Experimental and Modeling Studies of a Micro Direct Methanol Fuel Cell

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Abstract

The Direct Methanol Fuel Cell (DMFC) has attracted much attention due to its potential applications as a power source for transportation and portable electronic devices. Based on the advantages of the scaling laws, miniaturization promises higher efficiency and performance of power generating devices and the MicroDMFC is therefore an emergent technology. In this work, a set of experiences with a MicroDMFC of 2.25 cm^2 active area are performed in order to investigate the effect of important operating parameters. Maximum power density achieved was 32.6 mW/cm^2 using 4M mehanol concentration at room temperature. Polarization curves are compared with mathematical model simulations in order to achieve a better understanding of how parameters affect performance. The one-dimensional model used in this work takes in account coupled heat and mass transfer, along with the electrochemical reactions occurring in a direct methanol fuel cell and was already developed and validated for DMFC in previous work [1-3]. The model is also used to predict some important parameters to analyze fuel cell performance, such as water transport coefficient and methanol crossover. This easy to implement simplified model is suitable for use in real-time MicroDMFC simulations.

Keywords: MicroDMFC; Experimental Studies, Modelling, Heat and Mass Transfer.

1 Introduction

In the last few years, the growing interest in portable devices (laptop computers, 3G cellular phones and internet-enabled PDAs) has stimulated the research on miniaturized portable fuel cells to overcome batterie limitations [4]. Micro Fuel Cells can compete with batteries in the low power range (0-30 W). Mostly due to the lack of effective miniaturized hydrogen storage technologies, a liquid fuel like methanol could be the best option to reach a high power density with an attractive cost-to-power ratio. MicroDMFCs can also operate at ambient temperature, leading to a reduction on thermal management challenges for small systems. Small DMFCs with various degrees of microfabrication have been reported [5, 6]. Regarding design parameters, the most common materials used as carrier substrate are silicon and stainless steel. Stainless steel leads to high fuel cell performances. Cha [7] used numerical simulation to compare the performance of several cell designs. The central part of the MicroDMFC is the proton exchange membrane. Methanol crossover across the membrane is one of the most important problems to solve. High methanol concentration provides achievable energy density but it also causes severe methanol crossover through the membrane resulting in a mix potential at the cathode and could lead to lower cell performances Concerning the different concepts of fuel delivery and handling, the MicroFCs are categorized as passive and active [8]. An active system needs moving parts to feed oxidant or fuel to the cell requiring power to operate. Channels configuration is crucial to an efficient reactants distribution for active MicroDMFCs. A passive cell requires no external power. The design optimization demands for a better understanding of the flow dynamics. The control of the multiphase flows at the microscale is a crucial issue. The CO_2 bubbles formed at the anode can disturb and eventually block the flow. On the cathode side the water produced is injected into the channels and the developed two-phase flow plays a central role in fuel cell water management [9]. Both experimental and modeling studies are still needed to overcome or minimize the problems caused by an inadequate water and heat management. Despite the importance of water management in determining the MicroFC performance, no detailed design optimization has been reported. Numerical simulation [1-3, 8, 9] works help to optimize MicroDMFCs. In this work, an experimental study using an "in-house" designed microDMFC with an active area of 2.25 cm^2 is presented. A set of experiments to study the influence of methanol concentration and reactants flowrate on cell performance was performed. A steady state, one-dimensional model accounting for coupled heat and mass transfer, along with the electrochemical reactions occurring in a fuel cell, already developed and validated for DMFC [1-3], was used to predict MicroDMFC performance. Polarization curves predicted by the model are compared with the

experimental ones and the experimental resusts are explained under the light of predicted important parameters, such as the water transport coefficient (α) and methanol crossover.

2 Modeling Studies

The 1D model previously developed and validated takes into account coupled heat and mass transfer, along with the electro chemical reactions occurring in a fuel cell. The detailed description of the model is provided in reference [1]. The most relevant model parameters used for the simulations presented in this work are displayed in Tab. 1. Remaining parameters can be found in [1]. Model predictions are compared with experimental results obtained as described in Section 3.

Fig 1. MicroDMFC picture.

For most of the experiments reported, the flowrates used corresponded to a stochyometric factor (ζ) of 1 for the methanol solution and 3 for air for a current density of 1A/cm^2. Alternative flowrates were also used to investigate the flowrate effect, corresponding to a stoichiometric factor of 1, 2 and 3 for both reactants.

