Experimental investigation of a natural circulation fuel delivery system on the performance of an air breathing direct methanol fuel cell with liquid electrolyte layer

SATEESH KUMAR MANUPATI[1,*] , NAGA SRINIVASULU GOLAGANI[1] and
SRINIVASA REDDY BADDURI[2]

[1]Department of Mechanical Engineering, NIT Warangal, Warangal, Telangana 506001, India
[2]Department of Mechanical Engineering, KITS Warangal, Warangal, Telangana 506015 , India
e-mail: satyamanunitw@gmail.com

Abstract. Direct methanol fuel cells (DMFC) has proven to be the most promising option for charging portable electronic devices. The performance of a DMFC depends mainly on methanol crossover (MCO) and elimination the pumping power to pump fuel greatly enhances cell performance. Hence, the current study is aimed at achieving two objectives: delivery of fuel without any parasitic power consumption (losses) and reduction of MCO; the performance of a DMFC was analyzed experimentally at different operating conditions. To pump the fuel without any external power source, the inherently developed CO_2 bubbles at the anodic flow channel were utilized. In other words, byproduct of the fuel cell reactions provided the required power for pumping and hence the requirement of an external pump was eliminated. The effect of the working parameters such as reactants 'methanol concentrations, flow rates and incorporation of liquid electrolyte (LE) between two half membrane electrode assemblies was examined on the performance of DMFC. It is observed that the incorporation of LE between two half Membrane Electrode Assembly (MEAs) electrolyte assemblies reduced the MCO in an LE-DMFC and better performance was reported when compared to conventional DMFC, at an optimal flow rate of 2 ml/min with 3M methanol concentration. Further, the effect of methanol concentration and flow rates on the cell performance is also compared and analyzed. The better performance was achieved in a conventional DMFC (8.09 mW/cm^2). The corresponding LE maximum power is 8.8 mW/cm^2, which is 9.14% higher in comparison with conventional DMFC value. The piled hydrophilic LE layer thickness of 1.5 mm and H_2SO_4 (diluted sulfuric acid) is used as LE layer and electrolyte respectively.

Keywords. Natural circulation; liquid electrolyte; methanol flow rate; methanol concentration; CO_2 clogging.

1. Introduction

Due to imprudent energy usage, the world is currently facing an alarming threat over increased number of electronic devices. As portable electronic devices become more and more popular, their energy levels are increasing at an alarming rate. In this regard, fuel cell technology is the front runner due to its enormous potential to convert chemical energy directly into electricity [1]. The concept of direct methanol fuel cell (DMFCs) is derived from the Polymer Electrode Membrane (PEM), and is a subset of PEM fuel cell. Gaseous hydrogen is replaced with liquid methanol. While it has some advantages, it also has some disadvantages, including transport issues, bulky storage requirements and very high flammability. Compared to hydrogen gas, methanol has a higher energy density, is denser, and requires less storage space. DMFCs are considered to be highly promising renewable energy sources for stationary and portable applications. This technique is an innovative way to generate small-scale electricity using direct methanol fuel cells (DMFC) used in cell phones, laptop computers, MP3 players LCD-TVs, digital cameras, and autonomous devices [2]. Despite this DMFC development has encountered serious challenges in accommodating all the necessary components. These includes fuel delivery, air delivery, membrane electrode assembly (MEA), component interconnections, and system assembly, as well as elimination of CO_2 bubbles in natural convection.

A conventional method of eliminating CO_2 bubbles fuel cells are pumped with CO_2 bubbles along with fuel into fuel reservoirs [3]. Consequently, the gas separates from the liquid due to buoyancy and is delivered in to the atmosphere. Such orientation-dependent liquid separation

processes in portable devices are prone to liquid drain. In DMFCs, CO_2 gas bubbles pose serious clogging issue due to the anode channel's enhanced surface tension force, caused by scaling. When a DMFC channel becomes blocked, it reduces the effective mass-transfer area, which results in a reduction in performance. To remove the bubbles, the pump requires considerable parasitic power. Gas bubbles formation in the anodic channels may also significantly increase pressure and worsen methanol crossover (MCO) effects. In contrast, a natural circulation feed flow rate increases with an increase in current density, and is also unsteady at low current densities [4].

For the active and precise delivery of methanol fuel to DMFCs, various pumps have been proposed. In addition to the packaging penalty for the discrete pump, the power loss from the pump is the most significant disadvantage of passive fuel delivery of fuel cells. Fuel can be delivered without power-consuming components by a pressurized fuel reservoir, though the fuel cannot be recirculated and recycled. It is also important to control the pressure at the anodic channels to eliminate unexpected methanol crossover. Additionally, several technologies have been investigated for passively delivering methanol to an anodic chamber. Mixing pure methanol and water, delivering it to the reaction chamber can be achieved by diffusion along porous media and surface tension-induced transportation. However, passive fuel delivery methods are ineffective at agitating and controlling fuel concentration in situ at the reaction chamber. Although a suggestion has been made that DMFC systems could be powered by the anode's byproduct.

Furthermore, a buoyancy force - based natural convection results in the delivery of fuel without any energy consumption. In addition natural circulation also increases the energy density and power density [5]. It is possible to automatically regulate power generation by supplying an external load with reaction-generated gas bubbles. Increasing the load leads to faster electrochemical reaction thus generating a higher electrical current. In this way, CO_2 bubbles are created at a higher pace and the fuel is circulated faster. Surface tension will most likely prevail over buoyancy in a channel (i.e., bubble clogging). This technology is used to develop a novel channel structure that provides directional growth and gas venting for liquid pumping [6].

Methanol solution is initially injected into all parts of the flow field, including flow field channel, inlet and outlet tubes and fuel tank, During DMFC discharge bubbles of CO_2 gas are produced continuously, which generate liquid-gas mixture in the exit tube and anode flow channel and. A driving force is generated due to the density difference in the liquid methanol solution and the two-phase mixture of the flow loop. Through a vent valve at the top of the fuel tank, CO_2 gas is released from the methanol solution and separated from it, thus flowing downward into the DMFC and upward into the fuel tank.

To distribute liquid fuel with minimal packaging penalties, the natural circulation system structure is integrated to anodic channels of a DMFC. In addition, parasitic energy loss is avoided by discrete micro pumps. A self-regulating control of fuel delivery by external electric load is also supported by intrinsic relationship between the bubble generation rate and pumping rate. Contrary to that, the reported mechanism is independent of orientation since it is not gravity-dependent. The Pumping mechanisms can be embedded in the channel conceptually, without having to use any complex multi-compartment configurations or pistons. Unlike passive fuel delivery approaches, the mechanism reported in this paper uses active pumping, which benefits agitation of the fuel and reaction kinetics in the channel. The embedded natural circulation mechanism uses gas byproduct to eliminate two ancillary components simultaneously, which previously hindered the development of DMFC systems, i.e. the air pump and the fuel pump. As shown in figure 1, this simplifies and integrates the anode side configuration seamlessly.

Additionally, the intrinsically generated methanol crossover in DMFCs is another major challenge that needs to be addressed. As a result of this, fuel waste is produced along with mixed potential. This results in a decrease in voltage output, and the DMFC system displays a noticeable reduction in energy and power density. As of today, PEM technology with low crossovers is far from mature.

