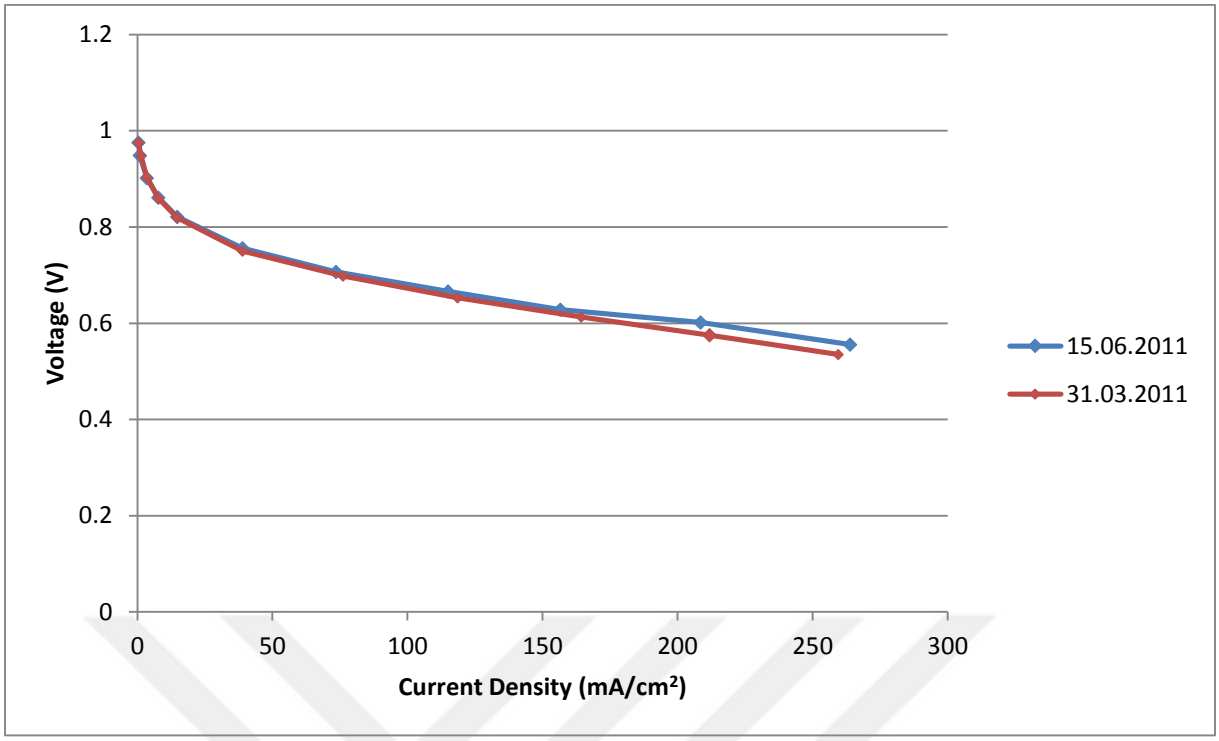



**Figure 4.1 Plots of the polarisation curves for the flow rate of 0.2 SLM of $H_2$ in 2 different days**

Figure 4.2 shows the polarisation curves for a flow rate of 0.3 of $H_2$ which are obtained at the discussed operating conditions. The polarisation curve (purple line) is notably different from the others. This may be explained by the date of the experiment which influences the humidification level of the membrane. Although, the fuel gases are fully humidified since the inlet gases are humidified at high temperature of $80^0$ C and the humidification level of reactants are measured before the introduction of gases into the fuel cell by the sensors, the performance of fuel cell is affected by the humidification level of the membrane especially with the anode side. This is due to the fact that Nafion membrane has low ionic conductivity in dry conditions [30]. The transport of protons from anode side to the cathode side increases with humidification degree of membrane which has a positive impact on the fuel cell efficiency. The produced water is transported from cathode side to anode side by a back diffusion process which increases the transport of protons to cathode side. Therefore, it is important to run the fuel cell in non-stopping period to get adequate membrane hydration. This period may be up to one week. It is possible on this test that the fuel cell is run for one day. This was not enough time to suitable humidification of the membrane. It may be possible

to conclude that the fuel cell requires a few runs before obtaining accurate results to ensure that membrane is humidified suitably.

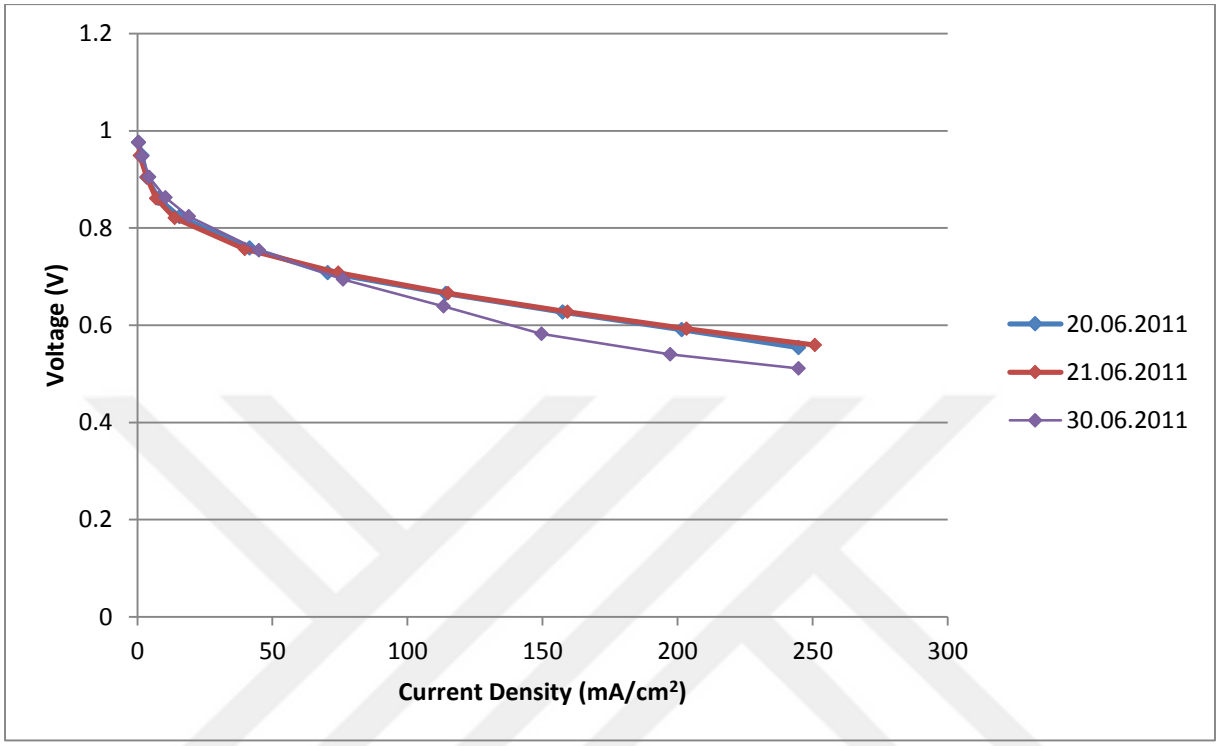



**Figure 4.2 Plots of the polarisation curves for the flow rate of 0.3 SLM of $H_2$ in 3 different days**

Figure 4.3 presents the polarisation curve for 0.4 SLM $H_2$, dots (red) present the results for lower voltages and some repeated points. Since the polarisation curve ends in the medium current density region, the whole polarisation curve which has 3 current density regions could not be obtained. Thus, the experiment is repeated in order to see the performance of the cell in the high current density area. The voltage is adjusted as possible as low to obtain high current density and observe the characteristic of polarisation curve in this region. The line is used to aid visual clarity.

