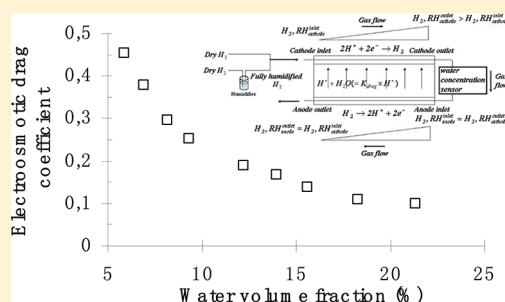


In-Situ Measurement of Electroosmotic Drag Coefficient in Nafion Membrane for the PEMFC

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S Supporting Information

ABSTRACT: A new method based on hydrogen pump has been developed to measure the electroosmotic drag coefficient in representative PEMFC operating conditions. It allows eliminating the back-flow of water which leads to some errors in the calculation of this coefficient with previously reported electrochemical methods. Measurements have been performed on 50 μm thick Nafion membranes both extruded and recast. Contrary to what has been described in most of previous published works, the electroosmotic drag coefficient decreases as the membrane water content increases. The same trend is observed for temperatures between 25 and 80 $^{\circ}\text{C}$. For the same membrane water content, the electroosmotic drag coefficient increases with temperature. In the same condition, there is no difference in drag coefficient for extruded Nafion N112 and recast Nafion NRE212. These results are discussed on the basis of the two commonly accepted proton transport mechanisms, namely, Grotthuss and vehicular.



1. INTRODUCTION

In proton exchange membrane fuel cell (PEMFC), protons are generated by oxidation of hydrogen at the anode. They pass through the polymer electrolyte membrane, and then, they react at the cathode taking part to the electrochemical reduction of oxygen which leads to water production. Thus, the membrane is the transport medium of protons, but it also acts as insulator and as gas separator. Nowadays, perfluorosulfonic acid (PFSA) membranes, such as Nafion from DuPont De Nemours, are the most commonly used in PEMFC. Indeed, they show excellent chemical stability and good mechanical properties, as well as high proton conductivity, when they are hydrated.^{1–3} Their proton conductivity and, as a consequence, fuel cell performance strongly increases with their water content. Thus, it is necessary to keep high membrane hydration level to obtain high performance.^{4,5} Therefore, membrane water content, often expressed in the average number of water molecules per sulfonic acid group $[\text{H}_2\text{O}]/[\text{SO}_3\text{H}] = \lambda$, is one of the most critical parameter in PEMFC.⁶

During PEMFC operation, the local membrane water content is fixed by the local water concentrations at the anode and at the cathode. They depend on the gas inlet flow, pressure and relative humidity, but also on the upstream water production as well as on the water repartition between the anode and the cathode. Moreover, this repartition is leaded by two opposite water flows. On one hand, the proton current through the membrane drags water molecules from the anode to the cathode. This phenomenon is known as electroosmosis. On the other hand, water is

produced at the cathode side and the resulting concentration gradient leads to a water flow from the cathode to the anode usually called back-flow. These two water flows must be managed; otherwise, either the drying of the anode or the flooding of the cathode can lower PEMFC performance and durability.

In summary, water management is a fundamental issue in PEMFC. The ultimate goal would be to keep homogeneous water profile through the membrane and a high hydration level thanks to an optimal control of working parameters. This requires a fine understanding of the water transport phenomena in proton exchange membrane. These phenomena are still under debate and, especially, the evolution of the value of the electroosmotic drag coefficient with temperature and membrane water content is not well-known.

The electroosmosis is quantified by the electroosmotic drag coefficient (K_{drag}), which is defined as the average number of water molecules per proton dragged through the membrane. The water flow across the membrane is only due to electroosmosis when there is only a gradient of proton chemical potential through the membrane and no gradient of water chemical potential. In the case when the chemical potential gradient of water is not null, it leads to a water flow which is added to the electroosmotic flow. This gives a net flow higher than the electroosmotic flow whether the gradient of water activity is

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opposite to the direction of protons and smaller in the opposite case. A water chemical potential gradient always exists during PEMFC operation because of water production of the cathode. So it is not possible to determine the electroosmotic drag coefficient during PEMFC operation.

In previous studies, the values of K_{drag} measured by different techniques are widely scattered.

Fuller and Newman have measured K_{drag} in cell with two compartments in which they control separately the concentration of aqueous solutions of LiCl.⁷ The two compartments are separated by a Nafion stripe. Thus, there is a gradient of water activity between the two extremities of the Nafion stripe. As a consequence, there is probably a water flow through the membrane due to water diffusion. K_{drag} was obtained from the measurement of the difference of electrostatic potentials between two platinum electrodes immersed in the two sealed compartments under H₂ atmosphere. Thus, no current pass through the two electrodes and, as a consequence, there is no net protons flow through the membrane. They found that K_{drag} is equal to about 1.4 for λ between 5 and 14, and K_{drag} drops to 0 for dry membrane. With the same technique, Zawodzinski et al. found a constant $K_{\text{drag}} = 1$ for $\lambda = 2-14$.⁸ The physical phenomena which are assessed with this method are rather different from those occurring when there is a flow of proton through the cell.

Meier and Eigenberger have measured the value of K_{drag} thanks to a technique that has been proposed by LaConti et al.^{9,10} The experimental device consists of two compartments separated by a Nafion membrane and containing both a 0.1 M HCl solution in which is immersed an electrode Ag/AgCl. A capillary is fixed on each compartment so as to determine the evolution of water volume when a fixed current density of $1.6 \text{ mA} \cdot \text{cm}^{-2}$ is imposed. They observed an increase of the level of water in the capillary at the cathode side and a decrease at the anode side. They ascribed this variation of volume to a water flow from one compartment to the other induced by a flow of protons, that is to say, by the electroosmosis. According to the authors, there is formation of gas bubbles on one electrode. Nevertheless, the cell voltage is not given. So, the electrochemical reactions which occurred are difficult to establish. Contrary to what the authors claim, the current may not only come from the proton flux. Although they also pretend to control the water content within the membrane, the way they proceed is not explained. This appears to be difficult since the membrane is in contact with an acid solution at fixed concentration, that is to say, with a fixed water activity. However, the amount of water in the membrane is directly dependent on water activity. K_{drag} increases from 1.3 to 6 for λ between 12 and 40. Finally, the value of 40 for λ is very high and difficult to achieve. The only way to reach such a value is to put the membrane in hot water avoiding any further drying by keeping it into water. According to Ise et al., LaConti et al. found a linear increase of K_{drag} from 0 in dry state to 4 or 5 in fully hydrated membrane.¹¹ No temperature dependence has been observed. For all reasons detailed above, the results remain questionable.

Ge et al. used a method based on hydrogen pump to measure the value of K_{drag} as a function of the temperature and of the relative humidity.¹² They found an increase of K_{drag} from 0.3 to 1.1 for an increase in λ from 2 to 12. Moreover, K_{drag} increases with temperature for λ higher than 4. In their setup, two flows of hydrogen were equilibrated at two different relative humidities and sent to each side of a Membrane Electrode Assembly (MEA) made of Nafion N117-CS membrane. So, a water concentration

gradient was imposed through the membrane. It leads to a flow of water in the same direction than the flow of proton imposed by the current. In this case, the water flow that crosses the membrane that was used to calculate the value of K_{drag} corresponds to the sum of electroosmotic flow and water diffusion flow. As a consequence, in this work, K_{drag} is overestimated.

