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Study of Electro-osmotic Drag Coefficients in Nafion Membrane in Acid, Sodium and Potassium Forms by Electrophoresis NMR

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Abstract

The water electro-osmotic drag coefficient of a cation _ K_{drag}(cation)_ is defined as the number of water molecules which is dragged by a cation when it goes through a membrane at equilibrium state (i.e. in the absence of water concentration gradient within membrane). This coefficient is one of the key elements for modeling the water balance through Nafion membrane in a proton Exchange membrane Fuel cell (PEMFC). In this work, we have applied the method of electrophoresis NMR (ENMR) to determine the coefficient of electro-osmotic drag (K_{drag}) within Nafion prepared in different cationic forms (H^+, Na^+ and K^+). Applying, in all cases, the same method for determining K_{drag} of Nafion membrane in many cationic forms should be appropriate in order to apprehend the mechanisms of water transport which occur in this membrane. This method consists in measuring the phase of the water NMR signal under the application of an electric current in a diffusion-like experiment, this phase being proportional to the flux of water within Nafion. The results show that the electro-osmotic coefficients of water within Nafion depend on the type of counter-cation and on the water content of Nafion. Due to proton lability, the electro-osmotic drag coefficient of water within Nafion in the acid form ($K_{drag}(H^+)$) is the lowest among the three studied cationic forms. In a dehydrated state of Nafion, the $K_{drag}(H^+)$ is lower than 1, suggesting here that the hopping mechanism is favored. In the case of Nafion in sodium and potassium forms, K_{drag} of these cations is always higher than 1. This can be rationalized by the vehicular mechanism and also by a strong interaction between the water solvation of the cation and the cation itself.

Keywords: Nafion, electro-osmosis, K_{drag}, Electrophoresis NMR, counter-cations

1. Introduction

Nafion is a perfluoronated polymer containing a certain amount of sulfonated groups. This feature confers to Nafion some particular properties such as a good ionic conductivity when hydrated. Until now, Nafion membrane is widely applied in many processes such as in electrodialysis for demineralization purpose or in Proton Exchange Membrane Fuel Cell (PEMFC) for energy production [1-4]. For this latter application, Nafion membrane has to be maintained at sufficient water content for ensuring a good protonic conductivity, since the fuel cell performance depends on the hydration level of the membrane. It is well-known that a PEMFC is an electrochemical cell which consumes hydrogen at the anode and oxygen at the cathode to produce both electrical energy and water in gas and/or liquid form at the cathode side. The water produced at the cathode can diffuse through Nafion membrane to the anode due to the water gradient between the two electrodes. On the other hand, protons generated at the anode can drag an amount of water when they go through the Nafion membrane by electro-osmosis. The balance between these two opposite fluxes constitutes the hydration level within a Nafion membrane. Thus, a good water management in a PEMFC is essential to extend the durability of the electrochemical cell. For that, we have to apprehend the water behavior in a running fuel cell. One of the options is to model the two main transport phenomena which are diffusion and electro-osmosis. As both phenomena are coupled, a model can be devised provided that reliable data are available for each phenomenon.

Indeed, Nafion is the most studied membrane in literature due to its particular structure and its good protonic conductivity [5-7]. Consequently, there is a myriad of data about Nafion. However due to the scattering of literature data, it appears difficult to achieve an appropriate choice. In the case of electro-osmosis for instance, there is a lot of methods leading to the measurement of the water electro-osmotic drag coefficient of Nafion membrane in the acid form. Among all available methods in the literature [8], we can mention (i) the electro-osmotic drag cell, (ii) the radiotracer drag cell, (iii) hydrogen pump, (iv) activity gradient and (v) electrophoresis NMR (ENMR).

The electro-osmotic drag cell is a cell which is composed of two compartments separated by a membrane. Each compartment is filled with an appropriate electrolyte. A current is applied between the two compartments thus generating ion fluxes. As ions are hydrated, they cross the membrane with their hydration water molecules. This is an electro-osmotic flux. By measuring the change of volume in each compartment, it is possible to calculate an electro-osmotic flux and also a coefficient of electro-osmotic drag. The method of radiotracer is similar. Instead of measuring a change of volume, it is the amount of isotopic species which determines the electro-osmotic flux. Concerning hydrogen pump, as its name indicates, protons are generated at the anode by reducing hydrogen and they are consumed at the cathode after they have crossed the membrane. By contrast to (i) and (ii), this method works in the gas phase and it is supposed to simulate an operating PEMFC. Consequently, the coefficients of electro-osmotic drag obtained with method (i) and (ii) are higher than with (iii). Indeed, Zadwozinski et al. applied method (i) for measuring the electro-osmotic drag coefficients within a Nafion in acid form [9]. They reported that K_{drag} varies between 2.0 and 2.9. Applying a similar method, Pivovar and al. [10] found K_{drag} coefficients greater than 3 for Nafion membrane in acid form. Using a radiotracer method, Verbrugge et al. [11] reported that the electro-osmotic drag coefficient of Nafion in the acid form depends on sulfuric acid concentration and varies between 3

