Study of a DMFC crossover at different temperatures using a polarization curve model.

Miguel A. Raso[1*], Óscar Santiago[2], Eleuterio Mora[3], Emilio Navarro[2], Teresa J. Leo[3]

[1] *Departamento de Química-Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040-Madrid, España*
[2] *ETSI Aeronáuticos-Universidad Politécnica de Madrid, Pza. Cardenal Cisneros 3, 28040 – Madrid, España*
[3] *ETSI Navales-Universidad Politécnica de Madrid, Avda. Arco de la Victoria 4, 28040 – Madrid, España*

(*) Pres. and corresp. author: marg@ucm.es

Keywords: Direct Methanol Fuel Cell, Modelling, Electroosmotic drag, Permeability, Diffusion

1. Introduction

Direct methanol fuel cells (DMFC) represent a promising technology for low-power portable or stationary applications because of the transport and handling advantages provided by the use of liquid and easily accesible fuel, with high energy density (5.54 kWh/kg) [1].

Its large-scale use depends on the solution of two technical problems that drastically reduce its efficiency, the kinetics of the oxidation reaction of methanol and the transfer of unreacted fuel from the anode to the cathode through the polymeric membrane, known as "crossover" [1].

This transfer takes place in the proton conductive polymer membranes both by diffusion through their pores and by electroosmosis, i. e., the dragging of the methanol molecules by the protons that pass through the membrane during the fuel cell operation.

The study of the fuel crossover is one of the most sensitive aspects to consider when designing a power generation system of which a DMFC is part, especially during low power operation, when the significance of this phenomenon in the reduction of the electric efficiency of the fuel cell is maximum [2].

2. Experimental

A house made single DMFC has been used to carry out polarization curves and gravimetric CO_2 measurements. The membrane electrode assembly has been prepared with Nafion® 117 and commercial electrodes, Pt/C (1 mg·cm^{-2}) for the cathode and Pt-Ru/C (3 mg·cm^{-2}) for the anode. Polarization curves have been measured according to the procedure described in [3, 4] at 20, 30, 40, 50, 60 and 70°C and with two different methanol-water solutions, 1 mol·L^{-1} and 1.5 mol·L^{-1}. Methanol (MeOH) was supplied by Panreac (99.9% purity) and Millipore water has been used to prepare the aqueous solutions. During tests the single cell was continuously supplied with aqueous methanol solution at 3 mL·min^{-1} to the anode and pure oxygen at 250 mL·min^{-1} to the cathode.

Permeability measurements on Nafion 117 were performed in a previous work [5].

In gravimetric tests the CO_2 generated at the anode and the cathode were captured by $Ca(OH)_2$ saturated solutions and the mass of the $CaCO_3$ produced is weighthed.

3. Results

The polarization curves have been fitted with a semiempirical model described in [6], whose parameters are the pseudo-order of the methanol oxidation reaction, the charge transfer coefficient of the anode, the membrane resistance to the protonic conduction and the diffusion coefficient of the anode backing layer.

The results show a clear increase of the charge transfer and anode diffusion coefficients with temperature, whereas the resistance decreases. The crossover predicted by the semiempirical model, in terms of current density j_{cross}, is shown in Figure 1. It has been calculated at a total current density of 8 mA·cm^{-2} to avoid the influence of the CO_2 crossover.

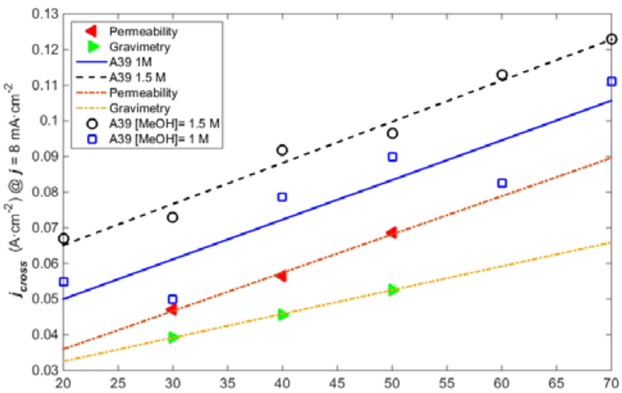

Figure 1. Predicted crossover at 8 mA·cm^{-2} and several temperatures (○ 1.5 M methanol, □ 1 M methanol polarization curves). ◀ Calculated crossover from permeability measurements (1 M methanol) [5]. ▶ Calculated crossover from CO_2 production gravimetric measurements (1 M methanol) [5].

