

# PERFORMANCE OF PEM LIQUID-FEED DIRECT METHANOL - AIR FUEL CELLS

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## Abstract

A direct methanol-air fuel cell operating at near atmospheric pressure, low-flow rate air, and at temperatures close to 60°C would tremendously enlarge the scope of potential applications. While earlier studies have reported performance with oxygen, the present study focuses on characterizing the performance of a PEM liquid feed direct methanol-air cell consisting of components developed in house. These cells employ Pt-Ru catalyst in the anode, Pt at the cathode and Nafion<sup>®</sup> 117 as the PEM. The effect of pressure, flow rate of air and temperature on cell performance has been studied. With air, the performance level is as high as 0.437 V at 300 mA/cm<sup>2</sup> (90 °C, 20 psig, and excess air flow) has been attained. Even more significant is the performance level at 60°C, 1 atm and low flow rates of air (3-5 times stoichiometric), which is 0.4 V at 150 mA/cm<sup>2</sup>. Individual electrode potentials for the methanol and air electrode have been separated and analyzed. Fuel crossover rates and the impact of fuel crossover on the performance of the air electrode have also been measured. The study identifies issues specific to the methanol-air fuel cell and provides a basis for improvement strategies.

## Introduction

A liquid-feed type direct methanol fuel cell using proton-exchange membrane electrolyte was developed under an ARPA-sponsored program [1,2]. This fuel cell operates on aqueous solutions of methanol as fuel, and oxygen or air as the oxidant. The cell delivers as high as 0.5 V at 300 mA/cm<sup>2</sup> at 90°C and employs a Pt-Ru anode and a Pt cathode with Nafion<sup>®</sup> 117 as the electrolyte. Among the significant advantages of this cell are its overall simplicity, ease of removal of carbon dioxide produced from the anode stream, and inherent ability to maintain the membrane at high levels of hydration. A 5-cell stack based on this concept was recently constructed by Giner Inc. and was tested at JPL. The liquid feed direct methanol fuel cell is now being actively considered by DOE and DOD for stationary, portable, and transportation applications. In order that the direct methanol fuel cell become a viable power source for many applications and from an overall system standpoint, it is essential that the fuel cell operates on air as an oxidant near atmospheric pressures, at low air flow rates, and at low to moderate temperatures. Therefore, this study focuses on characterizing the performance of liquid feed direct methanol-air cells developed in house, in order to identify the causes that limit cell performance, and design appropriate modifications.

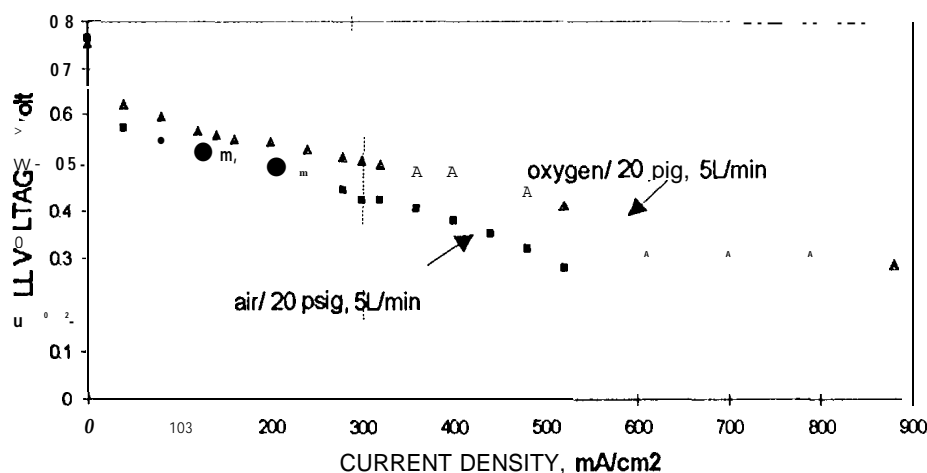
## Experimental Approach

The approach included: a) characterizing and assessing the effects of flow rate, pressure and temperature on the cell performance, b) measuring individual electrode