Luo et al. also used the hydrogen pump to determine the value of K_{drag} as a function of water content at ambient temperature and for $\lambda \approx 22.5$ as a function of temperature.¹³ They found a linear increase in K_{drag} from 1.1 to 1.9 as the membrane water content increases from 11 to 18. For $\lambda \approx 22.5$, K_{drag} increases from 1.7 to 2.5 as the temperature increases from 20 to 80 °C. In the setup, a stripe of Nafion N117 is used to separate two compartments both containing water. One side of each extremity of the membrane is in contact with water of one compartment. An electrode is stuck on the opposite side and is in equilibrium with a dry hydrogen flux. The stripe is under stress between a gasket and a plate between the two compartments. A constant voltage of 1.2 V is applied between the two electrodes leading to a protons flow through the plane of the membrane stripe from one compartment to the other. The water molecules dragged by the protons flow lead to a modification of water volume in each compartment, which is measured thanks to capillaries. However, the values of current density and of hydrogen flux are not known. In each compartment, there is a flow of water through the membrane thickness from the side in contact with water to the side in contact with the flux of hydrogen. So, hydrogen is, at least, partially hydrated. The local relative humidity of each flux of hydrogen is not known and could be different from one compartment to the other if the two hydrogen flows are not the same. This would lead to a parasitic water flows. Anyway, all these flows are not taken into account in the calculations of K_{drag} . Moreover, the water content within the membrane stripe between the compartments is not known whereas the protons flow crosses this part. For all these reasons, the results are questionable.

For the first time, Ise et al. applied electrophoretic NMR to measure the value of the electroosmotic drag coefficient.¹¹ They found a value around 2.5 for K_{drag} for a fully hydrated membrane. In this setup, several membranes have been stacked together so as to have enough signal to measure K_{drag} . As the total thickness of the stack is important (around 8 mm), a high voltage between the two sides of the stack (up to 300 V) is necessary to obtain an appropriate current density. Such high voltage may lead to water electrolysis and other parasitic electrochemical reactions such as carbon corrosion. So, the current that is measured is probably not only due to the flow of protons. Finally, water electrolysis can induce a water concentration gradient through the stack leading to some uncertainty in the measurements.

In this work, we present a method based on hydrogen pump so as to measure the electroosmotic drag coefficient. This method allows avoiding water concentration gradients across the membrane thickness. Measurements are conducted on Nafion membrane in PEMFC single cell test and in representative operating conditions.

2. EXPERIMENTAL SECTION

2.1. Membrane Electrode Assembly (MEA) preparation.

The electroosmotic drag coefficient was measured in Nafion N112 and NRE212 (50 μm in thickness) from Dupont De Nemours. Their equivalent weight, corresponding to the weight of dry polymer

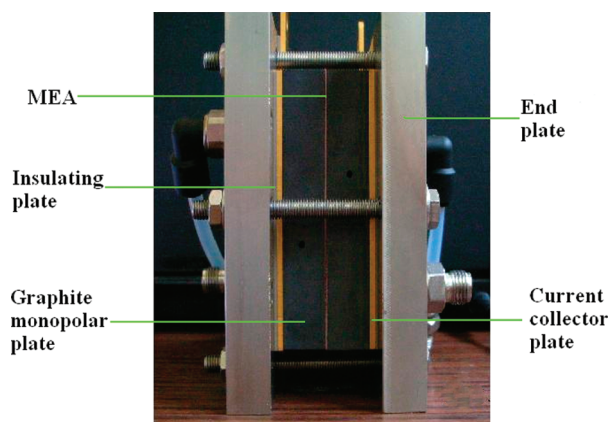


Figure 1. Picture of single test fixture used for electroosmotic drag coefficient measurement (same as for PEMFC tests).

required to neutralize an equivalent basis, is about $1100 \text{ g} \cdot \text{mol}^{-1}$. The membranes were used without any pretreatment. Membranes were hot-pressed at 3.5 MPa and 135°C during 210 s between two commercial electrodes (CE) E-LAT, LT 120 E-W SI (BASF fuel cell) to obtain a membrane electrodes assembly (MEA). The electrodes consisted in a gas diffusion layer (GDL) with a microporous layer, and a catalyst layer. Pt loading in the catalyst layer is around $0.5 \text{ mg} \cdot \text{cm}^{-2}$ according to the supplier. Another type of MEA has been made with Nafion NRE212 using homemade electrodes. Catalyst layer made with Tanaka 50 wt % Pt/C catalyst have been deposited onto each side of the membrane by decal process to obtain a catalyst coated membrane (CCM). Anode and cathode Pt loadings of the CCM were respectively of 0.28 and $0.26 \text{ mg} \cdot \text{cm}^{-2}$. A commercial GDL, SGL 25BA, has been stacked on each side of the CCM within the cell. This GDL consisted of a carbon fiber paper with 5 wt % of PTFE. There is no microporous layer. So, the structures (especially porosity) of the two electrodes (CE, LT 120 E-W SI and homemade CCM with SGL25BC) are very different. As a consequence, their water transport properties may differ strongly. CE (Commercial Electrode) and HM (Home-Made) will be used in the following for MEA made with CE electrodes and CCM, respectively.

2.2. Sorption Isotherms. Water content of membrane samples as a function of water activity or relative humidity (RH) was determined by gravimetric method using «Symmetrical Gravimetric Analyzer SGA-100» equipped with a microbalance and a dew point analyzer. All the samples are used without any pretreatment. Each sample was dried out during 240 min at 60°C under dry gases in the same chamber in which the sorption measurement was carried out. The weight change at the end of the protocol is lower than 0.001 wt % in 10 min. Once the drying process was done, the membrane weight was considered as the dry weight (weight corresponding to 0% RH), and then the sorption measurement started at a given temperature, from 5% RH to 95% RH, per step of 5%. Water content was determined for each RH until no weight evolution higher than 0.001% was observed over 10 min. Water content was determined from the weight difference between dry state and wet state. The membrane Nafion NRE212 has been used for the sorption isotherm measurements at 25°C .

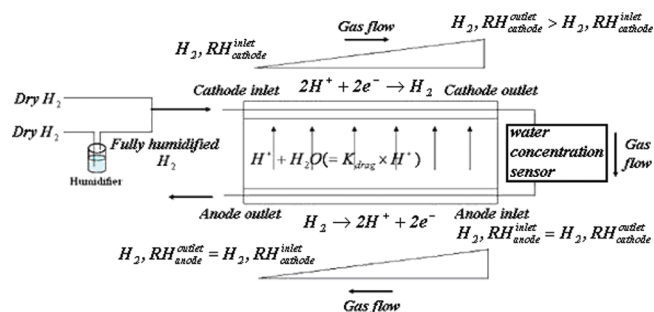


Figure 2. Schematic representation of the first hydrogen pump setup without water concentration gradient between each side of the membrane.

