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Measuring electro-osmotic drag coefficients in PFSA membranes without any diffusion assumption

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Abstract

An original set-up derived from the now standard hydrogen pump set-up is presented. The system enables isolation of the electro-osmosis as the lone macroscopic mass transport phenomenon, by minimizing or suppressing other external gradients, keeping the total pressure as the unique adjustment macroscopic parameter. The Electro-Osmotic Drag (EOD) coefficient was determined using 4 Nafion™ MEA (XL, 115, 117, 1110) as material, for temperature values in the 50-80°C range, relative humidity (RH) values in the 30-90% range and current densities ranging from 1.2 up to 1000 mA cm⁻². Pure Nafion™ membranes exhibit the same behaviours with EOD coefficients between 0.8 and 1 and which do not depend on the current density or RH. Nafion™ XL based MEA show a singular behaviour with an EOD coefficient sometime as low as 0.4 and which depends on the RH.

I. Introduction

The hydrogen fuel cells are promising energy converters, having the advantage to produce water as main ultimate product. However, the management of water within the system remains problematic and will probably remain crucial as catalyst performance allow reaching very high current density. Durability issue is also related to water management [1, 2]. In a real working fuel cell system, water is generally introduced in feed channels for core membrane humidification purpose but it is also produced internally along the cathode side through the electrochemical reduction of molecular oxygen. Within the volume of the cell, the water can be transported by different phenomena occurring simultaneously. In the membrane, four transport phenomena can be involved in water transport: diffusion, electro-osmosis, permeation and thermo-osmosis. They arise from different local gradients: concentration, electrochemical potential, pressure and temperature. If temperature and pressure difference between each side of the membrane can be suppressed or minimized, separating electro-osmosis from diffusion is a very difficult task.

Indeed, electro-osmosis is the water drag by the protons from the anode to the cathode occurring when the driving force is the electric field. This water flow often creates a water concentration difference between the two sides of the membrane, which in turn gives rise to water transport by diffusion, generally depicted as “back diffusion” as it is directed from cathode to the anode.

In this context, numerous experimental methods have been developed for electro-osmosis study, under conditions close to hydrogen or methanol fuel cells. The different existing experimental set-ups were usefully reviewed few years ago by Pivovar [3], detailing advantages and drawbacks of each system. Some experimental methods and results were also presented in the review of Kusoglu and Weber [4]. Among the different methods, the so-called hydrogen pump set-up has emerged as a promising system for the electro-osmosis phenomenon study. As it is one of the

“fuel cell” or “membrane-electrode assembly” method, it allows being close to the operating conditions of the fuel cells. It was adapted and modified several times and numerous studies are reported in the literature [5-8].

Some authors adapted the experimental conditions to reduce water diffusion, some of them take diffusion into account in the model used for the analysis of the experimental results ; Ge et al. [8] developed a pseudo two dimensional model to separate diffusion and electro-osmosis contribution to water transport through the membrane. This calculation step necessarily introduced some uncertainty within the results obtained, as the precise diffusion law within most of the membrane materials studied remain a matter of debate, and might exhibit non-Fickian behaviour. This may explain why a large discrepancy is visible among the experimental values reported and the trends towards effect of current density, temperature and relative humidity in the literature [4, 6, 9].

The system presented in this work tries to resolve this issue by creating specific working conditions which let the electro-osmosis as the main transport phenomenon. The experimental set-up is derived from a general hydrogen pump set-up but its originality is that it enables, for the first time, the determination of the Electro-Osmotic Drag (EOD) coefficient independently of any prior diffusion phenomenon study or assumption on diffusion phenomenon magnitude as the external water concentration all around the MEA remains uniform.

The experimental results presented here can help to advance the understanding and the modelling of the electro-osmosis phenomenon, as realized by different teams [10-13].

II. Description of the experimental method

The experimental method proposed in this study was derived from a standard hydrogen-pump system. As in a hydrogen pump, the cell is composed of a membrane sandwiched between two electrodes and two gas diffusion layers. Humid hydrogen flows in the channel at the anode. By applying a potential difference between the anode and the cathode, hydrogen oxidizes at the anode. The protons cross the membrane and the hydrogen reduces at the cathode. While flowing through the membrane, the protons carry water molecules creating the so-called electro-osmotic water flow. Due to the hydrogen and electro-osmotic flows through the membrane, the water content of the gas may vary along the channel and give rise to water transport by diffusion through the membrane.

The original development of the presented experimental method is the control of the total pressure of the cell ensuring that the gas mixture composition is uniform in the whole cell. In that way, water transport through the membrane occurs by electro-osmosis only, diffusion being removed. A schematic description of the cell is given in *figure 1* showing that the anode outlet was connected to the cathode inlet, a dew point sensor being located between the two compartments. This sensor was not used for its absolute accuracy but for its sensitivity, which minimizes the experimental uncertainty. It was indeed used to indicate if the dew point temperature is increasing or decreasing as a function of time just after the current is applied.