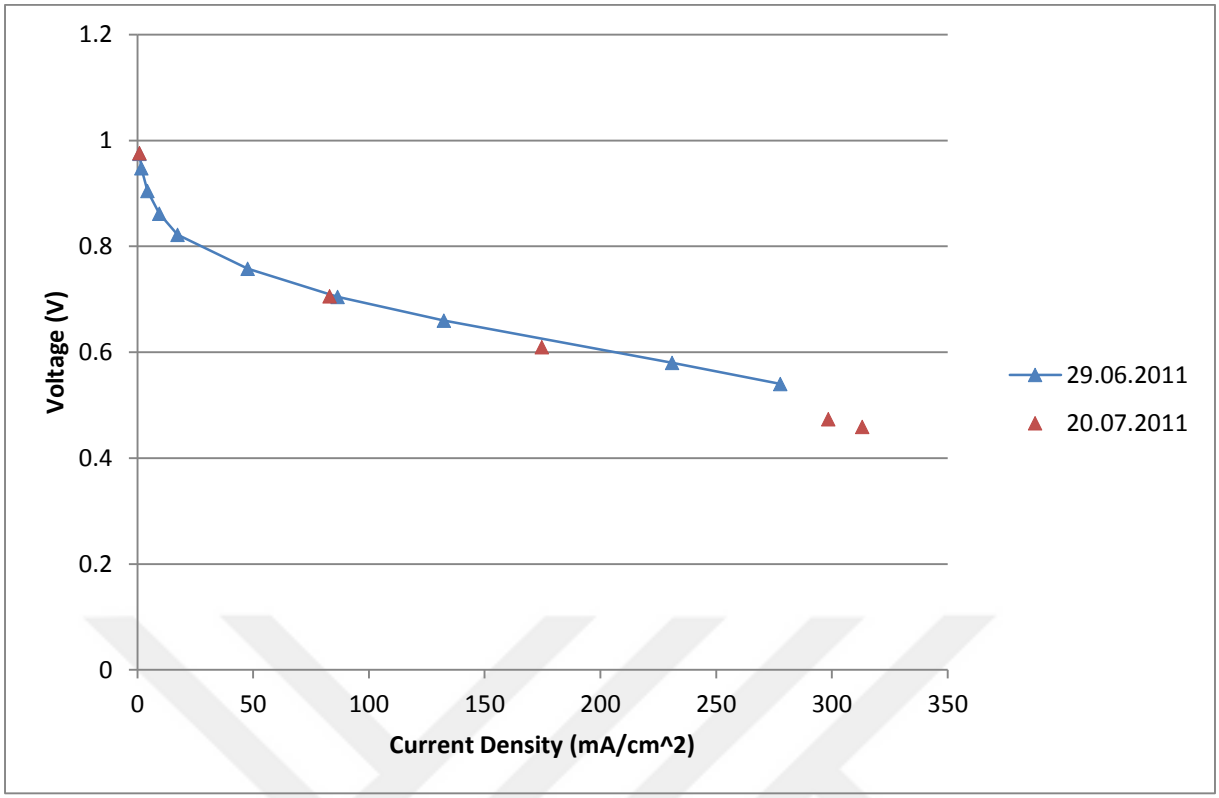



**Figure 4.3 Plots of the polarisation curves for the flow rate of 0.4 SLM of $H_2$**

Figure 4.4 shows the average result for the flow rate of 0.3 $H_2$ SLM and 0.4 $H_2$. The results for 0.3 $H_2$ SLM is calculated considering results from Figure 4.2. However, the values of 30.06.2011 (purple line) is removed from the average in Figure 4.5 since it appears to be an outlier compared to other values and there is no suspicion that the membrane may not be humidified adequately on this occasion.

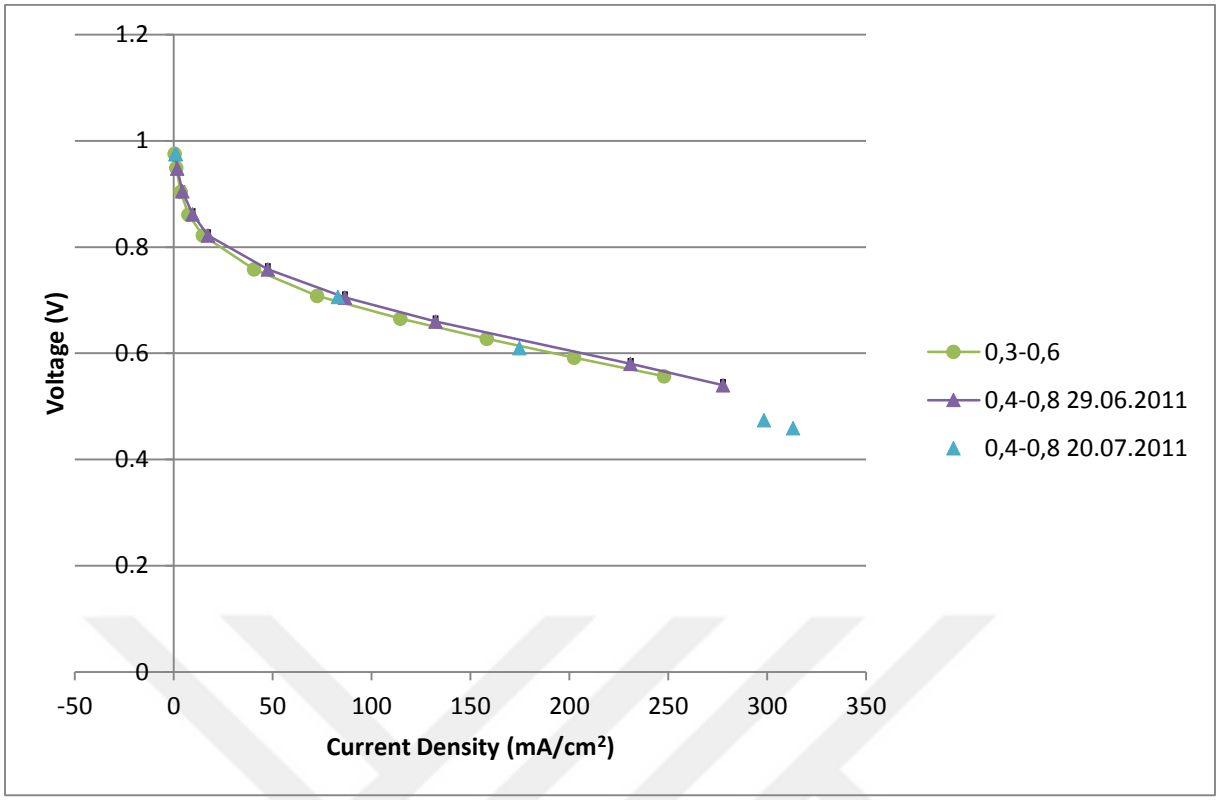



**Figure 4.4 Plots of the polarisation curves for 0.3 SLM of $H_2$ (average) and 0.4 SLM of $H_2$, from Figure 4.3**

The effect of flow rate on the cell performance is presented in Figure 4.5. The results using different fuel flow rates are obtained and compared to each other. It can clearly be seen that the performance of the cell is improved with an increasing fuel flow rate, but the improvement of the cell efficiency is not much. The current density of the cell increased relatively as the fuel flow rate increased. Finally, 280 mA/cm$^2$ current density is observed with 0.4 SLM flow rate of the hydrogen. This might be owing to the fact that sufficient fuel is supplied to the cell as well as rising humidity level. Since the fuel is fully humidified before going to the cell which might help increasing the humidity level of membrane. As it is already mentioned that the humidity level of membrane increases the transport of protons to the cathode side and this improves the fuel cell efficiency. In those experiments, the flow rate of air is also increased. This has an effect on the removing the product water and increasing the concentration level of oxidant. Jang et al (2008) found out that higher cathode flow rate increases the performance of the cell. As the concentration of oxygen increases with higher flow rate the activation over potential decreases as long as sufficient fuel is supplied. In this study, there is not a notable difference in the activation over potential and this may be

explained by the enough presence of oxidant at the cathode. However, Jang et al did not find any clear evidence for the anode flow rate [31]. As shown Figure 4.5 the increase on the cell performance is not significant. This may be either hydrogen is completely consumed while there is excess air at the cathode or oxygen is completely consumed while there is excess hydrogen at the anode. Fixing the flow rate of hydrogen or air will limit the performance of the cell [26]. However, in these experiments this is unlikely to happen since the experiments are run with the stoichiometry of 2. The increase in the fuel cell efficiency in the medium current density region may also be explained by the decrease in ohmic losses. The ohmic losses are functions of ionic and electronic resistance. Ionic losses can be expressed as follows [27];

$$r^{ion} = t_m / \sigma_{ion} \quad \text{(Eq. 4.1)}$$

tm represent the thickness of the membrane and $\sigma_{ion}$ represent the ionic conductivity of the membrane. Increasing fuel flow rate means a higher introduction of water into the cell which raises the humidification degree of the membrane. This potentially results in an increase in the ionic conductivity of the membrane. Since the ionic conductivity of the membrane increases the ionic resistance as well as ohmic resistance decreases.

These experiments derived the question of testing the fuel cell performance for the low flow rate in order to obtain a whole polarisation curve and determining the sufficient fuel flow rate is an important issue in terms of saving the fuel. Since hydrogen production and storage are a challenging area for fuel cells.

