A Direct Methanol Fuel Cell with low methanol crossover and high methanol concentrations: modelling and experimental studies

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Abstract

The direct methanol fuel cell (DMFC) with proton exchange membrane (PEM) as electrolyte and liquid methanol/water as the energy carrier is a promising power source for micro and various portable electronic devices (mobile phones, PDA's, laptops and multimedia equipment). However a number of issues need to be resolved before DMFC can be commercially viable such as the methanol crossover and water crossover which must be minimised in portable DMFC's.

In the present work, a detailed experimental study on the performance of an «in-house» developed DMFC with 25cm^2 of active membrane area, working near ambient conditions (ambient temperature and pressure) is described. Tailored MEAS (membrane electrode assemblies), with different structures and combinations of gas diffusion layers (GDL), were designed and tested in order to select optimal working conditions at relatively high methanol concentration levels without sacrificing performance. The experimental polarization curves were successfully compared with the predictions of a steady state, one-dimensional model accounting for coupled heat and mass transfer, along with the electrochemical reactions occurring in the DMFC recently developed by the same authors. The influence of the anode gas diffusion layer media, the membrane thickness and the MEA properties on the cell performance is explained under the light of the predicted methanol crossover rate across the membrane.

Keywords: *DMFC, High methanol concentrations, Tailored MEAs, Methanol crossover, Fuel Cell Performance.*

1 Introduction

Within the last years, there has been an increased interest in direct methanol fuel cells (DMFCs) as they are a promising power source for micro and portable applications since methanol is a liquid at room temperature, has high energy density, is easy to handle, and easy to store and distribute. However, a number of issues need to be solved before DMFC can be commercially viable. These include the slow anode kinetics arising from a multi-step fuel oxidation process at the anode which results in higher anodic overpotentials, and the fuel crossover from anode to cathode. The crossover not only lowers the fuel utilization, but also degrades the cathode performance and generates extra heat. Therefore, optimizing design and operating condition are critical in improving the DMFC performances.

The direct methanol fuel cell is a multiphase system involving simultaneous mass, charge and energy transfer. All these processes are intimately coupled, resulting in a need to search for optimal cell design, such as membrane thickness and gas diffusion layers structures, and operating conditions, such as cell temperature, methanol concentration, cathode pressure and methanol and air flow rate. A good understanding of these complex interacting phenomena emerges as an important role in optimizing the performance of a DMFC. While several works continue in order to elucidate the fundamental electrochemical reaction mechanisms, to explore new catalyst compositions and structures and to develop new membranes and methods to prevent methanol crossover, important system issues relevant to DMFC are emerging, such as water management, gas management, flow field

design, electrode structure and optimization of the operating conditions.

Some work has been done in order to find the optimal operating conditions [1-9]. These studies revealed that optimised operating conditions are elevated cell temperatures to improve the anode reaction, high air stoichiometries to prevent cathode flooding and dilute methanol solutions to mitigate methanol crossover. Although more concentrated methanol solutions would be preferable in order to achieve energy densities needed for portable power applications, but the use of concentrated methanol solutions at the anode is limited by the significant increase of methanol crossover flux with methanol concentration. So, low methanol crossover in a DMFC is essential for using high methanol concentration in portable power applications.

There are a few studies on DMFCs operating with high methanol concentration, with different membranes and gas diffusion layers and most of them were performed under high temperature and pressure. However less severe conditions (ambient temperature and pressure) are favourable especially for portable applications.

In their work Liu et al. [10] described a new MEA designed to achieve, simultaneously, low water crossover, low methanol crossover and high power density. The authors performed extensive experimental parametric studies to elucidate the effects of material properties, MEA fabrication processes and operating conditions and observed that the important material properties are the membrane thickness and structure of the cathode gas diffusion media. The authors suggest that the key operating parameters are the methanol crossover and the cathode stoichiometry, cell temperature and current density.