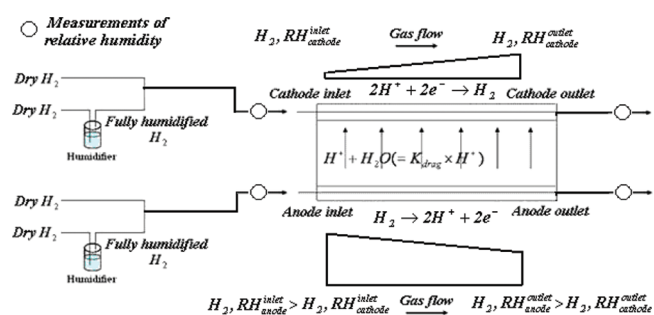


Figure 3. Schematic representation of the second hydrogen pump setup in coflow configuration with water concentration gradient between each side of the membrane.

2.3. Experimental Set-up. The measurements of the electroosmotic drag coefficient have been made in a PEMFC single cell test with an active area of 5 cm^2 . The cell consisted in a stack of end plate, electric insulating plate, current collector plate and graphite monopolar plate, on each side of the MEA, as shown in Figure 1. A single serpentine channel is machined on the monopolar plates. The rib and channel widths are respectively 0.8 and 1.4 mm.

The cell has been used in hydrogen pump mode. The cell is supplied with hydrogen and a relative humidity controlled by mixing a stream of dry hydrogen and a stream of humidified hydrogen. Current is fixed thanks to a potentiostat/galvanostat/impedance meter VSP associated with a 20 V/20A VMP2B booster (Bio-Logic SAS). At the anode, there is an oxidation of hydrogen to form protons which pass through the membrane which are then reduced at the cathode where they form hydrogen. The cathode outlet is directly connected to the anode inlet located on the opposite side of the MEA. As a consequence, the water concentration in the channel is the same on two opposite sides of the membrane in each point of the gas flow, as shown in Figure 2. Both sides of the MEA are in contact with a single gas flows. There is only one gas inlet and one gas outlet in the setup which are the cathode inlet and the anode outlet, respectively. This singular gas flow configuration has been chosen so as to minimize or avoid completely any water concentration gradient through membrane thickness.

At the cathode, the water concentration, and consequently the RH, increases from the inlet to the outlet where the molar water concentration in $\text{H}_2\text{O}/\text{H}_2$ mixture was measured under steady state (with and without current) thanks to a gas concentration sensor Piezocon (Lorex Industries, Inc.) (Figure 2). On the

Table 1. Example of Gas Inlets and Outlets Relative Humidities with and without Current during Measurements with the Second Method (With Gradient)

Nafion NRE212CE hydrogen flow ^a : 2000 N mL · min ⁻¹ stoichiometry = 2200					
<i>i</i> = 0				<i>i</i> = 26 mA · cm ⁻²	
anode inlet	cathode inlet	anode outlet	cathode outlet	anode outlet	cathode outlet
55.4%	42.1%	52.4%	45%	51.4%	46.1%

^a Total hydrogen flow.

contrary, the RH decreases from the anode inlet to the outlet. The water concentration accuracy of the sensor is $\pm 0.05\%$ of the measured value. Time resolution is lower than one second.

A second setup, also operated in hydrogen pump mode, has been used for checking the results obtained from the first method, as shown in Figure 3. In this configuration, two hydrated flows of hydrogen were sent to the cell in coflow configuration at two different RH (controlled by the same mixing gas system than the one used in the first method). The inlet RH has been chosen so as to keep higher relative humidity at the anode than at the cathode along the channel from the inlet to the outlet, and whatever the current density. Without current, there is a water flow from anode to cathode due to the gradient of relative humidity (Table 1). With current, the water flow induced by electroosmosis is added to the former water flow since it is in the same direction than the proton flow. In this method, it is sure that there is no back-flow of water because the electroosmotic flow is in the same direction than the water flow induced by the gradient of relative humidity. The two flows can be determined separately thanks to water balance with and without current as described above.

This method has already been reported in the literature.¹² Nevertheless, simple calculation of the amount of water that flows through the membrane, based on the experimental values of water diffusion coefficient in Nafion as a function of relative humidity available in the literature, show that the authors did not send enough water to keep a gradient between each side of the membrane. As a consequence, the values of the electroosmotic drag coefficient reported by Ge et al. are not reliable.

2.4. Method Description. 2.4.1. Principle

2.4.1.1. First Method. For the first method, the electroosmotic drag coefficient can be calculated from the values of water concentration with and without current.

Without current, it has been checked for a few values of RH that the water concentration $C^{i=0}$ was identical in the whole setup by measuring water concentration at the system inlet and outlet and also at the cathode outlet.

The inlet water flow $\phi_{\text{H}_2\text{O}}^{\text{inlet}}$ can be obtained by measuring the water concentration at the cathode outlet without current, knowing the inlet hydrogen flow ϕ_{H_2} :

$$C^{i=0} = \frac{\phi_{\text{H}_2\text{O}}^{\text{inlet}}}{\phi_{\text{H}_2\text{O}}^{\text{inlet}} + \phi_{\text{H}_2}} \Rightarrow \phi_{\text{H}_2\text{O}}^{\text{inlet}} = \frac{C^{i=0}}{1 - C^{i=0}} \times \phi_{\text{H}_2} = \phi_{\text{H}_2\text{O}}^{i=0} \quad (1)$$

All the concentrations are molar concentrations and flows are expressed in $\text{mol} \cdot \text{s}^{-1}$.

Once the $C^{i=0}$ is measured, current I (A) is applied and the water concentration at the cathode outlet increased due to the electroosmosis. When a steady state was reached, the value of $C^{i \neq 0}$ is constant and allows calculating the electroosmotic drag

coefficient as follows:

$$\begin{aligned} C^{i \neq 0} &= \frac{\phi_{\text{H}_2\text{O}}^{\text{inlet}} + \phi_{\text{drag}}}{\phi_{\text{H}_2\text{O}}^{\text{inlet}} + \phi_{\text{drag}} + \phi_{\text{H}_2} + \frac{I}{2 \times N_A \times e^-}} \\ \Rightarrow \phi_{\text{drag}} &= \frac{C^{i \neq 0}}{1 - C^{i \neq 0}} \times \left(\phi_{\text{H}_2} + \frac{I}{2 \times N_A \times e^-} \right) \\ - \phi_{\text{H}_2\text{O}}^{\text{inlet}} &= \phi_{\text{H}_2\text{O}}^{i \neq 0} - \phi_{\text{H}_2\text{O}}^{i=0} \quad (2) \end{aligned}$$

Where N_A and e^- are respectively the Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$) and the elementary charge ($1.6 \times 10^{-19} \text{ C}$), ϕ_{drag} is the electroosmotic flow in $\text{mol} \cdot \text{s}^{-1}$ and is equal to the water flow at the cathode outlet with $\phi_{\text{H}_2\text{O}}^{i \neq 0}$ and without current $\phi_{\text{H}_2\text{O}}^{i=0}$. The term $(I/(2 \times N_A \times e^-))$ comes from the hydrogen formation by the reduction of proton at cathode.

The electroosmotic drag coefficient can then be determined by

$$K_{\text{drag}} = \frac{\phi_{\text{drag}}}{\phi_{\text{protons}}} = \frac{\phi_{\text{drag}}}{\frac{I}{N_A \times e^-}} \quad (3)$$

2.4.1.2. Second Method. For the second method, the electroosmotic drag coefficient can be calculated from the measurements of relative humidity with and without current. Without current, the water concentrations have been measured at the anode and at the cathode inlets and outlets so as to determine the water flow. This water flow is considered to be a pure diffusive flow described by the Fick equation as the driving force is a concentration gradient of water. It will be called diffusive flow in the following. With current, electroosmotic flow is added to the water diffusive flow, and could be calculated by measuring the water concentration at anode/cathode outlet. Once the electroosmotic flow is obtained, the electroosmotic drag coefficient can be determined using eq 3. The detailed calculation of the diffusive flow and the electroosmotic flow is reported in the appendix.