characteristics, and c) measuring the crossover rates of methanol. These investigations were carried out on JPL-developed components. The anode catalyst was **Pt-Ru** (prepared in house), and the cathode catalyst was Pt (fuel cell grade, Johnson Matthey). Specifically designed anode and cathode structures prepared on porous carbon substrate were bonded under heat and pressure to a **pre-conditioned Nafion<sup>®</sup> 117** membrane to form a membrane-electrode assembly. The active area of the electrodes was typically 25 cm<sup>2</sup> unless stated otherwise. Each electrode had 4 mg/cm<sup>2</sup> of catalyst. The cells were characterized with respect to their overall electrical performance under various conditions of temperature and pressure of the oxidant. Substitution of hydrogen for air or oxygen at the cathode converts this electrode into a dynamic hydrogen electrode that can be effectively used as a reference to monitor the methanol fuel electrode. The ohmic resistance of the cell at 1 kHz was also measured. Polarization curves (corrected for ohmic resistance) for individual electrodes were obtained. Methanol crossover rates were measured by estimating the carbon dioxide content of the cathode exit stream using a Horiba VIA-510 analyzer.

### Results and Discussion

Figure 1 presents the difference in performances of liquid feed direct methanol fuel cells operating on air and oxygen at 20 psig (2.36 atm) and 1 L/rein of the oxidant. The loss in performance to the extent of 90 mV at 300 mA/cm<sup>2</sup>, is attributed to a combination of mass transfer effects in the catalyst layer and porous backing of the cathode and is similar to that observed with the hydrogen-oxygen fuel cell[3]. The cell is capable of sustaining high current densities as in the hydrogen/air fuel cell. Results on the separation of the cell voltage into individual electrode potentials are presented herein later show that under conditions of high stoichiometric flows and pressures as high as 20 psig, the cell is limited in voltage over most of the current density range by the performance of the anode unlike in the hydrogen/air fuel cell. From Fig. 1 it is seen that the methanol-air fuel cell operating on excess air flow at 20 psig and 90 °C sustains 300 mA/cm<sup>2</sup> at 0.437 V, and with oxygen as the oxidant the cell voltage is as high as 0.520V.



**Fig.1 :** Performance of liquid feed methanol fuel cell on oxygen and air at 90°C, 1 M methanol, active area 25 cm<sup>2</sup>.

To our knowledge, the performance shown in Figure 1 is the highest reported in the published literature under the specified conditions. On the basis of the ohmic resistance of the Nafion<sup>®</sup> 117 membrane, the cell voltage could be about 40 mV higher using a Nafion<sup>®</sup> 112 membrane with the penalty of increased crossover of methanol. The effect of temperature and pressure of air at high/low flow rates on the cell performance is presented in Figures 2 and 3. Results show that the effect of pressure on the cell voltage is more significant at low flow rates than high flow rates. Likewise, the effect of flow rate is less significant at higher pressures. The impact of working at ambient pressure on the cell voltage is the greatest at low flow rates and low temperature.