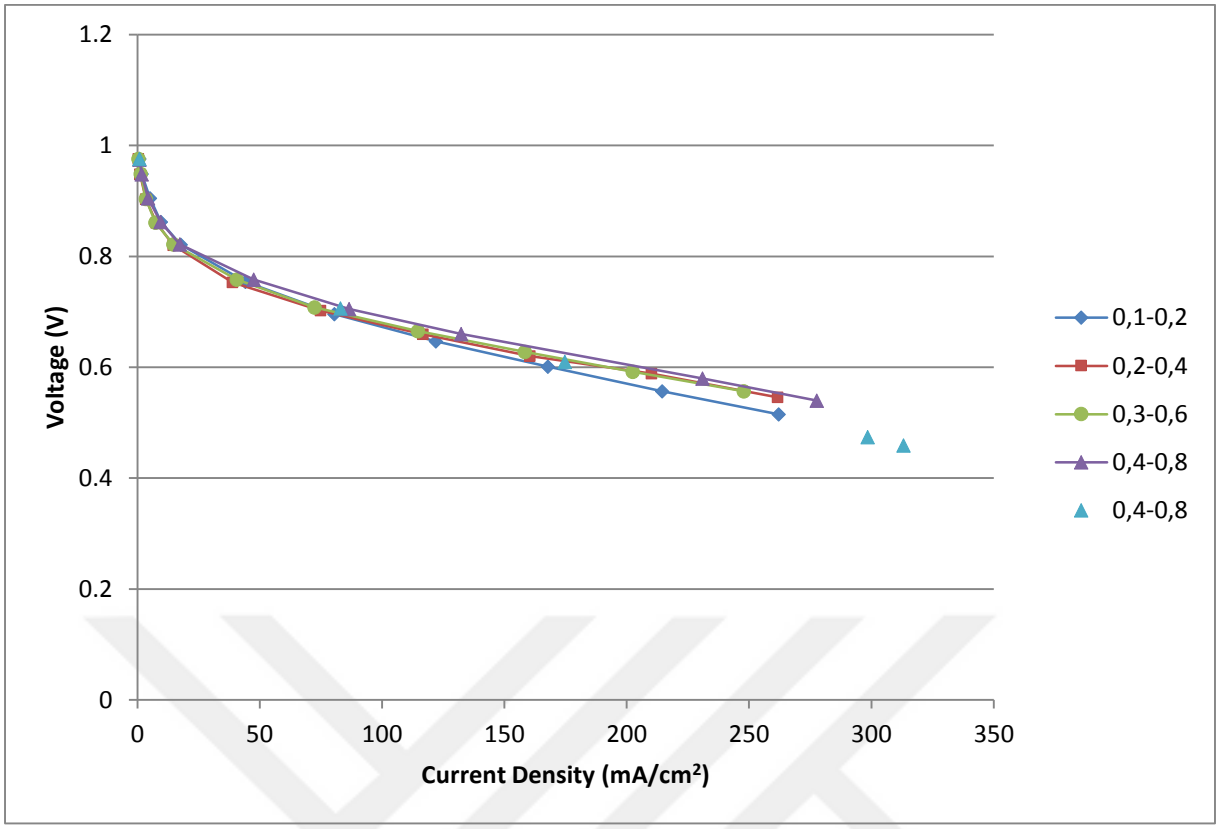



**Figure 4.5 Performance comparison among high flow rates (the flow rate of anode side is shown on the left, the flow rate of cathode side is shown on the right, both are presented in SLM), dots represent repeating experiment for some values.**

### Investigation of Low Fuel Flow Rates

Figure 4.6 exhibits the performance of the cell for 0.05 SLM hydrogen flow rate. The blue and red lines show the results of the experiments in different days. The Green dots are also obtained by setting low voltages in order to see the performance of the cell in the high current density region. From the Figure 4.6 it appears to be observed concentration losses, but there appear to be a strange kink in the points in the high current density region. It is expected that the polarisation curve has a smooth line as observed in the low and medium current density region. This may be caused due to the fact that high fluctuations are observed in the current and the data is recorded manually which can increase the accuracy of the results. The experiments for the flow rate of 0.05 SLM are repeated 3 times for the lower voltages and the results are presented in Figure 4.6.

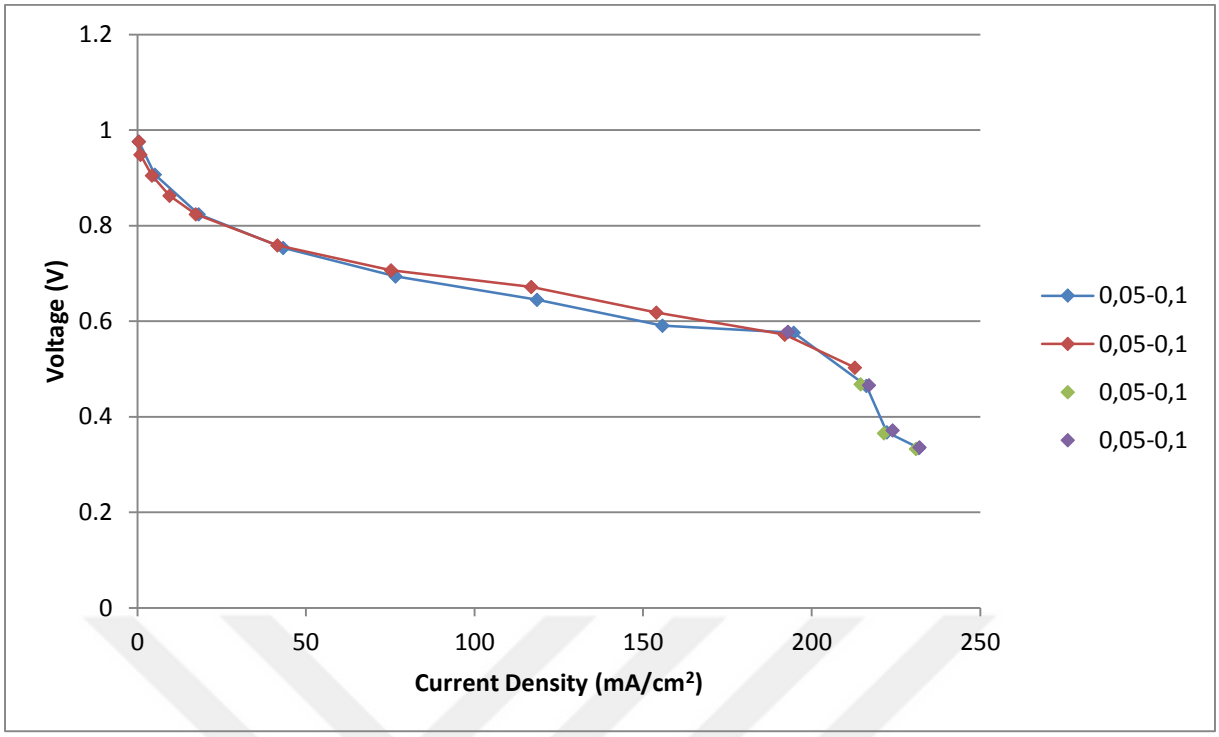



**Figure 4.6 Plots of the polarisation curve for (0.05 SLM $H_2$)**

The lowest level of fuel flow rate is presented in Figure 4.7. The stoichiometric ratio is used as 5. Since mass flow controller at the cathode side ranges up to 5 SLM which means that the flow rate control ranges ± 0.05. This also allowed making a comparison between the two hydrogen flow rates since air flow rate is fixed at 0.1 SLM. The clear concentration losses are observed in Figure 4.7. Concentration losses become dominant when the diffusivity of reactants to the catalyst surface lower than the rate of consumption. Since the reaction rate is high in the high current density region and there is not enough reactant diffusion to maintain the reaction consumption rate, a sharp drop in the cell potential is observed as seen in Figure 4.7. Since the concentration and partial pressure of reactants are low for the lower fuel flow rates, the cell efficiency deteriorates.

