Modeling and Simulation of Micro Direct Methanol Fuel Cells

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Abstract

Fuel cells have unique technological attributes: efficiency, absence of moving parts and low emissions. 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. With the advance of micromachining technologies, miniaturization of power sources became one of the trends of evolution of research in this area. Based on the advantages of the scaling laws, miniaturization promises higher efficiency and performance of power generating devices, so, MicroDMFC is an emergent technology. Models play an important role in fuel cell development since they facilitate a better understanding of parameters affecting the performance of fuel cells. In this work, 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 in [1-3], is used to predict Micro DMFC performance. The model takes in account all relevant phenomena occurring in a DMFC. Polarization curves predicted by the model are compared with experimental data existing in literature and the model shows good agreement, mainly for lower current densities. The model is used to predict some important parameters to analyze fuel cell performance, such as water transport coefficient and leakage current density. This easily to implement simplified model is suitable for use in real-time MicroDMFC simulations.

Keywords: MicroDMFC, Mathematical Modelling, Heat Transfer, Mass Transfer.

1 Introduction

Nowadays, consumers demand for portable, power-hungry devices (3G-cellular phones, laptop computers and internet-enabled PDAs) has stimulated researchers and industry to develop advanced miniaturized portable fuel cells to overcome systematic limitations of conventional batteries [4-7]. Medicine is also a demanding field for miniature fuel cells as implantable micro-power sources [8]. Micro Fuel Cells (MicroFC) can compete with batteries in the low power range (0-30 W). The PEM fuel cell and in particular the Direct Methanol Fuel Cell (DMFC) have potential to meet these requirements. Mostly due to the lack of effective miniaturized hydrogen storage technologies a liquid fuel like methanol is the best option to achieve a high power density with an attractive cost-to-power ratio. MicroDMFCs can operate at ambient temperature reducing the thermal management challenges for small systems. Small DMFCs with various degrees of microfabrication have been reported [8, 9]. The

central part of the MicroDMFC is the proton exchange membrane. Methanol crossover 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, lowering cell performance. Concerning the different concepts of fuel delivery and handling, the MicroFCs are categorized as passive and active [10]. An active system needs moving parts to feed oxidant or fuel to the cell requiring power to operate. A passive cell requires no external power. The air-breathing operation mode is normally used in these types of cells. Most of the works on MicroFCs rely on active systems but there is an increasing interest in the passive cells. The channel design determines the flow distribution in MicroFCs. Cha [11] used numerical simulation to compare the performance of several designs. 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. Understanding how the bubbles affect the flow resistance in the channels is essential to develop air breathing operation. 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 [12]. The channels must be designed for low pressure drop to avoid excessive parasitic power losses and must operate in a regime adequate to maintain a proper overall water balance. Despite the importance of water management in determining the MicroFC performance, no detailed design optimization has been reported. Numerical simulation [1-3, 10, 12] works help to optimize MicroDMFCs. In this work, 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], is used to predict Micro DMFC performance. Polarization curves predicted with this model are compared with literature results presented in [13] .

2 Modelling Studies

The 1D model is already developed and validated. The detailed description of the model is provided in reference [1]. The main assumptions are presented here:

- the fuel cell is assumed to operate under steady-state conditions;
- the transport of heat and mass through the gas diffusion and catalyst layers is assumed to be a diffusion pre dominated process and the convection effect is negligible;
- mass transport in the diffusion layers and membrane is described using effective Fick models;
- the thermal energy model is based on the differential thermal energy conservation equation (Fourier's law);
- pressure gradient across the layers is negligible;
- only the liquid phase is considered in the anode side, hence, carbon dioxide remains dissolved in the solution;

- gaseous methanol and water are considered in the cathode;
- solutions are considered ideal and dilute;
- local equilibrium at interfaces is represented by partition functions;
- the catalyst layers are assumed to be a macro-homogeneous porous electrode, hence, reactions in these layers are modeled as homogeneous reactions;
- anode kinetics is described by step mechanism, with a rate expression similar to that used by Meyers et al. [14];
- the anodic and cathodic overpotential is constant through the catalyst layers;
- cathode kinetics is described by Tafel equation;
- methanol and water transport through the membrane is assumed to be due to the combined effect of the concentration gradient between the anode and the cathode and the electro-osmosis force;
- the anode and cathode flow channels are treated as a continuous stirred tank reactor (CSTR). Accordingly, the composition and temperature inside the flow channels are uniform and equal to their values at the channel outlet;
- the heat generation by electrochemical reactions occurring in the catalyst layers is considered;
- when compared with the heat generated by electrochemical reactions and overpotential, the heat released by joule effects is ignored;
- the contact thermal resistance between the graphite plates and the gas diffusion layers is negligible;
- the anode and the cathode streams act as heat transfer fluids; hence, they remove heat from the cell at their outlet temperatures;
- the temperatures of the external walls of the cell are known;
- the heat flux generated in the catalyst layers is assumed to be constant.

