Experimental investigations on passive direct methanol fuel cell integrated with liquid electrolyte layer

A Thesis submitted in partial fulfillment of the requirements for
the award of the Degree of

DOCTOR OF PHILOSOPHY

In
MECHANICAL ENGINEERING

by

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CERTIFICATE

This is to certify that the dissertation work entitled — **Experimental investigations on passive direct methanol fuel cell integrated with liquid electrolyte layer**, which is being revised thesis submitted by **Mr. Muralikrishna Boni (Roll No. 715034)**, is a bonafide work submitted to the Department of Mechanical Engineering, National Institute of Technology, Warangal in partial fulfillment of the requirement for the award of the degree of **Doctor of Philosophy in Mechanical Engineering.**

To the best of our knowledge, the work incorporated in this thesis has not been submitted elsewhere for the award of any degree.

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Dedicated

to

- My beloved parents and family
- All my teachers

APPROVAL SHEET FOR Ph.D

This Thesis entitled “**EXPERIMENTAL INVESTIGATIONS ON PASSIVE DIRECT METHANOL FUEL CELL INTEGRATED WITH LIQUID ELECTROLYTE LAYER”** by **Muralikrishna Boni (Roll no:715034)** is approved for the Degree of Doctor Philosophy

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DECLARATION

This is to certify that the work presented in the thesis entitled **“EXPERIMENTAL INVESTIGATIONS ON PASSIVE DIRECT METHANOL FUEL CELL INTEGRATED WITH LIQUID ELECTROLYTE LAYER”** is a bonafide work done by me under the supervision of Prof. S. Srinivasa Rao and Dr. G. Naga Srinivasulu, and was not submitted elsewhere for the award of any degree. I declare that this written submission represents my ideas in my own words and where others' ideas or words have been included; I adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea / data / fact / source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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ABSTRACT

Fuel cell is an electro-chemical energy conversion device, which converts the chemical energy of the fuel directly into electrical energy. Among the different types of fuel cells, the passive direct methanol fuel cell (DMFC) is most suitable for small capacity applications such as charging of portable electronic devices. In the passive DMFC, the supply of the reactants, viz., diluted methanol at the anode and oxygen at the cathode is through diffusion and natural convection respectively. The passive DMFC suffers from a major disadvantage that the Nafion membrane allows the flow of methanol fuel from the anode side to cathode side (methanol crossover), and leads to mixed overpotential losses. The aim of the present thesis is to reduce the methanol crossover and enhace the reaction rate in the conventional DMFC by adapting different modifications in the cell such as incorporattion of liquid electrolyte layer in between the two half MEAs, selection of effective anode catalyst supports, optimized open ratio of the perforated current collector, usage of combined perforated and wire mesh current collectors, and different alcholic fuel additives to methanol fuel.

The influence of the Liquid Electrolyte (LE) layer thickness on the passive DMFC performance was experimentally evaluated by varying the LE layer thickness from 1.5 mm to 2.5 mm (1.5 mm, 2.0 mm and 2.5 mm), and methanol concentration from 1mol/cm^3 to 12 mol /cm^3. In all these experiments, diluted sulfuric acid of 1 mol/cm^3 concentration was used as the liquid electrolyte material. From the results, it is observed that in the entire range of experimentation the LE-DMFC with 2 mm thick LE layer gave the best performance at 5M methanol concentration.

A comparative study was carried out by conducting experiments to evaluate the performance of a conventional passive DMFC and an LE-DMFC by incorporating a two layer catalyst of Pt-Ru/black (inner layer) and Pt-Ru/C (outer layer) on the anode side of the passive DMFC. From the experimental results, it is observed that throughout the range of methanol concentrations from 1mol/cm^3 to 12 mol /cm^3, the cell incorporated with two layers of anode catalyst support along with the liquid electrolyte layer exhibited the best performance.

The effect of open ratio of the perforated current collector (PCC) on the passive DMFC performance was evaluated experimentally by using PCCs with three different ORs, i.e., 45.40%, 55.40% and 63.05%. In the total range of experimentation, it is observed that the PCC with OR of 55.40% and at 3M methanol concentration gave the best cell performance.

In the next phase of study, experiments were conducted on the passive DMFC by using a combined current collector having a combination of Perforated current collector (ORs of 45.40%.55.405 and 63.05%) and Wire Mesh Current Collector (WMCC) (ORs of 45.40% and 38.70%).The methanol concentration was varied from 1M -5M. From the results, it is observed that among the nine combinations of the current collectors, the combined current collector with PCC of OR 55.40% and WMCC of OR 38.70% exhibited the highest cell performance at 5M of methanol concentration.

Further, experimental studies were carried out to evaluate the performance of a passive alcoholic fuel cell with different single alcoholic fuels (ethanol, 1-propanol, 2-propanol, 1-methanol), and their additives to methanol as the anodic fuels, i.e., additives of ethanol, 2-propanol, 2-propanol + ethanol. From the results, it is observed that among the four single alcoholic fuels, 2-propanol was giving better cell performance compared to the other alcoholic fuels. In the present range of experimentation with all the fuel additives, 2-propanol additive at 2 mol/cm^3 concentration added to 4M methanol concentration produced the maximum power density.

Thus, in the present work different techniques were employed aimed at improving the performance of a passive DMFC.

Key words: Passive DMFC, Liquid electrolyte layer, Anode catalyst supports, Wire mesh current collector, Alcohol additives.

CONTENTS

Chapter 1 **Introduction** **Page no**

Chapter 2 **Literature Review**

List of figures

List of tables

Table title **Page no**

ABBREVIATIONS

FC-Fuel cell

DMFC-Direct methanol fuel cell

PEMFC-Proton exchange membrane fuel cell

MOR-Methanol oxidation reaction

ORR-Oxidation reduction reaction

MPD-Maximum power density

MCD-Maximum current density

MEA-Membrane electrode assembly

CL-Catalyst layer

GDL-Gas diffusion layer

OR-Open ratio

CC-Current collector

PCC-Perforated current collector

WMCC-Wire mesh current collector

MCO-Methanol crossover

Chapter1

1. Introduction

Industrialization and automation are increasing the energy consumption day by day. In the present scenario, 85%[1] of the energy generated is mainly from the fossil fuels such as coal, natural gas and oil. Non-conventional energy sources such as solar, wind, tidal, geothermal and bio fuels are contributing for a minor amount of energy generation. Among the recent developments, fuel cells have the advantages of high energy density, high energy conversion efficiency, low emissions, low operating temperatures, stress-free handling and noise-free operation. Fuel cell (FC) technology provides a viable solution to meet the energy requirement of small power applications.

Fuel cells are electrochemical energy conversion devices, which directly convert the chemical energy of the fuel into electrical energy. Fuel cells are categorized into Proton Exchange Membrane (PEM), molten carbonate, phosphoric acid, alkaline and solid oxide fuel cells based on the electrolyte material. Among all the types of fuel cells, Direct Methanol Fuel cell (DMFC), which is a sub-category of the proton exchange membrane type fuel cell, is an important energy source for charging of portable electronic devices. In the DMFC, when liquid fuel is used, it will produce a higher volumetric energy density compared to other fuels. The DMFC has the advantages of low fuel cost, small operating temperature and pressure range, easy re-fuelling, simple operation, simple structure design and light weight compared to the Proton Exchange Membrane Fuel cells. The present thesis work deals with different techniques aimed at improving the performance of the DMFC. A brief summary on the evolution of the DMFC is described in the subsequent sections in this chapter.

1.1 History of the fuel cell

For the first time in 1839, Sir William Grove introduced the basic operating principle of the fuel cell to the scientific community [2]. Later in 1842, Grove produced a 50-cell stack and named it as "gaseous voltaic battery". After Grove's invention, it took almost a century to reintroduce the FCs to the scientific community. In 1937, F.T. Bacon began to work on the practical FC, and he successfully built a 6 kW output stack by the end of the 1950s. In the early 1960s, Grubb and Niedrach built a fuel cell using solid ion-exchange membrane electrolyte. Primarily, sulfonated polystyrene based membranes were employed as the electrolytes, and there after Nafion membranes were substituted. The Nafion membrane has shown greater performance and durability, and is the most common membrane in use. This type of FC is generally called as the polymer electrolyte membrane fuel cell or the proton exchange membrane fuel cell.

In the early 1960s, PEM fuel cell (PEMFC) was first used in the Gemini space program and that FC was developed by General Electric, based on the work of Grubb and Niedrach. Following the Gemini Program, FCs were also used in the Apollo program, to produce electricity for life support and communications. These FCs were made by Pratt and Whitney based on the Bacon's patents. Due to their high cost, use of the FC systems was limited in space applications and in some special applications. In 1990, Ballard Power systems started development of PEMFC systems. The strategy of Ballard was to reduce the cost of the fuel cell by using low cost materials and fabrication techniques. In 1993, Ballard Power Systems demonstrated FC powered buses. In 1993, Energy Partners demonstrated the first passenger car operating on PEMFCs. At the end of the century, almost all car manufacturers picked up on this activity and had built and illustrated the FC-powered vehicle. The timeline of FC development history is shown in Fig.1.1.

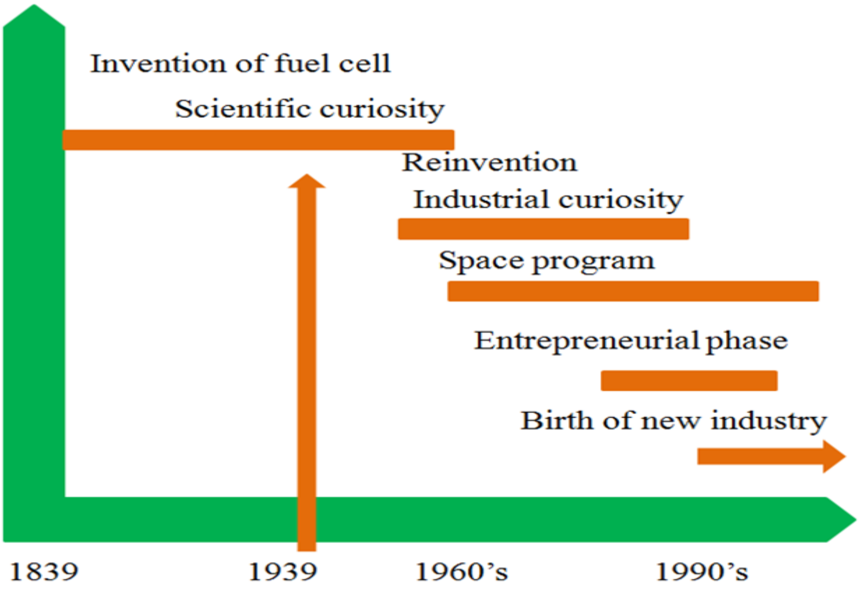


Fig. 1.1History of the evolution of fuel cells

1.2 Types of fuel cells

Fuel cells are classified based on the electrolyte material. Six types of fuel cells are available as of now. These are sub divided into high temperature and low temperature fuel cells. Solid Oxide Fuel Cell (SOFC) and Molten Carbonate Fuel Cell (MCFC) are the high temperature FCs, which operate under temperature range of 600-1000^{0}C. The low temperature FCs is Phosphoric Acid Fuel Cell (PAFC), Alkaline Fuel cell (AFC), Proton Exchange Membrane Fuel cell (PEMFC) and Direct Methanol Fuel cell (DMFC). The details of all these types of FCs are given in Table1.1.

Table.1.1 Outline of different types of fuel cells[1]

Fuel cell type	**PEMFC**	**DMFC**	**HT-PEMFC**	**AFC**	**PAFC**	**MCFC**	**SOFC**
Operating Temperature (^{o}C)	40-80	25-80	100-200	60-220	170-220	600-650	600-1000
Fuel	H_2	CH_3OH	H_2	H_2	H_2	$H_2$and CH_4	$H_2$and CH_4 and CO
Catalyst	Pt	Pt and/ or Pt-Ru	Pt	Pt	Pt	Ni	Ni
Carrier ion	H^+	H^+	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Electrolyte	Solid polymer	Solid polymer	Solid polymer	Aqueous KOH	Aqueous H_3PO_4	Molten carbonate	Ceramic
Output power range	Watts/Kilowatts	Watts	Watts/Kilowatts	Watts/Kilowatts	Kilowatts	Kilowatts/Mega watts	Mega watts
Limitations	High catalyst cost, water management and catalyst poisoning	Methanol crossover	Solid polymer electrolyte and composite bipolar plate	Expensive catalyst, sensitive to poisoning, and water management	Expensive catalyst, corrosive electrolyte, and electrolyte management	Corrosive electrolyte, high cost materials, and degradation	Expensive materials and degradation
Applications	Portable devices, electrical equipment, automotive and domestic	Portable power applications	Portable devices, electrical equipment, automotive and domestic	Space, military	Electrical equipment, Transportation and stationary applications	Stationary and distributed power generator	Power plants, combine heat and power, and stationary
Advantages	High power density, short start-up time, and low temperature	Short start-up time and low temperature	High CO tolerance, separate water management is not required	Low cost materials and high performance	Low cost electrolyte, long time performance and reliable	High quality waste heat and high efficiency	High quality waste heat, fuel flexibility and high efficiency

The present work deals with DMFC, which is a sub-class of the PEMFC. The details of the PEMFC and DMFC are discussed here in the next sections.

1.2.1 Proton Exchange Membrane Fuel cell (PEMFC)

Proton Exchange Membrane Fuel Cell (PEMFC) is also known as polymer electrolyte membrane fuel cell. It had a solid thin polymer membrane (Nafion, which was developed by DUPONT). Hydrogen and oxygen are used as the reactants. The PEMFC has the advantages of small operating temperature, simple structure design and light weight, when compared to the other fuel cells. The operation temperature of PEMFC is about 80 ^{o}C, which results in low start-up time. PEMFC design is suitable for usage in automobile applications.

The main problem associated with the PEMFC is water management and humidification of the membrane. The water generated at the cathode during reaction process blocks the flow of oxygen for the chemical reaction process. Due to the higher flow rates and higher current density regions, more heat is generated. The Nafion membrane cannot withstand this high heat. So, humidified reactants should be supplied on anode and cathode side. This humidification process increases the complexity of the system. The energy density of PEMFC is less and bigger tanks are required for storing of hydrogen.

1.2.2 Direct Methanol Fuel Cell (DMFC)

DMFC is a sub category of the PEMFC, which converts the chemical energy of methanol fuel directly into electricity. Humidification of Nafion membrane is not a problem due to the use of liquid methanol at the anode side. Methanol, also known as wood alcohol, is produced by destructive distillation of wood or naturally by anaerobic metabolism of bacteria. Thus, methanol fuel is a renewable energy. The merits of the methanol fuel are their ease of storage at room temperature and atmospheric pressure compared to hydrogen fuel. Hydrogen fuel is stored in composite cylinders at high pressure and low temperature. Energy density of the methanol (18.8 MJ/kg) fuel is higher than that of hydrogen (0.72 MJ/kg) fuel. The DMFC had low working temperature, which results in low start-up time, easy handling. DMFC has fast charging capacity of devices, which is compatible with the conventional batteries like Li-ion, NiCd batteries. DMFCs are suitable for charging of portable power devices like laptops, personal digital assistances, music players and mobile phones.

Direct methanol fuel cells are catageorized into the following three types:

a) Active DMFC

b) Air-Breathing DMFC (AB-DMFC), and

c) Passive DMFC

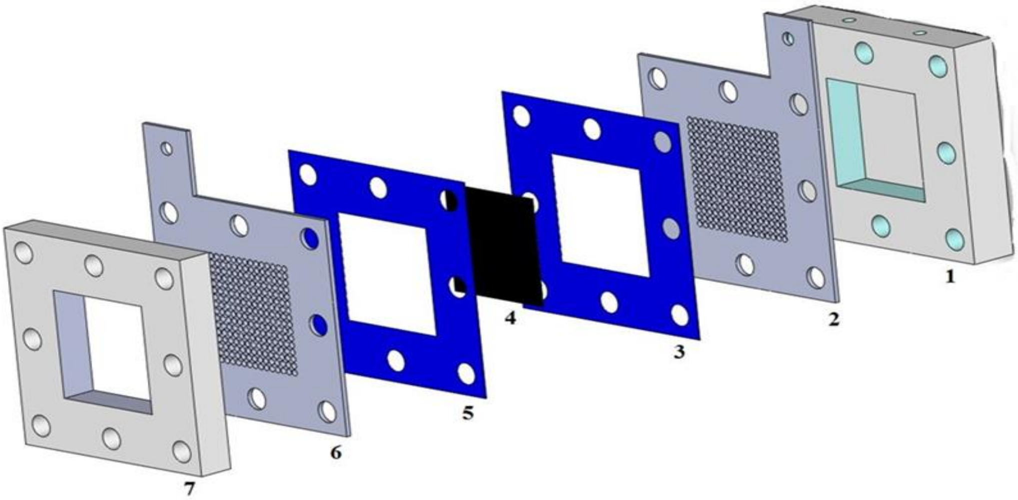
Over the past few years, a lot of research was carried out on the active DMFC. While operating condition of the active DMFC requires liquid supply pump, air pump and also a control system for regulation fuel and oxidant. The integration of this equipment to the small power charging applications is very difficult. Another disadvantage is consumption of additional power by the air pump and fuel pump, which results in decrease of the net power output. These difficulties in the operation of the active DMFC are making it less attractive for portable energy applications.

The Air-Breathing DMFC (AB-DMFC) is a semi-active DMFC. In the AB-DMFC, the fuel (diluted methanol solution) is supplied by external devices such as pumps at the anode side. At the cathode side, oxygen is taken from the atmosphere by natural convection and capillary action. The whole assembly is similar to the active DMFC except the cathode side. But, even in this type of fuel cell also, the fuel pump requires additional power, which makes it less attractive. These drawbacks of the active DMFC and the air-breathing DMFC are reduced by designing a simple structure, called the passive DMFC, which suits well for portable power applications.

In the passive DMFC, the fuel and oxidant supply take place by passive condition, i.e., by passive supply of methanol and air breathing by natural convection. While in the conventional passive DMFC system, the diluted methanol solution is directly exposed to the anode side of the MEA through current collector, the cathode side MEA is exposed to the atmosphere for air breathing via the cathode current collector. The passive DMFC has advantages of simple structure, light weight, no external device for the supply of reactants and also reduced parasitic power losses. This system is more suitable for charging of portable power applications. The present work focuses on the passive DMFC system. The construction details and working principle of the passive DMFC is described in the subsequent sections.

1.3 Construction of the passive DMFC

Fig.1.2 shows a schematic of the passive DMFC. The main components of the passive DMFC are membrane, catalyst layers, diffusion layers, current collectors and Teflon gaskets. The details of these components are discussed in the following sections.



1. Anode methanol reservoir	2.Anode current collector
3.PTFE gasket for anode side	4. MEA
5.PTFE gasket for cathode side	6. Cathode current collector
7.Cathode end plate	

Fig.1.2 Schematic of the passive DMFC

I. *Membrane (PEM)*

The membrane is considered as the heart of the DMFC. Through the membrane, the hydrogen ions are transported from the anode catalyst layer to the cathode catalyst layer, and for this, the membrane needs to possess relatively high proton conductivity. Also, the membrane should be chemically and mechanically stable in the fuel cell environment. Perfluorocarbon-sulfonic acid ionomer (PSA) membrane is usually used in the PEMFCs. Dupont developed the membranes based on a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer (Nafion family) and are considered as the best material for the membrane. A fully humidified membrane conducts the protons effectively. Therefore, it is essential to keep the membrane hydrated.

II. *Catalyst Layers (CLs)*

In a DMFC, there are two CLs on both sides of the membrane. These CLs are placed between the membrane and GDLs on the anode and cathode sides respectively[3]. All the electrochemical reactions take place at the catalyst layer. The catalyst layer must have high intrinsic activity, larger active surface area, high ionic and electric conductivity, porosity for reactants entry as well as product removal. Usually, bimetallic catalyst of Platinum (Pt) and Rutheniun (Ru) is preferred as the catalyst on the anode side in the DMFC, because of its great stability and reactivity. Pt is generally in the form of tiny particles and these small Pt particles are reinforced on the carbon particles to offer a high surface area. A catalyst layer with Pt supported on carbon is depicted in Fig.1.3.

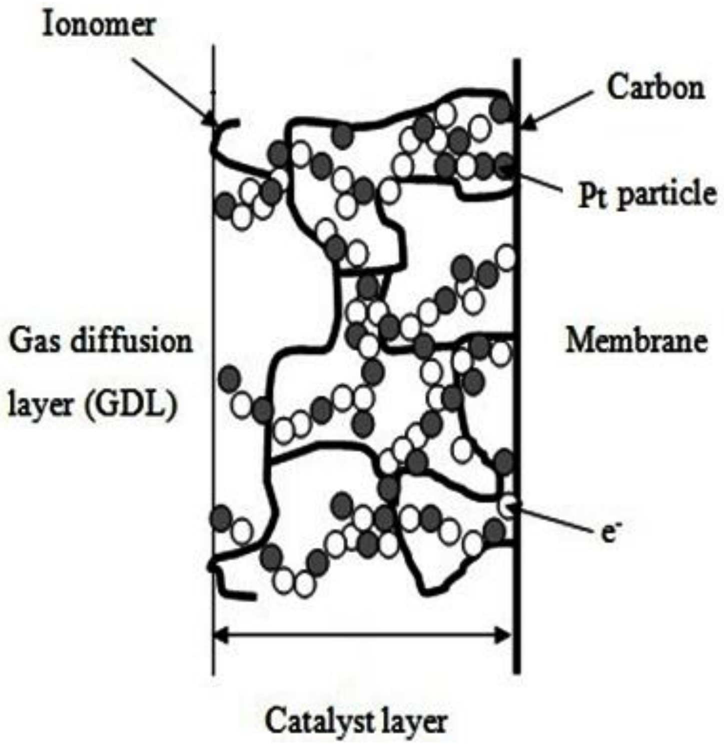


Fig.1.3 Catalyst layer[4]

III. *Gas Diffusion Layers (GDLs)*

There are two GDLs bonded to the anode and cathode catalyst layers. Usually hydrophobic carbon fiber paper or cloth is used as the GDL, and it is called the substrate. A microporous layer (MPL) with hydrophobic property is applied to the catalyst side of the substrate [5]. The hydrophobicity is usually attained through application of Poly Tetra Fluoro Ethylene (PTFE). The SEM images of carbon fiber paper and cloth are shown in Fig. 1.4. The following are some key functions of the GDL.

- It works as a passageway for transport of the reactants from the flow channels to the reaction site.
- It works as a passageway for evacuation of products (water) from the reaction site to the flow channels.

- It works as a heat conductor.
- It conducts the electrons from CL to the current collector via bipolar plate.

The membrane electrode assembly (MEA) is the combination of membrane, CLs and GDLs.

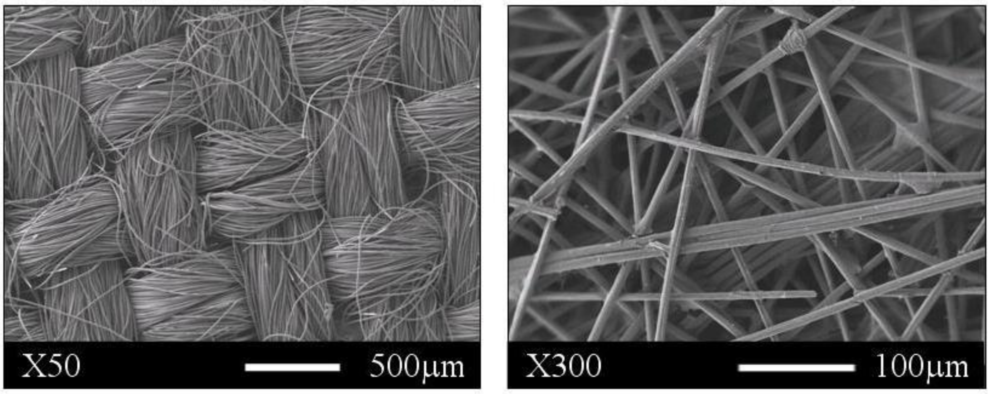


Fig.1.4 GDL material: carbon cloth (left) and carbon paper (right)[6]

IV. *Current collectors and Gaskets*

In the passive DMFC, mostly metal current collectors are used and two current collectors, one on either side of the anode and cathode are used. The main function of the current collector is to hold the MEA in correct position and to facilitate the flow of electrons produced during the chemical reaction process. Internal electrical resistance of the fuel cell depends on the pressure acting on the current collectors. Low pressure acted on the current collector increases the internal resistance, and high pressure damages the MEA. As a result optimum pressure is to be applied on the current collectors. The current collectors should possess high electrical conductivity, corrosion resistance and mechanical strength. Fuel at the anode side and oxidant at the cathode side are delivered through the channels of the current collectors to the catalyst reaction sites. Different designs of fuel channels used such as circular, square, rectangular, parallel and non-parallel are widely used in the passive DMFC.

Gaskets are fixed in between the current collector and the MEA. They help in providing a proper sealing and to maintain a precise conatact between the current collectors and the MEA. The thickness of the gaskets also influence the fuel cell performance. Lower thickness reduces the interal electrical resistance of the fuel cell.

V. End plates

In the passive DMFC, the end plates are made up of Poly-methyl methacrylate (PMMA). In the DMFC relatively small amount of heat is generated and these PMMA plates are capable of withstanding this small heat. Also, the transparent PMMA plates permit the visualization of the CO_2 bubbles generated at the anode side. In the passive DMFC, the anode end plate acts as the methanol reservoir. It has two holes on the top of the plate. Of these two holes, one hole is used for filling of methanol and the other hole is used for exhaust of CO_2. .The cathode end plate had a square shaped opening of area equal to the active area of the cell for air breathing. Both the end plates had drilled holes for passing the bolts and thereby making a leak proof joint.

1.4 Working principle of the passive Direct Methanol Fuel Cell

Fuel cells are electrochemical energy conversion devices, which convert chemical energy into electrical energy. In the DMFC, the chemical energy of methanol is converted into electrical energy through an electrochemical reaction process. The basic working principle of the passive DMFC is shown in Fig.1.5.The diluted methanol fuel (water and methanol) is supplied at the anode side of the membrane. It gets split into protons (H^+) and electrons, and a small amount of CO_2 is also produced. The produced protons pass through the membrane and reach the cathode side of the membrane. The electrons flow through the external electrical circuit and finally reach the cathode side of the membrane. The oxygen from the atmospheric air is also present near the cathode side of the membrane. Thus, near the cathode side of the membrane, the protons, electrons and oxygen combine to form a by-product, i.e., water. The reactions taking place at the anode, cathode and in the overall FC are shown below:

Anode side:

$$MOR: CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{1.1}$$

Cathode side:

$$ORR: \quad {}^3\!/_2\, O_2 + 6H^+ + 6e^- \rightarrow 3H_2O + heat \tag{1.2}$$

$$Overall: CH_3OH + {}^3\!/_2\, O_2 \rightarrow CO_2 + 2H_2O + heat \tag{1.3}$$

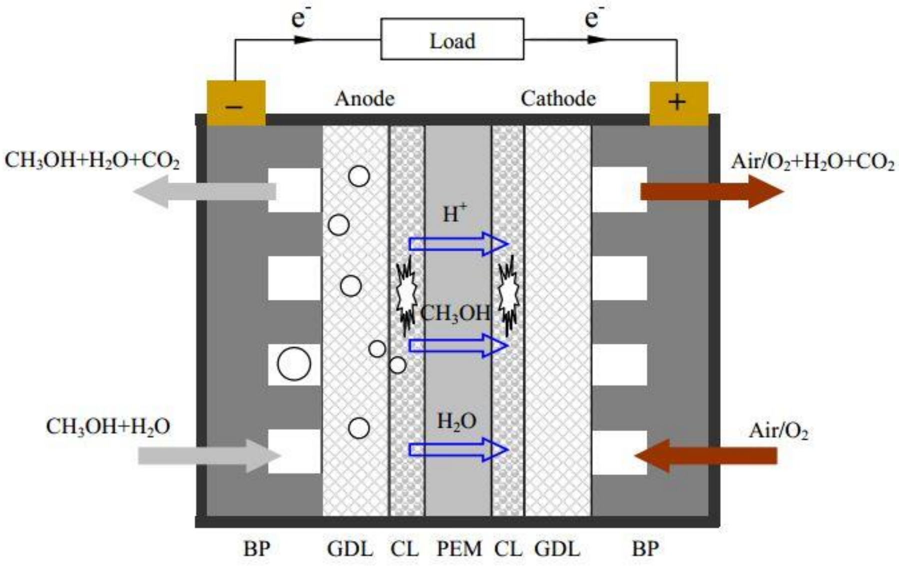


Fig.1.5 Working principle of the passive DMFC

1.5 Performance of the Passive DMFC

The performance of the passive DMFC can be summarized with a graph of its current-voltage characteristics. This graph shown in Fig.1.6, called the i–V curve (solid line), displays the voltage output of the FC for a given current output. An ideal fuel cell would supply any amount of current (as long as it is supplied with sufficient fuel), while maintaining a constant voltage determined by thermodynamics [7]. In practice, the real output voltage of a fuel cell is less than the ideal thermodynamically predicted voltage. Besides that a further increase in the current drawn results drop in FC output voltage and limits the total power output. The power (P) output of a fuel cell is given by the product of current and voltage

$$P = V * \mathrm{I} \qquad (1.4)$$

Power density curve of a fuel cell can be drawn from the data obtained from fuel cell *i*-V curve. The power density, which is the product of voltage and current density shows a parabolic trend of increase in power density with increase in the current density, which reaches a peak value and then decreases with increase in the current density. A typical power density curve (dotted line) is shown in Fig.1.6. The FC voltage is given on the primary *y*-axis (left), while the power density is given on the secondary *y*-axis (right).

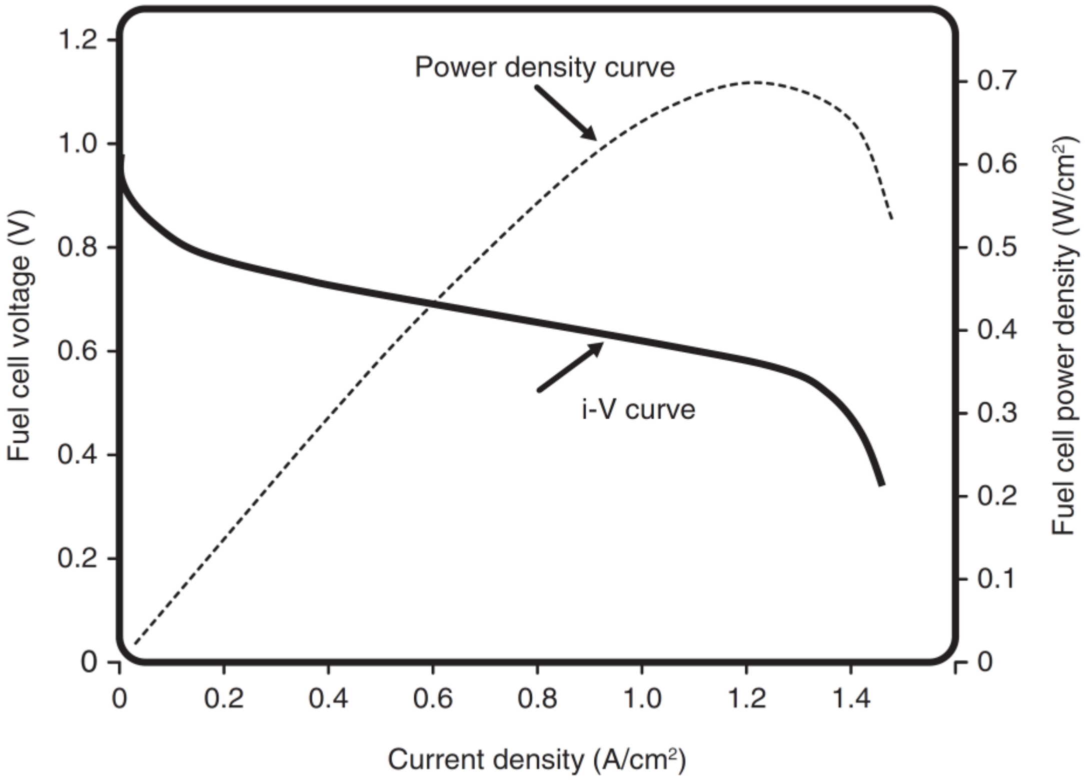


Fig.1.6 Polarization and performance characteristics of a fuel cell [7]

The current generated in a FC is directly proportional to the quantity of fuel consumed. It is difficult to keep the fuel cell at a high voltage under the current load. The output voltage of the fuel cell is displayed in the electronic load bank for a given current. The actual open circuit voltage (OCV) of the fuel cell is less than the ideal value, i.e., 1.21V. Compared to the reversible cell voltage, which is supposed to be a flat curve of constant voltage for all values of current density, the actual cell voltage was lower than reversible voltage. The actual cell potential decreases with increase in current density and this phenomenon is called as irreversible losses. The difference between the reversible cell voltage and the actual cell voltage is due to the irreversible losses inside the cell. These losses were mainly due to activation, ohmic and concentration losses. A typical polarization curve of the fuel cell is shown in Fig. 1.7.

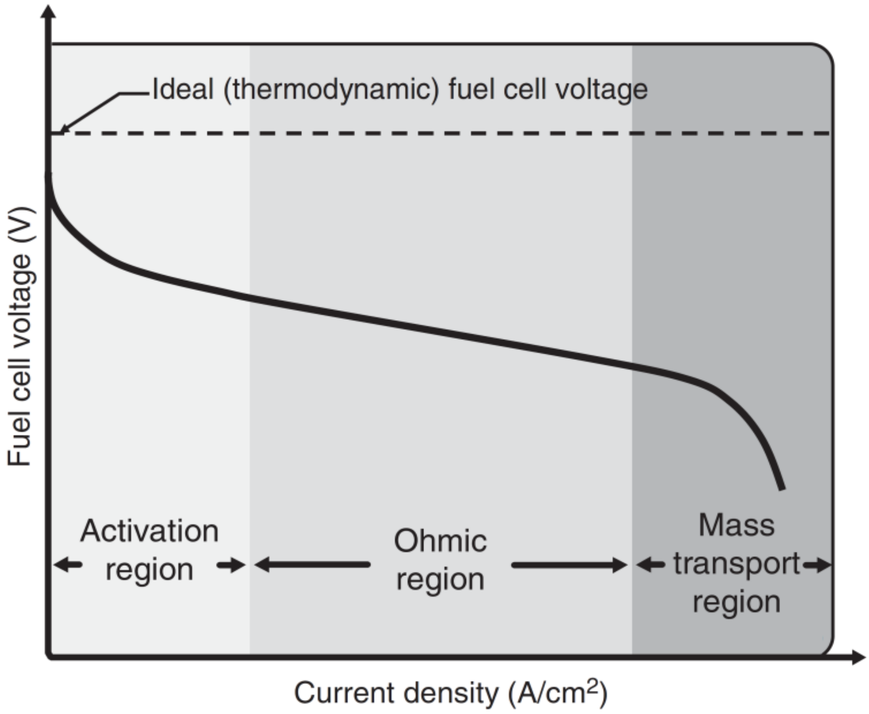


Fig.1.7 Polarization curve with irreversible losses of a fuel cell

The actual cell voltage generated by the FC is the subtract of all losses (activation, ohmic and concentration) from the reversible thermodynamic voltage.

$$\boldsymbol{V_{cell} = E_{cell} - \eta_{activation} - \eta_{concentration} - \eta_{ohmic}} \tag{1.5}$$

Where E_{cell} thermodynamic equilibrium potential

$\boldsymbol{V_{cell}}$ = actual cell voltage

$\boldsymbol{\eta_{activation}}$ = Activation losses

$\boldsymbol{\eta_{concentration}}$ = Concentration losses

$\boldsymbol{\eta_{ohmic}}$= Ohmic losses

These three losses have more influence on the Fuel cell (FC) performance. The output voltage drop in the first region (at lower current density) of the polarization curve is mostly effected by the activation losses. At the middle region (second region), the voltage drop is mostly influenced by the ohmic losses. Finally, the mass transport losses are highly effective in the higher current density region (third region).

1.6 Organization of the Thesis

The thesis comprises of 9 chapters. Chapter 1 outlines a short introduction of the passive DMFC. The literature review on the DMFC is provided in chapter 2. The gaps observed from the literature review and the thesis objectives are also presented in chapter 2. Experimental methodology with the passive DMFC is presented in chapter 3. In this chapter the description of the experimental set-up and components of the passive DMFC are discussed. Experimental results in consort with research objectives are presented in chapter 4 to chapter 8. In chapter 4, the influence of Liquid Electrolyte (LE) layer thickness on the passive DMFC performance is presented. Comparative study of the anode catalyst supports of carbon and carbon black on the performance of the passive DMFC is presented in chapter 5. Results of experimentation aimed to study the effect of open ratio of the perforated current collector and methanol concentration on the performance of the passive DMFC are discussed in chapter 6. In chapter 7, the combined effect of the perforated and wire mesh current collectors on the performance of a passive DMFC are presented. In chapter 8, the effect of blending of different alcohol additives to the methanol fuel on the performance of a passive DMFC are discussed. Finally, the overall conclusions drawn out of this research and some recommendations for future research are given in chapter 9. Appendix covers research output in the form of peer-reviewed journal and conference papers.

Chapter 2

Literature Review

A significant number of theoretical and experimental studies have been carried out by many researchers on Direct Methanol Fuel Cells (DMFCs). Experimental testing is the commonly used approach for understanding and predicting the DMFC performance. Some empirical and mathematical models have also been proposed in the literature to comprehend and analyze the performance of DMFCs. The objective of the current literature review is to present an overview of the DMFC development.