In this study, the effect of design parameters, such as membrane thickness and gas diffusion layers materials, on the cell performance of a DMFC operating with relatively high methanol concentrations was investigated. The cell performance was evaluated and analysed by measuring the current-voltage characteristics at ambient conditions (atmospheric pressure and ambient temperature). The experiments were performed with an «in-house» developed DMFC with 25 cm^2 of active area and some results are compared and explained under the light of the predictions of a recently developed one-dimensional model [11].

2 Experimental set-up

2.1 Apparatus

The fuel cell test station was manufactured by Fideris Incorporated. In one compact unit, the Methanol Test Kit (MTK) station comprises a methanol handling system, an oxidant gas handling system and a linear electronic load. To obtain the highest performance of the fuel cell test equipment, Fideris Incorporated recommends operation of all equipment using the FCPower software. This software package has been written especially for the fuel cell researcher to provide compete control of all aspects of fuel cell testing. A schematic drawing of the experimental apparatus used in this work is shown in Figure 1.

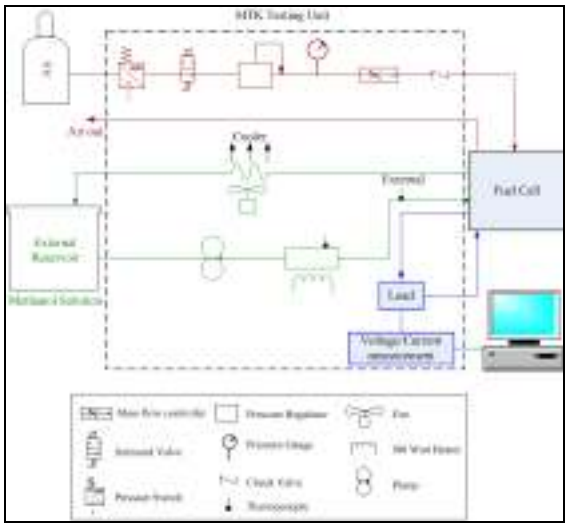

Fig. 1. Schematic diagram of the experimental set-up.

The loadbank subsystem acts as a large variable power resistor which is capable of controlling the amount of impedance by selecting either how much current is passed through the loadbank, the voltage across the loadbank or power dissipated by the loadbank. The computer constantly monitors both current and voltage and these parameters are used to calculate and track the amount of power that the loadbank is dissipating at any one time. This experimental system also provides control over anode and cathode flow rates, cell operating temperature, air pressure and methanol temperature. The anode flow rate is controlled and measured by a magnetic drive gear pump which allows a maximum methanol solution rate of 85 ml/min. Included in the recirculating loop are a heater equipped with over temperature protection and a cooling system which can cool the methanol solution to ambient temperature. The cathode mass flow is controlled and measured by a mass flow controller (MFC) and the gas flow rate can be set to a maximum of 10 l/min.

2.2 Fuel cell Design

The experimental fuel cell consists of two aluminium end plates, two gold plated copper connector plates, two monopolar graphite plates with machined serpentine flow fields, two diffusion layers, two catalyst layers and a membrane (Figure 2). The membrane used was Nafion 117 and Nafion 212 (DuPont) the catalyst was Pt-Ru on the anode

side with a loading of 4 mg/cm^2 and Pt-black on the cathode side with a loading of 4 mg/cm^2. The anode gas diffusion layers used were carbon cloth type A (E-TEK) or carbon paper TGPH060 (Toray) both with a PTFE content of 30 wt.%. The cathode gas diffusion layers used were ELAT carbon cloth (E-TEK), carbon paper TGPH060 (Toray) or carbon cloth type A (E-TEK) all with a PTFE content of 30 wt.%.

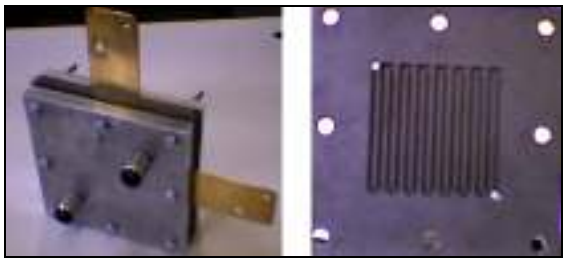

Fig. 2. «In-house» designed DMFC (left) with serpentine flow field (right).

