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REVIEW

# Liquid feed passive direct methanol fuel cell: challenges and recent advances

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**Abstract** This paper provides an overview of technological challenges and recent advances in the liquid feed passive direct methanol fuel cells (DMFC). Important issues viz. species management, thermal management, methanol crossover, sluggish anode kinetics, durability and stability, and cost are discussed in detail. Methanol management, water management, oxygen management, and carbon dioxide management are covered under species management. The present technological status is given and future research directions are suggested.

**Keywords** Passive direct methanol fuel cell · Liquid feed · Mass transfer · Heat transfer · Durability · Cost

## Introduction

Fuel cell is an electrochemical device which converts chemical energy of the reactants directly into the electrical energy [1–3]. Generally, the hydrogen, which has the highest energy content by weight (33,320 Wh kg$^{-1}$), is used as fuel in the fuel cells [4]. Fuel cells, based on the electrolyte used, can be classified mainly into five types: polymer electrolyte membrane fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC) [1, 2, 5–12]. These different fuel cells differ in their operating temperatures, efficiencies, power outputs, costs, and typical applications.

PEMFCs are low temperature fuel cells having operating temperature between 30 and 100 °C. These cells possess the highest power density of all the fuel cell types and fast start-stop capability. PEMFCs use solid electrolyte, which makes sealing of electrodes easier [13–15]. The PEMFC, based on the fuel used, can be categorized into two types: hydrogen-fuelled PEMFC ($H_2$-PEMFC) and direct liquid fuel cell (DLFC) [16–18].

DLFC is a promoted type $H_2$-PEMFC, which utilizes, instead of gaseous hydrogen, the liquid fuels such as methanol, ethanol, formic acid, etc. The DLFC has important advantages, over the $H_2$-PEMFC, viz. easy handling, storage, transportation and distribution of liquid fuel, high theoretical energy density, elimination of fuel reformer, elimination of fuel humidifiers (easy membrane hydration), etc. [16, 17, 19]. Based on the name of the liquid fuel used, the DLFCs can be renamed as direct methanol fuel cell (DMFC), direct ethanol fuel cell (DEFC), direct formic acid fuel cell (DFAFC), direct hydrazine fuel cell (DHFC), direct ethylene glycol fuel cell (DEGFC), direct dimethyle ether fuel cell (DDEFC), etc.

Methanol is a readily available and low cost fuel which can be produced from almost any hydrocarbon compound including natural gas, coal, biomass, methane, etc. It has a high theoretical energy density (gravimetric energy density, 5.5 kWh kg$^{-1}$ and volumetric energy density, 4.6 kWh L$^{-1}$). Methanol, with only carbon-hydrogen bonds, has a very simple and weak chemical structure, and hence, exhibits high electrochemical activity compared to other organic fuels. Therefore, methanol is the most preferred fuel for the DLFC and the DMFC is the most studied DLFC in the recent past [20–30]. The DMFC has the potential to be used in a broad range of applications including the low power applications such as portable electronic devices as well as the high power

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applications such as automobiles. The DMFCs can be categorized into active DMFC and passive DMFC, based on the method of fuel feed [17, 31–40], and into liquid feed DMFC and vapor feed DMFC based on the physical state of the fuel used [17, 31, 32, 41–43].

The active DMFC requires extra balance-of-plant components such as pumps, fans, and blowers for the supply and removal of the reactants and products. Whereas, passive DMFC relies on passive means such as diffusion, natural convection, gravitation, and capillary action for the same. Compared to active DMFC, the passive DMFC has simple and compact structure, exhibits lower parasitic power losses (higher energy density) and therefore suitable for portable applications.

In a vapor feed DMFC, fuel (methanol–water mixture) is fed in vapor state, whereas in a liquid feed DMFC, fuel is fed in liquid state. Vapor feed DMFC requires a separate vaporizer system which makes the system complex and increases the parasitic power loss. On the other hand, liquid feed DMFC operates near room temperature and offer several advantages over the vapor feed DMFC such as simpler and compact structure, lower parasitic power losses, and easier thermal management, and therefore best suited for portable applications.

This paper presents a comprehensive review of the experimental and theoretical studies on the liquid feed passive DMFC (hereby referred as passive DMFC only). The remainder of this paper is organized as follows: "Liquid feed passive DMFC: construction and working" gives brief description about the construction and working of the passive DMFC; "Species management" to "Cost" reviews the various challenges and recent advances related to passive DMFC. "Species management" provides details on the different species management issues viz. methanol management, water management, oxygen management, and carbon dioxide management. Objectives of each management and methods adopted to achieve the objectives are discussed. Advances in the thermal management issue are given in "Thermal management." Recent developments to reduce the methanol crossover (MCO) and to improve the anode kinetics are presented in "Methanol crossover" and "Sluggish anode kinetics," respectively. "Durability and stability" presents the recent researches concerning the durability and stability of the passive DMFC. The researches aimed to reduce the cost of the passive DMFC are discussed in "Cost." Finally, a summary is given in "Concluding remarks."

## Liquid feed passive DMFC: construction and working

The schematic diagram of a passive DMFC is shown in Fig. 1. It mainly consists of an anode end plate with fuel reservoir, an anode current collector (ACC), a membrane electrode assembly (MEA), a cathode current collector (CCC), and a cathode end plate. Gaskets are used, to provide perfect sealing, between the cell components. Small holes are provided on the anode end plate for fuel injection and carbon dioxide exhaust. The MEA is composed of anode diffusion layer (ADL), anode catalyst layer (ACL), polymer electrolyte membrane (PEM), cathode catalyst layer (CCL), and cathode diffusion layer (CDL). The function of anode and cathode current collector is to collect current generated in the MEA, to support the MEA and to provide passage for reactants and products. Typically, 1–3 mm thick stainless steel plate with perforated hole arrays is used as current collector. The function of anode and cathode diffusion layer is to provide porous surface for the respective catalyst layer to adhere on it, to distribute the reactants uniformly over the catalyst layer, and to conduct electrons to the respective current collector. The diffusion layer is made of wet-proofed (teflonized) carbon cloth or carbon paper (known as backing layer) and a micro-porous layer (MPL). The MPL is composed of carbon particles and polytetrafluoroethylene (PTFE) and facilitates more uniform distribution of the reactants on the catalyst layer. The wet-proofing of diffusion layer helps facilitating the two-phase mass transport on both anode and cathode sides. The catalyst layer (anode and cathode) structure is aimed to provide the three-phase boundary of catalyst, reactant, and proton conductor. It is composed of appropriate catalyst to promote electrochemical reaction, Nafion ionomer to conduct proton, and the hydrophobic PTFE to facilitate two-phase flow. Usually, Pt-Ru bimetallic catalyst is used at anode and bare Pt catalyst is used at cathode. The PEM separates the anode and cathode side, permits proton flow, and restricts electron flow. Typically, sulfonated fluoroethylene, an ion conducting polymer developed by DuPont (Nafion®), is used as PEM.

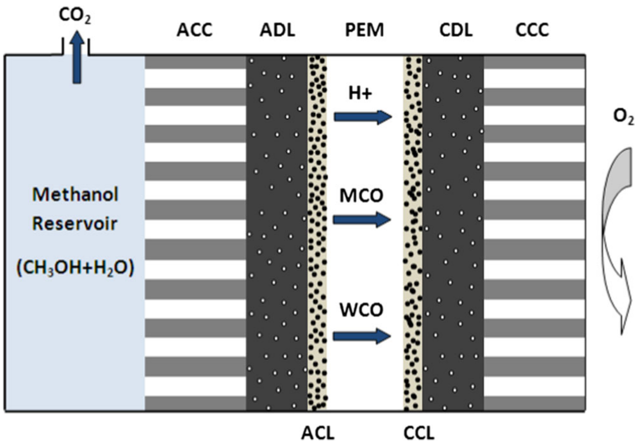

**Fig. 1** Schematic of passive DMFC

The methanol water mixture stored in the fuel reservoir is transported through ACC and ADL mainly due to diffusion and reaches the ACL. At ACL, some of the methanol is oxidized to generate proton, electron, carbon dioxide, and heat, which is termed as methanol oxidation reaction (MOR) and can be written as:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- + \text{heat} \qquad (1)$$

The remaining methanol and water, unused at ACL, permeates through the PEM by the mechanism of diffusion and electro-osmotic drag and reaches the CCL. The permeation of methanol and water through the PEM is termed as methanol crossover (MCO) and water crossover (WCO), respectively. At CCL, the crossovered methanol is oxidized to produce water and carbon-dioxide and causes mixed potential which leads to decrease in cell voltage. The carbon dioxide generated at ACL moves counter-currently, towards the fuel tank and vented out of the cell. The electrons and protons, which are produced in the MOR, flow through an external circuit and through PEM, respectively, and reach the CCL. The oxygen, present in the atmospheric air, transported through the CCC and CDL and reaches the CCL where it combines with proton and electron to generate water and heat. This is termed as oxygen reduction reaction (ORR) and can be written as:

$$^3/_2 O_2 + 6H^+ + 6e^- \rightarrow 3H_2O + \text{heat} \qquad (2)$$

The water at cathode is vented out of the cell by diffusion and natural convection. The generated heat is dissipated to the ambient air on the cathode side and to the methanol solution on the anode side. The overall reaction in a passive DMFC can be written as:

$$CH_3OH + {}^3/_2 O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \qquad (3)$$

## Species management

### Methanol management

Methanol, stored in the reservoir, passes through ACC and ADL, by process of diffusion and natural convection to reach the ACL. At ACL, some of the methanol gets consumed in anode electrochemical reaction, while remaining methanol crosses the PEM and reaches the CCL. As described earlier, the permeation of methanol through PEM is termed as MCO. However, it is very difficult to control the mass transfer of methanol in a passive DMFC; certain objectives, related to the methanol transport (objectives of effective methanol management), for efficient cell operation can be defined as:

#### *Uniform distribution of methanol at ACL*

A uniform distribution of methanol at the ACL is highly desirable for the effective cell performance. A non-uniform distribution of methanol may lead to several fuel starving locations at ACL and therefore many catalyst particles may remain unutilized and results in decreased cell performance. The uniformity of methanol distribution at ACL mainly depends on the ACC's structure. Chen et al. [44] found that the methanol concentration at ACL under the ACC rib is less than that under the ACC open area. A more uniform distribution of methanol can be achieved by using the ACC with higher open ratio. The smaller rib width on the ACC, which leads to a shorter mass transfer distance in the in-plane direction, shows more uniform distribution of methanol at ACL. Achmad et al. [45] compared the passive DMFC stack performance with different anode plate designs to maximize the methanol distribution. It was found that the anode plate with higher open ratio exhibits better methanol distribution. Shrivastava et al. [46] examined the feasibility of the stainless steel wire mesh as current collector in the passive DMFC. More uniform fuel distribution at catalyst layer was achieved with the wire mesh current collectors compared to those with conventional perforated plate current collectors.