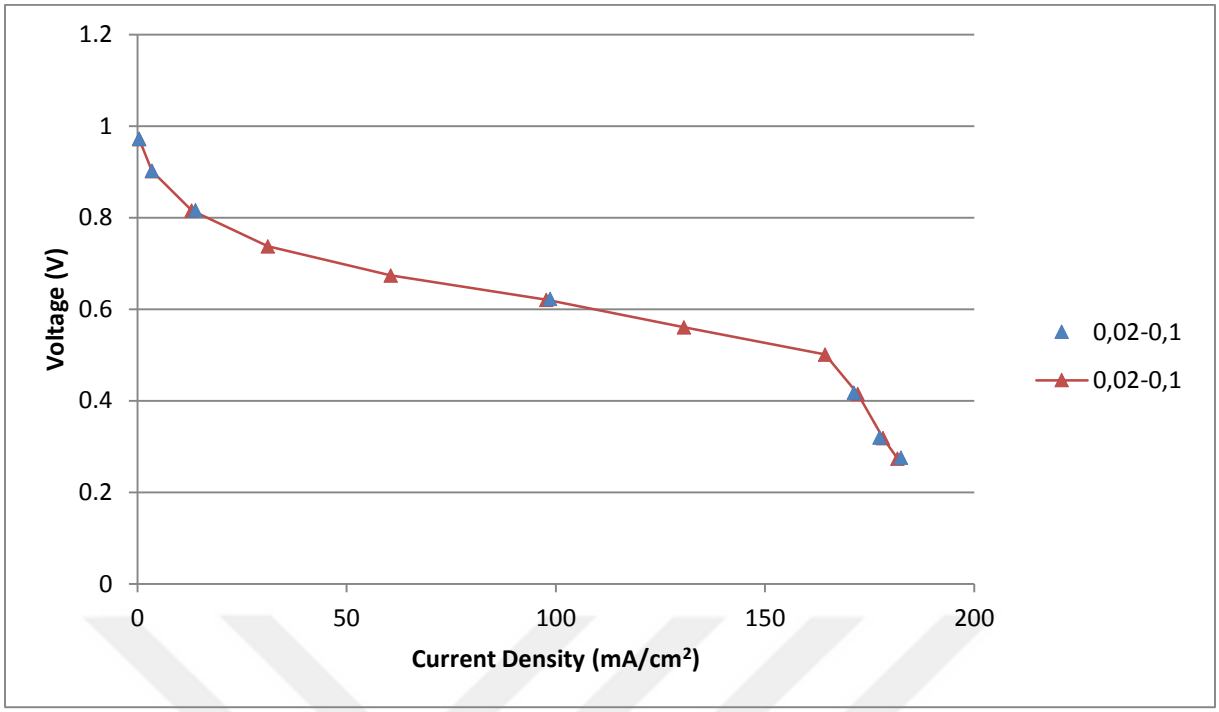



**Figure 4.7 Plots of the polarisation curve for (0.02 SLM $H_2$)**

It is explicitly seen from Figure 4.8 that the performance of the cell decreases with the decreasing fuel flow rate. This could be due to the fact that there is not sufficient hydrogen at the anode. As the hydrogen flow rate increases, the current density improves. Comparing to flow rate of hydrogen 0.02 and 0.05 with each other, a visible increase in the performance is seen. This might be owing to a rise in the hydrogen level as well as an increase the degree of humidification of the membrane. In the medium current density region ohmic losses are dominant. Since the fuel is humidified at a higher temperature ($80^0$ C), increasing mass of fuel means more water goes into the cell. This contributes to increase the humidification of membrane and could potentially decrease the ionic resistance of the membrane. As ionic resistance of the membrane decreases, the ohmic losses decrease which contributes to increase the performance of the cell in the medium current density region.

Another interesting point with low fuel flow rate of these experiments is that the concentration losses can be seen in the high current density region. In this region, water production is high and it is difficult to remove the water with low level of flow rate. This could cause flooding in the gas diffusion layer or at the active area of membrane. In the high current density region low saturated fuel is the best condition since the membrane is already with the product water and water inlet with the fuel.

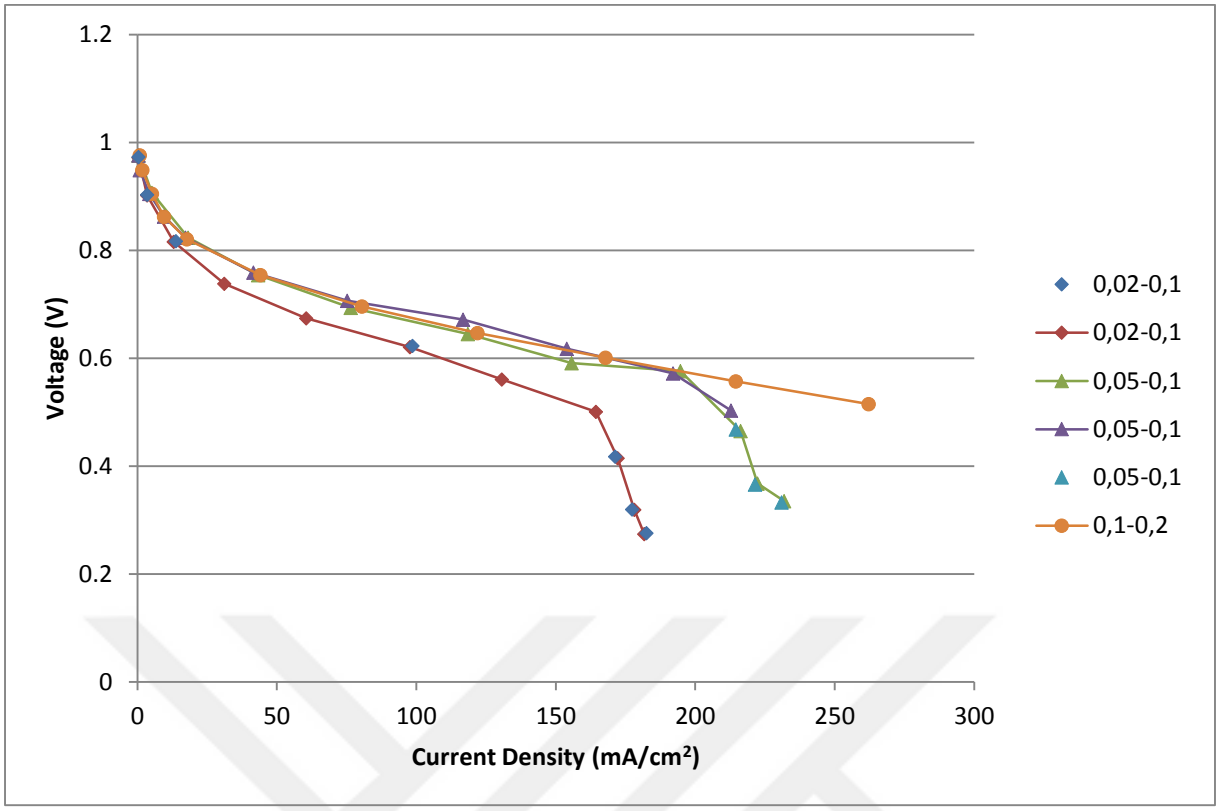



**Figure 4.8 Performance comparison among low flow rates (the flow rate of anode side is in SLM), dots represent repeating experiment for some values.**

The polarisation curves behaviour for low fuel flow rates is obtained as expected apart from the kinks in the high current density region. This might be slow diffusion of reactants to the catalyst surface which causes fluctuations in the current.

### 4.2 Effect of Pressure on the PEMFC Performance

The impact of gas pressure on the cell performance is also studied. The pressure is regulated using a pressure regulator placed downstream of test station. The cell is operated at ambient temperature. Humidified hydrogen and air are used at $80^0$ C with the flow rate of 0.1 SLM and 0.2 SLM, respectively. Figure 4.9 exhibits the effect of changing both the anode and cathode sides operating pressure from 10 psi to 34 psi. The cathode side can be pressurised up to 34 psi and the anode side can be pressurised up to 21 psi. This might be because of the fact that inlet gas pressure is set to 3 bar (3 bar ≈ 44.1 bar) just before the flow controller and the pressure differential is required between inlet and outlet for circulation of gas. Therefore, the

upper limits are chosen as 34 psi cathode side pressure and 21 psi anode side pressure. The experiments are run for 3 different cathode and anode pressures in 3 different days at constant flow rate of inlet gases.