For the first time in 1839, Sir William Grove demonstrated the working principle of a fuel cell. After his demonstration, it took almost one decade to re-introduce the fuel cell to the scientific community. Being enthralled with Grove's invention, Bacon began experimenting on fuel cells in 1939, and was successful in 1959 in constructing a fuel cell stack of 6 kW output power. Based on Bacon's patents, Pratt and Whitney made fuel cells. General Motors made trials with a fuel cell operated van by the mid-1960s. In the meantime, the U.S. Space Program continued to effectively make use of fuel cells. In the 1960s, many industries recognized that fuel cells can be used in different applications, but because of their high manufacturing cost and technical difficulties, fuel cells did not have the capacity to work in tandem with other energy conversion devices. In the 1980s, the Canadian Government sponsored the preliminary development work of fuel cells, which was supported by Ballard Power Systems. Later in 1989, the company decided to on concentrate on fuel cell systems for transportation and stationary applications.

Passive DMFCs are being widely used in the industry especially in leave alone applications. Research is going on to understand the working of the DMFC, identify the challenges, and methods of improving the performance of the DMFC. The following sections show the literature review in explaining details of these challenges and the efforts that are being made in the direction of overcoming them. The gaps identified in the literature and the objectives of the current research work are also presented in the end of this chapter.

2.1 Studies on methanol crossover reduction methods

Passive DMFC is extremely simple in operation and maintenance. However, the technical problems associated with the poor performance of the passive DMFC are methanol and water crossover across the membrane, which create mixed over-potential losses, and catalyst poisoning on the cathode side. But, with modifications of the membrane, it is possible to reduce the methanol crossover to some extent. The following section shows the details of this literature.

Casalegno and Marchesi[8] experimentally and analytically studied the factors that affect the performance of the DMFC. Methanol crossover was found to be one of the main reasons for the poor performance of the DMFC. It was found out that among the different means of methanol crossover diffusion was the major reason. Kim et al.[9], [10]numerically analysed the performance of a passive DMFC with and without incorporation of liquid electrolyte layer [LE] in between two half MEAs. It was observed that the introduction of LE layer would considerably reduce the methanol crossover and improve the cell performance, compared to the cell configuration without LE layer. Cai et al.[11] numerically and experimentally analysed the performance of a passive DMFC with Liquid electrolyte (LE) layer. From their studies, it was concluded that the LE-DMFC produces 30% more peak power density as compared with the basic cell configuration of no LE layer. Similarly, Kordesch et al.[12]conducted experiments on the performance of an active DMFC by modifying the membrane with the introduction of a circulating electrolyte. It was observed that the electrolyte layer placed between the membrane electrode assemblies (MEA) helps in reducing the methanol crossover. Ouellette et al.[13]–[16]experimentally and numerically analysed the effect of flowing electrolyte (FE) medium (formic acid and sulphuric acid) and membrane thickness on the performance of active DMFC. It was observed that with sulphuric acid as the electrolyte, there was a 34% increment in the cell performance. The results also showed that thinner anode and thicker cathode membranes yielded better fuel cell performance.

Sharghi et al.[17] made experimental studies on an active DMFC by varying the concentration, channel thickness and flow rate of the FE. It was observed that cells having thicker membranes with 0.6mm FE channel and 2M methanol concentration solution produced higher peak power density. Kablou et al.[18]studied experimentally the influence of operating conditions on the performance of a five cell FE-DMFC stack. It was observed that the cell that was operated with higher inlet methanol flow rate, higher methanol concentration and higher flow rate of electrolyte had given better performance. Coplan et al.[19], [20] conducted experimental and numerical investigations on the effect of the membrane structure and other operating parameters on the performance of a FE- active DMFC. It was noticed that higher peak power density was obtained by higher velocities of air, anode fuel and the flowing electrolyte. It was also observed that increase in the FE inlet velocity leads to a reduction in the methanol crossover.

Duivesteyn et al.[21], [22] proposed a numerical simulation to evaluate the performance of a DMFC with the introduction of a porous FE. It was observed that in the active DMFC, the inlet velocity of the FE had negligible hydrodynamic implications and, the use of thin FE channel had enhanced the cell performance. Kim et al.[23] carried out experiments by introducing a thin metal barrier in between the two half MEAs of a passive DMFC. It was observed that the metal barrier coupled DMFC configuration would reduce the methanol crossover effectively, and the cell performance improved by 37.5% compared to the original configuration of no metal barrier. Sun et al.[24] experimentally studied the effect of incorporating a molecular sieve in the membrane on the performance of a DMFC. It was observed that after the membrane was modified with the molecular sieve membrane, the methanol diffusion rate through the membrane was effectively suppressed, which was about four times lower than with the original Nafion membrane. Milad et al.[25] used multi-layered membranes with and without coating of cellulose nanocrystals (CNC) and studied their effect on the DMFC performance. It was observed that CNC coated multi-layered membranes increased the fuel cell performance by 38%, when compared to the Nafion 115 membrane. Yuan et al.[26] developed a gradient porous medium on the anode side for analysed the passive DMFC performance. It was observed that incorporation gradient porous medium reduced the methanol crossover and simultaneously enhanced the CO_2 removal rate. Yousefi et al.[27] experimentally analyzed the effect of relative humidity, environmental temperature and cell orientation on the passive DMFC performance. It was observed that low relative humidity and higher temperature produced maximum power densities, and vertical orientation of the cell gave better performance.

Jung [28] experimentally studied the impact of anode Microporous Layer (MPL) on the DMFC performance. It was observed that the anode MPL resulted in restricting the methanol crossover and improved the cell performance. Liu et al.[29] conducted experiments on a passive DMFC by using microporous layer coated (CML). This CML was composed of carbon nanotubes and ammonia oxide. It was observed that the use of this CML improved the performance of the cell by up to 30.3%. It was also noticed that the water removal capacity near the cathode and gas transferring property of the gas diffusion layer were improved. Sudaroli and kolar [30] studied the impact of PTFE loading on the anode MPL and membrane thickness on the DMFC performance. It was observed that the cells with a thin membrane and 10% PTFE loading on the anode MPL enhanced the cell power output by 24% as compared with thicker membrane.

Zhang et al.[31] conducted experiments on an air breathing DMFC by applying PTFE MPL coating on the cathode. It was concluded that the PTFE MPL coating decreased the methanol crossover as well as the back flow of water from the cathode to the anode. Krishnamurthy and Deepalochani [32] studied experimentally the effect of PTFE -MPL coating on the cathode on the DMFC performance. It was observed that the 20% of PTFE loading on the cathode back layer yielded better cell performance. Sang and Lee [33] studied the effect of varying different operating parameters such as the cell methanol concentration, anode flow rate, cathode flow rate, cathode back pressure on the DMFC performance. It was observed that the methanol crossover was decreased at lower cathode back pressure.

Thus, from the literature review, it can be observed that most of the studies aimed at solving the major problems of water and methanol crossovers in the DMFC by modifying the membrane. Most of the researchers have focused on the influence of flowing electrolyte channel for the reduction of the MCO in an active DMFC. In addition to this, some of the researchers used porous materials on the anode, and introduced structural changes in the MEAs (membrane electrode assemblies) to control the methanol cross over. Similarly, cathode microporous layer was also studied as a means to reduce the water crossover. It appears very little research work was carried out on the use of intermediate liquid electrolyte layer in a passive DMFC. Thus, there is scope to conduct experiments with liquid electrolyte layer with larger active area.

2.2 Studies on the anode catalyst supports

The performance of the passive DMFC is strongly affected by methanol crossover (MCO). MCO can be decreased by effective utilization of methanol on the anode side, and simultaneously retarding the flow of methanol from the anode to cathode side. It is learnt from the literature that the activation losses and methanol crossover can be reduced by selecting suitable anode catalyst supports for enhancing the electro-catalyst activity.

Kim et al.[34] experimentaly analysed the performance of a DMFC with different cathode catalysts viz., Pt black, Pt/C, Pt/black (inner layer)+Pt/C, Pt black (outer layer)+Pt/C. It was observed that Pt black (inner layer) + Pt/C gives better fuel cell performance among the four MEAs. This was due to the enhanced Oxygen Reduction Reaction (ORR) activity and reduced methanol crossover. Liu et al.[35] investigated the influence of three different types of catalysts: Carbon black, Multi walled Carbon Nanotube (MWNT), reduced Graphene Oxide (rGO) on the cathode side of the DMFC. It was noticed that Pt/ MWNTs catalyst exhibited superior long term stability than the other supports, and Pt/r GO had higher ORR activity.

Glass et al.[36] carried out experiments on the influence of anode catalyst layer thicknesses on the DMFC performance. The catalyst layer thicknesses was varied from 1 mil to 8 mils (1mil=2.54µm) with a Pt/Ru loading varied from of 0.25 mg/cm^2 to 2mg/cm^2. It was observed that 4mil layer of 2mg/cm^2 loading produced the highest peak power density and the 8 mil layer with 0.25 mg/cm^2 loading produced highest normalised power density compared with respect to 1 mil layer at 0.25 mg/cm^2 and 0.5 mg/cm^2. Chen et al.[37] conducted experiments to study the effect of cathode catalyst layer of 20% wt. Nafion (S-CCL), double cathode catalyst layer (D-CCL),10 % wt. of Nafion and PTFE (M-CCL) on the passive DMFC performance. It was inferred that the M-CCL contained fuel cell produced the highest peak power density compared to the other two, i.e., D-CCL and S-CCL. Liu et al.[38] analysed the effect of nano-porous Pt-Co alloy nano-wire catalyst membranes on the DMFC performance. It was found that the Pt-Co alloy nano-wire catalyst on the anode side exhibited better MOR compared to the Pt/C catalysts.

Giorgi et al.[39]developed a bimetallic catalyst of platinum and gold nano-particles and studied their effect on the DMFC performance. It was found that the bimetallic catalysts increased the electro-catalyst activity, and gold decreased the Pt poisoning. It was also observed that the fuel cell performance improved by three times compared to the conventional catalysts of Pt-Ru nanoparticle. Abdullah et al.[40] examined the effect of different types of catalyst supports of Pt-Ru/TiO_2-CNF, Pt-Ru/C, Pt-Ru/CNF, and Pt-Ru/TiO_2 on the DMFC performance. It was inferred that TiO_2-CNF catalyst support produced 5.54 times more current density with reference to the commercial Pt-Ru/C catalyst, because of highest catalytic activity of the bimetallic Pt-Ru compared to the other electro catalysts. Fuentes et al.[41] studied the influence of Pt-Ru catalyst supports of TiO_2 and Nb-TiO_2 on the DMFC performance. It was noticed that Nb-TiO_2 support increased the catalyst activity by 83% compared to the same catalyst with carbon support.

Kakati et al.[42] conducted experiments to study the impact of anode catalysts of Pt-Ru /Mo on multiwall carbon nanotubes and Pt-Ru/MWCNT on the DMFC performance. It was shown that the Pt-Ru /Mo on multiwall carbon nanotubes catalyst has higher electro catalytic activity compared to the Pt-Ru/MWCNT catalyst. Kang et al.[43] studied the effect of anode catalysts of pure Pt, Pt-Ru and Pt_5Ru_4M (M is either of Ni, Sn and Mo) on methanol oxidation reaction (MOR). It was observed that MOR of Pt-Ru/Ni electro catalysts was greater than that of Pt-Ru catalyst. Yang et al.[44] made a comparative study of PtRu-Sn and Pt-Ru catalysts on the MOR process.It was observed that the PtRu-Sn electrocatalyst increased the MOR compared to the Pt-Ru catalyst. Rosli et al.[45] conducted experimental studies to understand the influence of cathode catalyst of 5% wt. and 10% wt. Pd/C as well as in steps of 2, 4, 6 mg/cm^2 on the DMFC performance. It was observed that the optimal conditions of 10% wt. Pd/C and in steps of 4 mg/cm^2 gave the best performance. Zhou et al.[46] reported that Pt-Ru/C catalyst for DMFC and Pt-Sn/C catalyst for DEFC on anode side shown better fuel cell performance compared to pure Pt catalyst.

From the above literature review, it is observed that the most of the studies are related to different catalyst supports on the anode and cathode sides, viz., Pt/Ru, PtRu-Sn, Pt-Ru Ni, to enhance the MOR with a single coated catalyst layer on the anode side. Some studies were related to the two layer catalyst on the cathode side. Thus, there is scope to analyses the two layer catalyst with different supports on the anode side for reduction of methanol crossover.

2.3 Studies on the perforated current collector and wire mesh current collectors

Design of the current collectors plays a major role in the working and performance of a passive DMFC. In the passive DMFC, the current collectors are made with different shapes of perforations such as circular, rectangular, hexagon, triangular, etc. Through these openings in the current collectors, the reactants flow from the end plates to the membrane, i.e., the anodic fuel from the anode end plate to the membrane, and oxgen from the cathode end plate to the membrane. The main functions of the current collectors are to hold the MEA in the correct position and to act as current conductors for the passage of the electrons produced during the chemical reaction in the cell. The elctrons produced near the anode during the reaction will be collectd near the anode current collector, and flow through the external circuit and reach the cathode current collector. In addition to this, the current collectors also facilitate uniform distribution of the fuel and oxidant to the reaction sites. The major challenge associated with the design of the current collectors is to have an appropriate open ratio of the current collector such that the methanol crossover is reduced and a good contact between the MEA and the current collector is obtained.

Xue et al.[47] studied experimentally the effect of geometry of circular holes on the cathode current collectors on the performance of a DMFC. It was observed that the current collector with small uniformly sized holes was better at the cathode side. Kim et al.[48] designed current collectors with different shapes of the openings such as rectangular, circular and triangular shapes. It was noticed that the circular opening exhibited the best cell performance among the three shapes. Gholami et al.[49] experimentally analysed the effect of current collector channel configurations on the passive DMFC performance. It was observed that better fuel cell performance was obtained with combination of non-uniform parallel channels, with an open ratio of 53.76% on the anode, and a perforated flow field with an open ratio of 34.5% on the cathode side compared to the uniform channels. Xianqi et al.[50] conducted experiments on a passive DMFC fitted with parallel and perforated current collectors. It was concluded that with the perforated and parallel current collectors on the cathode and anode sides respectively, the fuel cell produced the maximum power density.Yang et al.[51] performed experimental studies on a passive DMFC fitted with different current collector(CC) structures. It was found that circular current collector on the cathode side and parallel CC on the anode side were the best combination that gave better fuel cell performance. Wang et al. [52] experimentally analysed the effect of collector channel patterns, current collector open ratios on the passive DMFC performance. It was observed that the vertical stripe pattern (VSP) is preferred for both anodes and cathodes due to the upward reaction products drift by natural convection. Open ratio of 45.6% and 35.8% are found to yield the best performance for anode and cathode, respectively.

Chen at al.[53] studied the performance of a DMFC with metal porous current collectors on the cathode side. It was observed that the metal porous current collectors on the cathode side enhanced the diffusion rate of oxygen and faster water removal due to the small pore size. Qin-Zhi et al. [54] from their experimental studies on a passive DMFC observed that parallel current collectors on the anode side increased the CO_2 bubble removal and enhanced the cell performance. Hen et al.[55] conducted experiments on the flow field structures of vertical parallel-fence (S1), horizontal parallel-fence (S2), composite structure (S3) based on the combination of a vertical parallel-fence and a sintered porous metal fibre felt (SPMFF), and composite structure (S4) composed of an open parallel-fence and SPMFF. It was observed that the vertical parallel fence (S1) and composite structure (S3) gave better fuel cell performance at lower and higher methanol concentrations respectively. In the composite structure, CO_2 bubbles resists methanol crossover (MCO) at concentrated solutions (i.e., 8M) and at diluted solutions CO_2 was quickly removed from the reaction sites. Braz et al. [56] conducted experiments on the passive DMFC with different current collector materials of Ti, stainless steel and SS with gold coated. It was observed that the Ti on the anode side and SS on the cathode side combination fitted fuel cell produced the higher maximum power density compared to other combinations.

Borello et al.[57] evaluated the performance of a passive DMFC fitted with perforated current collectors of 36% and 38% open ratios. It was observed that the higher open ratio (38%) current collector incorporated fuel cell gave better fuel cell performance. Yuan et al.[58] fabricated circular-hole-array (CHA) current collectors with open ratios of 50.24% and 28.26%, and parallel-fence (PF) current collectors with open ratio of 75.04% and 63.49% and studied their effect on the passive DMFC performance. It was observed that the combination of CHA with an open ratio of 50.24% and PF with an open ratio of 63.49% produced the maximum peak power density (MPD). Calabriso et al.[59] designed a current collector with stainless steel plates (SS316) with circular openings and with open ratios of 17% and 35%. It was observed that the current collector with open ratio of 35% produced greater peak power density at 2M of methanol concentration. Braz et al. [60] experimentally investigated the effect of current collector open ratio (34%, 41% and 64%) on the passive DMFC performance. It was observed that the current collector with lower open ratio of 34% gave better fuel cell performance than the other two current collectors. Yuan et al. [61] experimentally investigated the effects of methanol concentration and discharge current on the bubble in the pores of the diffusion layer of the passive DMFC. It was noticed that the both show that the size and number of anode CO2 bubbles are highly correlated with cell operating conditions. More and smaller bubbles are easily generated when the anode reaction is more intense. Munjewar and Thombre[62] analysed the effect of current collector roughness on the performance of a passive DMFC. It was revealed that the optimum surface roughness of 0.869 µm yielded better fuel cell performance. The optimum surface roughness decreased the contact resistance and increased the reactant flow into the catalyst layer.

Similarly, Shrivastava et al.[63] experimentally investigated the influence of wire mesh current collectors (WMCC) with supporting plate structure on the passive DMFC performance. It was observed that the optimized configuration of WMCC with an open ratio of 41% and supporting plate open ratio of 57.8% gave better fuel cell performance. Scott et al. [64] studied the effect of stainless steel meshes for the discharge of CO_2 bubbles at the anode portion of the passive DMFC. It was observed that a thick mesh with low voidage and rough surface gave better fuel cell performance. Ranjan et al.[65], [66] conducted experiments to study the influence of expanded metal mesh and supporting plate open ratios on the passive DMFC performance. It was observed that a combination of expanded metal mesh with an open ratio of 48.22% and supporting plate with an open ratio of 56.25% fitted fuel cell produced the maximum power density. Shao et al.[67] developed a novel design of anode structure, with titanium mesh coated with deposition of Pt-Ru. It was revealed that the coated deposition has good physical properties and resists the methanol crossover, which yielded better performance at lower methanol concentrations as compared with the conventional porous titanium mesh.

Falcao et al. [68] conducted experiments by adding wire mesh current collectors (with open ratios of 31%, 38.70%, 44.3% and 51.9%) in between the MEA and the perforated current collectors and studied their effect on the performance of a passive DMFC. It was noticed that the incorporation of wire mesh current collector with an open ratio of 38.70% gave higher power density compared to the other combinations. The wire mesh current collectors reduced the MCO and enhanced the fuel cell performance. Zhang et al.[69] experimentally examined the influence of incorporating different open ratio tin coated stainless steel wire meshes (open ratio of 33.09, 44.65, 53.58, 57.15 and 59.68 in between the MEA and the flow field on the performance of an active DMFC. It was observed that the incorporation of wire mesh with 33.09% open ratio gave better fuel cell performance compared to the other combinations of meshes. Bincy George and Raghuram Chetty [70] experimentally analysed the influence of catalyst coated Ti mesh with different open ratios on the passive DMFC performance. It was observed that the optimum configuration was found with PtRu on an 80 mesh (47% open ratio) Ti anode and a Pt/C coated GDL with 40 mesh (71% open ratio) Ti as a cathode gave better fuel cell performance. Thus, there is scope to analyze the effect of PCCs and wire meshes with different open ratios on the performance of a passive DMFC.

The literature review has been summarized with respect to the thickness and open ratio of current collectors, MEA structure and catalyst loading as shown Table.2.1.

Table 2.1 Summary of the literature review

Author	**Thickness (mm)**	**Open ratio (%)**	**MEA structure, Catalyst loading (Anode/Cathode)**	**Remarks**
[57]	-	38,36	-	-Higher open ratio of CC (38%), homogenous distribution of the fuel on the catalyst area.
[60]	0.5	34.41,64	N117 3/1.3	Lower open ratio (34%) reduced methanol crossover and increased the electron collecting area.
[71]	0.5	35,17	N117 CL-4/4	-Higher open ratio (35%) CC remove the CO_2 bubbles from the reaction sites easily and produced higher power at lower methanol concentration (2M).
[72]		32.21	-	-Small size of holes on the cathode side with constant open ratio gave uniform distribution the oxygen on the reaction area.
[73]	1	95% porosity	N115 4/2	Porous CC on the cathode side enhanced the oxygen transport.

2.4 Studies on different alcoholic fuels and fuel additives

Hydrogen is the most ideal fuel to be used in a fuel cell because of its electrochemical activity. However, the disadvantages associated with hydrogen such as low density, high volume requireement and the safety concerns make it less attractive for some applications. In such applications, instead of hydrogen, alcholic liquids can be used as fuels in the fuel cells. Alcholic fuels have the merits of easy storage, transport, higher energy density and easy membrane hydration. Thus, these fuels are being considered as fuels for fuel cells. Liquid alcohol fuels such as methyl alcohol (methanol), ethyl alcohol (ethanol), n-propyl alcohol (1-propanol, 2-propanol), and 2-butanol are the possible alternatives to hydrogen to be used as the fuels in the fuel cells.

Yang et al. [74] experimentally investigated the influence of blending of ethanol into the methanol fuel on the DMFC performance. It was observed that the addition of ethanol in the methanol fuel increased the cell voltage drop. Wang et al.[75] carried out experiments on a DMFC by using a blend of hydrogen peroxide and methanol as the anodic fuel. It was observed that the addition of hydrogen peroxide increased the peak current density compared to only methanol as the fuel. Cao et al.[76] made comparative studies with direct methanol and addition 2-proponol with methanol as the anodic fuel in a DMFC. It was observed that addition of 2-propanol enhanced the fuel cell performance up to 200 $mA.cm^{-2}$, and also increased the electrical efficiency by 1.5 times compared to the DMFC. Najmi et al. [77] studied the effect of addition of NaOH to the methanol fuel on the passive DMFC performance. It was observed that the addition of NaOH to methanol produced four times more power density as compared to the normal passive DMFC. Munjewar et al.[78] experimentally analysed the effect of mixing 2-proponol to methanol on the DMFC performance. It was observed that the addition of 2-proponol increased the cell performance by 63%.

Lamy et al.[79] carried out experiments with different alcoholic fuels such as methanol, ethanol, 1-propanol and 2-propanol by using a phosphoric acid doped polybenzimidazole (PBI) membrane in the Direct alcoholic fuel cell (DAFC). It was observed that methanol fuel gives better fuel cell performance compared to other alcoholic fuels. Lee et al.[80] experimentally studied the effect of electro-oxidation of methanol, ethanol and 2-propanol by using Interdigitated Array Electrodes (IDAEs). They also analysed the imapact of Pt and Pt-Ru electrodes on the anode side. It was observed that the addition of Ru enhanced the oxidation currents and reduced the onset potential of the alcohol fuels. Gojkovic et al.[81] reported that the addition of 2-propanol in methanol increased the oxidation rate compared to the individual operating cells of methanol and 2-propanol. Gupta et al.[82] conducted experiments with ethanol and 2-propanol as the fuels in a direct alcohol fuel cell. It was observed that 2-propanol was promising fuel for the Direct Alcoholic Fuel Cell (DAFC) compared to ethanol. Thus, there is scope to analyse the effect of different alcohols and belnds of alcohols with methanol as the fuels in the alcoholic fuel cells and evaluate their performance.

2.5 Research gaps identified from literature review

- From the above literature review, it was observed that in the DMFC the methanol and water crossover were reduced by incorporating a flowing electrolyte channel in between the two half MEAs of the active DMFCs, and very less literature was available on the impact of liquid electrolyte layer insertion on the performance of the passive DMFC.
- Different types of anode catalyst were used on the anode side of the DMFCs with single layer, with carbon and carbon supports. On the cathode side, two layer catalysts of Pt/C+ Pt/Carbon black were used for enhanced DMFC performance. Very less work was available on the effect of two layer catalyst on the anode side with different supports.
- From the literature, it is observed that most of the research work focused on the influence of open ratios of the perforated and wire mesh current collectors individually. Very little literature was available on the combination of different open ratios of wire meshes with single circular open ratio current collector.
- Most of the published research work is related to the single alcoholic fuel used as the anodic fuel and the effect of blending of the alcohol fuels on the performance DMFC was not thoroughly evaluated.
- In the literature, different researchers attempted modelling studies on the passive DMFC. From the review of the literature it is observed that methanol crossover is a major issue in the operation of the passive DMFC. Based on the literature review, different techniques have been identified to address the above issue.

2.6 Objectives of the present research work

The objectives of the present experimental work are as follows:

- To fabricate and experimentally investigate the influence of liquid electrolyte thickness aimed at enhancement of passive DMFC performance.
- To enhance the performance of a passive DMFC by incorporation of different catalyst supports (carbon and carbon black) on the basis of anode side reaction kinetics.
- To study experimentally the effect of perforated current collector open ratio for enhanced performance of the passive DMFC.
- To investigate the influence of combined wire mesh and perforated current collector aimed at improved electrical conductivity.
- To experimentally study the effect of different alcoholic fuel additives to the methanol as the anodic fuels on the performance of the passive DMFC.

Chapter 3

Experimental methodology

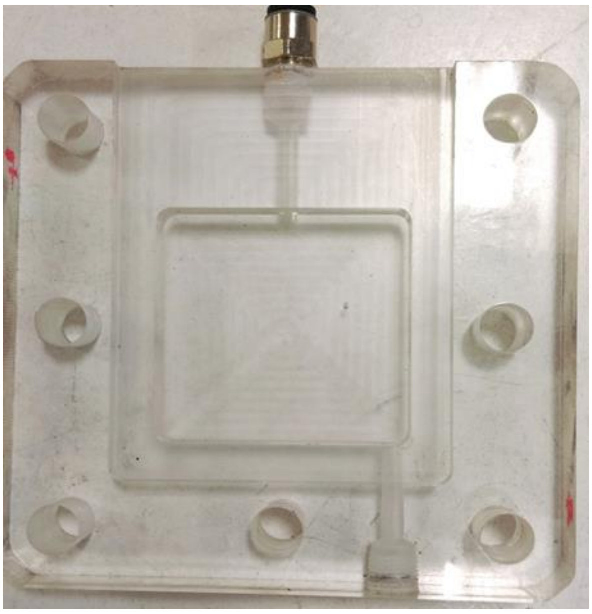
3.1Introduction

A passive direct methanol fuel cell (DMFC) assembly was fabricated in the Fuel cell Laboratory of NIT, Warangal. The cell is designed with an active area of 25 cm^2 (5 cm x 5 cm). The details of the parts of the passive DMFC and the different steps involved in the fabrication of the passive DMFC assembly are presented in this chapter.

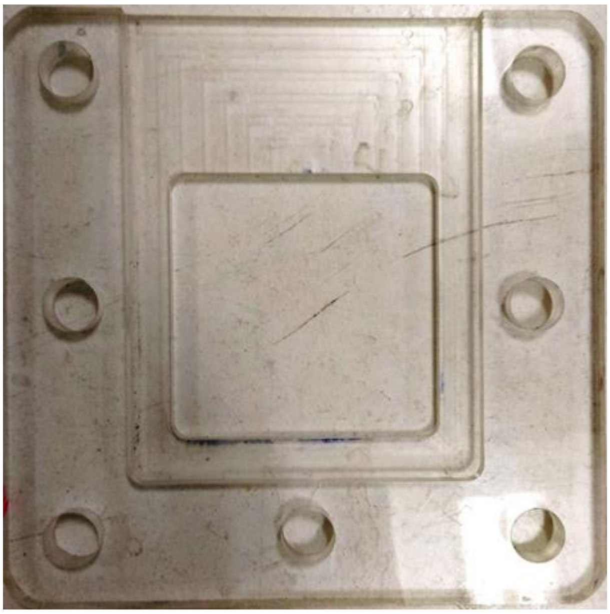
3.2 Passive direct methanol fuel cell

The main components of the passive DMFC include the anode and cathode side end plates, current collectors, gaskets and Membrane Electrode Assemly (MEA). A schematic daigram of the conventional passive DMFC (C-DMFC) as shown in Fig.1.2.

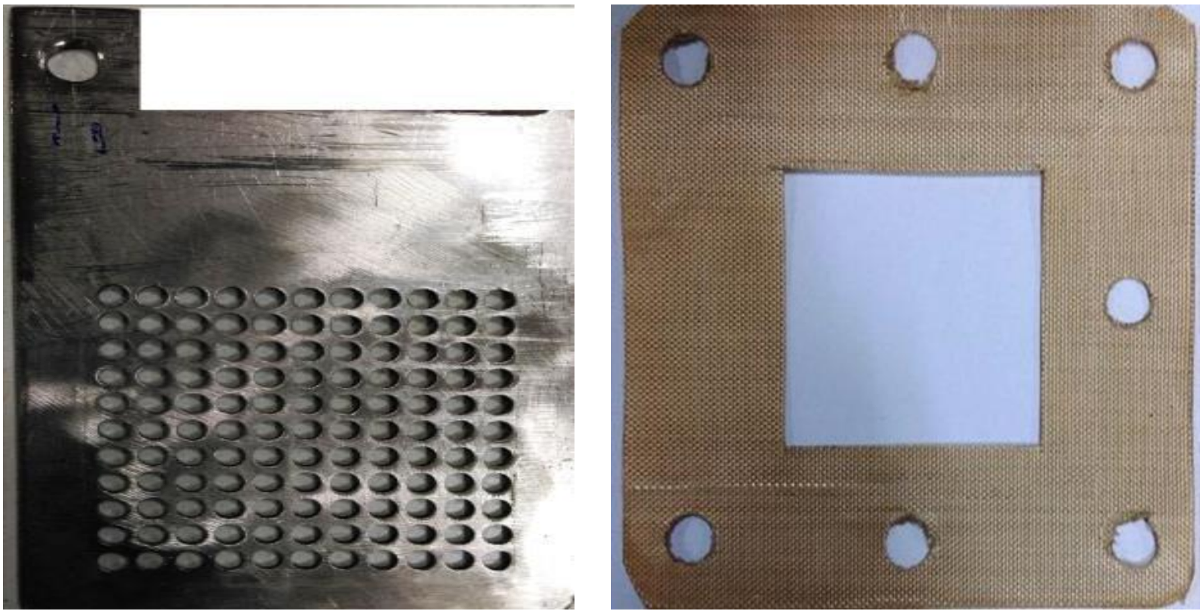
3.2.1Material:



(a)



(b)



(c) **(d)**

Fig.3.1 Passive DMFC components (a) Anode end plate (b) Cathode end plate (c) Perforated current collector (d) Teflon gasket

(a) End plates

The two end plates (anode and cathode end plates) were made up of Poly-methyl methacrylate (PMMA) material of 18 mm thickness. The anode end plate also acts as the reservoir of the anodic fuel, i.e., methanol. The reservoir has a capacity of 25 ml. One hole of 3 mm diameter was drilled on the top surface of the anode end plate. This hole is used for filling of methanol in the beginning of the experimentation. This hole also helps in the exhaust of the CO_2 gas produced near the anode side of the membrane during the reaction. The cathode end plate has a square opening of area equal to the active area of the cell, i.e., 25 cm^2, and this opening was exposed to the surrounding atmosphere. This opening on the cathode end plate allows air (oxygen) from the ambient to the cell through natural circulation. Holes were also drilled on the four sides of end plates to firmly hold them for making an assembly of the cell using bolts and nuts. The anode and cathode end plates are shown in Figs. 3.1 (a) and (b) respectively.

(b) Current collectors

The current collectors permit the flow of the reactants from the end plates to the membrane, i.e., the anodic fuel from the anode end plate to the membrane, and oxgen from the cathode end plate to the membrane. The elctrons produced near the anode during the reaction will be collectd near the anode current collector, and flow through the external circuit and reach the cathode current collector. From the cathode current collector, the elctrons reach the membrane and complete the reaction. Thus, the current collectors also act as current conductors. Different configurations of current collectors such as Perforated curent collectors, wire mesh current collectors are used in the fuel cells. Two perforated current collectors, one on either side of the anode and cathode, made of stainless steel 316L material of 2 mm thickness, were used in the conventional DMFC. Fig.3.1 (c) shows the perforated current collectors used in the present experimnetal set-up.

(c) Gaskets

Two, 0.23 mm thickness, Teflon coated glass fiber gaskets were used in the configuration. The gaskets help in providing proper sealing and maintaing a precise conatact between the current collectors and the MEA. Fig. 3.1 (d) shows a photo of the gasket.

(d) Membrane Electrode Assembly (MEA)

The MEA is the most important component of the fuel cell. The MEA consists of five different layers, viz., (i) diffussion layers (called as Gas Diffusion Layers) on the anode and cathode sides (ii) Catalyst layers on the anode and cathode sides, and (iii) the membrane. The constructional details of these layers are described in the following sections.

(i) Gas Diffusion layers (GDL)

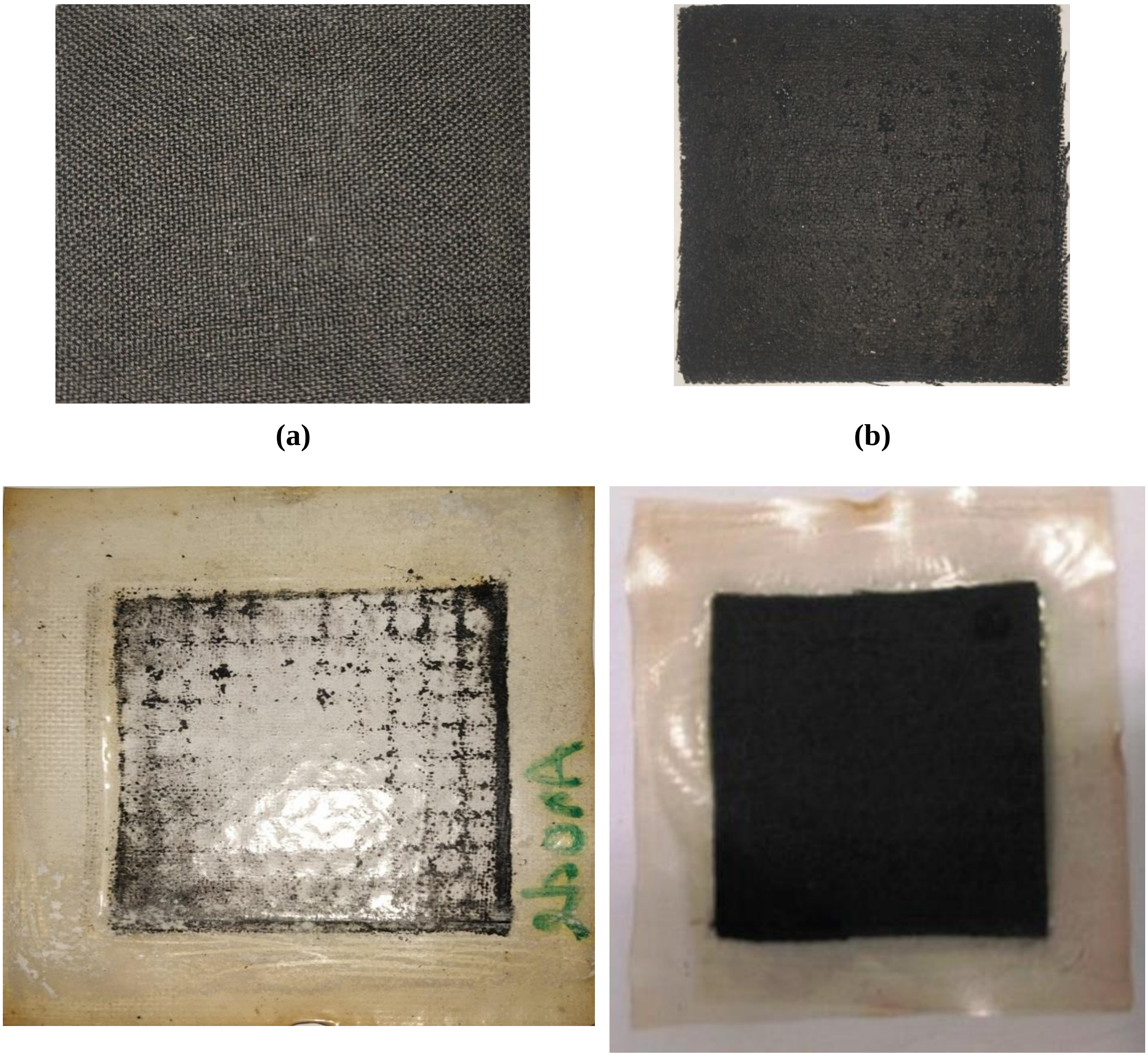
There are two GDLs bonded to the anode and cathode catalyst layers. Hydrophobic carbon fibre paper or cloth was used as the GDL, and it is called the substrate. A micro-porous layer (MPL) with hydrophobic property was applied to the catalyst side of the substrate. The hydrophobicity is usually attained through application of Poly Tetra Fluoro Ethylene (PTFE). Fig.3.2 (a) shows the carbon cloth GDL of area 50 mm x 50 mm, used in the conventional DMFC.

(ii) Catalyst layers (CL)

In a passive DMFC there are two Catalyst Layers (CLs), one on either side of the membrane. These CLs are placed between the membrane and GDLs on the anode and the cathode sides respectively. All the electrochemical reactions take place at the catalyst layers only. Catalysts of Pt-Ru/C and Pt/C were used on the anode and cathode sides respectively. Fig.3.2 (b) shows the photo of the catalyst layers of area 50 mm x 50 mm used in the present experimentation.