#### *High energy density*

In a passive DMFC, increase in methanol feed concentration leads to the change in following three phenomena; combined effect of which decides the cell performance. (i) Increase in MCO, which adversely affect the cell performance. (ii) Decrease in mass transport loss or concentration polarization (as methanol flux towards ACL increases), which enhances the cell performance. (iii) Increase in cell temperature, resulted from increased heat released by the oxidation of increased MCO, which enhances the electrochemical activity and therefore enhances the cell performance. In a passive DMFC, the optimum cell performance is obtained at a moderate level of methanol feed concentration (usually, between 2 and 4 M) and on increasing or decreasing the methanol concentration beyond this range; the cell performance decreases.

The above discussion indicates that for optimum cell performance, the methanol availability at ACL should be sufficient to minimize the mass transport loss, the MCO should be low to minimize the cathode overpotential, and the cell temperature should be high to enhance the electrochemical activity. The cell temperature depends, mainly, on the amount of crossovered methanol. The MCO occurs mainly due to the diffusion and hence largely depends on the methanol concentration (methanol availability) at the ACL. It means methanol concentration at ACL is the only independent parameter and all other viz. MCO and cell temperature depends on it. Therefore, for optimum cell performance, the methanol concentration at ACL (the only controllable parameter) should be at adequate level to provide the best compromise between the fuel availability, MCO, and the cell temperature. For a fixed methanol feed concentration, the methanol concentration at ACL changes with change in the amount of current produced from the cell. Therefore, it is very difficult to keep the methanol concentration at ACL, somehow, at the adequate level to get always the maximum cell performance. To the author's best knowledge, no technology is available at present, to keep the methanol concentration at ACL always at the optimum level for every value of current drawn.

The passive DMFC, in general, is operated with relatively diluted methanol feed concentration (2–4 M) to maintain the methanol concentration at ACL at adequate level and to get optimum cell performance. The use of diluted methanol solution lowers the specific energy of the cell and lead to shorter operational time of the cell for each fuel charge. Using concentrated methanol solution in the reservoir may increase the methanol concentration at ACL beyond adequate level, which can decrease the cell performance. Therefore, using the concentrated methanol solution in the reservoir and simultaneously maintaining the methanol concentration at ACL at adequate level is an important objective of effective methanol management. To accomplish this, many researchers modified the anode structure of the cell by inserting a methanol barrier layer and therefore increasing the mass transfer resistance between methanol reservoir and ACL as shown in Fig. 2 [47–56]. Different materials such as porous carbon plate [47–49], micro fluidic-structured flow field [52], Nafion membrane [53], porous PTFE plate [49], and porous metal-fiber sintered plate [54–56] were used as methanol barrier layer. These cells are referred as high concentration methanol feed passive DMFC and is a new class of passive DMFC, which requires species management objectives and various technical issues different from those for diluted methanol feed DMFC. This paper considers the studies related to the diluted methanol feed passive DMFCs only.

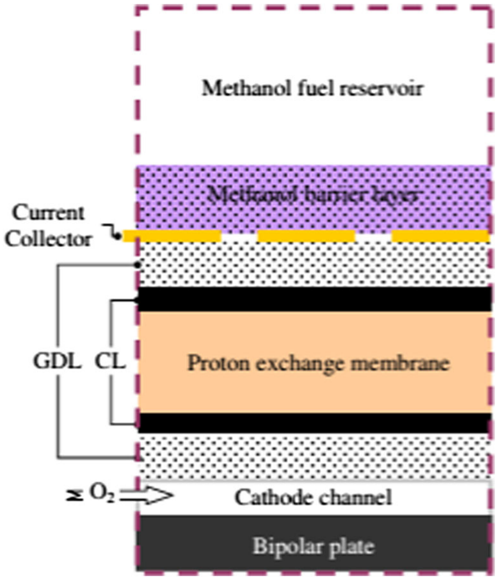

**Fig. 2** Schematic of high concentration methanol feed passive DMFC [49]

### *Minimum methanol loss*

In a passive DMFC, total methanol consumption can be divided into three parts:

i. The methanol used for producing useful current (cell current).
ii. The methanol which permeates through PEM.
iii. The methanol vapor carried out of the cell with the release of carbon dioxide gas on the anode side.

The fuel efficiency is defined as the ratio of amount of fuel converted into useful electrical energy to the total amount of fuel used. The studies aimed to reduce methanol wastage, frequently uses this term in the discussions. For the effective passive DMFC operation, the fuel efficiency must be high. The fuel efficiency of the passive DMFC can be increased by following methods:

i. By reducing MCO. Detailed discussion on the methods to reduce MCO is provided in the "Methanol crossover."
ii. By reducing the amount of methanol vapor carried out with the release of carbon dioxide. Rice and Faghari [57] showed by the numerical analysis that the methanol vapor carried out from the system with the release of carbon dioxide is approximately one fifth of the total methanol consumed in the chemical reactions. Prakash et al. [58, 59] described a novel carbon dioxide venting technology using polymer membranes (poly(dimethyl siloxane, PDMS) and poly(1-trimethyl silylpropyne, PTMSP)), which separates carbon dioxide from methanol and allows only carbon dioxide to escape out of the cell.
iii. By optimizing the structural parameters and operating conditions. Many experimental [60–62] and theoretical studies [63, 64] reveal that the fuel efficiency decreases, mainly due to increase in MCO, with increase in methanol feed concentration. Therefore, the highest fuel efficiency can be achieved by using the lowest possible methanol feed concentration. However, the highest power density of a passive DMFC is obtained with relatively higher methanol feed concentration (2–4 M). Jewett et al. [63] plotted the variation in the product of power density and fuel efficiency with methanol feed concentration and thereby suggested an optimum methanol feed concentration of 2 mol kg$^{-1}$, since it gives the best compromise between power density (21 mW cm$^{-2}$) and fuel efficiency (63.0 %). A bit different results were presented by Lai et al. [62] as they investigated the effect of methanol feed concentration on fuel efficiency at different current density and found that the fuel efficiency decreased from 46.9 to 17.4 % when methanol feed concentration increased from 1 to 8 mol L$^{-1}$ at the lower current density of 11.1 mA cm$^{-2}$. However at a relatively higher current

density of 44.4 mA cm$^{-2}$, the fuel efficiency increased from 14.7 to 31.3 % when methanol feed concentration increased from 1 to 8 mol L$^{-1}$.

Liu et al. [65] studied experimentally the effect of PEM thickness on the fuel efficiency and the results obtained are shown in Fig. 3. Three PEMs: Nafion 112, Nafion 115 and Nafion 117, were used for the analysis. The MCO is inversely proportional to the membrane thickness. The thickest membrane (Nafion 117) exhibited the highest fuel efficiency, whereas the thinnest membrane (Nafion 112) yielded the worst fuel efficiency and therefore it was recommended to use thicker membrane to achieve higher fuel efficiency. Similar recommendation was made by Lai et al. [62] as well.

In the recent past, significant researches have been carried out for the effective methanol management in a passive DMFC. However, most of the researches mainly focus on improving the energy density. Only few works deal with improving the methanol distribution at ACL and to reduce the methanol loss from reservoir. More work is anticipated in this direction. Methanol concentration at ACL governs the concentration polarization, MCO, cell temperature, and the cell performance. Techniques should be developed to keep the methanol concentration at ACL always at the optimum level for wide range of current drawn.

## Water management

Water management is crucial in the passive DMFC and it has a great impact on the power output, efficiency, performance stability over long-term operation, etc. The following are the objectives to be achieved for effective water management.

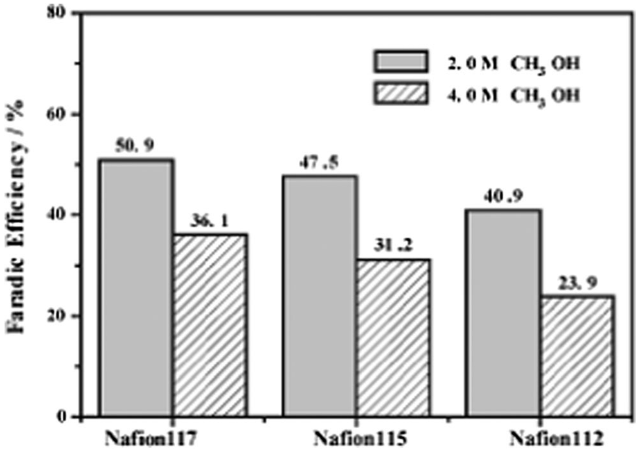

**Fig. 3** The effect of PEM thickness on fuel efficiency of passive DMFC [65]

### *Uniform distribution and sufficient availability of water at ACL*

Water, together with methanol, should be distributed uniformly over the ACL. A non-uniform distribution of water may create several location in the ACL unutilized for electrochemical reaction and reduces the cell performance. The discussion presented in "Uniform distribution of methanol at ACL" for the uniform distribution of methanol equally applies on the uniform distribution of water as well.

At the anode, one molecule of water is required for oxidation of one molecule of methanol, i.e., stoichiometric ratio is 1:1. But, in actual, much diluted methanol solution (water to methanol molecular ratio >1:1) is used in the passive DMFC to accomplish a complete oxidation of methanol (which releases six electrons). Insufficient availability of water for anode reaction may cause incomplete methanol oxidation, which results in formation of intermediate products such as formic acid (HCOOH) and formaldehyde (HCHO, it is highly toxic) and in lesser electron production as given below:

$$CH_3OH + H_2O \rightarrow 4H^+ + 4e^- + HCOOH \quad (4)$$

$$CH_3OH \rightarrow 2H^+ + 2e^- + HCHO \quad (5)$$

Therefore, to avoid this, sufficiently diluted methanol solution should be used. This objective of water management is readily fulfilled in the conventional passive DMFCs as diluted methanol solution is fed to avoid MCO; however, this can be a serious issue if concentrated or pure methanol is used.