Oliveira. V.B *et al* [7] pioneered the study of MEAs with different configurations and coalescences of gas diffusion layer GDL to predict MCO transport across the membrane at high methanol concentrations. They noticed that the DMFCs suffer from electro-osmotic drag and methanol diffusion, respectively, which prevents the use of materials appropriate for gas diffusion layers (carbon paper and cloth at the anode and cathode GDL respectively) on the anode side of high concentrated methanol solutions. Jung *et al* [8] experimentally examined the effect of membrane thickness on passive DMFC performance. In their study, they found that an increase in membrane thickness lowers MCO while increasing ohmic resistance. Kim *et al* [9] analyzed the performance of a single DMFC. They found reduced methanol crossover and a 37.5% performance improvement compared to the reference system at 3.0M methanol concentration. Liu *et al* [10] made membrane electrode assembly with an anode catalyst layer as catalyst diffusion medium (CDM) in addition of hydrophobic microporous layer (MPL) at cathode, to reduce the methanol crossover. They observed that MPL with carbon cloth exhibited lower methanol and water crossover compared to MPL without carbon cloth. Yong *et al* [11] found that the introduction of cathode diffusion layer led to an increase in power stability and mitigated PTFE loading in the backing layer during the continuous fuel cell operation. Kang *et al* [12] conducted an experimental investigation to study the effects of cathode air humidification and hydrophobic anode MPL on methanol crossover. They observed that compared to MEA
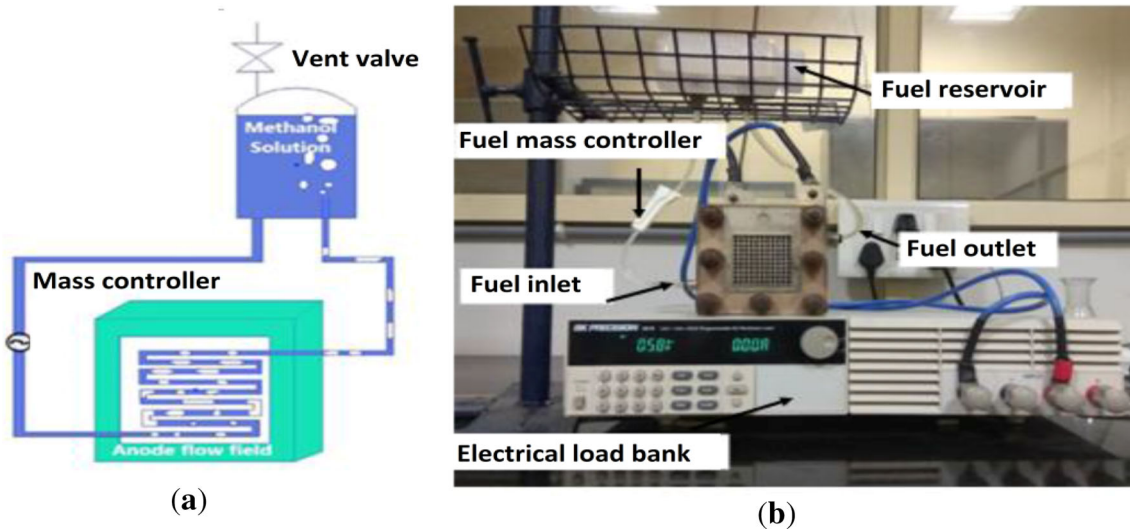
Figure 1. (a) Schematic of complete natural circulation fed system. (b) Photograph of the complete experimental set-up.

without MPL anode, the performance of MEA with the anode did not decline much as methanol concentration increased. Song *et al* [13] designed a novel MEA for lower water and MCO in an air–breathing DMFC. They introduced a microporous layer (MPL) to the cathode backing layer to reduce the thickness of membrane, water crossover and MCO. Liu *et al* [14] analysed the outcomes of variation in membrane thickness (Nafion 112,115,117) at various methanol concentrations. They noticed that the thicker membrane Nafion 112 performed better at lower methanol concentration (2M). Kim *et al* [15] studied the impact of mitigating MCO through the Nafion polymer electrolyte membrane when palladium (Pd) nanophases were added to the membrane in order to enhance DMFC performance. Enhancement in cell performance was reported to be superior at high methanol concentrations because of the phenomenon of Pd-impregnated Nafion membrane compression. Choi *et al* [16] studied the process of plasma etching and palladium sputtering to modify the surface of a Nafion membrane. They noticed that combining plasma etching and palladium sputtering caused a notable reduction in methanol crossover.

In order to minimize the problem of MCO in the performance of DMFC, some of the researchers accomplished the changes in Nafion membranes. The composite polymer materials were shown an excellent substitute to commercial MEAs compared to commercial MEAs with higher methanol concentrations. Kordesch *et al* [17] proposed a new flowing electrolyte (FE) concept to reduce the MCO. Ouellette *et al* [18–20] were experimentally investigated the effects of FE media such as formic acid (CH_2O_2) and sulfuric acid (H_2SO_4). They reported that the addition of FE to active DMFCs resulted in enhanced performance. Colpan et al. [21–23] came out an experimental study by changing the dimensional modeling of flowing electrolyte (FE) to

evaluate the performance characteristic of DMFC. They found an increase in electrical efficiency by 57% where FE-DMFC was used in lieu of DMFC.

For different operating conditions, Kjeang *et al* [24] simulated MCO by convection and diffusion with a 3D numerical computational fluid dynamics (CFD) model. Compared to conventional DMFCs, they identified a reduction of MCO, and also determined that electrolyte channel orientation had a significant impact on methanol crossover. To investigate the effects of channel thickness, volume flux and porous material properties on flow in FE-DMFC, Duivesteyn *et al* [25] simulated porous flowing electrolyte layer. Based on their study, they recommended that thinner electrolyte channels, higher volume flux, and porous materials should be used to optimize performance of cell. Sharghi *et al* [26] evaluated the performance of FE-DMFC (diluted H_2SO_4) along with multiple combinations of Nafion polymer electrolyte membranes (N-212/N-117).

They noticed that the density of power increased when thinner FE channel was decreased at 2M methanol concentration. Similarly Adan *et al* [27] explored the effect of sulfonated polysulfone/Zirconium hydrogen phosphate composite membrane performance on Nafion 115 membrane. They showed that the composite membranes produced 13% more performance than Nafion115 membrane in a DMFC. Ahmad *et al* [28] analyzed new organic-inorganic hybrid membranes of various different compositions ZP-PBI (zirconium phosphate (ZP) and polybenzimidazole (PBI)). They concluded that the Nafion-PBI 1% -ZP 1% produced the better performance compared to the commercial Nafion117 membrane. Lee *et al* [29] achieved a reduction in methanol crossover in air breathing DMFC. Their results reported that composite membranes produce greater power densities over Nafion membranes.
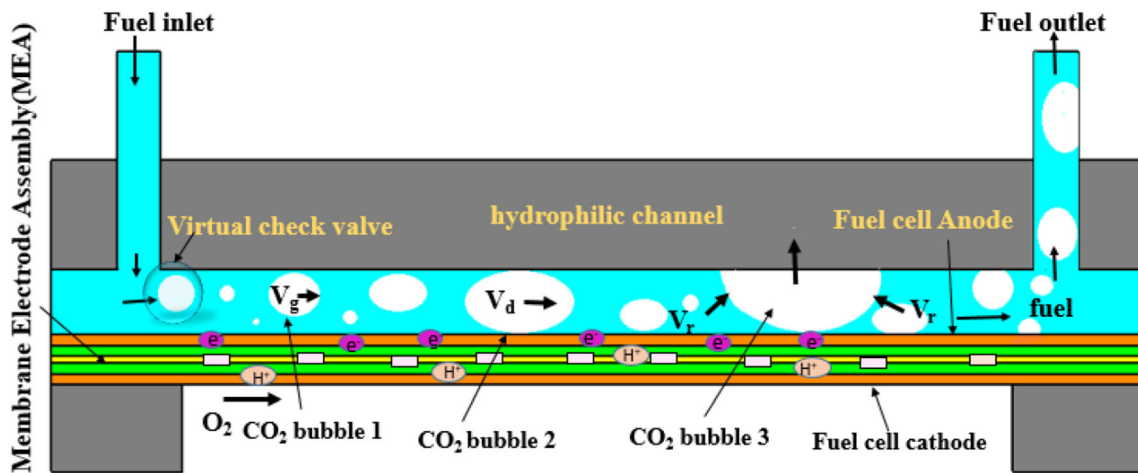
Figure 2. Schematic description of the embedded natural circulation of liquid fuel by intrinsic CO_2 bubbles.