2.4.2. Experimental Conditions. For each measurement, hydrogen stoichiometry is fixed and chosen to be between 275 to 2200. This means that the hydrogen flow is 275 to 2200 times more important than the one required for the electrochemical reaction. Such high stoichiometric ratio allows having a maximum RH difference lower than 10% between inlet and outlet at each electrode. On one hand, the hydrogen produced at the cathode or consumed at the anode represents a very small part of the total hydrogen flow. On the other hand, the amount of water dragged by electroosmosis is much lower than the inlet water flow.

Even if the variation of RH does not exceed 10% maximum, the membrane water content is not homogeneous in the setup from the inlet to the outlet. This induces incertitude on the value of λ which is taken into account in the results.

In this work, two ways of controlling these stoichiometric parameters have been used. In the first method, the hydrogen flow was kept constant at $500 \text{ N mL} \cdot \text{min}^{-1}$, and the current density was calculated to keep a given stoichiometry. It will be named “constant flow” in the following. In the second one, the hydrogen flow rate was adapted to have a given stoichiometry. It will be named “adjusted flow” in the following. The kind of method used will be specified in each case. The current density ranges between 20 and $100 \text{ mA} \cdot \text{cm}^{-2}$.

During the experiments, electrochemical impedance spectroscopy (EIS) measurements are performed with and without current thanks to the potentiostat/galvanostat/impedancemeter. EIS measurements have been performed between 100 kHz and 1 Hz with 10 points per decade after 4 periods of stabilization and values are averaged on 4 periods. The ohmic resistance of the MEA is ascribed to the modulus of the complex impedance at the higher frequency for which its imaginary part is zero. The system was considered to be equilibrated when this resistance did not evolve anymore. For each RH, the typical equilibrating time was between 1 h and 1 h 30 minutes. Two minutes are required to reach equilibrium after starting the protons pump.

The current was kept constant, and chosen so as to keep the voltage below 1 V to avoid other parasitic electrochemical reactions (as oxidation of Pt, water electrolysis, carbon corrosion). The cell temperature was controlled over the range from 25 to 80°C to obtain the electroosmotic drag coefficient at different temperatures. Nevertheless, as the gas lines are not warmed, the dew point of gases is limited to 25°C which corresponds to 7% RH at 80°C .

With the second experimental setup (with gradient), the relative humidity is measured using Rotronic HC2 sensor with an accuracy of 0.8% RH.

All the measurements have been carried out under atmospheric pressure at the system outlet. The pressure drop between system inlet and outlet has been measured. It does not exceed 20 mbars. Even if this value of pressure drop is low, it leads to a small and measurable difference in the RH for a fixed molar water concentration. This pressure drop has been taken into account into the calculation of the water molar concentration from the RH measurements in the second method. It has no impact for the first method as the Piezocon sensor measures directly the water molar concentration. The effect of such pressure on the measurement is negligible.

2.4.3. Limitations. In spite of all our efforts to reach a “perfect” configuration, the two methods have their own limitations which are described below.

2.4.3.1. First Method. The value of K_{drag} presents uncertainty that could not be exactly assessed since the method and the calculation are based on two main hypotheses.

First, there is no water concentration gradient across the membrane. This implies that there are no water transport limitations within the electrodes. Indeed, if the setup intrinsically induces that the relative humidity is the same within the channel at the two opposite sides of the MEA along the hydrogen flow, there could be a gradient between the channel and the membrane surface within the electrodes because of their limitations of water transport. As a consequence, there could be a water gradient between each side of the membrane which depends on the water

transport properties of the electrodes (depending on their porosity, thickness, and tortuosity) and on the value of the water flow between anode and cathode imposed by the current. It can be noticed that the water transport limitations within the electrodes can lead to water concentration gradients within their thickness but also within their plane, that is to say between the middle of the rib and the channel. This effect may be lowered thanks to convection induced by the pressure drop along the gas flow, especially for high values of hydrogen flow.

Second, the current density is homogeneous on the whole cell, either from the inlet to the outlet but also in front of the ribs and of the channels. The repartition of current density is governed by the difference in MEA local performance. Since there is a small difference of water concentration between the inlet and the outlet, there is also a small difference in membrane water content and hydrogen partial pressure, that is to say, in MEA resistance and in activation and transportation overpotentials. As a consequence, electrochemical performance of the proton pump may be different at the inlet and at the outlet of the setup. Since the kinetic of the hydrogen oxidation and proton reduction reactions are very fast and the maximum difference in hydrogen partial pressure within the cell is only 31,7 mbars (saturation water pressure at 25°C), the main contribution to overpotential is the ohmic drop. Considering that the cell voltage is the same on the whole surface of the MEA, the repartition of current density is not homogeneous at this scale. Moreover, current is collected by the rib. So, the path for electrons is longer when they are produced in front of the channel than in front of the rib. This could result in a small difference of local current density between the rib and the channel which mainly depends on the in-plane conductivity of the GDL.

To resume, the more the conditions are homogeneous within the whole setup the more accurate is the measurement. In spite of the efforts to lower the inhomogeneities by using a very small current density and a high gas stoichiometry associated with an extremely precise concentration sensor, there is necessarily a difference in water concentration between compartment inlet and outlet so as to be able to measure the flow of water. As written previously, this homogeneity is taken into account into the error in the membrane water content. Nevertheless, this could lead to very small difference in current density between setup inlet and outlet. Anyway, there may be some local differences in working conditions, especially between the rib and the channel, because of transport limitations (water, gas and electrons) within the electrodes. It is important to precise that these errors, if they can give rise to uncertainty in the value of K_{drag} , can not modify the dependence of K_{drag} as a function of water content and temperature.

2.4.3.2. Second Method. The second method is much more complicated to realize than the first one. Moreover, the hydration level of the membrane could not be determined with as much precision as in the first one because the relative humidity is different at the anode and at the cathode on two opposite sides of the membrane and in each point of the gas flow. Finally, in order to determine the electroosmotic flow it is necessary to know the diffusive flow induced by the concentration gradient of water when current flows through the cell. In our calculations, we assume that this flow is the same with and without current. It is obviously wrong. Indeed, the average water concentration gradient between anode and cathode is lower with current than without. As a consequence, the diffusive flow used for the calculation of the electroosmotic drag coefficient is

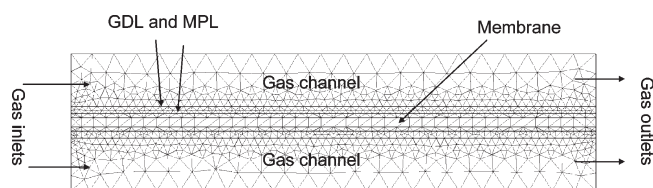


Figure 4. Simplified cell representation used for the simulations.

