

A Review on Direct Methanol Fuel Cell and Its Contemporary Status

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Abstract

The Direct Methanol Fuel Cell (DMFC) has been designed from the start to be appropriate for a wide range of appliances, including stationary and portable electrical applications, since it is regarded as a particularly promising energy source in renewable energies. It uses polymer electrolyte membrane (PEM) fuel cell technology for its ion or proton conducting electrolyte. Their key benefit is the simplicity with which methanol fuel and energy-densifying stable liquid may be transported in all climatic circumstances. Other benefits include cheaper fuel production costs, less flammability risk, and enhanced energy security and availability. It emits hydrogen and carbon dioxide but no sulphur, nitrogen, or other hazardous gases. This review paper highlights advancements in DMFC technology from its inception to the present day, with the ultimate goal of improving overall DMFC performance by addressing issues such as performance influence on operating temperature and pressure parameters; stacking; methanol and water cross-over; current collectors, optimization of gaskets, supporting plates, cathode channel configuration; experiments on portable power supply sources, and multi anodes over the last 15 years. It also identifies research needs for future efforts.

Keywords: *DMFC, energy source, current collectors, methanol cross over, water cross over, power density.*

INTRODUCTION

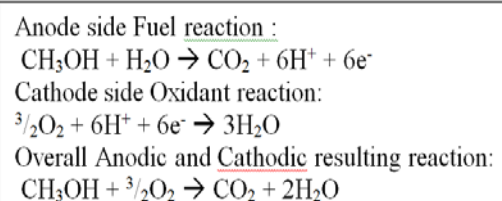
A fuel cell, which is similar to a battery in that it transfers chemical energy from reactants into electricity, is one of the sources of electricity. It differs from a battery in that it produces electricity constantly as long as fuel and an oxidant are available. It offers benefits such as clean byproducts, extremely low or no emission of oxides of nitrogen and sulphur, runs silently, has no moving parts, additional fuel processing to satisfy demand requirements, and a high energy density. Methanol is a popular fuel for Direct Methanol Fuel Cells (DMFC). Methanol is a reasonably affordable and widely accessible fuel with a high specific energy density, rapid refilling, and strong transport and storage capabilities. It functions at a low temperature and pressure in fuel cell applications, requiring no extra liquid electrolyte. The compact cell architecture makes it ideal for portable applications.

EMERGENCE OF DMFC

The benefit of the direct methanol fuel cell over the hydrogen fuel cell is that it employs methanol in liquid form without the requirement for external reforming. The Jet Propulsion Laboratory in Pasadena, California, devised, designed, and produced DMFC cells. They were

intended to power the Armed Forces as well as NASA's space applications. Methanol fuel is easier to store and has a higher energy density than compressed hydrogen or other gaseous fuels. DMFC currently has low efficiency and requires more platinum loading than other fuel cells, resulting in higher prices. On the other hand, DMFC is likely to be a major source of power for mobile and portable devices. DMFC also makes use of PEM membrane. However, in addition to platinum, additional catalysts such as ruthenium are required on the anodic side of the membrane to break the chemical bonds in the reaction to create carbon dioxide, hydrogen ions, and free electrons. In DMFC, free electrons flow from the cell's anode to the cathode through an external circuit, while hydrogen protons are transmitted across the electrolyte membrane. Electrons from the anode and hydrogen ions react with the oxidant to generate water at the cathode. Table 1 shows the reactions.

Table 1:-DMFC Reactions



REVIEW ANALYSIS

Table 2:-DMFC studies

S.No	Name of the Author	Approach	Area of investigation
1	Jiabin Ge, Hongtan Liu <i>et al.</i> [1]	Experiment	Performance study
2	Zhen Guo and Amir Faghri <i>et al.</i> [2]	Development technique	Fuel cell stacks
3	Yingli Zhua <i>et al.</i> [3]	Design, Development and Testing	Planar air breathing of stacks
4	Chao Xu <i>et al.</i> [4]	Experiment	Methanol and water crossover
5	Yean-Der Kuana <i>et al.</i> [5]	Experiment	Design of Current Collectors
6	Sasan Yousefi <i>et al.</i> [6]	Experiment	Study the characteristics
7	Naveen K <i>et al.</i> [7]	Design and development	Wire mesh current collectors
8	Andrea Calabriso <i>et al.</i> [8]	Design, Development and Testing	Study of mono-polar PDMFC
9	Ranjan K. Mallick <i>et al.</i> [9]	Experiment	Current Collectors and support plate.
10	David Ouellette <i>et al.</i> [10]	Modelling	Flow fields
11	Luwen Wang <i>et al.</i> [11]	Development and Experiment	Bipolar DMFC
12	Tobias M. Brueckner <i>et al.</i> [12]	Experiment	Operation of a multi-anode PEM electrolysis cell

Several research scholars studied, investigated, designed, developed mathematical analysis and iterations, modeling, system improvement and experiments on DMFC. Approach of these scholars tabulated in Table 2.