(iii) Membrane

The membrane is considered as the heart of the passive DMFC, through which there will be transport of hydrogen ions (protons) from the anode CL to the cathode CL. The membrane needs to possess relatively high proton conductivity. Also, the membrane should be chemically and mechanically stable in the fuel cell environment. Perfluorocarbon-sulfonic acid ionomer (PSA) membrane was used in the DMFC. Nafion 117 membrane with an area of 75 mm x 75 mm was used in the present experimentation, and is as given in Fig.3.2 (c).



(a) **(b)**

(c) **(d)**

Fig.3.2 Parts of the MEA (a) Gas diffusion layer (GDL) (b) Catalyst coated GDL (c) Nafion membrane (d) MEA

3.2.2 Fabrication of the MEA

The Membrane electrode assembly with an active area of 25 cm^2 (5.0 cm × 5.0 cm) was made by hot pressing of a Nafion117 membrane at 135^0C, 8 MPa for 3 min. Before starting the hot pressing, the organic and inorganic impurities were eliminated from the Nafion membrane by boiling the membrane in 3 wt. % H_2O_2 solution for one hour, followed by subsequent cleansing in deionised (DI) water. Later, it was boiled in 0.5 M H_2SO_4 solution for around 1 hour and lastly boiled in DI water for one hour. The anode and cathode backing layers were fabricated of carbon cloths with 20% polytetrafluoroethylene (PTFE). The anode and cathode catalyst layers were processed by distribution of sufficient quantity of the catalyst into the solutions containing of DI water, Nafion solution and isopropyl alcohol. The catalyst on the cathode side was 60 wt. % Pt/C with a cathode loading of 2mg/ cm^2, and the anode side catalyst was 60 wt% Pt-Ru/C with a loading of 4 mg/cm^2. The complete assembly of the MEA is shown in Fig.3.2 (d).

3.3 Assembly of the Passive DMFC

The passive DMFC assembly consists of the end plates, current collectors and the MEA along with the gaskets. All these parts of the DMFC were assembled by using nuts and bolts. The bolt and nut assembly was tightened to an applied torque of 5 N-m. The assembly of the passive DMFC is shown in Fig.3.3.

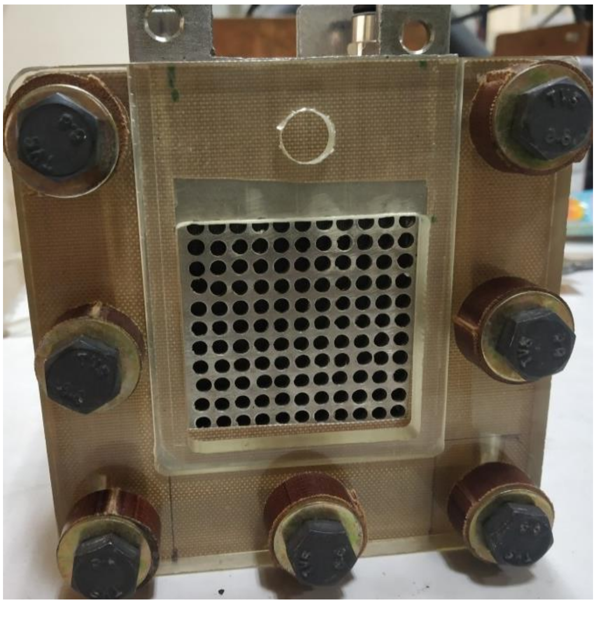


Fig.3.3 Complete assembly of the passive DMFC

3.4 DC Electronic load bank

DC electronic load bank was used to measure the voltage, current and power values according to input conditions as shown in Fig.3.4.

3.4.1 Specifications of the DC Electronic load bank

- BK precession-Model-8510
- Voltage-0-120V
- Current:0-120A
- Power:0-600W
- Built-in high resolution (0.1 mA/1 mV)

Fig.3.4 DC electronic load bank

3.5 Experimental procedure

The procedure for each experiment is as follows:

- Diluted methanol solution of different concentrations was prepared.
- The prepared methanol solution was poured into the reservoir of anode end plate using a pipette.
- The fuel cell assembly was checked for leakage of liquid fuel.
- Before starting the experiment, the new MEA was activated for a period of 12 hours at 1M of methanol concentration with constant load.
- All the experiments were carried out at room temperature and relative humidity of 60-70% and with the cell being kept in horizontal position. The anode was placed on the upper side and the cathode was placed on the bottom side respectively.
- The electrode terminals of the fuel cell were connected to a DC electronic load bank as shown in Fig.3.4.
- The experimental set-up was kept in switched on condition for one hour at open circuit voltage to attain steady state conditions as shown in Fig.3.5.

- The voltage readings for each current were recorded after steady state conditions are attained.
- Each experiment was repeated for three times for checking consistency of the readings.

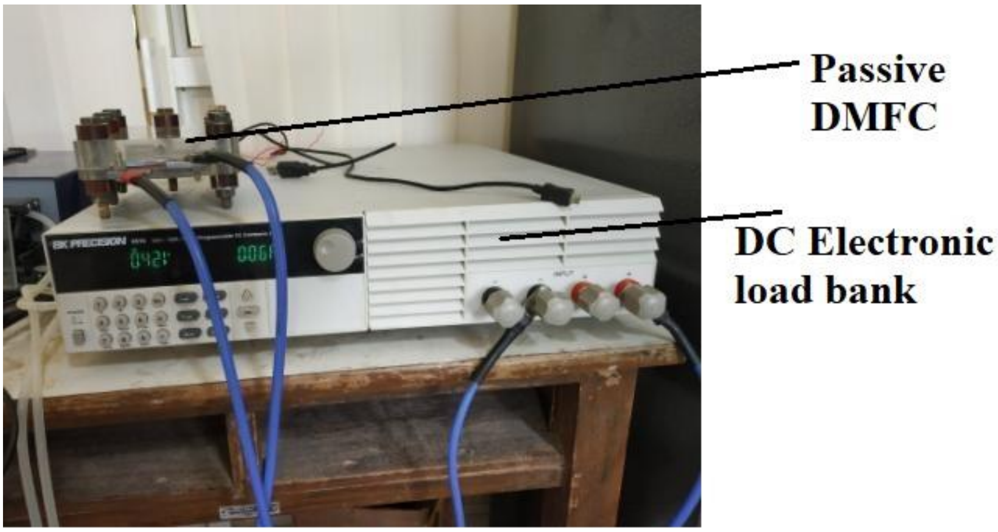


Fig.3.5 Experimental set-up of the passive DMFC

Table.3.1 Experimental operating conditions

Parameter	**Operating range**
Activation time period	12 hours at 1M of methanol concentration.
Constant voltage during activation	0.2 V
Relative humidity	60 % -80%
Operating temperature	Room temperature (20^0C-28^0C)
Operating pressure	Atmospheric pressure
Methanol concentration	1M to 12M
Cell orientation	Horizontal

To meet the objectives of the present work as discussed in Chapter 2, experiments were conducted in five stages as described below:

1. In the first stage of experimentation, the influence of Liquid Electrolyte (LE) layer thickness on the performance of the passive DMFC was analysed. Tests were conducted on a passive DMFC by varying the electrolyte layer thickness from 1.5 mm to 2.5 mm and the methanol concentration was varied from 1M to 12M.

2. The second stage of experimentation was aimed at making a comparative study of the anode catalyst supports of carbon and carbon black on the performance of the passive DMFC.

3. The third stage of experimentation was aimed to analyze the effect of open ratio of the perforated current collector with respect to methanol concentration on the performance of the passive DMFC.

4. In the fourth stage of experimentation, the combined effect of perforated and wire mesh current collectors on the performance of a passive DMFC was studied.

5. In the fifth stage of experimentation, the effect of blending different alcohol additives to the methanol fuel on the performance of a passive DMFC was analyzed experimentally.

   The results of these experiments are discussed in the subsequent chapters respectively.

Chapter 4

To fabricate and experimentally investigate the influence of liquid electrolyte thickness aimed at enhancement of passive DMFC performance.

Passive DMFC is extremely simple in operation and maintenance. However, the technical problems associated with the poor performance of the passive DMFC are methanol and water crossover across the membrane, which create mixed over-potential losses, and catalyst poisoning on the cathode side. By incorporating the modifications in the membrane, it is possible to reduce the methanol crossover. The present work aims to incorporate the modifications in the membrane by introducing a Liquid Electrolyte (LE) layer in between the two half membrane electrode assemblies (MEA). Methanol concentration is an important parameter that influences the performance of the Passive DMFC, conventional DMFC as well as liquid electrolyte layer (LE-DMFC). Before evaluating the effect of the Liquid electrolyte layer thickness on the performance of the passive DMFC, experiments were conducted on a Conventional passive-DMFC (i.e., no electrolyte layer in the MEA) to establish the effect of methanol concentration. Experiments were conducted by varying the methanol concentration to demonstrate the effect of methanol crossover. Later, experiments were conducted by incorporating a liquid electrolyte layer in between the two half MEAs of the passive DMFC to evaluate the effect of the liquid electrolyte layer thickness on the performance of the cell. The analysis of these results is presented in this chapter.

4.1 Effect of methanol concentration on the performance of a conventional passive DMFC

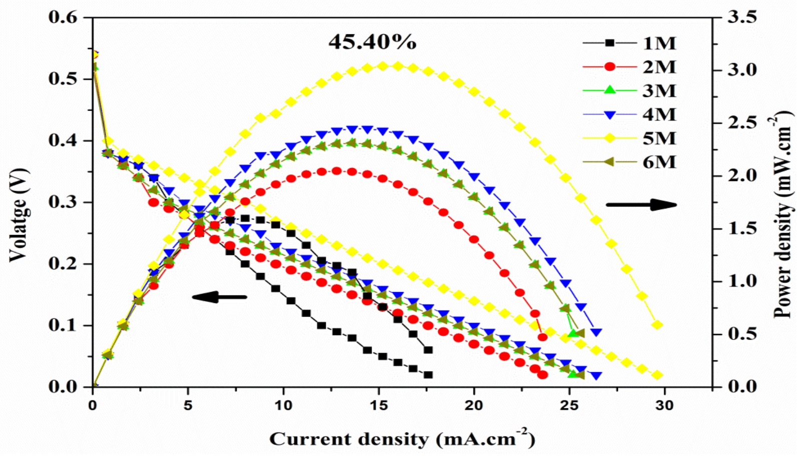


Fig.4.1 Polarization and power density characteristics of the passive DMFC for different methanol concentrations

In this phase of experimentation the effect of methanol concentration on the performance of a conventional passive DMFC (C-DMFC) was studied. Pt-Ru/C and Pt/C catalysts were used on the anode side and cathode sides respectively. The methanol concentration was varied from 1M to 6M. A current collector with an open ration of 45.40% was used for this experimentation. Experiments were conducted by varying the methanol concentration from 1M to 6M. For each methanol concentration, experiments were conducted by varying the current density, and the corresponding cell voltage and power density were measured. Fig.4.1 shows the polarization and power density characteristics of the C-DMFC. It can be seen from the polarization curves that for any methanol concentration, as the current density is increased, the cell voltage gradually drops. This voltage drop is steeper at smaller methanol concentrations, and the slope of the polarization curve gradually increases with increase in the methanol concentration. The smallest slope is observed for 5M methanol concentration. However, at 6M concentration, once again the slope is steeper and is inferior to even 4M methanol concentration.

The power density, which is the product of voltage and current density shows a parabolic trend of increase in the power density with increase in the current density, reaches a peak and then decreases with increase in the current density. With increase in the methanol concentration, the maximum power density increases and also the operating range gets widened. This trend continued for the increase in the methanol concentratrion from 1M to 5M. With further increase in the methanol concentration to 6M, the cell performance deteriorated. At 6M methanol concentration, the power density is lowere than that with 4M methanol concentration. Thus, it can be observed from the figure that at 5M methanol concentration, the cell generated the MPD and MCD of 3.04 mW cm^{-2} and 29.6 mA cm^{-2}, respectively.

Compared to the reversible cell voltage,which is supposed to be a flat curve of constant voltage for all values of current density the actual cell voltage is lower.The difference between the reversible cell voltage and the actual cell voltage is due to the losses in the cell.These losses are the sum total of activation losses, ohmic losses and concentration losses. At smaller methanol concentrations (say for 1M), the cell voltage falls steeply with increase in the current density. It is because at lower methanol concentration, sufficient amount of methanol is not available for the reaction, and the activation losses will be dominant. As the methanol concentration is increased, the slope of the polarization curve becomes flatter, the peak power density produced increases and the operating range of the cell also increases.This is because with increase in the methanol concentration, the reaction kinetics of the cell improve and this results in better output of the cell. This trend continued with increase in the methanol concentration from 1M to 5M. However, with further increase in the methanol concentration, i.e., at 6M methanol concentration, the cell performance deteriorated and is even inferior to 4M methanol concentration. This can be attributed to the concentration losses. At higher methanol concentrations, the MCO from the anode to the cathode increases. This creates the mixed overpotential losses. Because of this, cathode side catalyst poisioning, cathode water flooding, wastage of fuel, obstruction of oxygen flow and also deterioration of the quality of the membrane occur.Water is produced at the cathode catalyst layer (water flooding) due to the mixed overpotential, and the water bubbles so formed block the pores of the diffusion layer (GDL) obstructing the flow of oxygen to the reaction sites. This results in sharp detoriation in the performance of the cell.

From this experimentation, it is concluded that the performance of a conventional passive DMFC increases with increase in the concentration of the anodic fuel, but at higher concentrations the methanol cross over dominates and adversely affects the cell perfomance and there exists an optimum methanol concentration at twhich the cell performance is the highest.

It was observed from the literature that the incorporation of an additional electrolyte layer can considerably reduce the MCO and improve the cell performance. In the present work, liquid electrolyte layer was considered for evaluation. In the next phase the experiments were conducted to evaluate the effect of liquid electrolyte layer thickness on the performance of the passve DMFC.

4.2 Assembly of the Liquid electrolyte-passive DMFC

The MEA of the conventional DMFC was modified by inserting a liquid electrolyte layer in between the two half MEAs. Initally the catalyst was coated on the diffussion layers of the anode and cathode sides. After that the two layers were hot pressed on the Nafion membrane individually.The hot pressed parts are called as half MEAs on the anode side and cathode side. Piled hydrophilic filter papers were soaked in an acidic nature electrolyte (1M dilute sulfuric acid) soltion.These soaked filter papers were placed between the two half MEAs and then assembled. The soaked filter papers is named as the Liquid Electrolyte (LE) layer. The thickness of the LE layer was estimated by the number of paper piles. This membrane with a liquid electrolyte layer sandwiched between the two half MEAs is called as the Composite MEA or LE-MEA. Fig.4.2 shows different steps in the fabrication of the LE-MEA. The composite MEA, placed in between two Teflon gaskets, was sandwiched between the anode and cathode current collectors. This assembly was fixed in between the cathode and anode end plates, which were made of acrylic material. The anode end plate serves as methanol reservoir and the cathode end plate with a square opening, was exposed to the atmosphere for air breathing. The entire assembly was tightened with an applied torque of 5N-m. Different steps of the complete assembly steps are shown in Figs. 4.3 and 4.4.

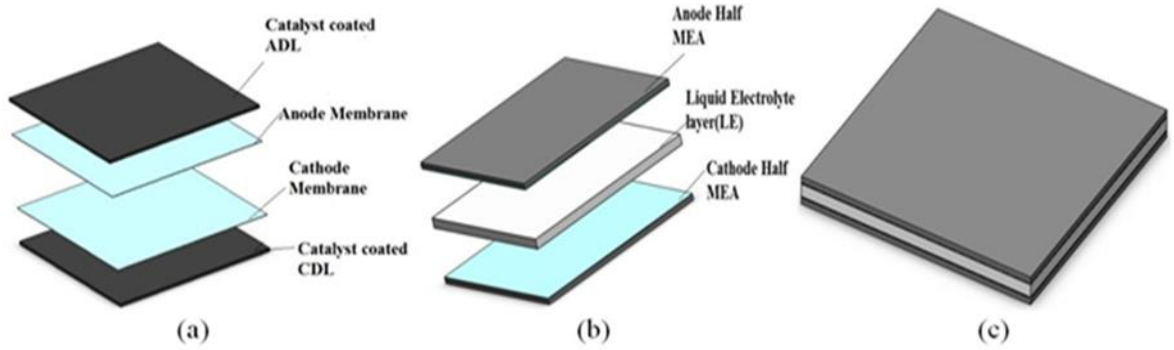
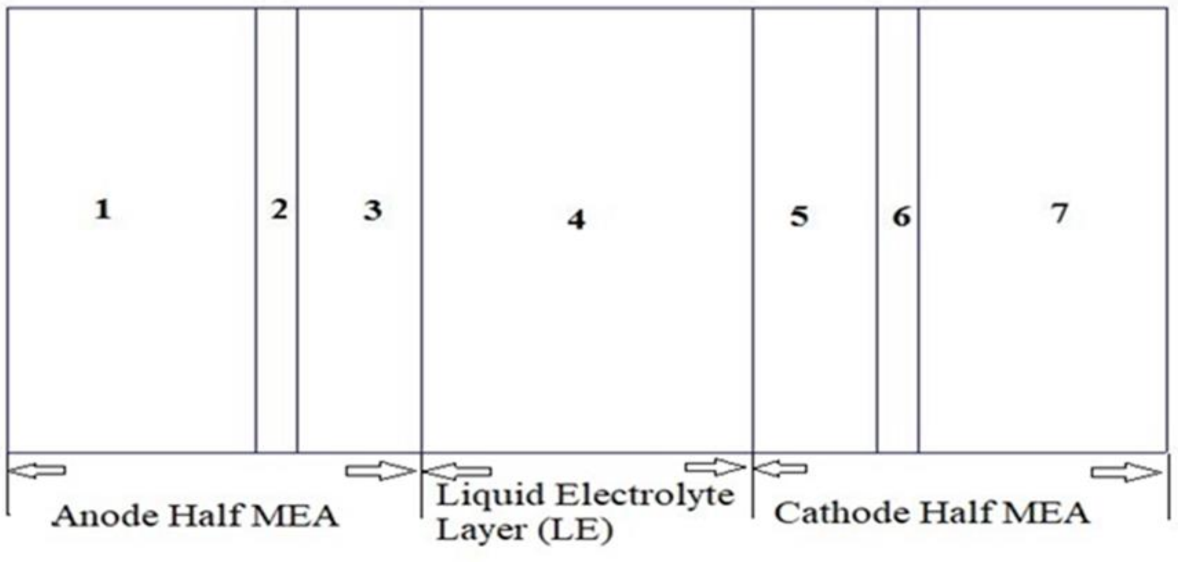


Fig. 4.2 Fabrication of the Composite MEA (a) Half MEAs before hot pressing (b) After hot pressing along with liquid electrolyte layer. (c) Composite MEA



1. Anode gas diffusion layer(ADL)
2. Anode catalyst layer(ACL)
3. Anode membrane
4. Liquid electrolyte layer
5. Cathode membrane
6. Cathode catalyst layer
7. Cathode gas diffusion layer.

Fig. 4.3 Schematic of Half MEAs with LE layer

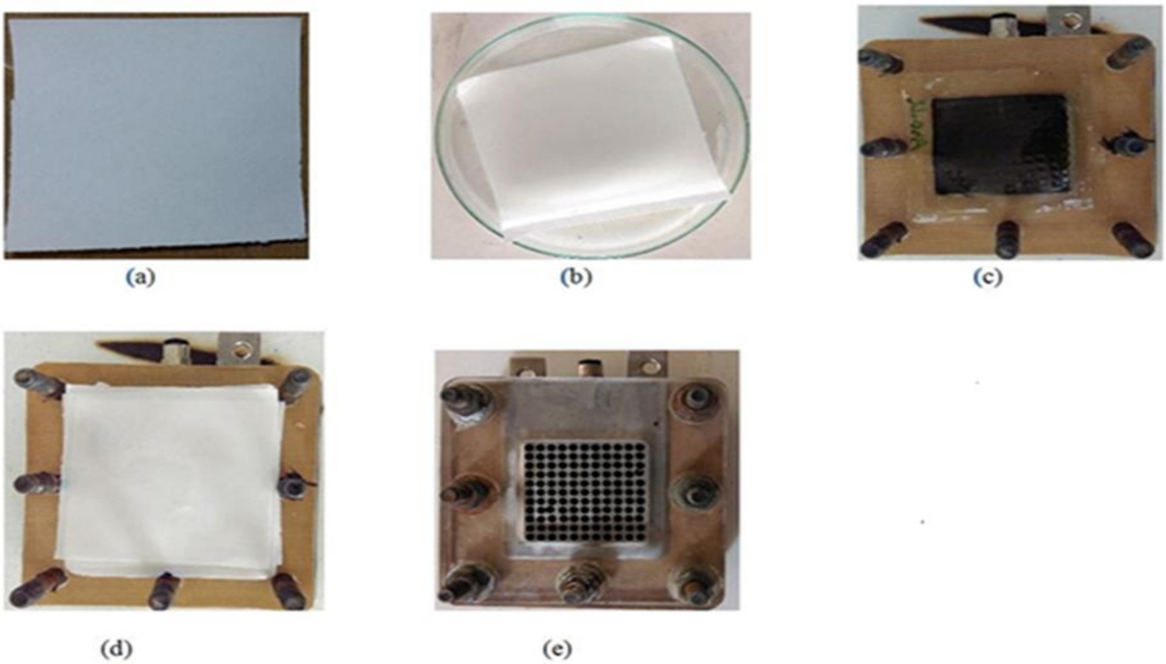
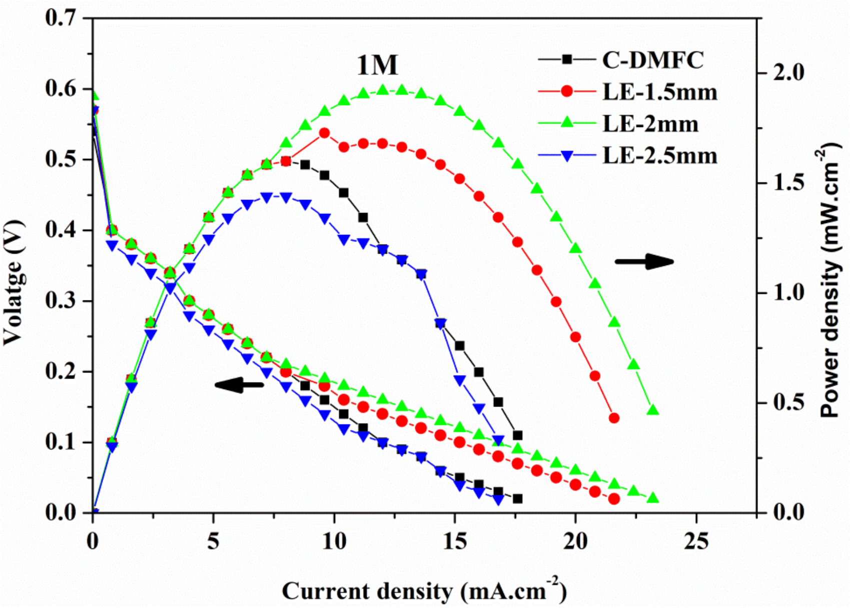


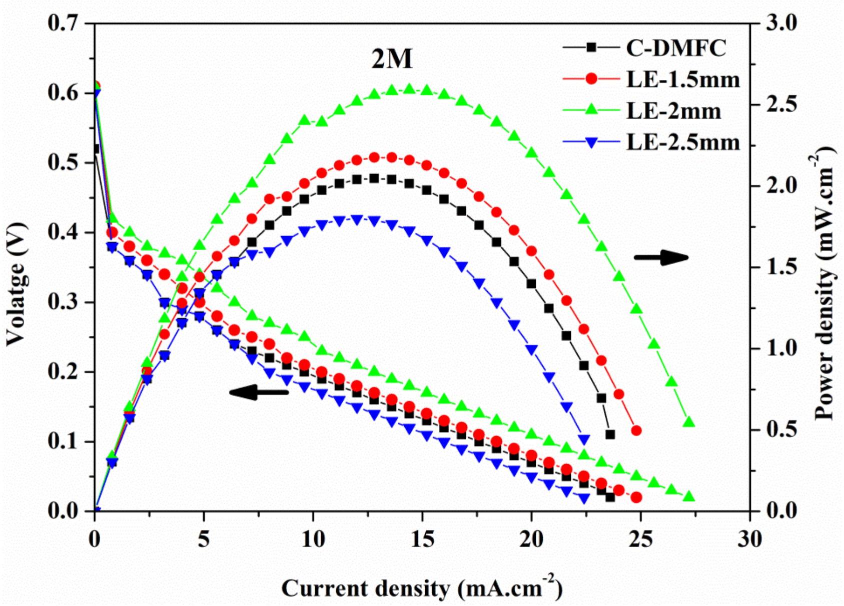
Fig.4.4 Assembly steps of LE-passive DMFC (a) Hydrophilic filter paper. (b) Hydrophilic filter paper soaking in diluted H_2SO_4 solution (c) Cell with anode half MEA (d) Piled filter papers placed over half MEA (e) Complete assembly of cell with the liquid electrolyte layer sandwiched between the two half MEAs.

The influence of the Liquid Electrolyte (LE) layer thickness on the performance of the passive DMFC is experimentally investigated. Tests were conducted on a passive DMFC by varying the liquid electrolyte layer thickness from 1.5 mm to 2.5 mm (1.5 mm, 2.0 mm and 2.5 mm), and the methanol concentration was varied from 1M to 12M. In all these experiments, diliuted sulfuric acid of 1M concentration was used as the liquid electrolyte material. Having established in the previous section that the performance of the conventional passive DMFC deteriorates beyond 5M methanol concentration, comparison was made between the Conventional passive DMFC and the LE-DMFC upto 5M methanol concentration only. However, to evaluate the performance of the LE-DMFC and to identify the optimum liquid electrolyte layer thickness and methanol concentration, experiments were conductd on the LE-DMFC upto 12M methanol concentration. These results are discussed in the following sections.

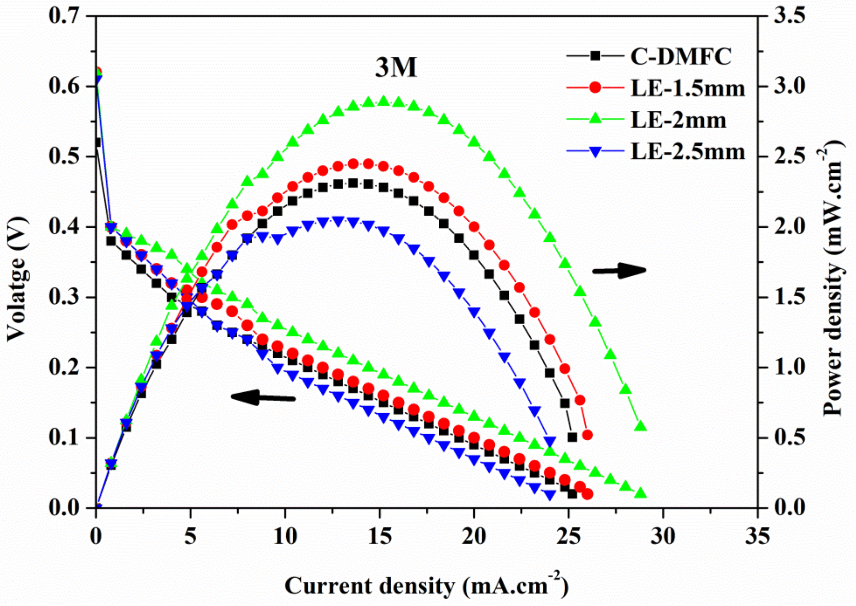
4.3 Effect of the Liquid electrolyte layer thickness



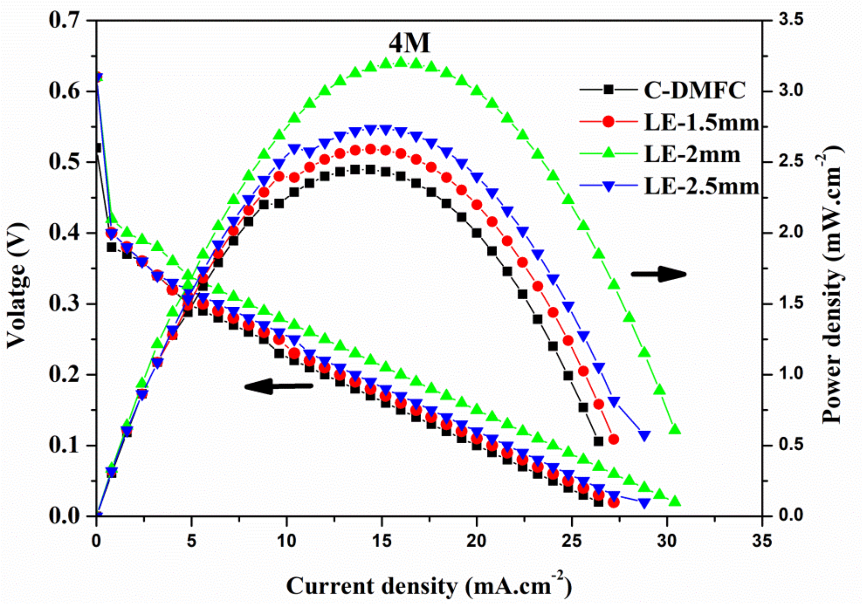
(a)



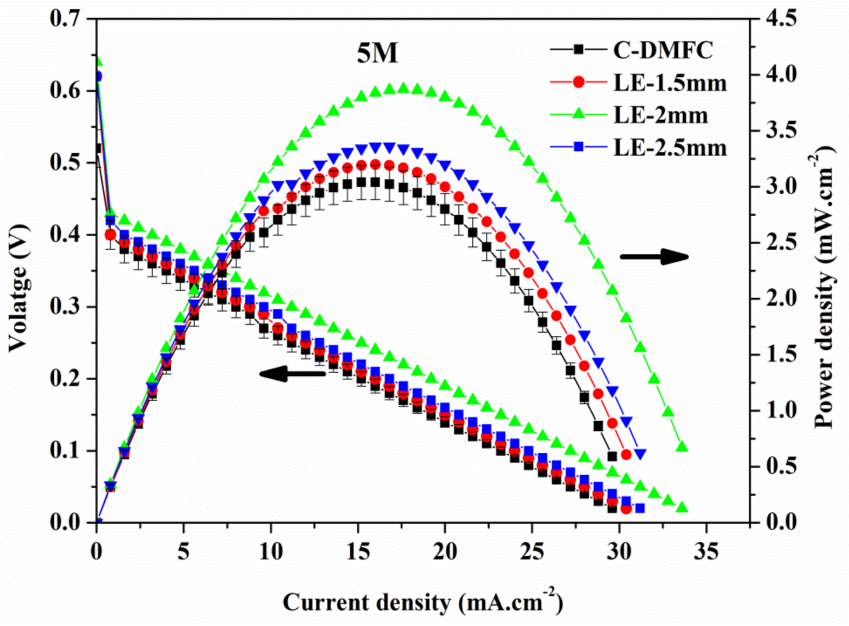
(b)


3M
C-DMFC
LE-1.5mm
LE-2mm
LE-2.5mm
Volatge (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
5
10
15
20
25
30
35

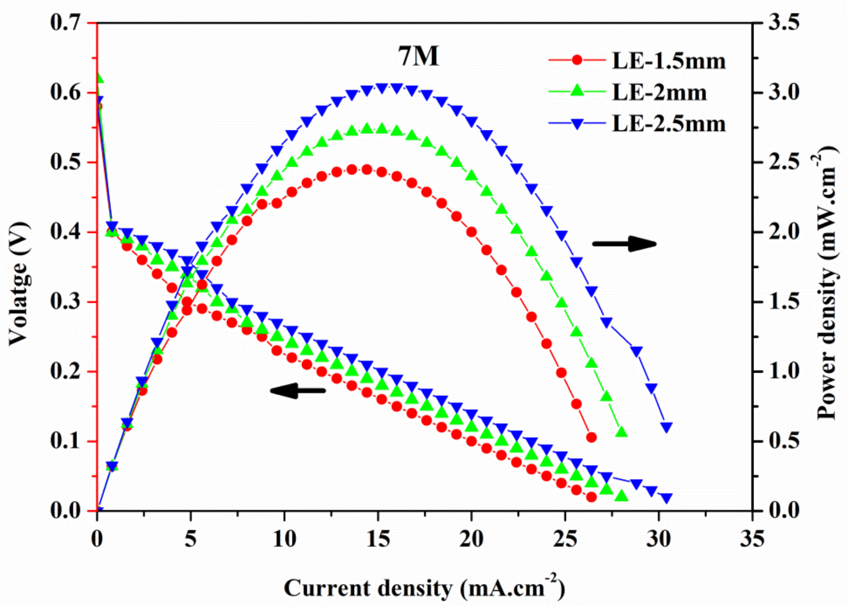
(c)


4M
C-DMFC
LE-1.5mm
LE-2mm
LE-2.5mm
Volatge (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
5
10
15
20
25
30
35

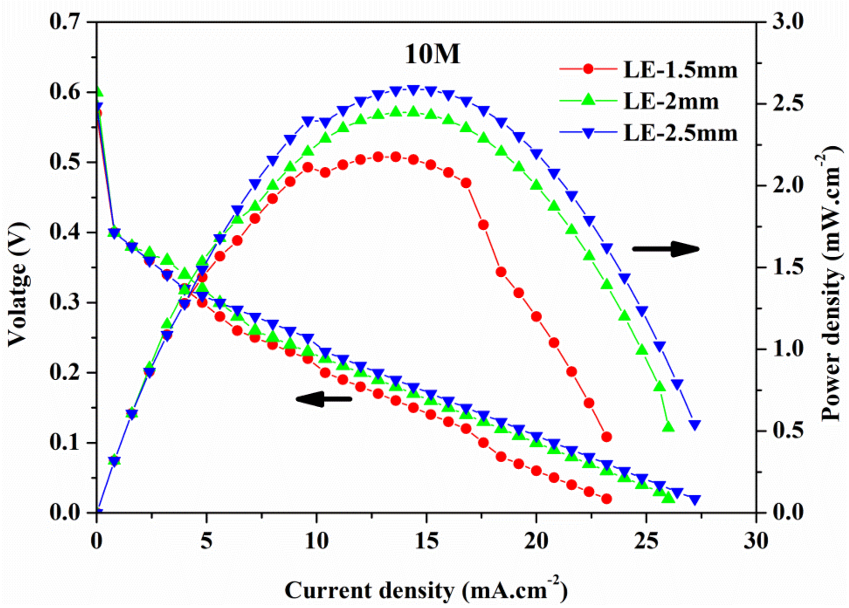
(d)


5M
C-DMFC
LE-1.5mm
LE-2mm
LE-2.5mm
Volatge (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
0
5
10
15
20
25
30
35

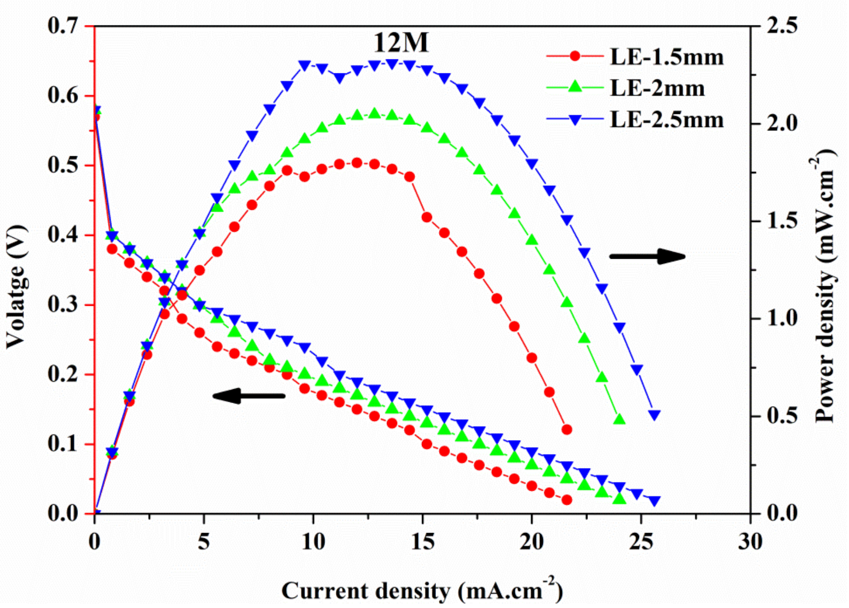
(e)


7M
LE-1.5mm
LE-2mm
LE-2.5mm
Volatge (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
5
10
15
20
25
30
35

(f)



(g)



(h)

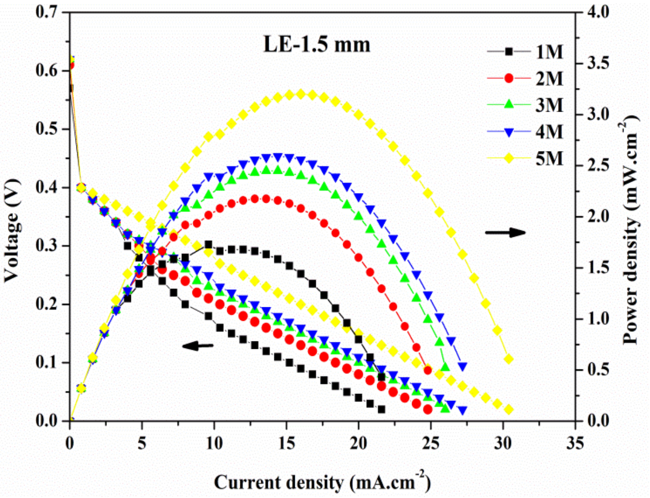
Fig.4.5 (a-h).Comparison of the performance of LE-DMFC with different liquid electrolyte layer thicknesses (1.5mm, 2mm and 2.5mm) for different methanol concentrations(1M to 12M)

Fig.4.5 (a-e) show the comparision of the performance of a conventional DMFC and LE-DMFC. It can be observed from Fig.4.5 (a) that for methanol concentration of 1M, there is no significant effect of the LE layer thickness on the cell performance at lower current densities. For 1M methanol concentration, the cell performance with any LE layer thickness is almost the same as that of the C-DMFC, i.e., without the LE layer. However, as the methanol concentration is increased from 1M to 5M, the influence of LE layer is reflected even at lower current densities also, as seen in Fig.4.5 (b-e). It can be observed that the cell performance improved by introducing the LE layer. The introduction of the LE layer reduced the methanol crossover and hence results in improved cell performance. However, the optimum LE layer thickness, which gives the best cell performance is not unique for all the methanol concentrations. It can be observed from Figs. 4.5 (a-c) that for methanol concentrations of 1M to 3M, the LE layer of 2 mm thickmess gives the best cell performance and, in the decreasing order of cell performance are LE-2.5mm DMFC, C-DMFC, LE-1.5mm DMFC and LE-2mm DMFC. As the concentration is increased from 3M to 5M, as can be seen from Fig.4.5 (d-e), the same LE-2mm DMFC gives the best cell performance, but the 2.5mm thick LE layer DMFC performance has also improved and, in the decreasing order of cell performance are LE-2mm DMFC, LE-2.5mm DMFC, LE-1.5mm DMFC and the C-DMFC. Thus, it can be observed that in the range of 1M to 5M methanol concentrations, the LE-2mm DMFC gives the best cell performance. It can also be seen that in the range of 1M to 5M methanol concentrations, the DMFC with higher LE layer thickness of 2.5mm is not giving the best cell performance. This can be explained as follows.