### *Reduce water crossover and cathode water flooding*

In a passive DMFC, water appears at CCL by three ways:

i. Non-reacting water at ACL permeates through PEM and reaches at CCL, which is termed as WCO.
ii. Water generates at CCL by cathode electrochemical reaction.
iii. Water generates at CCL by oxidation of crossovered methanol.

The water at CCL can be evacuated out of the cell only by natural convection. If the rate of water removal is low, water may accumulate on the cathode side of the cell, resulting in so-called water flooding problem. The liquid water may block the pores of diffusion layer and therefore obstruct the oxygen transport. The insufficient oxygen at CCL may cause decrement in the cell performance. As compared to the active DMFC, the water flooding problem is more serious in the passive DMFC as the capacity of water removal in the passive DMFC is less than that in the active DMFC. Therefore, for efficient cell operation, it is very important to eliminate the cathode water flooding problem. The cathode flooding is a problem of higher concern in a diluted methanol feed passive DMFC compared to the high concentration methanol feed passive DMFC. Following are the methods to control the cathode water flooding problem:

(a) Enhance rate of cathode water removal

If the rate of water transport from the CCL to the ambient air becomes equal to the rate of water appearing at the CCL, then the net water accumulation at the CCL will be zero and the cathode water flooding can be avoided. As the water transport from the CCL to the ambient air is by passive means only, it is very challenging to enhance it.

Several researchers modified the cathode structure to enhance the cathode water removal. Chen and Zhao [66] used porous metal foam as CCC of the passive DMFC and found the cell yielded better and much more stable performance than the cell with conventional perforated plate current collector. One of the reasons for enhancement in the cell performance was the better water removal at the cathode as a result of the enhanced water transport by capillary action in the porous metal foam. The effect of current collector design on the passive DMFC performance was studied by Gholami et al. [67] and it was found that the water removal is easier in the parallel channel current collector compared to the perforated plate current collector. Moreover, non-uniform parallel channels with negative channel slop in the CCC can be more effective in the water removal. Chen et al. [68] investigated a passive DMFC with stepwise hydrophobicity distributed CCL and found that the stepwise hydrophobicity distribution favors the removal of water from the cathode via gasification and is beneficial for the effective water management.

Wang et al. [69] treated the surface of an aluminum-based CCC by plasma electrolyte oxide, composed of $Al_2SiO_3$ and $Al_2O_3$, to prepare a super-hydrophilic coating [69]. It was found that the liquid water spreads quickly and water droplet does not form on the surface of treated CCC and the cathode water flooding was avoided. To remove cathode water, Hashim et al. [70] proposed a cathode design which consists of 1.0 mm vertical channels for water to flow under gravitational force without disturbing the air transport path.

The cell operating condition also has significant impact on the cathode water removal. Lai et al. [71] investigated the passive DMFC performance with different cell orientations and found that the passive DMFC with horizontal orientation and anode facing upward least suffered with cathode water flooding compared to vertical orientation and horizontal orientation with anode facing downward. It was due to more effective removal of liquid water by the gravity and therefore the cell exhibited the best long-term performance. Chan et al. [72] suggested operating the passive DMFC at higher temperature for effective removal of cathode water as the increased cell temperature enhances the water evaporation rate on the air-breathing cathode. Guo et al. [73] developed a three-dimensional transient model to investigate the mass transfer characteristic in the cathode of a passive DMFC. They found that an adequate cell current density and appropriate cathode pressure could facilitate better water removal. Also, the porosity of CCL has definite effect on the cathode water removal. Some of the researchers insisted using active feed of oxygen on cathode side, while using the passive feed of methanol at the anode in a DMFC as active oxygen feed can be effective for removing the cathode water [74]. This type of the DMFC is referred as semi-passive DMFC.

(b) Reduce water crossover

In the passive DMFC, WCO occurs by three different mechanisms: diffusion, electro-osmotic drag (EOD) and hydraulic permeation (convection) (Fig. 4). Diffusion occurs due to the water concentration gradient across the PEM. The protons moving from anode to cathode drag water molecules with them which is known as EOD. The hydraulic permeation occurs due to the pressure gradient across PEM. The WCO not only causes anode water loss but also exaggerates cathode water flooding. Previous studies [75] showed that the rate of water produced at CCL could be lower than the rate of WCO, indicating that the WCO is the primary cause of cathode water flooding. Therefore, to control the cathode water flooding, it is necessary to control the WCO.

The WCO is influenced by operating conditions of the passive DMFC such as current density, methanol feed concentration, etc. In a passive DMFC, the WCO increases with increase in current density, mainly due to increase in EOD (more number of protons drags more

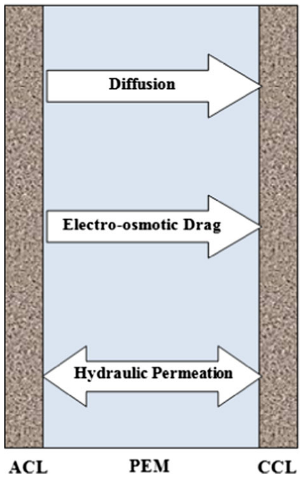

**Fig. 4** Mechanism of WCO in a passive DMFC

water molecules) (Fig. 5) [61, 76–78]. Therefore, to alleviate WCO, the cell should be operated at low current density. However, the WCO remains almost same for all the methanol concentration indicating that methanol concentrations below 4 M have negligible influence on the WCO [61, 76]. Xu et al. [61] pointed out that the diffusion-driven WCO flux from anode to cathode was almost offset by the water back convection (hydraulic permeation) from cathode to anode as they found net water transport co-efficient 2.6, very close to the electro-osmotic drag coefficient of the membrane (2.5). With the increase in the cell temperature, the diffusion coefficient and electro-osmotic drag coefficient increase and therefore the WCO increase [79].

The effect of MEA structure on the WCO in a liquid-feed DMFC was studied by Yang and Zhao [78]. It was found that the WCO can be reduced by decreasing the permeability of ACL, and by increasing the hydrophobic level of ACL. The total rate of WCO was much lower for a thicker membrane (Nafion 117) than that for a thinner membrane (Nafion 112).

(c) Reduce methanol crossover

Water produced due to the oxidation of crossovered methanol at CCL contributes significantly to the cathode water flooding. The techniques reducing MCO will be also helpful in reducing cathode water flooding. The details on how to reduce MCO is given in "Methanol crossover."

(d) Enhance water back flow

One of the potential solutions for reducing cathode water flooding is to transport the water back from the cathode to the anode, which is referred as water back flow. The water back flow not only reduces the cathode water flooding but also reduces the external supply of water for the anode reaction and therefore provides opportunity to operate the cell with concentrated methanol solution. The water back flow is achieved by creating a hydraulic pressure gradient between cathode and anode with higher hydraulic pressure at the cathode.

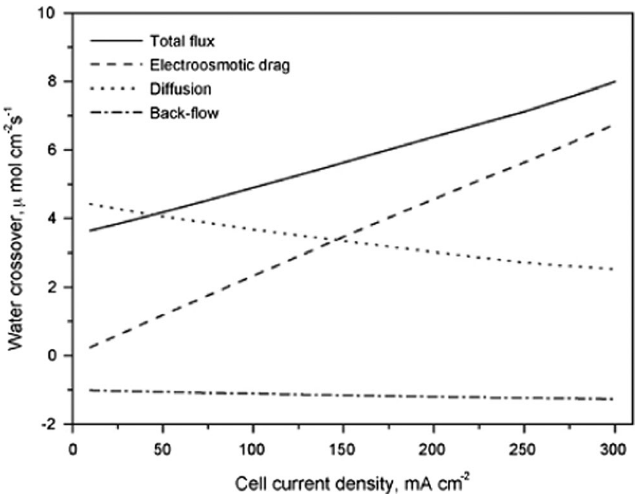

**Fig. 5** Variation in WCO flux through membrane [78]

Cao et al. [80] used a double MPL cathode in the passive DMFC. The inner MPL was made of Ketjen Black carbon with 50 wt% of PTFE and outer MPL was made of Vulcan XC-72R carbon with 25 wt% of PTFE. The Novel MEA facilitated more effective water back flow from cathode to anode and therefore the cell exhibited lower cathode flooding (Fig. 6), higher performance, and more stability than the cell with conventional MEA. Jewett et al. [81] used two additional CDLs to enhance water back flow and achieved an increase in water balance coefficient from −1.930 to 1.021 in a passive DMFC operated with 3.0 mol kg$^{-1}$ methanol solution at a current density of 33 mA cm$^{-2}$. Kim et al. [82] developed MEA with diffusion layers containing hydrophilic nano-particles and found that water back diffusion increased several times than that for the conventional MEA. A CDL that utilizes mesoporous carbons with uniform mesopores and high pore volume was fabricated and tested by Cao et al. [83] for the passive DMFC and it was revealed that the novel CDL structure can promote the water back flow from cathode to anode and therefore the cell delivered a power density of 31.4 mW cm$^{-2}$ with enhance discharge stability. Moreover, addition of fluorinated Vulcan XC-72R into the cathode MPL [84], addition of hydrophobic air-filter layer at the cathode [76], addition of a hydrophobic water management layer at the cathode [61], and addition of hydrophobic water leak proof layer on the both sides of the CCC [85] were the other techniques adopted for enhancing water back flow in the passive DMFC.

Large number of studies helps to alleviate the issue of cathode water flooding to a great extent; however, further studies are essential to eliminate it completely. It is essential to improve understanding of the two-phase flow of water and air at the cathode side in order to provide sufficient oxygen for the cathode reaction and to reduce cathode flooding problem.

## Oxygen management

Oxygen from ambient air transported through CCC and CDL by the process of diffusion and natural convection and reaches the CCL, where it gets consumed in cathode electrochemical reaction and in oxidation of crossovered methanol. Following are the tasks to accomplish effective oxygen management.