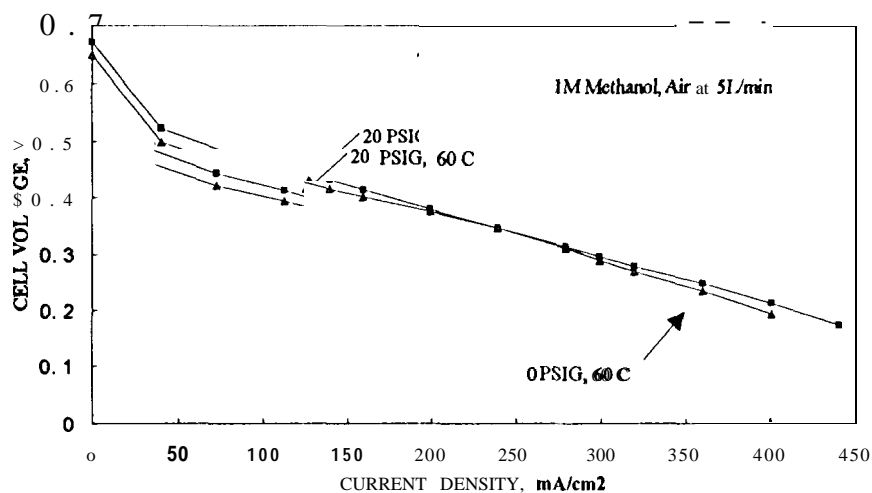


Fig. 2: Performance of direct methanol liquid feed fuel cell on air at 0 psig and 20 psig at 5 L/min and 60°C.

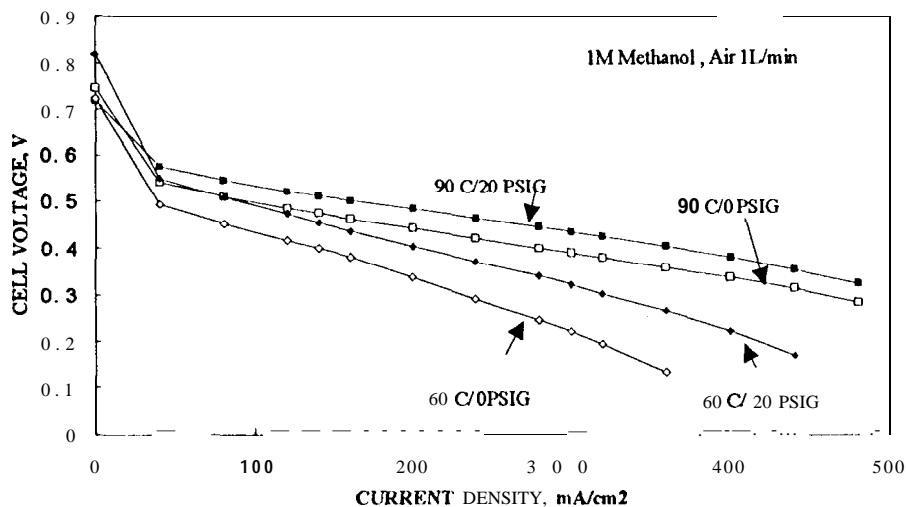


Fig. 3: Effect of pressure and temperature on the operation of direct methanol-air cells at air flow rate of 1 L/min.

These results demonstrate that a current density of  $150 \text{ mA/cm}^2$  can be sustained at  $0.4 \text{ V}$  at  $60^\circ\text{C}$ , at ambient pressure and low flow rate ( $1 \text{ L/rein}$ ) of air, This performance level makes the methanol-air fuel as practical power source for many applications.

In order to determine the individual electrode contributions to the cell voltage at low flow rates and ambient pressure, a separation of the electrode potentials was accomplished as described above. These results are presented in Figure 4.