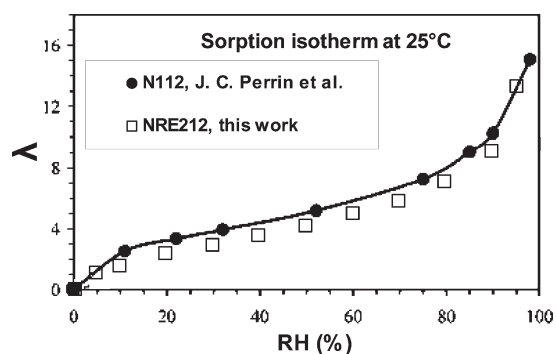


Figure 5. Comparison of sorption isotherms of Nafion NRE212 obtained in this work and Nafion N112 by J. C. Perrin et al.^{16,17}

overestimated. Thus, the value of the electroosmotic drag coefficient is underestimated. Nevertheless, this difference is probably negligible.

A way to overcome this limitation is to use a model in order to evaluate the diffusive flow. The model represents a simple 2D geometry (Figure 4) taking into account the cell channels, the GDL/MPL layers and the membrane. In a first step, the diffusion through GDL and MPL is supposed not to be a limitation to mass transport, compared to the diffusion within the membrane. The phenomena taken into account are Navier–Stokes fluid flows in the channels, Darcy–Brinkman fluid flow in the porous GDL and MPL, diffusion and electroosmosis in the membrane. The current density distribution along the channels is supposed to be uniform and the temperature is supposed to be constant. Boundary conditions are the fluid flows and composition (vapor content) at the channels inlets, and the pressures at the outlets.

The model was implemented in the Comsol Multiphysics simulation software coupled with Matlab. Two simulation steps are necessary to evaluate the electroosmotic drag coefficient. First, the diffusion coefficient in the membrane used in the model is fitted in order to obtain the same outlet relative humidity with the model that with the experiment at zero current. Then, this diffusion coefficient (but not the water diffusive flow!) is kept constant and the drag coefficient is fitted so that the computed outlet humidity matches the experimental value.

3. RESULTS AND DISCUSSION

3.1. Sorption Isotherms. Figure 5 shows the sorption isotherm of Nafion NRE212 at 25 °C. The membrane water content λ within the setup is calculated from this sorption curve at 25 °C whatever the temperature. For an average value of RH within the setup, the incertitude on RH, that is to say the difference in relative humidity between the cathode inlet and outlet, allows determining the error in λ from the sorption curves. The results obtained in this work are compared to the sorption isotherms on

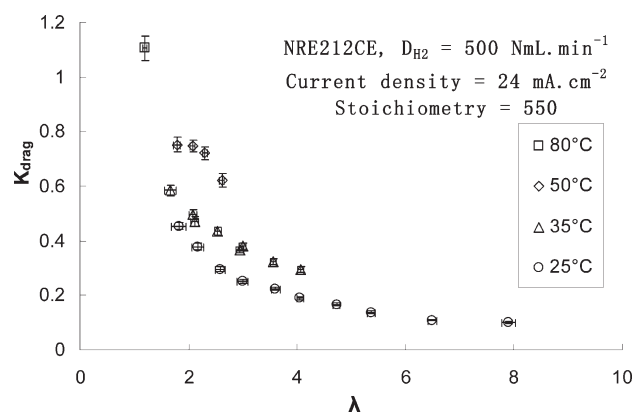


Figure 6. Electroosmotic drag coefficient in Nafion NRE212CE, as a function of water content λ at different temperatures, obtained with constant flow of 500 N mL \cdot min⁻¹ and stoichiometry rate of 550.

Nafion N112 obtained by J. C. Perrin et al. using Nuclear Magnetic Resonance (NMR) in Figure 5.^{16–18} The difference in water content is the same over the RH range. This could be explained by the fact that in this work, the λ at RH = 0% was considered to be equal to 0 which is certainly not true. So, an uncertainty related to the dry weight should be added to the values. The NMR has the main advantages to be a quantitative method allowing determining the exact number of protons (water molecules) within the polymer.

3.2. Electroosmotic Drag Coefficients. **3.2.1. Study of First Method Reliability on NRE212.** The electroosmotic drag coefficient of Nafion NRE212CE MEA decreases as the water content increases, whatever the temperature (Figure 6). These results have been obtained in constant flow and a gas stoichiometry of 550 that corresponds to a current density of 24 mA \cdot cm⁻². At 25 °C, K_{drag} varies from 0.45 for $\lambda \approx 1.8$ –0.1 for $\lambda \approx 7.9$. At 50 °C, K_{drag} varies from 0.74 for $\lambda \approx 1.8$ to 0.6 for $\lambda \approx 2.6$. This dependency with water content is contrary to the results obtained in the majority of the previous studies. In many of those studies, lower electroosmotic drag coefficient at lower hydration level was interpreted by the reduced mobility of water molecules and by the increased interaction between water and polymer, in a narrower hydrophilic channel of the Nafion structure. Nevertheless, according to modeling developed by Seeliger et al., the proton transport increases significantly with increasing humidity in aqueous pore structure of the Nafion membrane.¹⁴ In this work, the proton conduction mechanism is dominated by the Grotthuss structural diffusion mechanism, which describes the proton transport by breaking and formation of hydrogen bond, without net flow of water molecules. Otherwise, as described in the article of Dippel and Kreuer, the mobility of proton in Nafion, obtained from Nernst–Einstein relation and measurements of conductivity, is closely related to the self-diffusion coefficient of water at low degrees of hydration.¹⁵ This is explained by the transport of hydronium H₃O⁺, which is well-known as the vehicular mechanism of proton transport. This means that water molecules are transported by protons. The same authors using pulse field gradient NMR also show that the diffusion coefficient of protons is higher than the oxygen (water) diffusion coefficient in aqueous solution of HCl for concentrations between 2 and 8 mol \cdot L⁻¹. These values of concentration correspond to the proton concentration in the hydrophilic channel of Nafion for λ ranges between 5 and 17.

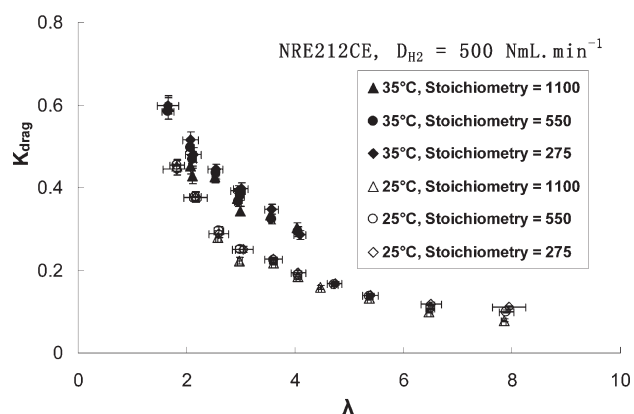


Figure 7. Comparison of electroosmotic drag coefficients in Nafion NRE212CE obtained with constant flow of 500 N mL·min⁻¹, for different stoichiometry 275, 550, and 1100 (with current densities of 48, 24, and 12 mA·cm⁻², respectively).