Helen *et al* [30] was synthesized and characterized a composite membrane containing α-zirconium phosphate and s and sillicotungstic acid to reduce MCO in DMFC. The α-zirconium phosphate and sillicotungstic acid increased the proton conductivity in Nafion115 composite membrane, which and resulted in better performance than commercial Nafion 115 membrane. Yin *et al* [31, 32] numerically evaluated the impact of adding a liquid electrolyte layer (LE) between two half MEAs on DMFC performance. They noticed that the optimized layer thickness of 2 mm significantly reduced methanol crossover in the fuel cell. Boni *et al* [33, 34] investigated the effects of an LE layer by placing two half MEAs between two half MEAs in air-breathing DMFC. Their results concluded that an optimized LE-layer thickness of 2 mm and concentration of 1M LE (H2SO4) mitigated the methanol crossover respectively, and they also found that it enhanced power densities performance compared to the conventional air-breathing DMFC.

Literature survey reveals that the majority of studies are focused on the performance of active fuel delivery systems. Some studies focus on the effect of methanol concentrations, flow rates and deteriorations of MCO in relation to active DMFC performance. Very few studies have worked on a natural circulation fuel delivery system for DMFC and on LE effect on DMFC performance. These studies were aimed at avoiding parasitic consumption of external devices and transferring fuel at the anode with different operating parameters instead of determining the total performance of a single fuel cell. A natural circulation fuel delivery system has been designed to investigate the performance of a natural circulation fuel delivery system under different operating conditions such as electric current density and liquid electrolyte concentration. Using a DMFC model, DMFC performance can also be directly compared to that of LE-DMFC.

2. Working mechanism

Figure 2 illustrates how the natural circulation mechanism works. This natural circulation is caused by the prevailing bubble pumping mechanism [5]. In order to pump bubbles, three major actions must be performed inside a liquid-filled channel. (a) The augmentation of bubbles through a virtual check valve, (b) the dislodgment of bubbles at the hydrophilic-hydrophobic junction and (c) the non-directional discharge of bubbles by a porous membrane.

Consider a channel made of SS material, with its inner surface dampened by liquid (e.g., methanol mixed with water). A dry channel can be automatically primed with liquid by capillary action. In contrast, air is forced into a liquid channel by a positive pressure. The extreme pressure necessary to compress gas into a water-filled channel can be calculated as follows:

$$\Delta P^{max} = \frac{4\sigma}{d} cos\theta_{rec}$$

The surface tension of the liquid-gas interface is σ, the receding contact angle between the liquid on the inner surface of the channel is θ_{rec}, and the hydraulic diameter is *d*. Since the pressure ΔP^{max} is inversely proportional to the size of the channel (*d*). In contrast to bubble intrusion, the entrance to a smaller channel serves as an efficient check valve when liquid is present. Virtual check valve of this type has been used in many different micro devices. In this case, an inlet and outlet are placed on opposite extreme corners of the fuel filled flow channel, and all of this is connected to a fuel reservoir with tubes (silicon). The inlet tube set is placed at the inlet by installing a small regulator (i.e., controller) to regulate the mass to a desired flow before entering the celland the outlet tube set at the outlet, to control fuel flow direction between the hydrophilic channel and hydrophobic membrane as shown in figure 2.

During the fuel cell reaction, the channel necks are pushed in contrast to the air bubbles, which produces CO_2 between the two necks. As a result, the small gas bubble blocks the flow of leftward liquid while allowing rightward liquid to flow forward. If the channel necks are hydrophilic, a virtual check valve is created. Otherwise, CO_2 bubbles will grow into the hydrophilic channel and push liquid fuel towards the rightward with them. Once the bubble touches a hydrophobic channel, an addition rightward displacement is induced by the difference in the surface energy throughout the junction. As long as the bubble generation rate of the hydrophobic membrane is sufficient, any DMFC system will operate with a virtual check valve that periodically allows in fresh fuel. So through the pores of the nanoscale membrane, bubbles are trapped and effectively removed. In this way, by directing bubble growth in the anodic channel and removing non-directional (symmetric) bubbles, there is more efficient directional pumping of the liquid fuel than if the anodic channel is closed, as there is no circulation of fuel. At the fuel outlet, a set of channel necks is equipped to arrest bubbles from accidently entering in to downstream channels and obstructing liquid flow.

3. Experimentation

3.1 *Device fabrication*

The schematic and photograph views of the embedded natural circulating DMFC are shown in figures 3 and 4. In DMFC, there are two anode plates, two cathode plates, two gas diffusion layers and MEA (E-TEK). The anodic and cathodic current collectors are fabricated by wire-cut technique. These plates themselves works as a current collector in the fuel cell. The anodic channel is configured with a single serpentine channel of width 2.0 mm, 2.0 mm depth and 1.0 mm rib. The cathode has uniform perforated circular holes with an open ratio of 45.34%, as shown in figure 4. Both anodic and cathodic plates were fabricated with a thickness of 2 mm stainless steel (SS) 316L material. Transparent poly methyl methacrylate (PMMA) is used for both the anode and cathode end plates to display gas evolution and two-phase transportation within the anode flow field. To make sure adequate electrical contact resistance and to avoid fuel leakage sufficient clamping force was applied. Between the MEA and DMFC components, two silicon rubber and PTFE (polytetrafluoroethylene) gaskets were inserted to distribute the clamping pressure and prevent fractures in end plates.

Anode and cathode current collectors are connected by mean of a porous membrane sandwiched between them and clamped with enough force. A small mechanical manual valve
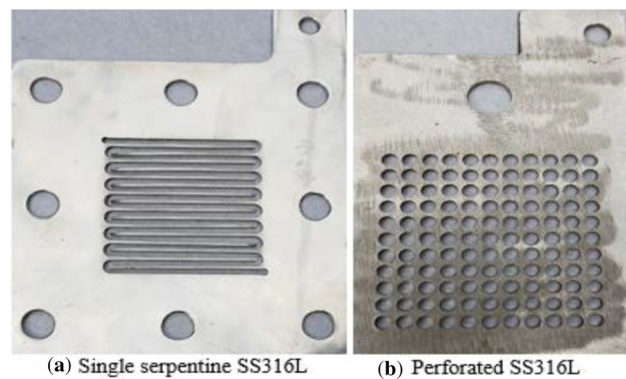