Table 1 – Model parameters values used in simulations.

Parameter	Value	Reference
U_{O_2}	1.24 V	[10]
U_{CH_3OH}	0.03 V	[10]
$\partial E / \partial T$	-1.4 $\times 10^{-4}$V/K	[11]
κ	0.036 S/cm	[10]
a	1000 cm^{-1}	[10]
$I_{0\,ref}^{CH_3OH}$	$9.425 \times 10^{-3} \exp\left((35570/R)(1/353 - 1/T)\right)$ A/cm^2	[11]
$I_{0\,ref}^{O_2}$	$4.222 \times 10^{-6} \exp\left((73200/R)(1/353 - 1/T)\right)$ A/cm^2	[11]
k	7.4×10^{-4}	[10]
λ	2.8×10^{-9} mol/cm^3	[10]
α_A	0.52	[10]
α_C	1.25	[10]
K_{4-6}, K_{8-9,H_2O}	0.8	Assumed
K_{8-9,O_2}	1.25	Assumed
K_7	0.001	Assumed
n_d	$2.9 \exp\left(1029 \times (1/333 - 1/T)\right)$	[11]

3 Experimental Data

In the present work, all the components of the active micro DMFC were "in house" designed, except the MEA. A Nafion 117 membrane (catalyst load of 4mg/cm^2 in both sides) with 2.25 cm^2 active surface area from FuelCellsEtc was used. The basic cell design consists in two acrylic terminal plates and two golden stainless steel current collectors with serpentine design. The thickness of stainless steel plate is 300 μm and 20 channels width and length are respectively, 375 μm and 1.5 cm. The cell is presented in Fig. 1.The experimental rig consists in a rotameter for air flow, a peristaltic pump (Control CO) for methanol flow and

an electrochemical station (Zahner) to obtain polarization curves. In order to study the effect of the methanol concentration on the cell performance, three different concentrations were used: 3M, 4M and 5M.

All the experiments were performed at room temperature, a condition of special interest bearing in mind portable applications.

4 Results and Discussion

The model used in this work is rapidly implemented with simple numerical tools: Matlab and Excel.

In Fig. 2 the predicted polarization curves for 3, 4 and 5 M methanol solutions are compared with experimental data.

The effect of the methanol concentration on the DMFC performance generally reflects two phenomena: increase of the methanol concentration leads to an increase on the coverage of the electrocatalyst sites by methanolic species, but also to an increase of the concentration gradient between the anode and cathode side, with a consequent increase in the crossover through the Nafion membrane. Another point that should be accounted for is the fact that the polarization behavior in the mass transfer region is directly related to the methanol concentration, so an increase in the limit current density is achieved with an increase in methanol concentration.
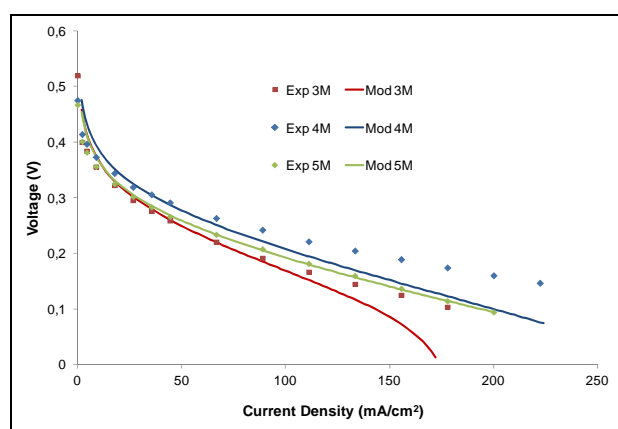

Fig. 2. Comparison of the model predictions of polarization curves for different methanol concentrations; dots: experimental data, lines: model predictions. Operating conditions: temperature 20 ºC, pressure 1 atm. Methanol/Air flow rates of 0.11 /130 ml/min.