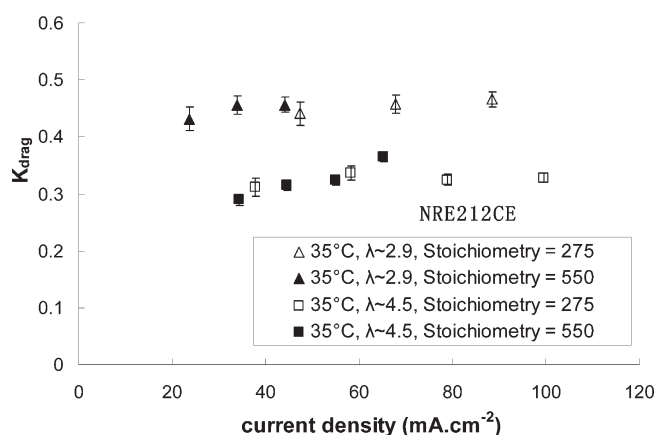


Figure 8. Electroosmotic drag coefficient in Nafion NRE212CE as a function of current density, obtained with adjusted flow, for two stoichiometries 275 and 550.

This difference increases as the concentration of proton in the aqueous phase decreases. In that case, this is an evidence of a purely diffusive process with mobile counterion. This means that proton transfer can occur without any movement of water. This corresponds to structural diffusion, for example Grotthuss mechanism.¹⁵ Thus, this result is interpreted as an increase of the Grotthuss transport mechanism to the detriment of the vehicular mechanism when the proton concentration decreases. This explains the high proton conductivity of aqueous acid solutions in comparison with the hydraulic limitations.

In our case, we measure a net flow of water associated with protons. Our hypothesis is that there is a statistical balance (in number and time) between the two previously cited proton transport phenomena within the membrane as in aqueous solutions. One in which the protons “jump” from one water molecule to the other by hydrogen bond breaking and forming (Grotthuss mechanism) and another in which the protons move with only one water molecule (vehicular mechanism). In that sense, only the second mechanism leads to a net flow of water and not the first one. We consider that the Grotthuss mechanism is diffusive. In our experiment, we measure the net flow of water.

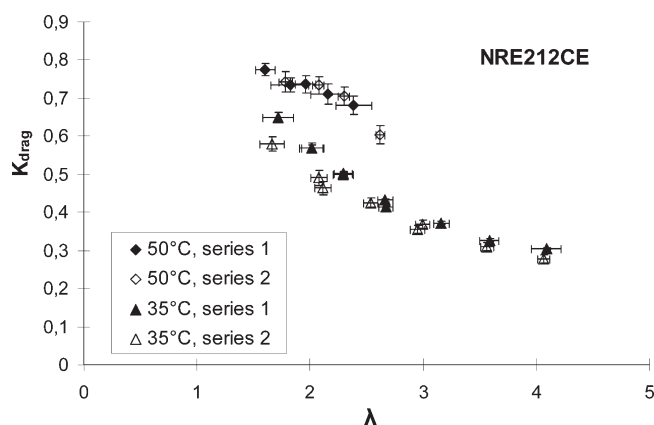


Figure 9. Comparison of electroosmotic drag coefficients in Nafion NRE212 as a function of water content λ , obtained in two series of measurement on the same NRE212CE MEA. H₂ flow rate and the current density so as the stoichiometry rate have not been fixed in these measurements.

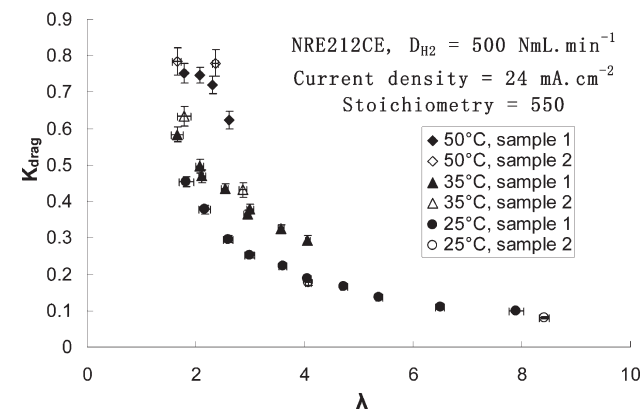


Figure 10. Comparison of electroosmotic drag coefficients in Nafion NRE212 as a function of water content λ , obtained in two series of measurement on two different NRE212CE MEA. H₂ flow rate and the current density have been fixed at 500 N mL·min⁻¹ and 24 mA·cm⁻² with the corresponding stoichiometry rate of 550.

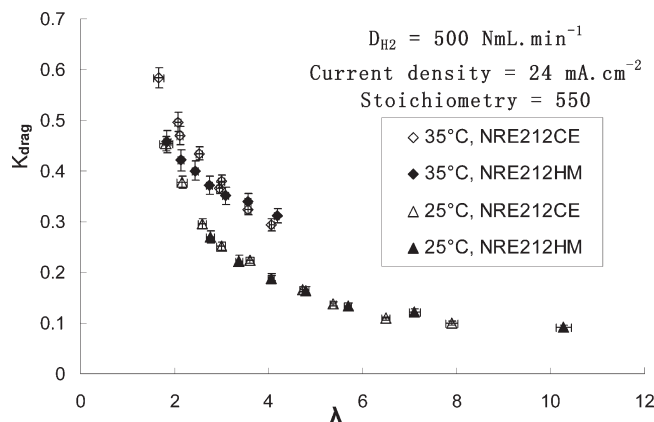


Figure 11. Comparison of electroosmotic drag coefficients in NRE212CE and NRE212HM using the electrodes developed in this laboratory, at 25 and 50 °C, as a function of water content.

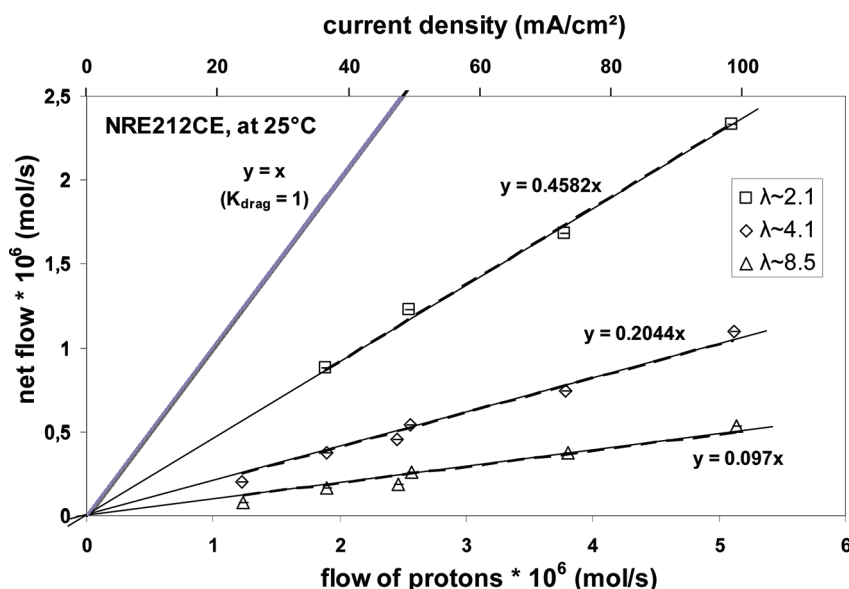


Figure 12. Net flow as a function of current density in Nafion NRE212CE membrane at 25 °C. the points have been obtained with adjusted H₂ flow, for two stoichiometry rates 275 and 550.