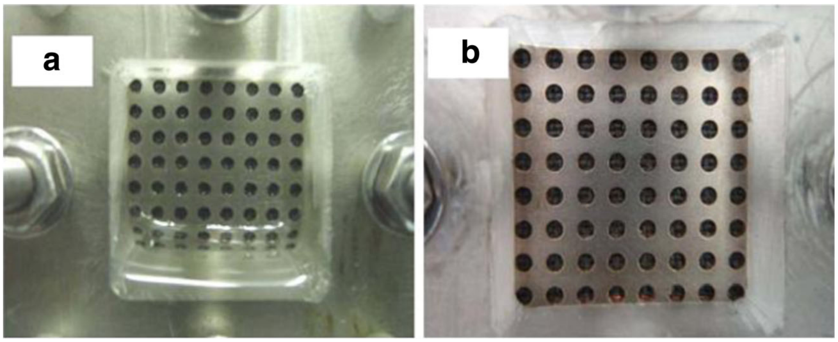

**Fig. 6** Photograph of the passive DMFC cathode with **a** conventional MEA and **b** MEA with double MPL cathode during a continuous operation at 40 mA cm$^{-2}$ for 3 h [80]

### *Sufficient availability and uniform distribution of oxygen at CCL*

Oxygen, in sufficient quantity, must be available at the CCL for the electrochemical reaction. Otherwise, the insufficient availability of oxygen may lead to increase in concentration polarization, especially at high current densities, which may result in inferior cell performance. The sufficient availability of oxygen at CCL can be accomplished by minimizing the mass transport resistance for oxygen between CCC and CCL. The resistance to the oxygen mass transport is offered by the accumulated water at the cathode and by physical structure of the cathode. The researches for reducing cathode water flooding are also helpful in reducing mass transport resistance for oxygen.

Water accumulated at CCL may occupy several catalyst locations and lead to non-uniform distribution of oxygen. The structure of CCC also affects the oxygen distribution at the CCL. The oxygen concentration at the CCL under the current collector rib is found lower than that under the current collector opening [76, 86]. The non-uniform distribution of oxygen at CCL results in several oxygen starving locations which decreases the cell performance. Therefore, for effective cell operation, the oxygen should be uniformly distributed over the CCL.

Researchers showed that the oxygen transport in the passive DMFC is affected by the MEA design, the CCC structure, and the cell operating conditions. Chen and Zhao [66] used porous metal foam as CCC in the passive DMFC and claimed better cell performance compared to the cell with conventional perforated plate current collector. The better cell performance was attributed, mainly, to the increased oxygen transport rate due to the larger specific transport area of metal foam and lower cathode flooding. Chen and Zhao, in another study [87], replaced the conventional diffusion layer with a Ni–Cr alloy metal foam plate. The new MEA exhibited lower overall mass transport resistance and higher transport rate of oxygen and thus improved the passive DMFC performance.

Reshetenko et al. [88] introduced pore-forming materials, ammonium carbonate and ammonium hydrocarbonate, in the CCL of an air-breathing DMFC. It was seen that, upon decomposition during MEA fabrication, the ammonium carbonate increases the macropores formation, while ammonium hydrocarbonate increases the mesopores formation and therefore results in the increased porosity of the cathode, which enhances the oxygen transport rate. Chen et al. [68] compared the performance with single-layer catalyst cathode, double-layer catalyst cathode, and multi-layer catalyst cathode in the MEA of passive DMFC (Fig. 7). The conventional single layer catalyst cathode contained 20 wt% Nafion content, the outer layer of double layer catalyst contained 10 wt% Nafion and 10 wt% PTFE, while the inner layer, adjacent to the PEM, contained 20 wt% Nafion. The multi-layer catalyst cathode was fabricated by adding one more catalyst layer containing 15 wt% Nafion and 5 wt% PTFE on the double-layer catalyst cathode, and in this way, the stepwise distribution of hydrophobicity on the cathode was achieved. The total platinum loading of 4 mg cm$^{-2}$ was maintained in every cathode. It

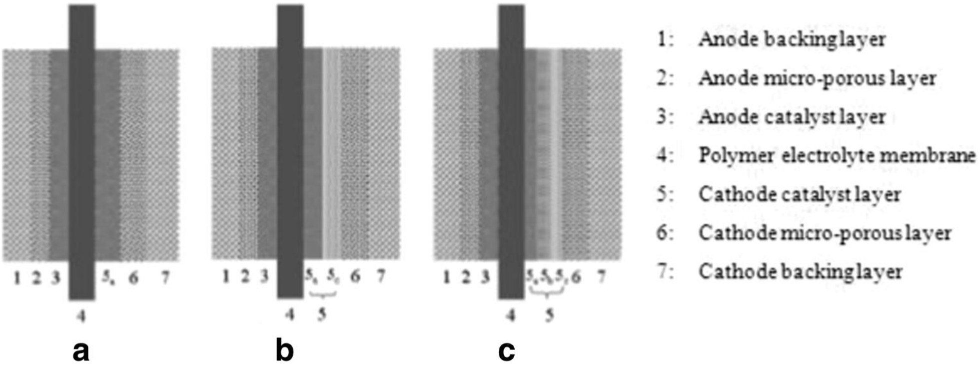

**Fig. 7** Schematic diagram of MEA with **a** single layer catalyst cathode; **b** double layer catalyst cathode; and **c** multi-layer catalyst cathode [68]

was found that the hydrophobicity gradient on the cathode can accelerate the oxygen transport and enhance water back diffusion, and therefore the passive DMFC with multi-layer catalyst cathode delivered the best performance. Cao et al. [83] prepared a CDL by coating the slurry of mesoporous carbon (2.0±0.2 mg cm$^{-2}$ carbon loading) and PTFE (20 wt%) onto the carbon cloth and compared it with conventional CDL, which contained XC72R carbon. The passive DMFC with mesoporous carbon CDL performed better than the passive DMFC with conventional CDL. It was due to suitable pore size and pore structure of mesoporous carbon, which enhanced the oxygen transport in the cathode and therefore increased oxygen concentration at CCL was achieved.

### *Clean air*

The passive DMFC cathode is kept open and exposed to the surrounding atmosphere and hence can be harmed by dust particles and chemicals present in the air. Moreover, due to the open cathode, the passive DMFC cannot be operated in the rainy situations as the rain water may block the cathode pores and disrupt the oxygen transport. To eliminate these problems, it was suggested to use the air filters at the cathode of the passive DMFC [63, 76, 81]. The four air filters: oil sorbents, expanded PTFE, porous polyethylene-I, and porous polyethylene-II, different in thickness, mean pore size, and porosity, were tested in a passive DMFC by Jewett et al. [63, 81]. The incorporation of cathode air filter also affects the air transport, water transport, heat transport, and the overall cell performance. However, the run time of the cell was decreased slightly with the incorporation of air filter but the average power density was unaffected. Among the different air filters, the oil sorbent was chosen the best as it exhibited better overall water management, better cell performance, and the deep filtration characteristic.

Limited studies were found on oxygen management issue of the passive DMFC. The present open cathode structure does not permit the passive DMFC operation in the rainy and high dust situations. It is essential for the commercialization that the passive DMFC should be made operational in these extreme situations as well.

## Carbon dioxide management

In the passive DMFC, carbon dioxide is produced due to anode electrochemical reaction. Then, it flows counter-currently towards the fuel reservoir due to the buoyancy force (Fig. 8) and escape out of the cell from the vent provided in the fuel reservoir. If the carbon dioxide is not effectively removed, it gets accumulated on the ACL, reducing the availability of catalyst sites for anode electrochemical reaction. Moreover, carbon dioxide can block the pores of ADL and occupy the openings of ACC, thereby increasing the mass transport resistance for methanol and leads to decrease in the cell performance [89]. The major task of carbon dioxide management is, therefore, to remove carbon dioxide quickly and continuously from the passive DMFC.

The carbon dioxide evolution is affected by the anode structure and the operating conditions. The rate of carbon dioxide production is directly proportional to the current produced by the cell. Carbon dioxide is produced at a higher rate and its removal become more difficult at a higher current density [44, 90]. To achieve higher limiting current and to provide better conditions for anode reaction, the effective removal of carbon dioxide, especially at a higher current, is essential [91]. The removal of the carbon dioxide becomes easier, due to the lesser mass transport resistance, on increasing the open ratio of the ACC [44, 92]. The larger rib width of ACC makes more difficult the carbon dioxide transport from the rib region to the open region, and thus leads to higher gas saturation under the rib region [44]. Yang et al. [93] showed that the parallel channel current collector, due to the higher open ratio, allows easy removal of carbon dioxide compared to the perforated plate current collector.

The horizontal orientation of the passive DMFC with anode facing upward exhibits more effective removal of carbon dioxide and hence more stable cell performance compared to horizontal orientation with anode facing downward and vertical orientation of the cell [71, 94]. In a unique study, Liu et al. [95] proposed a magnetic-coupled passive DMFC for the effective carbon dioxide removal. Magnetic field was created by placing two chrome ferrite magnets, with intensity 200 mT, 3 cm away from the cell. It was found that the Lorentz force, generated by the magnetic field, promoted the carbon dioxide removal and as a result the cell performance was improved by 12.5 %.

Effective carbon dioxide management is essential for high performing passive DMFC. Studies focusing specifically on carbon dioxide management are rare. Both experimental and theoretical studies are needed on this issue. The carbon dioxide evolution heavily depends upon the cell orientation. The

**Fig. 8** Photograph of the carbon dioxide bubble coming out from the openings of ACC in a passive DMFC [92]

passive DMFC should be designed in such a way that it must have effective carbon dioxide evolution in all the orientations.

## Thermal management

At ACL, heat is generated due to the anode overpotential and heat is consumed in the anode electrochemical reaction. At CCL, heat is generated due to the cathode overpotential, oxidation of crossovered methanol, and due to cathode electrochemical reaction, while heat is consumed in the evaporation of liquid water. The net heat generated in the passive DMFC is dissipated to the methanol solution in the reservoir at the anode side and to the ambient air at the cathode side. The aim of effective thermal management in a passive DMFC is to minimize heat loss, so that the cell temperature can be maintained at a sufficiently high level. A higher cell temperature increases the electrochemical kinetics at both electrodes and therefore increases the cell performance. In a passive DMFC, the cell temperature is deeply related with the MCO. The permeated methanol reacts with oxygen at cathode and releases heat which increases the cell temperature. That is why the increase in cell temperature is treated, in many studies, as an indication of increased MCO rate [44, 57, 76, 94, 96, 97].