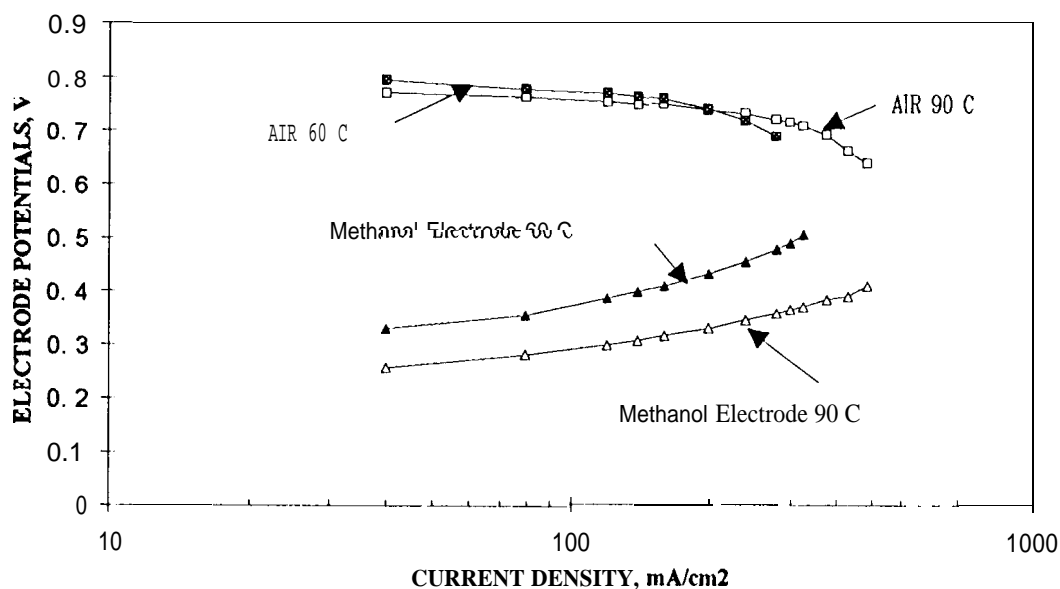


Fig. 4: Individual electrode potentials vs. dynamic hydrogen electrode in a direct methanol air fuel cell operating under ambient pressure air at  $1 \text{ L/rein}$  and  $1 \text{ M}$  methanol

These results suggest that although the polarization at high current densities arises from the air electrode, the methanol electrode is the most significant contributor to the polarization at low/medium current densities. In order to improve the performance in the range of  $100\text{-}300 \text{ mA/cm}^2$  significant improvement in the activity of the anode catalyst is required. At  $60^\circ\text{C}$  the overpotential at the anode is higher (by at least  $75 \text{ mV}$ ) than the value at  $90^\circ\text{C}$  throughout the range of current densities. Results shown in Fig.4 establish that significant cathode polarization is observed at  $300 \text{ mA/cm}^2$  at  $60^\circ\text{C}$  at low flow rates

The steady state crossover rates for methanol have been measured by estimating the carbon dioxide content in the cathode stream. The crossover rate is expressed as a parasitic current density. The present technique for measurement of crossover rates yields much more consistent values compared to earlier measurements[4] and the present method is now considered the most direct and reliable of those tested so far. The crossover rate is found to decrease with increasing current density, and also increases with temperature. Results presented in Figure 5 is a comparison of the crossover rates at  $60^\circ\text{C}$  and  $90^\circ\text{C}$ . The decrease of crossover rate at high current density arises from the increased

utilization of methanol at high current densities. This supports the view that improving the utilization of methanol at the anode is a promising approach to achieving lower crossover rates. The impact of methanol crossover on the performance of the cathode is very significant. Improvements in anode performance can be completely offset by reduction in potential of the air electrode over a wide range of current densities.