2.3 Experimental conditions

In the experiments, a DMFC with an active area of a 25 cm^2 was used operating at ambient conditions (atmospheric pressure and ambient temperature) by feeding aqueous methanol solution to the anode and dry air to the cathode.

Two different methanol concentrations (2M and 5M) as well as some design parameters such as the anode and cathode gas diffusion layer material and the membrane thickness were tested. The methanol flow rate was set at 3 ml/min and the air flow rate at 3.6 l/min.

3 Results and discussion

The performance of the fuel cell designed in this study was determined by a set of tests, in order to obtain the cell polarization and power curves. The tests consisted of applying a load to the cell, measuring the corresponding voltage value and then calculating the cell power. The influence of methanol concentration, gas diffusion layers characteristics and membrane thickness on the cell performance was carefully investigated.

In a previous work, Oliveira et al. [11] developed a semi-analytical one-dimensional model considering the effects of coupled heat and mass transfer, along with the electrochemical reactions occurring in a DMFC. The model can be used to predict the methanol, oxygen and water concentration profiles in the anode, cathode and membrane as well as to estimate the methanol crossover rate, the net water transport coefficient (α) and the temperature profile across the cell.

In this work, the developed model is used to predict the polarization curves for two different methanol concentrations (2M and 5M). In these experiments carbon cloth was used as anode and cathode gas diffusion layers. The model predictions and experimental results are compared in Figure 3. As can seen from the plots the model describes well the experimental results for the entire range of current densities.

Model predictions are useful to better understand experimental results. In this work, model predictions of methanol crossover rate through the membrane are used to explain some experimental results.

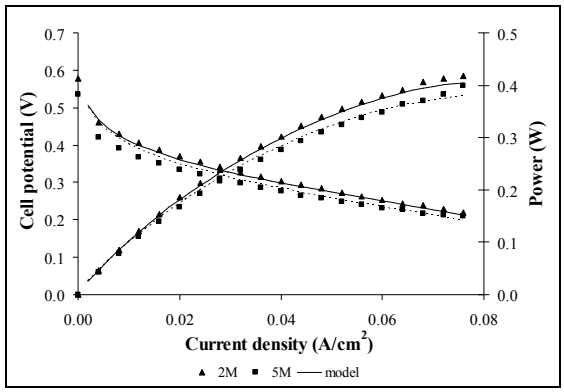

Fig. 3. Comparison of the model predictions on cell performance and power; dots: experimental data, lines: model predictions. Operating conditions: methanol concentration 2M and 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min. Gas diffusion layers materials: carbon cloth at the anode and at the cathode.

3.1 The effect of anode gas diffusion layer

Two structural parameters of the diffusion layer affect the fuel cell performance: i) the tortuosity, which influences the species transport and ii) the surface properties, the wettability and roughness, controlling the droplet/bubble attachment or coverage on the diffusion layer surface. Carbon cloth is more porous and less tortuous than carbon paper. Gaseous carbon dioxide is produced by the anode reaction and must be removed from the diffusion layer by the anode flow. If the carbon dioxide bubbles cannot be removed from the catalyst surface they cover the surface decreasing therefore the effective mass transfer area.

As can be seen from Figure 4, for high methanol concentrations, the level of methanol crossover is also high. Since the carbon paper is less porous than carbon cloth, it limits the amount of methanol reaching the catalyst layer and consequently the methanol that crosses the membrane. The use of carbon paper will probably induce less significant levels of methanol crossover.