As can be seen in Fig. 2, the open-circuit voltage, predicted by the model, is much lower than the thermodynamic equilibrium cell voltage because of methanol crossover. This prediction is in accordance with experimental data. The open circuit voltage is higher for lower methanol concentrations. It is observed that, for this operating conditions, a methanol solution concentration of 4M leads to better performances. Usually, for micro-sized DMFCs, optimal methanol concentrations are higher than for large cells because methanol transport in micro channels is more difficult requiring a higher methanol concentration. According to Fig. 2, the model predictions adjust well experimental performance curves, especially for low current density values. Generally, DMFC models predict less accurately the experimental data at low voltages, where complex phenomena, like water flooding, may occur. The present model describes well the experimental results for low current densities due to the integration, on the model development, of the mass transfer effects at the cathode side. The most significant discrepancies between the model and experimental data are for conditions near the limiting current densities due to the fact

that the model neglects two-phase flow effects. Under these conditions, the bubbles considerably reduce the limiting current density of the cell. However, this model is easier to implement and has shorter simulation times than the ones considering two phase flow effects.

Fig. 3 shows the predictions of the methanol crossover as a function of current density for different methanol feed concentrations. At the cathode, the methanol that crosses the membrane reacts with oxygen in a corrosion reaction.
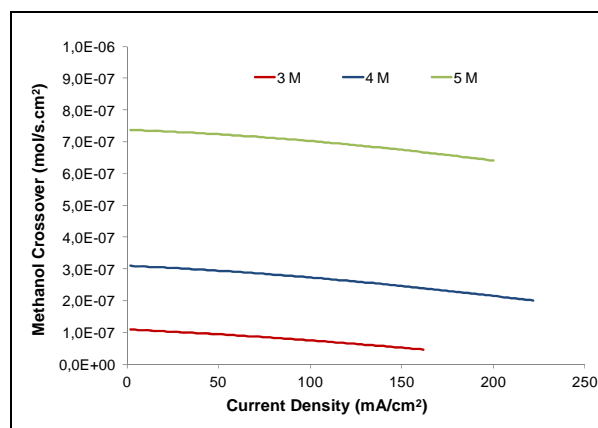

Fig. 3. Model prediction for methanol crossover for different methanol feed concentrations. Operating conditions: temperature 20 ºC, pressure 1 atm, Methanol/Air flow rates of 0.11 /130 ml/min.

As can be seen in Fig. 3, the methanol crossover can be reduced using low methanol concentrations and high current densities. The methanol crossover decreases with current density for all concentrations. This provides a check that the transport equations, used in the development of this simple model, give a physically meaningful influence of methanol concentration at the anode feed on the methanol losses. Although, for these operating conditions, the advantages resulted from a higher coverage of the electrocatalyst sites by methanolic species combined with the negative effects of the increase on methanol crossover when higher methanol concentrations are used resulted in better performances for a methanol concentration of 4M.

In Fig. 4, model predictions of α (defined as the ratio of the net water flux though the membrane from the anode to the cathode normalized by protonic flux) as a function of methanol feed concentration for different current densities, are presented.

It can be observed that methanol concentration has significant impact on α values. It should be noted that positive values of α corresponds to a net water flow from anode to cathode while negative values indicates that the net flow occurs in the opposite side. High methanol concentrations result in low values of α. It is also evident that for higher values of the current density the impact of metha-

nol concentration decreases. The model used predicts the correct trends for the impact of the current density on water crossover. There are, as much as the authors are aware, no accurate experimental data of α to validate the model.
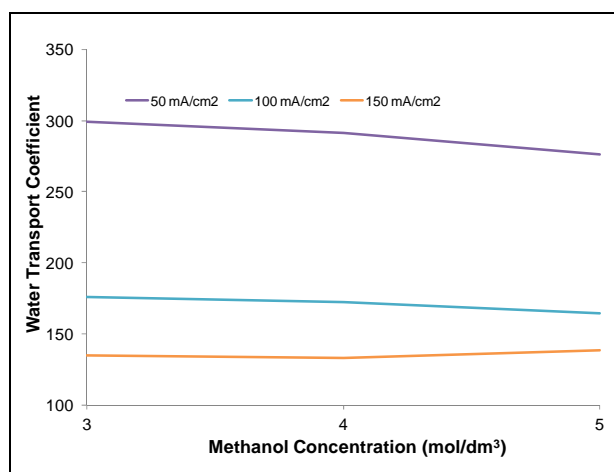

Fig.4. Influence of methanol concentration on the net water transport coefficient at different current densities. Operating conditions: temperature 20 ºC, pressure 1 atm. Methanol/Air flow rates of 0.11 /130 ml/min.

Reactant flowrates could have strongly influence on cell behavior. Efficient removal of carbon dioxide gas bubbles and liquid water produced at the anode and cathode side, respectively, must be maintained to allow the access of reactants to the catalyst sites.