As the experimental principle reported here is, to the best of our knowledge, new, the authors like to describe briefly the general method of the measurement, its advantages, the typical sequence of a standard run and the actual data extraction process.

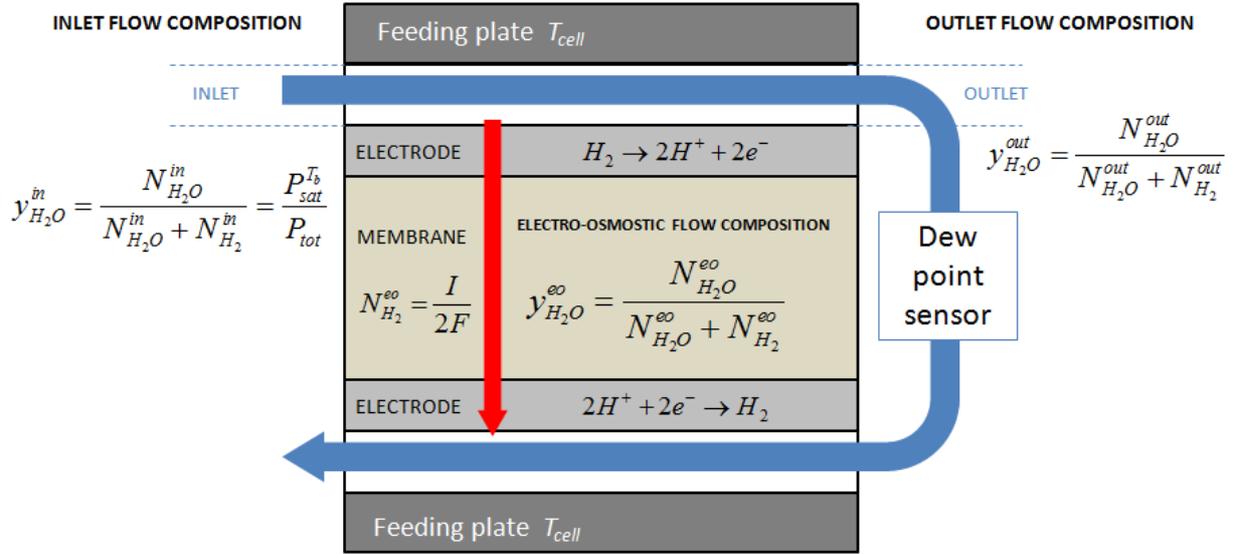


Figure 1. Schematic description of the operating cell

The main parameters used in this study were the flow compositions -or the water molar fractions in the gas mixture. They were defined at the inlet and at the outlet of the anode channel, and through the membrane:

$$y_{H_2O}^i = \frac{N_{H_2O}^i}{N_{H_2O}^i + N_{H_2}^i} \quad i=in.,out.,eo \quad (1)$$

$N_{H_2O}^{in,out}$ and $N_{H_2}^{in,out}$ are the vapour and hydrogen molar flux (mol s^{-1}) at the inlet and at the outlet of the anode, and $N_{H_2O}^{eo}$ and $N_{H_2}^{eo} = I/2F$ are the molar electro-osmotic liquid water and hydrogen flux (mol s^{-1}) through the membrane.

During the experiment, the current density I is initially set to 0 A and humid hydrogen flows in the cell. The dew point temperature measured by the sensor is constant and equal to the bubbler temperature (T_b) used for hydrogen humidification.

Just after applying the current, three different regimes can occur:

- In the first regime, the measured dew point temperature increases. In this case, the electro-osmotic flow composition $y_{H_2O}^{eo}$ is lower than the inlet composition $y_{H_2O}^{in}$, thus enriching with water vapour the gas flow analysed by the detector.
- In the second regime, the measured dew point temperature decreases. In this case, the electro-osmotic flow composition is higher than the inlet composition, thus reducing the amount of water in gas mixture.

In those two first regimes, the gas flow composition is not uniform in the channel at the anode and at the cathode, and the corresponding gradient of water concentration gives rise to water transport by diffusion through the membrane in addition to the electro-osmosis.

- However, it exists a third regime (named the equilibrium regime) for which the dew point temperature reported by the sensor remains constant when the current is applied. In this case the inlet flow composition is equal to that of the electroosmotic flow. This particular regime can then be used to determine the EOD coefficient.