The most relevant model parameters used for these simulations are presented in Tab. 1. Remaining parameters can be found in [1].

Table 1 – Model parameters values used in simulations.

Parameter	Value	Reference
U_{O_2}	1.24 V	[15]
U_{CH_3OH}	0.03 V	[15]
$\partial E / \partial T$	-1.4×10^{-4} V/K	[16]
κ	0.036 S/cm	[15]
a	1000 cm^{-1}	[15]
$I_{0\ ref}^{CH_3OH}$	$9.425 \times 10^{-3} \exp\left((35570 / R)(1/353 - 1/T)\right)$ A/cm^2	[16]

$I_{0\ ref}^{O_2}$	$4.222\times10^{-6}\exp\big((73200/R)(1/353-1/T)\big)$ A/cm^2	[16]
k	2.0×10^{-4}	assumed
λ	2.8×10^{-9} mol/cm^3	[15]
α_A	0.52	[15]
α_C	1.55	[15]
K_{4-6}, K_{8-9,H_2O}	0.6	assumed
K_{8-9,O_2}	1.25	assumed
K_7	0.001	assumed
ξ_{CH_3OH}	$2.5\times x_{CH_3OH}$	[15]
n_d	$2.9\exp\big(1029\times(1/333-1/T)\big)$	[16]

Model predictions are compared with experimental results presented in [13]. In this work, the authors evaluated the performance of a microDMFC with 2.25 cm^2 of MEA active area with four types of flow fields. The best design (multiserpentine) was chosen for comparison with model simulations. In this design, the channel width and depth were 375 μm and 300 μm, respectively. The MEA used was Nafion 112. Air flow rate was 50 cm^3/min and methanol flow rate was 0.0503 cm^3/min for all simulated conditions. More details on the experimental work can be found in reference [13] .

3   Results and Discussion

The model used in this work is rapidly implemented with simple numerical tools: Matlab and Excel.
In Fig. 1 the predicted polarization curves for 1, 2, 3, 4 and 5 M methanol solutions are compared with experimental data from [13].
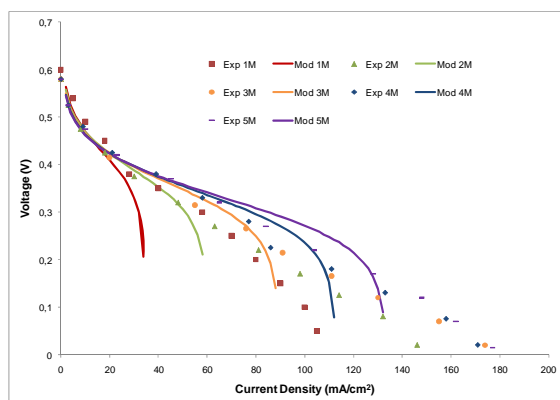

Fig. 1. Comparison of the model predictions of polarization curves for different methanol concentrations; dots: experimental data from [13] , lines: model predictions. Operating conditions: temperature 20 ℃, pressure 1 atm, q_{Air}= 50 cm^3/min and $q_{Methanol}$= 0.0503 cm^3/min.

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.

It can be seen that for low current densities and higher feed methanol concentrations the cell performance is lower. Higher methanol concentrations induce higher methanol crossover values. At the cathode side, methanol reacts with the oxygen to form a mixed potential. Hence, a higher methanol concentration leads to a higher mixed potential, inducing a lower cell performance. According to Fig. 1, the model predictions adjust well experimental performance curves presented by [13], specially 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. As we can see in Fig. 1 the present model describes well the experimental results for low current densities due to the integration, on the model, 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. Comparing with models which take into account two-phase flow effects [17], the present model predictions are worse at high current densities where the influence of two-phase flow effects is more important. 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.
Figure 2 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. Therefore the leakage current formed due to methanol oxidation represents fuel losses. Expressing the methanol crossover in terms of a leakage current gives a more understanding idea of the effect of the loss in efficiency due to methanol crossover. As can be seen in Fig. 2, the leakage current can be reduced using low methanol concentrations and high current densities. The leakage current 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 in the anode feed on the methanol losses.
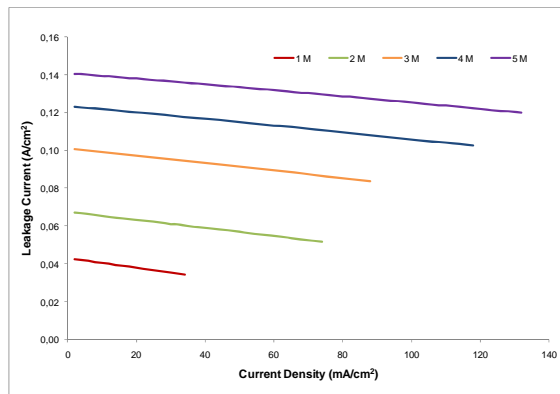