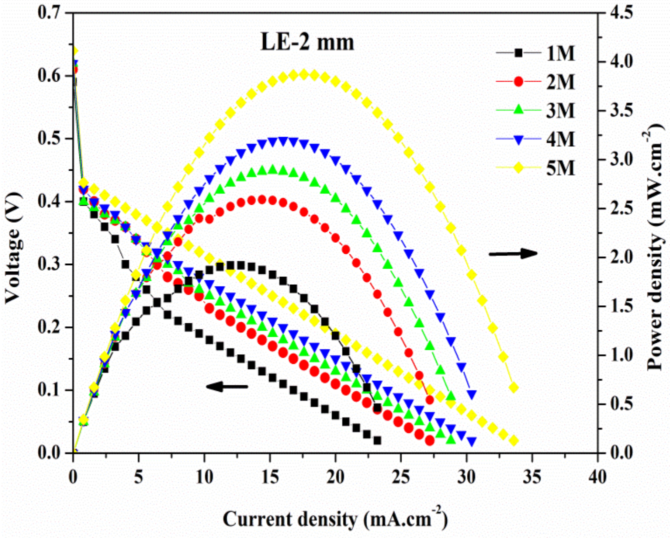
The introduction of LE layer in the cell no doubt decreases the methanol crossover [10], but increases the ohmic resistance of the cell also. The thickness of the LE layer determines the proportions of these two effects. The cell performance depends on the cumulative effect of the decrease in the methanol crossover and the increase in the ohmic resistance due to the introduction of the LE layer. Thus, at lower methanol concentrations of 1M to 5M, 2mm is the optimum LE layer thickness, which gives the best cell performance, as seen in Fig.4.5 (a-e).

As the methanol concentration is increased from 7M to 12M, 2.5mm LE layer gives the best cell performance as seen in Figs.4.5 (f-h). In the decreasing order of cell performance are LE-2.5mm DMFC, LE-2mm DMFC and LE-1.5mm DMFC. As the methanol concentration increases, the potential for MCO from the anode to the cathode increases. The introduction of the liquid electrolyte layer retards this methanol crossover, and thicker LE layer would perform better in this regard. Eventhough the introduction of a thicker LE layer causes greater ohmic resistance, the effect of decrease in the methanol crossover dominates. Hence, in the range of 7M to 12M methanol concentrations, 2.5 mm thick LE layer gave better performance compared to the 2 mm and 1.5 mm thick LE-DMFC. Thus, at lower methanol concentrations 1M to 5M, 2 mm thick LE layer gave the best cell performance, while at higher methanol concentrations of 7M to 12M, 2.5 mm thickness LE layer gave the best cell performance.

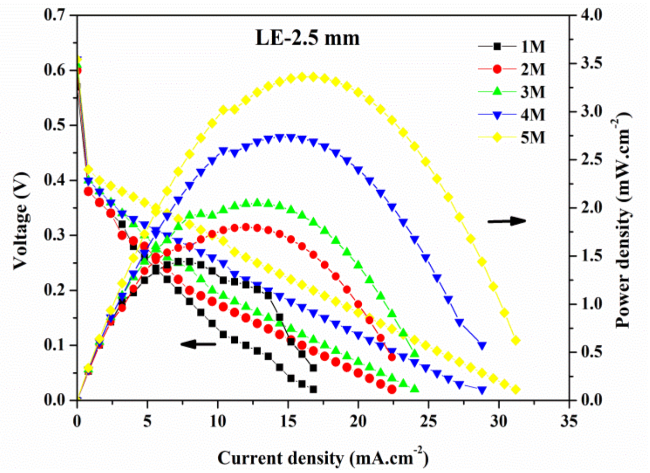
The variation of the peak power density and the maximum current density with respect to methanol concentrations for different LE layer thicknesses are shown in Figs.4.7 and 4.8. In the range of 1M to 5M methanol concentrations, 2 mm thick LE layer gives the best cell performance with a minimum increment of 20% to a maximum increase of 31.71% in the peak power density as compared with the C-DMFC. Similarly, the maximum current density also increases with a minimum of 13.51%to a maximum of 31.81% as compared to the C-DMFC.



(a)



(b)



(c)

Fig.4.6 (a-c) Polarization curves of LE-DMFC with different thickness of 1.5 mm,2 mm and 2.5 mm.

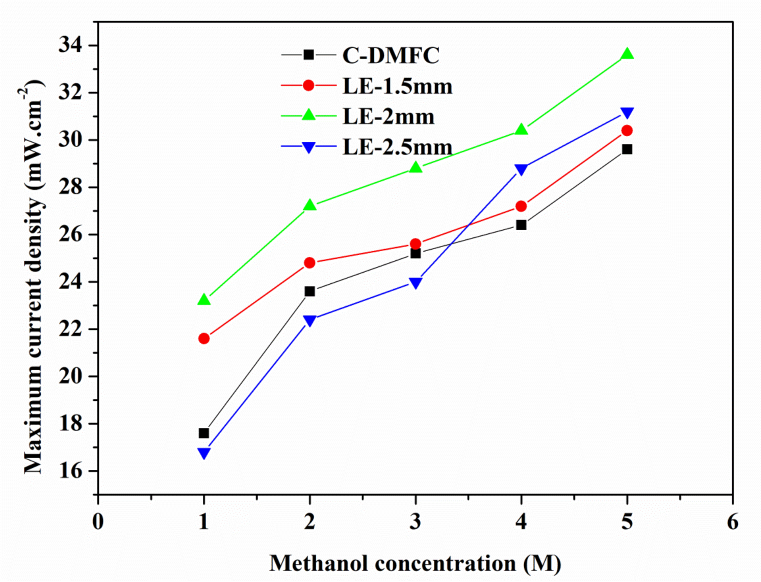


Fig.4.7 Variation of maximum current density with respect to methanol concentrations from 1M to 5M of C-DMFC and LE-DMFC

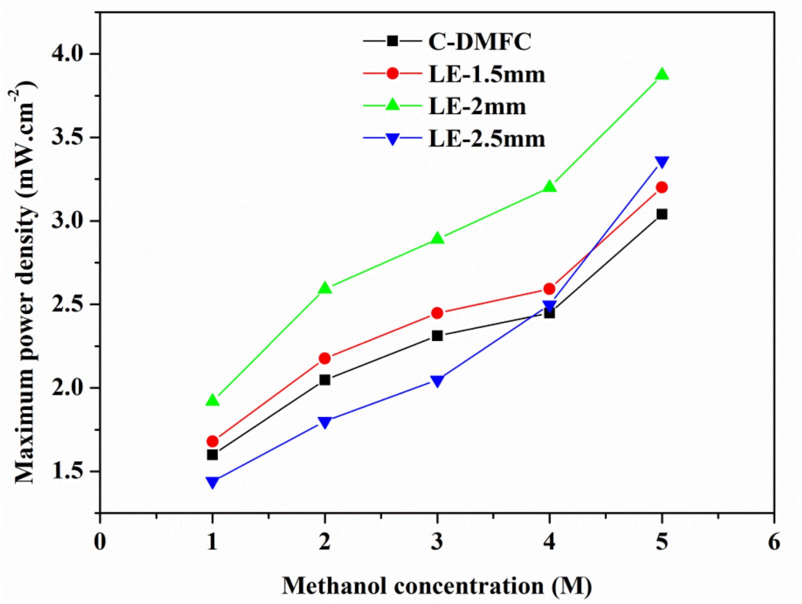


Fig.4.8Variation of maximum power density with respect to methanol concentrations from 1M to 5M of conventional and LE-DMFC

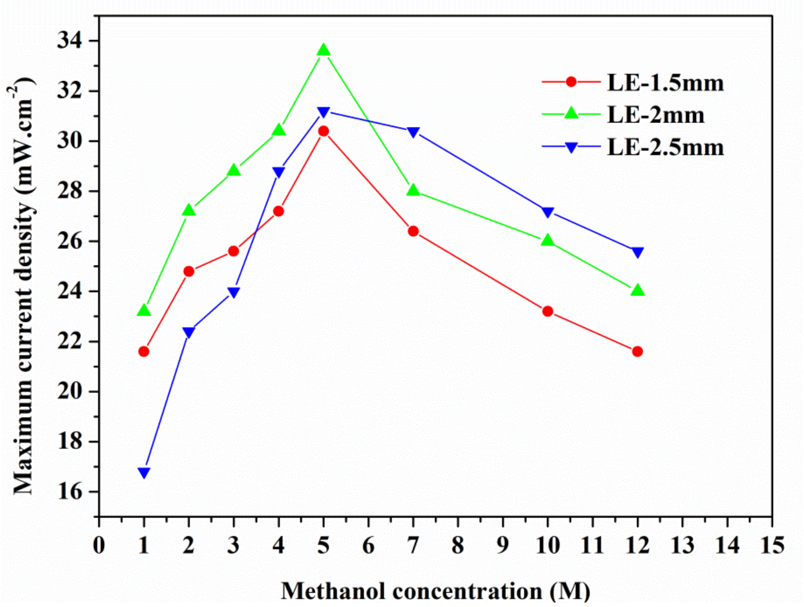


Fig.4.9 Variation of maximum current density with respect to different methanol concentrations from 1M to 12M of LE-DMFC

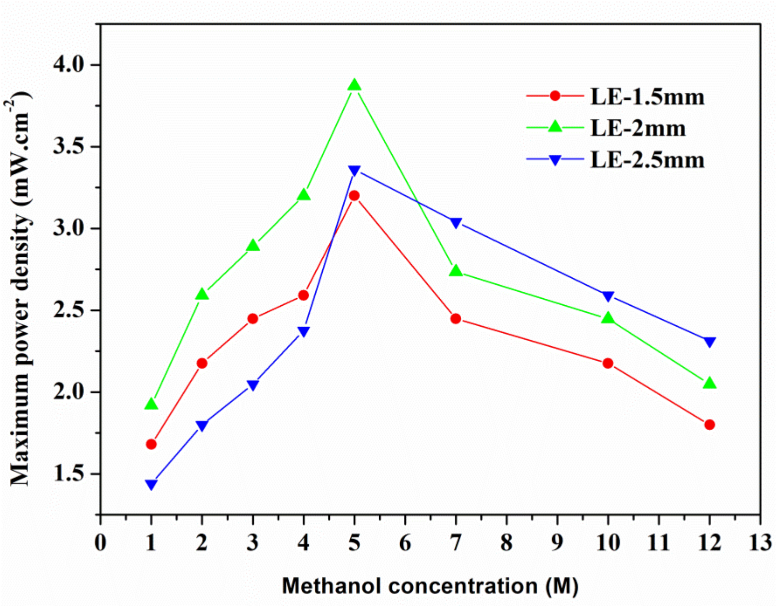


Fig.4.10 Variation of maximum power density with respect to methanol concentrations of 1M to 12M for LE-DMFC

Figs.4.9 and 4.10 show the variation of MPD and MCD in the entire range of methanol concentrations from 1M to 12M for different LE layer thickesses. It can be seen that at methanol concentration beyond 5M, the performance of all the LE-DMFC cells detoriate with a dropping slope. Among the three LE layers of 1.5 mm,2 mm and 2.5 mm thicknesses, LE-2.5 mm DMFC gives better cell performance in the range from 5M to 12M of methanol concentrattion. It is kown that the change in the performance of the C-DMFC with the introduction of LE layer is due to the Grothus mechanism. Because of the Grothus mechanism, water and methanol crossover components of electro-osmotic drag(EOD) in the LE layer decrease. However, increase in the LE layer thickness restics the flow of protons through the membrane i.e, ohmic resistance increases. It can be observed from the figures that in the entire range of 1M to 12M methanol concentrations, and among the three different LE layers of 1.5mm, 2.0 mm and 2.5mm, the 2mm thick LE layer gives the best cell performance at a methanol concentration of 5M. Corresponding to this best performance, the maximum current density is 33.6 mA.cm^{-2}, which is a 13.51% improvement compared to C-DMFC. Similarly, the maximum power density is 3.872 mW cm^{-2}, which is a 30.71% increment as compared to C-DMFC.

4.3.1 Summary

In the present work the influence of LE layer thickness on the performance of liquid feed passive DMFC was studied for various inlet methanol concentrations (varied from 1M to 12M). Three different LE layer thicknesses of 1.5mm, 2mm and 2.5mm were considered. The results of this study revealed that the LE layer thickness has a significant effect on the cell performance. The following major conclusions are drawn from the experimental results:

- Methanol concentration has a significant influence on the performance of conventional passive DMFC. As the methanol concentration is increased from 1M to 5M, the cell performance increased to a peak value, and with further increase in the methanol concentration to 6M, the cell performance studied. The MPD and MCD of the conventional passive DMFC at 5M methanol concentration are 3.04 mW cm^{-2} and 29.6 mA cm^{-2} respectively.
- From the experimental results, it is observed that a modified MEA with incorporation of the liquid electrolyte layer has significant effect on the cell performance. However, the optimum LE layer thickness is not unique for all the methanol concentrations. In the range of 1M to 5M methanol concentrations, 2mm thick LE layer gave the best cell performance, while in the range of 7M to 12M methanol concentration, 2.5mm thick LE layer gave the best cell performance.
- For any LE-DMFC (for all the thicknesses of 1.5mm, 2mm and 2.5mm) the cell performance improved with increase in the methanol concentration, reached a maximum at 5M methanol concentration and then deteriorated with further increase in the methanol concentration.
- In the entire range of experimentation covering methanol concentrations of 1M to 12M and among the three LE layer thicknesses of 1.5mm, 2mm and 2.5mm, the LE-DMFC with 2 mm thick layer gave the best performance at 5M methanol concentration. The corresponding MPD and MCD are 3.872 mW.cm^{-2} and 33.6 mA.cm^{-2}, which are around 30.71% and 13.51% greater than the corresponding C-DMFC values respectively.

Chapter 5

To enhance the performance of a passive DMFC by incorporation of different catalyst supports (carbon and carbon black) on the basis of anode side reaction kinetics

The performance of the passive DMFC is strongly affected by methanol crossover. MCO can be reduced by effective utilization of methanol on the anode side, and simultaneously retarding the flow of methanol from the anode to cathode side. It is learnt from the literature that the activation losses and methanol crossover can be reduced by selecting a suitable anode catalyst supports for enhancing the electro-catalyst activity. The present experimental work focussed on carbon and carbon black catalyst supports on the anode side with the aim of increasing the reaction rate and therby reducing the methanol crossover. Experiments were conducted to evaluate the performance of a conventional passive DMFC and LE-DMFC by incorporating a two layer catalyst of Pt-Ru/black (inner layer) and Pt-Ru/C (outer layer) on the anode side. The results of these experiments are presented in this chapter.

5.1 Fabrication of the Anode catalyst supports

Fabrication of the conventional Membrane Electrode Assembly (MEA) was already discusssed in sec.3.2.2. It was felt that the MCO can be considerably reduced by replacing the single layer anode catalyst with a two layer catlyst. In this two-layer catalyst, the first layer was coated with Pt-Ru/black catalyst on the diffusion layer with a loading of 2.5 mg.cm^{-2} and the second layer was coated with Pt-Ru/C catalyst layer with a loading of 1.5 mg.cm^{-2}. A schematic of the two layer catalyst is shown in Fig.5.1. After the first and second stages, the layers were hot pressed at a temperature of 135 ^{0}C and pressure of 8 MPa. Experiments were conducted to compare the effect of this two layer anode catalyst support with the single layer anode catalyst. Experiments were conducted on the C-DMFC and the LE-DMFC using both the single layer as well as the two layer anode catalyst supports. In all these four sets of experiments, the cathode catalyst was the same, i.e., Pt/C (60%) with a loading of 2 mg.cm^{-2}. The details of these four sets of MEAs are given in Table 5.1. For the MEA-1, only one layer of Pt-Ru/C, conventional anode catalyst was used, MEA-2 based anode catalyst has two layers of catalyst supports i.e., Pt-Ru/black (inner layer) and Pt-Ru/C (outer layer), MEA-3 and MEA-4 are same as the MEA-1 and MEA-2 respectively, but liquid electrolyte layer is incorporated in between the two half MEAs (i.e., LE-DMFC). Piled hydrophilic filter papers were soaked in an acidic nature electrolyte (1M dilute sulfuric acid) soltion.These soaked filter papers were placed between the two half MEAs and then assembled. The pile of soaked filter papers is named as the Liquid Electrolyte (LE) layer. A 2 mm thick liquid electrolyte (LE) layer was considered in the present experiments. In each one of these four sets experiments were conducted by varying the methanol concentration also. With the C-DMFC, i.e., MEA-1 and MEA-2 incorporated cells; the methanol concentration was varied from 1M to 5M. For the LE-DMFC, i.e., MEA-3 and MEA-4 incorporated cells; the methanol concentration was varied from 1M to 12M. A perforated current collector with an open ratio of 45.40% was used for all these four sets of experiments. Experiments were also conducted to evaluate the long term operation of the passive DMFC for these four MEAs at 5M of methanol concentration. The results of all these experiments are discussed in the following sections.

Table.5.1 Constructional details of different MEAs

Type of MEA	**Anode catalyst**	**Cathode catalyst**
MEA-1(one layer each on the anode side and cathode side)	Pt-Ru/C (60 %) catalyst with a loading of 4 mg.cm^{-2} on anode side	Pt/C (60%) with a 2 mg.cm^{-2} cathode side.
MEA-2 (Two layers on the anode side and one layer on the cathode side)	Pt-Ru/black (60%) catalyst with a loading of 2.5 mg.cm^{-2} and Pt-Ru/C (60%) with a loading of 1.5 mg.cm^{-2} on anode side.	
MEA-3 (One layer of catalyst along with LE)	Pt-Ru/C (60 %) catalyst with a loading of 4 mg.cm^{-2} on anode side with addition of LE layer	
MEA-4(Two layers of catalyst along with LE)	Pt-Ru/black (60%) catalyst with a loading of 2.5 mg.cm^{-2} and Pt-Ru/C (60%) with a loading of 1.5 mg.cm^{-2} on anode side with addition of LE layer.	

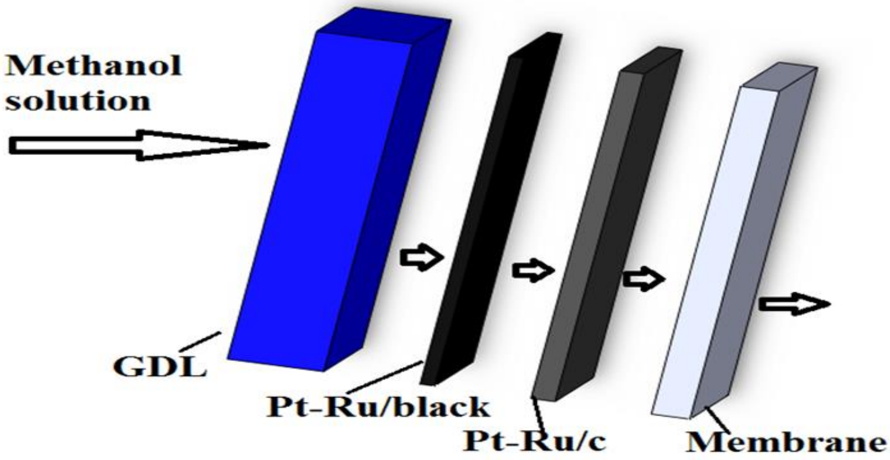
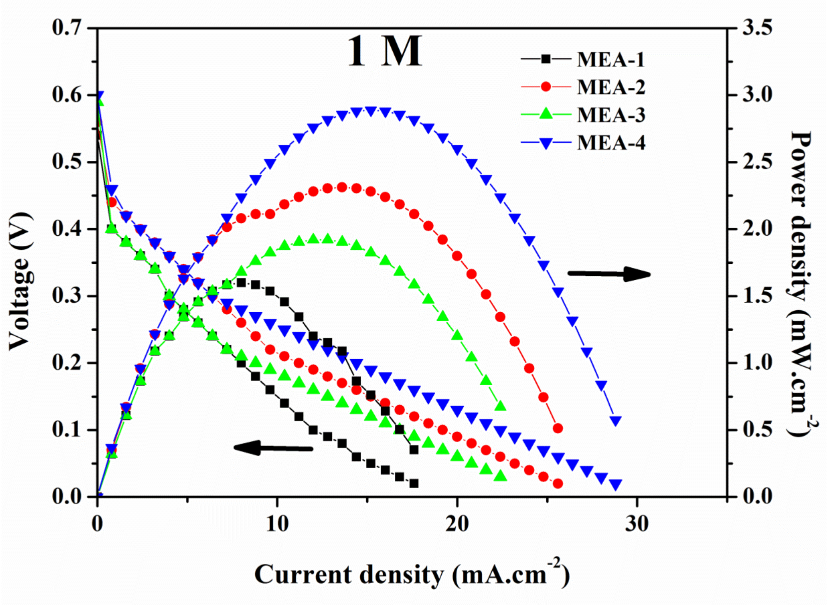
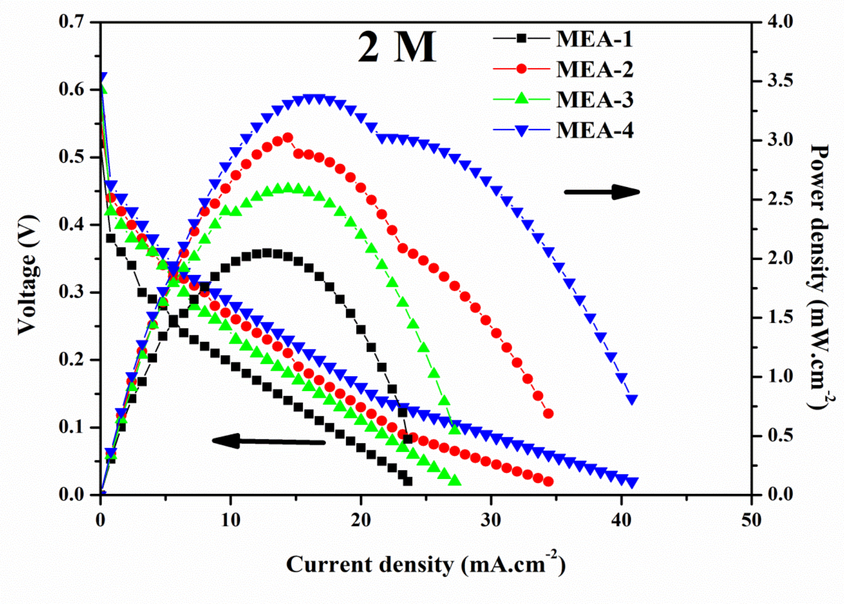


Fig.5.1 Schematic of the anode side half MEA-2.

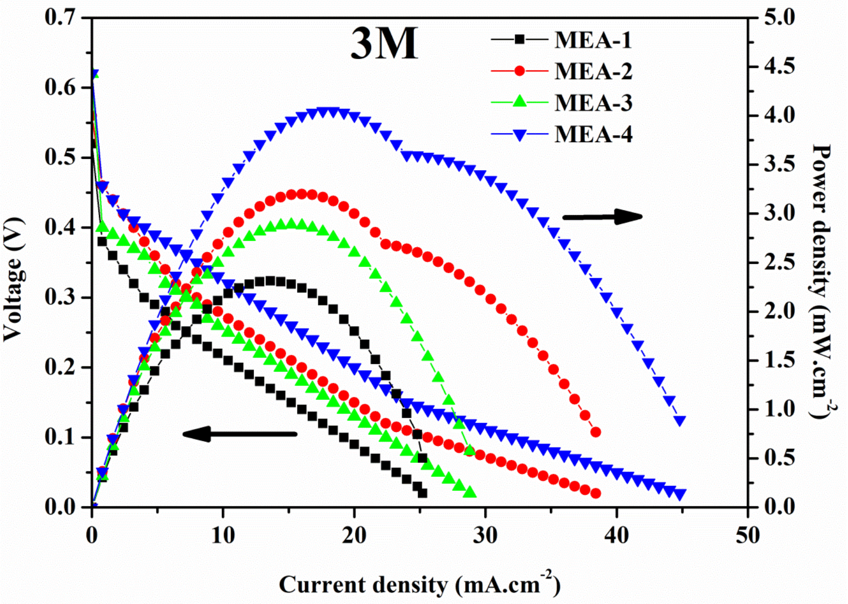
5.2 Effect of the anode catalyst supports on the performance of a passive DMFC



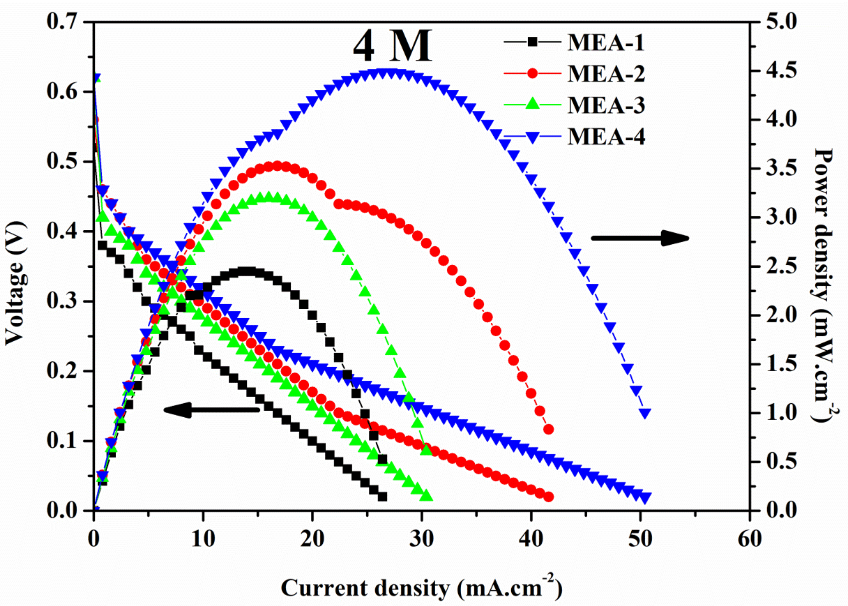
(a)


2 M
MEA-1
MEA-2
MEA-3
MEA-4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
10
20
30
40
50

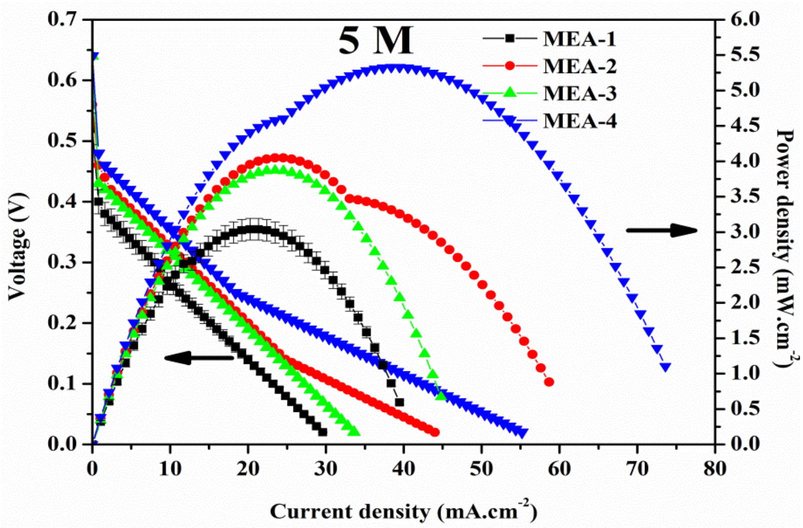
(b)


3M
MEA-1
MEA-2
MEA-3
MEA-4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
0
10
20
30
40
50

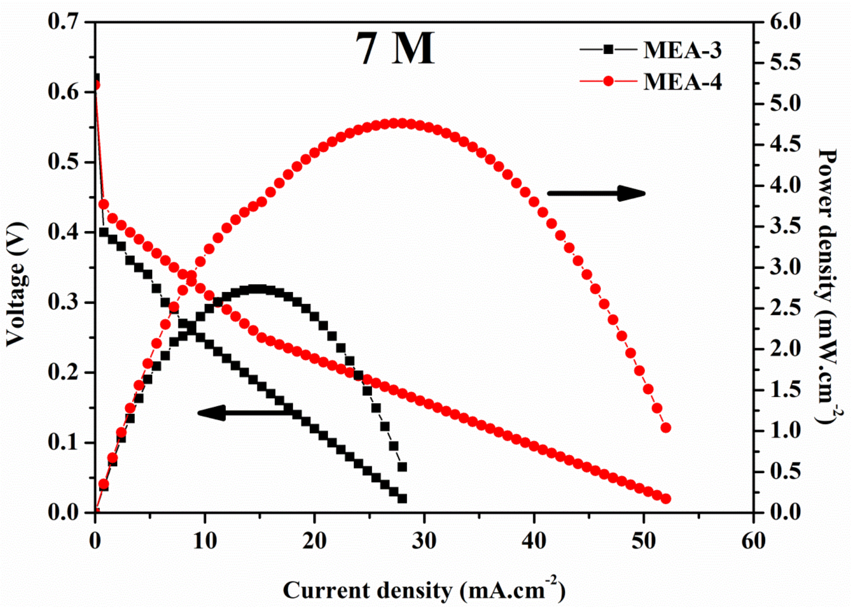
(c)


4 M
MEA-1
MEA-2
MEA-3
MEA-4
Voltage (V)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Power density (mW.cm^{-2})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Current density (mA.cm^{-2})
0
10
20
30
40
50
60

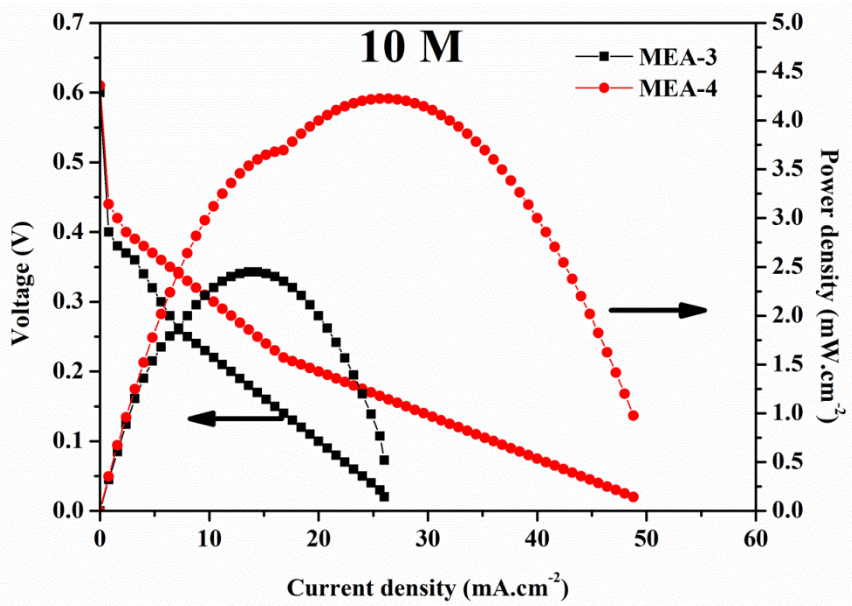
(d)


5 M
MEA-1
MEA-2
MEA-3
MEA-4
Voltage (V)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Power density (mW.cm^{-2})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
Current density (mA.cm^{-2})
0
10
20
30
40
50
60
70
80

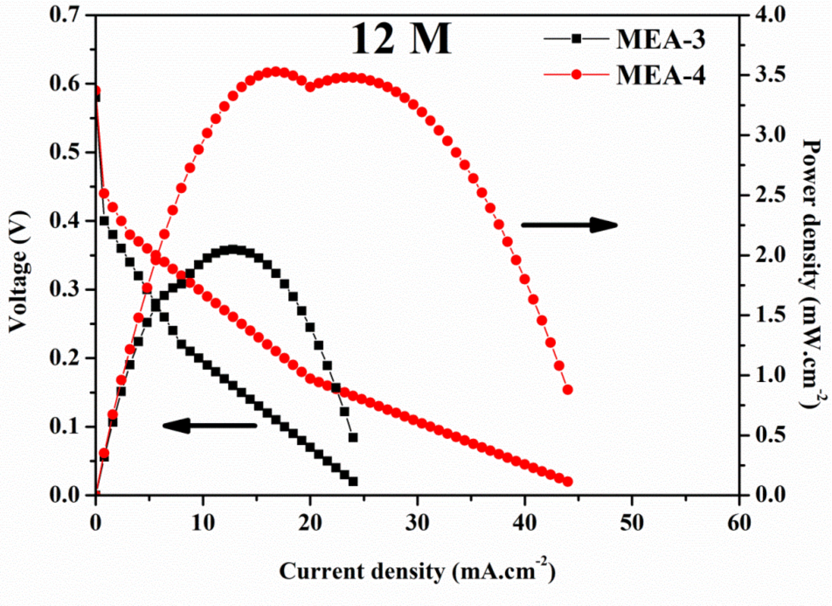
(e)


7 M
MEA-3
MEA-4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
10
20
30
40
50
60
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0

(f)


10 M
MEA-3
MEA-4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
10
20
30
40
50
60
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

(g)



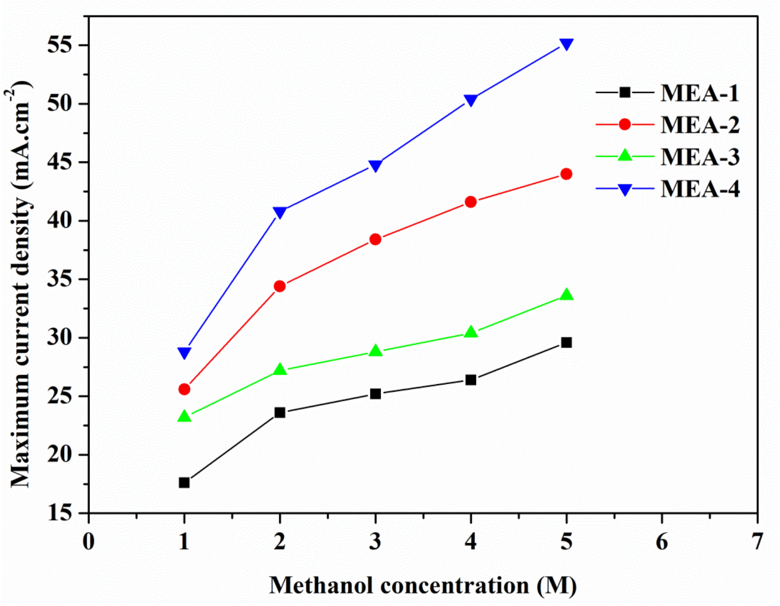
(h)

Fig.5.2 (a-h) Comparison of different catalyst supports of with and without incorporated Passive DMFC

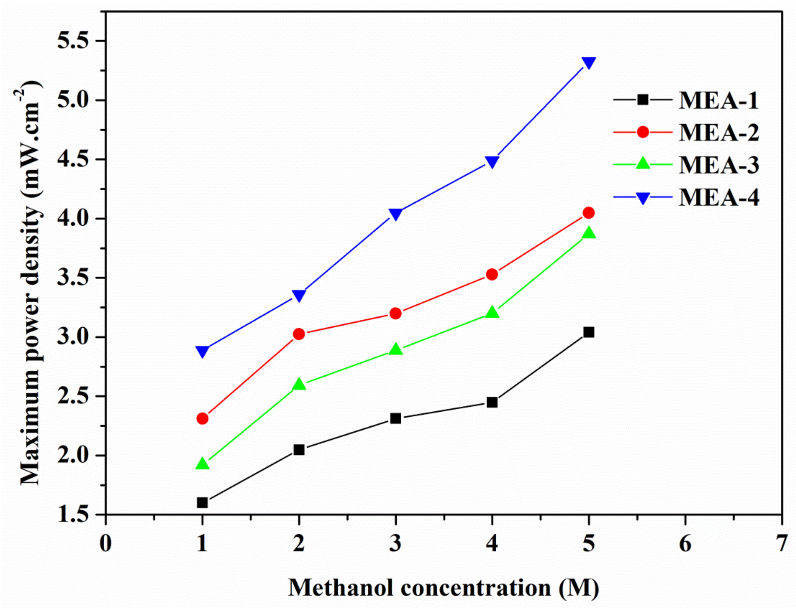
Figs. 5.2 (a-h) shows the polarization and power density curves of the passive DMFC with the four different MEAs. Methanol Crossover (MCO) is one of the major problems that adversely affects the fuel cell performance. MCO occurs due to Diffusion, electro-osmotic drag and pressure gradients mechanisms. Out of the three mechanisms, diffusion is the major contribution for MCO. It can be observed from this Figs. 5.2 (a-e) that performance of each one of these four cells is improving with increase in the methanol concentration. This is due to the reason that with increase in the methanol concentration more amount of methanol reaches the anode catalyst layer. This enables more amount of methanol being consumed on the anode side reaction

It can also be observed from the Figs. 5.2 (a-e) that any methanol concentration, the cell with MEA-4 gives the highest performance. MEA-4 has two layers of catalyst support, i.e., the Pt-Ru/black (inner layer) and Pt-Ru/C (outer layer) with LE layer inserted in between two half MEAs. Initially, the diluted methanol solution enters the Pt-Ru/black catalyst layer through the diffusion layer. Here, faster reaction of the methanol solution takes place because Pt-Ru/black has higher electrochemical surface activity. In this first layer, more amount of methanol fuel is consumed and the remaining methanol solution reaches the second layer of conventional Pt-Ru/C catalyst layer. Here some reaction takes place and some more methanol will be consumed. Added to this since this MEA-4 is having the LE layer, the methanol cross over will be retarded. The cumulative effect is the cell with MEA-4 is giving the highest performance. On the other hand MEA-1 based cell is giving the lowest performance. The MEA-1 based cell has only one layer of anode catalyst of Pt-Ru/C and without the LE layer. The Pt-Ru/C layer has lower electrochemical activity compared to Pt-Ru/black catalyst. Thickness of the Pt-Ru/black catalyst is lower than Pt-Ru/C catalyst and porosity is higher than conventional catalyst (Pt-Ru/C). The Pt-Ru/black catalyst increases the poisoning tolerance and stability of the catalyst. Single layer of Pt-Ru/black catalyst layer on the anode side increases the tendency of the MCO due to lower thickness and higher porosity of the catalyst. Finally, the passive DMFC performance increment is due to the enhanced reaction kinetics and reduction of MCO with the help of two layer catalyst and LE layer. The MPD and MCD is produced by the cell at 5M of methanol concentration when the MEA-4 is incorporated. It can also be observed from the figures that in the decreasing order of performance of the cells with MEA-4, MEA-2, MEA-3 and MEA-1 respectively. This indicates that two layers of catalyst (MEA-2) has more positive effect on the cell performance than a single layer catalyst along with liquid electrolyte layer (MEA-3). This can be explained as the catalysts layers help in increasing the rate of reaction and thereby reducing the methanol crossover. On the other hand the liquid electrolyte layer only retards the methanol crossover.