Jiabin Ge, Hongtan Liu, et al. [1] did the experiments to find out how well a direct methanol fuel cell works overall under different operating conditions, including

the effects of operating temperature, methanol concentration, cathode humidification temperature, anode flow rate, and cathode flow rate. According to the findings of these investigations, operational temperature has a dual influence on cell performance. The performance of the cell improves with operating temperature, but after a certain threshold, the negative effect of temperature takes over. As a result, there is

a maximum current density, which increases as cell voltage lowers. The optimal methanol concentration for this specific cell design is between 1M and 2M with air as the oxidant, however with a greater air flow rate, the unfavourable effect of methanol crossing is alleviated. Also, when pure oxygen is used as the oxidant, the "crossover effect" of methanol is greatly reduced. These results show that the best cathode design and operating conditions allow for much higher concentrations of methanol, which makes the overall fuel weight much lighter. Humidification does not have a substantial effect on the cathode side, hence it is not required for DMFC. Up to a certain point, the anode flow rate has a big effect on how well the cell works. After that point, increasing the anode flow rate doesn't make much of a difference. Increasing the air flow rate usually makes a cell work better, but not as much as increasing the anode flow rate. Similarly, once the air flow rate reaches a particular level, any additional increase has little impact.

Zhen Guo, Amir Faghri et al. [2] investigated ways of developing planar air-breathing direct methanol fuel cell stacks. The planar fuel cell stack construction allows fluids to diffuse into and out of the cell, making it ideal for portable power

source applications, procedures for design and development that began with small single cells, progressed to huge single cells, and eventually concentrated on stacks. The stack's modular architecture also allows it to be built independently of the other components of the fuel cell system. The MEA and GDLs are laminated together to minimise electrical/ionic contact resistance, which also aids in the elimination of related heavy hardware. The concentration of methanol has a considerable impact on the output power density and the cell operation temperature. In this investigation, the power density was maximised when 2.0 and 3.0 M methanol solutions were utilised. At ambient circumstances, the four-cell stack had a maximum power density of around 30.0 mWcm².

Yingli Zhua et al. [3] conceived, constructed, and tested an 8-cell planar DMFC twin-stack with a total active area of 32 cm². With 4 M methanol concentration and passive operation, a maximum power density of 16.9 mWcm² was reached. The tin-plated mesh resulted in a 40% drop in internal resistance and a 46% improvement in power density. A novel CO₂-driven fuel feed mechanism was developed that can self-regulate the

feeding rate in response to changes in the fuel cell's discharging current. With the usage of 80 ml of 4M methanol, the stack outfitted with this fuel-feed mechanism effectively powered a sensor node for 39 hours. Feeding rates may be tuned for varied methanol concentrations by using larger gas outlets and feed pipes. As a result, it is envisaged that with improved design, a longer operation period with the same fuel loading will be possible.

Chao Xu et al. [4] conducted experiments to better understand the methanol and water crossover over the membrane in order to construct highly effective passive DMFCs. The methanol crossover, water crossover, and fuel efficiency were all tested experimentally in a passive liquid-feed DMFC at various methanol concentrations and current loads in this study. A WML in the cathode's influence on methanol and water crossover was also examined. The performance of the passive DMFC was discovered to be highly dependent on the heat and water behaviour of the passive DMFC, which also controlled the methanol and water crossover over the membrane. The methanol crossover rose as current density increased, but fuel efficiency improved first and then fell marginally. In the test range, the water crossing rose

approximately linearly with current density, and the net water-transport coefficient was practically constant. It was also shown that, while the methanol crossover and fuel efficiency were highly dependent on methanol concentration, the water crossover was almost the same for varying methanol concentrations. The results also revealed that, while the WML in the cathode increased cathode flooding and oxygen transport resistance, it resulted in a significant decrease in both water and methanol crossing over the membrane.

Yean-Der Kuana et al. [5] investigated the influence of two essential elements in the design of collectors for planar-type DMFCs, the total free open ratio and the total perimeter length of the free openings, on current collectors by comparing different hole layouts. Cell performance was low in the low total free open ratio range, while raising the total free open ratio greatly enhanced the mass transfer of reactants and products, resulting in better cell performance. The surface contact area between the current collectors and MEA becomes critical in the larger total free open ratio range, and further increases in the total free open ratio may not improve cell performance because the higher total free open ratio leads to higher surface contact resistance due to a lower total

contact area between the MEA and current collectors. Because of the greater permeability of the current collectors, they raise the methanol crossover even further. A longer total perimeter length of openings always gives better cell performance under the same total free open ratio because it shortens the diffusion length between the free open areas and the closed areas behind the current collectors for the reactants and products, and mass transfers are smoother. Current collectors on planar-type DMFCs should be designed with the proper total free open ratio and total contact area in mind. It is also advised that the total free opening circumferential length be increased. A 50% total free open ratio and a larger total free opening perimeter length with a 10 × 10 hole arrangement are proposed for the current applications.