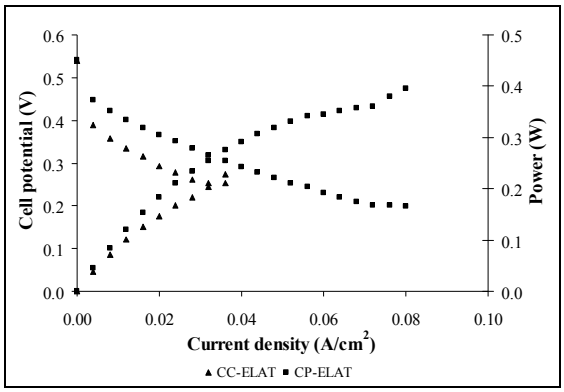

Fig. 4. Influence of anode gas diffusion layers on cell performance and power. Operating conditions: methanol concentration 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min. Gas diffusion layers materials: ELAT (E-TEK) at the cathode.

This effect is shown in Figure 5 confirming that the methanol crossover rate through the membrane is lower when carbon paper is used as anode gas diffusion layer material. Lower methanol crossover rates lead to higher fuel cell performances.

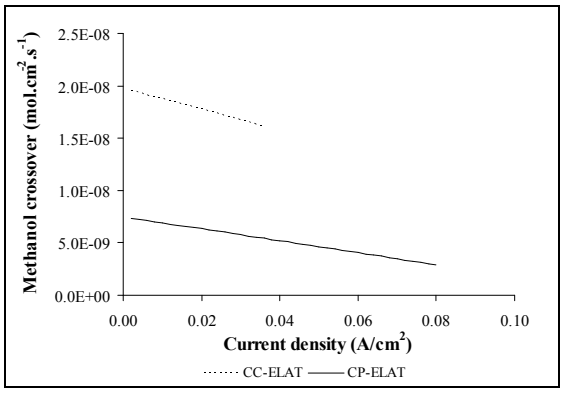

Fig. 5. Model predictions of the methanol crossover rate for different anode gas diffusion layers. Operating conditions: methanol concentration 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min. Gas diffusion layers materials: ELAT (E-TEK) at the cathode.

3.2 The effect of the cathode gas diffusion layer

Figure 6 shows the cell polarization and power curves for three different cathode diffusion media. It seems clear that the carbon cloth material shows the best performance. It should be noted that the variation in performance with different gas diffusion media at the cathode results from the cell internal resistance and the ability of facilitating the oxygen transport. The carbon cloth electrode has an increased capacity to remove the liquid water and thus can contribute to avoid severe flooding at the cathode catalyst layer. Decreasing the water coverage on the cathode diffusion layer surface will benefit the oxygen access to the catalyst site. Also when compared to carbon paper, the carbon cloth with its low tortuosity imposes a lower transport resistance with higher oxygen concentration. Due to the importance of oxygen polarization under high current densities, the differences in performance and power for the two curves are higher under these conditions.

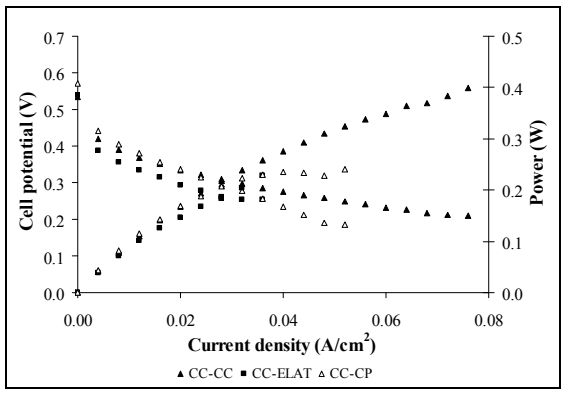

Fig. 6. Influence of cathode gas diffusion layers on cell performance and power. Operating conditions: methanol concentration 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min. Gas diffusion layers materials: carbon cloth at the anode.

3.3 The effect of the membrane thickness

Figures 7 show the cell polarization and power curves for three different membranes, Nafion 117, 115 and 212. The most considerable differences in fuel cell performance for the three membranes used were found at low current densities. As can be seen from the plots the thicker membrane, Nafion 117, revealed no appreciable mass transfer limitations even at high current densities regime. It should be noted that methanol transport through the cell is enhanced or diminished by using different membrane thicknesses. Figure 8 shows the methanol crossover rate through the membrane for the three membranes used. As expected, thicker membranes generate lower methanol crossover rates, which lead to an increase in the fuel cell performance. Therefore, the cell using Nafion 117 and Nafion 115 have the higher electrochemical performances.