In Fig.5 experimental results obtained for different air flowrate values are compared with model predictions.
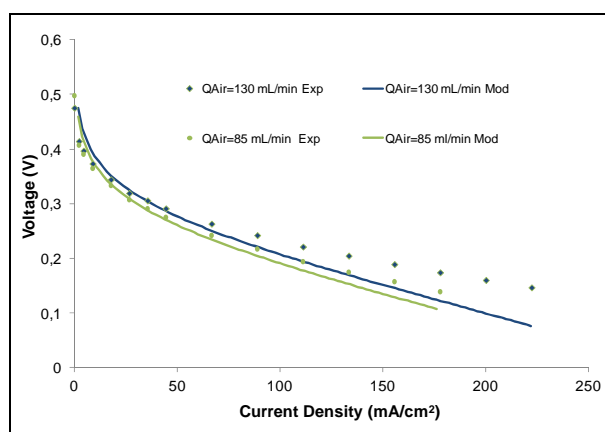

Fig.5. Comparison of the model predictions of polarization curves for different air flowrates; dots: experimental data, lines: model predictions. Operating conditions: methanol concentration of 4M, temperature 20 ºC, pressure 1 atm. Methanol flow rate of 0.11 ml/min.

Model predictions are in accordance with experimental data revealing that better cell performances are obtained with higher air flowrates. A high flow rate forces the oxygen to span the ribs of microchannels and disperse oxygen in the entire gas

diffusion layers and also helps on water drops removal.

In Fig.6, experimental results to evaluate the effect of methanol flowrate are compared with the model predictions.
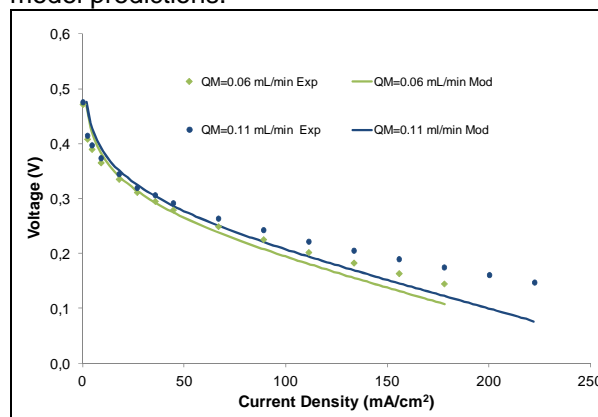

Fig.6. Comparison of the model predictions of polarization curves for different methanol flowrates; dots: experimental data, lines: model predictions. Operating conditions: methanol concentration of 4M, temperature 20 ºC, pressure 1 atm. Air flow rate of 130 ml/min.

As can be seen in Fig.6, for the flowrate range studied, both experimental and simulated data reveal better performances for higher methanol flowrates. For these operation conditions, higher methanol flow rates lead to a high methanol concentration along the flow channels and consequently high methanol concentration in the catalyst layer, facilitating the anode reactivity. Also, higher flow rates are more efficient in carbon dioxide bubbles removal at the anode side leading the pathway free for the fuel and consequently more fuel reaches the anode catalyst layer.

Comparing model simulations and experimental results from Fig. 5 and Fig. 6, it can be concluded that the model adjusts well experimental data. As said before, model adjustments are better for low current densities because of two-phase flow effects are neglected on model development.

5 Conclusions

In this paper a set of experiments with an "in-house" designed microDMFC are presented in order to evaluate the effect of some important operating parameters (methanol concentration and reactants flowrates) at room temperature, a condition of special interest taking in mind portable applications. Analyzing experimental results it can be concluded that, for the operating conditions studied and cell design, fuel cell performance can be improved using a methanol concentration of 4M, high methanol flowrates and high air flowrates. A steady-state, 1D model accounting for coupled heat and mass transfer, along with the electrochemical reactions occurring in the DMFC is used to predict micro DMFC performance. Some relevant parameters on fuel cell performance, like water transport coefficient and methanol crossover

are also simulated. The model adjusts well experimental data for low current density values. The most significant discrepancies between the model and experimental data occur for conditions near the limiting current densities due to the fact that the model neglects two-phase flow effects. Parameters simulated by the model are very useful to explain fuel cell performance and allow optimization of fuel cell operating conditions. The presented model can be a useful tool to improve Micro DMFC understanding and to optimize fuel cell design. The model can be used in real-time system level MicroDMFC calculations.

6 Acknowledgements

7 References

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