Figs.5 (f-h) show the comparison of the performance of the LE-DMFC with a single layer of catalyst and two layers of catalyst, i.e., MEA-3 and MEA-4 respectively with the variation of methanol concentration from 7M to 12M. In the range of 7M-12M methanol concentration also, the cell with MEA-4 only gives the best performance compared to the cell with MEA-3. MEA-3 has a single layer of anode catalyst along with the LE layer in between the two half MEAs, while MEA-4 has two layers of anode catalyst along with the LE layer in between the two half MEAs. Thus it can be concluded that even in the case of LE DMFC also, the two layer catalyst is giving the best performance.

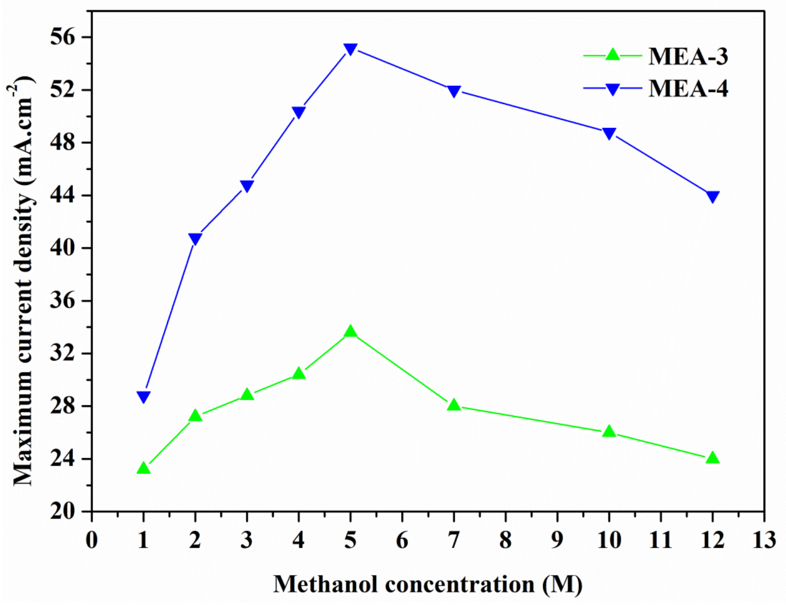


(a)

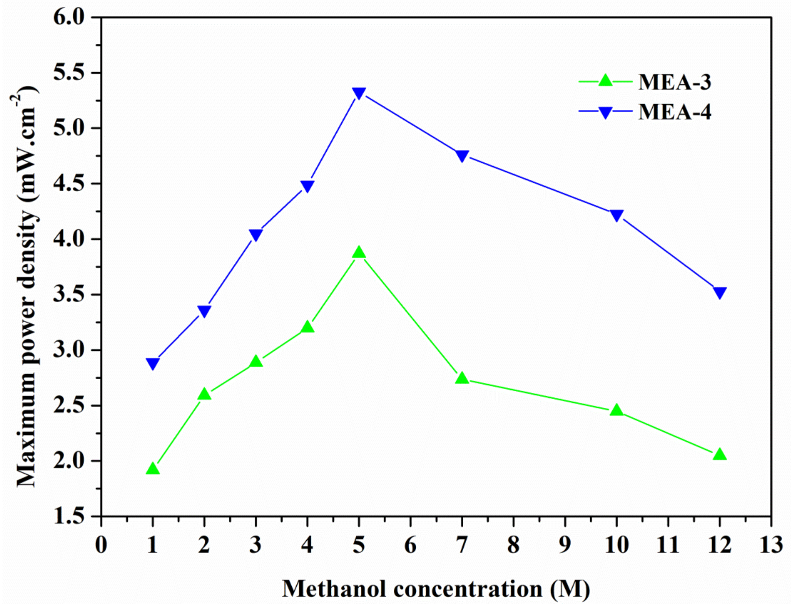


(b)

Fig.5.3 (a-b) Comparison of the maximum current density and maximum power density of the cells with four MEAs in 1M to 5M methanol concentration range.



(b)



(b)

Fig.5.4 (a-b) Comparison of the maximum current density and maximum power density of the LE-DMFC with MEA-3 and MEA-4 in 1M to 12M methanol concentration range.

Figs 5.3 (a and b) show the comparison of the MCD and the MPD for the cells with the four MEAs in the range of 1M to 5M methanol concentration. It can be observed from the figures that there is a monotonous increase in the MCD and MPD with increase in the methanol concentration for each one of the four cells and throughout this range of methanol concentration the cell with MEA4 has the highest performance.

Figs. 5.4 (a and b) show the comparison of the MCD and the MPD of the LE-DMFC with single layer and two layer anode catalyst support in the range of 1M to 12 M methanol concentration. It can be observed from the figure that throughout this range, the cell with MEA-4 gives the best performance. It can be observed that the cell performance doesn't increase monotonously with increase in the methanol concentration. Initially the cell performance increases with increase in the methanol concentration up to 5M concentration and then decreases with increase in the methanol concentration. It can also observe from the figures that the best performance is obtained at 5M methanol concentration. The highest MPD and MCD are produced at 5M of methanol concentration for the MEA-4 based fuel cell, which are 5.328 mW.cm^{-2} and 55.2 mA.cm^{-2} respectively. The lowest values of the MCD and MPD are produces by MEA-1 incorporated in the fuel cell, which are 3.04 mW.cm^{-2} and 29.6 mA.cm^{-2} respectively. The MEA-4 based fuel cell produces maximum power density and maximum current density of 75.26% and 86.48% respectively, higher than the conventional single catalyst layer fuel cell with no liquid electrolyte layer, i.e., MEA-1. The values of the MCD and MPD for the four MEAs at 5M of methanol concentration are given Table.5.2.

Table.5.2 Maximum power density and Maximum current density produced at 5M of methanol concentration.

Type of MEA	**Maximum current density (mA.cm^{-2})**	**Maximum power density (mW.cm^{-2})**
MEA-1	29.6	3.04
MEA-2	41.6	4.048
MEA-3	33.6	3.872
MEA-4	55.2	5.328

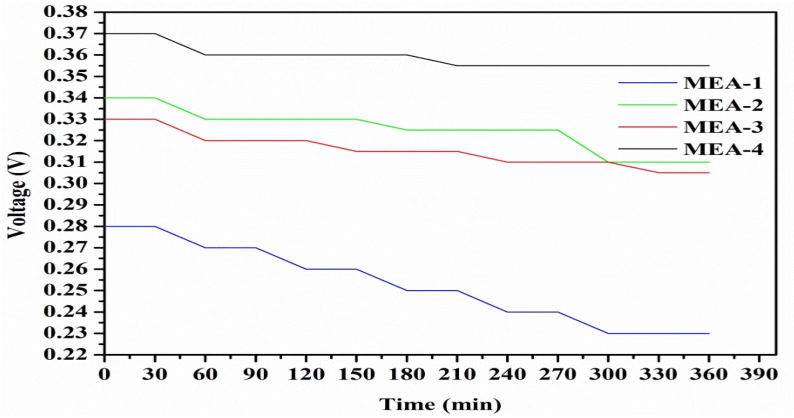


Fig.5.5 Long term operation of the passive DMFC for four different MEAs at 5M of methanol concentration.

Fig.5.5 shows the comparison of the long term operation of the fuel cells incorporated with the four MEAs at 5M of methanol concentration. In each of these cases, the cell was operated at a constant current density of 9.6 mA.cm^{-2}. It can be noticed from the figure that the higher and lower voltage stability was exhibited by the MEA-4 and MEA-1 incorporated cells respectively. Higher voltage stability of the MEA-4 is due to the reduced cathode over-potential losses. The cathode over-potential losses depend on the methanol and water crossover. The Methanol and water crossover are more for MEA-1based fuel cell. On the other hand the methanol and water crossover were considerably reduced for the MEA-4 incorporated cell, because the MEA-4 has two layers of anode catalyst and the liquid electrolyte layer in between the two half MEAs. It can also be observed from the figure that in the increasing order of the voltage stability are the MEA-1, MEA-2, MEA-3 and MEA-4 incorporated cells respectively.

5.2.2 Summary

This experimental study deals about the performance of a passive DMFC fitted with four different MEAs, i.e., with a single layer of anode catalyst and two layers of anode catalyst; with the incorporation of liquid electrolyte layer ad without the liquid electrolyte layer, viz., MEA-1, MEA-2, MEA-3 and MEA-4. Liquid electrolyte layer is incorporated in the MEA-3 and MEA-4. From the experimental results, it is observed that among the four different MEAs, the MEA-4, which has two layers of anode catalyst along with the liquid electrolyte layer, gives the best cell performance for the whole range of methanol concentration from 1M to 1M. . From the present study, the following conclusions are drawn:

- It was observed that throughout the range of methanol concentrations from 1M to 12M, the cell incorporated with MEA-4 (having two layers of anode catalyst support along with the liquid electrolyte layer) exhibited the best fuel cell performance. The lowest performance was obtained for the conventional fuel cell which incorporated MEA-1 (a single layer of anode catalyst and no liquid electrolyte layer). It was attributed that the highest performance of the cell with MEA-4 was due to the enhanced reaction kinetics and reduced methanol crossover.
- It was also observed the best performance was obtained at 5M methanol concentration for all the cells.
- The maximum current density and maximum power density produced by MEA-4 based fuel cell are 5.328 mW.cm^{-2} and 55.2 mA.cm^{-2} at 5M of methanol concentration

respectively. These are 75.26% and 86.48% higher than conventional based fuel cell of MEA-1 at 5M of methanol concentration.

- It was also observed that in the decreasing order of performance are the cells with MEA-4, MEA-2, MEA-3 and MEA-1 respectively. This indicates that two layers of catalyst (MEA-2) has more positive effect on the cell performance than a single layer catalyst along with liquid electrolyte layer (MEA-3). This can be explained that as the catalysts layers help in increasing the rate of reaction and thereby reducing the methanol crossover. On the other hand the liquid electrolyte layer only retards the methanol crossover.
- For the long term operation of fuel cell, MEA-4 incorporated fuel cell gave good voltage stability compared to other three MEAs.

Chapter 6

To study experimentally the effect of perforated current collector open ratio for enhanced performance of the passive DMFC

Design of the current collectors plays a major role in the working and performance of a passive DMFC. In the passive DMFC, the current collectors are made with different shapes of perforations such as circular, rectangular, hexagon, triangular, etc. Through the openings in the current collectors, the reactants flow from the end plates to the reaction area i.e., the anodic fuel from the anode end plate to the membrane, and oxgen from the cathode end plate to the membrane. The elctrons produced near the anode during the reaction will be collectd near the anode current collector, and flow through the external circuit and reach the cathode current collector. From the cathode current collector, the elctrons reach the membrane and complete the reaction. Thus, the current collectors also act as current conductors. The major challenge associated with the design of the current collectors is to have an appropriate open ratio of the current collector such that the methanol crossover is reduced and a good contact between the MEA and the current collector is obtained. In the present work, the effect of the open ratio of the perforated current collector on the performance of a C-DMFC was analyzed by varying the current collector open ratio (45.40%, 55.40% and 63.05%). Experiments were also performed to evaluate the effect of incorporating a liquid electrolyte layer in the MEA on the cell performance corresponding to each one of these three current collectors. The details of these experimental studies are presented in this chapter.

6.1 Experimentation

Perforated current collectors, made of 2mm thick SS316L material were used in the present experimentation. Three perforated current collectors with open ratios of 45.40%, 55.40% and 63.05% were fabricated. The details of these current collectors are shown in Table.6.1 and Fig.6.1. The Open ratio (OR) of the current collector is defined as the ratio of the total area of the openings in the current collector to the total reactive area. These perforated current collectors were placed in between the end plates and the MEA on the anode and cathode sides.

Table.6.1 Three different open ratios of the perforated current collectors

S.no	**Diameter of the hole (mm)**	**Number of holes**	**Open ratio (%)**
1	3.80	100 (10x10)	45.40
2	2.48	225 (15x15)	55.40
3	2.47	256(16x16)	63.05

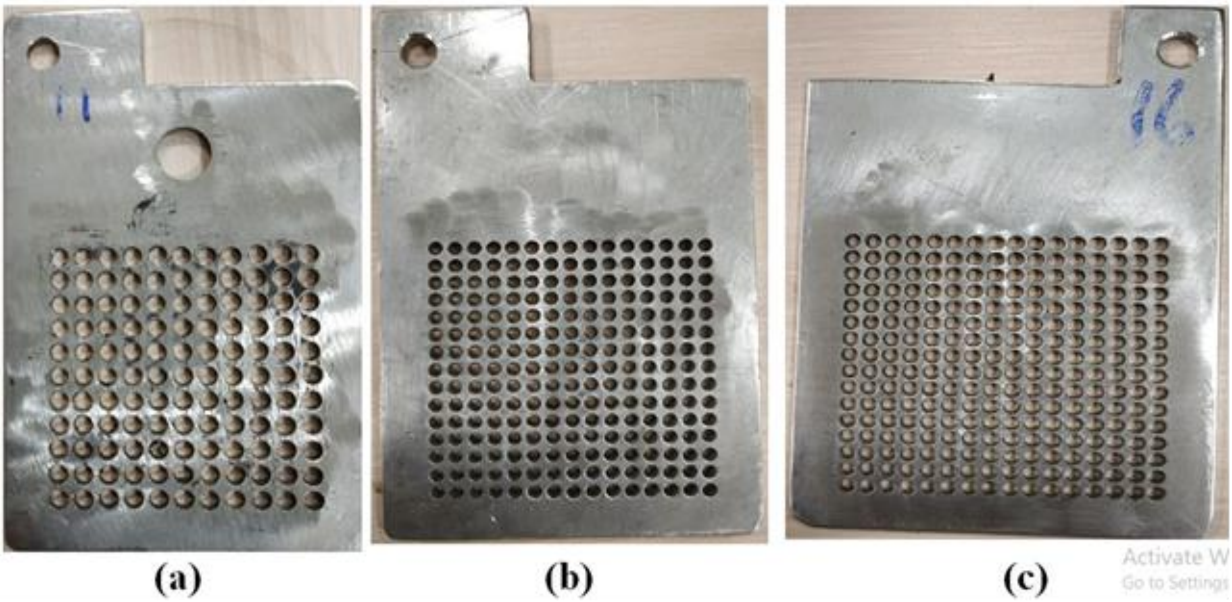

(a) (b) (c)

Fig.6.1 Current collectors with three different open ratios (a) 45.40% (b) 55.40% (c) 63.05%

Experiments were carried out to evaluate the impact of the OR of the current collector on the performance of the passive DMFC. Having established in the earlier studies that a two layer anode catalyst gives better performance, the same is used in the present experimentation also, i.e., the anode catalyst has two layers of catalyst supports i.e., Pt-Ru/black (inner layer) and Pt-Ru/C (outer layer. On the cathode side a single layer of Pt/C (60%) with a loading of 2 mg.cm^{-2} was considered. Experiments were conducted with the objectives of identifying the effect of methanol concentration for a given open ratio of the current collector, and identifying the optimum combination of open ratio for the current collector and methanol concentration to give the best fuel cell performance. Later, experiments were also conducted by incorporating a 2 mm thick liquid electrolyte layer (Piled hydrophilic filter papers soaked in 1M dilute sulfuric acid soltion) using these three current collectors. This study was extended to analyses the long term stability of the C-DMFC and LE-DMFC fitted with 45.40% current collector at 5M of methanol concentration. Finally, visualization study of the fuel cell fitted with 63.05% current collector at 5M of methanol concentration.

6.2 Effect of the current collector open ratio on the performance of C-DMFC

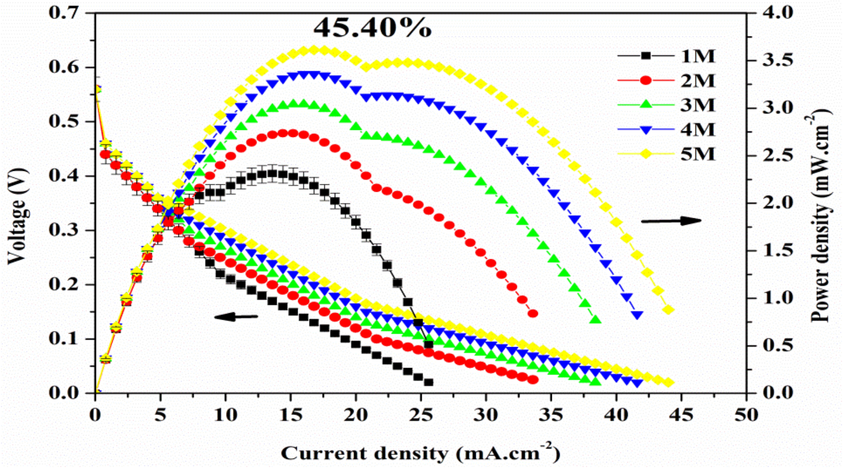


Fig.6.2 Effect of methanol concentration on the cell performance for the cell with current collector of 45.40% open ratio.

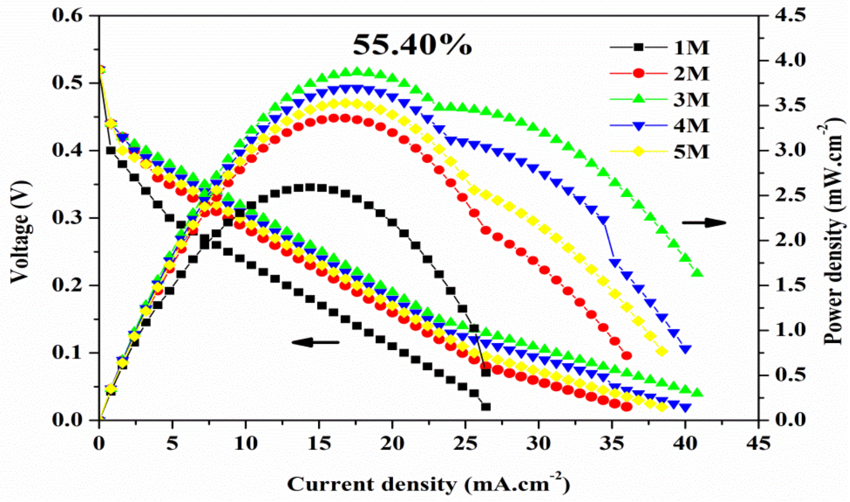


Fig.6.3 Effect of methanol concentration on the cell performance for the cell with current collector of 55.40% open ratio.

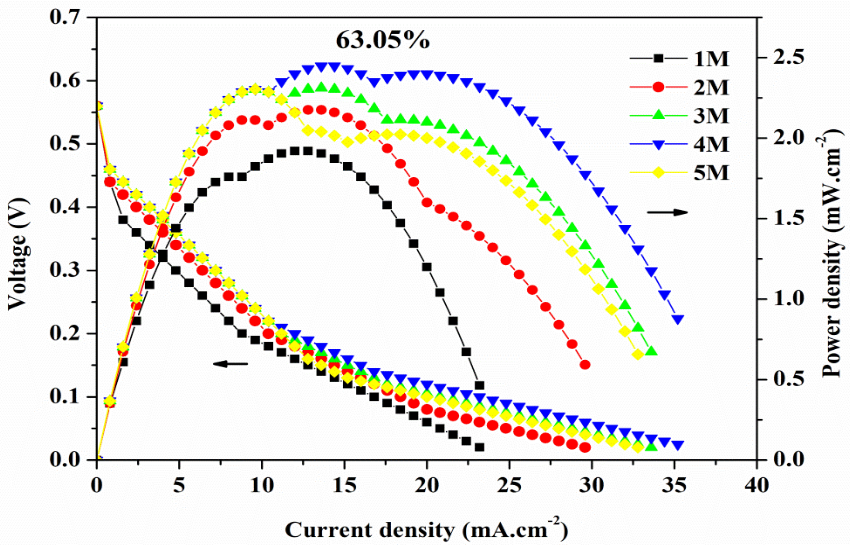
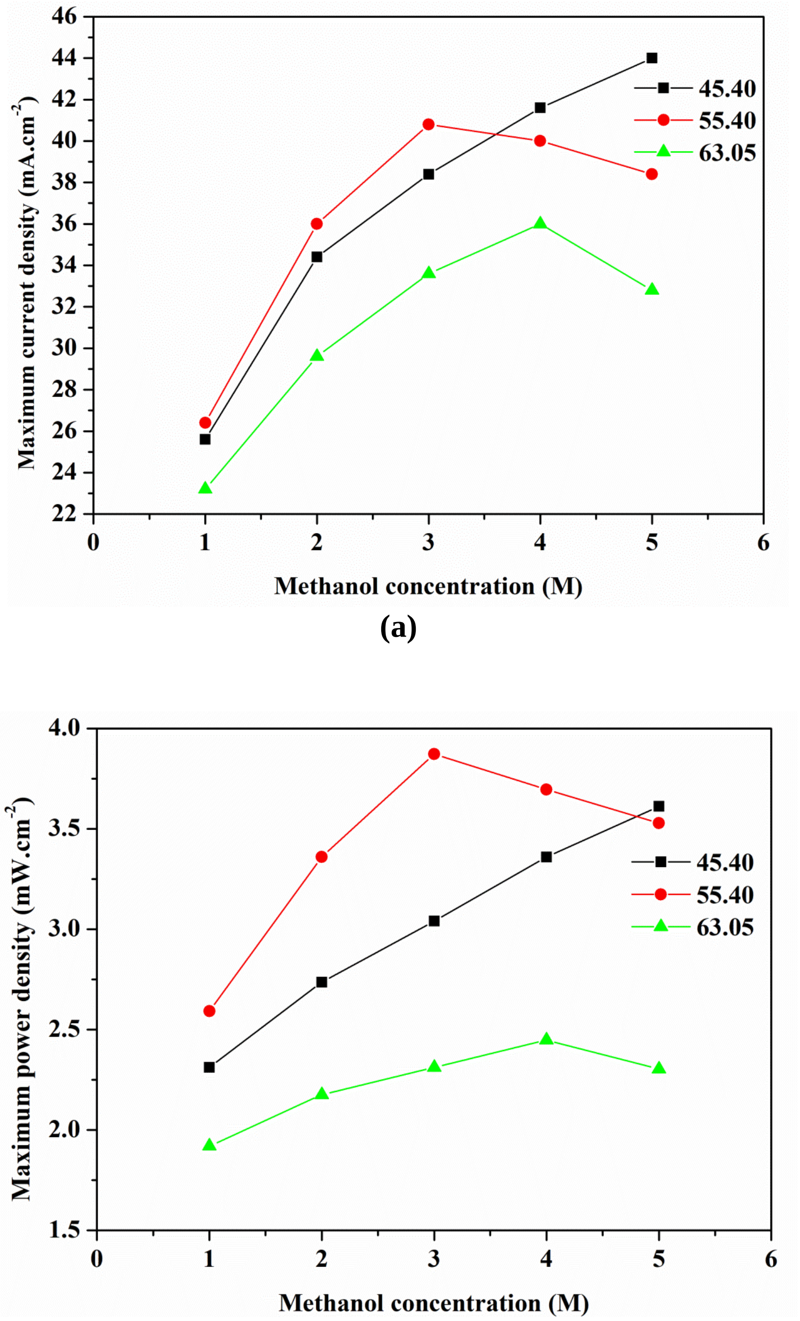


Fig.6.4 Effect of methanol concentration on the cell performance for the cell with current collector of 63.05% open ratio.

Fig. 6.2 depicts the performance characteristics of a passive DMFC using current collector of open ratio 45.40% at different methanol concentrations. It can be seen from the figure that as the methanol concentration ~~is~~ increases, the cell performance is increased. It can be observed that both the MCD and MPD of the cell increased monotonously with increase in the methanol concentration. The MPD and MCD were produced by the cell at 5M methanol concentration. The MCD and MPD of fuel cell with current collector of open ratio 45.40% are 44 mA.cm^{-2} and 3.612 mW.cm^{-2} respectively. Similarly, Figs.6.3 and 6.4 show the performance characteristics of the passive DMFC using current collectors with open ratios of 55.40% and 63.05% respectively. It can be seen from Fig. 6.3 that the effect of methanol concentration is not monotonous as in the case of the current collector with 45.40% open ratio, i.e., the cell performance does not increase continuously with increase in the methanol concentration. Initially, the cell performance improved with increase in the methanol concentration up to 3M and with further increase of methanol concentration from 3M-5M, the cell performance deteriorated. The MCD and MPD for the fuel cell with current collector of 55.40% open ratio are 40.8mA.cm^{-2}and 3.872mW.cm^{-2} respectively at 3M methanol concentration. Similarly, it can be observed from Fig. 6.4 that for the fuel cell with current collector of 63.05% open ratio, the impact of methanol concentration on the cell performance is not monotonous. Initially, the cell performance enhanced with increase in the methanol concentration from 1M-4M and then decreased with further increase in the methanol concentration from 4M to 5M.The MCD and MPD produced by the cell are 36mA.cm^{-2} and 2.448mW.cm^{-2} at 4M of methanol concentration. It can be seen that there is no uniform effect of methanol concentration on the cell performance with different current collector open ratios. The optimum value of the methanol concentration which gives the best cell performance depends on the open ratio of the current collector also.

It can be explained that increase of the current collector open ratio has a mixed effect on the cell performance. On one hand, increase in the current collector open ratio increases the area for the passage of the reactants and hence promotes the mass transfer of the reactants. Thereby it enhances the reaction rate and improves the cell performance. Similarly, it also facilitates easy removal of the products of reaction (CO_2 at the anode and H_2O at the cathode) from the reaction sites. This is a favourable effect for enhancing the cell performance. On the other hand, increase in the open ratio of the current collector, leads to increased methanol crossover from the anode to the cathode, causing mixed overpotential on the cathode side reaction area. Because of this mixed overpotential, the fuel utilization rate decreases, and the unreacted methanol obstructs the transport of oxygen on the cathode reaction sites. This adversely affects the cell performance. Similarly, increase in the open ratio of the current collector reduces the contact area of the collector with the reaction sites. This decreases the current collector’s ability to conduct more electrons and thus adversely affects the cell performance. Similarly, the methanol concentration also has mixed effects on the performance of a DMFC. On the positive side, increase in the methanol concentration increases the diffusion of methanol through the anode diffusion layer and anode catalyst layer, and thus makes available more amount of methanol for the reaction near the membrane. On the negative side, when the concentration of methanol is more, the potential for the MCO from the anode to the cathode increases. This causes increased mixed overpotential losses and results in the deterioration of the cell performance. Thus, the cell performance is a manifestation of the cumulative effect of favourable and adverse effects due to the open ratio of the current collector and the methanol concentration.



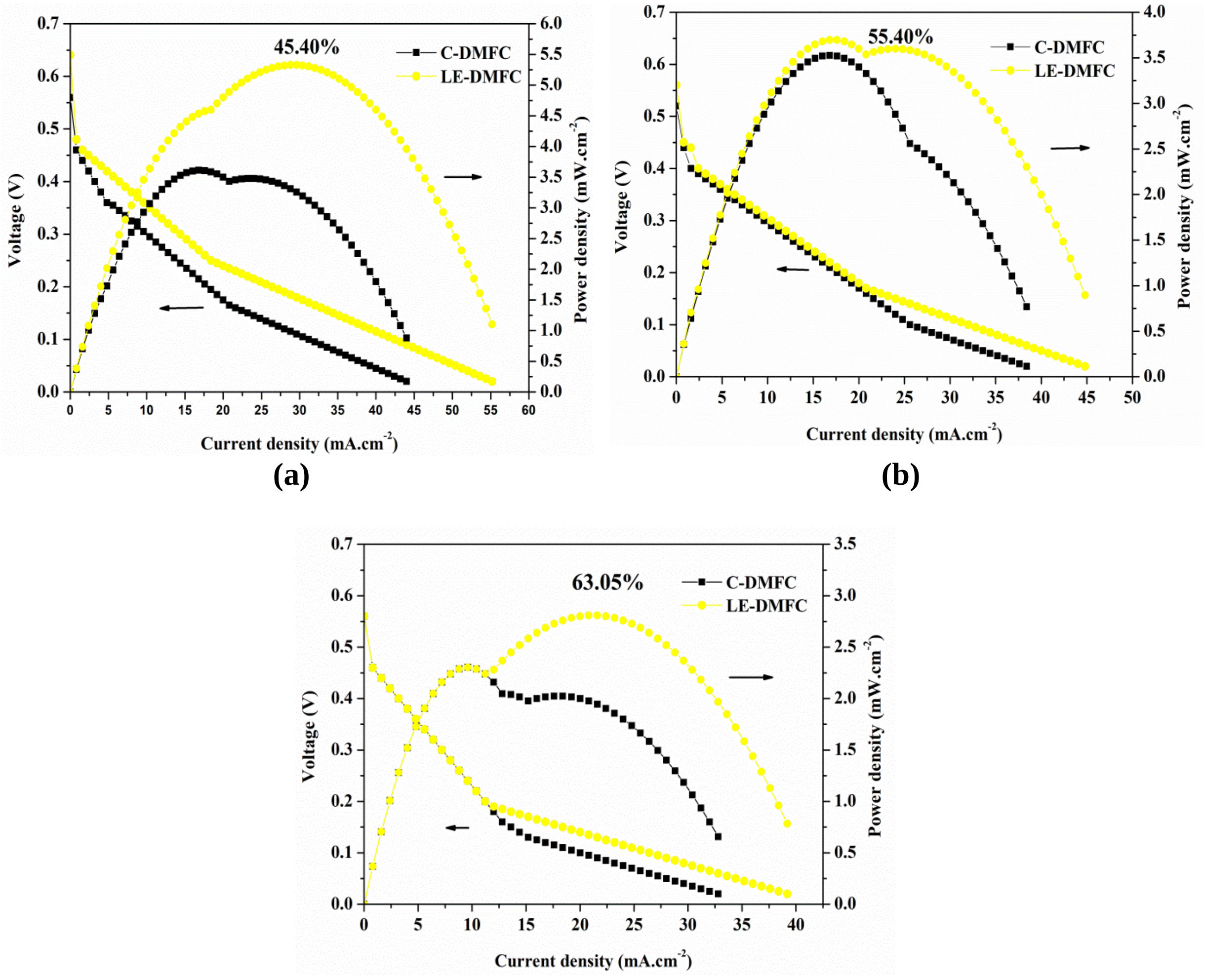
(a)

(b)

Fig.6.5 (a) and (b) Variation of the maximum current density and maximum power density with open ratio of the current collector.

Figs.6.5 (a) and (b) show the variation of the MCD and MPD with different methanol concentration for the three different open ratios of the current collector. It can be noticed that the MPD and MCD increase with increase in the methanol concentration from 1M-5M for the 45.40% current collector. For the 55.40% open ratio current collector, the MPD and MCD increase with increase in methanol concentration from 1M-3M and then decreases. For the current collector with an open ratio of 63.05%, the MCD and MPD increase with increase in the methanol concentration from 1M-4M and then decrease. It can be seen that in the present range of methanol concentrations of 1M to 5M and for the current collector open ratios of 45.40%, 55.40% and 63.05%, the fuel cell with current collector of 55.40% open ratio exhibited the best performance of maximum values of current density and power density at 3M methanol concentration. At 5M of methanol concentration, the 45.40% open ratio current collector based fuel cell produced the MCD and MPD compared to the other two current collectors. Among three current collectors of different open ratios and present range of 1M to 5M methanol concentration, the fuel cell with current collector of 55.40% open ratio exhibited the best performance by producing MCD and MPD of 40.8mA.cm^{-2}and 3.872mW.cm^{-2} respectively at 3M methanol concentration.

6.2.1 Effect of liquid electrolyte layer



(a)

(b)

(c)

Fig.6.6 (a), (b) and (c) Effect of the liquid electrolyte layer on the performance of the fuel cell at 5M of methanol concentration for the three current collectors with different open ratios.

Figs. 6.6 (a), (b) and (c) show the polarization characteristics of a passive DMFC with and without incorporation of LE layer in the MEA for the fuel cell employing current collectors of three different open ratios at 5M methanol concentration. It can be observed from the figure that in all the three cases of current collector open ratios, the performance of the fuel cell improved by incorporating the liquid electrolyte layer. It can be explained that in a passive DMFC, the cell performance is strongly affected by methanol and water cross-over. The incorporation of the liquid electrolyte layer considerably reduces this MCO and hence improves the cell performance as discussed in chapter-4. In general, the incorporation of an additional layer increases the ohmic resistance and impairs the cell performance. The cumulative effect of reduction in the methanol crossover and increase in the ohmic losses of the cell determine the overall effect of incorporating a liquid electrolyte layer on the fuel cell performance.

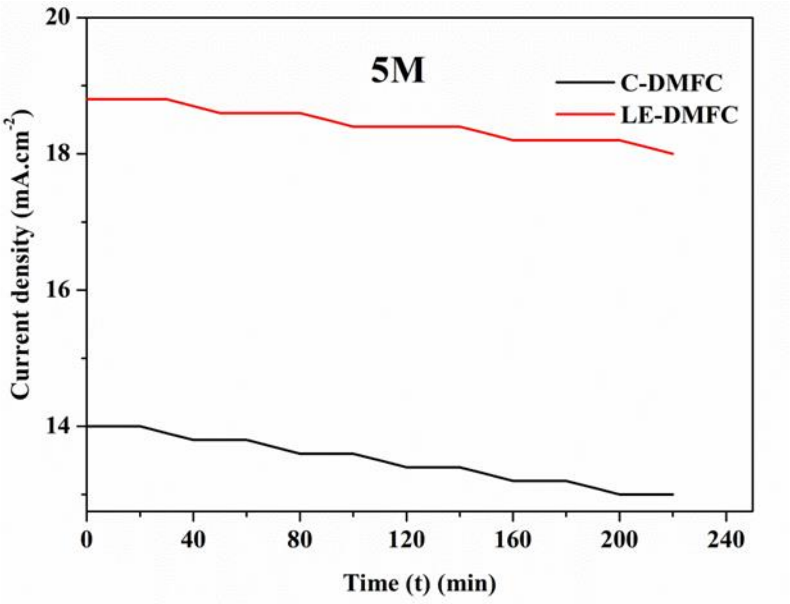
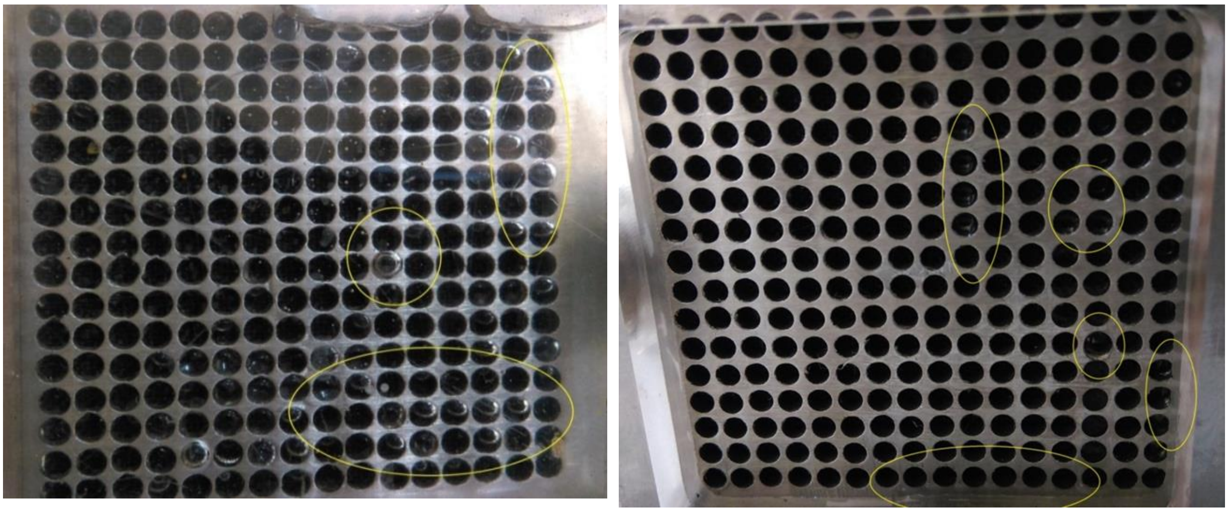


Fig.6.7 Comparison of the long term operation of the LE-DMFC and C-DMFC.

