

Study on a Passive Vapor Feed Direct Methanol Fuel Cell with High Methanol Concentration

F. A. Halim, U. A. Hasran, M. S. Masdar, and S. K. Kamarudin

Abstract—An extensive research has been carried out to improve the performance of direct methanol fuel cells (DMFCs) using low methanol concentration below 5 M either in active or passive conditions due to methanol crossover (MCO) problem which the methanol crosses over the membrane and reacts directly with oxygen at cathode. However, a low methanol concentration leads to a low energy density of the fuel cell system and a short runtime which cannot meet the requirement of commercialization. Therefore, it is important to use a high concentration of methanol in DMFC to achieve a high energy density. This study was done to improve the performance of passive vapor feed DMFC by using high methanol concentrations from 12 M (molarity) to neat methanol. From the results obtained, it was showed that the performance of passive vapor feed DMFC that used high methanol concentration improved. It was a linear dependence of current density on methanol concentration which is the current density increased when the methanol concentration increased up to neat. The linear dependence of current density on the concentration suggested that the cell operation was under the rate controlling by the methanol transport. Therefore, it can conclude that high methanol concentration can leads to high energy density achieved by the DMFCs.

Index Terms—Direct methanol fuel cell, energy density, methanol concentration

I. INTRODUCTION

Direct methanol fuel cell is a renewable source of fuel and can offer high power and energy density, low emissions, ambient operating conditions and fast and convenient refueling. It is an appropriate power supply for electronic device [1], [2]. DMFC operates either in active or passive mode. Active DMFC works with additional devices to deliver reactant to the cell such as pump or blower. In contrast with passive DMFC, it eliminates any usage of additional devices in the operation which fuel is stored in fuel reservoir and oxygen supplied to cathode by air-breathing. Completely passive DMFC is preferable due to its simplicity in design and suitable for portable application compared to active DMFC [3]. Based on the previous studies on DMFC, optimum concentration that produces maximum power density for active DMFC is about 1M to 2M while 4M for passive DMFC [4]. Further increasing the methanol concentration will leads in methanol crossover

problem. This problem occurred when the methanol diffuses through the membrane, reacts at the cathode side and lowers the conversion efficiency [5]. Methanol crossover also results in a waste of fuel [6]. High methanol concentration will cause high methanol crossover rate through the membrane and reduce the cell performance. However, high methanol concentration enables the DMFC to obtain high performance compared to low methanol concentration [4]. An alternative way to lessen this problem is to operate the DMFC in vapor feed because the methanol crossover rate is much lower than in the liquid feed DMFC and the methanol can be fed with high concentration or neat methanol [7]. In vapor feed DMFC, methanol evaporates from nearly pure liquid methanol source and condenses into a highly dilute methanol solution at the anode side. The liquid methanol and air can be delivered in passive manner by natural convection and capillary force [8]. Vapor feed direct methanol fuel cell has potential for a shorter start-up time because of the mass diffusivity is several orders of magnitude greater than in liquid phase. It also has potential to have a higher operating temperature and thus increasing the reaction rates which resulting in higher power outputs [9].

Study on vapor feed DMFC operating with high methanol concentration or neat methanol was reported by some researchers. Hae Kyoung Kim proposed a vapor fed passive DMFC to achieve high energy density by using pure methanol for mobile application. The passive vapor feed DMFC with a humidified MEA showed 20–30mWcm⁻² for 15 days with a maximum power of 36mWcm⁻². It also showed 70% higher fuel efficiency and 1.5 times higher energy density for a 4 h operation than the liquid feed passive DMFC. In this work, a porous fired alumina, porous foam, barrier, and vaporizer were used for feeding and controlling methanol in the vapor phase [10]. Guo et al provided a vapor feed DMFCs with passive thermal or fluids management systems. Pure methanol was delivered by the wick structures from a liquid methanol reservoir to an evaporation pad. The liquid was evaporated by different heating manners such as electrical heating, catalyst burning and heat recovery from the cell itself. The results showed that the vapor feed DMFC reached a power density of 16.5 mW/cm² at a current density of 60 mA/cm² [3]. Besides that, Eccarius *et al.*, introduced a vapor-fed DMFC with completely passive operation on both anode and cathode sides and the effect of methanol concentration on the fuel cell performance were investigated. A polydimethylsiloxane (PDMS) membrane was applied as an evaporator through which the liquid methanol could be evaporated automatically into vapor phase without any energy input [11]. Instead of using a membrane as the vaporizer,

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F. A. Halim and U. A. Hasran are with the Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia (e-mail: fahimah.engukm@gmail.com).