Cell temperature depends on the cell operating parameters such as methanol feed concentration, current density, ambient temperature, air humidity, cell orientation, etc. and on the cell structural such as current collector design, PEM thickness, etc. The cell temperature increases with increase in methanol feed concentration (Fig. 9). The MCO rate increases with increase in methanol feed concentration, which release more heat upon oxidation at cathode [44, 57, 61, 76, 96–99]. The cell temperature increases with increase in current density. At high current densities, the ohmic overpotential and mass transfer overpotential becomes high and therefore higher heat is released per unit time (Fig. 9) [44, 61, 76, 96, 97, 99–101].

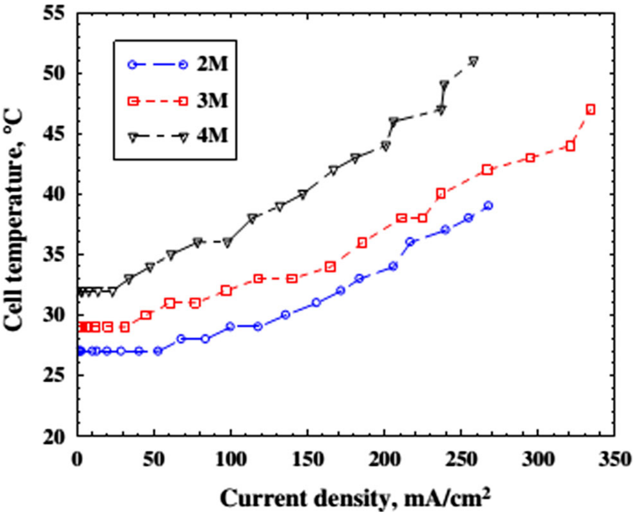

**Fig. 9** Variation in cell temperature with current density for different methanol feed concentrations [61]

The higher ambient temperature causes lower heat loss from the cell and results in higher cell temperature [57, 97]. The cell temperature increases with increase in air humidity as the increase in air humidity decreases the water removal rate at cathode and thus decreases the latent heat loss [57, 76]. The cell operating orientation also affects the passive DMFC temperature. A vertical orientation of the cell exhibits higher MCO and therefore yields higher cell temperature compared to that with horizontal orientation [94]. In the vertical orientation, cell temperature gradually increases from the bottom to the top of the cell due to counterclockwise circulation of methanol solution caused by natural convection. In the horizontal orientation, the cathode temperature is higher than the anode temperature as the net heat generated at the cathode is much greater than that generated at the anode [99].

At lower current densities, the passive DMFC with higher open ratio of the current collectors exhibits higher cell temperature. Whereas at higher current densities, the cell with lower open ratio of the current collectors exhibits higher cell temperature. At lower current densities, the higher open ratio of the ACC yields higher MCO rate and that leads to higher heat release rate and higher cell temperature. Whereas at higher current densities, the heat generated by ohmic and mass transfer overpotentials becomes dominant (over decrease in MCO rate). Mass transfer overpotential increases with decrease in open ratio which results in higher cell temperature at a lower open ratio of the current collector [44]. A higher rib width on the current collector exhibits higher mass transport overpotential and higher resistance to heat transfer on the cathode and thus yields higher cell temperature [44]. Chen and Zhao [66] used porous metal foam (Ni–Cr alloy) current collector at the cathode of a passive DMFC and achieved a higher cell temperature compared to the conventional perforated plate current collector, which was due to the lower effective thermal conductivity of the porous structure. The PEM thickness also influences the passive DMFC temperature. The thinner membrane yields higher cell temperature due to higher rate of MCO [65].

Significant research has been conducted in the recent past to understand the relation between the cell temperature and the cell performance. A higher cell temperature improves the electrochemical kinetics but also increases the MCO rate. Optimization of the cell temperature for optimum cell performance is not been done yet. Moreover, the cell design and component structure should be modified to minimize the heat dissipation.

## Methanol crossover

Methanol, when crosses the PEM and reaches the cathode, affects the passive DMFC performance in the following ways:

i. Methanol reacts with oxygen at CCL, creating mixed potential which results in cell voltage loss.
ii. The poisoning of cathode catalyst (Pt).
iii. MCO contributes in cathode water flooding that decreases the cell performance.
iv. Decrease in fuel efficiency.
v. Destruction of PEM (Nafion membrane).

MCO contributes the largest portion of the irreversibilities inside the passive DMFC [102]. For effective cell operation, the MCO should be as low as possible. The MCO is caused by three mechanisms: diffusion, EOD, and hydraulic pressure difference across membrane. The diffusive mass transport is the dominant contributor of the total MCO followed by the EOD, while the hydraulic pressure difference contributes least to the total MCO (Fig. 10). The total MCO increases with increase in methanol feed concentration [44, 61, 100, 103–105]. The diffusion MCO is proportional to the methanol concentration gradient across PEM. The methanol concentration at ACL and hence the methanol concentration gradient across PEM increases with increase in methanol feed concentration, which increases the diffusion MCO and the total MCO [64]. EOD is caused by dragging of the methanol molecules by protons moving from anode to cathode. The EOD component of MCO depends on the amount of current generated from the cell and on the methanol fraction at the ACL-PEM interface. In general, EOD increases with increase in current density. However, the methanol concentration at ACL decreases, which decreases the diffusion component of MCO, on increasing the current density. At lower methanol feed concentration, methanol concentration at ACL decreases sharply with increase in current density and the total MCO decreases with increase in current density (Fig. 11). Whereas, at higher methanol feed concentration, sufficient methanol is available at ACL, the methanol concentration and therefore the diffusion-driven MCO does not decreases much with increase in current density. The EOD component of MCO, which increases with increase in current density, becomes dominant and the total MCO increases with increase in current density [44, 99, 102]. To achieve minimum MCO, the passive DMFC should be fed with diluted methanol solution and must be operated at higher current density.

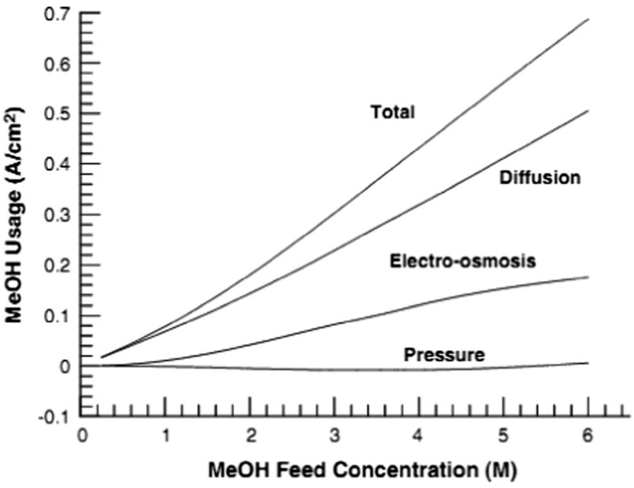

**Fig. 10** Methanol crossover vs. methanol feed concentration at maximum power density of passive DMFC [64]

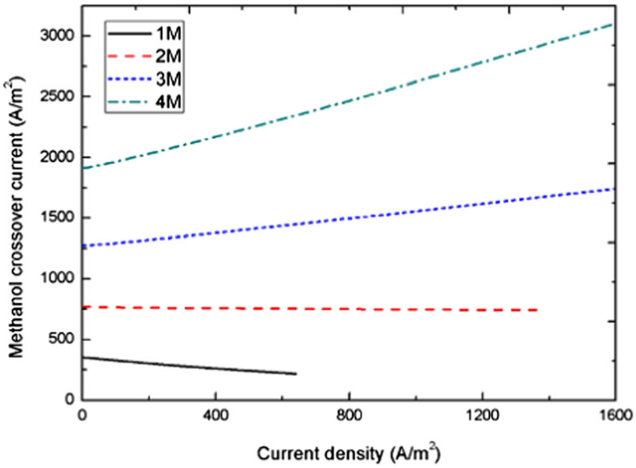

**Fig. 11** Variation in MCO with current density at different methanol feed concentrations [99]

The passive DMFC with vertical orientation exhibits higher rate of MCO, due to the stronger natural convection, compared to that with horizontal orientation [94]. The thicker membrane (Nafion 117) yields lower MCO due to the lower methanol concentration gradient across membrane [65, 92].

In order to reduce the MCO in the passive DMFC, following approaches have been used in the recent past:

i. Maintaining low methanol concentration at ACL

MCO is proportional to the methanol concentration at ACL, and therefore, the most preferred approach to reduce the MCO is to maintain the methanol concentration at ACL as low as possible. This can be achieved by using diluted methanol solution (<4 M) in the reservoir [60, 66, 67, 87, 94, 96, 102, 103, 106, 107]. But, the use of diluted methanol solution in the reservoir decreases the specific energy of the cell and therefore reduces the operation time in a single fuel recharge. To increase the specific energy, the concentrated methanol must be used in the passive DMFC which, however, can drastically increase the MCO. The target of using of concentrated methanol solution at reservoir, while maintaining the methanol concentration at ACL at a lower level, can be achieved by inserting a methanol barrier layer between methanol reservoir and ACC [47–56] as shown in Fig. 2.

ii. Using highly active anode catalyst

The passive DMFC mostly utilizes Pt-Ru bimetallic catalyst at anode, which exhibits very slow rate of methanol oxidation reaction. A highly active anode catalyst can promote the rate of anode electrochemical reaction and, therefore, can be helpful in maintaining the methanol concentration at ACL at a lower level in order to reduce the MCO [108, 109]. The details on the past researches aimed to enhance the anode catalyst activity are given separately in the "Sluggish anode kinetics." Despite huge research in this direction, Pt-Ru catalyst is still the best. The rate of anode electrochemical reaction can also increased by using very high catalyst loading, but it will increase the fuel cell cost tremendously.

iii. Use of thicker membrane

A thicker membrane (such as Nafion 117) offers high resistance to the methanol transport and hence reduces the MCO. However, a thicker membrane also exhibits lower proton conductivity and decreases the cell performance [65, 92]. Studies are being carried out to enhance the proton conductivity of the membrane so that the thicker membranes can be used to reduce the MCO without compromising the cell performance.