In addition to the equation (1), the gas composition at the inlet of the cell $y_{H_2O}^{in}$ can also be given as a function of the total pressure P_{tot} of the cell:

$$y_{H_2O}^{in} = \frac{P_{sat}(T_b)}{P_{tot}} \quad (2)$$

Where $P_{sat}(T_b)$ is the saturated pressure at the operating temperature T_b of the bubbler used for the hydrogen humidification. The hydrogen RH at the inlet of the cell is:

$$RH^{in} = \frac{P_{sat}(T_b)}{P_{sat}(T_{cell})} \quad (3)$$

RH^{in} was fixed by setting the bubbler temperature T_b and the cell temperature T_{cell} which was assumed uniform.

Thus, in order to reach the particular third regime for a given water activity RH^{in} , the inlet composition of the gas is modified by tuning the total pressure according to equation (2).

As it is explained in the next section, the EOD coefficient was then deduced from the total pressure and from the bubbler temperature. This is a definite advantage over other methods that require a mass balance and thus are sensitive to the gas flow rates.

Data extraction process

As previously explained, the original idea is to adjust the total pressure P_{tot} in order that the composition of the inlet humidified hydrogen becomes equal to the electro-osmotic flow composition. By definition, the EOD coefficient noted ξ , is the ratio of the molar water flow $N_{H_2O}^{eo}$ by the molar flow of protons which is twice the hydrogen molar flow through the membrane.

$$\xi = \frac{N_{H_2O}^{eo}}{2N_{H_2}^{eo}} \quad (4)$$

It can be given as a function of the electro-osmotic flow composition:

$$\xi = \frac{1}{2} \frac{y_{H_2O}^{eo}}{1 - y_{H_2O}^{eo}} \quad (5)$$

Achieving the same gas composition at the inlet $y_{H_2O}^{in}$ and at the outlet $y_{H_2O}^{out}$ (location of the RH sensor) of the anode channel requires having:

$$y_{H_2O}^{eo} = y_{H_2O}^{in} \quad (6)$$

This condition is satisfied experimentally by varying the total pressure P_{tot} .

From equations (2, 5, 6) the experimental EOD coefficient is obtained as a function of the experimental equilibrium pressure P_{tot}^{eq} leading to the third regime and of the bubbler temperature:

$$\xi = \frac{1}{2} \frac{P_{sat}(T_b)}{P_{tot}^{eq} - P_{sat}(T_b)} \quad (7)$$

During the experiments, the total pressure was varied (increased or decreased) and the current was applied until the third regime was reached allowing determination of the EOD coefficient.

A detail of a typical experimental run is given in *figure 2*.

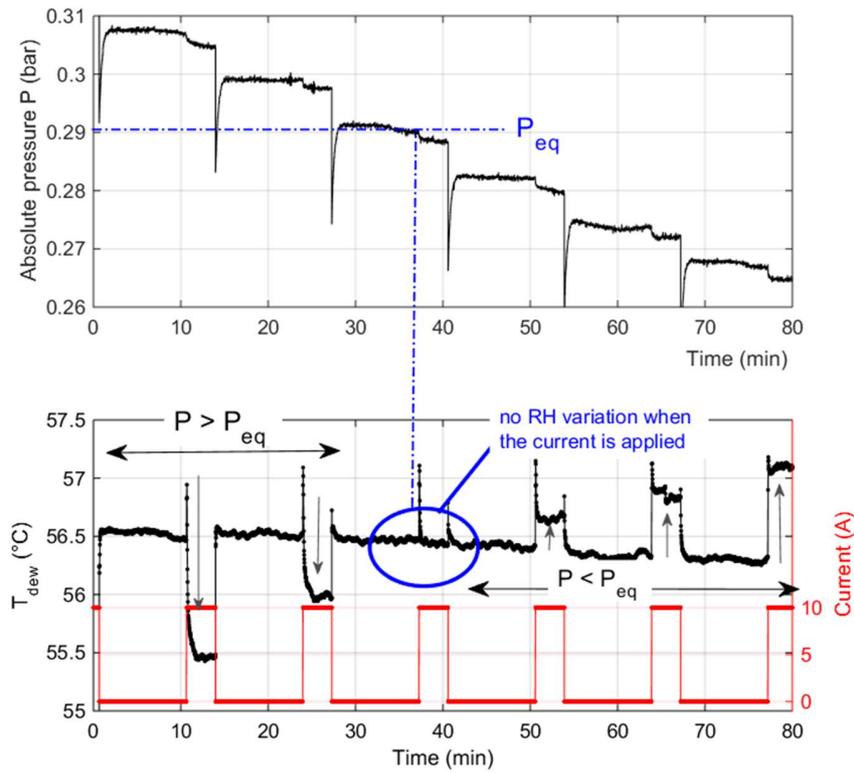


Figure 2. Typical run for N115. Top: total pressure applied to cell ; bottom: dew point temperature at the outlet and current density variations with time

In this example, the total pressure was scanned between 308 and 268 mbar by 10mbar steps. For the setting value of the total pressure, humid hydrogen flows in the cell during about 10 minutes without current loading. Then the current was set to the selected value during 3 minutes. As it is presented in *figure 2*, when the total pressure P_{tot} is higher than 290 mbar, the dew point temperature at the anode outlet decreases after the current is applied and when it is lower than 290 mbar, the dew point temperature increases. So, the equilibrium total pressure for this run, taken as an example, was found to be 290 ± 10 mbar.