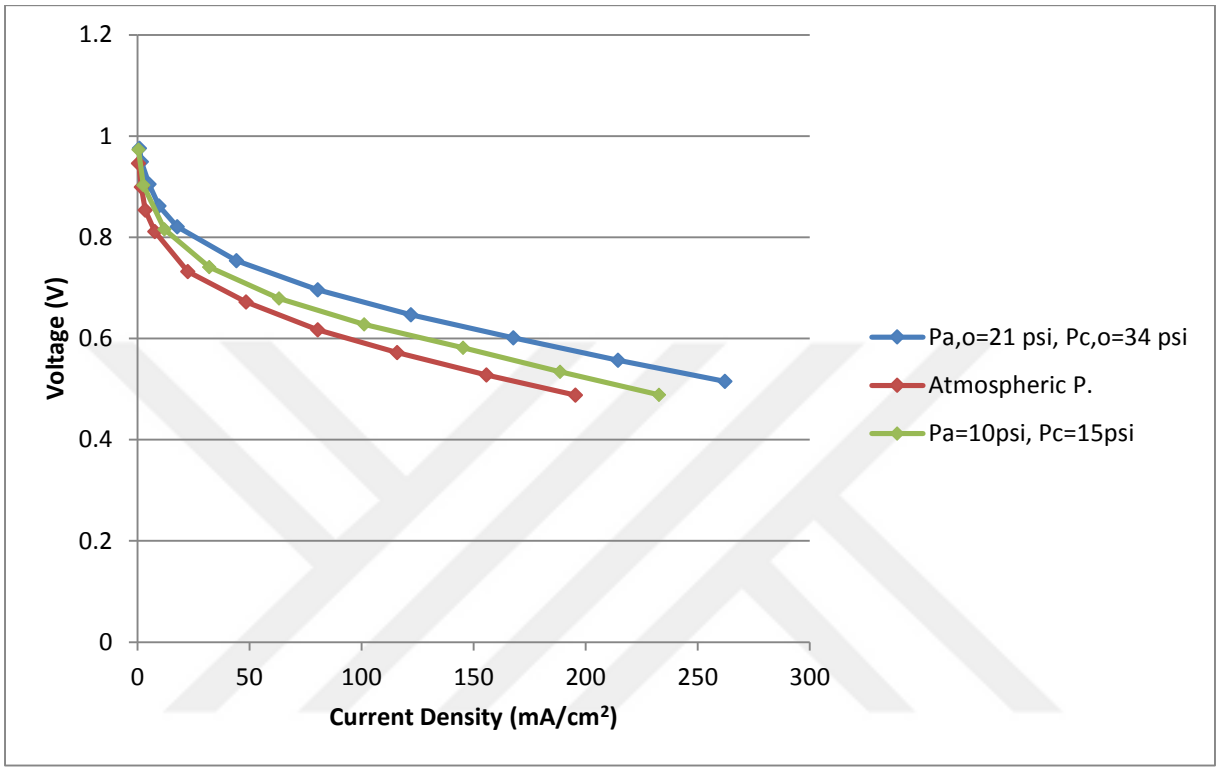



**Figure 4.9 Effect of operating pressure (left is anode side, right is cathode side)**

It can be seen from the Figure 4.9 that the performance of the cell improves when the operating pressure increases. This might be explained using Nernst equation. An increase in the partial pressure of the reactants and product flows lead to higher open circuit voltage in the equation. Nernst equation can be expressed as follows [32]:

$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{\left(P_{H2} \times \sqrt{P_{O2}}\right)}{P_{H2O}}\right) \quad \text{(Eq. 4.2)}$$

$E^0$ which is about 1.2 V is the limit voltage at standard pressure; $P_{H2}$ represents partial pressure of hydrogen where $P_{O2}$ and $P_{H2O}$ present partial pressures of oxygen and water.

The improvement on the cell performance can be explained with elevated open circuit voltage in the Nernst equation (Eq. 4.1). When the operating pressure is increased, the partial

pressure of reactant gases increase. The raised pressure increases exchange current density and this elevates open circuit voltage and improves the cell performance. Another effect of elevated pressure can be increasing diffusivity of the reactant gases [30]. As the partial pressure of gases increase, the diffusivity improves which might help decreasing the mass transport limitation problem. Mass transport limitation is one of the challenges for fuel cells which deteriorate the performance. Decreasing mass transport limitation improves the cell performance.

The anode side and cathode side pressure also have an effect on the performance. The cathode side is pressurised higher than the anode side in those experiments. The pressurised cathode improves the cell performance better than the pressurised anode [30].. This might be due to the fact that product water transport from cathode to anode improves the humidity level of membrane. The ionic conductivity of the membrane increases with the increasing humidity level. This enhances the performance of the cell especially at the high current density region. Since water production rate is high at the high current density region, more water can be transported from the cathode side which ensures higher hydration of the membrane. Another effect of pressurised cathode side is that the oxygen reduction reaction rate increases with the high pressure since the partial pressure of oxygen increases.

Another factor which might have an effect on the cell performance with raised pressure is that humidification. The increase in the cell performance with higher pressure can also be due to the fact that less water is needed to humidify the membrane at higher pressures. This means that the humidity ratio of gases increase very quickly and even more with higher pressure which explains the performance improvement in Figure 4.9.

### 4.3 Empirical Models

The performance of the fuel cell is characterised by polarisation curve (current versus voltage). The I-V curves are obtained for different fuel flow rates. The experimental data is used in predicting the kinetic parameters of the cell at different fuel flow rates and an analytical model is used in describing the polarisation curves.

The actual voltage of the cell is usually lower than the ideal voltage of the cell due to irreversible losses mentioned in Section 2.3.1. These voltage losses tend to increase as current drawn from the cell increases. There are a number of parameters which influence the voltage

losses such as kinetics of the electrochemical reactions on the electrodes, internal resistance of the cell, and mass transport limitations [24]. The activation losses are caused by the slow electrode reaction kinetics; ohmic losses are due to the ion transport in the electrolyte and electronic resistance to the electron transport and concentration losses occur owing to mass transport limitations [24].

The relationship between cell potential and current density is given as follows [33]:

$E= E_0- b \log i- Ri$ (Eq 4.3)

Where

$E_0= E_r + b \log i_0$ (Eq 4.4)

In the equation $E_r$ is the reversible cell potential for the cell, R is the resistance which is mainly caused ohmic resistance of the membrane and $i_0$, b are the Tafel parameters for oxygen reduction which is given below:

$b= \frac{RT}{\alpha F}$ (Eq 4.5)

α presents the transfer coefficient which has a strong impact on the cell performance. It is typical value is about 1 and $i_0$ represents the exchange current density which is shows the rate of reactions both forward and backward at the equilibrium[2].

The whole relationship between the cell potential and current density considering the concentration polarisation losses is given by the equation below [34]:

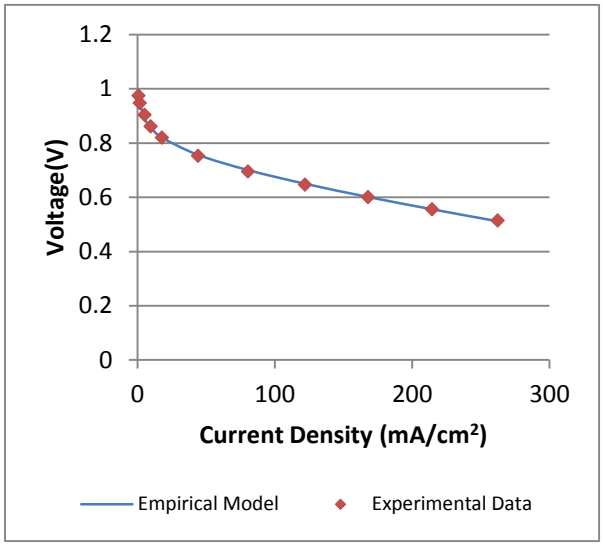
$E= E_0 –b \log i- Ri- m\exp(ni)$ (Eq.4.6)

m and n have an impact on concentration losses.

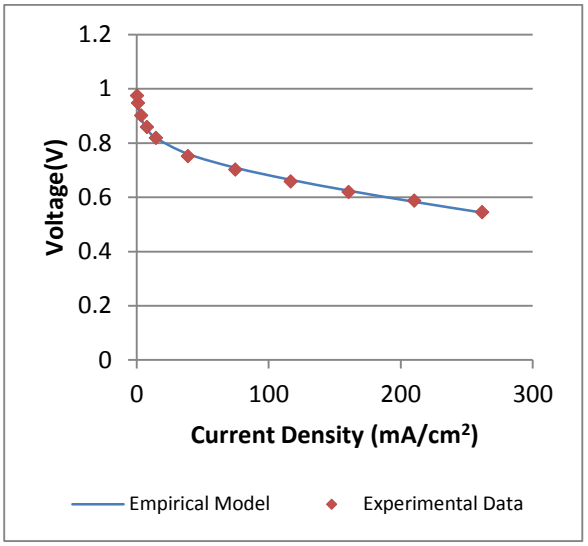
**Table 4.2 Kinetic parameters for different flow rates.**

| **Fuel flow rate (SLM)** | **$E_0$ (V)** | **b (V)** | **R(Ω $cm^2$)** |
|---|---|---|---|
| 0.1 | 0.632± 0.010 | 0.05±0.002 | 0.714± 0.041 |
| 0.2 | 0.633± 0.012 | 0.046± 0.002 | 0.577± 0.051 |
| 0.3 | 0.640±0.012 | 0.045± 0.002 | 0.602± 0.050 |
| 0.4 | 0.647± 0.018 | 0.047± 0.003 | 0.648± 0.065 |

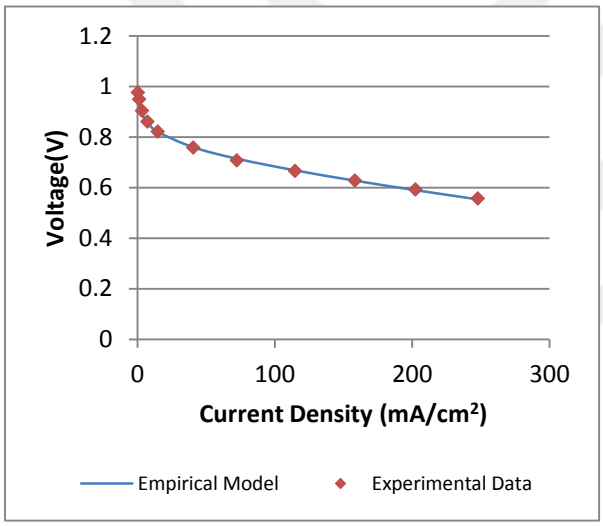
A nonlinear regression analysis is used to calculate kinetic parameters of the cell taking into account different operating fuel flow rates using the experimental data. The polarisation curves in Figure 4.10 show how the model fits with the experimental data for high fuel flow rates. Equation 4.3 is used in this case as the results show no concentration losses.