iv. Use of methanol-tolerant cathode catalyst

The cathode catalysts with high activity towards oxygen reduction reaction and inactivity towards oxidation of crossovered methanol (methanol tolerant) can provide a solution for reducing mixed-potential at cathode [19, 110–115]. Several metal cluster compounds such as palladium-based alloys, such as Pd–Co, Ni, and Cr [116], carbon-supported palladium-cobalt-noble metal (Au, Ag, Pt) nanocatalysts [117], carbon-supported-Pt-Pd-alloy [118], transition-metal macrocycles and ruthenium-based chalcogenides [119], Pd–$WO_3$, and Pd–$SnO_2$ [120] were investigated as methanol-tolerant catalysts. The methanol-tolerant catalysts do not actually restrict MCO. The permeated methanol at cathode, however not oxidized, vent out of the cell by evaporation and natural convection. Therefore, this approach cannot reduce fuel loss and cannot be considered as a complete solution of the MCO.

v. Development of membranes with low methanol permeability

The Nafion membranes possess high proton conductivity, high chemical and thermal stability, but it is highly permeable to methanol and hence it is considered most responsible for the MCO in a passive DMFC. The development of the membrane to suppress MCO should be without compromising other important properties such as ionic conductivity, chemical and thermal stability, and cost. The latest development in the membranes for achieving low methanol permeability can be divided into two categories:

a. Development of alternate membranes

Several membranes, considered as alternate to existing Nafion membrane, have been developed in order to reduce the MCO [121–124] such as membranes based on sulfonated poly(ether ether ketone) (SPEEK), membranes based on Poly(imide)s, acid-doped polybenzimidazoles (PBIs), membranes based on grafted copolymers such as poly(ethylene-tetrafluoroethylene) (ETFE), sulfonated poly-styrene membranes (SPS), poly(vinylidene fluoride) (PVDF) membranes, membranes based on block copolymers (sulfonated poly(styrene-b-ethylene-r-butylene-b-styrene) (S-SEBS)), triblock copolymer of sulfonated poly(styrene-isobutylene-styrene) (S-SIBS), cross-linked PVA-PAMPS [poly(vinyl alcohol) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid)] composites, poly(ethylene tetrafluoroethylene) (ETFE) membranes, etc.

Rambabu and Bhatt [125] prepared an alternative membrane by incorporating polystyrene sulfonic acid (PSSA) functionalized multi-walled carbon nanotubes (PSSA–MWCNTs) into sulfonated polyether ether ketone (sPEEK) matrix by solution casting procedure. The sPEEK–PSSA–CNTs membrane exhibited lower MCO and better DMFC performance compared to pristine sPEEK and Nafion membrane. Diaz et al. [126] compared the methanol permeability in phosphoric acid-doped membranes based in poly[2,2-(m-phenylene)-5,5-bibenzimidazole] (PBI) and poly[2,5-benzimidazole] (ABPBI) with commercial Nafion 117 membrane. The MCO in the ABPBI was higher than PBI, but 1 order of magnitude lesser than the Nafion® 117 in the temperature range 20–90 °C. The ratio of proton conductivity and the MCO coefficient for the ABPBI membrane was much higher as compared to Nafion and PBI membrane.

b. Modification in existing Nafion membrane

The several research works have been carried in the recent past to modify Nafion membrane in order to make them less methanol permeable. The modification in the Nafion membrane is achieved by:

- Making a composite membrane by blending Nafion membrane with organic or inorganic materials:

  Different types of composite membranes were developed for the DMFCs [122, 127] such as Nafion membrane blended with organic materials (Nafion/polypyrrole, Nafion/poly(1-vinylimidazole), Nafion/polyfurfuryl alcohol (PFA), Nafion/polyvinylidene fluoride (PVdF), and Nafion/polyvinyl alcohol (PVA)), Nafion membrane blended with inorganic materials (sulfonated organic silica, zirconium phosphate, zeolite and montmorillonite), and organic–inorganic hybrid membranes. Molla and Compan [128] prepared a composite membrane for DMFC by depositing the Nafion® polymer between PVA nanofibers. The Nafion/PVA composite membrane showed linear variation of the resistance to MCO with the membrane thickness. As compared to pristine Nafion® membranes, the composite membrane showed a remarkable reduction, 1 order of magnitude, in the MCO. Ahmad et al. [129] developed organic–inorganic hybrid membrane by casting mixtures of zirconium phosphate (ZP), polybenzimidazole (PBI), and Nafion dispersion in dimethylacetamide. Hybrid Nafion-PBI-ZP membrane formed a dense and fine structure with high water content, which facilitated better proton conductivity compared to Nafion 117 membrane. The MCO for the hybrid membrane was almost four times lower than that for the Nafion 117 membrane.

- Providing film coating on the Nafion membrane surface

  Chiu et al. [130] sputter deposited PTFE on the Nafion 117 surface and found that coated PTFE film act as a barrier for methanol and therefore effectively reduces the MCO, whereas the proton conductivity was not significantly influenced. Trioctylphosphine (TOP)/Pd composites have been synthesized and applied to the surface Nafion 115, by Tian et al. [131], to be acting as methanol barrier in the DMFC. The modified surface was crack-free and adhered well with Nafion membrane. The TOP/Pd-modified Nafion membrane showed reduced MCO and better cell performance compared to bare Nafion 115 membrane.

  More details on the membrane development can be found in the articles of Lufrano et al. [121], Ahmad et al. [122], Neburchilov et al. [123], and Wang et al. [124].

  MCO is one of the major causes of decreased cell performance and is considered as a major challenge among the researchers. A lot of studies have been carried out in the recent past to encounter the MCO. Some success has been achieved in reducing the MCO, but the results so far are not sufficient to solve this problem and more research is needed in this direction to achieve the breakthrough.

## Sluggish anode kinetics

At the passive DMFC anode, the oxidation of methanol occurs at a much slower rate compared to that of hydrogen in the $H_2$-PEMFC causing higher activation overpotential in the passive DMFC. The complete oxidation of methanol at anode produces carbon dioxide and releases six electrons and six protons and is a complex series of various intermediate reaction steps as shown in Fig. 12 [132, 133]. At the top left is fuel, methanol, and at the right-bottom is product, carbon dioxide. Any route can be adopted to move from methanol to carbon dioxide. But, the most preferred route is the route with consecutive one right step and one down step as; this route contains the stable compounds viz. formaldehyde ($CH_2O$) and formic acid (HCOOH). Initially, Pt was used as anode catalyst in the DMFCs. It can be seen in Fig. 12 that, during methanol oxidation, carbon monoxide (CO) can be an intermediate product. The carbon monoxide act as poison for the Pt catalyst, and therefore to eliminate catalyst-poisoning, a more active alloy catalyst, Pt-Ru (atomic ratio 1:1), is now being used. The oxygen containing species adsorbs on the Ru atoms at lower potentials and promotes the oxidation of CO to $CO_2$ [134–136]. Recently, Sahin and Kivrak [137] studied the effect of addition of ruthenium to the carbon supported Pt and Pt-Ru catalyst for methanol oxidation. Pt–Ru (25:1) catalyst presents the best electrochemical activity and CO tolerance compared to Pt–Ru (3:1), Pt–Ru (1:1), and Pt catalysts.

The anode kinetics can be further improved by following ways:

i. Development in preparation methods of catalysts to achieve narrow nano-scale size and uniform distribution of catalyst, high dispersion of catalyst on catalyst support, uniform composition throughout the catalyst particles. The impregnation method [138], colloidal method [139], and micro-emulsion method [140] are the main methods adopted for preparing carbon-supported Pt-Ru catalyst.
ii. Developing catalyst support materials to achieve fine dispersion, high utilization, and stability of the catalyst particles. Different carbon-based materials viz. carbon nanotubes, carbon nanofibers, nanowires, mesoporous carbon and graphene, as well as non-carbonaceous materials viz. titania, alumina, indium oxides, ceria, zirconia nanostructures, and conducting polymers were used as catalyst support [141–143].
iii. Developing new and improved catalysts. Different anode catalysts developed for DMFCs includes platinum-based catalyst (binary catalyst: PtRu, PtOs, PtSn, PtW, PtMo, etc. [136]; ternary catalyst: Pt–Pd–Ru [144], Pt-Pd-Co [145], Pt-Ru-Mo [146]; quaternary catalyst: Pt–Ru–Ir–

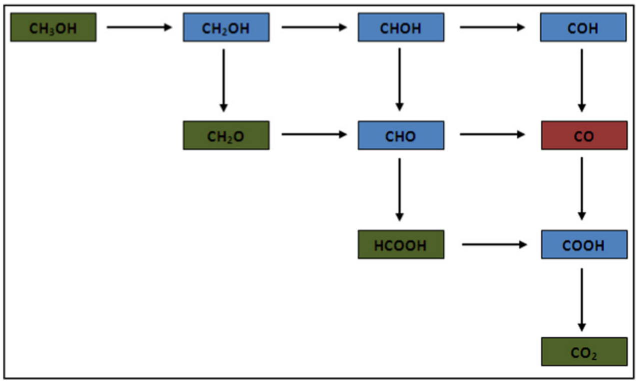

**Fig. 12** Methanol oxidation pathway at the DMFC anode [132, 133]

Sn [147], Pt-Ru-Ir-Ni [148]), non-platinum catalyst [149–151] (such as Pd-Ni alloy, gold nanoparticles onto a polyaniline (PANI) grafted multiwall carbon nanotube (MWNT-g-PANI) matrix, metal free carbon nitride nanotube), non-platinum catalyst based on transition metal carbides [152], and non-platinum catalyst based on promoted transition metal oxides [153] (such as $TiO_2$ modified by Pt, $TiO_2$ modified by Pd, etc.). The activity of non-platinum catalysts, in general, is much lower than that of platinum catalysts. But, non- platinum catalysts have the advantages of low price and strong resistance to poisonous substance.

More detailed discussion on the development of anode catalysts can be found in the articles of Liu et al. [136], Basri et al. [142], Serov and Kwak [152], and Tiwari et al. [154].

A great progress has been made in developing catalyst preparation method, developing catalyst support, and developing new catalyst with noble and non-noble metals, and improved anode kinetics were claimed, further improvements are required with respect to reliability, repeatability, and sensitivity. Most importantly, non-nobel catalysts with improved electrochemical activity must be developed.