Fig. 2. Model prediction for methanol crossover for different methanol feed concentrations. Operating conditions: temperature 20 ºC, pressure 1 atm, $q_{Air}=$ 50 cm^3/min and $q_{Methanol}=$ 0.0503 cm^3/min.

The model predictions of the net water transport coefficient , α (defined as the ratio of the net water flux though the membrane from the anode to the cathode normalized by protonic flux), are presented in Fig. 3 as a function of current density for different methanol feed concentrations. 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.
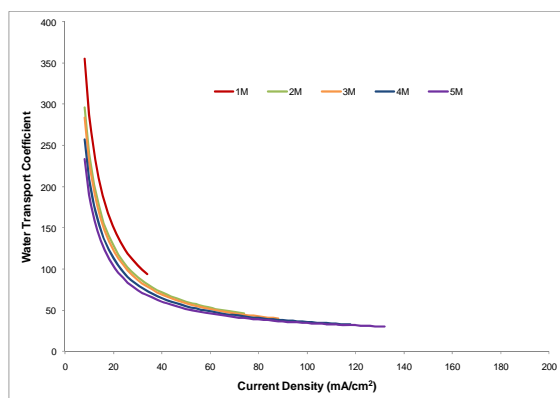

Fig. 3. Model predictions of the net water transport coefficient for different methanol concentrations. Operating conditions: temperature 20 ºC, pressure 1 atm, $q_{Air}=$ 50 cm^3/min and $q_{Methanol}=$ 0.0503 cm^3/min.

Fig. 3 shows that for all the methanol concentrations used the values of α are positive, although they are higher for low methanol concentrations. For low methanol concentrations there is almost always a higher water concentration

at the anode side, especially for the lower values of current density. The transport of water due to electro-osmotic drag and diffusion towards the cathode is dominant. For high methanol concentrations the water produced in the cathode gives higher water concentrations in the cathode side. Therefore the water transport from the anode to the cathode is lower corresponding to small values of α. Working under low or even negative values of α, (corresponding to lower water crossover) may be essential to enable operation of a DMFC under high concentration of methanol in the feed solution, increasing the fuel cell performance.
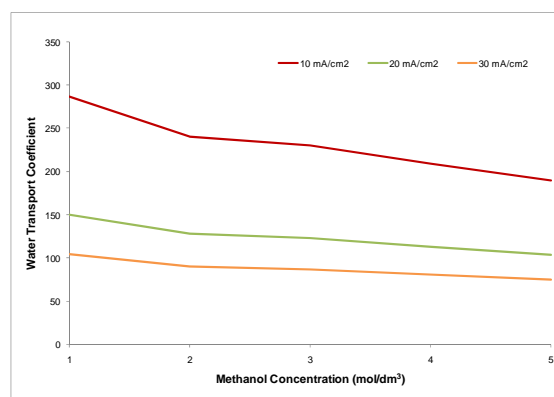

Fig. 4. Influence of methanol concentration on the net water transport coefficient at different current densities. Operating conditions: temperature 20 ºC, pressure 1 atm, $q_{Air}=$ 50 cm^3/min and $q_{Methanol}=$ 0.0503 cm^3/min.

In Fig. 4, model predictions of α as a function of methanol feed concentration for different current densities are presented. It is evident that the methanol concentration has significant impact on α values. As already referred, high methanol concentrations result in low values of α. It is also evident that for higher values of the current density the impact of methanol 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 data of α to validate the model. Liu et al. [18] determined values of α for a reasonable set of operating conditions, but used an indirect method for performing the measurements. The trends predicted with this 1D model are in accordance with the ones proposed by Liu et al. [18].