Fig. 6.7 shows the variation of the current density with respect to time at constant voltage of 0.25V for the fuel cell fitted with current collector of 45.40% open ratio. It can be observed that current density drop is more for the conventional DMFC compared to the LE-DMFC. This can be attributed to the MCO. MCO losses are more in the C-DMFC. The methanol crossing the membrane reaches the cathode and reacts with oxygen to produce water (in the form of bubbles). These water bubbles resist the oxygen flow into the cathode reaction sites and deteriorate the cell performance with time.



(a) **(b)**

Fig.6.8 (a) and (b) Formation of CO_2 bubbles on the anode current collector, and water bubbles on the cathode current collector with current collector of 65.03% open ratio at 5M methanol concentration.

Besides the above performance studies, physical studies were also made. The formation of CO_2 and water bubbles were observed on the anode and cathode side as shown in Figs.6.8 (a) and (b) corresponding to the operation of the cell at a current density 25 $mA.cm^{-2}$. During the anodic reaction process, electrons, protons and carbon dioxide bubbles are produced near the anode. The produced electrons pass through the external circuit and reach the cathode. The protons pass through the membrane and reach the cathode side. At the cathode side the electrons, protons and oxygen combine and produce water (in the form of bubbles). More number of CO_2 gas bubbles was generated at higher current densities and higher methanol concentrations due to greater reaction rates. The CO_2 gas bubbles resist the methanol flow to the anode reaction sites. Similarly, on the cathode side the water bubbles block the flow of oxygen to the cathode side reaction sites. Both of them deteriorate the cell performance with time.

6.2.2 Summary

The present work is on the experimental investigation of the influence of current collector open ratio at different methanol concentrations on the performance of a passive DMFC. Experiments were conducted with current collectors of three different open ratios, viz., 45.40%, 55.40% and 63.05% in the range of 1M to 5M methanol concentration. It was observed that the open ratio of the current collector has significant effect on the performance of a passive DMFC. The effect of incorporating a liquid electrolyte layer in the MEA was found as further improvement in the performance. Based on the experimental results, the following conclusions are drawn:

- The cell performance is a strong function of the current collector open ratio. The best open ratio of the current collector which gives the best cell performance is also a function of the methanol concentration.
- In the present range of experimentation of methanol concentration from 1M to 5M, the current collector with 45.40% open ratio gave the best performance at 5M methanol concentration; while the current collector with 55.40% open ratio gave the best performance at 3M methanol concentration, and the current collector with 65.03% open ratio gave the best performance at 4M methanol concentration.
- At 3M methanol concentration, the current collector with an open ratio of 55.40% exhibited the best cell performance, while at 5M methanol concentration, the CC with an OR of 45.40% gave the best cell performance.
- In the total range of experimentation, the optimum molar concentration and open ratio of current collector are 3M and 55.40% respectively in the present range of the parameters, which gave the best cell performance.
- The incorporation of the liquid electrolyte layer was found to further improve the performance of the cell for all the three open ratios of the current collector.

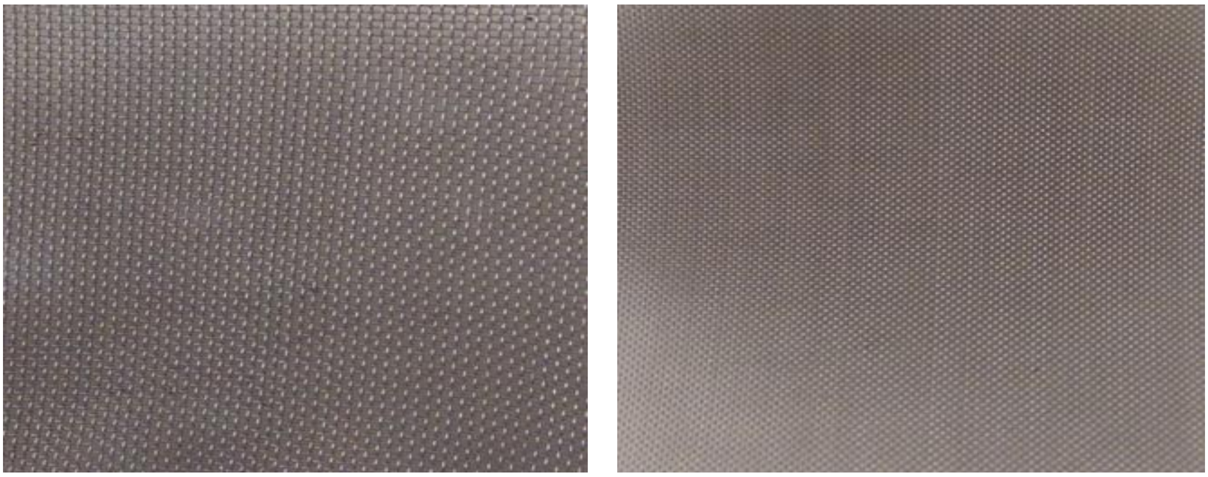
Chapter 7

To investigate the influence of combined wire mesh and perforated current collector aimed at improved electrical conductivity

In a passive DMFC mostly metal current collectors are used on either side of the cell, i.e., on the anode and cathode sides. The main functions of the current collectors are to hold the MEA in the correct position and to act as current conductors for the passage of the electrons produced during the chemical reaction in the cell. The current collector should possess high electrical conductivity, corrosion resistance, low thermal conductivity and good mechanical strength. In addition to this, the current collectors also facilitate uniform distribution of the fuel and oxidant to the reaction sites. The current collectors also have a major role in controlling the flow of the reactants and hence the methanol crossover across the membrane. It was observed from the literature [63] that an additional wire mesh current collector besides the perforated metal current collector sometimes enhances the performance of the fuel cell. In the current research work an experimental study was carried out to evaluate the effect of the combine perforated and wire mesh current collectors on the performance of a passive DMFC. Perforated current collectors with three different open ratios (45.40%.55.405 and 63.05%) and wire mesh current collectors with two different open ratios (45.40% and 38.70%) were considered for the present study. The analysis of these experimental results is presented in this chapter.

7.1 Assembly of the combined perforated and wire mesh current collectors

The assembly of the passive DMFC with a single perforated current collector was discussed in Sec.3.3. This assembly is modified to incorporate both the perforated and the wire mesh current collectors. The wire mesh current collector (WMCC) is placed in between the perforated current collector (PCC) and the MEA on both the anode and cathode sides. Perforated current collectors with three different open ratios (45.40%.55.405 and 63.05%) and wire mesh current collectors made of stainless steel (SS316) with two different open ratios (45.40% and 38.70%) were considered. Fig.7.1 shows the photos of the wire mesh current collectors and Fig.7.2 shows the combined current collector assembly. The specifications of the wire mesh current collector are shown in Table.1.



(a) (b)

Fig.7.1 SS Wire mesh current collectors of open ratios (a) 45.40% (b) 38.70%

Table.7.1 Specifications of the wire mesh current collectors

S.no	Mesh	SWG	Wire diameter(mm)	Size of opening (mm)	Open Ratio, %
1.	32	33	0.2540	0.6619	45.40
2.	26	30	0.3150	0.6010	38.70

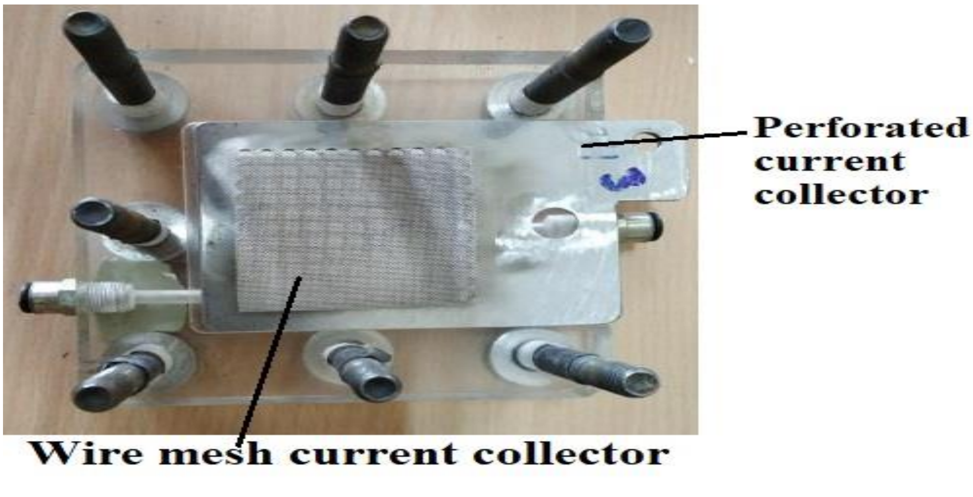


Fig.7.2 Assembly of the combined wire mesh current collector and perforated current collector

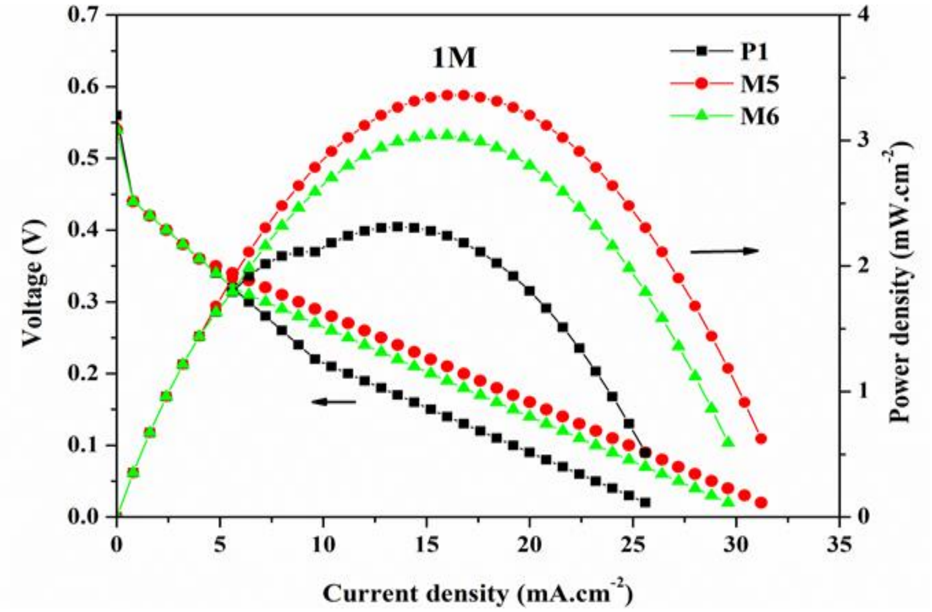
Experiments were carried out to evaluate the effect of the combined wire mesh and perforated current collectors on the performance of the passive DMFC. Having established in the earlier studies that a two layer anode catalyst gives better performance, the same is used in the present experimentation also, i.e., the anode catalyst layers were made of 60% Pt-

Ru/black+ Pt-Ru/C with a loading of 2.5 mg.cm^{-2} and 1.5 mg.cm^{-2} respectively. The cathode catalyst layer was coated with 60% Pt-Ru/c with a loading of 4 mg.cm^{-2} and Nafion 117 membrane with an active area of 25 cm^{2} was used. A total of nine combinations of the combined current collectors were made using the three PCCs and the two WMCCs, as shown in Table.7.1. For each assembly of the combined current collector, experiments were performed by varying the methanol concentration from 1M -5M to identify the optimum combination which gives the best performance. Experiments were also conducted to evaluate the long term operation of the passive DMFC. The results of all these experiments are discussed in the following sections.

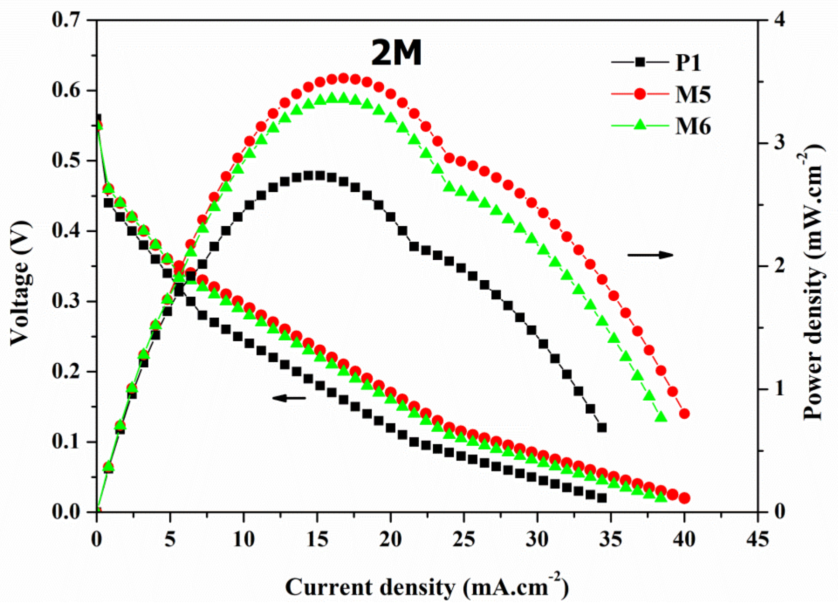
Table.7.2 Combinations of the perforated current collectors with wire mesh current collectors.

S.No	**Perforated-Current collector (PCC) open ratio (%)**	**Number of holes**	**Wire mesh-Current collector (WMCC) open ratio (%)**	**Combination of current collectors**
1	45.40	100 (10x10)	38.70	M5
2	45.40	100 (10x10)	45.40	M6
3	45.40	100 (10x10)	-	P1
4	55.40	225 (15x15)	38.70	M1
5	55.40	225 (15x15	45.40	M2
6	55.40	225 (15x15)	-	P2
7	63.05	256 (16x16)	38.70	M3
8	63.05	256 (16x16)	45.40	M4
9	63.05	256 (16x16)	-	P3

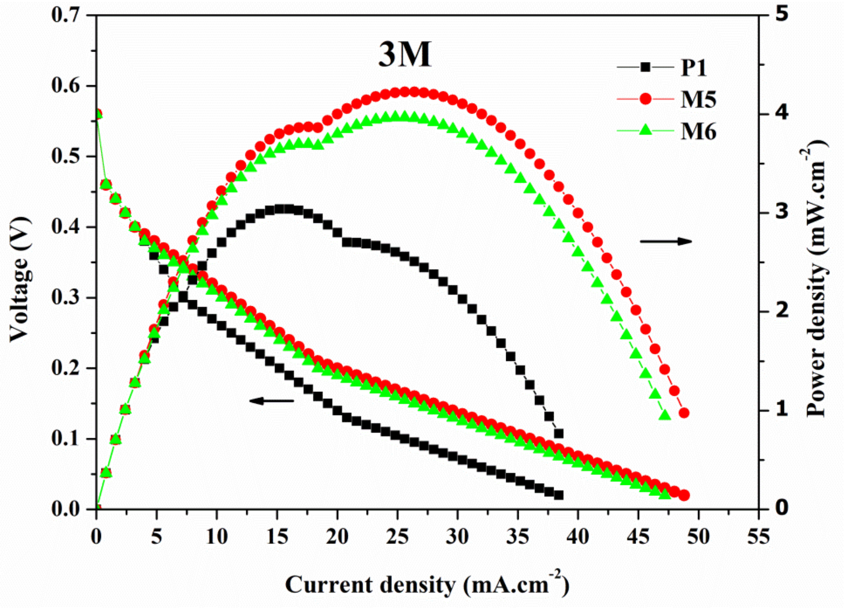
7.2 Effect of the combined perforated and wire mesh current collectors on the performance of the passive DMFC at different methanol concentrations



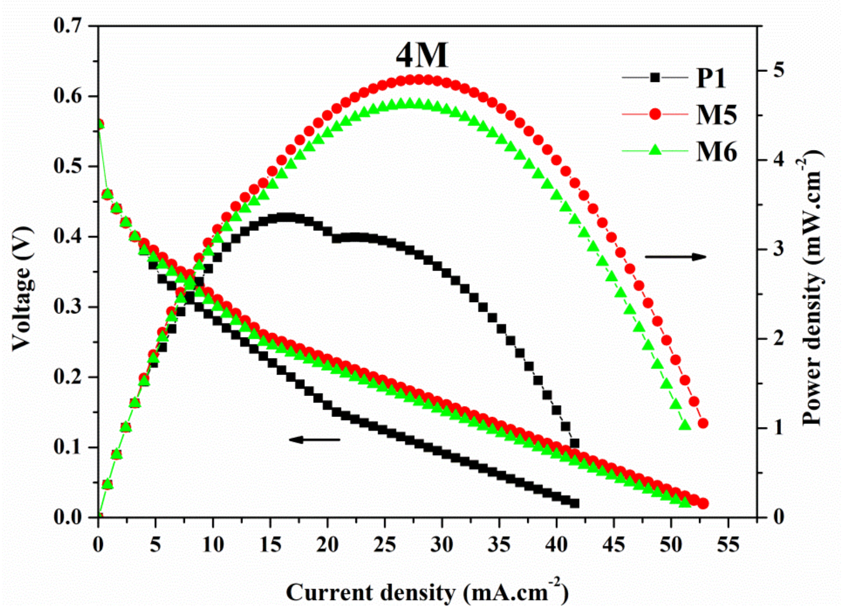
(a)



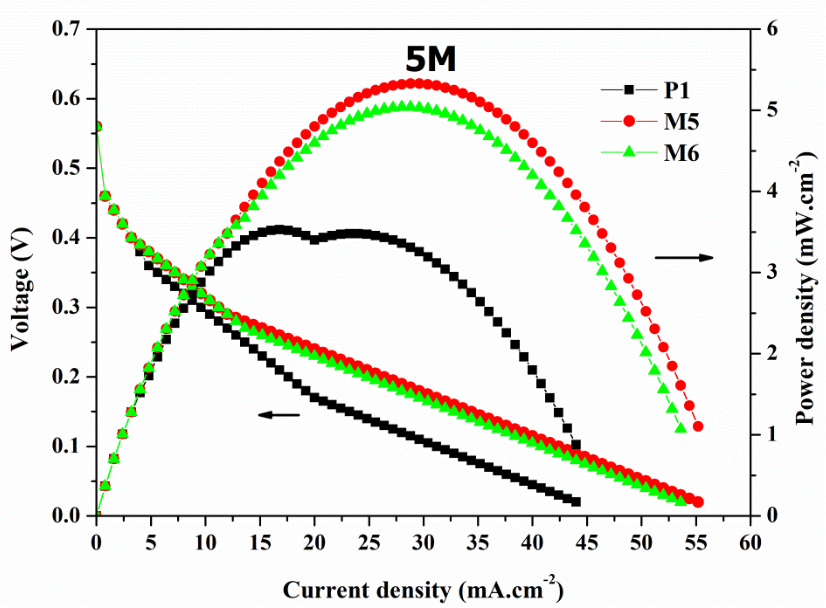
(b)


3M
P1
M5
M6
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
0
5
10
15
20
25
30
35
40
45
50
55

(c)


4M
P1
M5
M6
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
0
5
10
15
20
25
30
35
40
45
50
55

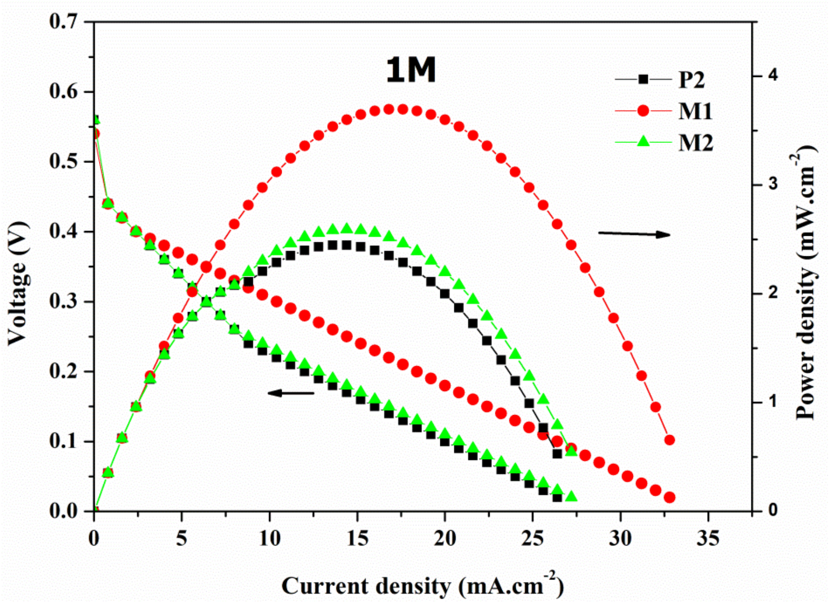
(d)



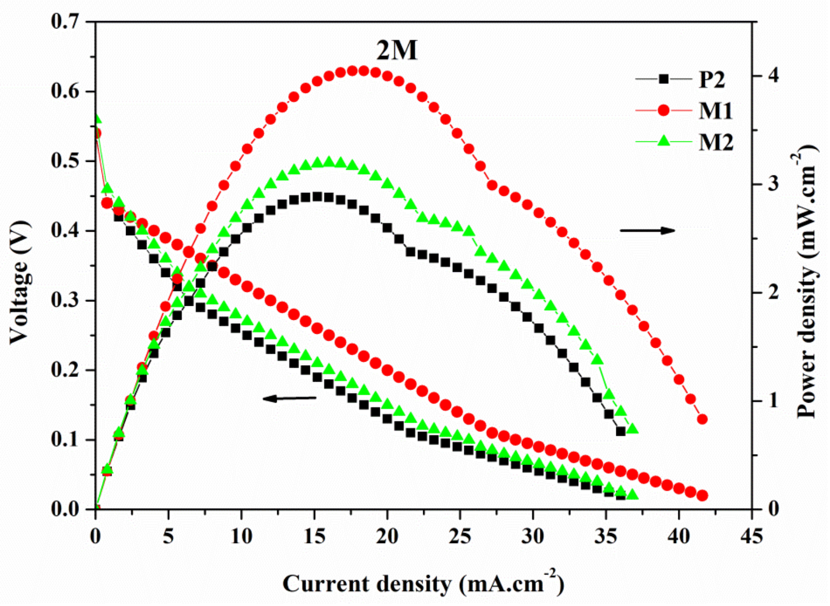
(e)

Fig.7.3 Effect of the WMCCs on the performance characteristics of the fuel cell fitted with PCC of OR 45.40% at different methanol concentrations.

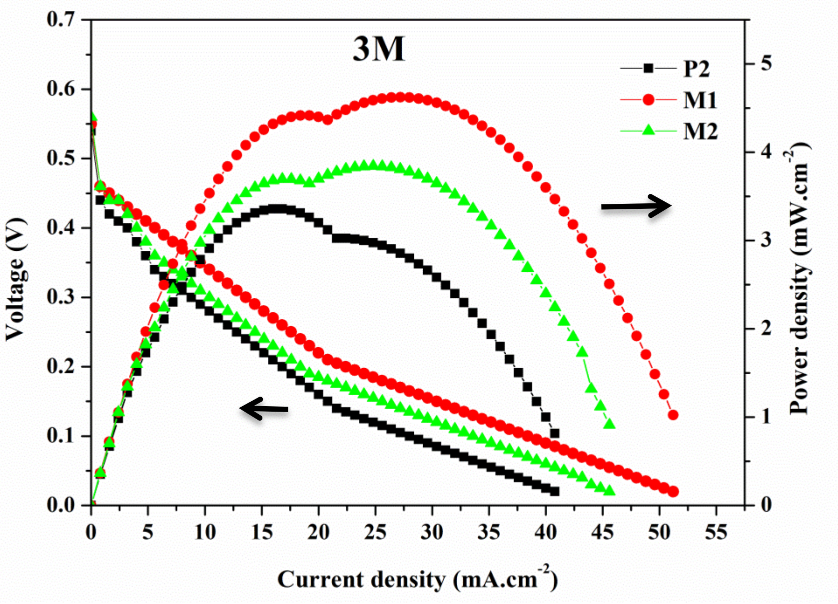
Fig.7.3 (a-e) show the polarization characteristics of the fuel cell incorporated with PCC of OR 45.40% and the combinations with WMCCs 1 and 2, i.e., P1, M5 and M6. The effect of variation of methanol from 1M to 5M is shown in Fig.7.3 (a to e) respectively. From the Fig. 7.3, it is observed that the fuel cell with the M5 combination current collector produced the highest maximum power densities compared to other two current collectors at any methanol concentration in the range of 1M-5M. The lowest performance was observed with the fuel cell fitted with the P1 type current collector. The M5 type current collector was having a combination of PCC with 45.40% OR and WMCC with 38.70% OR, while the P1 type was having only a PCC with 45.40% OR.


1M
P2
M1
M2
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
0
5
10
15
20
25
30
35

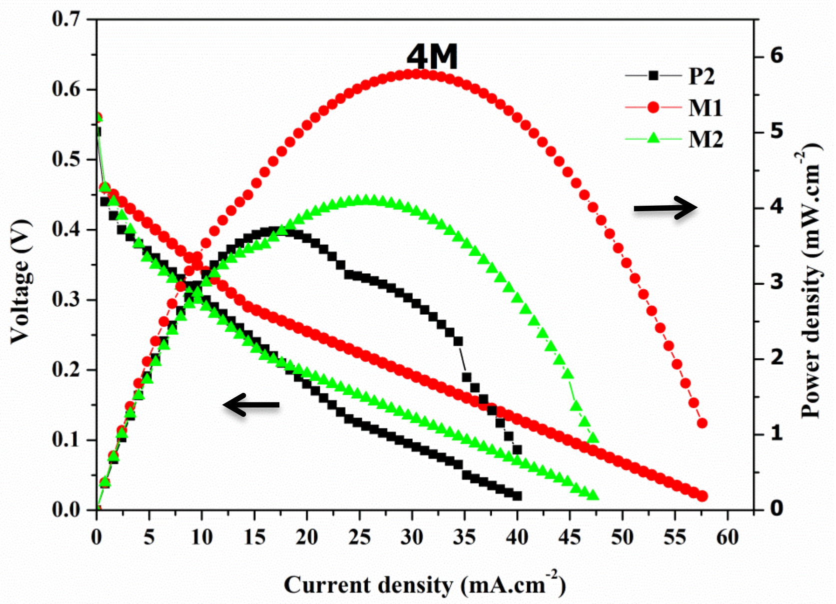
(a)


2M
P2
M1
M2
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
0
5
10
15
20
25
30
35
40
45

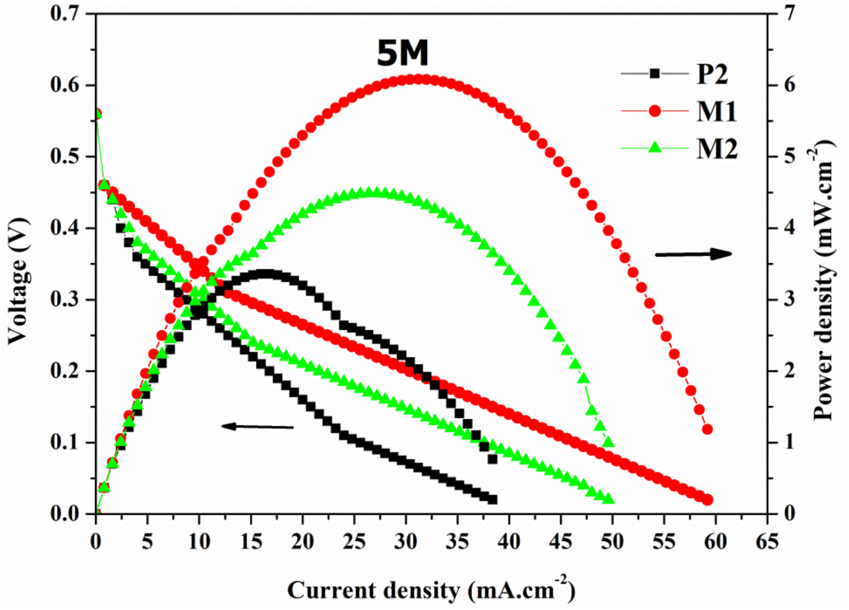
(b)


3M
P2
M1
M2
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
0
5
10
15
20
25
30
35
40
45
50
55

(c)


4M
P2
M1
M2
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
6
0
5
10
15
20
25
30
35
40
45
50
55
60

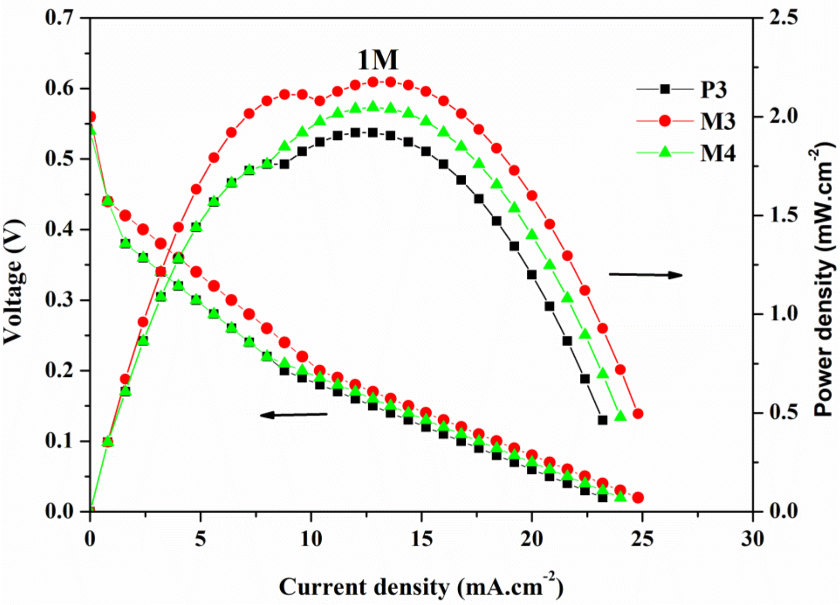
(d)



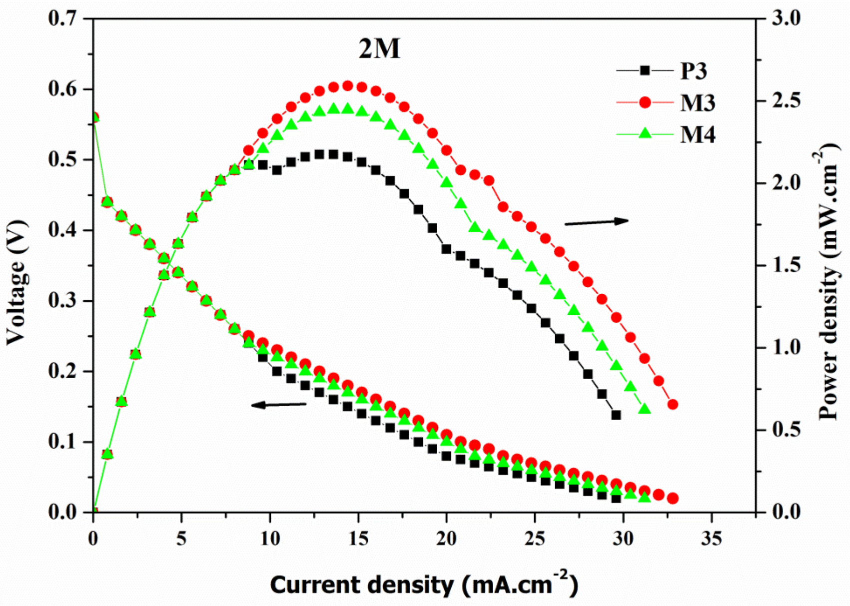
(e)

Fig.7.4 Effect of the WMCCs on the performance characteristics of the fuel cell fitted with PCC of OR 55.40% at different methanol concentrations.

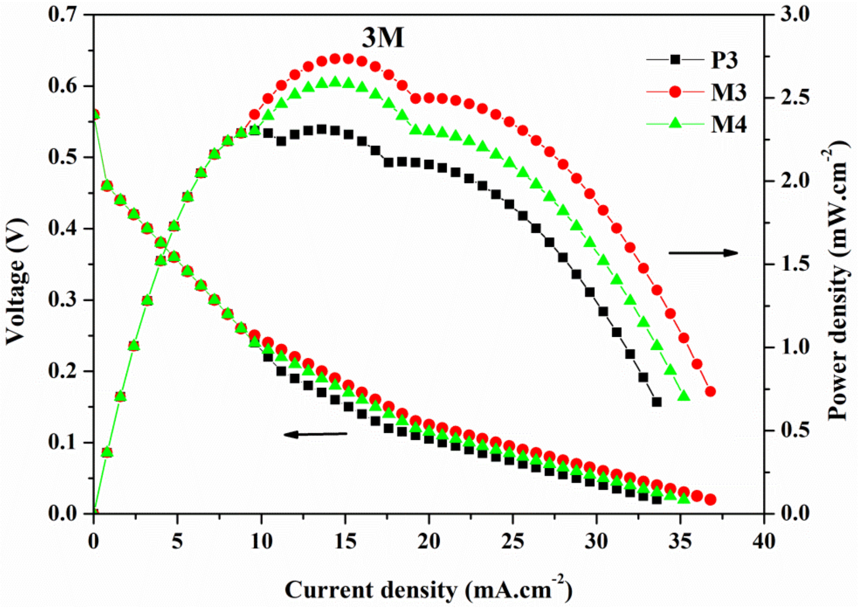
Fig.7.4 (a-e) show the polarization characteristics of the fuel cell incorporated with PCC of OR 55.40% and the combinations with WMCCs 1 and 2, i.e., P2, M1 and M2. The effect of variation of methanol from 1M to 5M is shown in Figs.7.4 (a to e) respectively. From the Fig.7.4, it is observed that the fuel cell with the M1 combination current collector produced the highest maximum power densities compared to other two current collectors at any methanol concentration in the range of 1M-5M. The lowest performance was observed with the fuel cell fitted with the P2 type current collector. The M1 type current collector was having a combination of PCC with 55.40% OR and WMCC with 38.70% OR, while the P2 type was having only a PCC with 55.40% OR.