III. Experimental set-up

Figure 3 gives a global schematic view of the experimental set-up

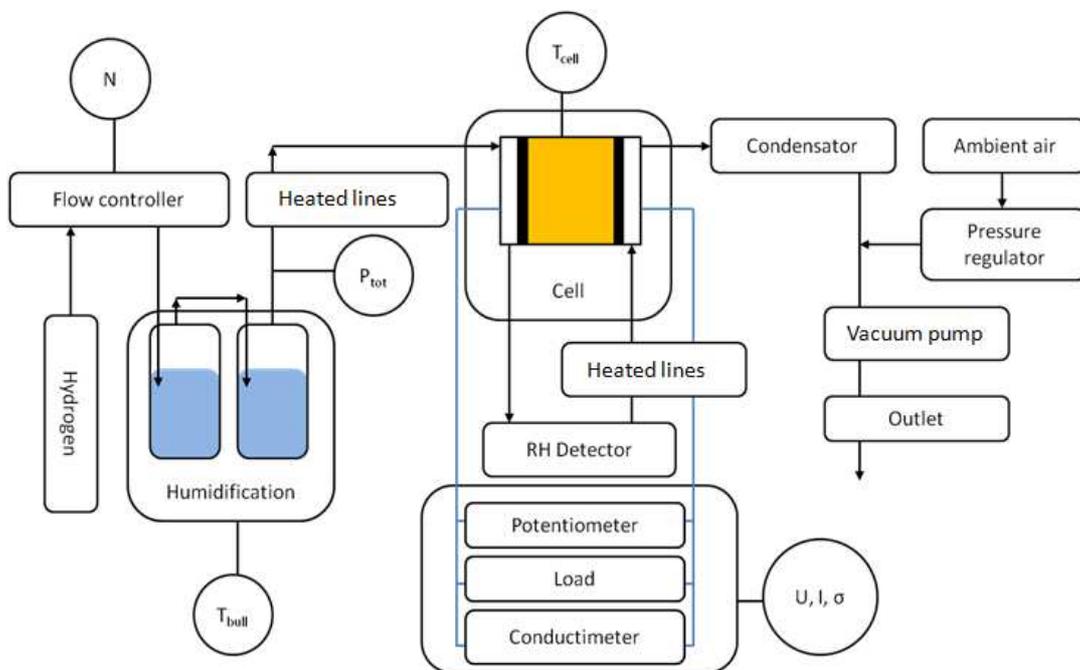


Figure 3: Schematic of the experimental set-up.

The hydrogen humidification was realized using two home-made bubblers each being composed of a 2-liters tank. They were connected in serie in order to ensure a good equilibrium between liquid and gas phases, independently of the gas flow. This provided the required stability of the water content of the gas at the inlet of the cell, and yield a very stable dew point temperature T_b ($\Delta T_b < 0.1^\circ\text{C}$). Each bubbler was calibrated using an optical dew-point detector (©MICHELL Instruments, Optidew chilled mirror hygrometer), providing an overall $\pm 0.1^\circ\text{C}$ uncertainty. All the components were connected using standard stainless steel tubes and connectors (SWAGELOK® Company), with exception of the tubes connecting the cell to the gas supply which was in PTFE to ensure electrical insulation of the cell. All the lines were heated to avoid vapour condensation. The cell temperature was controlled using a water circuit embedded in the cell plates and connected to a thermostatic bath (LAUDA™ RE306) monitored by a Pt100 probe ($\Delta T_{cell} < 0.1^\circ\text{C}$). The gas management was carried out using flow controllers (BROOKS® SLA 5850S).

A vacuum pump (VACUUBRAND MZ 2D NT) and a pressure controller (BROOKS® 5866E) were used for the total pressure adjustment. A pressure regulator (BRONKHORST) allows choosing the outlet total pressure. This set-up is entirely automated and driven using the Labview® software. The pressure instruction has been automated according a specific algorithm to faster converge towards the equilibrium pressure. The hydrogen stoichiometry goes from 1.25 to 2 depending on the applied current density. Those values were found to achieve a good compromise between sensitivity and absolute gas flow value so that the flow in the dew point detector is high enough to achieve good measurement. If the stoichiometry was too high, the relative variations of the *RH* would be too low as compared to the *RH* detector sensitivity. If the stoichiometry was too low, the gas flow would be too low relatively to the dead-volume of the

RH detector chamber. Water vapour was condensed at the outlet of the cell to prevent the vacuum pump to be filled with liquid. A home-made Pelletier's effect condenser was used for exhaust water recovery. An external milliohm meter (HIOKI Company) was used for the conductimetry measurements, using the high-frequency (@1kHz) impedance method.

