A passive DMFC with membrane for diffusion controlled methanol feed

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Abstract - *Transport of methanol to the anode of a passive Direct Methanol Fuel Cell (DMFC) for varying concentration of methanol was studied using Nafion membranes of varying thickness namely, 50, 125, 175m. The maximum power density was achieved with 1M aqueous methanol in the case of Nafion 112 as passive methanol transport layer (PMTL). Higher power density was achieved with 4M aqueous methanol while the power density decreased for concentrations higher than 4M in the case of Nafion 115 and Nafion 117. Maximum power density of 21 mW* cm^{-2} *was obtained with Nafion 115 membrane as PMTL for 4M aqueous methanol at ambient conditions.*

Key Words: Passive Direct Methanol Fuel Cell; Transport; Methanol; Membranes; Power density.

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) have been an important area of research for application in portable electronic devices, such as notebook computers, personal digital assistants (PDAs), music systems and cellular telephones due to their advantages in terms of high energy density, simplicity and fast recharging [1-3]. However, in order to be commercially feasible, it is necessary to eliminate power losses from auxiliaries such as fuel and reactant feed pumps, methanol and liquid level sensors, which are used in the active DMFCs. Passive DMFCs without such auxiliaries, have much simpler structures and are being investigated [4-6].

Operating parameters and design of the passive DMFCs are crucial to enhance their performance. The operating parameters such as temperature, methanol flow rate and its concentration, and design aspects like passive methanol feed system, CO_2 removal from anode are mainly limiting the cell performance. The optimal methanol concentration was reported to be 4.0 M for passive DMFCs [7, 8]. Yang et al. [9] reported that much higher exposure ratio of the parallel flow field on the anode and perforated flow field on the cathode increased the delivery of fuel and oxygen, respectively resulting in enhanced performance. In passive DMFCs [10], higher temperature at cathode improves natural convection due to temperature difference between the MEA and the atmospheric air leading to enhanced performance.

Presently, one of the most challenging problems for the passive DMFCs is supply of methanol at a desired flow rate and concentration from the reservoir tank to the anode. However, high and low methanol concentration lead to methanol crossover with resultant mixed potential on the cathode and low energy density, respectively [10]. Hence, some researchers [11-16] have made improvements in the fuel delivery system to increase the methanol feed concentration. Abdel kareem et al. [11-13] reported that while employing a porous carbon plate because of the increased mass transfer resistance higher concentration of methanol could be used. Kim et al. [14, 15] employed hydrogels in methanol fuel cartridges to control methanol diffusion rate from the fuel reservoir to the anode. Yang and Liang [16] reported on a DMFC system with passive fuel delivery based on liquid surface tension. In the present study, we report on the use of Nafion membrane of varying thickness as passive methanol transport layer (PMTL) for supply of methanol; in a diffusion-controlled mode to the anode. To the best of our knowledge, this kind of approach of passive delivery of methanol to the anode has not been reported.

2. EXPERIMENTAL

Exploded view of passive DMFCs as shown in Fig. 1(A), was designed, fabricated and tested in this study. The membrane electrode assembly (MEA) procured from M/s Johnson Matthey used in this study had 4 mg cm^{-2} loading of carbon-supported 1:1 Pt/Ru catalyst on the anode and 2 mg cm^{-2} loading of carbon-supported Pt on the cathode. This MEA was sandwiched between anode and cathode graphite flow field plate, which was then clamped between two transparent acrylic fixture plates. Anode and cathode flow field plate machined into parallel windows and perforated holes, respectively. A step of 0.5 mm width and 0.5 mm depth was machined along the circumference of the parallel windows for removal of CO_2 as shown in Fig. 1(B). A reservoir of 5.0 mL capacity was built in the anode fixture. 1M methanol solution from the built-in reservoir was supplied to the anode reaction zone through PMTL (Nafion 117 membrane) which was assembled between methanol reservoir tank and the anode flow field plate. Atmospheric air was supplied as an oxidant to the cathode reaction zone by natural convection. Bitrode T2000 electrical load interfaced to a computer was employed to record the voltage - current curves. The polarization curves were obtained in potentio static mode and discharge current was obtained at a constant voltage of 0.4V. At three current densities like 25, 50 and 75 mA cm^{-2} the concentration of CO_2 gas (in ppm) was measured by using CO_2 gas sensor (Vaisala CO_2 sensor M170) as shown in Fig. 1 1(B). Similarly electrochemical experiments were carried out with Nafion 115 and 112 membranes as PMTL for varying methanol concentration (1M, 2M, 3M, 4M and 5M).