Table 2. Details of the Measurements and Calculations Performed Using the Second Method

Nafion NRE212CE hydrogen flow = 2000 N mL · min ⁻¹ ; active surface of electrode = 5 cm ²													
<i>i</i> = 0							<i>i</i> ≠ 0						
RH anode inlet %	RH anode outlet %	RH cathode inlet %	RH cathode outlet %	average lambda	diffusive water flow (×10 ⁶) mol · s ⁻¹	diffusion coefficient (×10 ⁶) cm ² · s ⁻¹	current density mA	RH anode outlet %	RH cathode outlet %	net flow (×10 ⁶) mol · s ⁻¹	electroosmotic flow (×10 ⁷) mol · s ⁻¹	<i>K</i> _{drag}	
28.0	25.3	14.2	16.8	2.1	1.27	1.36	129	24.3	17.8	1.78	5.13	0.38	
34.8	32.1	21.4	24.3	2.5	1.35	1.60	257	30.2	25.8	2.19	8.36	0.31	
41.6	38.7	28.5	31.4	2.8	1.42	1.61	257	37.2	32.8	2.12	7.05	0.26	
48.3	45.4	35.2	38.1	3.2	1.42	1.49	257	44.2	39.2	1.99	5.65	0.21	
55.4	52.4	42.1	45	3.7	1.46	1.48	257	51.4	46.1	1.99	5.30	0.20	
62.3	59.3	49.5	52.7	4.2	1.53	1.63	515	57.4	54.3	2.45	9.17	0.17	
81.0	76.6	64.1	68.2	5.4	2.13	1.33	515	75.7	69.5	2.74	6.08	0.11	
91.6	86.8	72.6	77.3	6.6	2.38	0.85	515	85.7	78.2	2.96	5.76	0.11	

That is to say, we measure only the second mechanism. We measure that the contribution of this mechanism to the net flow decreases as the increasing membrane water content (or as the concentration of protons within the hydrophilic domains of the ionomer decreases). According to us, this is consistent with the measurements made in aqueous solutions of acids. This trend may be explained by the decrease of interactions between charged species as the proton concentration decreases. The energy of the hydrogen bonds may decrease with the proton concentration. So, it is easier to break and form them which is in favor of the Grotthius mechanism. However, in aqueous solutions anion are mobile whereas they are fixed in ionomer. We consider that it does not change the proton conducting mechanisms but their balance. The effect of proton concentration may be accentuated in ionomers by the confinement within the hydrolytic domains.

For a given water content, *K*_{drag} increases with temperature (Figure 6). This result is consistent with all the studies previously

published and corresponds to an increasing contribution of the vehicular mechanism.

The effect of stoichiometry has also been studied by fixing the hydrogen flow at 500 N mL · min⁻¹. No significant difference has been observed by applying three different current densities (48, 24, and 12 mA · cm⁻²) for three different stoichiometric rates (275, 550, and 1100) (Figure 7).

As it can be seen on Figure 8, the values calculated for *K*_{drag} does not seem to depend on gas stoichiometry or on current density with our setup. This result is in accordance with negligible transport limitation within the electrodes.

The measurements have been repeated twice on the same MEA NRE212CE at 35 and 50 °C only. No significant difference is observed between the two series of results (Figure 9). Neither the hydrogen flow rate, nor the current density have been fixed in these measurements so as the stoichiometry rate is not constant. To check if we can obtain repeatable results, another series has been done with the same MEA structure but changing the sample.

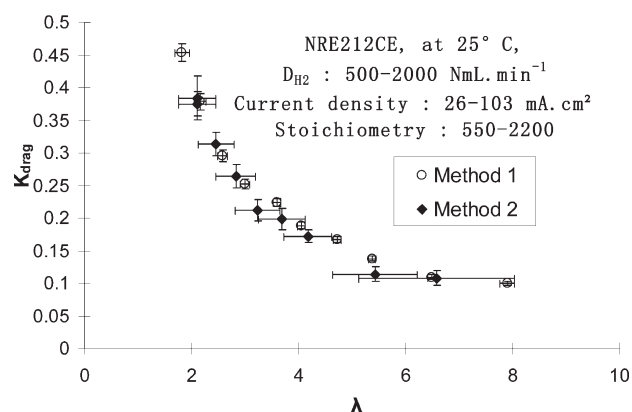


Figure 13. Comparison of electroosmotic drag coefficients obtained by using the two methods: method 1 with direct jet of gas flow from cathode outlet to anode inlet; method 2 with imposed water gradient through the membrane.

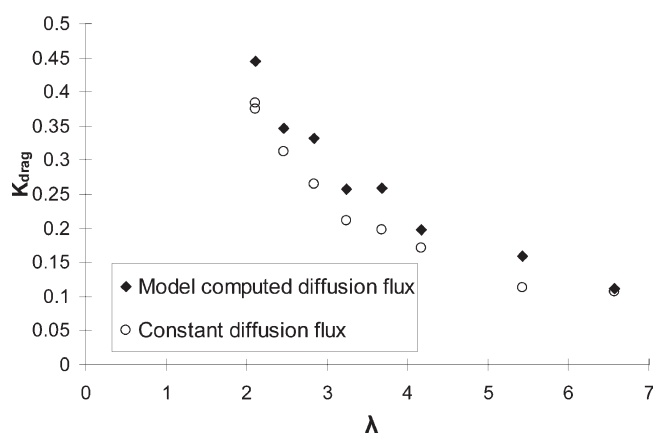


Figure 14. Comparison of results obtained at 25 °C using the model supposing a constant diffusion flux and when computing the diffusion flux.

As shown in Figure 10, the results are quite similar with the two samples. These measurements in Figure 10 have been done with hydrogen flow rate and current density fixed at 500 N mL · min⁻¹ and 24 mA · cm⁻², respectively, which corresponds to a stoichiometry of 550. So our measurements appear to be both reproducible and repeatable.

To check if the water transport limitations in the electrode could have any impact onto the calculated values of K_{drag} , measurements have been performed with the same membrane NRE212 but with two different electrodes (NRE212CE and NRE212HM). In these measurements, the hydrogen flow rate and the current density have been fixed at 500 N mL · min⁻¹ and 24 mA · cm⁻², respectively, which correspond to a stoichiometry of 550. As shown in Figure 11, there is no difference in K_{drag} with the two samples, at 35 and 50 °C. So, two very different electrode structures, with probably very different transport properties, give the same values for K_{drag} . This is, for us, another evidence of the reliability of our results.

If there is a water concentration gradient across the membrane because of transport limitations within the electrodes, there would be a back-flow in the opposite direction of the protons flow. As a consequence, the flow measured in our experience would be a net flow (ϕ_{net}) corresponding to the

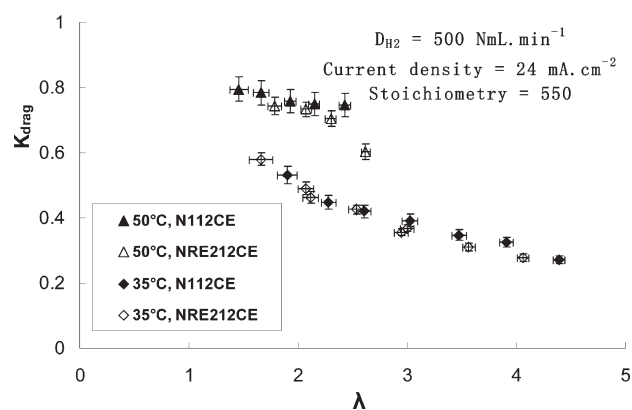


Figure 15. Comparison of electroosmotic drag coefficients in Nafion N112CE and Nafion NRE212CE, at 35 and 50 °C, as a function of water content λ .

sum of the electroosmotic flow (ϕ_{drag}) and the back flow, ($\phi_{\text{back-flow}}$) described as follows:

$$\phi_{\text{net}} = \phi_{\text{drag}} - \phi_{\text{back-flow}} = \frac{i \times S \times K_{\text{drag}}}{1000 \times F} - D_{\text{diff}} \times S \times \Delta C_W \quad (8)$$

Flows are expressed (mol · s⁻¹); i is current density in (mA · cm⁻²), S is the active surface of MEA (cm²); ΔC_W is water concentration gradient between anode and cathode (mol · cm⁻⁴).