(a) Single serpentine SS316L   **(b)** Perforated SS316L

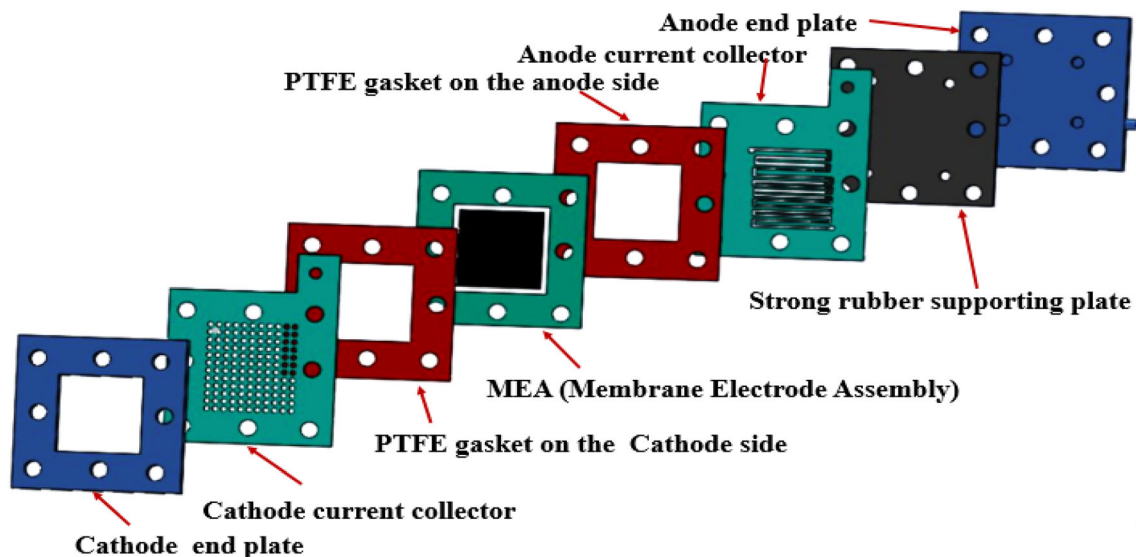**Figure 4.** Photograph of the anode and cathode current collectors.

Figure 3. Exploded view of direct methanol fuel cell.

is attached to the fuel inlet and outlet via a silicon tubing. By removing the bubbles during the fuel operation, a controlled experiment can be performed. By connecting the fuel inlet and outlet directly to the fuel cartridge, flow resistance and bubble clogging can be reduced. This is the result of a fluidic loop that is driven by natural-circulation. The MEA must, however, be charged with diluted methanol fuel and pumped by means of an external pump during the activation process. Using this method, the fuel cartridge serves as an inlet, and the fuel used can be discharged through the fuel outlet. Once MEA is activated, the external pump is turned off.

3.2 *Fabrication and activation of a MEA*

The MEA, an active area of 25 cm^2, was fabricated by hot pressing of Nafion membrane at 135°C and 8 Mpa for
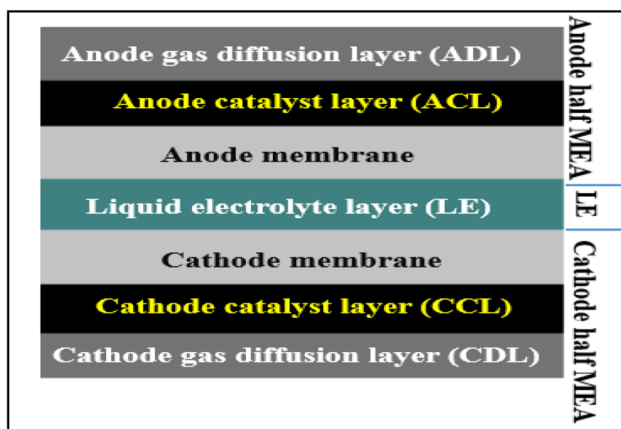
Figure 5. Schematic of LE layer with Half MEAs.

3 min. Before hot pressing of MEA, it was boiled in 3 wt.% of H_2O_2 for 1 hr, and then deionized (DI) water for 1 hr and finally in 0.5 M H_2SO_4 aqueous solution to activate the membrane. In boiled DI water, MEA was further refined to remove organic and inorganic impurities of H_2SO_4 from the Nafion membrane. Layers of carbon cloth were used as anode and cathode backings, with polytetrafluoroethylene (PTFE) coating at 20%. Carbon particles packed at 1 mg/cm^2 and PTFE loaded at 30% were used as microporous diffusion layers on the backing layers. A catalyst ink diffusion layer was applied to the electrodes. In order to prepare catalyst ink, suitable amounts of the catalyst were dispersed in solutions composed of DI water, Nafion solution and isopropyl alcohol. The cathode side catalyst contains 60 wt.% Pt/C with a loading of 2 mg/cm^2, and the anode side catalyst contains 80 wt.% Pt-Ru/C. Hence, this design enables higher hydraulic pressure to be formed so that water can flow from the cathode to anode more freely.

3.3 *Incorporation of liquid electrolyte in DMFC*

In DMFC (C-DMFC), the MEA consists of a single set of elements, this contains a diffusion layer and a catalyst layer along with membrane on both cathode and anode side. However, in incorporation of liquid electrolyte DMFC (LE-DMFC), the LE layer was incorporated between two MEAs and then assembled. In order to fabricate the liquid electrolyte layer, hydrophilic filter papers were piled up and soaked in diluted sulfuric acid solution. Based on the number of papers piled in one pile, the LE layer's thickness can be estimated. In half MEA, the diffusion layers and
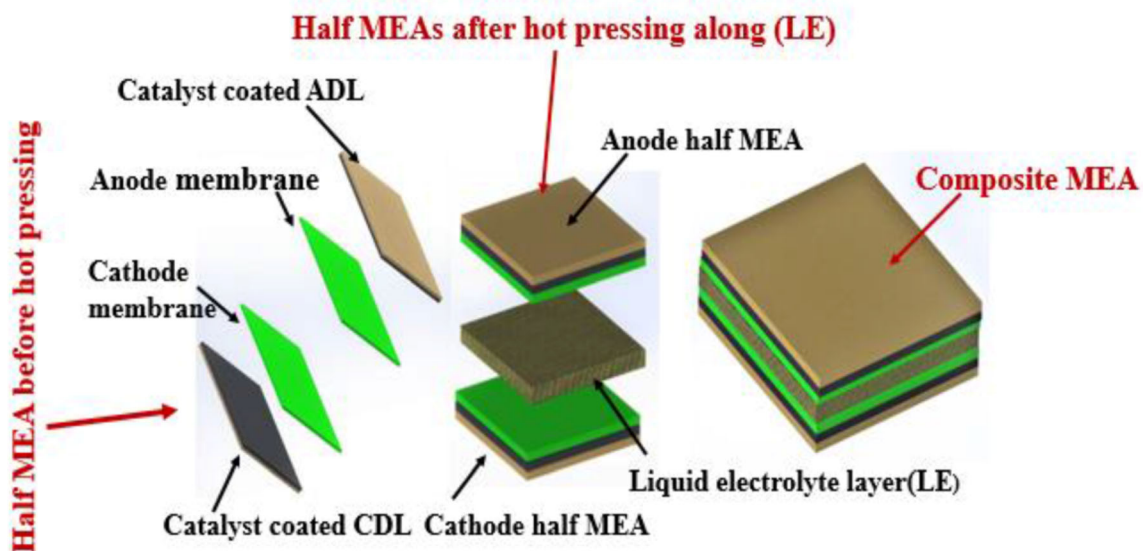

Figure 6. Various steps in fabricating of composite MEA.

catalyst layers are connected by a hot pressing process to the membrane. Figures 5 and 6 show the schematic fabrication of complete LE MEA process, which is also called as composite MEA. After completion, the composite MEA is sandwiched between the components of DMFC by applying a torque of 5 N-m to tighten the entire DMFC as shown in figure 7.