M. S. Masdar and S. K. Kamarudin are with Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia, and Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

Abdelkareem *et al.*, also investigated the performance of passive vapor feed DMFC by using a porous carbon plate (PCP) to deliver methanol vapor to the anode under different cell voltages of 0.1, 0.2 and 0.3 V for different methanol concentration. As a result, high methanol concentration over 20 M could be efficiently used to produce the relatively power density of 30 mW cm^{-2} for more than 10 h. Catalyst used are Pt and Pt-Ru black for the cathode and anode which has loading of $10 - 12 \text{ mg/cm}^2$ [12]. Abdelkareem *et al.*, [13] utilized porous carbon plate to vaporize the methanol and it resulted in high power density at high methanol concentration. From the previous study on DMFC fed with high methanol concentration, the structure differs from the conventional DMFC where methanol barrier layer employed between the methanol reservoir and membrane electrode assemblies. This was done to control the methanol crossover rate and increases the cell performance [14]. In this study, we investigated the effect of methanol concentration on the fuel cell performance which varied from 12 M to pure methanol. The DMFC was operated in completely passive means as the methanol is stored in a fuel reservoir and the oxygen supply is relied on the air-breathing. The methanol was vaporized by using a PDMS membrane which employed between fuel reservoir and anode current collector.

II. METHOD OF EXPERIMENT

A. MEA Preparation

The MEA was prepared by using a carbon cloth as anode and cathode backing layer. Pt-Ru black and Pt black were used as the catalyst for the anode and cathode, respectively. The catalyst was prepared by dispersing in a solution of deionized water, isopropyl alcohol and 5 wt.% Nafion solution. The ink was coated on the carbon cloth that was coated with carbon black as gas diffusion layer. The catalyst loading for both electrodes were 12 mg/cm^2 with an active area of 4.84 cm^2 . Nafion 117 membrane was used as the electrolyte membrane. The membrane was pretreated by the following procedure. The membrane was immersed in deionized water and heated up until 80°C for 1 hour. Then, the membrane was immersed in 3% hydrogen peroxide (H_2O_2) at 80°C for 1 h and then, washed with deionized water for 20 min. After that, it was immersed in 1 M sulfuric acid (H_2SO_4) at 80°C for 1 h and washed again with boiled deionized water until it is neutral. PDMS membrane was placed between fuel reservoir and anode current collector as a pervaporation membrane to supply methanol in vapor phase. The current collectors used in this experiment were graphite plates for anode and cathode side. The MEA was fabricated by hot pressing at 350°C and 5MPa for 3 min.

B. Measurement of the Cell Performance

In this experiment, all the tests were carried out in passive mode at ambient condition (289K and 1 atm). Different concentration of methanol solution (5 ml) was fed into the fuel reservoir by a syringe through an open tube. The concentration was varied from 12 M to neat methanol and time versus current density at the different cell voltages of 0.05, 0.06, 0.07 V was measured for 3 h operation. The

measurement was conducted by using a potentiostat or galvanostat.

III. RESULT AND DISCUSSION

A. Time Versus Current at Different Constant Cell Voltages

Fig. 1 and Fig. 2 show the result of current density at cell voltage of 0.05V and 0.06 V with different methanol concentration that ranged from 12M to neat methanol. From the figure, it was found that the current density was initially decreased and within few minutes, it became nearly constant with time. The figure also indicated that the nearly stable current density increased with increasing of methanol concentration. The current density was nearly constant with time may due to the employment of the PDMS membrane which can regulate the methanol transfer rate from the reservoir to the anode and reduce the methanol crossover from anode to cathode. The current density achieved with neat methanol was about 34 mAcm^{-2} and 30 mAcm^{-2} for cell voltage of 0.05 V and 0.06 V respectively which was operated for 3h. However, at 0.07 V of cell voltage, the current density increased with methanol concentration up to 21 M. Fig. 3 shows the variation of current density for different methanol concentration at cell voltage of 0.07 V. Initially, the current density for each concentration was rapidly decreased to a certain value before it becomes nearly stable. The nearly stable current density increased with the increasing methanol concentration up to 21 M, then decreased from 20 mAcm^{-2} to 15 mAcm^{-2} from 21 M to neat methanol. The decrease of current density would be due to the high methanol crossover for neat methanol compared to other concentrations.

