Review on utilization of the pervaporation membrane for passive vapor feed direct methanol fuel cell

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Abstract. The Direct Methanol Fuel Cell (DMFC) is a promising portable power source for mobile electronic devices because of its advantages including easy fuel storage, high energy density, low temperature operation and compact structure. In DMFC, methanol is used as a fuel source where it can be fed in liquid or vapor phase. However, the vapor feed DMFC has an advantage over the liquid feed system as it has the potential to have a higher operating temperature to increase the reaction rates and power outputs, to enhance the mass transfers, to reduce methanol crossover, reliable for high methanol concentration and it can increase the fuel cell performance. Methanol vapor can be delivered to the anode by using a pervaporation membrane, heating the liquid methanol or another method that compatible. Therefore, this paper is a review on vapor feed DMFC as a better energy source than liquid feed DMFC, the pervaporation membrane used to vaporize methanol feed from the reservoir and its applications in vapor feed DMFC.

1. Introduction
A Direct Methanol Fuel Cell (DMFC) is an electrochemical energy conversion device that converts the chemical energy of methanol fuel directly into electricity and a little of heat for as long as fuel and oxidant are supplied, without combustion as an intermediate step. The DMFC is an attractive candidate for mobile power sources, such as Notebooks PCs, handheld PCs, cellular phones, PDAs, etc. The advantages of DMFC are easy fuel storage, low operating temperature and simple design [1]. In spite of these advantages, the commercialization of DMFC is still hindered by several technological obstacles, namely low active catalyst for methanol oxidation, methanol crossover (MCO) through the polymer electrolyte membrane (PEM) in the membrane electrode assembly (MEA), mass transport and water management [2]. In this review, the focus was on the vapor feed DMFC as a better energy source than liquid feed DMFC. Pervaporation membrane is looked into as a medium to vaporize methanol fuel and its applications in vapor feed DMFC is reviewed.

2. Active and passive DMFC
In terms of fuel and oxidant delivery schemes, DMFC can be classified either as active-feed or as passive-feed DMFC [3]. Table 1 shows the differences between active and passive DMFC system [4]. Active DMFC operates with the help of external devices. In active-feed DMFCs, methanol solution is usually delivered by a liquid pump, while the oxidant, oxygen from surrounding air, is supplied by a
gas blower or fan [3]. The active system has more reliability, gives a better performance and is more convenient for controlling operating conditions such as temperature, methanol concentration and methanol flow rate [5]. However, parasitic energy losses are inevitable due to the power consumption from pump operation [6].

In contrast, the concept of a passive DMFC is that a DMFC can perform stand-alone operations, which eliminates the need for external devices to pump methanol and blow air into the cell. Therefore, a passive system has some advantages over an active system as they are simpler and more compact. Furthermore, parasitic energy losses can be reduced to enhance the overall system efficiency by using a concentrated methanol solution, and this potentially results in high reliability, low cost, high fuel utilization and high energy density which is favorable in portable device application [4]. Every movement of methanol and oxygen in passive systems occurs naturally. Oxygen diffuses into the cathode from the ambient air due to the air-breathing action of the cell and methanol diffuses into the anode driven by a concentration gradient between the anode and the fuel reservoir.

Table 1. Differences between active and passive DMFC.

|                  | Active                                      | Passive                                      |
|------------------|---------------------------------------------|----------------------------------------------|
| Definition       | Operate with auxiliary devices to deliver methanol at anode and to supply air at cathode | Operate without any auxiliary devices to deliver methanol at anode and to supply air at cathode |
| Cost             | High                                        | Low                                          |
| Volume           | Requires large volumes                      | Compact cell design                          |
| Application      | Incompatible for portable devices           | Compatible for portable devices              |
| Design           | Complex                                     | Simple                                       |

3. Vapor feed DMFC

One of the fundamental factors that prevent faster development of DMFC technology is MCO from the anode to the cathode. The MCO rate is roughly proportional to the methanol concentration at the anode [7]. A higher methanol concentration leads to a higher methanol permeation rate [8]. Therefore, in order to reduce MCO, it is necessary to regulate the methanol feed concentration [7]. The DMFC usually shows the highest performance at low concentrations of methanol from in the range of 2-3 M under active conditions and about 5 M under passive conditions due to the MCO [9, 10]. However, a low methanol concentration used in DMFC can lead to a low energy density of the fuel cell system and thus a short runtime, which cannot meet the requirement of the commercialization [11]. To ensure that DMFC are compact enough for portable devices, produce adequate power and are lightweight, fuel should be supplied as concentrated methanol solutions, or even neat methanol [12]. Vapor feed fuel delivery system is an alternative to operate the DMFC with high methanol concentration or even pure methanol without suffering high MCO because MCO in vapor feed DMFC is lower compared to liquid feed DMFC [13].