3.4 *Experimental set-up and test conditions*

To measure current and voltage, a direct current 8510 programmable electronic device was used. During the process of obtaining the stable voltage, a time interval of one minute was allowed. An activation period of 12 h was performed with a flow rate of 2 mL/min at a methanol molar concentration of 1 M prior to performing the experiment. Experiments were conducted in a vertical position, with relative humidity of 60–70%.

4. Results and discussions

In this experiment, flow rates in a natural circulation system with methanol concentrations and a LE layer were studied experimentally to determine the impact on DMFC performance. Initial stage of experiments were carried out to analyse the natural circulation. In the second stage, tests were carried out to analyze the influence of flow rates, which has varying from 0.5 ml/min to 5 ml/min at different methanol concentrations (1M–4M). To identifying the effect of flow rates at an adopted methanol concentration, a series of experiments were conducted to identify the optimal flow rate and methanol concentration to achieve better cell performance.

4.1 *Performance comparison of two different feed cells*

When an external device is used, both parasitic energy losses and packaging penalty of the system increases.
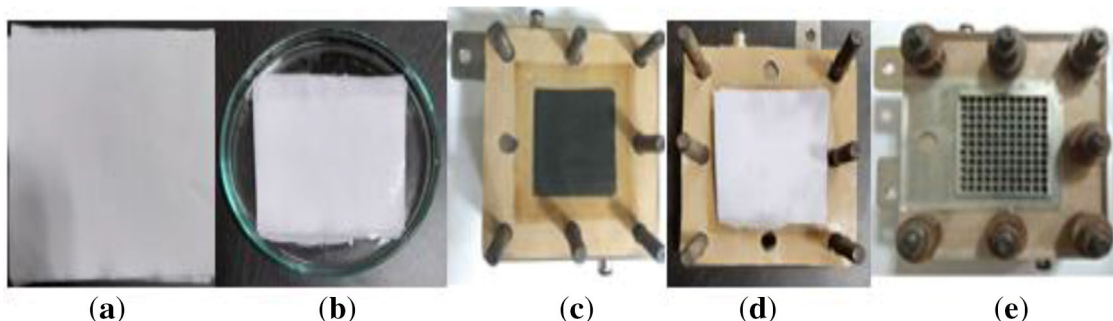

Figure 7. (a) Hydrophilic filter paper (b) Soaking of hydrophilic filter paper in diluted H_2SO_4 solution (c) Anode half MEA with cell (d) Piled hydrophilic filter paper on half MEA (e) Complete assembly of cell.
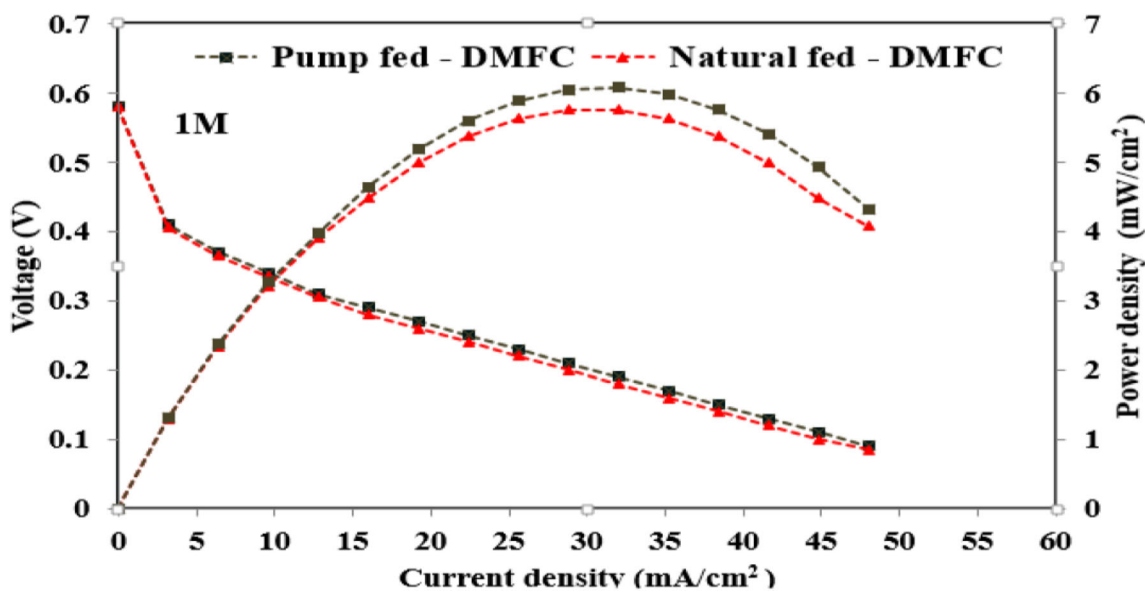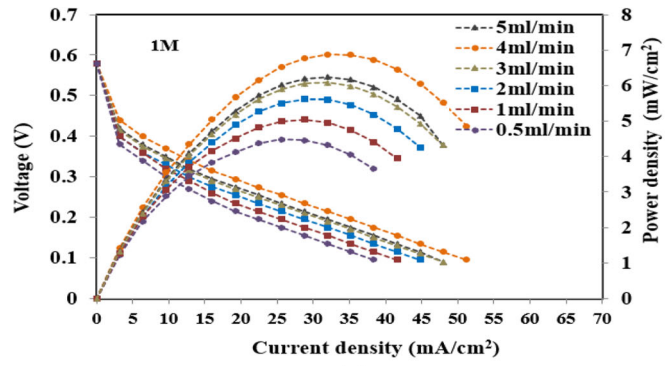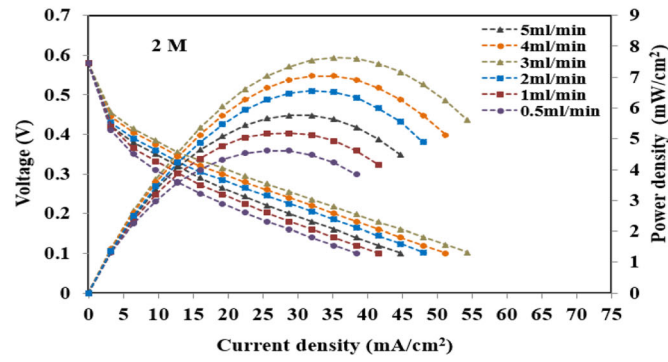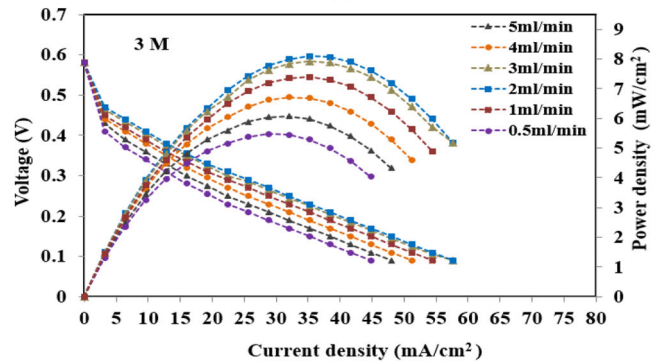

Figure 8. Performance comparison of pump fed-DMFC and natural fed– DMFs at 2 ml/min flow rate.