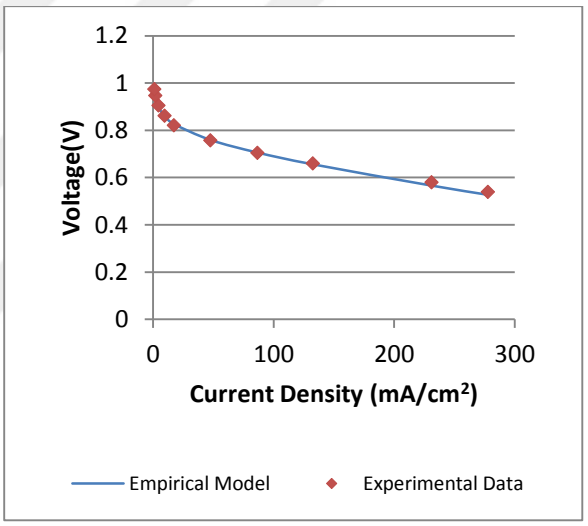

**a-) 0.1 SLM**




**b-) 0.2 SLM**




**c-) 0.3 SLM**




**d-) 0.4 SLM**

**Figure 4.10 Comparison between experimental (bullets) and empirical (lines) at different flow rate,a-) 0.1 SLM, b-) 0.2 SLM, c-) 0.3 SLM and d-) 0.4 SLM $H_2$, respectively.**

The polarisation curves are obtained experimentally and compared with the model at different fuel flow rates. It is seen that the efficiency of the cell increases with increasing fuel flow rate. This might be due to higher humidification degree of membrane and higher water production which makes the membrane much wetter. As a result of this the ionic conductivity of the membrane increases. These runs are done in the concentration losses are negligible

area. The low fuel flow rates are also used to observe the concentration impact and obtain the kinetic parameters in this area. A good agreement can be seen between the experimental and model. In the low current density region, the behaviour of the polarisation curves seems to be similar. This might be due to the fact that the operating temperature is the same. The kinetics of reaction tends to be similar at the same temperature. Another reason for identical behaviour of polarisation curves in the low and medium current density area might be slow reaction rate. The consumption of hydrogen is relatively low in these regions. However, there are other kinetic parameters that affect the kinetic of reaction. As the fuel flow rates rise, the efficiency of the cell increases since higher flow rate especially reduces the concentration losses. The kinetic parameters for different fuel flow rates are presented in the Table 4.2. It is expected that the ohmic resistance of the cell reduces with the flow rate since more humidified gases introduced into the cell. The fluctuations in the resistance might be due to the fluctuations in the humidity level of the membrane since the experiments are run in different date. The results might have some differences from one day to another because of the probability of membrane dry problem. As it can be seen from Figure 4.10 that the equation where no concentration losses models the polarisation curves which are obtained under different fuel flow rates.

Table 4.3 illustrates the kinetic parameters for low fuel flow rates. Since the impact of concentration losses are mostly seen in this region, the experiments are done with low flow rates to observe mass transport limitations in this area. The parameters of m and n which are described in the equation 4.6 and calculated using the nonlinear analysis are constant.

**Table 4.3 Kinetic parameters for low flow rates.**

| **Fuel flow rate (SLM)** | **$E_0$ (V)** | **b (V)** | **R(Ω $cm^2$)** | **m(V)** | **n($cm^2$/A)** |
|---|---|---|---|---|---|
| 0.02 | 0.621± 0.036 | 0.047±0.006 | 1.127± 0.249 | $2.364x10^{-9}$ | 101.311 |
| 0.05 | 0.669± 0.058 | 0.041± 0.01 | 0.886± 0.365 | $6.628x10^{-7}$ | 54.54 |

The figures 4.11- 4.14 show the effect of concentration losses as well as activation and ohmic losses. Figure 4.12 and 4.14 present all the data which are obtained and the data used in model. Comparing the polarisation curves, it can be seen that there is a good agreement between the model and the data using these calculated parameters.

It can be seen from table 4.2 and 4.3 that the value of $E_0$ increases with the fuel flow rate. However, they are different for low and high fuel flow rates. This might be due to fact that the expression equation and the date which the fuel cell is run are different. The increase in $E_0$ might be due to the fact that an increase in the temperature results in an increase in the current density [23]. As it can be seen from the equation 4.4 that $E_0$ is a function of $i_0$ (exchange current density). The fuel cell is run at the room temperature (about $25^0$ C). However, inlet gas temperature is set to $35^0$ C for the anode side and $50^0$ C for the cathode side. In addition to this, the inlet gas is humidified at $80^0$ C before introducing the cell. As increasing fuel flow rate, more gas entering the cell which might have an effect of increasing the temperature of the cell. This increase in the cell temperature may result in an increase in the exchange current density. An increase in $E_0$ might increase the cell voltage as can be seen from the equation 4.3 and 4.6. The exchange current density increases with the temperature of the cell and this decreases activation losses [35].

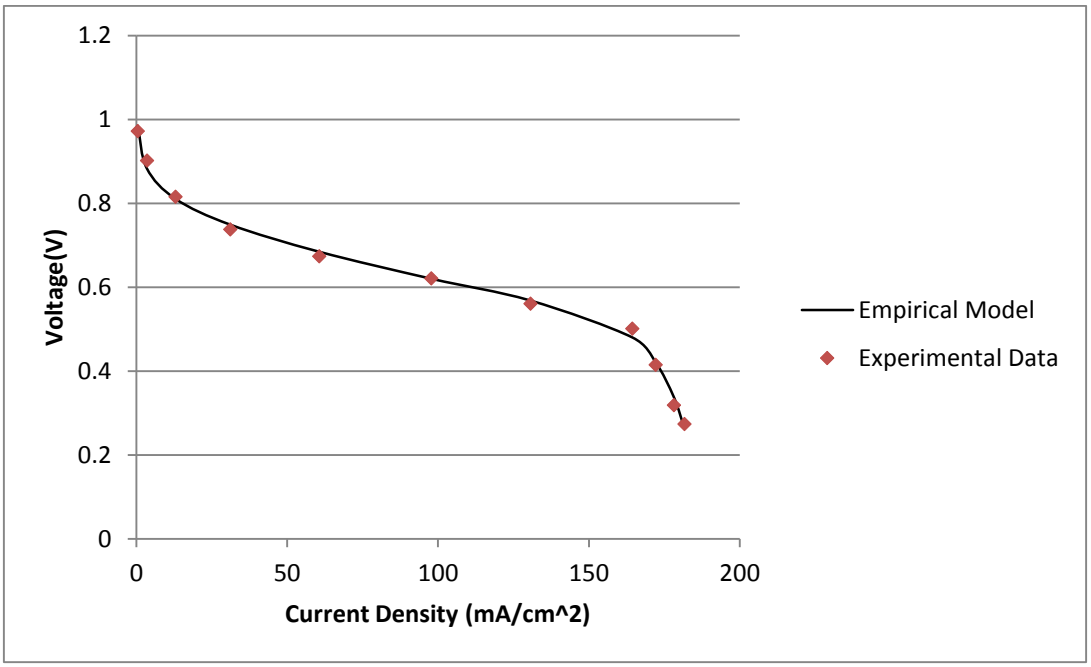



**Figure 4.11 Comparison between experimental (bullets) and empirical (lines) at the flow rate of 0.02 SLM.**

Another potential impact which could cause an increase in $E_0$ might be the increase the concentration of the reactants. Since the fuel flow rate increases, the concentration as well as partial pressure of reactant increase, this might also increase the exchange current density. Since the chemical reaction rate is the proportional to partial pressure of the reactants. However, there are other variables that affect the exchange current density such as materials and porosity of the electrode, distribution and dimension of catalyst particles [36]. Thus, further study can be done for different membranes with different properties.