Sasan Yousefi et al. [6] constructed and evaluated an experimental passive direct methanol fuel cell to assess the characteristics of open circuit voltages under different operating circumstances such as ambient temperature, cell orientation, and methanol concentration. The effect of fuel cell orientation on cell performance was looked at. When the concentration of methanol increases, the open circuit voltage (OCV) values

decrease because a higher mixed potential leads to lower OCV values in the cell. Experiment results also showed that increasing the ambient temperature causes more natural convection inside the fuel cell. Methanol crossover is facilitated by the enhanced natural convection. As the mixed potential increases, the OCV of passive air-breathing DMFC decreases. The experimental findings revealed that cell orientation has a significant impact on cell performance and fuel cell open circuit voltage. Due to cathode flooding and carbon dioxide bubble generation in the anode, the passive DMFC with the anode angled downward performs poorly. Vertical operations consistently outperformed horizontal operations. The faster electrochemical kinetics of electrodes caused by a higher rate of methanol crossover led in enhanced performance in the vertical cell configuration.

Naveen K et al. [7] studied the viability of woven wire mesh as a current collector in a passive DMFC, designing and fabricating a unique single-cell fixture. As current collectors, several wire meshes are utilised. For each mesh, the supporting plate is optimised. The performance of the DMFCs-W and DMFCP is compared. Based on the experimental results, it was

established that the supporting plate was a crucial component of the DMFCs-W. The performance of DMFCs-W varies with different supporting plate designs, and the best cell performance may be obtained by using a single supporting plate configuration. The unique supporting plate arrangement varies depending on the wire mesh current collector. Because wire mesh shape impacts mass transfer pattern, cell electrical resistance, and so on, it has a substantial impact on cell performance. It has been discovered that a mesh consisting of moderately thick wires improves cell performance. Due to improved capillary action, meshes with thin wires and micro-sized apertures (wire mesh-E; DMFC-E) display excellent in-plane mass transfer and retain optimal cell performance across a broad range of supporting plate configurations. When the optimal supporting plate arrangement is unknown, the wire mesh-E can be employed in a passive DMFC with supporting plates with an overly high number of ribs without affecting cell performance. DMFCs-W have better fuel distribution at ACL and attain higher cell temperatures than DMFCs-P. The stainless steel wire mesh is identified as a suitable material for use as a current collector in the passive DMFC and as a potential alternative to the standard

perforated plate current collector in this study.

Andrea Calabriso et al. [8] built, tested, and constructed a monopolar PDMFC. The varied assembly configurations were chosen to examine their influence on the passive air-breathing direct methanol fuel cell; the first stage was to improve the cell's behaviour using different thicknesses of silicone and PTFE gaskets. On the anodic side, two silicone gaskets provided the optimum performance. Because of decreased contact resistance between GDLs and current collectors, the internal resistance of the fuel cell reduces as gasket thickness and stiffness decrease. Following the selection of the gasket arrangement, two pairs of stainless steel plates SS316 with OR 17% and OR 35% were evaluated with molar concentrations ranging from 1 M to 4 M. Voltage to current and power density curves were measured and compared. They demonstrated that with a smaller crossing area, various molar concentrations behave essentially identically. Fuel cross-over appears to be reduced at lower molar concentrations at greater current densities, with the highest performance at 2 M. The generation of CO₂ bubbles in the perforations of the anode plate denies the reactant access to the active region of the MEA at high

current density, limiting power density. During the experiments, a tiny short-circuit current was recorded between the electrodes. It adds to a reduction in overall cell voltage and, as a result, power. The following research steps will concentrate on the investigation of different hole shapes in order to facilitate the removal of CO₂ bubbles, as well as the use of various current collector materials capable of further reducing the internal resistance of the cell and eliminating the short circuit phenomenon. In the field of portable applications, a PDMFC stack appears to be a promising candidate to replace batteries in all electronic devices with low power supply due to the high overall energy conversion efficiency, easy refilling, and low emissions, particularly referring to the potential use of renewable and sustainable resources and new technologies such as hydrogenative chemical recycling of carbon

Ranjan K. Mallick et al. [9] built to test the practicality of a single passive DMFC fixture's EMCC. The performance of the passive DMFC is measured and compared with various combinations of supporting plates and EMCCs for this purpose. Based on the findings of the experiments, it was determined that the supporting plate is a crucial component in passive DMFCs with

expanded metal mesh as the current collector. The supporting plate designs impact cell performance, and the best performance may be obtained by adjusting its open ratio by altering the rib arrangement and rib thickness. In this investigation, the peak power density was obtained with a 5x5 supporting plate with a 2.5 mm rib thickness and a 56.25% open ratio. The passive cell with the EMCC outperforms the conventional passive cell with the conventional perforated current collector, and the EMCC also allows for better fuel distribution at the anodic catalyst layer and increases operating temperature when compared to the conventional perforated current collector. Because the mesh type and geometry of the EMCC affect mass transfer resistance and overall ohmic resistance, they have a significant impact on cell performance. It has been discovered that passive DMFC with coarse mesh, greater strand width, and thicker EMCC functions better.