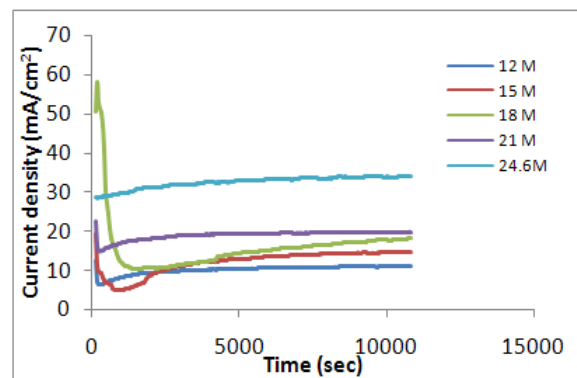


Fig. 1. Current density for different methanol concentration at cell voltage of 0.05V.

B. Effect of High Concentration on Power Density

Fig. 4 shows the maximum power density achieved by the cell for different methanol concentration at different cell voltage. The maximum power density increases with the increasing of methanol concentration and cell voltage. However, the highest maximum power density about 5 mWcm^{-2} was obtained at cell voltage of 0.07 V with methanol concentration of 15 M. Further increased of methanol concentration to neat methanol produced a lower maximum power density compared to 15 M methanol concentration. This was occurred may due to the high methanol crossover and water problem with neat methanol operation.

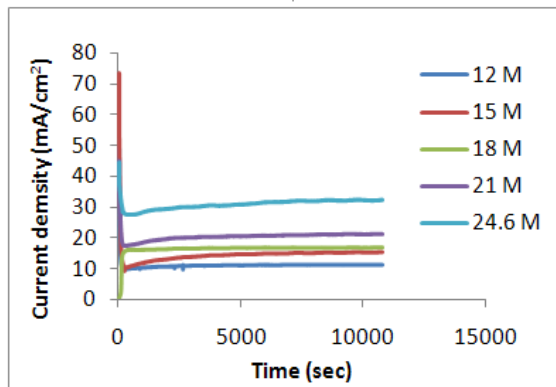


Fig. 2. Current density for different methanol concentration at cell voltage of 0.06V.

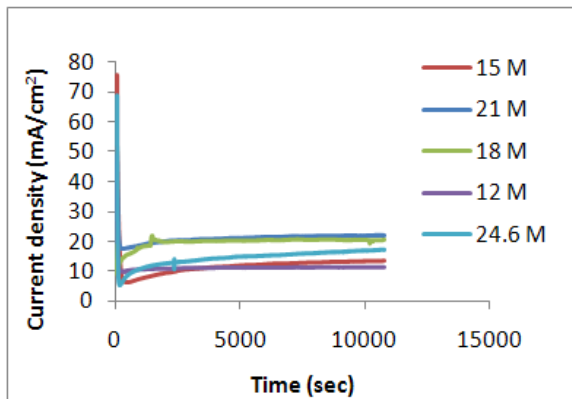


Fig. 3. Current density for different methanol concentration at cell voltage of 0.07V.

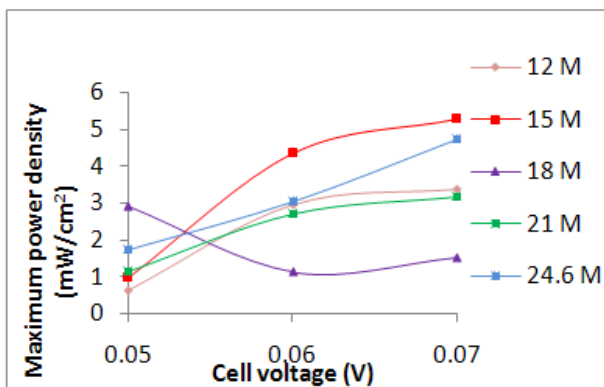


Fig. 4. Maximum power density achieved with different methanol concentration and different cell voltage

IV. CONCLUSION

The effect of methanol concentration on the fuel cell performance which was varied from 12 M to neat methanol under different cell voltage, 0.05 V, 0.06 V and 0.07 V was investigated. From the results obtained, the current density produced by the fuel cell increased with increasing methanol concentration. High methanol concentration can be used that produced a high constant current density of 34

mAcm^{-2} and 30 mAcm^{-2} at 0.05 V and 0.06 V with neat methanol operation for 3 h. The maximum power density increased with increasing of cell voltage and methanol concentration. The highest maximum power density obtained from this experiment was at 0.07 V cell voltage and 15 M of methanol concentration which was about 5 mWcm^{-2} .

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Fahimah Abd Lah Halim is with Universiti Kebangsaan Malaysia, UKM Bangi, Selangor, Malaysia.