Since methanol is a very volatile substance, it can easily be evaporated and delivered to the fuel cell through the vapor phase. In a vapor feed passive DMFC, methanol from reservoir tank will be transported to the vaporizer to generate methanol in vapor phase due to the high volatility of liquid methanol [14]. The vaporizer can be a pervaporation membrane or a heated porous pad [2]. Next, methanol vapor will go through the vapor transport layer (VTL), which is a hydrophobic porous layer used to transport methanol vapor to the anode diffusion layer (DL), and simultaneously to prevent liquid from being transported through it. Then methanol is transported through the ADL to the reactive sites in the catalyst layer (CL), on which the electrochemical oxidation of methanol takes place [2]. In methanol oxidation reaction, methanol will react with water to produce proton, electron and carbon.
dioxide. Hydrogen ions formed from this oxidation pass through the PEM to reach the cathode where more electrons are used to reduce oxygen [15]. In oxygen reduction reaction, oxygen then reacts with the electrons and protons to produce water.

3.1. Differences between vapor feed and liquid feed DMFC
The electrochemical oxidation reaction of methanol for both vapor feed and liquid feed DMFC takes place mainly in liquid phase [2]. However, there are some differences between the vapor feed DMFC and liquid feed DMFC [2], as shown in Table 2.

| Table 2. Differences between active and passive DMFC. |
|------------------------------------------------------|
| **Vapor feed DMFC**                                   | **Liquid feed DMFC**                                |
| Methanol fuel fed in vapor phase                      | Methanol fuel fed in liquid phase                   |
| Uses concentrated methanol solution or neat methanol as fuel | Uses diluted methanol solution as fuel               |
| Methanol fuel supplied to the fuel reservoir is converted to vapor phase before being fed at anode | Methanol fuel fed directly into anode from methanol tank in liquid form |
| Methanol vapor condenses to form diluted methanol solution in the anode DL and CL | Liquid methanol vaporizes from the diluted solution into the gas phase with the removal of gas CO2 |
| Water needed in the anode for methanol oxidation needs to be recovered from the cathode | Water needed for the anodic reaction may be directly supplied from the diluted methanol solution feed |

3.2. Advantages of vapor feed DMFC
A vapor feed DMFC has potential over a liquid feed system in several ways. One of its advantages is its potential to have a higher operating temperature [2, 14] as it exists in vapor state, thus increasing the reaction rates and in turn results in relatively low MCO.

Rice and Faghri [14] found that the vapor feed DMFC also has the potential for shorter start-up time because the mass diffusivity is several orders of magnitude greater than in liquid phase. Thus, the vapor feed system has an advantage in the mass transfer process [16], which results in higher power outputs and leading to the better cell performance. Kamarudin et al. [5] supported this by stating that the cell voltage and power density achieved for liquid feed are significantly lower than those obtained with a vapor feed system, while Fukunaga et al [16] reported that a vapor feed has higher activity than liquid feed due to the higher methanol concentration used as fuel.

Vapor feed DMFCs on working at higher temperature also has the following advantages [17]: (1) Methanol ionization step carried out to produce protons proceeds more rapidly in these cells; (2) Higher temperature results in higher catalytic electrode activity and the faster reaction leads to reduction in methanol fuel crossover; (3) Higher operation temperatures could drastically reduce or eliminate carbon monoxide poisoning of platinum or possibly even allow platinum to be replaced by much less expensive catalysts.

4. Critical issue of vapor feed DMFC
Vapor feed DMFC need to overcome some major challenges in order to operate passively in high methanol concentration, namely MCO through the PEM and water management in the fuel cell [4].
4.1. Methanol crossover (MCO)

MCO is the process by which unreacted methanol is transported from the anode through the PEM to the cathode, where it reacts directly with oxygen, so that no current is produced from the cell [7]. It is caused by the driving forces of concentration gradient, pressure gradient and electro-osmosis [18]. Fuel crossover phenomenon is one of the issues that can reduce the voltage and the fuel utilization efficiency of a DMFC [19], as well as contributing to fuel wastage. Hence, the rate of MCO needs to be reduced to alleviate its impacts on the DMFC performance.