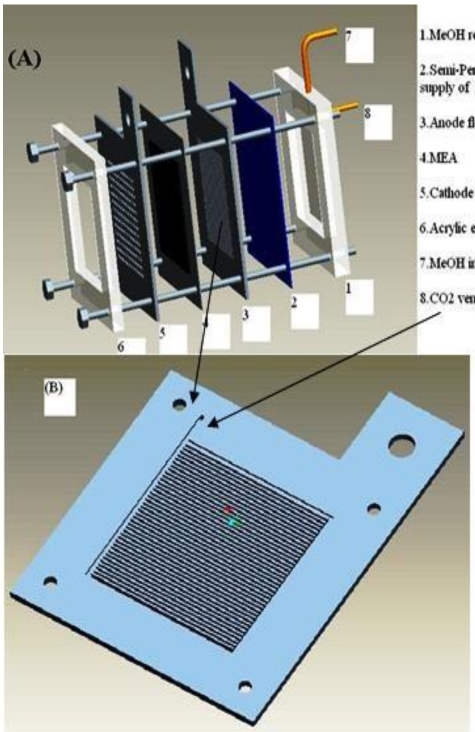

Fig-1: (A) Schematic of exploded view of the passive DMFCs cell fixture. (B) Provision for CO_2 removal in a passive DMFC

3. RESULTS AND DISCUSSION

The amount of methanol delivery by passive feeding (diffusion) to reaction layer from reservoir is a function of methanol concentration and PMTL thickness that determines the cell performance. In Chart 2, the influence of the PMTL such as Nafion 112; Chart 2(A), Nafion 115; Chart 2(B), and Nafion 117; Chart 2(C) with varying methanol concentration (1M, 2M, 3M, 4M and 5M) on the performance of passive DMFCs are given. In Chart 2 (A), it is clearly seen that higher performances at 1 and 2M while lower performances at 3, 4, and 5M methanol are obtained. With increase in methanol concentration increased methanol crossover resulted in decreased performance. Chart 2(C) shows that on replacement of PMTL i.e. Nafion 112 with Nafion 117, comparatively low performance at lower concentrations (1M and 2M) and enhanced performance at higher methanol concentrations (3M and 4M) are obtained, which is attributed to the decrease in methanol transport flux (MTF) due to increase in PMTL thickness from 50 to 175 m. Chart 2(B) shows the results obtained on replacement of PMTL i.e. Nafion 112 with 115. The polarization curves obtained for methanol concentrations 1M, 2M and 3M follow similar trend. A peak power density of 21 mW/cm-^{2} is obtained with 4.0 M methanol. However, in all cases with 5 M methanol, the OCV decreased, indicating that significant methanol crossover from anode to cathode causes decrease in cell performance. The maximum power density is obtained for optimal passive methanol feeding by diffusion with PMTL using Nafion 115 membrane and 4M methanol. In passive DMFC single cell studies, the methanol crossover and methanol transport flux are obtained from the following equations.

$$\text{Volume methanol crossed over} = \begin{pmatrix} \text{Initial volume in the reservoir} - \\ \text{Final volume in the reservoir} - \\ \text{Volume reacted} \end{pmatrix} \quad (1)$$

$$\text{Methanol Transport Flux} = \left[\frac{\begin{array}{c} \text{Volume of methanol crossed over} + \\ \text{Volume of methanol used for oxidation} \end{array}}{\text{Area of PMTL} \times \text{Time}} \right] \quad (2)$$