The parameters of b and R generally decrease with increasing fuel flow rate. However, there is some fluctuations. This might be due to the change in the humidification level of membrane. Since the experiments were run in different days. This decrease is expected in the results. Since the resistance of the cell is mainly due to ionic resistance of the membrane. As ionic conductivity decreases with rising fuel flow rate as discussed, the ionic resistance of the cell decreases. The decrease in b (Tafel slope) may due to an increase in transfer coefficient. The Tafel slope is a function of transfer coefficient. As the transfer coefficient increases, b decreases. The high fuel flow rate might increase transfer coefficient which could cause a decrease in b.

The parameters of m and n are important to understand mass transport limitations. However, the physical meanings of them are not well understood. The calculated values of m and n are presented in the table 4.3. These values are similar to Kim et al [33]. It was found that the m values in the range of $10^{-19}$ and $10^{-9}$ means the mass transport limitation is minimal [33]. However, the higher value of n means it has dominant impact on the mass transport limitations. It might be said that n is more responsible for the quick drop in the voltage in the high current density region. As it can be seen from table 4.3 that the value of n is higher which means that the experimental fit in this study is good.

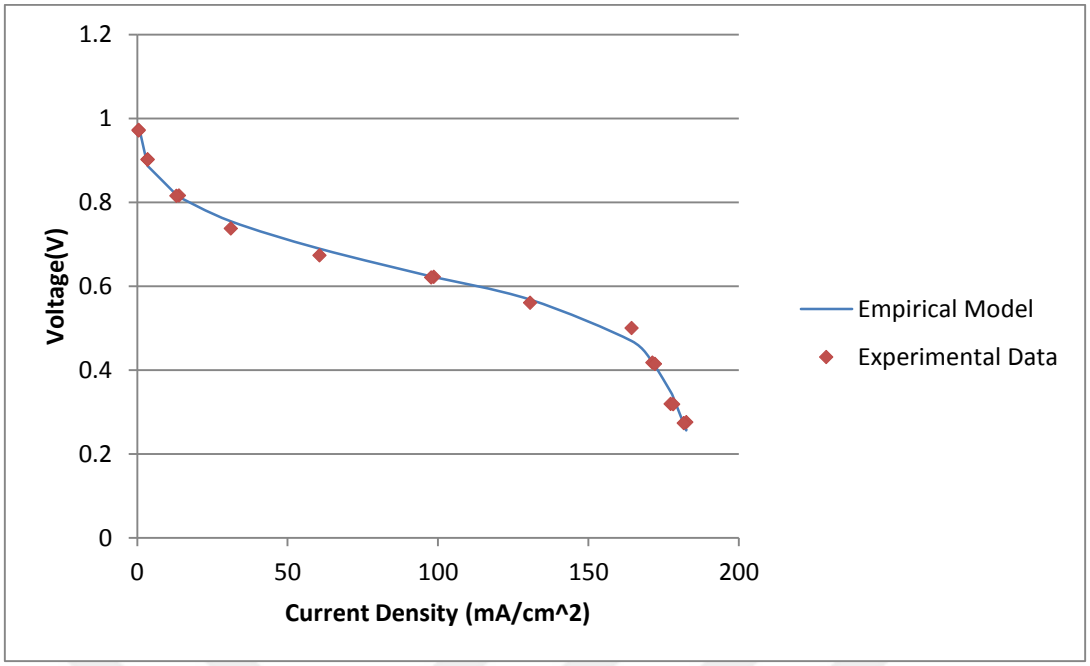



**Figure 4.12 Comparison between experimental (bullets) and empirical (lines) at the flow rate of 0.02 using all the experimental data from Figure 4.8**

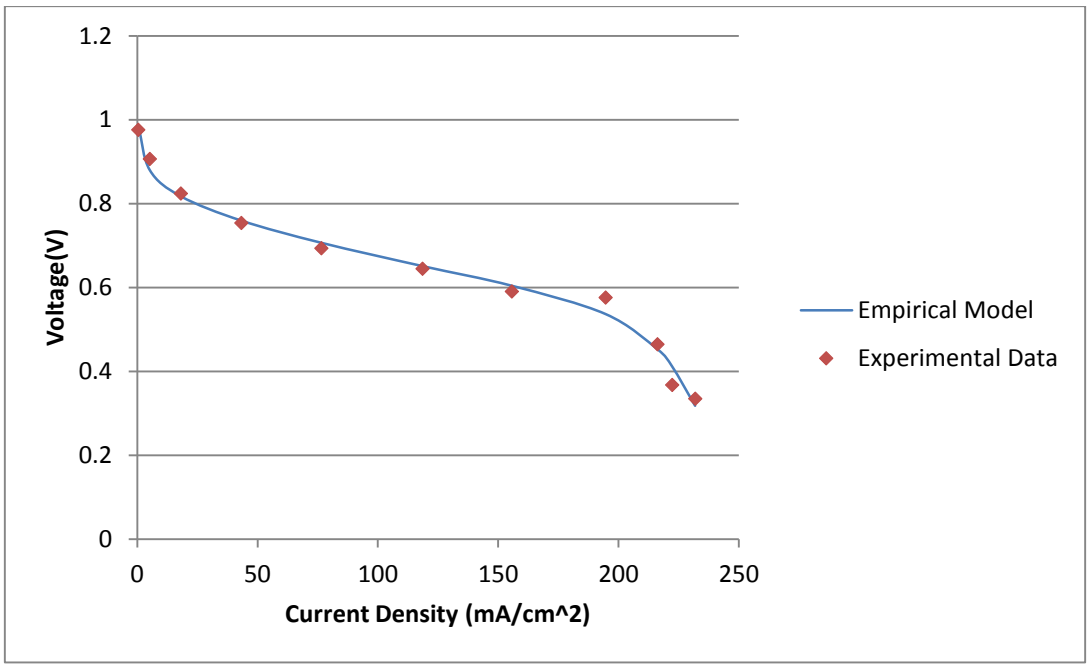



**Figure 4.13 Comparison between experimental (bullets) and empirical (lines) at the flow rate of 0.05 SLM.**

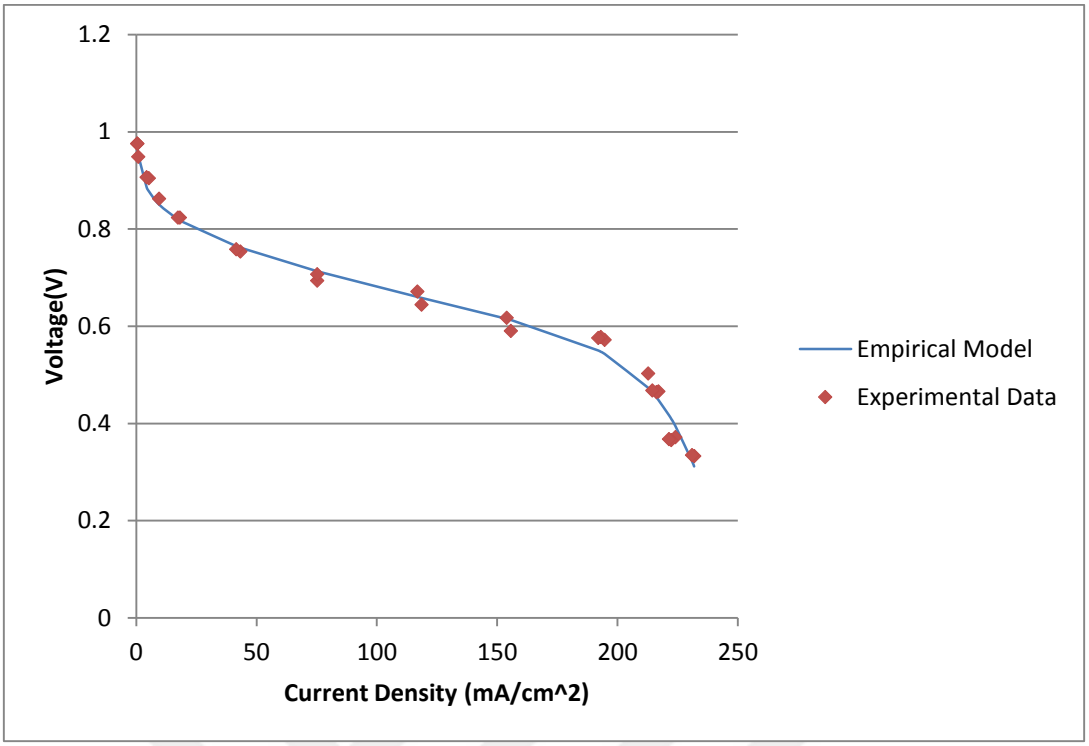



**Figure 4.14 Comparison between experimental (bullets) and empirical (lines) at the flow rate of 0.05 using all the experimental data from Figure 4.8**

An analytical semi empirical model for estimation of some parameters of the polarisation curves of the cell is described using different fuel flow rates. The experimental data and model fitted reasonably. The effect of fuel flow rate can be described as proportional to temperature and pressure of the reactants. Since, the temperature and pressure of the reactant seem to have more effect on the kinetic parameters of the cell. The impact of pressure and temperature can be studies as a further research.

