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Experimental measurement technique for the assessment of the fuel crossover diffusion coefficient in the membrane electrode assembly of a direct methanol fuel cell

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Abstract

Since the cross-over still seems to be the main issue of the direct methanol fuel cells, an experimental evaluation of the diffusive cross-over is performed. Even if the relationship of the rate through the membrane is the sum of the three terms of diffusive, osmotic and drag, the diffusive component is also present at open circuit lowering the Open Circuit Voltage of the single cell up to 50 % with respect to the Nernst potential. The goal of the research is to develop a direct measurement technique of the crossover that can provide the effective values of the parameters that characterize the membrane electrode assembly. The experimental set up consists in the pressure, flow and temperature control and acquisition using Labview. A sensitive analysis for three values of temperatures at 60°C, 65°C and 70°C is performed for first. Then, a small overpressure was generated in the cathode side by a valve located at the cathode outlet. A set of pressure were analysed for 0, 30 and 90 mbar of overpressure at the cathode. The tested fuel cell has a commercial Nafion 117 membrane and carbon paper gas diffusion layers 700 cm² large. Preliminary results show that the differential concentration term seems to be significantly larger than the osmotic term. The diffusion coefficients are useful for fuel cell modelling and for the calibration of the operating conditions in the sensor less DMFC systems.

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1. Introduction

Since the main issue of the Direct Methanol Fuel Cell (DMFC) is the fuel cross-over [1] the research in this field is focused on the replacement of the electrolytic membrane with new materials. It requires a deep knowledge of the phenomena occurring in the membrane electrode assembly. Numerical simulation strongly help the understanding of the transport phenomena occurring in the fuel cell aiming to explore new design to reduce the drawbacks of the technology. Therefore, it is of deep interest the accurate evaluation of the parameters and coefficients used in numerical simulations to carry out a faithful reproduction of the physical phenomena occurring in DMFCs during operating conditions. It is also interesting for the characterization of the crossover rate in DMFC stacks for sensor less systems, where the control of the molar concentration in the anode circuit is performed by algorithms which use correlations between operating parameters (such as temperature and OCV) and fuel rate consumption that includes the fuel cross-over [2] [3] [4]. The experimental cross-over evaluation was already investigated with indirect measurement techniques such as CO₂ measurement in the cathode [5], but it does not take into account the unreacted methanol at the cathode, and with conventional LSV (Linear Sweep Voltammetry) [6]. In this paper, an experimental technique for the direct evaluation of the diffusive cross-over is performed determining the volume of fuel lost during operation and the global diffusive coefficient for the Membrane Electrode Assembly (MEA). The change in behavior of the diffusion coefficient depending on temperature and pressure is also investigated through sensitive analyses.

Nomenclature

C_i	i -species concentration, [mol cm ⁻³]
D_i	i -species diffusive coefficient, [cm ² s ⁻¹]
F	Faraday constant, 96485 [C/mol]
J_i	i -species cross-over rate, [mol cm ⁻² s ⁻¹]
M	molecular weight, [g mol ⁻¹]
S	active area surface, [cm ²]
V	volume, [mL]
i	current density, [mA cm ⁻²]
k	permeability, [cm ²]
p	pressure [mbar]
t_m	membrane thickness, [m]
x_i	i -species molar fraction
w_i	i -species mass fraction

Greek Symbols

δ_i	i -species drag coefficient, [mol _{i} molH ⁺]
μ	dynamic viscosity, [Pa s]

2. Materials and Methods

To experimentally assess the fuel migration rate, the used technique of cross-over evaluation has been performed in a DMFC stack of 28 cells with 25 cm² of active area each (totally 700 cm²). The total volume of the channels at the anode and at the cathode is about 28 mm³ and the anode flow rate is set at 300 mL min⁻¹ whereas the air flow rate at 6 L min⁻¹ simulating the normal operation of the fuel cell. The MEAs are made of a Nafion 117 membrane with carbon paper as Gas Diffusion Layer (GDL) over the two electrodes. The DMFC stack has been installed on a test bench in Figure 1, in which the control and measurement of temperature has been performed by a thermostatic bath coupled with a heat exchanger and with four thermocouples, type K, placed at the inlet and outlet of the anode and the cathode.

2.1. Measurement procedure

The experiment consists in the evaluation of the discharging time of a well defined volume of fuel stored in the mixing tank where a couple of level sensors, connected to the logic unit, send a digital signal to switch on and off the dosing pumps. They deliver a determined volume of fluid on the basis of the consumption rate due to the cross-over. Two storages, a High Concentration Methanol Tank (HCMT) and a Deionized Water Tank (DWT) provide the liquid for fuel mixture. The flow rates at the anode and cathode are controlled respectively by a feeding pump, installed between the mixing tank and the heat exchanger, and a flow meter controller, equipped with an electric valve performing a feedback control with the flow sensor, placed downstream the compressor and before the fuel cell cathode inlet.