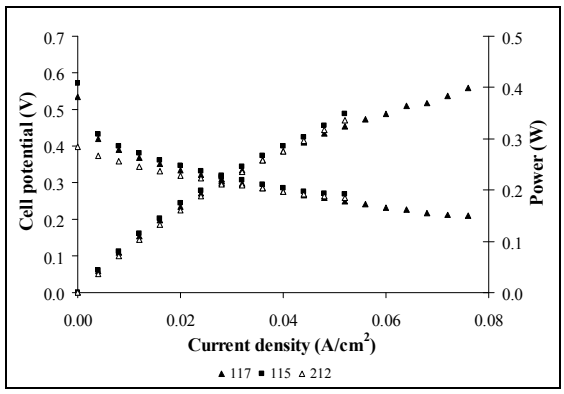

Fig. 7. Influence of membrane thickness on cell performance and power. Operating conditions: methanol concentration 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min. Gas diffusion layers materials: carbon cloth at the anode and at the cathode.

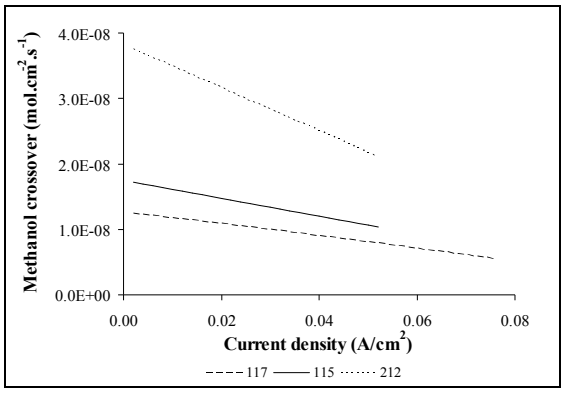

Fig. 8. Model predictions of the methanol crossover rate for different membrane thicknesses. Operating conditions: methanol concentration 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min. Gas diffusion layers materials: carbon cloth at the anode and at the cathode.

3.4 Tailored membranes

Following the results presented in the previous sections, the next goal was tailoring a MEA to achieve a better performance with higher methanol concentrations.

One membrane named commercial Nafion 117 was considered with 30 wt% carbon cloth type A (E-TEK) as gas diffusion layer on the anode and ELAT (E-TEK) on the cathode side. One tailored MEA with a thinner membrane Nafion 212, a 30% wet-proofed carbon cloth type A as anode and cathode gas diffusion layers was also proposed. Two different methanol concentrations 2M and 5M, were used to check if it is possible to work with high methanol concentration without significant sacrifice of fuel cell performance.

Figure 9 a) and b) show, respectively, the cell performance and power density for the two types of MEAs, using the two selected methanol concentrations of 2M and 5M. As is evident from the plots, for the lower methanol concentration used, the tailored MEA has a lower performance for the entire range of current densities, since the membrane used is thinner and generates a larger amount of methanol crossover, as can be seen in Figure 10. For a 5M methanol concentration, the tailored MEA has a much better performance and power density especially for medium to high current densities. This is due to the fact that in this region concentration overpotential is a major portion in the total overvoltage so a decrease in membrane thickness leads to a reduction on mass transfer resistance. Working with thinner membranes has advantages such as the cost and the possibility of working with a favorable water transport direction. Decreasing the membrane thickness enhances back transport of water, from the cathode to the anode, an essential operating condition when working with high methanol concentrations. According to the suggestions of [10] it is possible to reduce the methanol crossover using thinner membranes and thicker gas diffusion layers. This is confirmed with the predictions of methanol crossover generated for 5M methanol concentration which are higher for the commercial membrane.

The results obtained seem to point out optimized conditions for operation of DMFCs with tailored MEAs and high methanol concentrations with an increased performance.