David Ouellette et al. [10] simulated a three-dimensional, single-phase FE-DMFC with four distinct cathode channel topologies (serpentine, parallel serpentine, triple serpentine, and grid). The influence of current density on methanol concentration in the centre of the FEC is studied, as are the identified reasons. The

single serpentine flow field gave the best performance of the flow fields studied because it provided the most oxygen coverage on the CCL. The grid type flow field performed the worst, since the hydrodynamics inside the channel created locally diffusive-driven transport, which resulted in dead zones and a mass transport limiting regime.

Luwen Wang et al. [11] created and tested a bipolar passive DMFC stack for portable use. PMMA was chosen as the material for the bipolar plates. The current collectors were made from stainless steel sheet utilising wire cutting and laser beam cutting processes. To avoid electrochemical corrosion, a 3.5 mm Au coating was electroplated onto the current collectors. A unique current collector design was presented, which integrates internal and exterior electrical connections smoothly to minimise resistance loss. The stack was characterised by altering the methanol concentration and using different placement strategies. Methanol concentrations of 2M, 3M, 4M, and 5M were investigated. At 3M methanol concentration, the passive stack's highest power density was 18.7 mW/cm². The passive DMFC stack in mode B performs better and more consistently than mode A in discharging high currents for different

placement options (designated as A: vertical cathode air channels and B: parallel cathode air channels). Furthermore, the longevity of a bipolar passive DMFC stack was tested by powering an experimental fan for 100 days and achieving an attenuation ratio of 16.67% on the 100th day.

Tobias M. Brueckner et al. [12] used a multi-anode PEM electrolysis cell in anode polarisation mode to get steady-state polarisation data under regulated mass transport circumstances. This facilitates the assessment and comparison of organic fuel oxidation catalysts and gives data useful for determining their appropriateness for use in electrolysis and fuel cells. Higher voltage mass transport regulated electric currents offer estimations of reaction stoichiometries and aid in the discovery of catalysts with enhanced efficiency. A Platinum-Ruthenium (PtRu) black catalyst predominates in the two-electron oxidation of ethanol, ethylene glycol, and glycerol to the appropriate aldehyde, whereas Pt catalysts give more complete oxidation. The stoichiometry for glycerol oxidation at a 70% Pt/C catalyst reached 7.6 electrons at 0.9 V, indicating the formation of compounds such as glyceric acid, hydroxyl pyruvic acid, and tartronic acid. Metallic

oxide supports have been shown to boost the low potential activity of platinum catalysts for all of the fuels tested. Although less successful than alloying Pt with Ru, Sn oxide and Ru+Sn oxide supports can do this with less stoichiometry loss. This impact was particularly noticeable in ethylene glycol and glycerol, where the Pt/Ru+Sn oxide/C catalyst showed the most potential. The introduction of a Ru on Pt/C catalyst has also been demonstrated to boost low potential activities over Pt/C. However, the introduction of a Rh core lowered activity compared to Pt/C.

Fuel cells are constructed [13] and maintained [14] to be more durable and operable.

CONCLUSIONS

Literature review on the investigation revealed the following inferences.

1. Using a greater proportion of methanol in conjunction with a good cathode design and operating conditions may allow for a considerable reduction in total fuel weight and hence fuel cell power density.
2. Increasing the number of cells that can be stacked in the DMFC enhances cell performance.
3. Methanol fuel feeding rates may be tuned for varied concentrations by using larger gas outlet and feed pipe systems. As a result of this enhanced design, it is envisaged that longer operation times will be possible with the same fuel loading.
4. Optimizing the water management layer enhances cell performance.
5. Total free open ratio design optimization and a larger total free opening perimeter length improve DMFC performance.
6. Cell orientation other than horizontal / vertical for water and CO₂ disposal with minimal methanol cross over is possible.
7. The consistent horizontal and vertical progressive widening of mesh-openings from bottom to top improves gas scavenging and allows for uniform fuel flow.
8. Fuel cells with coarse mesh, greater strand width, and thicker EMCC are necessary for improved cell performance.

9. In comparison, the grid type flow field performed the worst, while the single serpentine flow field performed the best since it offered the most oxygen coverage on the CCL.

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