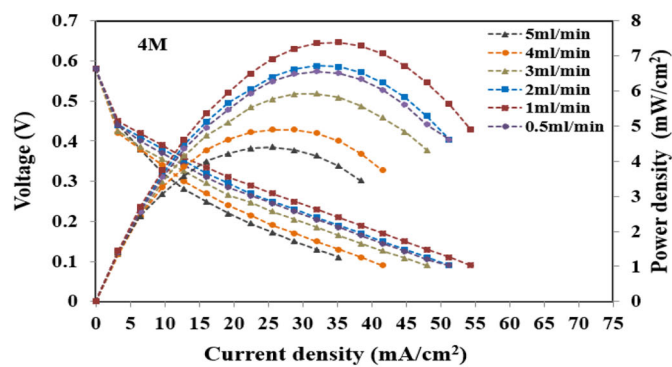**Figure 9.** (a–d) Effect of flow rates on the fuel cell performance at different methanol concentration.

These consequences tend to increase as the size of the system getting decrease, because variation in energy consumption of active components remains same as that of larger systems though the total utilizable energy of the system gets reduced. To overcome this issue, natural circulation fed system is employed. Figure 8 illustrates the performance comparison of 1M methanol concentration solution at 2 ml/min flow rate and a natural circulation fed cell and pump fed fuel cell. It is seen that at lower current densities, the performance of the natural circulation fed cell is almost equal to the pump fed cell. However, at higher current densities, there is a little drop in performance.

4.2 *Effect of methanol flow rates*

Figures 9(a–d) illustrate the performance characteristics of a natural circulation fed DMFC at different flow rates using 1–4 M methanol concentrations. It can be noted that the increased flow rate increases maximum power density. The maximum power density produced by natural circulation fed DMFC with 1 M methanol concentration at 4 ML/min is 6.88 mW/cm^2. Similarly figures 9(b–d) show the performance of natural circulation fed DMFC using 2M, 3M and 4M respectively. The flow rate effect in figure 9(b) is not monotonic, unlike in the case of 1M methanol concentration. At first, the cell performance improved with a rate of flow of 3 ml/min, but as the rate of flow increased to 5 ml/min, the cell performance declined. The maximum density of power of the cell with 2M methanol concentration was 7.55 mW/cm^2. It can be identified from figure 9(c) that for the cell with 3M methanol concentration, the influence of rate of flow on the performance is not monotonous. The cell performance improved with an enhancement in the rate of flow from 0.5 to 2 ml/min, and then degraded on further enhancement in the flow rate from 2 to 5 ml/min. The maximum density of power obtained by the fuel cell was 8.09 mW/cm^2 at 2 ml/min of flow rate. It can be seen from figure 9(d) that for the cell with 4M methanol concentration, the effect of rate of flow is not monotonous. The cell performance improved with enhancement of flow rate from 0.5 to 1 ml/min, and then degraded on further increase in the flow rate from 1 to 5 ml/min. The maximum density of power obtained by the fuel cell was 8.09 mW/cm^2 at 1 ml/min of flow rate. Various methanol concentrations did not affect fuel cell performance, indicating that fuel flow rate does not affect performance of fuel cell.

Fuel cell performance is affected by flow rate enhancement in a mixed manner. An increase in flow rate increases the area of fuel diffusion passage and mass transfer, which promotes reactions. Consequently, it increases the reaction rate and improves fuel cell performance. Boosting the fuel flow rate in the cell causes a mixed over potential at the cathode reaction site when MCO takes place from the anode to the cathode side. Consequently, the cathode oxygen transport is disrupted due to the mixed over potential, which lowers the fuel use rate. These factors adversely affect cell performance. Additionally, increasing the flow rate in the cell will decrease the reaction time with the reactants. As a result, the chemical reaction is no longer able to conduct more electrons which adversely impacts the fuel cell performance.

The increased concentration of fuel improves through the anode diffusion layer as well as through the anode catalyst layer. This results in more methanol being available near the membrane. Nevertheless, it has a negative effect, as the probability of methanol crossover from the cathode to anode increases when concentration of methanol. The deterioration of cell performance is caused by the increased mixing of over potential losses. Accordingly, cell performance is a reflection of the combined effect of fuel flow rates and methanol concentrations.

Figure 10 illustrates the variation of maximum power density with flow rate for four different methanol concentrations. The maximum power density enhances with enhancement in flow rate from 0.5 to 4 ml/min and then decreases for 1M methanol concentration. When flow rate is increased from 0.5 to 3 ml/min, the maximum power density increases and then decreases for 2M methanol concentration. With an increase in flow rate from 0.5 to 2 ml/min and 0.5 to 1 ml/min, respectively, the maximum power density of 3M and 4M methanol concentrations increases and then deteriorates due to MCO. This results decrease in current density and power density. Thus electrical efficiency and power density are reduced due this transport of methanol from anode to cathode. It was determined that in the current range of flow rates of 0.5 to 5 ml/min and for methanol concentrations of 1M, 2M, 3M and 4M, the fuel cell with 2 ml/min flow rate showed the highest power density at a 3M methanol concentration. Among six flow rates, the fuel cell with a flow rate of 2 ml/min produced the maximum power density of 8.09 mW/cm^2.
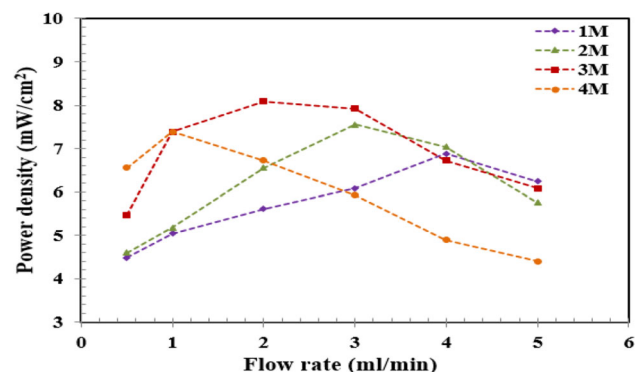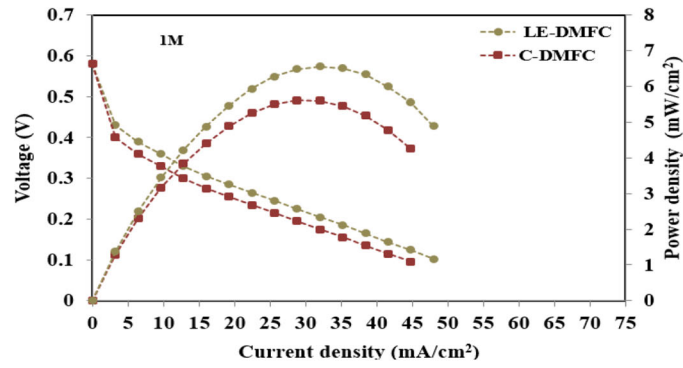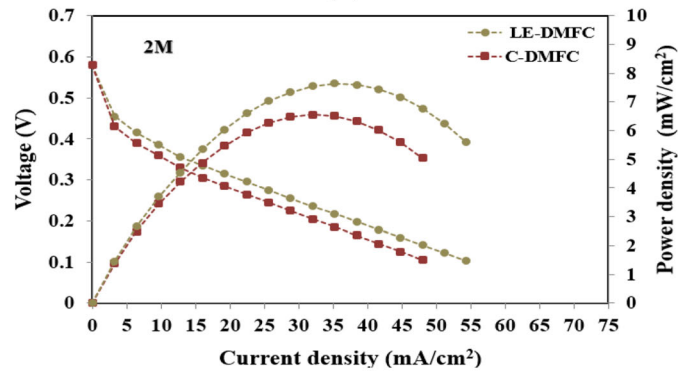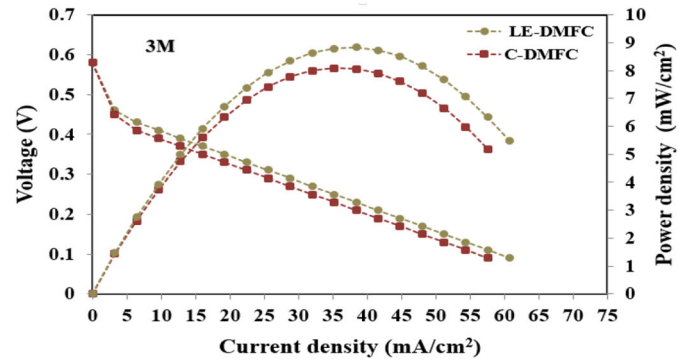