4 Conclusions

In this paper a steady-state, 1D model accounting for coupled heat and mass transfer, along with the electrochemical reactions occurring in the DMFC is used to simulate micro DMFC behavior. 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 are 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 allows choosing better 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.

5 Acknowledgements

6 Nomenclature

U_{O_2}	thermodynamic equilibrium potential of oxygen oxidation, V
U_{CH_3OH}	thermodynamic equilibrium potential of methanol oxidation, V
$\partial E / \partial T$	rate of change of electromotive force, V/K
κ	ionic conductivity of the membrane, S/cm
a	specific surface area of the anode, cm^{-1}
$I_{0,ref}^{CH_3OH}$	exchange current density of methanol, A/cm^2
$I_{0,ref}^{O_2}$	exchange current density of oxygen, A/cm^2
k	constant in the rate expression
λ	constant in the rate expression, mol/cm^3
α_A	anodic transfer coefficient
α_C	cathodic transfer coefficient
K	Partition coeficcient
ξ_{CH_3OH}	electro-osmotic drag coefficient of methanol
n_d	electro-osmotic drag coefficient of water

References

1. Oliveira, V.B., et al., Heat and mass transfer effects in a direct methanol fuel cell: A 1D model. *International Journal of Hydrogen Energy,* **33** (2008) (14): p. 3818-3828.

2. Oliveira, V.B., C.M. Rangel, and A.M.F.R. Pinto, Modelling and experimental studies on a direct methanol fuel cell working under low methanol crossover and high methanol concentrations. *International Journal of Hydrogen Energy,* **34** (2009) (15): p. 6443-6451.

3. Oliveira, V.B., C.M. Rangel, and A.M.F.R. Pinto, Water management in direct methanol fuel cells. *International Journal of Hydrogen Energy,* **34** (2009) (19): p. 8245-8256.

4. Hsieh, S.S., et al., A novel design and microfabrication for a micro PEMFC. *Microsystem Technologies,* **10** (2004) (2): p. 121-126.

5. Barbir, F., *PEM Fuel Cells - Theory and Practice.* 2005, Oxford: Elsevier Academic Press.

6. Motokawa, S., et al., MEMS-based design and fabrication of a new concept micro direct methanol fuel cell ([mu]-DMFC). *Electrochemistry Communications,* **6** (2004) (6): p. 562-565.

7. Wainright, J.S., et al., Microfabricated fuel cells. *Electrochimica Acta,* **48** (2003) (20-22): p. 2869-2877.

8. Kundu, A., et al., Micro-fuel cells--Current development and applications. *Journal of Power Sources,* **170** (2007) (1): p. 67-78.

9. Kamarudin, S.K., et al., Overview on the challenges and developments of micro-direct methanol fuel cells (DMFC). *Journal of Power Sources,* **163** (2007) (2): p. 743-754.

10. Faghri, A. and Z. Guo, Challenges and opportunities of thermal management issues related to fuel cell technology and modeling. *International Journal of Heat and Mass Transfer,* **48** (2005) (19-20): p. 3891-3920.

11. Cha, S.W., et al., The scaling behavior of flow patterns: a model investigation.

Journal of Power Sources, **134** (2004) (1): p. 57-71.

12. Fei, K., T.S. Chen, and C.W. Hong, Direct methanol fuel cell bubble transport simulations via thermal lattice Boltzmann and volume of fluid methods. *Journal of Power Sources,* **195** (2010) (7): p. 1940-1945.

13. Lu, Y. and R.G. Reddy, Effect of flow fields on the performance of micro-direct methanol fuel cells. *International Journal of Hydrogen Energy,* **36** (2011) (1): p. 822-829.

14. Meyers, J.P. and J. Newman, Simulation of the Direct Methanol Fuel Cell. *Journal of The Electrochemical Society,* **149** (2002) (6): p. A718-A728.

15. Garcia, B.L., et al., Mathematical Model of a Direct Methanol Fuel Cell. *Journal of Fuel Cell Science and Technology,* **1** (2004) (1): p. 43-48.

16. Chen, R. and T.S. Zhao, Mathematical modeling of a passive-feed DMFC with heat transfer effect. *Journal of Power Sources,* **152** (2005): p. 122-130.

17. Wang, et al., *Mathematical modeling of liquid-feed direct methanol fuel cells.* Vol. 150. 2003, Pennington, NJ, ETATS-UNIS: Electrochemical Society.

18. Liu, F., et al., *Low crossover of methanol and water through thin membranes in direct methanol fuel cells.* Vol. 153. 2006, Pennington, NJ, ETATS-UNIS: Electrochemical Society.