## Durability and stability

The durability can be defined as the ability of passive DMFC to resist permanent decay in the performance over time and is related to the decrease in cell performance which is irreversible. The stability can be defined as the ability to recover performance lost during continuous operation and is related to the decrease in cell performance which is reversible [155]. The fuel cell life-time requirement for portable application is around 5000 operating hours [156]. The passive DMFC, which is considered as a promising contender for powering portable devices, currently falls well below this requirement due to the severe performance degradation over the operational time. The performance degradation rate of DMFCs range between 10 and 25 $\mu V\ h^{-1}$, which is much higher compared to that of the $H_2$-PEMFCs [157]. To make the passive DMFC commercially feasible, it is essential to increase its durability and performance stability. The cause of performance degradation of the passive DMFC can be divided into two parts:

### Permanent degradation (Irreversible)

The passive DMFCs suffer from irrecoverable performance loss caused by change in microstructure of its components, change in transport properties, and reduction in catalyst activity. Following are the main cause of the permanent performance degradation of the passive DMFCs:

*Catalyst degradation*

In the passive DMFC, in general, the anode catalyst used is Pt-Ru alloy. Ruthenium (Ru) may crossover from anode to cathode via electro-osmotic water flux at high current densities, which can reduce the CO poisoning tolerance of the anode catalyst and affect adversely the anode kinetics [158–161]. Zainoodin et al. [159] confirmed the Ru crossover in the passive DMFC by energy dispersive spectroscopy (EDS) mapping results which is shown in Fig. 13. Some of the intermediate products of the methanol oxidation reaction such as carbon monoxide, formaldehyde, and formic acid may be adsorbed on the anode catalyst surface, which can prevent the further adsorption and oxidation reaction of fresh methanol [158]. Sintering and decomposition, agglomeration, growth, and dissolution of catalyst particles can occur during long-term operation of passive DMFC which lead to loss of active catalyst surface area and result in decreased cell performance [158, 159, 161]. Figure 14 shows the transmission electron microscope (TEM) image of CCL before (Fig. 14a) and after (Fig. 14b) the durability tests of a passive DMFC. Before the durability test (Fig. 14a), the size of Pt catalyst particles was small and particles were uniformly distributed on the catalyst support with minimal agglomeration. After the durability test (Fig. 14b), the growth of Pt catalyst particles and agglomeration were observed. Furthermore, the permeated methanol can poison the Pt/C catalyst at the cathode, which can results in decreased electrochemical activity [162]. The corrosion of the catalyst support (such as carbon black) occurs during the cell operation which is caused by reactant starvation at catalyst layers [158].

*Catalyst layer and diffusion layer degradation*

Change in hydrophobic and hydrophilic properties and change in pore size of the catalyst layer and diffusion layers occurs during the cell operation which can lead to difficulty in carbon dioxide removal on the anode side and increased water flooding on the cathode side [158, 159, 163].

*PEM degradation*

The Nafion® (Dupont™) membrane in the passive DMFC is subjected to mechanical, chemical, and thermal degradations. Mechanical degradation is related to formation of perforations, cracks, and pinholes that form during MEA fabrication, cell assembling, and cell operation. The chemical degradation of membrane occurs due to the “chemical attack” by the foreign ions and contaminants and cause change in chemical composition of the membrane as well as thinning of the membrane. The thermal degradation of the membrane refers to the decrease in ionic conductivity, mechanical strength, and other membrane properties due to

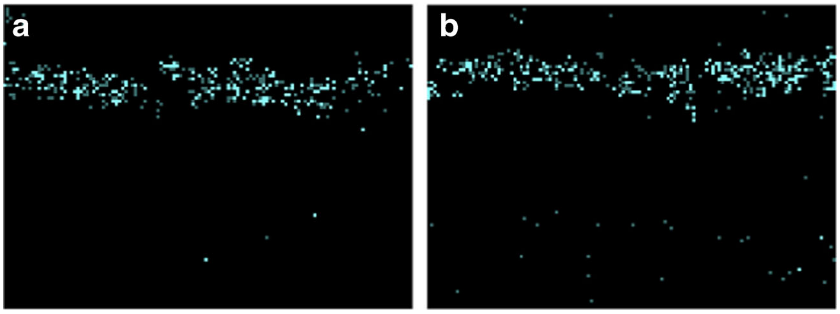

**Fig. 13** EDS mapping of the MEA cross-section **a** before durability test; **b** after durability test [159]

thermal cycling and cell operation at subfreezing and elevated (>80 °C) temperatures [155, 159, 161, 164].

*Current collector degradation*

The current collectors, in the passive DMFC, are usually made from stainless steel (SS) 316, printed circuit board (PCB), etc. [165–167]. These current collectors suffer from corrosion during the long-term operation and lead to increase in contact resistance between current collector and MEA [168]. Moreover, the accumulation of corrosion products on Nafion membrane significantly decreases its proton conductivity and leads to inferior cell performance [169]. To increase the corrosion resistance, various coatings such as platinum [72], gold [80], etc. are applied on the surface of the current collectors. Guo et al. [169] proposed combined coatings of 10 μm Nickel (Ni) and 2 μm gold (Au) on the PCB current collector and found that this coating, due to the existence of coating defects, was not able to endure halide attacking and exhibited progressive degradation during the durability test. It was recommended to develop a more effective coating, to resist corrosion, for the PCB current collectors. Yang et al. [170] showed that the SS316L, treated by passivation solution with 30 % (vol%age) $HNO_3$ and $Na_2MoO_4$ in room temperature 0.6 V vs saturated calomel electrode for 1 h, exhibited much better corrosion resistance, compared to bare SS316 and thus is suitable for use in passive DMFC environment.

Zainoodin et al. [159] investigated the MEA degradation in a passive DMFC with three different modes of operation: LT1—continuous operation with constant load, LT2—on–off operation with constant load, and LT3—on–off operation with variable load for a period of 3000 h. On comparing the polarization curve before and after the degradation test, loss in maximum power density of 49.5, 28.4, and 43.7 % for LT1, LT2, and LT3, highest loss with operation mode LT1, were observed. Transmission electron microscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy mapping confirm the catalyst agglomeration, carbon support corrosion, dissolution, and migration of Ru catalyst from anode to cathode which were different in magnitude with different operational mode.

## Temporary degradation (reversible)

The temporary or reversible degradation includes cathode water flooding, carbon dioxide accumulation at anode, etc. and can be recovered after operation interruption. The liquid water on the cathode blocks the pores of diffusion layer and obstruct the oxygen transport, whereas carbon dioxide accumulation disturbs the methanol transport at anode and both lead to decreased cell performance [159, 171, 172]. (Details have already been given in the sections “Cathode water flooding” and “Carbon dioxide management”).

Studies, in significant numbers, have been performed to investigate durability and stability of the DMFCs with more emphasis on the active feed DMFCs. The degradation behavior and mechanisms for the active feed DMFCs are, however, qualitatively true for the passive feed DMFCs as well and therefore the research papers dealing with durability of active feed DMFCs provide valuable information for passive DMFCs as well. But, separate studies for the passive DMFCs, to provide quantitative information on the performance

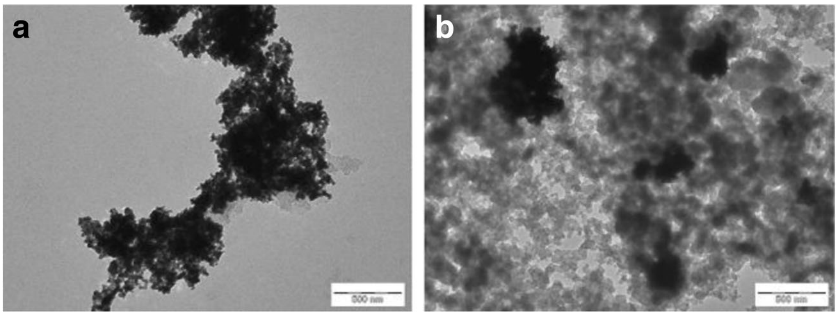

**Fig. 14** TEM image of CCL **a** before durability test; **b** after durability test [159]

degradation and, to develop effective mitigation strategies which are supposed to be different to those for active DMFCs due to difference in the operating conditions, are essential. Therefore, more research is recommended to further improve the durability and stability of passive DMFCs.

## Cost

The higher cost of passive DMFC compared to its competitor such as lithium (Li)-ion battery, for powering portable electronic devices, is a major hurdle for its commercialization. The total cost of a passive DMFC system includes material cost, fabrication cost, operating cost, maintenance cost, etc. Wee [156] performed a cost comparison between DMFC and Li-ion battery when used as power source in the laptop computer for average power output of 20 W and operational time of 3000 h. The manufacturing cost of DMFC system was estimated to be \$16.65 $W^{-1}$, much higher than that of the Li-ion battery system (\$0.77 $Wh^{-1}$). While, the energy consumption cost was slightly higher for DMFC (\$0.00051 $Wh^{-1}$), mainly due to higher fuel loss by MCO, than that for the Li-ion battery (\$0.00032 $Wh^{-1}$). It was recommended to reduce the MCO level to an order of magnitude of −9 and manufacturing cost to \$6.30 $W^{-1}$ in order to make the DMFC system as competitive as the Li-ion battery. Rashidi et al. [173] compared the DMFC system and Li-ion battery system for powering laptop, camcorder, and cell phone for an operational period of 4 years. As shown in Fig. 15, it was found that the Li-ion battery has a lower cost than the DMFC during the first year of operation; however, for the complete operational time of 4 years, the DMFC was proved cheaper than Li-ion battery as the battery needs to be replaced after 500 cycles of charging and discharging thereby increasing drastically the battery cost.