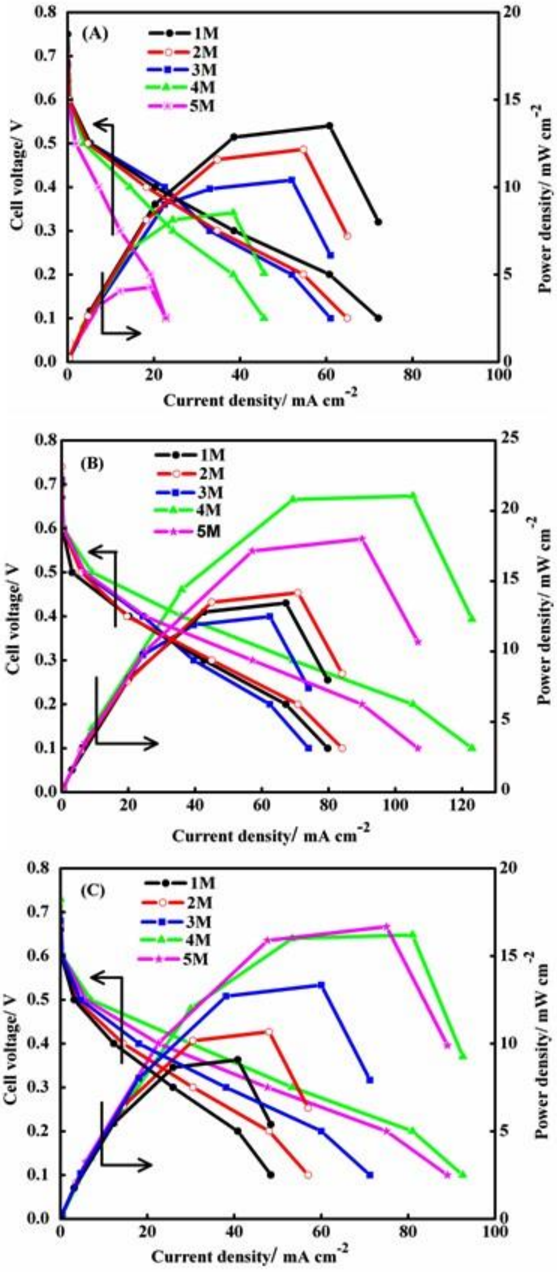

Chart. 1: Effect of passive methanol transport layer (A) Nafion 112, (B) Nafion 115 and (C) Nafion 117 membrane for varying methanol concentrations on performance of passive DMFCs.

Initial and final volume of methanol in the reservoir is noted for each test. Volume of methanol reacted is equivalent to faradaic oxidation of methanol. At constant current density of 40 mA cm^{-2}, the methanol crossover current density and MTF are calculated using the above equations, for various methanol concentrations and for different PMTL and the data are shown in Chart 2. Increase in the thickness of the PMTL from 50 to 175 m leads to decrease in MTF thus limiting the mass transport to the anode and consequently, methanol crossover in passive DMFCs.

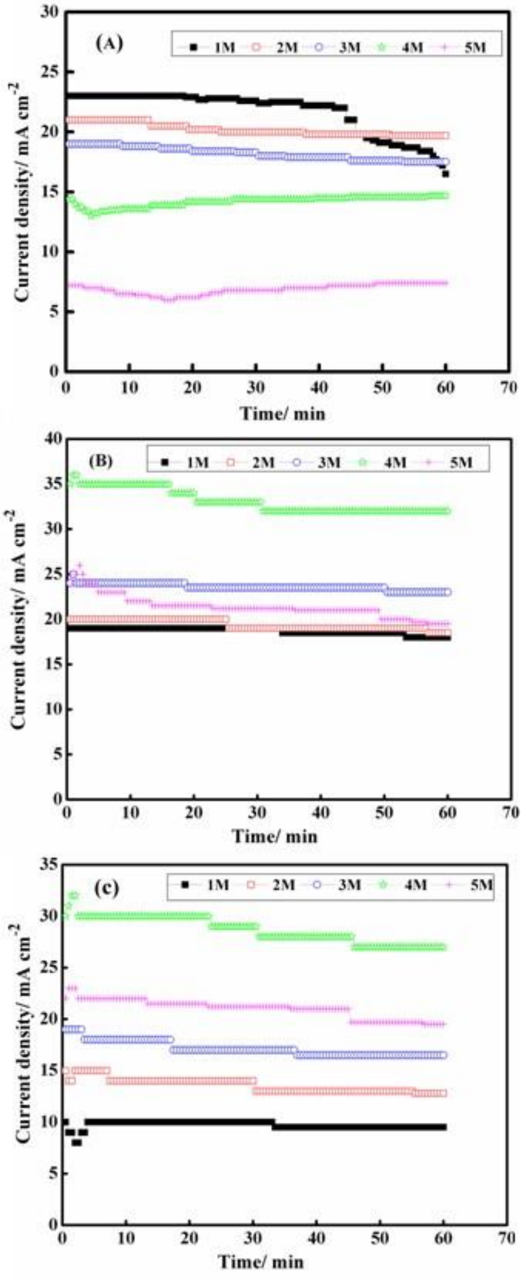

Chart. 2: Methanol crossover current density (solid lines) and methanol transport flux (dotted lines) with respect to varying methanol concentrations at 40 mA cm^{-2}.