1M
P3
M3
M4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
0
5
10
15
20
25
30

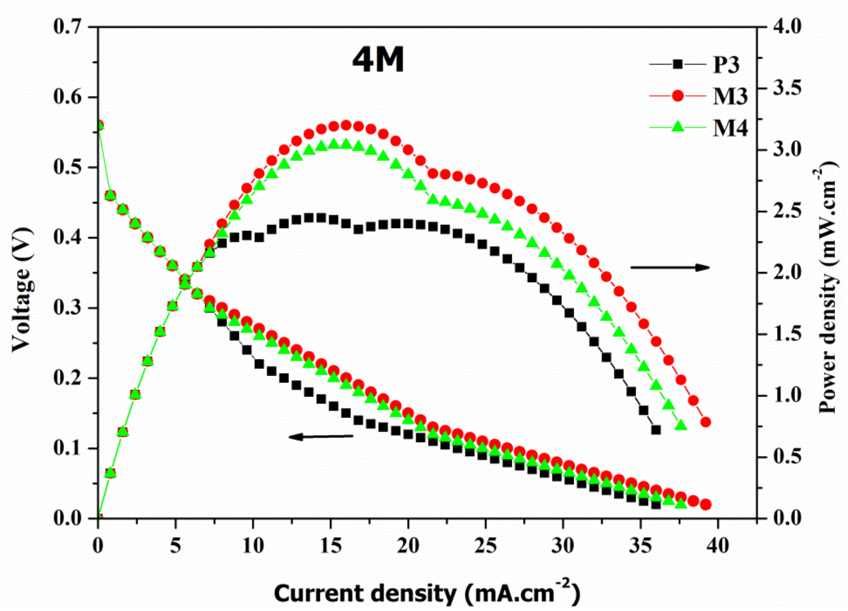
(a)


2M
P3
M3
M4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
5
10
15
20
25
30
35

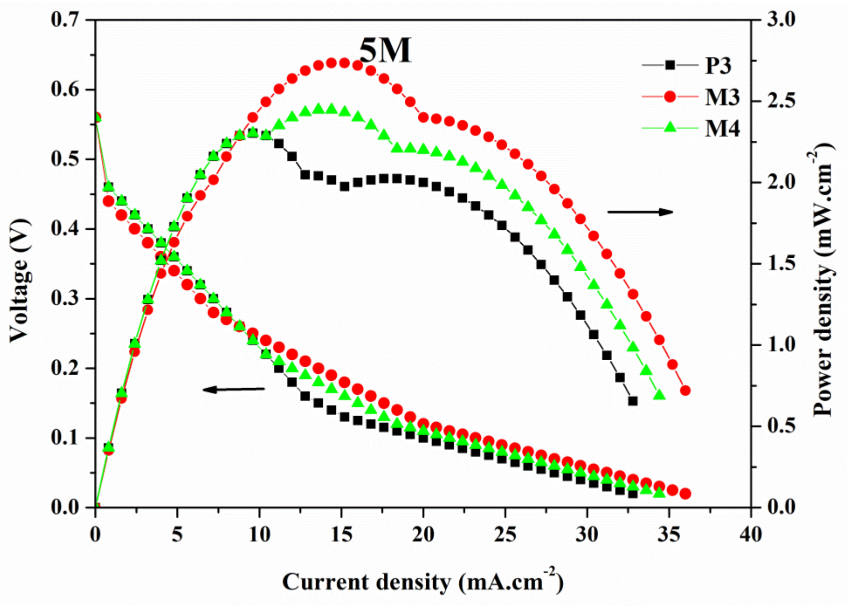
(b)


3M
P3
M3
M4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
5
10
15
20
25
30
35
40

(c)


4M
P3
M3
M4
Voltage (V)
Power density (mW.cm^{-2})
Current density (mA.cm^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
5
10
15
20
25
30
35
40

(d)

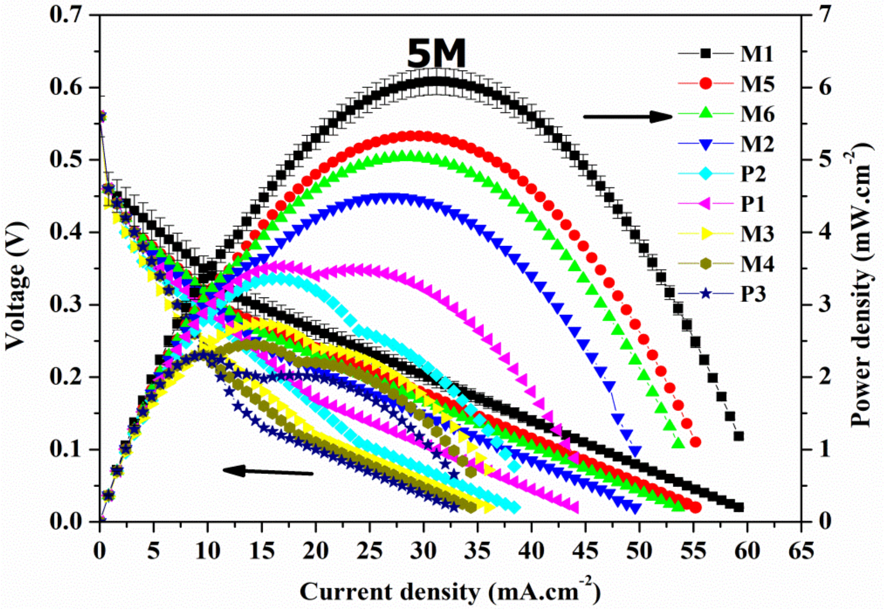


(e)

Fig.7.5 Effect of the WMCCs on the performance characteristics of the fuel cell fitted with PCC of OR 63.05% at different methanol concentrations.

Fig.7.5 (a-e) show the polarization characteristics of the fuel cell incorporated with PCC of OR 63.05% and the combinations with WMCCs 1 and 2, i.e., P3, M3 and M4. The effect of variation of methanol from 1M to 5M is shown in Figs.7.5 (a to e) respectively. From the Fig.7.5, it is observed that the fuel cell with the M3 combination current collector produced the highest maximum power densities compared to other two current collectors at any methanol concentration in the range of 1M-5M. The lowest performance was observed with the fuel cell fitted with the P3 type current collector. The M3 type current collector was having a combination of PCC with 63.05% OR and WMCC with 38.70% OR, while the P3 type was having only a PCC with 63.05% OR.

Fig.7.5 (a-e) show the polarization characteristics of the fuel cell incorporated with PCC of OR 63.05% and the combinations with WMCCs 1 and 2, i.e., P3, M3 and M4. The effect of variation of methanol from 1M to 5M is shown in Fig.7.5 (a to e) respectively. From the Fig. 7., it is observed that the fuel cell with the M3 combination current collector produced the highest maximum power densities compared to other two current collectors at any methanol concentration in the range of 1M-5M. The lowest performance was observed with the fuel cell fitted with the P3 type current collector. The M3 type current collector was having a combination of PCC with 63.05% OR and WMCC with 38.70% OR, while the P3 type was having only a PCC with 63.05% OR.



(e)

Fig.7.6 (a-e) Performance comparison of the different combinations of the wire mesh with perforated current collectors.

Figs.7.6 (a and b) depict the polarization and power density curves of the passive DMFC fitted with different combinations of the wire mesh and perforated current collectors at 5M methanol concentration. It can be seen from the Fig.7.6 that among the nine combinations, the fuel cell with M1 type combination of current collector gave the best fuel cell performance, and the P3 type PCC fitted fuel cell gave the lowest performance compared to the fuel cells fitted with the other combinations of current collectors. The M1 type combined current collector was made of a combination of PCC with 55.40% OR and WMCC with 38.70% OR while the P3 type current collector was a PCC having OR of 63.40%.

From the Figs. 7.3- 7.6, the following general conclusions can be drawn regarding the polarization characteristics. It can be seen from the figures that at any methanol concentration the effect of adding the wire mesh current collector is to increase the maximum current density, maximum power density and the operating voltage of the cell compared to the base configuration of only PCC. The current density corresponding to the maximum power density is increasing means the chemical reaction rate is increasing. This indicates that more amount of methanol is reaching the catalyst layers and more oxidation is taking place. It may be noted that the difference between the ideal voltage and the actual voltage of the cell is a measure of the losses in the cell. From the figures it is seen that the operating voltage of the wire mesh incorporated cell is always greater than the basic configuration of only PCC. This indicates that the losses are decreasing with the incorporation of the WMCC for every PCC, and for every methanol concentration. Similarly, it can also be observed that the operating range of the cell is getting widened with the incorporation of the WMCC for every basic PCC configuration and at every methanol concentration.

The reason for this behavior can be explained as follows. In the combined current collector configuration, the perforated current collector acts as a supporting plate for the wire mesh current collector. This supporting plate helps in providing better contact of the wire mesh current collector with the diffusion layer, thereby reducing the electrical contact resistance. Simultaneously, the incorporation of the wire mesh current collector increases the resistance to methanol crossover and thereby reduces the methanol crossover losses. Initially, on the anode side the diluted methanol fuel enters the PCC (having large openings), which allows more amount of fuel to flow. In the second stage, this fuel passes through the wire mesh current collector. At this junction, some amount of fuel is restricted, while the remainder of the fuel reaches to the catalyst reaction sites. It creates a lower methanol concentration gradient between the anode and cathode compartments. Thus, the reduced open ratio of the wire mesh current collector decreases the methanol crossover and enhances the fuel cell performance.

In the case of perforated current collectors, it can be seen from the construction that a large patch of solid material lies in between two openings. There will be no reactant flow through this solid patch. This reduces the effective reaction area of the membrane. On the other hand, in the case of WMCC, the WMCC is made of thin wires of small diameter. Thus, in between two openings of the WMCC, a smaller patch of solid space, equal to the diameter of the mesh wire only exists. This helps in not only improving the flow of the reactants but also makes it more uniform. The effective reaction area considerably increases, even though the Open ratio is small for the WMCC. This produces more uniform distribution of fuel on the catalyst reaction sites with wire mesh current collectors compared to the perforated current collectors. Thus, the PCC and WMCC combination provides more uniform distribution of the reactants at the catalyst layers and at the same time the current carrying capacity is not diminished. Thus, the incorporation of the WMCC aids in improving the performance of the fuel cell.

Table.7.3 Maximum power density values for nine combinations of current collectors

Methanol Concentration (M)/MPD	**P1**	**M5**	**M6**	**P2**	**M1**	**M2**	**P3**	**M3**	**M4**
1	2.312	3.36	3.04	2.448	3.969	2.592	1.92	2.176	2.048
2	2.736	3.528	3.36	2.888	4.048	3.2	2.176	2.592	2.448
3	3.04	4.224	3.968	3.36	4.624	3.844	2.321	2.736	2.592
4	3.36	4.9	4.624	3.696	5.776	4.096	2.448	3.2	3.04
5	3.528	5.328	5.04	3.36	6.084	4.488	2.304	2.736	2.448

It can be seen from the Table.7.3 that for the P1 type current collector there is a monotonous enhancement in the MPD with increase in the methanol concentration, but the rate of enhancement is less at higher methanol concentration. But, for the P2 and P3 current collectors, there is no monotonous enhancement in the MPD with increase in the methanol concentration, i.e., the MPD initially increases with increase in the methanol concentration, reaches a maximum, and then decreases with further increase in the methanol concentration. The MPD is obtained at 4M methanol concentration.

On the other hand, it can also be observed from the table that for the M1 and M2 combinations associated with the P2 current collector (OR 55.40%), and for the M5 and M6 combinations associated with the P1 current collector (OR 45.40%) there is a monotonous enhancement in the MPD with increase in the methanol concentration from 1M to 5M, whereas for the M3 and M4 combinations associated with P3 current collector, there is no monotonous enhancement of MPD with increase in the methanol concentration. For these M3 and M4 combinations the MPD is obtained at 4M methanol concentration.

Table.7.4 Percentage increase in maximum power density in the case of without incorporation of wire mesh current collectors

Methanol Concentration (M)/ % increase in MPD	**P1**	**M5**	**M6**	**P2**	**M1**	**M2**	**P3**	**M3**	**M4**
1		45.32	31.48		28.94	5.88		13.34	6.25
2		28.94	22.8		40.16	10.80		19.11	11.11
3		38.94	30.52		37.61	14.40		17.88	11.67
4		45.84	37.61		56.27	10.82		30.71	24.18
5		51.02	42.85		81.07	33.57		18.75	6.25

It can be observed from the Table.7.4, that at any methanol concentration M3 is better than M4, M1 is better than M2 and, M5 is better than M6 in terms of the performance. It can be observed that in all these three combinations , i.e., M5, M1 and M3 combinations, the WMCC is having an open ratio of (38.70%), and in the M6, M2 and M4 combinations, the WMCC is having an open ratio of (45.40%). This indicates that in between WMCC 1 (OR of 38.70%) and WMCC 2 (OR of 45.40%), WMCC 1, which is having smaller OR is giving better performance.

Table.7.5 Current density at MPD for nine combinations of current collectors

Methanol Concentration (M)/ Current density at MPD	**P1**	**M5**	**M6**	**P2**	**M1**	**M2**	**P3**	**M3**	**M4**
1	13.6	16.8	16	14.4	16.8	14.4	12.8	13.6	12.8
2	15.2	16.8	16.8	15.2	18.4	25.6	13.6	14.4	14.4
3	16	26.4	24.8	16.8	27.2	24.8	13.6	15.2	14.4
4	16.8	28	27.2	16.8	30.4	25.6	14.4	16	15.2
5	16.8	29.6	28.8	16.8	31.2	27.2	9.6	15.2	14.4

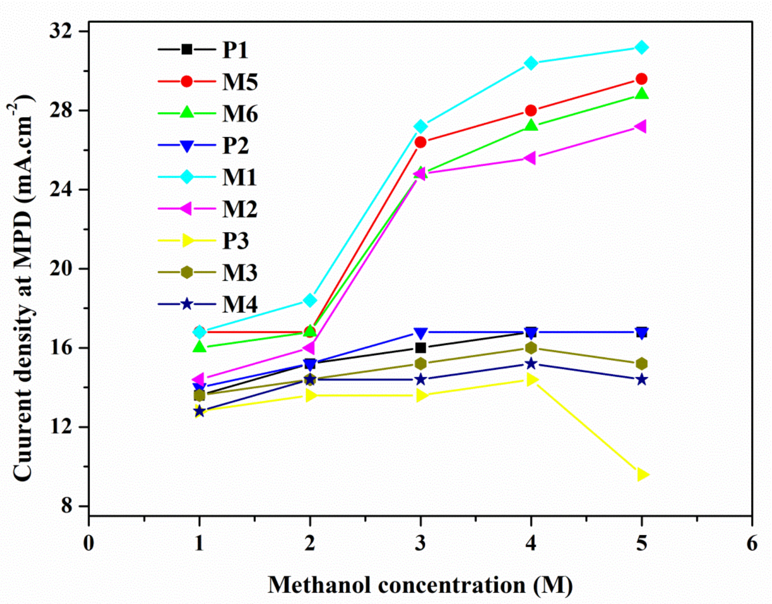


Fig. 7.7 Variation of current density at the MPD with respect to methanol concentration

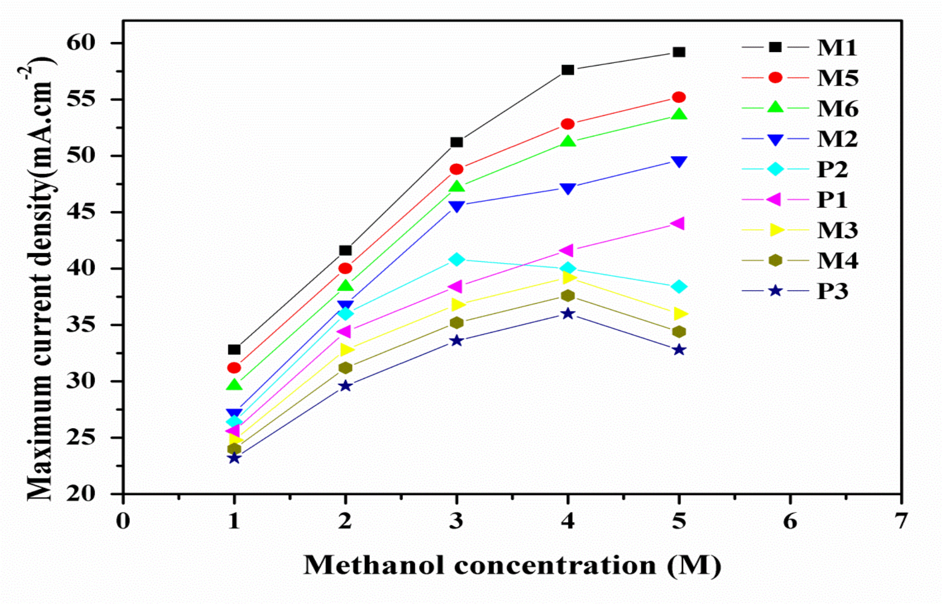


Fig.7.8 Maximum current densities of the passive DMFC with different combinations of WMCC and PCC.

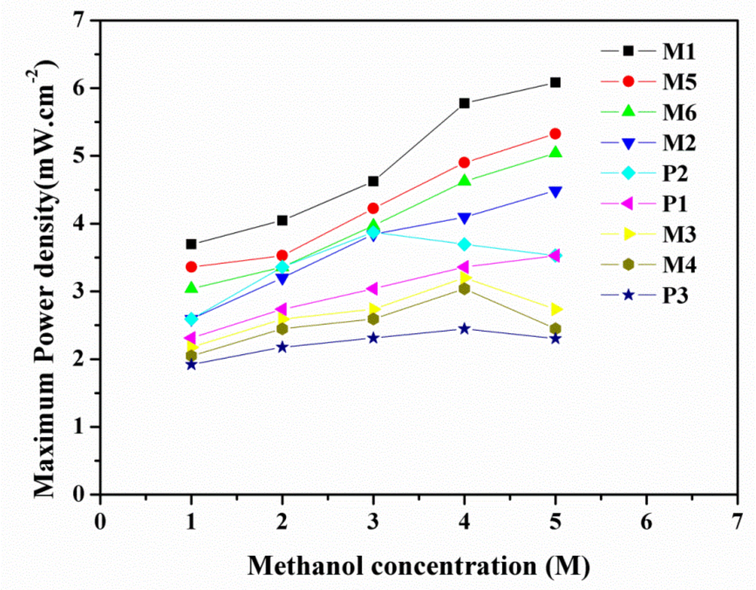


Fig.7.9 Maximum peak power densities of the passive DMFC with different combinations of WMCC and PCC

Figs. (7.7), (7.8) and (7.9) depict the variation of current density at maximum MPD, maximum current density of the cell and the maximum power density with respect to methanol concentration. The methanol concentration is varied from 1M-5M for the nine combinations of current collectors. From Fig. 7.7 it is observed that the current density at the MPD is increasing with increase in the methanol concentration for M1, M5, M6 and M2 type current collector fitted fuel cells, whereas for the other five combinations fitted fuel cell this current density at the MPD doesn’t monotonously increase with increase in the methanol concentration. From Figs. 7.8 and 7.9, it is observed that the MCD and MPD increase with increase in methanol concentration from 1M-5M for the M1, M5, M6, M2 and P1 combinations. For the P3, M4 and M3 combination current collectors, the maximum current densities and maximum power densities initially increase with increase in the methanol concentration from 1M-4M, and then decrease with further increase in the methanol concentration to 5M. Only for the P2 type current collector, the cell performance increases from 1M-3M and then decreases. Among the nine combinations of current collectors, the M1 type combination current collector fitted fuel cell produced the MCD and MPD at 5M methanol concentration. The MCD and MPD produced by the M1 incorporated fuel cell are 59.2 mA.cm^{-2} and 6.084 mW.cm^{-2} respectively, at 5M of methanol concentration. The P3 type current collector incorporated fuel cell produced the lowest MCD and MPD, which are 32.8 mA.cm^{-2} and 2.304 mW.cm^{-2} respectively, at 5M of methanol concentration.

It can be seen from the Figs. (7.7)-(7.9) that among the nine combinations M1 gives the best performance at all the methanol concentrations. In the decreasing order of performance are M1, M5, M6 and M2 combinations either in terms of the MPD or MCD or the current density at the MPD. The performance of the other five combinations is far inferior to these four combinations. Added to that it can also be observed that there is a monotonous increase in the performance with increase in the methanol concentration for these four combinations.

It can be observed from table 3 that performance of the fuel cell doesn't improve much with WMCCs also when the PCC was having an OR of 63.05%. The smallest improvement at any methanol was concentration was observed for M4 followed by M3 type current collectors associated with the P3 type PCC. At each methanol concentration in the lowest order of performance were P3 followed by M4 and M3 type current collector fitted cells. This is because of the large opening ratio of the PCC. That indicates that even with wire mesh combined current collectors also the OR of the PCC has a major influence on the performance of the DMFC.

7.2.1 Long term operation of wire mesh along with perforated and only perforated current collector

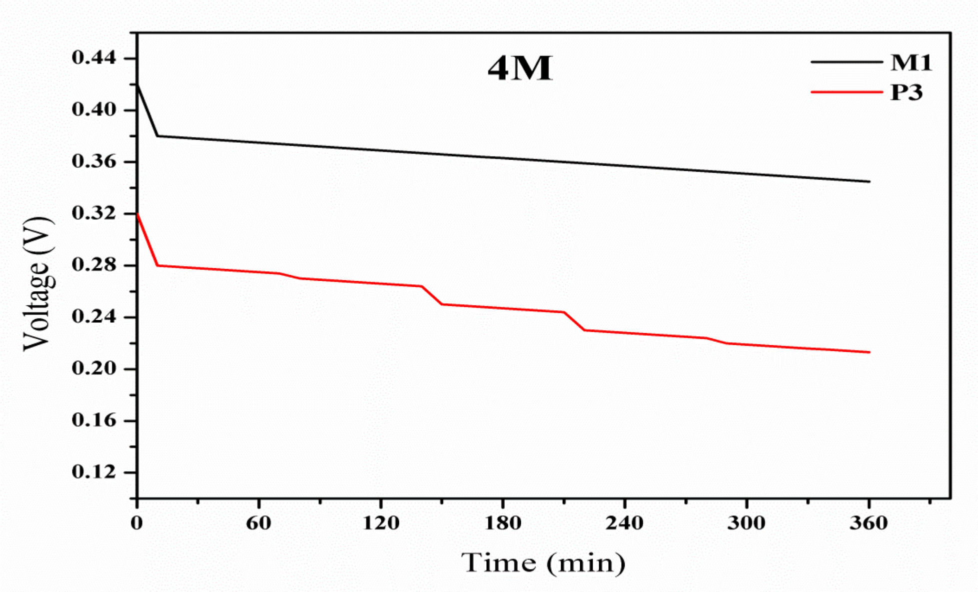


Fig.7.10 Comparison of the long term operation of M1 and P3 current collector fitted fuel cells.

Experiments were conducted to evaluate the long term performance of the fuel cell. Experiments were conducted continuously for a period of six hours for the M1 and P3 combinations of the current collectors at 4M of methanol concentration and at a constant current density of 25mA.cm^{-2}. The voltage–time characteristics are depicted in Fig.7.10. It can be seen from the figure the M1 type collector gives better stable output voltage compared to the P3 type current collector. This is because the methanol crossover losses are more predominant in the single perforated current collector of P3.These losses increase the cathode overpotential. More voltage drop occurred for the fuel cell with P3 type current collector compared to the M1 type current collector. Because of the methanol crossover, oxygen availability on the cathode reaction sites decreases and the performance deteriorates.

7.2.2 Summary

The present work experimentally studied the effect of the combined perforated and wire mesh current collectors at different methanol concentrations (1M-5M). Experiments were also carried out to evaluate the long-term stability of the fuel cell fitted with M1 and P3 current collectors. The following major conclusions are drawn from the experimental results:

- The incorporation of the wire mesh collector along with the perforated current collector in the fuel cell increased the operational range, the operational output voltage and the MPD of the fuel cell.
- In between the two wire mesh current collectors, the WMCC with 38.70% OR incorporated current collector combination gave better performance with all the three PCCs (of different open ratios).
- The effect of the incorporation of the WMCC was not uniform with all the three PCCs (of different ORs). The effect of the incorporation of the WMCC was minimum with the P3 type PCC, which indicates that the basic PCC has a significant effect on the performance.
- Among the nine combinations of the current collectors, the M1 type current collector combination incorporated fuel cell exhibited the highest performance and the P3 type current collector incorporated fuel cell gave the lowest performance. The maximum current densities and maximum power densities produced by M1 and P3 are 59.2 mA.cm^{-2}, 32.8 mA.cm^{-2}, 6.084 mW.cm^{-2} and 2.304 mW.cm^{-2} respectively.
- For long term operation, the fuel cell with M1 type combination of the current collector has greater voltage stability compared to the fuel cell with P3 type current collector.

Chapter 8

Effect of alcoholic additives to the methanol fuel on the performance of a passive DMFC

Hydrogen is mostly preferred to be used as a fuel in the fuel cell. This is due to the weak hydrogen-hydrogen bond, which gives a high electrochemical activity. But,hyrogen is not a freely available fuel. The production cost of hydrogen is more and the storage of hydrogen is also difficult. Added to that, hydrogen has low volumetric energy density compared to liquid fuels, and hence it requires large volume to store. Instead of hydrogen, alcholic liquids can be used as fuels in the fuel cells. Alcholic fuels have the merits of easy storage, transport, higher energy density and easy membrane hydration. Thus, these fuels are being considered as suitable fuels for fuel cells. Liquid alcohol fuels such as methyl alcohol (methanol), ethyl alcohol (ethanol), n-propyl alcohol (1-propanol, 2-propanol), and 2-butanol are the possible alternative fuels to hydrogen with high energy density. The present work deals about the performance analysis of a passive alcoholic fuel cell with different single alcoholic fuels and their additives as the anodic fuels. Ethanol, 1-propanol, 2-propanol, 1-methanol, and fuel additives of ethanol, 2-propanol, 2-propanol+ethanol to methanol were explored as the anodic fuels, and their impact on the performance of the FC was experimentally evaluated.

8.1 Results and discussion

Experiments were carried out to evaluate the effect of the different alcoholic fuels on the performance of a passive alcoholic fuel cell. Having established in the earlier studies that a two layer anode catalyst gives better performance, the same is used in the present experimentation also, i.e., the anode catalyst has two layers of catalyst supports, viz., Pt-Ru/black (inner layer) and Pt-Ru/C (outer layer). On the cathode side a single layer of Pt/C (60%) with a loading of 2mg.cm^{-2} was considered. Similarly, a perforated current collector (PCC) with an open ratio of 45.40% was used in the fuel cell. All the experiments were conducted at room temperature and RH of 60 to 70%. Experiments were conducted in two phases. The first phase of experiments was aimed at evaluating the performance of the passive fuel cell with different single alcoholic fuels as the anodic fuels. Ethanol, 1-propanol, 2-propanol and methanol were used as the single alcoholic fuels, and with each of these fuels, the fuel concentration was varied from 0.5M-5M. In second phase of experimentation, these single alcoholic fuels were added as additives to methanol and were used as the anodic fuels of the DMFC, and the performance of the DMFC was evaluated experimentally. Ethanol, 2-propanol and 2-propanol+ethanol were added to methanol, and with each of these additives, experimentation was carried out by varying the additive concentration from 0.5M-2.5M.The results of these experiments are discussed in the subsequent sections.

8.1.1 Performance evaluation of the fuel cell with different alcohols as the anodic fuel

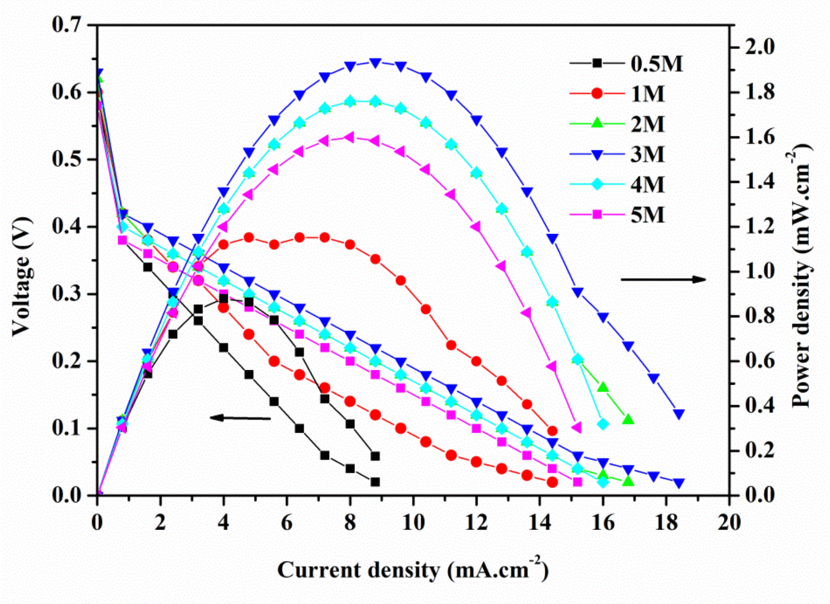


Fig.8.1 Polarization curves with 1-propanol as the anodic fuel

Fig.8.1 shows the polarization curves of the fuel cell with 1-propanol as the anodic fuel at different concentration of the fuel. It can be seen from the Fig.8.1 that the fuel cell performance increases with increase in the fuel concentration from 0.5 M-3M, and then after decreases. This enhancement of the fuel cell performance is due to the enhanced reaction kinetics with increase in the fuel concentration initially. However, at higher concentration of the fuel, the fuel crossover from the anode to the cathode side of the membrane increases and the cell performance deteriorates.

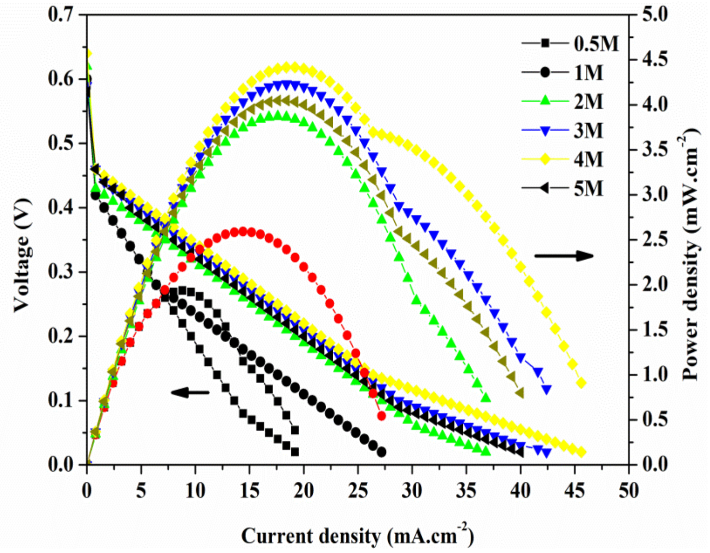


Fig.8.2 Polarization curves with 2-propanol as the anodic fuel

Fig. 8.2 depicts the performance characteristics of the fuel cell with 2-propanol as the anodic fuel. The concentration of the fuel was varied from 0.5M-5M. It can be seen from the figure that the fuel cell performance increased with increase in the 2-propanol concentration from 1M-4M.The maximum fuel cell performance was obtained at 4M concentration. With further increase in the concentration from 4M to 5M, the fuel cell performance decreased. The MCD and MPD produced by the 2-propanol fuel cell are 45.6 mA.cm^{-2} and 4.416 mW.cm^{-2} at 4M concentration.

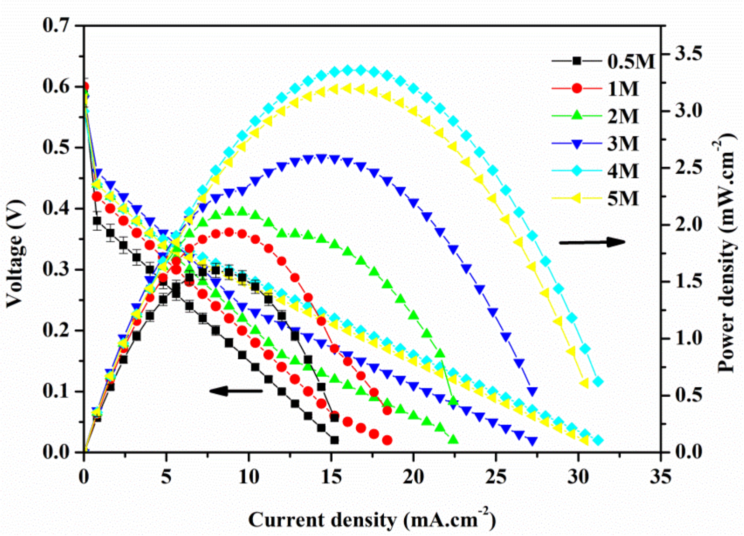


Fig.8.3 Polarization curves with ethanol as the anodic fuel

Fig.8.3 shows the polarization curves of the fuel cell with ethanol as the anodic fuel. Ethanol concentration was varied from 0.5M-5M. It can be observed from the figure that the fuel cell performance increased with increase in the ethanol concentration from 0.5M-4M and with further increase in the ethanol concentration from 4M-5M, the fuel cell performance deteriorated. The MCD and MPD produced by the ethanol fuel cell are 31.2 mA.cm^{-2} and 3.36 mW.cm^{-2} respectively at 4M ethanol concentration.

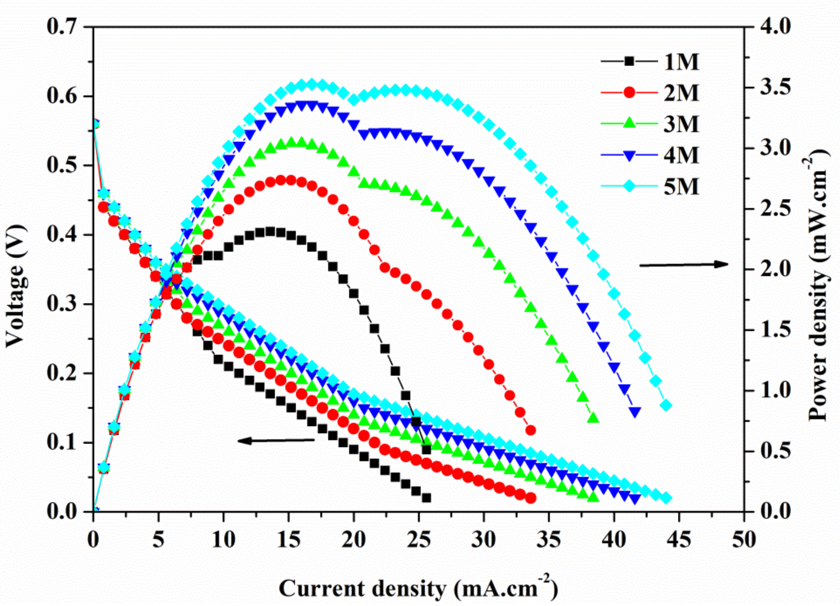


Fig.8.4 Polarization curves with methanol as the anodic fuel

Fig.8.4 shows the polarization curves of the DMFC. The methanol concentration was varied from 1M-5M. The fuel cell performance increased from 1M-5M of methanol concentration. The effect of methanol concentration on the performance of the passive DMFC was discussed in Sec.4.1.

Table.8.1 Comparison of the open circuit voltages (V) with the four alcohols as the anodic fuels

Anodic fuel/ Concentration`	**1-Propanol**	**Ethanol**	**2-Propanol**	**Methanol**
1M	**0.6**	0.59	**0.6**	0.55
2M	**0.62**	0.58	**0.62**	0.55
3M	**0.63**	0.58	0.62	0.56
4M	0.58	0.58	**0.64**	0.56
5M	**0.58**	0.56	**0.58**	0.56

It can be observed from the table.8.1, that the Open Circuit Voltage (OCV) is the highest for 2-propanol at most of the concentrations. In some cases, the OCV with 1-propanol is also highest.

Table.8.2 Comparison of the Maximum current density (mA.cm^{-2}) with the four alcohols as the anodic fuels

Anodic fuel/ Concentration`	**1-Propanol**	**Ethanol**	**2-Propanol**	**Methanol**
1M	14.4	18.4	**27.2**	25.6
2M	16.8	22.4	**36.8**	34.4
3M	18.4	27.2	**42.4**	38.4
4M	16	31.2	**45.6**	41.6
5M	15.2	30.4	**40**	44

It can be observed from the table.8.2, that the Maximum Current Density is the highest for 2-propanol and lowest for 1-propanol at any concentration.

Table.8.3 Comparison of the Maximum power density (mW.cm^{-2}) with the four alcohols as the anodic fuels

Anodic fuel/ Concentration`	**1-Propanol**	**Ethanol**	**2-Propanol**	**Methanol**
1M	1.152	1.936	**2.92**	2.312
2M	1.76	2.112	**3.872**	2.736
3M	1.936	2.592	**4.232**	3.04
4M	1.76	3.36	**4.416**	3.36
5M	1.6	3.2	**4.048**	3.528

It can be observed from the table.8.3, that the Maximum Power Density is the highest for 2-propanol and lowest for 1-propanol at any concentration.

Table.8.4 Comparison of the Current density at MPD(mW.cm^{-2}) with the four alcohols as the anodic fuels

Anodic fuel/ Concentration`	**1-Propanol**	**Ethanol**	**2-Propanol**	**Methanol**
1M	6.4	8.8	**14.4**	13.6
2M	8.8	9.6	**17.6**	14.4
3M	9.6	14.4	**18.4**	16
4M	8.8	16.8	**19.2**	16.8
5M	8	16	**18.4**	17.2

It can be observed from the table8.4, that the Current Density corresponding the Maximum Power Density is the highest for 2-propanol and lowest for 1-propanol at any concentration.

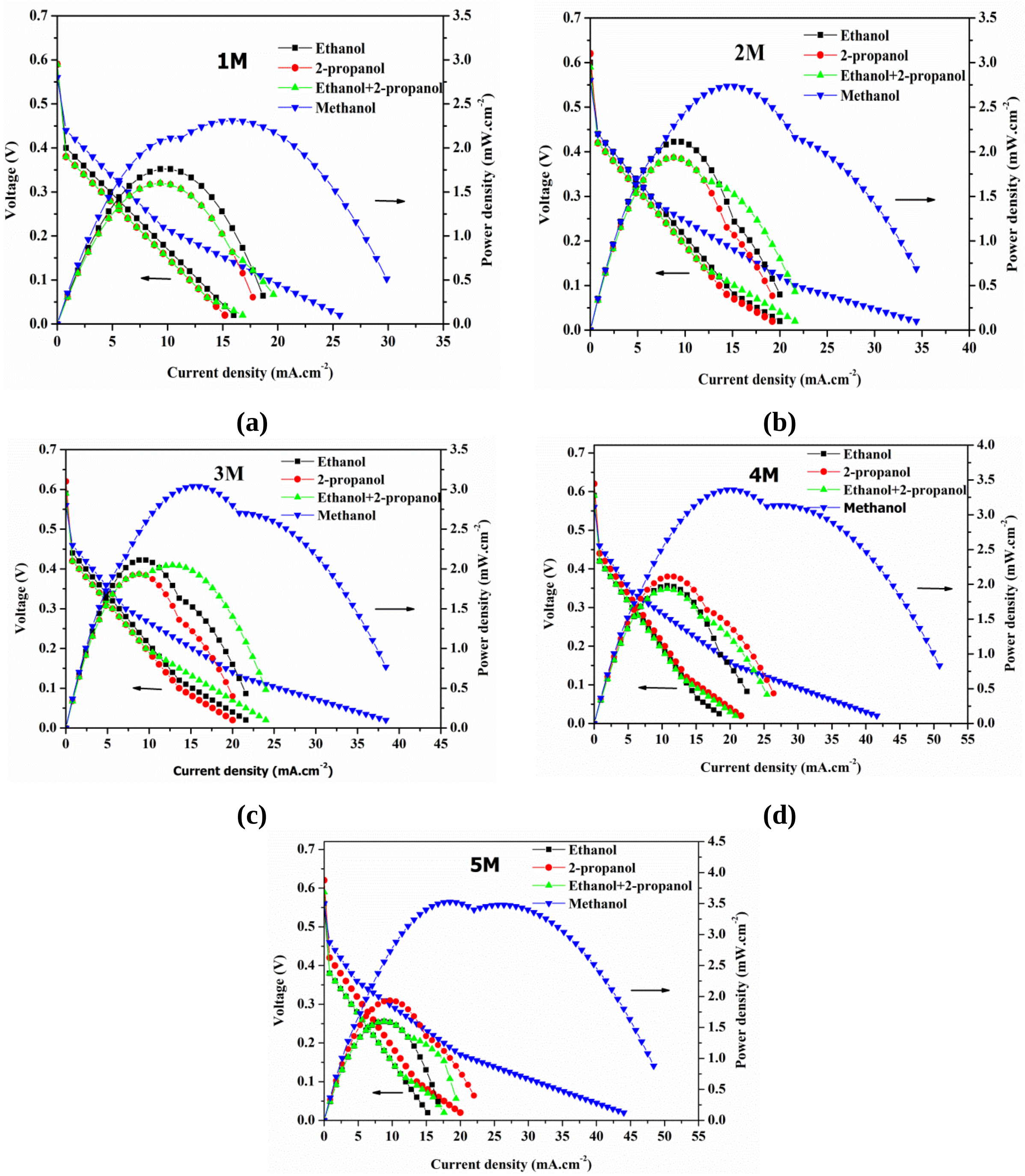
Table.8.5 Maximum power densities and the corresponding fuel concentration for different anodic alcoholic fuels.