In order to reduce the MCO, hydrogels was used as the fuel-diffusion-rate-controlling agent in passively operated flat pack type DMFCs [20]. The agent retards the fuel diffusion rate from the fuel reservoir remarkably, thus suppressing the MCO even at high fuel concentrations. Most of the liquid methanol that soaked into the hydrogel was possibly in vapor-liquid equilibrium [4]. Nakagawa et al. used the porous carbon late (PCP) as a support to prevent their passive DMFC from undergoing a significant loss of methanol due to the crossover and also being out of temperature control [21]. Nevertheless, degree of reduction in MCO was shown to depend on the properties of the PCP [21]. Flux of methanol through the PEM can be controlled by the diffusion resistance of the porous plate.

Abdelkareem et al. [22] used different methanol concentrations at different cell voltages and found that the effect of the pore structure and thickness of the porous plate, as well as the gas barrier thickness, influence the methanol transport and cell performance of their passive DMFC. As a result of mass transfer restrictions by employing the PCP, high methanol concentration over 20 M could be efficiently used to produce the relatively high power density of 30 mW cm$^{-2}$ for more than 10 h. MCO could be decreased by changing the open ratio of the anode vaporizer because the mass transfer resistance of methanol from the fuel reservoir to the anode CL increases [12].

4.2. Water management

Recently, water management system is more critical and challenging in a passive vapor feed DMFC than in a conventional liquid feed DMFC. The objectives of water management are to provide water for the anode reaction, remove water generated in the cathode layer and keep a high water content in the PEM to lower the proton conductive resistance [23]. Depletion of water inside the anode catalyst layer, especially at higher current densities, decreases the cell performance substantially [24]. Ideally, water needed for the anodic reaction should be completely recovered from water generated from the electrochemical reaction at the cathode, especially when fed with neat methanol [25].

According to Tsujiguchi et al [10], water required for the reaction at the anode side of a vapor feed DMFC, which operates with neat methanol as fuel, can be supplied from the cathode side through the PEM by back diffusion, resulting in a simple system with an increased energy density. Water management becomes a key issue at a higher operating temperature because the evaporative losses are much greater [14]. However, humidified MEA with a composite membrane of lower MCO and diffusion layers of hydrophilic nanomaterials can force the water with back diffusion from the cathode to the anode through the composite membrane [1].

Besides that, Guo and Faghri [7] used a micro porous sub-layer bonded to the cathode catalyst that effectively repels liquid from the cathode and into the PEM to manage water in miniature vapor feed DMFCs without the need for a complex micro-fluidics subsystem. These pores are too small and have a hydrophobic surface. Hence, liquid water that accumulates is pushed back in the other direction across the sub-layer to the anode, as is required for the anode reaction that uses even strictly neat methanol as the fuel.

Xu et al. [25] studied the effects of different water management approaches, that is the addition of a water management layer (WML) and a hydrophobic air filter layer (AFL), and the use of thinner PEM in a passive vapor feed DMFC to improve its water management and cell performance when neat methanol was directly used. They found that adding a WML and an AFL or thinning the membrane thickness greatly improved the water management capability as the water recovery from the cathode to the anode could be enhanced, leading to lower internal resistance, better membrane hydration and better cell performance. The MCO was also curbed and the fuel efficiency was increased.
Li and Faghri [12] studied a change in the cell structures of passive DMFC fed with neat methanol to improve water management system by adopting perforated covers with different open ratios at the cathode without increasing the cell volume or weight. The water management of the fuel cell could be improved by decreasing the open ratio at the cathode side as the water loss from the cathode side was reduced and the water back flow from the cathode to the anode was increased.

5. Pervaporation

Vapor feed direct methanol fuel cell was reported since early 1990s by utilizing an external device, such as an electric vaporizer, heater and so on. However, the external devices consume more additional energy and eventually reduce the total system efficiency. Hence, other methods to produce methanol vapor has been explored to overcome this problem. The most common way to deliver methanol vapor without any additional device is by using a pervaporation membrane which affects the phase change from the liquid methanol, which is contained within the fuel reservoir, to vapor phase [25].

Pervaporation is a membrane technical method that allows only one component of a particular mixture to pass through a non-porous or porous membrane. The phase separation membrane is employed between fuel reservoir and anode diffusion layer to separate mixture of liquids by partial vaporization. There are various types of pervaporation membrane used to vaporize methanol in the fuel reservoir such as silicone membrane [26], Nafion membrane [1, 12, 25, 27], and polydimethylsiloxane (PDMS) [24]. The pervaporation membrane is typically located between the fuel reservoir and anode DL in the DMFC system.

5.1. Mechanism of pervaporation membrane

There are three physical processes that are involved in the permeation of methanol through a pervaporation membrane, as shown in figure 1: (1) sorption of liquid methanol molecules from the reservoir tank at the feed side of the membrane; (2) diffusion of the dissolved methanol through the membrane; and (3) desorption of methanol vapor from the permeate side [28].