The concentrations of CO_2 at 25, 50 and 75 mA cm^{-2} are 420, 500 and 590 ppm, respectively. It is interesting to note that the measured concentration in ppm corresponds to the faradaic oxidation of methanol. The discharge current behavior of the cell is also tested at varying methanol concentrations at a constant voltage of 0.4V with different PMTLs as shown in Chart 3. The discharge current density obtained for 5M concentration is less than that for 4M concentration reiterating the fact that MTF is optimal at 4M concentration. A maximum load current density of 33 mA cm^{-2} obtained with PMTL of Nafion 115 membrane at 4.0 M methanol can be attributed to the optimized PMTL and methanol concentration.

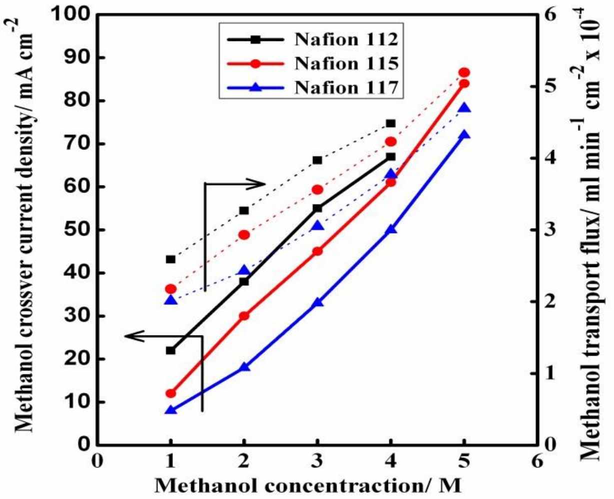

Chart. 3: Discharge current density at a constant voltage (0.4V) with different passive methanol transport layers: (A) Nafion 112, (B) Nafion 115 and (C) Nafion 117 for varying methanol concentrations.

In order to evaluate whether the passive DMFCs suffer from the oxygen mass transport limitation on the cathode, the limiting current density was measured with forced air on the cathode of a passive DMFC, also called as a semi-passive DMFC. Chart 4 shows the performance curve of passive and semi-passive DMFCs with optimized PMTL of Nafion 115 membrane and 4M methanol solution. In the performance curves, a difference in limiting current density of 15 mA cm between passive and semi-passive DMFCs indicates the oxygen mass transport limitation. It interesting to note that the overall passive fuel cell performance is limited by oxygen mass transport and not that by PMTL. In semi-passive DMFCs, a peak power density of 28 mWcm^{-2} is obtained, which almost matches the performance of active DMFCs.

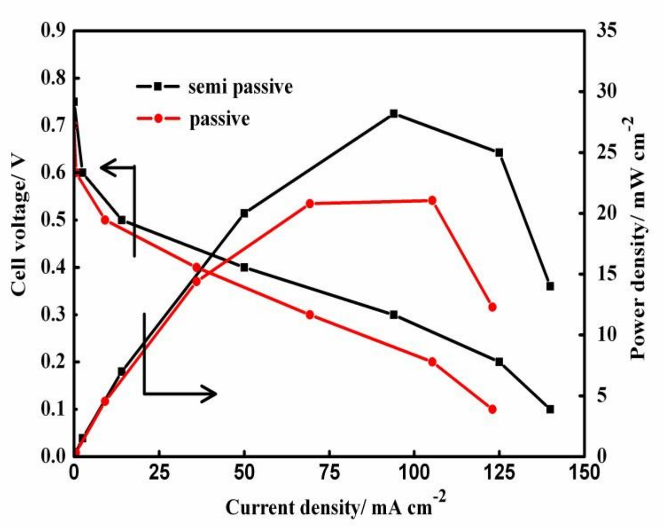

Chart. 4: Comparative performance of passive and semi-passive DMFCs

4. CONCLUSIONS

In a passive DMFC single cell, Nafion 115 membrane as a PMTL has MTF of 4×10^{-4}mL min^{-1} cm^{-2} controlled by diffusion with 4M methanol solution. Peak power densities of 21 and 28 mW cm^{-2} are obtained for passive and semi-passive DMFCs, respectively. The performance obtained in semi-passive DMFCs is comparable to that reported for active DMFCs at ambient conditions.

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