S. No	**Anodic fuel**	**Maximum power density (mW.cm^{-2})**	**Fuel concentration (M) for the maximum power density (mW.cm^{-2})**
1	1-Propanol	1.936	3M
2	Ethanol	3.36	4M
3	2-Propanol	4.416	4M
4	Methanol	3.528	5M

The details of the open circuit voltage, MCD, MPD and the current density at the maximum power density, and the corresponding fuel concentration are compiled in Tables 8.1 to 8. 5, respectively. It can be observed from the tables that 2-propanol is giving better fuel cell performance compared to the other three fuels, viz., 1-propanol, ethanol and methanol. The increasing order of performance of these four anodic fuels is: 1-propanol, ethanol, methanol and 2-propanol. Among the four anodic fuels considered in the present study, 2-propanol has higher energy density compared to other fuels, and also has higher Open Circuit Voltage (OCV). 2-propanol has lower crossover current density compared to methanol [27]. With oxidation of each methanol molecule, six electrons are produced, while for each 2-propanol molecule, 18 electrons are produced. In other words, with complete oxidation of each 2-propanol molecule, three times as large current is produced as compared to complete oxidation of each methanol molecule. Propanol and ethanol have lesser environmental effect compared to methanol. 2-propanol is nontoxic compared to methanol, and also fuel leakage of 2-propanol can be identified by smell. The main drawback of 2-propanol is that it quickly destroys the anode side catalyst compared to methanol. This should be avoided by frequently cleaning the catalyst area. The fuel cell operated with 2-propanol results in swelling of the Nafion membrane at higher concentrations.

8.1.2 Effect of alcohol fuel additives to methanol fuel

In the second phase of experiments, fuel additives of ethanol, 1-propanol, 2-propanol and ethanol+2-propanol were added to the basic fuel of the DMFC, i.e., methanol. The fuel additive concentration was varied from 0.5M to 2.5M, and the methanol concentration was varied from 1M-5M for each one of these four fuel additives. The results of these experiments are discussed in the subsequent paragraphs.



(a)

(b)

(c)

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Fig.8.5 (a-e) Polarization curves of the fuel cell with the fuel additives at 0.5M concentration and at different methanol concentrations in the range of 1M-5M.

Fig.8.5 (a-e) shows the polarization curves with different fuel additives at 0.5M concentration being added to methanol, and the methanol concentration being varied in the range of 1M-5M. Among all the fuels, pure methanol with no additive exhibited the highest performance. The maximum fuel cell performance was observed at 5M methanol concentration.

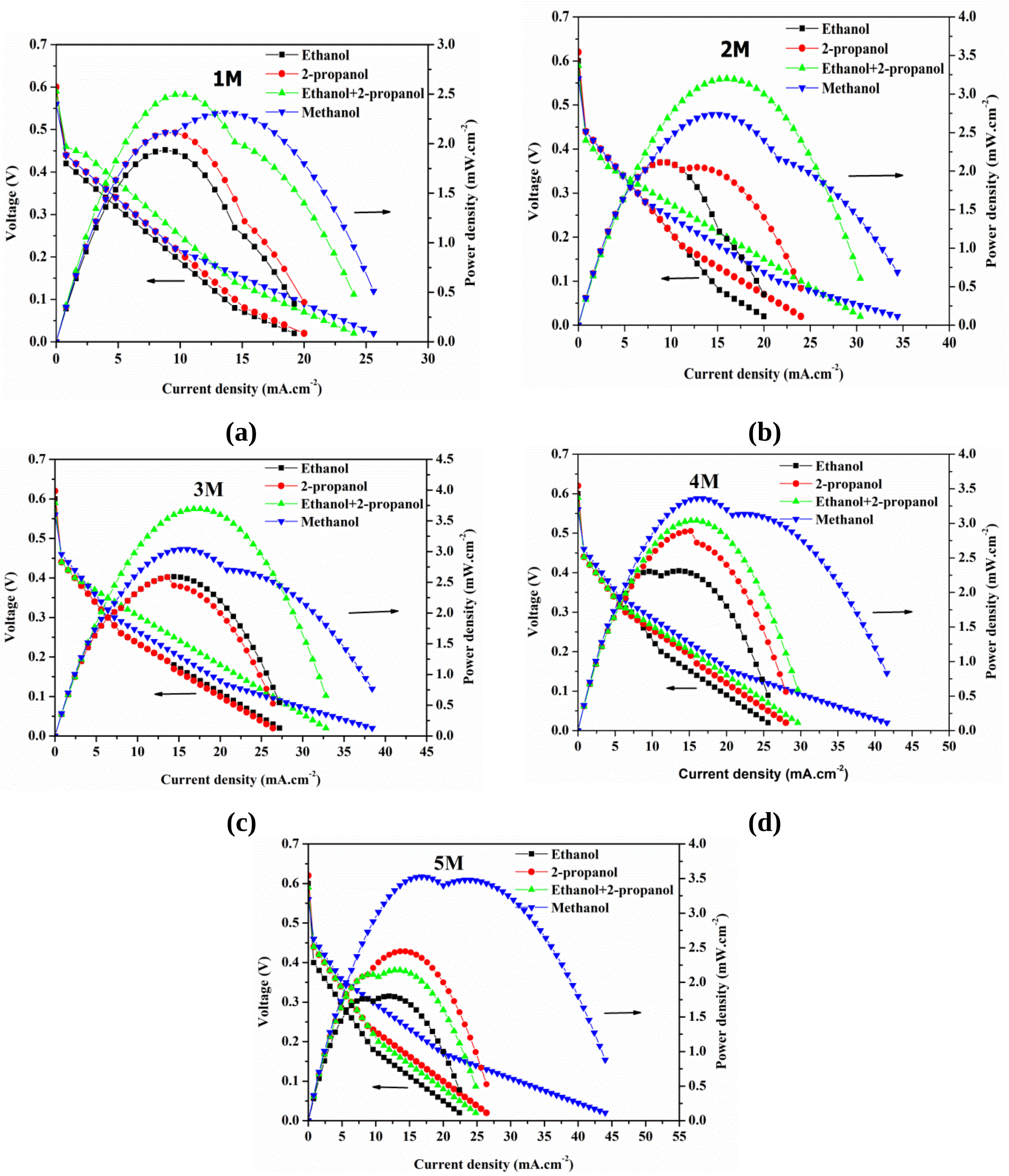

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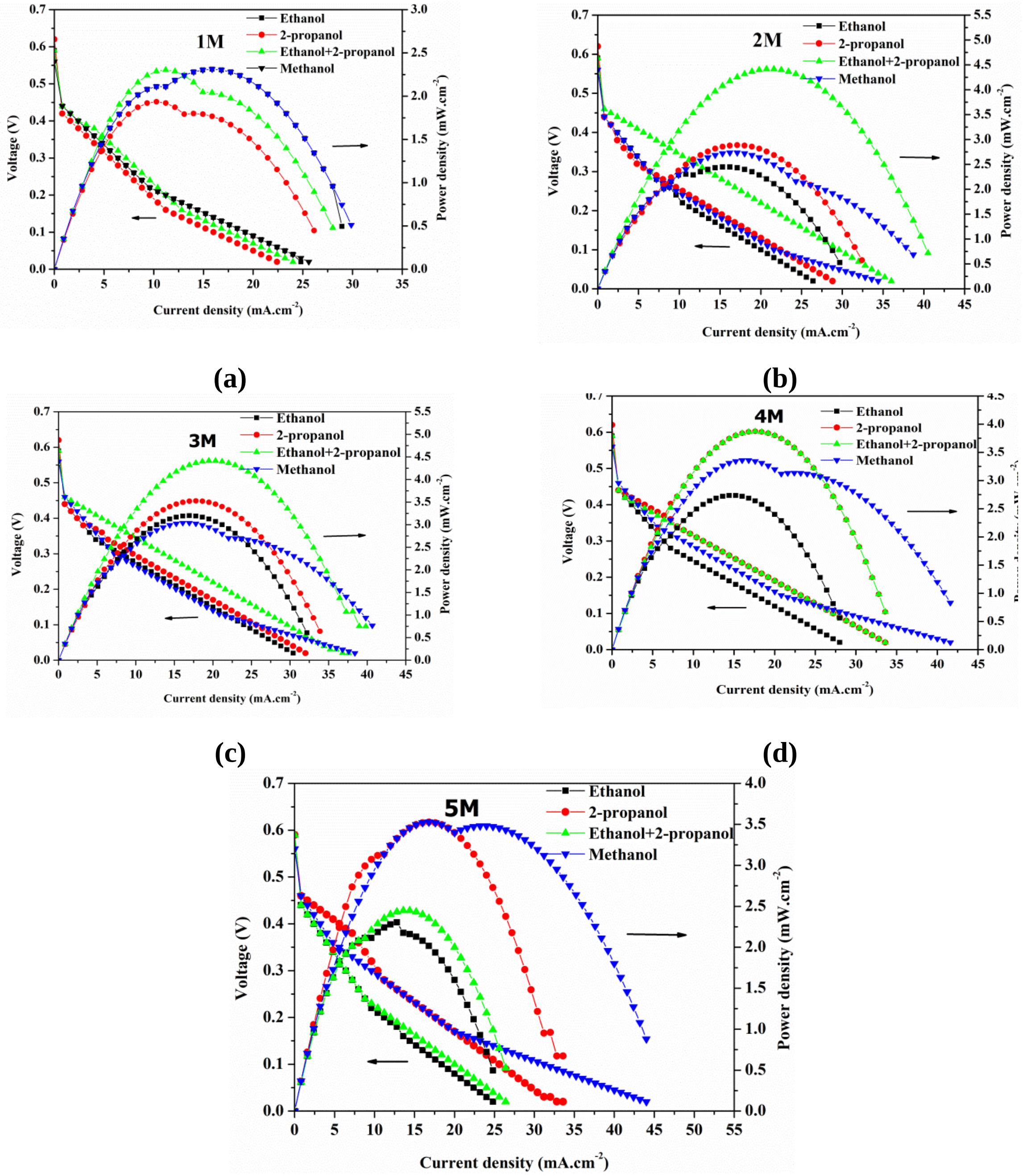
Fig.8.6 (a-e) Polarization curves of the fuel cell with the fuel additives at 1.0 M concentration and at different methanol concentrations in the range of 1M-5M.

Fig.8.6 (a-e) shows the polarization curves with different fuel additives at 1.0 M concentration being added to methanol, and the methanol concentration was varied in the range of 1M-5M. In the lower methanol concentrations up to 3M, ethanol+2-propanol fuel additive is giving better fuel cell performance. As explained earlier the enhanced electrochemical reaction kinetics associated with 2-propanol may be responsible for this. At higher methanol concentrations from 4M-5M, the fuel cell with pure methanol as the anodic fuel produced higher power density.



(a) (b)

(c) (d)

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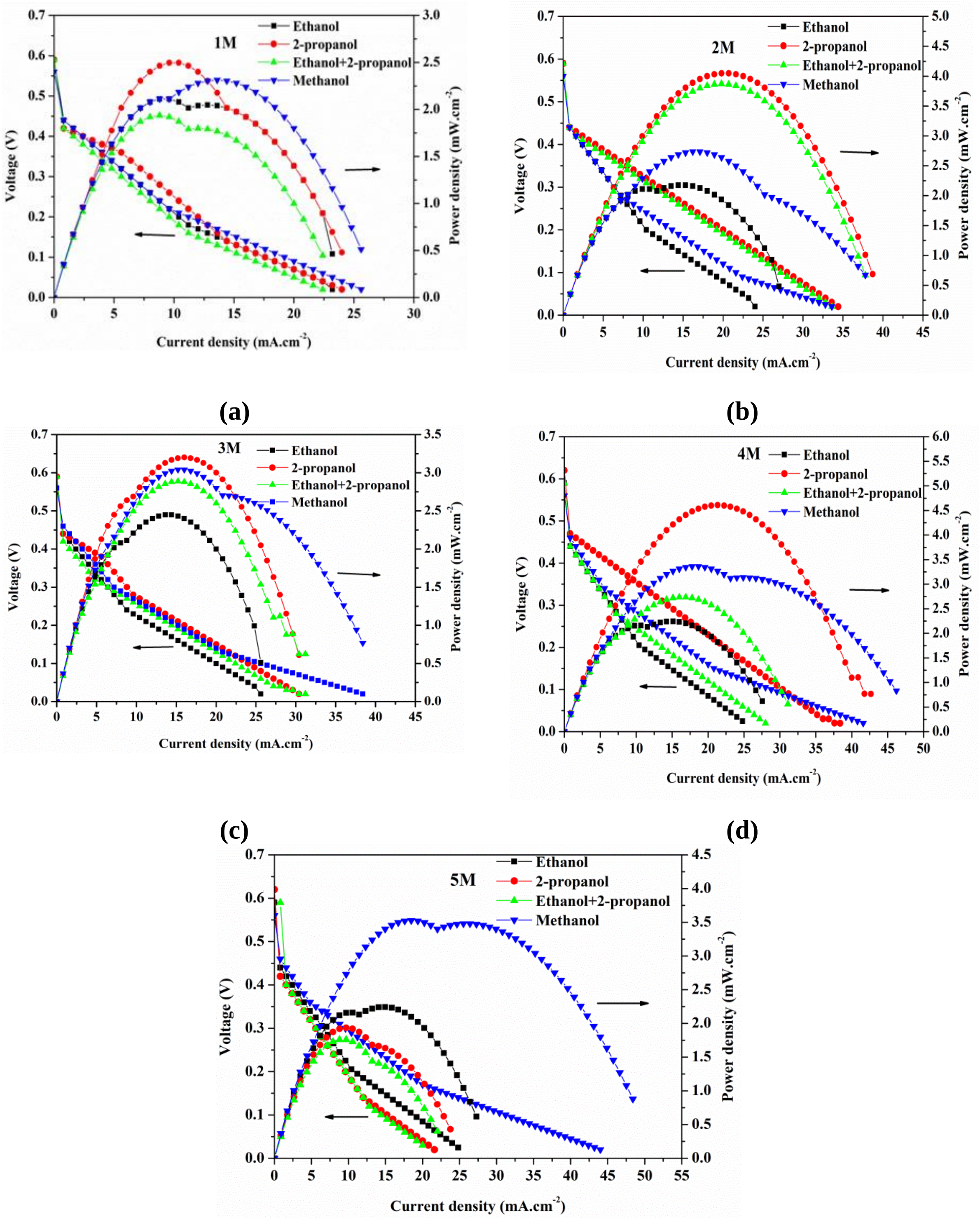
Fig.8.7 (a-e) Polarization curves of the fuel cell with the fuel additives at 1.5 M concentration and at different methanol concentrations in the range of 1M-5M.

Fig.8.7 (a-e) illustrates the polarization curves of the different fuel additives at 1.5M concentration added to methanol, and the methanol concentration was varied from 1M to 5M. Ethanol+2-propanol additive is giving better fuel cell performance from 1M-4M of methanol concentration. At 5M methanol concentration, pure methanol is giving the highest performance.



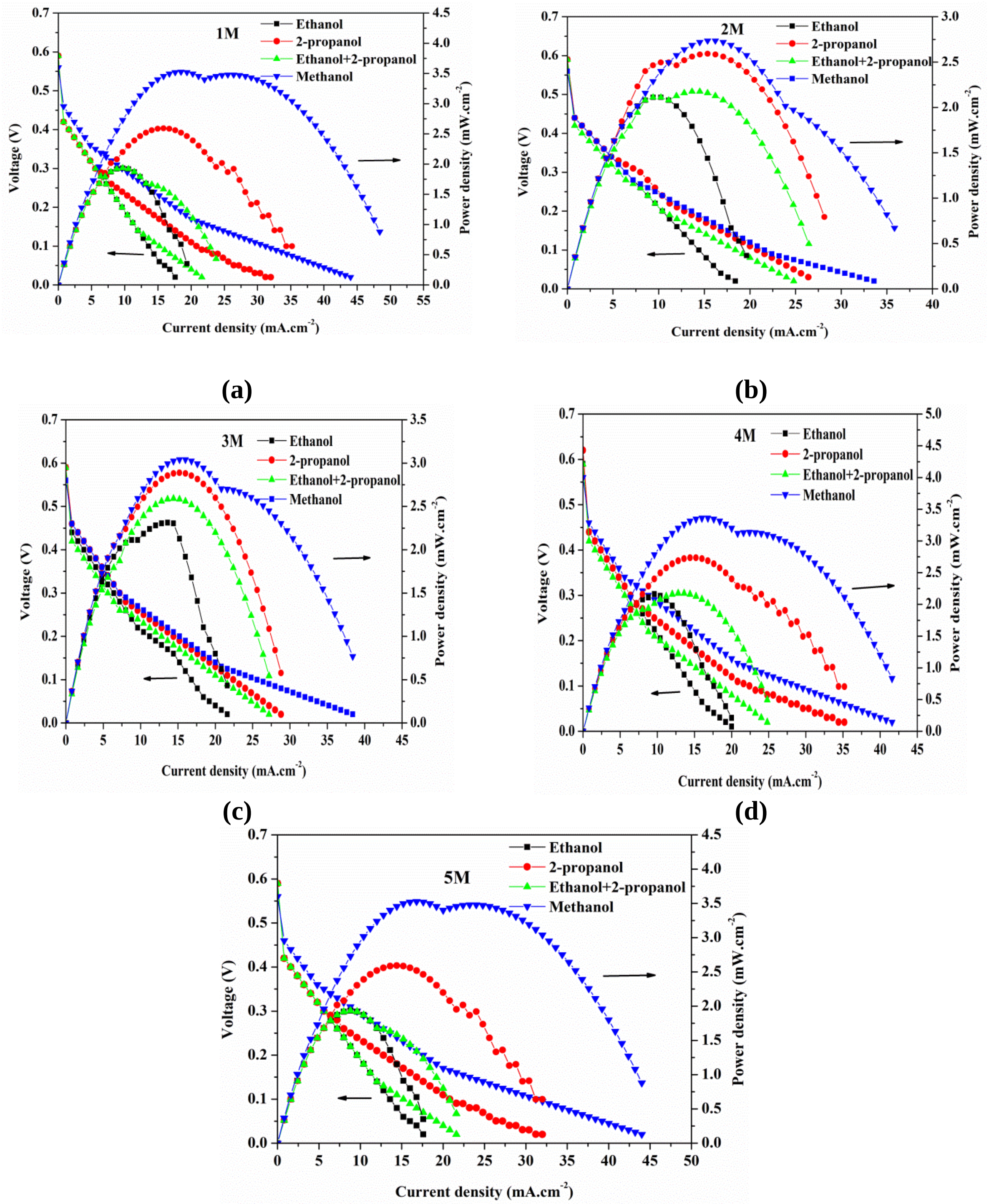
(a) (b)

(c) (d)

(e)

Fig.8.8 (a-e) Polarization curves of the fuel cell with the fuel additives at 2.0 M concentration and at different methanol concentrations in the range of 1M-5M.

The polarization curves of the 2M concentration fuel additive to methanol fuel in the range of 1M-5M are shown in Fig.8.8 (a-e).The maximum power density was produced by the 2-propanol additive fuel cell in the range of 1M-4M. At 5M methanol concentration, pure methanol fuel cell gave better performance.



(a)

(b)

(c)

(d)

Fig.8.9 (a-e) Polarization curves of the fuel cell with the fuel additives at 2.5 M concentration and at different methanol concentrations in the range of 1M-5M.

The polarization curves of the fuel additives at 2.5M concentration to methanol fuel is shown in Fig.8.9 (a-e). At 1M methanol concentration, 2-propanol fuel produced higher maximum power density. From 2M-5M methanol concentrations, pure methanol fuel cell produced the highest maximum power density.

Table.8.6 Maximum power density (mW.cm^{-2}) values at 0.5M concentration of the fuel additive

Methanol concentration/Fuel additive	**1M**	**2M**	**3M**	**4M**	**5M**
Ethanol	1.76	2.112	2.112	1.98	1.6
2-Propanol	1.6	1.936	1.936	2.112	1.936
Ethanol+2-Propanol	1.6	1.936	2.048	1.936	1.6
Methanol	2.312	2.736	3.04	3.36	**3.528**

At 0.5M of fuel additive, the pure methanol fuel cell has the highest MPD compared to the other three fuel additives.

Table.8.7Maximum power density (mW.cm^{-2}) values at 1M concentration of the fuel additive

Methanol concentration/Fuel additive	**1M**	**2M**	**3M**	**4M**	**5M**
Ethanol	1.936	2.112	2.592	2.312	1.8
2-Propanol	2.112	2.112	2.584	2.888	2.448
Ethanol+2-Propanol	2.496	3.2	**3.696**	3.04	2.176
Methanol	2.312	2.736	3.04	3.36	**3.528**

At 1M concentration of the fuel additive, the fuel cell with ethanol+2-Propanol additive fuel produced the highest MPD up to 4M of methanol concentration. However, at 5M of methanol concentration, pure methanol fuel cell gave better performance. It can also be observed that the highest MPD is with 3M methanol concentration and not at 5M methanol concentration.

Table.8.8Maximum power density (mW.cm^{-2}) values at 1.5M concentration of the fuel additive

Methanol concentration/Fuel additive	**1M**	**2M**	**3M**	**4M**	**5M**
Ethanol	2.312	2.448	3.2	2.736	2.304
2-Propanol	1.936	2.888	3.528	3.872	3.528
Ethanol+2-Propanol	2.304	4.4	4.416	3.870	2.448
Methanol	2.312	2.736	3.04	3.36	3.528

At 1.5M concentration of the fuel additive, ethanol+2-Propanol fuel additive produced the maximum MPD at 3M of methanol concentration compared to other fuel additives. However, at 5M of methanol concentration, pure methanol fuel cell gave better performance. It can also be observed that the highest MPD is with 3M methanol concentration, and not at 5M methanol concentration.

Table.8.9 Maximum power density (mW.cm^{-2}) values at 2M concentration of the fuel additive

Methanol concentration/Fuel additive	**1M**	**2M**	**3M**	**4M**	**5M**
Ethanol	2.112	2.176	2.448	2.244	2.244
2-Propanol	**2.496**	**4.048**	**3.2**	**4.608**	1.936
Ethanol+2-Propanol	1.936	3.872	2.888	2.736	1.76
Methanol	2.312	2.736	3.04	3.36	**3.528**

At 2M concentration of the fuel additive, 2-Propanol fuel additive produced the maximum MPD from 1M-4M of methanol concentration. However, at 5M methanol concentration, pure methanol fuel gave better fuel cell performance. It can also be observed that the highest MPD is with 4M methanol concentration and not at 5M methanol concentration.

Table.8.10 Maximum power density (mW.cm^{-2}) values at 2.5M concentration of the fuel additive

Methanol concentration/Fuel additive	**1M**	**2M**	**3M**	**4M**	**5M**
Ethanol	1.76	2.112	2.312	2.16	1.936
2-Propanol	1.936	2.592	2.888	2.736	2.592
Ethanol+2-Propanol	1.76	2.176	2.592	2.176	1.936
Methanol	**2.312**	**2.736**	**3.04**	**3.36**	**3.528**

At 2.5M concentration of the fuel additive, pure methanol fuel cell gave better performance for all concentrations of methanol from 1M to 5M and the highest MPD is produced with 5M concentration of methanol.

From the tables 8.6 to 8.10, it is observed that the maximum power density is produced by 2-propanol fuel additive at 2M of concentration and 4M methanol concentration, and is of value

4.608 mW.cm^{-2}. It can be explained that 2-propanol fuel results in enhanced reaction kinetics, and thus produce more heat. This produced heat increases the fuel cell temperature. Increased cell temperature again enhances the reaction kinetics. Mostly, an ethanol fuel additive is given the lowest fuel cell performance. At higher current density regions, the voltage drop is higher in 2-propanol fuel. These results indicate that in the higher current density regions poisoning of catalyst is higher. Due to this accumulated catalyst particles on the reaction sites the resistance to the mass transfer of fuel from the anode reservoir to the reaction sites increases and the reaction rate deteriorates. This should be avoided by periodical cleaning of the catalyst. At higher fuel additive concentrations in methanol fuel i.e., 2.5M concentration of the additives, increased CO_2 bubble formation occurs on the anode side. These produced bubbles offer resistance for mass transfer. That is the reason why at 2.5M concentration of the additives, pure methanol fuel cell is giving better performance for all the methanol concentrations.

8.1.3 Summary

This present experimental work deals about the performance evaluation of a passive alcoholic fuel cell with different alcohols, and alcohol additives to methanol as the anodic fuels, i.e., ethanol,1-propanol,2-propanol and methanol as the single alcoholic fuels, and also with ethanol, ethanol+2-propanol and 2-propanol as the fuel additives to methanol. When used as the single fuel, the individual alcohol fuel concentration was varied from 0.5M-5M, and when used as fuel additives, the concentration of the additives was varied from 0.5M-2.5M. For each fuel additive, the methanol concentration varied from 1M-5M. From the present study, the following conclusions are drawn:

- Among the four alcohols used as the anodic fuels, 2-propanol was giving better fuel cell performance compared to the other alcoholic fuels. The maximum power density produced by 2-propanol fuel cell is 4.416mW.cm^{-2} at 4M of concentration.
- The 1-propanol fuel cell produced the lowest power density compared to the other anodic fuels.
- The alcoholic additives clubbed with methanol as the fuel has a positive effect on the fuel cell performance.
- In the present of experimentation with all the fuel additives, 2-propanol additive produced the maximum power density at 2M concentration added to 4M methanol concentration.

Chapter 9

9.1 Conclusions

DMFC is becoming to be the most widely used fuel cell for small capacity portable applications. Different techniques are being employed to improve the performance of the DMFC. The present work deals with the performance evaluation of a Passive DMFC and the influence of Liquid electrolyte (LE) layer thickness at various inlet methanol concentrations ranging from 1M to 12M.Three different LE layer thicknesses of 1.5mm, 2mm and 2.5mm were considered. Experiments were also carried out to evaluate the effect of single layer and two layers of anode catalyst. Thus, four different combinations of MEAs were fabricated and the performance of the passive DMFC was evaluated with these four MEAs. Similarly, the effect of the open ratio of the perforated current collector (PCC) on the performance of the DMFC was studied by conducting experiments with PCCs of three different open ratios (45.40%, 55.40% and 63.05%). Experiments were also carried out to study the effect of combined perforated current collector and wire mesh current collector (WMCC) on the performance of the DMFC. Nine different combinations of current collectors made of three PCCs (OR of 45.40%, 55.40% and 63.05%) and two WMCCs (OR of 38.70 and 45.40%) were considered. Finally, the performance of the fuel cell was evaluated with different anodic alcoholic fuels such as ethanol, 1-propanol, 2-propanol, methanol, and the additives of these alcohols to methanol. From the present experimental study, the following conclusions are drawn:

- Methanol concentration has a significant influence on the performance of the conventional passive DMFC. As the methanol concentration is increased from 1M to 5M, the cell performance increased and reached a peak value at 5M concentration, and further increase in the methanol concentration to 6M, decreased the cell performance. The MPD and MCD of the conventional DMFC at 5M methanol concentration were 3.04 mW cm^{-2} and 29.6 mA cm^{-2} respectively for the DMFC fitted with PCC of 45.40% open ratio.
- The modification of the MEA by incorporating the liquid electrolyte layer has a significant effect on the cell performance. The optimum liquid electrolyte layer thickness which gives the best cell performance was found to be a function of the methanol concentration and not the same for all the methanol concentrations. In the range of 1M to 5M methanol concentrations, 2mm thick LE layer gave the best cell

performance, while in the range of 7M to 12M methanol concentration, 2.5mm thick LE layer gave the best cell performance.

- In the entire range of experimentation covering methanol concentrations of 1M to 12M and among the three LE layer thicknesses of 1.5mm, 2mm and 2.5mm, the LE-DMFC with 2 mm thick layer gave the best performance at 5M methanol concentration. The corresponding MPD and MCD are 3.872 mW.cm^{-2} and 33.6 mA.cm^{-2}, which are around 30.71% and 13.51% greater than the corresponding C-DMFC (i.e., no liquid electrolyte layer) values respectively.
- It was observed that throughout the range of methanol concentrations from 1M to 12M, the cell incorporated with the MEA having two layers of anode catalyst support along with the liquid electrolyte layer-MEA-4) exhibited the best fuel cell performance. The lowest performance was obtained for the conventional fuel cell which incorporated a single layer of anode catalyst and no liquid electrolyte layer - MEA-1). It was attributed that the highest performance of the cell with MEA-4 was due to the enhanced reaction kinetics and reduced methanol crossover.
- In the present range of experimentation of methanol concentration from 1M to 5M, the perforated current collector with 45.40% open ratio gave the best performance at 5M methanol concentration; while the current collector with 55.40% open ratio gave the best performance at 3M methanol concentration, and the current collector with 65.03% open ratio gave the best performance at 4M methanol concentration. In the total range of experimentation, the optimum molar concentration and open ratio of current collector are 3M and 55.40% respectively, which gave the best cell performance.
- In between the two wire mesh current collectors, the WMCC with 38.70% OR incorporated current collector combination gave better performance with all the three PCCs (of different open ratios).
- Among the nine combinations of the current collectors, the M1 type current collector combination (PCC of 55.40% and WMCC of 38.70%) incorporated fuel cell exhibited the highest performance, and the P3 type current collector (having only the PCC of 65.03% OR) incorporated fuel cell gave the lowest performance. The maximum current densities and maximum power densities produced by M1 and P3 are 59.2 mA.cm^{-2}, 32.8 mA.cm^{-2}, 6.084 mW.cm^{-2} and 2.304 mW.cm^{-2} respectively.

- Among the four alcohols used as the anodic fuels, 2-propanol was giving better fuel cell performance compared to the other alcoholic fuels. The maximum power density produced by 2-propanol fuel cell is 4.416mW.cm^{-2} at 4M of concentration.
- In the present of experimentation with all the fuel additives, 2-propanol additive produced the maximum power density at 2M concentration added to 4M methanol concentration.

9.2 Contributions

The present work includes design and fabrication of a passive direct methanol fuel cell with an active area of 25 cm^2. The important components of the passive DMFC are current collectors, membrane electrode assemblies and end plates on the anode and cathode sides. The perforated current collectors on the anode and cathode sides allow the methanol fuel and cathode oxidant in to the reaction sites. In this work, the current collector open ratio was optimized by conducting experiments over a range of open ratios. Methanol crossover (MCO) is a major reason for deterioration of the fuel cell performance. MCO can be reduced by incorporating a liquid electrolyte layer. The liquid electrolyte layer thickness was optimized by conducting experiments of three different thicknesses. Catalyst supports enhance the anode reaction rate. In the present work, carbon black was used as the anode catalyst support instead of carbon. Similarly, the effect of incorporating a wire mesh current collector between PCC and MEA on the cell performance was evaluated, by conducting experiments with mesh collectors of two different open ratios. Finally, the effect of alcohol additives along with methanol as the fuel to enhance the fuel cell performance was studied.

9.3 Limitations

The passive DMFC has lower power outputs compared to other fuel cells. This is due to the characteristic chemical kinetics of the methanol fuel cell. Some of the limitations are listed below:

- Reduced mass transfer to the reaction sites.
- Slower anode kinetic reaction rate.
- Lower power out puts.

9.4 Recommendations

- In the present study on the anode side, Pt-Ru bimetallic catalyst was used. Because of Ruthenium, reaction kinetics is very slow. To get higher reaction kinetics, it would be desirable to select a better bimetallic catalyst with Pt.
- One of the problems with methanol is that smaller amounts of methanol fuel reaches to the anode catalyst. This is because the methanol flow inside the cell takes place by diffusion process. The mass transfer rate of methanol can be enhanced by the incorporation of natural circulation fuel feed system through flow field plates.

9.5 Novelty of the present work

The present work aims at improving the performance of a passive Direct Methanol Fuel Cell by employing different techniques. Incorporation of liquid electrolyte layer in between the two half MEAs, optimization of thickness and open ratio of the current collector, incorporation of wire mesh current collectors, addition of two layer anode side catalyst support carbon black have contributed to substantial improvement in the performance of the passive DMFC.

9.6 Future scope

- To study the effect of multiple membranes instead of single membrane inside the MEA on the methanol crossover and cell performance.
- To evaluate the effect of solid methanol instead of liquid methanol as the anodic fuel on the performance of the fuel cell and the mass transfer losses.
- The MEA of fuel cell other than Nafion membrane can be explored to reduce cost of fuel cell.

Appendix-I

Uncertainty analysis

Experimental studies require performing uncertainty analysis to investigate the usual propagation of errors in the instrumentation. Each voltage value is measured three times to obtain more precise values at the same current density, and the mean values are taken for the analysis. The sample mean is expressed as:

$$X_{avg} = \frac{1}{n}\sum_{i=1}^{n} X_i$$

Where, X_i: individual measurement; X_{avg}: average of the measurement; and n: number of measurements.

Uncertainty in the measured experimental data is evaluated from standard deviation and is expressed as:

$$\sigma = U_x = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{avg})^2}{n-1}}$$

Where Ux: uncertainty of the measurement (x_i)

For the current density of 12 $mA.cm^{-2}$ for 45.40% open ratio current collector at 2M methanol concentration.

X_1=0.187 V, X_2=0.19 V and X_3=0.193 V

Measured uncertainty U_x=0.2%

Appendix-II

Cost details of the passive DMFC

The passive DMFC consists of anode end plate, cathode end plate, MEA and the current collectors. Among all these components the MEA is the heart of the cell. At present Nafion 117 used in the MEA is little bit expensive. Once this technology is matured and produced on mass scale, the MEA may be available at a cheaper price.

Cost details of the Passive DMFC

Name of the component	**Cost in Rs.**
Anode end plate (Acrylic)	500.00
Cathode end plate (Acrylic)	500.00
MEA (Nafion 117)	6000.00
Current collectors (SS316L) (Anode + cathode)	1500.00
Total cost	8500.00

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Publications:

S. No	Name of the journal	Paper title	Remarks Index
1	International journal of green energy (Taylor and Francis)	Influence of intermediate Liquid Electrolyte Layer on the performance of Passive Direct Methanol Fuel cell (DOI: https://doi.org/10.1080/15435075.2019.1671419)	Published (SCI)
2	Chemical papers (Springer)	Experimental investigations on the effect of current collector open ratio on the Performance of a Passive Direct Methanol Fuel Cell with liquid electrolyte layer (Published in online version, DOI: 10.1007/s11696-020-01277-0.)	Published (SCI)
3	Chinese Journal of Chemical Engineering (Elseveir)	Performance evaluation of the incorporation of different wire meshes in between perforated current collectors and Membrane electrode assembly on the Passive Direct Methanol Fuel Cell. (DOI: https://doi.org/10.1016/j.cjche.2020.07.038)	Accepted (SCI)
4	Asia-pacific journal of chemical engineering (Wiley)	Performance evaluation of an Air Breathing –Direct methanol fuel cell with different cathode current collectors with liquid electrolyte layer. (DOI: 10.1002/apj.2465)	Published (SCI)
5	Chemical Product and Process Modeling (Degruter)	Effect of Anode Diffusion Layer thickness and porosity on the Performance of Passive Direct Methanol Fuel cell. (DOI: http://sci-hub.tw/10.1515/cppm-2019-0029)	Published (Scopus/E SCI)
6	Korean journal of chemical engineering(Springer)	Experimental analysis of a two-cell Passive direct methanol fuel cell stack	Minor revision submitted (SCI)
7	Environmental progress and sustainable energy (Wiley)	Comparison of the anode side catalyst supports with incorporation of liquid electrolyte layer on the performance of a Passive Direct Methanol Fuel cell	Under Review (SCI)

Conferences

S. No	National/International	Name of the conference	Paper title	Place held
1	International	New Frontiers in Chemical, Energy and Environmental Engineering	Performance evaluation of an Air Breathing –Direct methanol fuel cell with different cathode current collectors	NIT Warangal, India.