Materials and cell assembly

The different tested MEAs were purchased from IonPower. They were essentially Catalyst Coated Membrane MEA (CCM) apart from one sample which was a Catalyst Coated Backing (CCB). Different membranes were tested: Nafion™ XL, Nafion™ 115, Nafion™ 117 and Nafion™ 1110 were used as received. The electrodes Pt loading was equal to 0.4 mg cm⁻² on both sides. GDL Sigracet 25BC (250 μm thick) were used as gas diffusion layers. Nafion™ 117 was tested with CCM (IonPower) and CCB (0.3mgPt/C on Sigracet 29BC from fuelcellstore.com hot pressed @T=135°C for 3min). High purity hydrogen 5.0 grade was purchased from MESSER, and deionised water was used for the humidification system.

A home-designed single cell with a 25 (5x5) cm² active surface area was used for all measurements. The MEA were built-up using PTFE gaskets (200 μm thick) and the cell was tightened with 5 N.m torque at room temperature before connection to the system. The brass gold plated 5x5 cm² plates are made of 25 straight parallel channels leading to a very low pressure drop.

Uncertainty estimation

The relative uncertainty of the EOD coefficient measurements was estimated. The Rankine isotherm was used to determine the saturation pressure

$$P_{sat}(T_b) = \exp\left(13.669 - \frac{5096.23}{T_b + 273.15}\right) \quad (8)$$

With ξ given by the equation (7), the relative uncertainty is written as equation (9):

$$\frac{\Delta\xi}{\xi} = (2\xi + 1) \frac{5096.23}{(T_b + 273.15)^2} \Delta T_b + \frac{2\xi}{\exp\left(13.669 - \frac{5096.23}{T_b + 273.15}\right)} \Delta P_{tot} \quad (9)$$

By taking $\Delta T_b = 0.5^\circ\text{C}$ and ξ close to 1, the first term represents a contribution close to 7 % of the total uncertainty and it decreases as the bubbler temperature increases. Besides, the second term only depends on the pressure step used to converge towards the equilibrium pressure ; it was set to $\Delta P_{tot} = 5$ mbar.

IV. Results and discussion

The experimental values of the EOD coefficient are given in figure 4 as a function of the current density, for the four membrane materials NXL, N115, N117 and N1110, at three cell temperatures 50°C (a), 60°C (b) and 80°C (c), and different values of the hydrogen RH at the inlet of the cell.

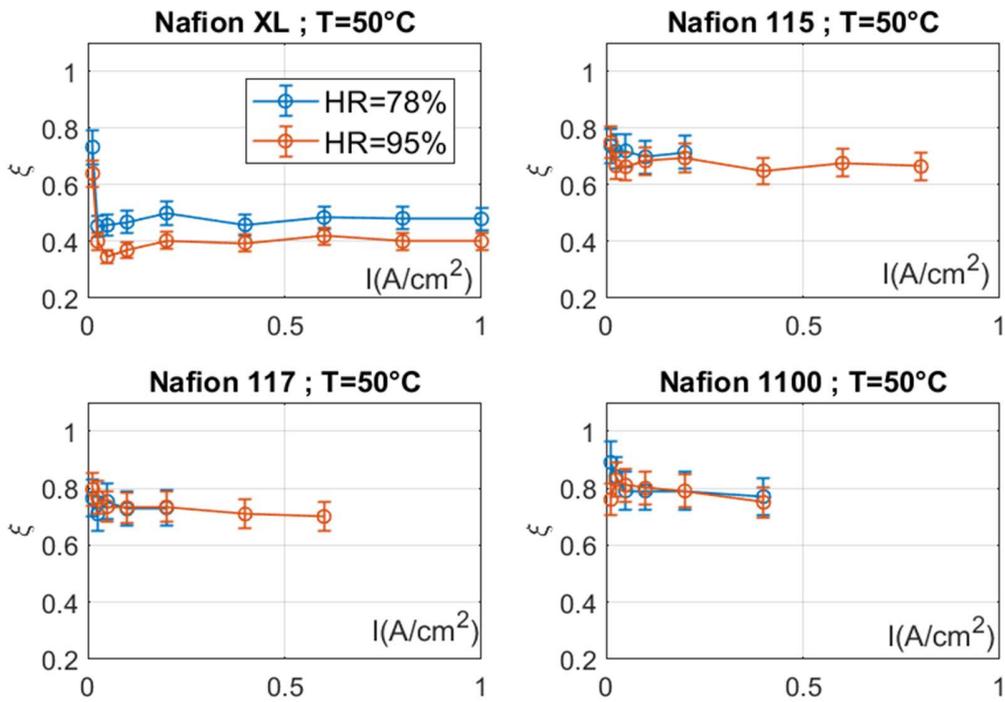


Figure 4,a : EOD coefficient for the 4 MEA as a function of the current density and two RH. $T=50^\circ C$