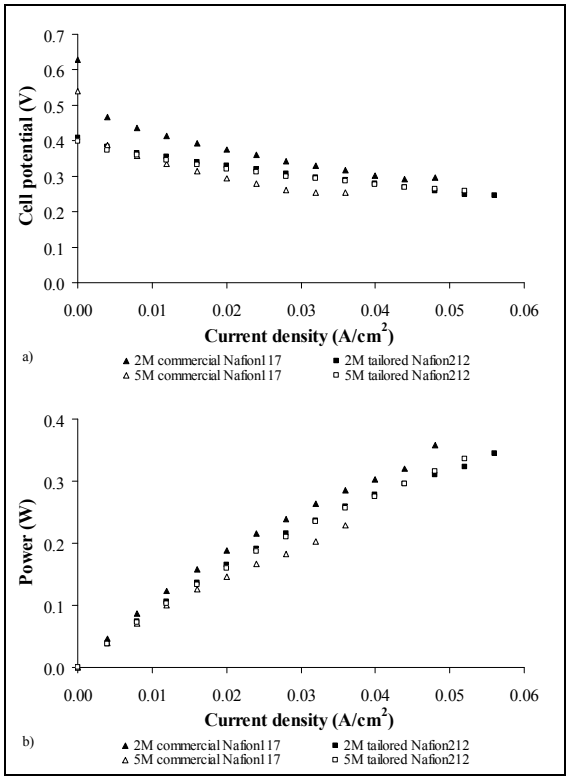

Fig. 9. Influence of MEA properties on a) cell performance and b) power. Operating conditions: 2M and 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min.

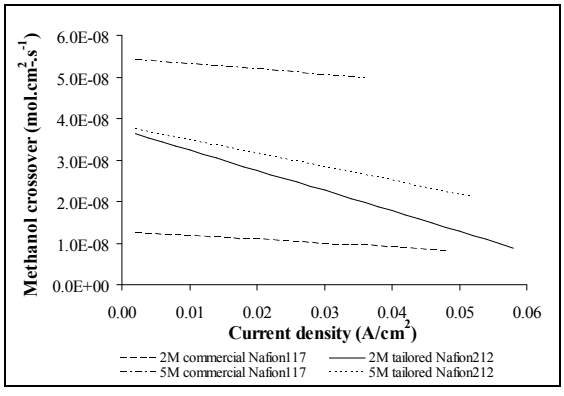

Fig. 10. Model predictions of the methanol crossover rate for different MEA properties. Operating conditions: 2M and 5M, methanol flow rate 3 ml/min and air flow rate 3.6 l/min.

4 Conclusions

Reducing the membrane water and methanol transport from the anode to the cathode of a DMFC is of significant importance to achieve higher cell performances and consequently increased power densities. The performance of a direct methanol fuel cell operating near ambient conditions (atmospheric pressure and temperature) and relatively high methanol concentrations has been carried out to systematically study the effects of the anode gas diffusion layer media, the cathode gas diffusion layer media and the membrane thickness on the cell performance. Using carbon paper instead of carbon cloth for anode diffusion layer increases the cell performance. These results were explained under the light of the predictions of the methanol crossover rate, from a recently developed model. For the cathode side, the use of carbon cloth instead of carbon paper increases the cell performance.

Thicker membranes lead to a lower methanol crossover rate at relative through the membrane increasing the fuel cell performance. However the use of thinner membranes has many advantages such as the enhancing of the back diffusion of water which is essential to work at high methanol concentrations. The possibility of using highly concentrated methanol solutions at the anode is limited by the significant water loss from the anode to cathode occurring in the DMFC due to electro-osmotic drag and molecular diffusion through the membrane.

As a result of these experimental results, a tailored MEA was proposed to achieve relatively low methanol crossover and high power density, operating at high methanol concentrations. The use of adequate materials for the gas diffusion layers enables the use of thinner membranes. The resulting MEA provides a basic element for future DMFC systems using high concentration or pure methanol.

Acknowledgements

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