The slope of the linear tendence of the data predicted from the polarization curves is clearly the same of that obtained from permeability measurements. Therefore, the methanol crossover can be explained by the overlapping of two phenomena: the methanol diffusion across the Nafion membrane increasing as temperature increases and methanol electroosmosis constant with temperature (see Table 1).

Table 1. Linear tendence of data in Figure 1

Data set	**Slope (mA·cm^{-2}·K^{-1})**	**Intercept (mA·cm^{-2})**
Polarization curves 1 M methanol	1.11±0.24	27.8±11.6
Polarization curves 1.5 M methanol	1.153±0.079	42.1±3.8
Permeability	1.073±0.079	14.5±3.2
Gravimetry	0.667±0.020	19.22±0.80

The difference between the calculated crossover from permeability measurements and the predicted one from the 1 M methanol polarization curves is a bit greater than the total current density (13.3 vs 8 mA·cm^{-2}), as it was observed in [6]. It was interpreted as the effect the methanol molecules dragged by each proton. The crossover difference for the 1.5 M methanol solution reaches 27.6±7 mA·cm^{-2}, and the permeability of methanol results to be almost constant with the methanol concentration [7], so the methanol electroosmosis must be twice the obtained for the 1 M methanol solution.

The gravimetric slope is two thirds the obtained from the polarization curves, implying that a molecule of methanol out of every 3 molecules crossing through the membrane to the cathode does not react with oxygen to produce CO_2, as already highlighted in [8].

4. Conclusions

These results confirm those obtained in [6], assuring that the study of the crossover of methanol can be carried out using a model for the curves of polarization of a DMFC.

This study confirms the conclusions in [6], extending their validity to the habitual temperature range of usage of DMFC.

Acknowledgements

The authors would like to acknowledge the Comunidad de Madrid and the European Social Funds through the Research Project S2013MAE-2975 PILCONAER and the Spanish Ministry of Economy and Competitiveness and European Regional Development Funds, through the Research Project ENE2014-53734-C2-2-R.

References

[1] J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, J. Wiley and Sons, Chichester 2003, cap.6, pp.140-161.

[2] M. Eikerling, A. Kulikovsky, *Polymer Electrolyte Fuel Cells, Physical Principles of Materials and Operation,* CRC Press, Boca Raton 2015, pp. 324-329.

[3] Leo, T.J.; Raso, M.A.; Navarro, E.; Sánchez de la Blanca, E.; Villanueva, M.; Moreno, B. *Int. J. Hydrog. Energy* 35 (2010) 11642–11648.

[4] T.J. Leo, E. Navarro, M.A. Raso, E. Sánchez de la Blanca, C. Redondo in *Resúmenes de las VI Jornadas de Ingeniería Termodinámica*, Córdoba (España) (2009).

[5] M.A. Raso, A. Soria, M.V. Barragán, T.J. Leo, O. Santiago, E. Mora, E. Navarro, in *Abstracts of IBERCONNAPICE 2016*, Torremolinos (España) (2016).

[6] T.J. Leo, M.A. Raso, E. Navarro, E. Sánchez de la Blanca. *J. Power Sources* 196 (2011) 1178-1183.

[7] M.P. Godino, V.M. Barragán, J.P.G. Villanueva, M.A. Izquierdo-Gil, C. Ruiz-Bauzá, B. Seoane. *Chem. Eng. J.* 162 (2010) 643-648.

[8] H. Dohle, J. Divisek, J. Mergel, H.F. Oetjen, C. Zingler, D. Stolten, J. Power Sources, 105 (2002) 274-282.