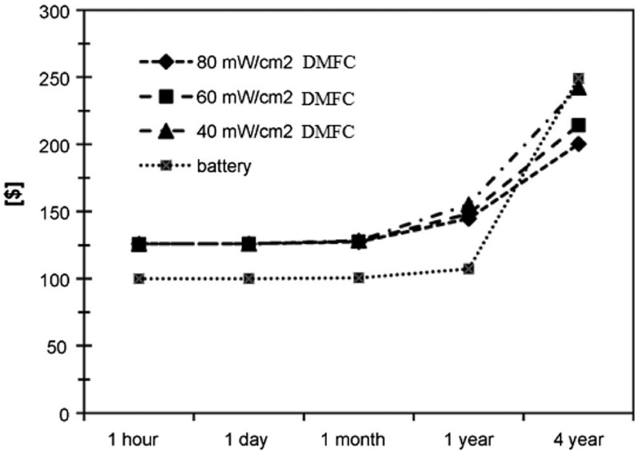

**Fig. 15** Cost comparison between DMFC system and Li-ion battery system for powering laptop computers

There are three main contributors to the higher cost of a passive DMFC system: (i) use of expensive Pt catalyst at both electrodes, (ii) use of expensive Nafion® membrane, and (iii) expensive precious metal coating (such as Pt, Au, etc.) on the current collector. The expensive platinum catalysts significantly increase the total price of passive DMFC system. The cost associated with the Pt catalyst can be reduced either by using non-Pt catalyst or by reducing the Pt catalyst loading. Huge research efforts have been made in recent years to develop low cost non-Pt catalysts for anode and cathode; however, the relatively lower electrochemical activity of these catalysts is still a big concern [152]. A passive DMFC, in general, utilizes a Pt-loading of 2–4 mg $cm^{-2}$ at each electrode. The Pt-catalyst loading can be reduced, while maintaining the similar performance of the cell, by improving the catalyst utilization towards electrochemical reactions [95, 174–184]. Recently, nano-structured catalysts and catalysts supports have been developed, which maximize the triple phase reaction boundary, and improve the catalyst utilization. Chen et al. [175] utilized electronspun nano fiber network anode catalytic layer in the MEA of a passive DMFC. The nano-structured anode with Pt-Ru loading 1.0 mg $cm^{-2}$ performed better and therefore achieved 55 % reduced anode catalyst loading, which was mainly due to the increase in catalyst utilization, than the conventional anode with Pt-Ru loading of 2.0 mg $cm^{-2}$.

The passive DMFC contains commercial Nafion 112, 115, and 117 as PEM, which contributes significantly to the total cost of the cell. Repeated attempts have been made to develop new membranes lesser fluorinated than Nafion in order to reduce the cost, but these membranes exhibited lower chemical stability and therefore lower durability compared to the Nafion membrane [70, 185]. Baglio et al. [182] utilized a low-cost fluorine-free membrane, composed of sulfonated polystyrene grafted to a polyethylene backbone, in a passive DMFC stack and compared its performance with the conventional Nafion 117 membrane. The cell with the fluorine-free membrane delivered a maximum power density of 18 mW $cm^{-2}$, lesser than the cell with conventional Nafion 117 membrane which delivered a maximum power density of 31 mW $cm^{-2}$. Considering the significant cost reduction, the fluorine-free membrane exhibited promising characteristics for application in passive DMFC.

The coating of the precious metals such as platinum, gold, etc. is applied on the current collectors to increase its corrosion resistance and to decrease the contact resistance between current collector and MEA. But, the coating increases the cost of passive DMFC significantly. Not much work has been found to provide a cheaper alternative for the existing current collectors, and hence, research in this direction is expected.

The past researches helped reducing the cost of passive DMFC; still, the cost is a major concern for the commercialization of the passive DMFC. More investigations are needed

**Table 1** Passive DMFC challenges and proposed solutions

| Challenges | Proposed solutions |
|---|---|
| Methanol management | |
| • Uniform distribution of methanol at ACL | • ACC with higher open ratio [44, 45] |
| | • Smaller rib width on ACC [44] |
| • Concentrated methanol feeding for high energy density of the cell | • Methanol barrier layer at anode [47–49, 52, 53] |
| • High fuel efficiency | • Reduce MCO |
| | • By reducing the amount of methanol vapor carried out by with the release of $CO_2$ [57–59] |
| | ✓Use of polymer membrane at $CO_2$ vent to separate methanol and $CO_2$ [58, 59]. |
| | • By optimizing the structural parameters and operating conditions |
| | ✓Use low methanol feed concentration [60–62] |
| | ✓Operate at high current density [62] |
| | ✓Use thicker membrane [65] |
| Water management | |
| • Uniform distribution and sufficient availability of water at ACL | • Use of diluted methanol solution |
| • Alleviating cathode water flooding | • Enhance water removal at cathode side |
| | ✓Use of porous metal foam as CCC [66] |
| | ✓Use of parallel channels on CCC [67] |
| | ✓Use of CCL with stepwise hydrophobicity distribution [68] |
| | ✓By providing a super-hydrophilic coating on the CCC [69] |
| | ✓CCC with vertically shaped channel [70] |
| | ✓Operating the cell with horizontal orientation and anode facing upward [71] |
| | ✓Operating the cell at higher temperature [72] |
| | ✓Active feeding of oxygen [74] |
| | • Reduce WCO |
| | ✓Operate the cell at low current density [61, 76–78] |
| | ✓Low cell temperature [79] |
| | ✓Decrease the permeability and increase the hydrophobic level of ACL [78] |
| | ✓Use of thicker membrane [78] |
| | • Reduce MCO |
| | • Enhance water back flow |
| | ✓Use of double MPL cathode [80] |
| | ✓Use of two additional CDLs [81] |
| | ✓MEA with diffusion layers containing hydrophilic nano-particles [82] |
| | ✓CDL with mesoporous carbons [83] |
| | ✓Addition of fluorinated Vulcan XC-72R into cathode MPL [84] |
| | ✓Use of hydrophobic air-filter layer at the cathode [76] |
| | ✓Addition of hydrophobic layer on the both sides of CCC [85] |
| Oxygen management | |
| • Sufficient availability and uniform distribution of oxygen at CCL | • Reduce cathode water flooding |
| | • Use of metal foam plate as CDL [87] |
| | • Introduction of pore-forming materials in the CCL [88] |
| | • Use of multi-layer catalyst cathode [68] |
| | • Mesoporous carbon CDL [83] |
| • Clean air | • Use of air filters at the cathode [63, 76, 81] |
| Carbon dioxide management | |
| • Remove $CO_2$ quickly and continuously | • High open ratio and low rib width on ACC [44, 92] |
| | • Use of parallel channel current collectors at anode [93] |

**Table 1** (continued)

| Challenges | Proposed solutions |
|---|---|
| | • Operate the cell with horizontal orientation and anode facing upward [71, 94]<br>• Create magnetic field around the cell [95] |
| Thermal management | |
| • Maintain the cell temperature at sufficiently high level | • Cell operation at relatively higher methanol concentration [61, 76, 96, 98, 99]<br>• Operate the cell at higher current density [76, 96, 100, 101]<br>• High ambient temperature and high humidity [57, 76, 97]<br>• Cell operation with vertical orientation [94]<br>• Use of porous metal foam as CCC [66]<br>• Use of thinner membrane [65] |
| Reduce methanol crossover | |
| • Reduce MCO | • Maintaining low concentration of methanol at ACL<br>✓Low methanol feed concentration [87, 94]<br>✓Use of methanol barrier layer [47, 48]<br>• Operate the cell at higher current density [44, 99, 102]<br>• Use thicker membrane [65, 92]<br>• Highly active anode catalyst<br>• Methanol tolerant cathode catalyst [19, 110, 113, 114]<br>• Low methanol-permeable membrane<br>✓Membranes alternate to Nafion [121, 122]<br>✓Modified Nafion membranes [128, 130, 131] |
| Sluggish anode kinetics | |
| • Improve anode kinetics | • Improvement in catalyst preparation methods for nano-sized, uniformly distributed catalysts [138–140]<br>• Develop catalyst support materials to achieve fine dispersion, high utilization and stability of the catalyst particles [141–143]<br>• New and improved anode catalyst [136, 144, 147, 148] |
| Durability and stability | |
| • Improve durability and stability | • Optimizing operating conditions [159, 171]<br>• Improvement in catalyst and membrane [158, 159, 161, 164]<br>• Corrosion resistant coating on current collectors [72, 80, 169, 170] |
| High cost | |
| • Reduce cost | • Reduce catalyst cost<br>✓Non-Pt catalyst [152]<br>✓Reduce catalyst loading [95, 174, 175, 177, 179, 181]<br>• Inexpensive membrane [70, 185]<br>• Less costly coating on the current collectors |

to further reduce the cost and to commercialize the passive DMFC. Specifically, the cheaper alternatives for the coating of current collector or the cheaper but high corrosion resistive current collectors should be developed.

The passive DMFC challenges and the solution proposed by researchers are listed in Table 1. It can be seen that significant research has been done for every challenge and many different solutions are proposed, but passive DMFC commercialization is still far away and therefore more extensive work in these direction is anticipated. Little research has been conducted on the durability and stability of the passive DMFC and particular attention is required on this issue.

## Concluding remarks

The liquid feed passive DMFC is a potential power source for portable applications moving into commercialization. In this review, the critical challenges and recent advances on the passive DMFC has been discussed. Immense progress has been made in encountering various technical issues and improving the passive DMFC performance in the recent past; still, many challenges exist. Further continuous research is needed to overcome these challenges and to achieve commercialization of the passive DMFC. Following points are the suggestions on the future research directions:

- Methanol concentration at ACL governs the concentration polarization, MCO, cell temperature, and the cell performance. Techniques should be developed to keep the methanol concentration at ACL always at the optimum level for wide range of current drawn.
- Cell components should be designed in order to achieve uniform reactant distribution at catalyst layers.
- It is essential to improve understanding of the two-phase flow of water and air at the cathode side in order to provide sufficient oxygen for the cathode reaction and to reduce cathode flooding problem.
- The present open cathode structure does not permit the passive DMFC operation in the rainy and high dust situations. Passive DMFC should be made operational in these extreme situations as well.
- The carbon dioxide evolution heavily depends upon the cell orientation. The passive DMFC should be designed in such a way that it must have effective carbon dioxide evolution in all the orientations.
- A higher cell temperature improves the electrochemical kinetics but also increases the MCO rate. Optimization of the cell temperature for optimum cell performance is not been done yet. Moreover, the cell design and component structure should be modified to minimize the heat dissipation.
- Fundamental studies to understand more clearly the mass transport and heat transport in the passive DMFC are needed in order to achieve effective species management and thermal management.
- MCO is still the major issue in the passive DMFC and breakthrough is needed in this direction.
- Non-nobel catalysts with improved electrochemical activity are needed to be developed.
- Performance degradation studies specifically focused on passive DMFC is recommended.
- Cheaper alternatives for the coating of current collector or the cheaper but high corrosion resistive current collectors should be developed.

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