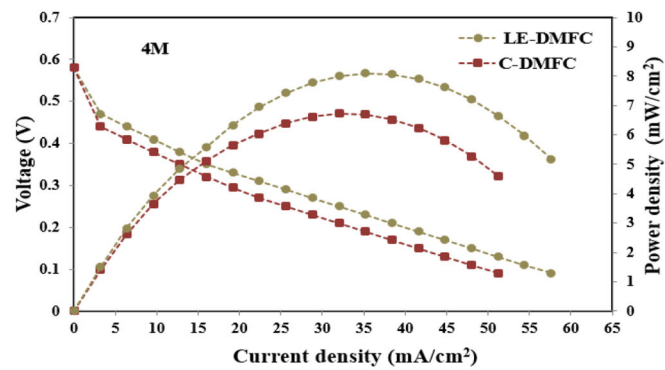**Figure 10.** Variation of maximum power density at different flow rates and methanol concentrations.

Figure 11. (a–d) Impact of the LE layer on the performance of the fuel cell at various methanol concentrations for the 2 ml/min flow rate.
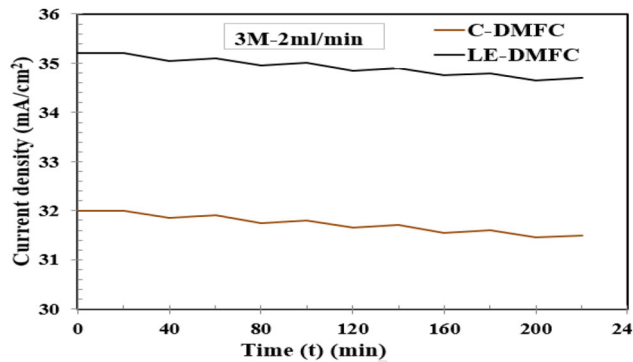
Figure 12. Comparison of the LE-DMFC and C-DMFC performance with long term operation.
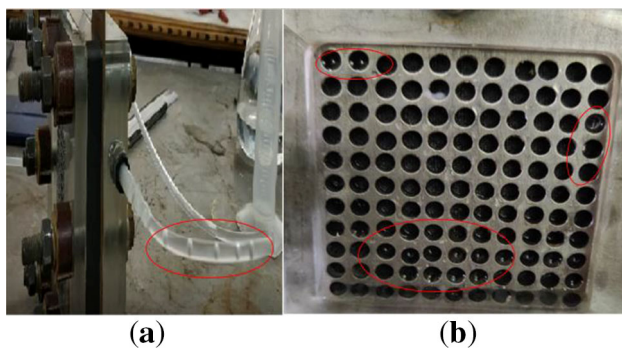

(a)   (b)

Figure 13. a, b Formation of CO_2 bubbles on the anode side and water bubbles on the cathode side at high current densities and methanol concetrations.

4.3 Impact of liquid electrolyte layer

Figures 11(a–d) illustrate the use of four different methanol concentrations and a monotonous 2 ml/min flow rate; this work examined the polarisation characteristics of the natural circulation-fed DMFC with and without an LE layer. In the figure, in all four methanol concentrations, the LE layer between two half MEAs enhances the performance of the fuel cell. DMFC performance is strongly affected by the crossover of methanol and water in natural circulation fed cells. On inclusion of LE layer, the crossover of methanol is reduced substantially and therefore fuel cell performance is increased. By adding an additional layer, the fuel cell performs less efficiently and ohmic resistance increases. Reduction of MCO and increasing ohmic losses of the fuel cell together determine the overall impact of implementing an LE layer on the performance of the fuel cell.

Figure 12 depicts the current density as a function of time for a fuel cell with a flow rate of 2 ml/min at a 3M methanol concentration at a constant voltage of 0.25 V.

It can be found that the density of current increases in LE-DMFC performance when compared to the conventional DMFC (C-DMFC). The drop in C-DMFC performance is attributed to methanol crossover losses. This methanol crossover says that the methanol molecules cross the PEM

membrane from anode to cathode side and react with oxygen to form water (in the form of bubble). Thus, water bubbles deteriorate the performance of fuel cells over time by preventing oxygen supply to the cathode reaction area.

Figure 13(a and b) depict CO_2 formation and water bubble formation on anode and cathode sides, measured at 25 mA/cm^2. Electrons, protons, and CO_2 bubbles are generated near the anode during the anodic reaction process. An external circuit transports the electrons generated at the anode to cathode. Through PEM, protons are transferred to the cathode side. In a cathode, electrons, protons and oxygen come together to form water molecules. Because of the higher reaction area and higher current density, more CO_2 bubbles are generated at higher methanol concentrations rates. In the reaction area, CO_2 gas bubbles create clogs that disrupt methanol flow. In the same way, the cathode side is prevented from receiving oxygen. In both cases, the fuel cell's performance degrades with time.

5. Conclusions

In the current experiment, a DMFC was built with an embedded natural circulation structure that actively delivered liquid fuel to the anode channel and stirred the fuel without the use of a separate, power consuming pumping component. On eliminating auxiliary devices, the packaging was greatly reduced. The influence of methanol flow rate and methanol concentrations was also investigated. Following are the major conclusions from the present work.

1. The maximum power density in active DMFC was observed to be 6.08 mW/cm^2. On eliminating the external fuel pump (i.e., for natural circulation DMFC) a maximum power density of 5.76 mW/cm^2 was observed.
2. The flow rate of a methanol showed mixed effects on the performance of fuel cell at different methanol concentrations. Optimum methanol concentration and flow rate are found to be 3 M, and 2 ml/min respectively. Thus, under these conditions the maximum power density of 8.09 mW/cm^2 was obtained.
3. On inclusion of LE layer, the crossover of methanol reduced substantially and fuel cell performance increased and maximum power density of 8.83 mW/cm^2 at 3 M methanol concentration was achieved.
4. The incorporation of LE layer (thickness of 1.5 mm) between two half MEAs resulted in better performance with an MPD of 8.83 mW/cm^2, which is 9.14% higher in comparison with conventional passive DMFC value.