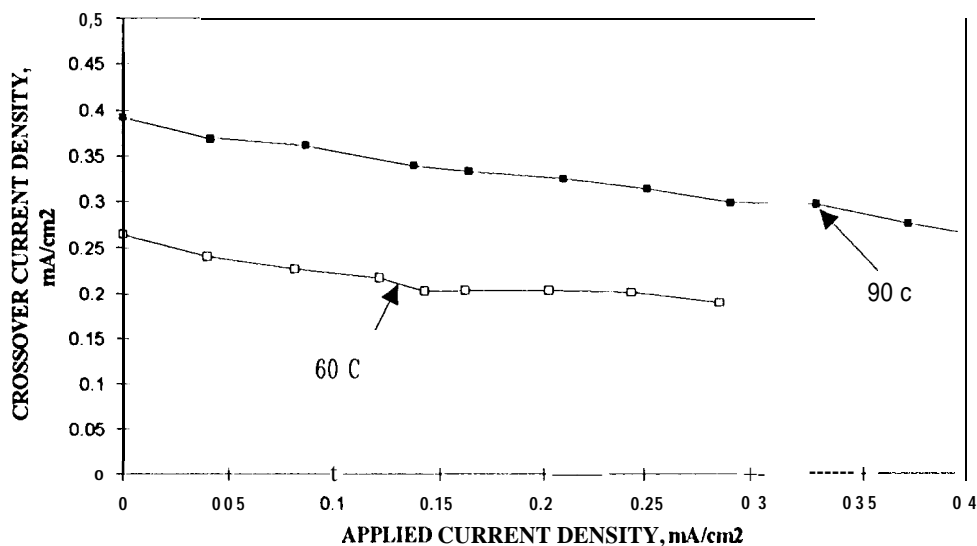


Fig. 5: Dependence of parasitic crossover current density on the operating current density of the direct methanol-air fuel cell operating on 1 M methanol and air at 20 psig, 5L/min.

The results presented in Figure 6 suggest that improvements in cathode performance to the extent of 50-70 mV can be achieved by prevention of fuel crossover. Also, reduction of methanol crossover will allow the use of higher concentrations of methanol that will result in improved kinetics of methanol electro-oxidation.

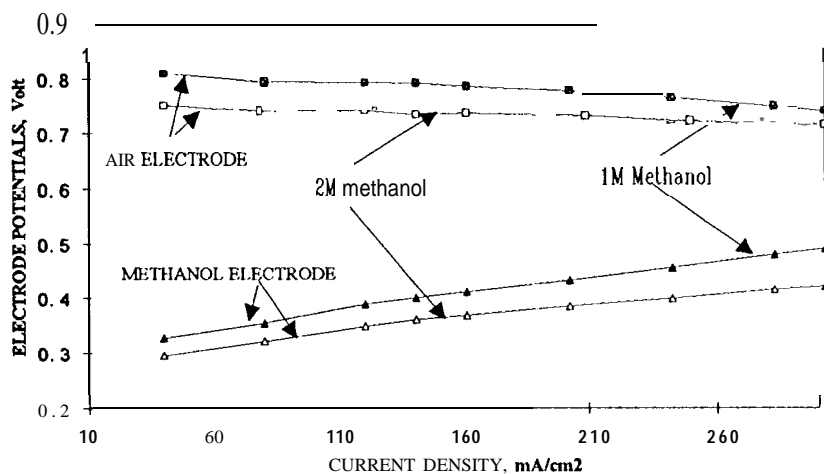


Fig.6: Individual Electrode Potentials vs. dynamic hydrogen electrode for direct methanol-air fuel cell operating at 60 oC, 0 psig and 5L/min of air.

## Conclusions

The liquid-feed direct methanol **fuel** cells developed at **JPL** perform at 0.437 V at 300  $\text{mA}/\text{cm}^2$  on air at 20 psig and 900C; with oxygen, the cell voltage of 0.52 V has been obtained under identical operating conditions. The effect of flow rate on **performance** is very significant at pressures close to ambient. With the latest improvements in electrode structure, 0.4 V has been attained at 150  $\text{mA}/\text{cm}^2$  at 60 °C and air flows at 3-5 times **stoichiometric**. These performance **levels** make the methanol **fuel** cell extremely suitable for practical applications. Measurement of individual electrode potentials show that improvements to the anode catalyst activity can greatly enhance the performance at 600C in the low to medium current density range, while improvement in the air electrode performance is also required at higher current densities. The decrease of crossover rate on applied load demonstrates that improvement of methanol utilization at the anode can reduce crossover rates significantly, Impact of the crossover of methanol on the cathode potential is shown to be about 70 mV. This study quantifies the scope for improvement in various parts of the **cell**.

## Acknowledgements

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