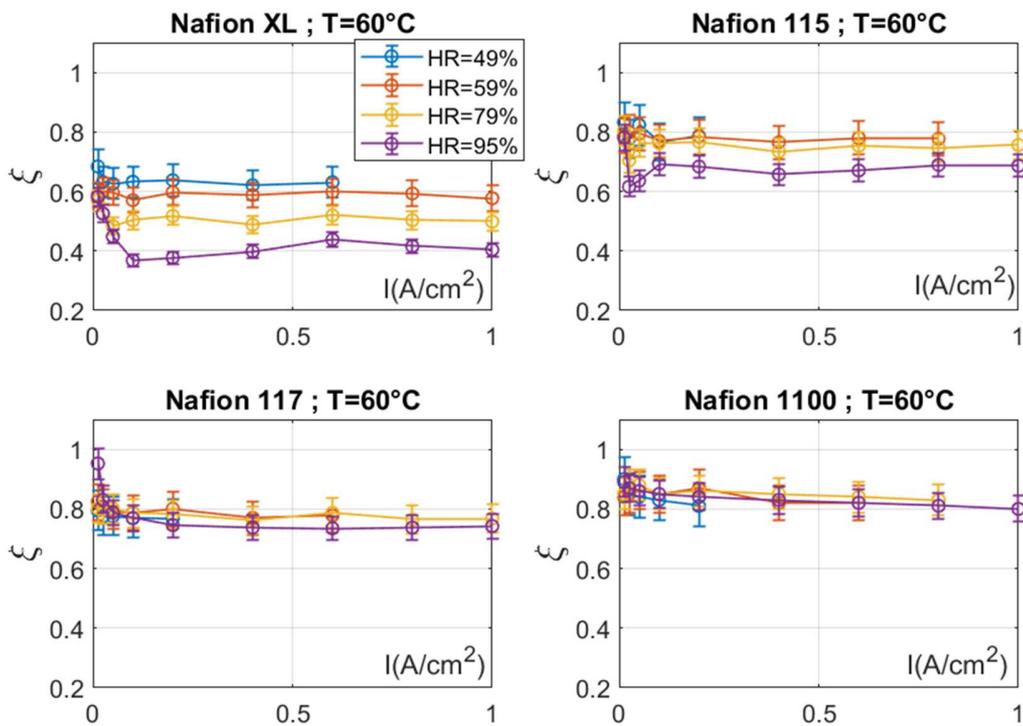


Figure 4,b : EOD coefficient for the 4 MEAs as a function of the current density and four RH. $T=60^\circ C$