Abbreviations

CDM	Catalyst diffusion medium
CFD	Computational fluid dynamics
C-DMFC	Conventional direct methanol fuel cell

DI	Deionized
DMFC	Direct methanol fuel cell
FE	Flowing electrolyte
GDL	Gas diffusion layers
LE	Liquid electrolyte
LE-DMFC	Liquid electrolyte liquid electrolyte
MCO	Methanol crossover
MPL	Microporous layer
PEM	Polymer Electrode Membrane
PTFE	Polytetrafluoroethylene
SS	Stainless steel

Acknowledgment

References

[1] Calabriso A, Cedola L, Del Zotto L, Rispoli F and Santori S G 2015 Performance investigation of Passive Direct Methanol Fuel Cell in different structural configurations. *J. Clean Prod.* 88: 23–28

[2] Boni M, Srinivasa Rao S and Naga Srinivasulu G 2020 Performance evaluation of an air breathing–direct methanol fuel cell with different cathode current collectors with liquid electrolyte layer. *Asia-Pacific J. Chem Eng.* 15: 1–10

[3] Wang L, He M, Hu Y, Zhang Y, Liu X and Wang G 2015 A "4-cell" modular passive DMFC (direct methanol fuel cell) stack forportable applications. *Energy.* 82: 229–235

[4] Ye Q and Zhao T S 2005 A natural-circulation fuel delivery system for direct methanol fuel cells. *J. Power Sources.* 147: 196–202

[5] Meng D D and Kim C J 2009 An active micro-direct methanol fuel cell with self-circulation of fuel and built-in removal of CO2 bubbles. *J. Power Sources.* 194: 445–450

[6] Hur J I, Meng D D and Kim C J 2012 Self-Pumping membraneless miniature fuel cell with an air-breathing cathode. *J. Microelectromechanical Syst.* 21: 476–483

[7] Oliveira V B, Rangel C M and Pinto A M F R 2009 Modelling and experimental studies on a direct methanol fuel cell working under low methanol crossover and high methanol concentrations. *Int. J. Hydrogen Energy.* 34: 6443–6451

[8] Bin Jung G, Su A, Tu C H and Weng F B 2005 Effect of operating parameters on the DMFC performance. *J. Fuel Cell Sci. Technol.* 2: 81–85

[9] Kim S, Jang S, Kim S M, Ahn C Y, Hwang W, Cho Y H, Sung Y E and Choi M 2017 Reduction of methanol crossover by thin cracked metal barriers at the interface between membrane and electrode in direct methanol fuel cells. *J. Power Sources.* 363: 153–160

[10] Liu F, Lu G and Wang C Y 2006 Low Crossover of Methanol and Water Through Thin Membranes in Direct Methanol Fuel Cells. *J. Electrochem Soc.* 153: A543

[11] Tang Y, Yuan W, Pan M, Tang B, Li Z and Wan Z 2010 Effects of structural aspects on the performance of a passive air-breathing direct methanol fuel cell. *J. Power Sources.* 195: 5628–5636

[12] Kang K, Lee G, Gwak G, Choi Y and Ju H 2012 Development of an advanced MEA to use high-concentration methanol fuel in a direct methanol fuel cell system. *Int J Hydrogen Energy.* 37: 6285–6291

[13] Song K Y, Lee H K and Kim H T 2007 MEA design for low water crossover in air-breathing DMFC. *Electrochim Acta.* 53: 637–643

[14] Liu J G, Zhao T S, Liang Z X and Chen R 2006 Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cells. *J. Power Sources.* 153: 61–67

[15] Kim Y M, Park K W, Choi J H, Park I S and Sung Y E 2003 A Pd-impregnated nanocomposite Nafion membrane for use in high-concentration methanol fuel in DMFC. *Electrochem commun.* 5: 571–574

[16] Choi W C, Kim J D and Woo S I 2001 Modification of proton conducting membrane for reducing methanol cross-over in a direct-methanol fuel cell. *J. Power Sources.* 96: 411–414

[17] Kordesch K, Hacker V and Bachhiesl U 2001 Direct methanol-air fuel cells with membranes plus circulating electrolyte. *J. Power Sources.* 96: 200–203

[18] Ouellette D, Colpan C O, Cruickshank C A and Matida E 2015 Parametric studies on the membrane arrangement and porous properties of the flowing electrolyte channel in a flowing electrolyte-direct methanol fuel cell. *Int J Hydrogen Energy.* 40: 7732–7742

[19] Ouellette D, Cruickshank C A and Matida E 2014 Experimental investigation on the performance of a formic acid electrolyte-direct methanol fuel cell. *J. Fuel Cell Sci. Technol.*

[20] Ouellette D, Colpan C O, Matida E and Cruickshank C A 2015 A single domain approach to modeling the multiphase flow within a flowing electrolyte - Direct methanol fuel cell. *Int. J. Hydrogen Energy.* 40: 7817–7828

[21] Colpan C O, Ouellette D, Glüsen A, Müller M and Stolten D 2017 Reduction of methanol crossover in a flowing electrolyte-direct methanol fuel cell. *Int. J. Hydrogen Energy.* 42: 21530–21545

[22] Colpan C O, Cruickshank C A, Matida E and Hamdullahpur F 2011 1D modeling of a flowing electrolyte-direct methanol fuel cell. *J. Power Sources.* 196: 3572–3582

[23] Colpan C O, Fung A and Hamdullahpur F 2012 2D modeling of a flowing-electrolyte direct methanol fuel cell. *J Power Sources.* 209: 301–311

[24] Kjeang E, Goldak J, Golriz M R, Gu J, James D and Kordesch K 2006 A parametric study of methanol crossover in a flowing electrolyte-direct methanol fuel cell. *J Power Sources.* 153: 89–99

[25] Duivesteyn E, Cruickshank C A and Matida E 2013 Modelling of a porous flowing electrolyte layer in a flowing electrolyte direct-methanol fuel cell. *Int. J. Hydrogen Energy.* 38: 13434–13442

[26] Sabet-Sharghi N, Cruickshank C A, Matida E and Hamdullahpur F 2013 Performance measurements of a single cell flowing electrolyte-direct methanol fuel cell (FE-DMFC). *J. Power Sources.* 230: 194–200

[27] Ozden A, Ercelik M, Devrim Y, Colpan C O and Hamdullahpur F 2017 Evaluation of sulfonated polysulfone/zirconium hydrogen phosphate composite membranes for direct methanol fuel cells. *Electrochim Acta.* 256: 196–210

[28] Ahmad H, Kamarudin S K, Hasran U A and Daud W R W 2011 A novel hybrid Nafion-PBI-ZP membrane for direct methanol fuel cells. *Int J Hydrogen Energy.* 36: 14668–14677

[29] Lee W, Kim H, Kim T K and Chang H 2007 Nafion based organic/inorganic composite membrane for air-breathing direct methanol fuel cells. *J. Memb Sci.* 292: 29–34

[30] Helen M, Viswanathan B and Murthy S S 2007 Synthesis and characterization of composite membranes based on α-zirconium phosphate and silicotungstic acid. *J. Memb Sci.* 292: 98–105

[31] Yin K M 2015 One-dimensional steady state algebraic model on the passive direct methanol fuel cell with consideration of the intermediate liquid electrolyte. *J. Power Sources.* 282: 368–377

[32] Yin K M 2008 A theoretical model of the membrane electrode assembly of liquid feed direct methanol fuel cell with consideration of water and methanol crossover. *J Power Sources.* 179: 700–710

[33] Boni M, Surapaneni S R, Golagani N S and Manupati S K 2021 Experimental investigations on the effect of current collector open ratio on the performance of a passive direct methanol fuel cell with liquid electrolyte layer. *Chem Pap.* 75: 27–38

[34] Boni M, Rao S S and Srinivasulu G N 2019 Influence of intermediate liquid electrolyte layer on the performance of passive direct methanol fuel cell. *Int. J. Green Energy.* 16: 1475–1484