6. Application of pervaporation membrane in vapor feed DMFC

Ren et al. [26] developed a passive vapor feed DMFC in which both the passive fuel delivery system and water management system were presented. Silicone membrane was used as the pervaporation
membrane and its surface properties were modified to make it more hydrophobic. The cathode structure was optimized to enable the supply of water from the cathode to the anode by back diffusion and back convection.

Kim et al. [1, 27] developed a semi passive vapor feed DMFC with a humidified MEA and proposed to achieve high energy density and high fuel cell efficiency simultaneously. Liquid methanol was supplied to the system by a syringe pump at a rate of 0.3 cm$^3$ h$^{-1}$ for the continuous supply of methanol from the fuel reservoir. Methanol was vaporized by Nafion 112 membrane and then diffused through a hydrophobic water barrier layer and buffer layer to get to the anode electrode. The pervaporation membrane, hydrophobic water barrier and buffer layer verify that the delivery of methanol is as a vapor phase and control the diffusion rate. The vapor feed passive DMFC with humidified MEA maintained the power density at 20-25 mW cm$^{-2}$ for 360 h and performed with a 70% higher fuel efficiency. The energy density achieved was 1.5 times higher than a liquid feed passive DMFC.

Li and Faghri [12] used Nafion 117 as their pervaporation membrane for a passive DMFC with neat methanol. The passive DMFC also consisted of methanol barrier which was made from a hydrophobic PTFE membrane placed between the fuel reservoir and pervaporation membrane. PTFE films were placed in both sides of anode and cathode as perforated covers. Furthermore, a gas mixing layer was added between the pervaporation membrane and anode current collector to increase the mass transfer resistance. The cell performance was found to be improved, the MCO was decreased and the fuel efficiency was increased, especially during high current density operation because more carbon dioxide gas was generated at a higher current density [12].

![Figure 2. Schematic of the passive vapor feed DMFC [25]](image)

Xu et al. [25] also used Nafion 117 membrane for their passive vapor feed DMFCs with neat methanol. As shown in figure 2, a supporting layer made of porous polyethylene was inserted into the methanol tank and attached tightly to the pervaporation membrane to avoid serious swelling deformation to the Nafion 117. A perforated PTFE film was inserted between the pervaporation membrane and the VTL to restrict the generation rate of methanol vapor. VTL have a hydrophobic surface so that it could function to adjust the transport rate of methanol vapor and simultaneously prevent the transport of liquid.

Meanwhile, Eccarius et al. [24] investigated the impacts of structure parameters and operating conditions for a passive vapor-feed DMFC with neat methanol. Their pervaporation membrane is the PDMS membrane, which is a well known hydrophobic membrane for removing organics from aqueous mixtures [29]. The evaporation rate of methanol into the vapor chamber was controlled by different open ratios of the solid plate attached to the PDMS membrane. In addition, several membranes with differing thickness, ion exchange capacity and specific conductivity were investigated and compared to study their role to reduce MCO in a vapor feed DMFC by Fokken and Lutter. However, PDMS was found to be too soft, flexible, easy to tear and viscoelastic, which means that the methanol liquid may permeate through this membrane in a long-term cell operation.
A novel porous carbon plate (PCP) with better durability than the pervaporation membranes was introduced to vaporize the methanol [9, 22, 30]. Abdelkareem et al. [9] investigated the performance of the passive vapor feed DMFC with and without the PCP under closed circuit conditions with different methanol concentrations ranging from 1 M to neat methanol. The MCO flux and water flux through the MEA with and without PCP were also analyzed. The maximum power density obtained at room temperature was 24 mW cm$^{-2}$ for methanol concentration of 2 M without the PCP, and this was reproduced at 16 M with PCP. In addition, the mass transfer for both methanol and water from the reservoir to the anode were significantly restricted by the PCP. Thus, high methanol concentrations could be efficiently used in order to get high power density. The back diffusion of water from the cathode to the anode through the PEM also occurred and this resulted in no flooding at the cathode, which was contrary to the case without the PCP.

7. Conclusion

Vapor feed DMFC have a better performance compared to liquid feed DMFC. MCO and water management are currently the main challenges faced by vapor feed DMFC because they have the most effect on the cell performance. Several common approaches to reduce MCO are modification of the PEM, addition of fuel-diffusion-rate-controlling agents such as hydrogel and PCP, usage of neat methanol as fuel and addition of water management layer on the cathode side to push more water backward from cathode to anode for membrane hydration in the methanol oxidation reaction. The most common way to deliver methanol vapor without any auxiliary device is by using a pervaporation membrane, which affects the phase change from methanol liquid contained within the fuel reservoir to methanol vapor.

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