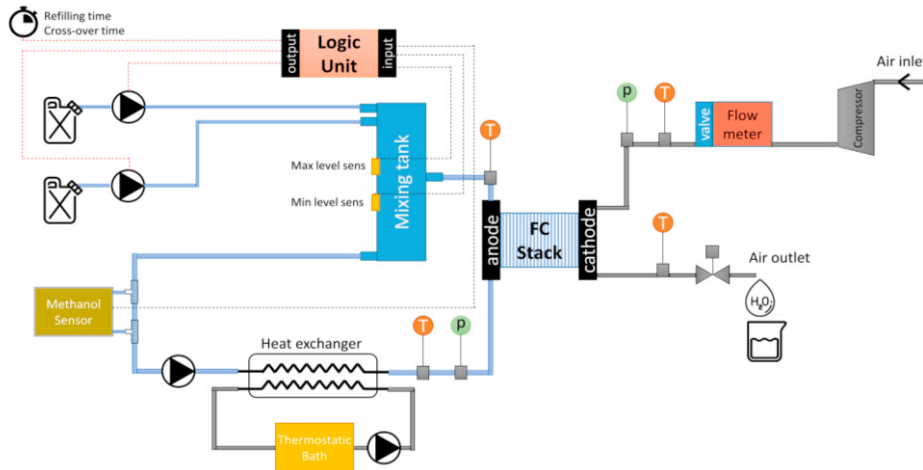


Figure 1 – Test bench scheme for cross-over evaluation

Every test consists of 10 cycles in which pumps refill the mixing tank. The first timer starts at the beginning of the test and stops at the end of the last refill, giving the cross-over time (Figure 1). The second timer starts when the low level sensor (LLS) switches off until the high level sensor (HLL) switches on again (the liquid reaches the maximum level in the Mixing Tank). The volume delivered by the pumps every cycle is around 13 mL.

The tests are performed at constant temperature at 60°C, 65°C and 70°C with an overpressure between cathode and anode of 0, 30 and 90 mbar.

In literature [2], the fuel cross-over is estimated to be due to three contributes as it is shown in (1).

$$J_i = D_{i,MEA} \frac{(C_{i,a} - C_{i,c})}{t_m} + \frac{C_{i,a} k_{MEA} \Delta p_{a,c}}{t_m \mu} + \delta_i \frac{i}{F} \quad (1)$$

The first contribute at the second member is the diffusive component, the second term is the pressure component and the third is the drag component of the cross-over.

In this paper, only the first two components are experimentally evaluated to determine the diffusion coefficient.

First, considering the generated current i and the differential pressure Δp between anode and cathode to be null, the rate of fuel through the membrane can be written as in (2).

$$J_{met,diff} = D_{met,MEA} \frac{\Delta C_{met,a,c}}{t_m} \cdot \frac{M_{mix}}{x_{met} \cdot \rho_{mix}} \quad (2)$$

While the rate of water can be written as in (3).

$$J_{H_2O,diff} = D_{H_2O,MEA} \frac{\Delta C_{H_2O,a,c}}{t_m} \cdot \frac{M_{mix}}{x_{H_2O} \cdot \rho_{mix}} \quad (3)$$

Considering V the volume of fluid delivered each refilling from dosing pump to the mixing tank the total diffusion rate is defined in (4).

$$J_{diff} = \frac{V}{S \cdot \Delta t} = J_{H_2O,diff} + J_{met,diff} = \frac{PM_{mix}}{t_m \cdot \rho_{mix}} \left(\frac{D_{H_2O,MEA} \Delta C_{H_2O}}{x_{H_2O}} + \frac{D_{met,MEA} \Delta C_{met}}{x_{met}} \right) \quad (4)$$

From (4), the diffusion coefficient through the MEA for methanol, with (5), and for water, with (6), can be evaluated.

$$D_{H_2O,MEA} = \frac{V}{S \cdot \Delta t} \frac{x_{H_2O} \cdot \rho_{mix} t_m}{PM_{mix} \Delta C_{H_2O,a,c}} \quad (5)$$

$$D_{met,MEA} = \frac{V}{S \cdot \Delta t} \frac{x_{met} \cdot \rho_{mix} t_m}{PM_{mix} \Delta C_{met,a,c}} \quad (6)$$

All the parameters in the (5) and (6) are known unless for the molar concentration of the species at the cathode (see equation (1)). We can assume, in first approximation as it was done for other researches [3], that the values $C_{i,c}$ are negligible compared to the anode GDL molar concentration, as if the whole quantity of the mixture that reaches the cathode Gas Diffusion Layer (GDL) would be instantaneously transported in the channel.

3. Results

The results from the experiment show that the diffusive cross-over increases as the temperature increases while the overpressure seems to be not significant at OCV condition (Figure 2).