For given working conditions (temperature and RH), the net water flow is the sum of the electroosmotic flow, which is proportional to the current, and the back-flow, which has no fundamental reasons to be linear with current.

As shown in Figure 12, the net water flow is proportional to current density. This is difficult to understand if the back flow is non negligible as described with eq 8. This means that the values of the slope correspond to K_{drag} measured in each point. Moreover, extrapolation to 0 A leads to a value of zero for K_{drag} .

3.2.2. Comparison between First and Second Methods. As described in the Experimental Section, a second method has been used to check the results obtained by the first method. With the second method, it is highly unlikely to have a back-flow. The gradient of relative humidity between the two compartments is in the same direction with and without current (Table 2). It leads to a water flow in the same direction than the electroosmotic flow. As shown in Figure 13, only a slight difference was observed between the two methods. The second one gives values for the electroosmotic drag coefficient only slightly smaller than with the first one. This is evidence of the reliability of the first method without any errors due to the back flow.

The electroosmotic drag coefficient calculated by using the model, instead of supposing the water flux due to the gradient of RH is constant, gives very close results (Figure 14). As expected, the electroosmotic drag coefficient is underestimated considering the constant diffusion flux but the overall trend is the same. Moreover, the values taking into account the real diffusion flux are closer to those obtained with the first method. Again, this confirms its validity.

3.2.3. K_{drag} on N112 Membrane. To check if the membrane fabrication process can modify water transport properties of Nafion, the extruded N112 membrane (50 μm in thickness) was compared to NRE212. As shown in Figure 15, there is no

difference in K_{drag} for N112 and NRE212. This means that the fabrication method does not influence the electroosmotic drag coefficient.

4. CONCLUSIONS

A new method based on hydrogen pump was developed to determinate the electroosmotic drag coefficient in Nafion proton conducting membranes. The influence of their water content has been studied for temperatures ranging between 25 and 80 °C. This method allows avoiding any parasitic water concentration gradient across the membrane thickness that would lead to errors on the values of this coefficient. Lot of attention has been paid to check the reproducibility and the reliability of the method.

The electroosmotic drag coefficient decreases with increasing membrane water content. This result is opposite to what is commonly accepted for proton conducting membranes. Reproducibility and repeatability of the method has been checked. Moreover, neither gas flows, nor current density, nor electrode structure, nor the type of Nafion membrane, have an influence of the calculated value of K_{drag} . All these results are for us strong evidence of the reliability of our method.

The results are consistent with the structural model of this perfluorosulfonic acid ionomer membrane (PFSA) with separation between hydrophilic and hydrophobic domains at the nanometre scale. The hydrophilic domains become larger and more continuous when the water content increases with water activity. This favors the Grotthus proton conducting mechanism (without net water molecules) detriment to the vehicular mechanism. This is also in accordance with the evolution of proton transport properties in acids solutions as a function of their concentration even if, in that case, the counterion is mobile in the liquid electrolyte. For a given water content, K_{drag} increases with temperature which is in accordance with all the previous works that have been published.

The setup will be adapted to make measurements up to 95% RH for temperature as high as 120 °C. Then measurements will be performed on the 25 μm thick NRE211 and the 125 μm thick N115 Nafion membranes so as to compare the results with those obtained on NRE212. The goal is to determine in which extent the water back-flow can be neglected. After checking these points, the study will be performed on other PFSA membranes such as Aquivion from Solvay Solexis and on hydrocarbon membranes, such as sulfonated PEEK.

■ ASSOCIATED CONTENT

S Supporting Information. Details on model description and the calculations, especially calculations of the incertitude. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) LaConti, A.B.; Hamdan, M.; McDonald, R.C. In *Handbook of Fuel Cells—Fundamentals, Technology and Applications*; Vielstich, W., Lamm, A., Gasteiger, H., Ed.; Wiley: Chichester, U.K., 2003; Vol. 3, Chapter 49.
- (2) Sethuraman, V. A.; Weidner, J. W.; Haug, A. T.; Protsailo, L. V. *J. Electrochem. Soc.* **2008**, *155*, B119.
- (3) Yoshitake, M.; Watakabe, A. *Adv. Polym. Sci.* **2008**, *215*, 127.
- (4) Banerjee, S.; Curtin, D. E. *J. Fluorine Chem.* **2004**, *125*, 1211.
- (5) Heitner-Wirguin, C. *J. Membr. Sci.* **1996**, *120*, 1.
- (6) Springer, T. E.; Zawodzinski, T. A.; Gottesfeld, S. *J. Electrochem. Soc.* **1991**, *138*, 2334.
- (7) Th., F.; Fuller, Newman, J. *J. Electroanal. Soc.* **1992**, *139*, 1332.
- (8) Zawodzinski, T. A.; Davey, J.; Valerion, J.; Gottesfeld, S. *Electrochim. Acta* **1995**, *40*, 297.
- (9) LaConti, A.B.; Fragala, A.R.; Boyack, J. R. *Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage*; McIntyre, J.D.E., Srinivasan, S., Will, F.G., Eds.; PV 77–6, The Electrochemical Society Softbound Proceedings Series; The Electrochemical Society: Princeton, NJ, 1977.
- (10) Meier, F.; Eigenberger, G. *Electrochim. Acta* **2004**, *49*, 1731.
- (11) Ise, M.; Kreuer, K. D.; Maier, J. *Solid State Ionics* **1999**, *125*, 213.
- (12) Ge, S.; Yi, B.; Ming, P. *J. Electroanal. Soc.* **2006**, *153*, A1443.
- (13) Luo, Z.; Chang, Z.; Zhang, Y.; Liu, Z.; Li, J. *Int. J. Hydrogen Energy* **2010**, *35*, 3120.
- (14) Seeliger, D.; Hartnig, C.; Spohr, E. *Electrochim. Acta* **2005**, *50*, 4234.
- (15) Dippel, T.; Kreuer, K. D. *Solid State Ionics* **1991**, *46*, 3.
- (16) Perrin, J. C.; Lyonard, S.; Guillermo, A.; Levitz, P. *J. Phys. Chem. B* **2006**, *110*, 5439.
- (17) Perrin, J. C.; , Ph. D Thesis, Université Joseph Fourier, Grenoble, <http://tel.archives-ouvertes.fr/tel-00115418/en>, 2006.
- (18) Guillermo, A.; Gebel, G.; Mendil-Jakani, H.; Pinton, E. *J. Phys. Chem. B* **2009**, *113*, 6710.