### 4.4 Effect of Operating Conditions on the SOFC Performance

Performance, cost, durability are very significant issues in terms of SOFC technology. There has been a lot of ongoing research in order to observe the cell performance under different operating conditions, degradation mechanisms and realistic approaches.

One of the important operating parameters of the cell is humidity. Hager at al [37] studied the effect of humidity for SOFC using lanthanum strontium manganite (LSM)- YSZ cathode . The cell was operated at different temperatures between $750^0$ and $850^0$ C. They used ≈ 4%

humidity in the air and looked for the performance of the cell under 1500 h operations. It was found that the voltages drops become significant in the cell with LSM- YSZ cathode performance at low temperatures ($750^0$C) and high current density. The temperature of the cell should be increased or the current density should be decreased to mitigate degradation. It is concluded that the SOFC with LSM-YSZ cathode performs worse when humidity in air introduced to the cell with ≈ 4%. Another study was done by Kim et al that the SOFC with LSM- YSZ cathode performance improves when ≈ 3% humidity air introduced the cell at $800^0$C. However, it is also indicated that as humidity increases, the cell voltage drop increases which deteriorates the cell efficiency.

Operating temperature of SOFC is another major factor which has an effect on the cell performance. A study was carried out by Serincan et al to observe temperature impact on a micro-tubular SOFC. It is found that the performance of the cell enhances with increasing temperature. Since ionic conductivity of the electrolyte, diffusivity and activation energies increase. An increase in diffusivity of fuel molecules (assumed hydrogen) means the fuel reaches the reaction site faster which significantly reduces the mass transport limitations as well as ohmic losses. However, the effect of the temperature on the cell performance depends on the cell types and materials used; the major impact is that a higher temperature improves the cell performance. Ohmic losses are predominant loss in SOFC which can be reduced by increasing the temperature [3].

Similar to other types of fuel cells, the performance of SOFC increases with increasing pressure. This might be owing to an increase in Nernst potential. The voltage is given with changing pressure as follows [3]:

$$\Delta V = 0.027 \ln(P_2/P_1) \quad \text{(Eq. 4.7)}$$

Since the gas concentration and partial pressure of gases increase with increasing pressure, the cell performance enhances. However, cathode gas pressure has greater impact on the cell performance than anode gas pressure. Since the cathode reaction happens slower than the anode reaction, even a small change in cathode reaction kinetics has better effect on the overall reaction. Increasing pressure at the cathode side makes the reaction rate of cathode comparable with the reaction rate of anode which makes the overall reaction faster. However, further increase in the cathode pressure will not have much impact on the overall reaction rate [38]. It might be said that cathode side pressure is more sensitive to the overall performance.

Fuel flow rate and fuel composition are also important parameters for determining SOFC performance. This is particularly significant for high current density region since the reaction rate is high and concentration losses due to mass transport limitations are dominant. In low and medium current density region the reaction rate is not high; therefore the impact of fuel flow rate might be seen mostly in high current density region. Low fuel flow rate results in a steep voltage drops in the high current density region. The fuel flow rate should be adjusted to desired current density since higher fuel flow rate does not increase the cell performance further. This might also waste the fuel. Fuel composition is another aspect in terms of the cell performance. It is found that the ratio of hydrogen in the fuel with ¼ improves the cell performance [38].

There are various parameters that affect the cell efficiency needed to be researched such as materials, types, fuel, operating conditions and so on. Operating parameters mainly depend on the cell. Since the properties of the components might be different from one to another. Thus, a detail study should be done for each type of cell for realistic conditions before the application.

# Chapter 5

## Conclusions and Recommendations for Future Work

The aims of this study were to investigate the effects of operation parameters for the fuel cell which was prepared in the fuel cell laboratory and determine the parameters of the cell using a semi-empirical model. The experiments were carried out for different fuel flow rates and pressure. The performance of the cell was characterised by I-V curve for each run. The performance of the cell was evaluated considering three fundamental losses; activation, ohmic and concentration. Finally, the experimental data was used to estimate the parameters of analytical model and describe the polarisation curves. Based on the results, the conclusions below have been found.

**1-** The performance of the cell increases with increasing fuel flow rates. However, there are other factors that affect the cell performance since the improvement in the cell performance increases slowly. This can be seen especially in the high current density region. It is found that the humidification level of the membrane has a great effect on the cell performance. Since the humidity level of the membrane increases ionic conductivity, ohmic losses decrease and the reaction rate increases. The increase in the cell performance might be due to the introducing more humidified gas into the cell which increases the humidification level of the membrane as well as the temperature of the cell. Another reason for the increase in the cell efficiency might be supplying enough reactants to the cell which might counteract the over potentials. However, the polarisation curves seem identical for low and medium current density region. This might be due to a small amount of hydrogen is used in the reaction in these regions since the reaction rate is slow in the low current density region. As the reaction ratio increases in the high current density region the impact of fuel flow rate can be seen clearly. The experiments for low fuel flow rate were done in order to observe the cell efficiency especially in the high current density region. The polarisation curves do not show the characteristic of I-V in the high current density region for high fuel flow rates. A steep voltage drop was observed in the high current density region for low fuel flow rates. This might be due to the concentration of reactants decrease quickly as the reaction rate is high and potential flooding problem in the cathode. Since reaction rate is high water production in this

region is high. As fully humidified gas is supplied to the cell, there is excess water in the cell which needs to be removed. It might be difficult to remove product water since fuel flow rate is low.

**2-** The operating pressure for this particular PEM fuel cell was also studied. It is observed that the cell efficiency increases with increasing pressure. This is because the partial pressure of the reactant increases as pressure increases. As the diffusivity of gases and exchange current density increase, the efficiency of the cell improves. The cathode pressure has greater effect on the cell performance than anode pressure. The cathode reaction takes place slower than the anode reaction. A small change in the cathode reaction rate affects the overall reaction rate greater than anode side.

**3-** Interpretation of the cell potential against current density has gaining a lot of attention because of the difficulty of obtaining the kinetic parameters of the cell experimentally. Especially when air is used as an oxidant, predicting the cell performance in the medium and high current density region becomes important due to ohmic and concentration losses. An empirical equation and a nonlinear regression are used to fit the cell potential against current density in this study. The experimental data is obtained at different fuel flow rates. The kinetic parameters of the cell calculated and presented. The results are shown excellent fit with experimental and model. The behaviour of polarisation curves tends to be similar in the low and medium current density area. However, the behaviour of polarisation curve is different in the high current density region due to mass transport limitation. The parameters of m and n are calculated and presented in order to predict concentration losses. The physical meanings of these parameters are not clear. It is found that the value of n is greater than the value of m. This might be due to the fact that n has greater impact on concentration losses than m. The value of m ranges $10^{-9}$ to $10^{-7}$ which may cause less effect on the voltage drops in the high current density region. It is also investigated that the resistance which mostly contributes to ohmic losses fluctuates with different fuel flow rate. It is expected that the resistance will decrease since ionic conductivity of membrane increases. This fluctuation might be due to change in humidity degree of membrane from one day to another.

**4-** Influence of various operating conditions on the cell performance is significant. Based on the current study, investigating of the impact of fuel flow rate for the cathode and anode and investigating the humidity impact on the cell performance can be studied for the future work. With sufficient time, the MEA can be prepared using different GDLs with different properties and permeability and electronic conductivity of the GDL will be investigated. The different loading of PTFE GDL can also be studied as further research.

**5-** There are also other kinetic parameters which affect the cell performance such as exchange current density, transfer coefficient, limiting current density, and so on. With sufficient time, these kinetic parameters can be obtained as a future work. These parameters can be used to optimise the structure of the electrode and membrane which might help to predict the cell efficiency at various operating conditions as well as increasing the efficiency. The model also can be used to interpret the cell performance in terms of applications such power density, energy efficiency of the system as a function of current density.

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