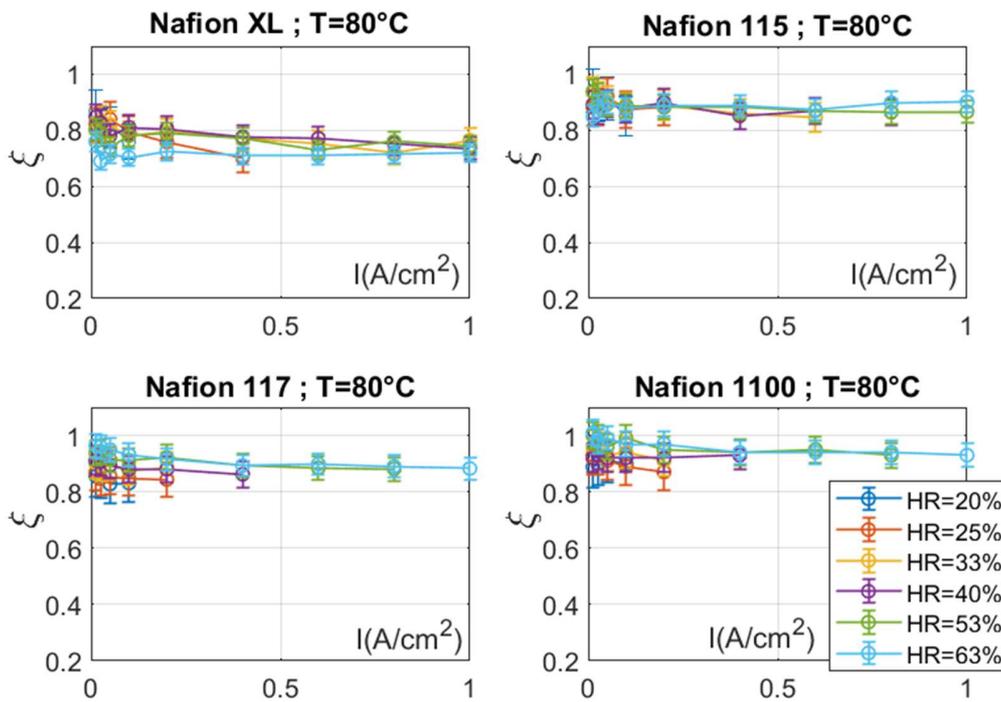


Figure 4,c : EOD coefficient for the 4 MEAs as a function of the current density and six different relative humidities. $T=80^{\circ}\text{C}$

General comments

All the EOD coefficients measured were smaller than one. Except at the low current densities (smaller than 0.1 A cm^{-2}), it appears that the EOD coefficient does not depend on the current density. Values obtained for pure Nafion™ membranes of different thicknesses were about the same even if they seemed to slightly increase with the membrane thickness. The smallest values were obtained for the XL membrane, which is a very thin membrane composed of Nafion™ polymer and an internal reinforcement. The uncertainties are in the order of $\pm 5\%$.

EOD variation with the temperature

For the pure Nafion™ membranes (115, 117 and 1100) the EOD coefficient does not depend on the RH but only on the temperature. In figure 5, the EOD coefficient is plotted as a function of the temperature for the Nafion™ 117 membrane. For the temperature range considered, the EOD coefficient seems to vary linearly with the temperature and it is lightly smaller at the higher current density although the respective confidence intervals overlapped.

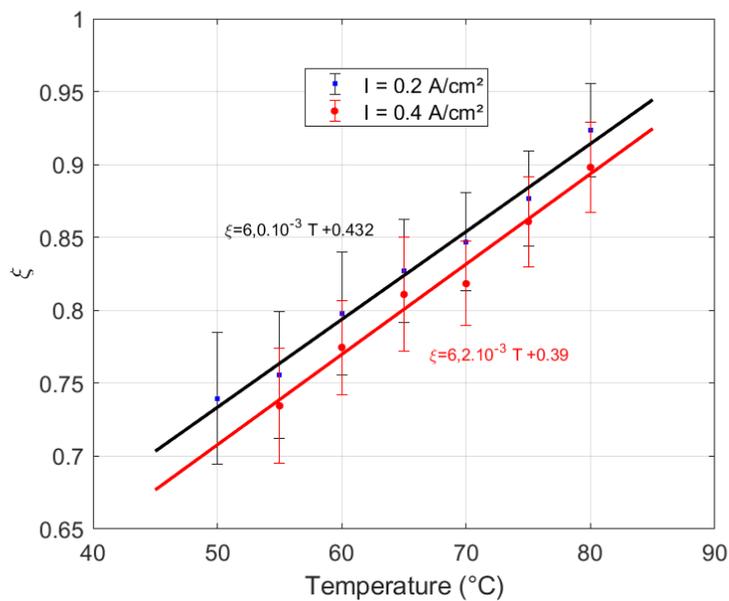


Figure 5 : EOD coefficient as a function of the temperature for a CCM with Nafion™ 117 and two current densities. $RH=70\%$.

Ge et al [8] observed a EOD coefficient varying with the temperature for a given water content, but as they consider that the water content of the membrane is a function of the RH and of the temperature, they concluded that at fixed RH the EOD coefficient did not depend on the temperature.

As reported by Kosuglu and Weber [4], the increase of the EOD coefficient with the temperature is commonly attributed to the presence of ions larger than H_3O^+ .

The behaviour of the XL membrane is singular. The same kind of sensitivity is observed with respect to the temperature but an additional variation appears with respect to the *RH* for the lowest temperatures (50°C & 60°C): the EOD coefficient decreases when the *RH* of hydrogen increases. This variation of the EOD coefficient as a function of the *RH* disappears for the highest temperature (80°C).

EOD variation with current density

Except at the low current densities, the EOD coefficient presented in *figure 4* does not depend on the current density. Variations at low current densities may be due to the uncertainties linked to the small water flow. The results of Peng et al. [5] presented the same independence from the current density. These results are in accordance with the idea that the EOD coefficient measured should be an intrinsic one.

EOD variation with *RH*

Without considering the results obtained at the lowest current density (because of the uncertainties) or with the heterogeneous Nafion™ XL based MEA, it appears that the *RH* has a small impact on the EOD coefficient. These results are clearly different from most of the results presented in the literature [4] which show an increase of the EOD coefficient with the water content of the membrane and therefore with the *RH* of the gas.