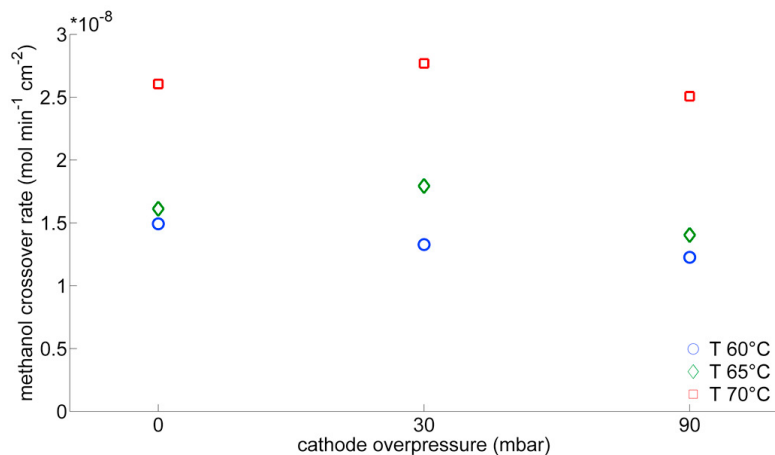


Figure 2 – Volume flow rate migration in dependence on temperature and cathode overpressure

The dependence from temperature is not linear and the resulting data for 60°C are slightly lower than 65°C. They lay in the same range of values between $1.2 \cdot 10^{-8}$ and $1.7 \cdot 10^{-8}$ mol cm⁻² min⁻¹. The diffusion coefficients are determined by (5) and (6) where the term Δt accounts for the cross-over time, which is the time needed for all the 10 cycles of the test. The amounts for the other terms of the equations are listed in Table 1.

Table 1 – Used parameters for diffusion coefficient calculation

Parameter	
Membrane surface area, S	700 cm ²
Methanol molar fraction, x_{met}	0.017
Water molar fraction, x_{H_2O}	0.983
Methanol differential molar concentration, ΔC_{met}	1 mol/L
Water differential molar concentration, ΔC_{H_2O}	53 mol/L
Mixture density, ρ_{mix}	994 kg/m ³
Mixture molar weight, PM_{mix}	0.018 kg/mol
MEA Thickness, t_m	400 μm

The diffusion coefficients of water and methanol with a standard deviation of a 5% are plotted in Figure 3. The diffusion coefficient slight decreases when the cathode overpressure increases, for both water and methanol.

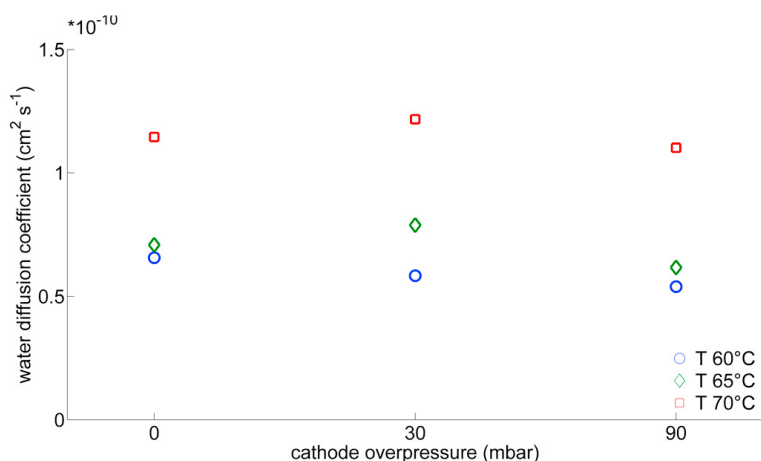


Figure 3 – Diffusion coefficients of methanol (top) and water (bottom) through the MEA

From the experiments, results show a tendency of the diffusion coefficient to grow up depending on temperature. While it is about $0.6 \cdot 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at 60°C , it increases by 50 % at 70°C with a mean value of $1.1 \cdot 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. The values experimentally measured are in line with the usual values used in other numerical works [4].

4. Conclusion

In this work, a measurement technique for the characterization of the fuel cross-over through the membrane electrode assembly is developed. The technique allows the determination of the diffusion coefficient through the recording of the discharge time of a well defined fuel volume supplied from a dosing pump in a mixing tank. The test bench was also equipped by a series of pressure transducers and thermocouples allowing the control of the temperature and pressure in the two electrodes. The tests shown that the diffusion coefficients increases as the temperature increases with a change of about the 40% whereas the permeation component due to the cathode overpressure seems to be not significant and the amount of permeated methanol water solution do not change. The registered permeation rate is around $1.5\text{--}2.5 \cdot 10^{-8} \text{ mol min}^{-1} \text{ cm}^{-2}$. The temperature dependence also seems to be nonlinear and while the increase of the permeation rate between 60°C and 65°C is about 14 %, it strongly increases between 65 and 70°C of about the 60%. The determination of the factors characterizing the water methanol permeation through the exposed technique is extremely useful especially for numerical simulations and for stack characterization used in sensor less DMFC systems where the reintegration of fresh fuel is controlled by algorithms. The future step of the research is the development of a protocol for the determination of the other factors dependent on current density of the DMFC stack such as the drag coefficient.

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