For the Nafion™ XL membrane at low temperature (50°C & 60°C) and to a lesser extent for Nafion™115 at 60°C, the unexpected results of Peng et al. [5] are confirmed: the EOD coefficient decreases as the water content of the membrane increases. Peng et al. [5] considered

these results consistent with the decrease of the concentration of protons within the hydrophilic domains of the membrane as the water content increases, and therefore with the decrease in the fraction of protons transported by the vehicular mechanism (hydronium transport) compared to the Grotthus or hydrogen bond breaking and forming mechanism. This is in agreement with the ab-initio calculations of Choe et al [13] that suggested that more water in the membrane increases hopping transport of protons which reduces the EOD coefficient. However, the exhaustive characterization of Nafion™ XL realized by Shi et al. [17] shows that the water uptake, the through plane conductivity as a function of the relative humidity, and the conductivity changes with the temperature of this membrane is very similar to Nafion™212. Therefore, the composite nature of the Nafion XL membrane seems not enough to explain the discrepancy with the other membranes tested. It is thus likely that this difference in behavior is due to the higher water content of the XL membrane that is produced by casting compared to other extruded membranes [18].

EOD variation with the electrode nature

Few studies were conducted with different membranes and different membrane-electrodes assemblies.

The results obtained for Nafion™117 with CCM and CCB electrodes are compared in *figure 6*. It can be concluded that the method used to build the electrode-membrane assembly has no detectable influence on the water transport by electro-osmosis using our set-up. Peng et al. [5] compared the EOD coefficient obtained for extruded Nafion™112 and Nafion™RE212 (50 μm) which was tested with commercial and homemade electrodes. They observed that the fabrication

process of the membrane, as the electrode structure have not influenced the determined EOD coefficient by means of their set-up.

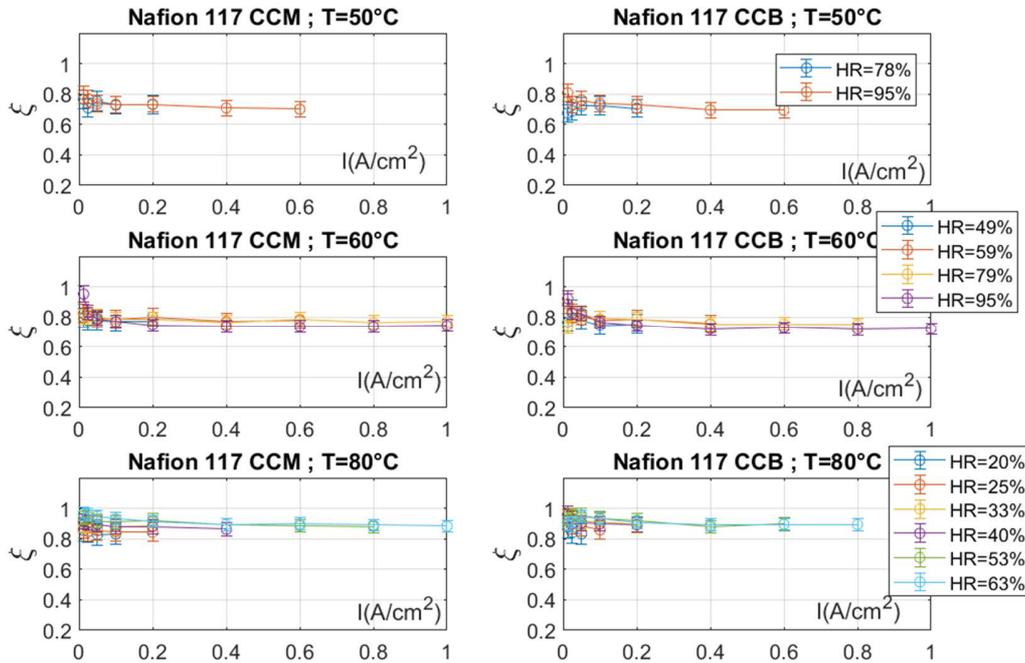


Figure 6 : influence of the electrode nature on the measurement. CCM at left and CCB at right

V. Conclusion

The system presented here was proven efficient in determining the net electro-osmotic drag coefficient under a large range of RH (20% - 95%), temperature (50-80°C) and current density up to 1 A cm⁻², relevant within the fuel cell context without requirement of a prior diffusion study. Its robustness is based on the fact that the observable is the absolute pressure. No water balance is achieved, eliminating errors due to uncertainty in flow rates and absolute humidities.

Pure Nafion™ membranes (115,117 & 1100) exhibit about the same behaviour: the EOD coefficients measured do not depend on the current density or on the RH but is an increasing function of temperature. Its value is always inferior to one for equilibrium with water vapour. The

behaviour of thinner Nafion™ XL membrane is singular. The associated EOD coefficient decreases with the RH as low as $\xi=0.4$ at 60°C, 95%RH. This singularity remains to be explained.

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