and 8. Applying the hydrogen pump technique, K_{drag} is found in the range 0.1 to 0.8 [12-13]. However at higher water contents, Luo et al. [14] reported K_{drag} values from 1.2 to 2 for Nafion® 117. Thus it appears illusory to rely on literature results for modeling purpose. Other disadvantages are the influence of the experimenter and the electrolyte concentration at which the experiments are performed. Moreover, those methods, which use an electrolyte as a medium for ionic conductivity, are not immune to other phenomena, such as diffusion or osmosis, which may occur during the measurement.

In this work, we focus on the determination of the electro-osmotic drag coefficients within a Nafion membrane. As the electro-osmotic drag coefficient is defined as the number of water molecules which move with an ion in the absence of any concentration gradient, we have turned to the ENMR (Electrophoresis Nuclear Magnetic Resonance) method for the following reasons. Firstly, ^{1}H NMR is a good tool for characterizing water content within a Nafion membrane because of the fluorinated backbone of the latter. Thus, the only signal we can measure comes from the water molecules that hydrate the sulfonated sites (SO_3^-) and protons if Nafion is in acid form. Secondly, this method does not use an electrolyte solution like methods (i) and (ii). Thirdly, the measurement is very fast in comparison with the time required for the preparation of samples. Therefore, we can safely assume the absence of any concentration gradient in the course of NMR measurement.

Although this method was already applied to measure the electro-osmotic drag coefficients of Nafion in acid form [15], we have extended it to study other cationic forms of Nafion such as sodium and potassium forms of Nafion. By studying these cationic forms of Nafion, we can distinguish the influence of each mechanism on the water transport within the Nafion membrane. Indeed, it is well-known that proton can be transported by two different mechanisms: (i) vehicular mechanism by sulfonated sites and (ii) by hopping via water molecules (Grotthuss mechanism) [16]. Contrary to the proton cation, the other cations cannot be transported via hopping mechanism, since they cannot make inter/intra bonds with water molecules. Moreover, the comparison of electro-osmotic drag coefficients of Nafion in different cationic forms obtained with the same method should be more relevant than with different experimental methods. Furthermore, we present in this work the adaptation of the ENMR method to a powerful wide-bore 600 MHz NMR spectrometer possessing spectroscopy and imaging facilities. This equipment allowed us to deal, among other things, with relatively large samples and thus to have a better control of the water content within Nafion membrane. The details of this method as well as the preparation of samples are described below.

2. Experimental section

2.1 Materials

Nafion® 117 was purchased from Ion Power. The chemical products such as the acids (HCl 37%, HNO_3 65%, H_2SO_4 98%), the salts with a purity >98% (Na_2SO_4 and K_2SO_4) and peroxide water (33%) were purchased from Sigma-Aldrich. Gas Diffusion Electrode sheets (GDE) from Baltic Fuel Cells were used as received. They were loaded with 1 mg Pt.cm^{-2} and were hydrophobic at 5%.

2.2 Membrane samples in H^+, Na^+ and K^+ forms: cleaning and conditioning

In this study, we have to deal with membranes having different amount of water content expressed by λ (the number of H_2O per number of SO_3^-). Knowing the shrinking issue of Nafion membrane according to water content, we prepared membrane samples with 3 different diameters: 15, 16 and 17 mm. We could then choose the diameter of samples according to the required hydration of samples, our aim being to prepare samples with the same diameter whatever membrane water content. The 3 different diameters of samples were obtained using a piece cutter set.

All samples were cleaned and prepared in acid form before being exchanged in other cationic forms. The samples in acid form were obtained following the protocol described in a previous paper [17]. The sodium and potassium forms of Nafion were obtained by cation exchange with samples in acid form. We used Na_2SO_4 and K_2SO_4 solutions at 0.05 M in this study. The cationic exchange step consists in immersing samples in an appropriate solution containing the required cationic form. To make sure that the exchange step has properly taken place, we repeated the cation exchange step at least 5 times with an interval of 12 hours at each bath. Before being used, Nafion samples prepared both in different cationic forms (H^+, Na^+ and K^+) and in different diameter sizes (15, 16 and 17 mm) were separately kept in a solution at 0.1 N containing the same cationic form.

2.3. Samples preparation for ENMR experiments.

The cell for ENMR experiments is home-made. Briefly, this cell is composed of a Plexiglas® tube and a hollow Teflon® tube of 18 mm internal diameter. When cleaned and conditioned in a cationic form, Nafion samples were first dried between two sheets of absorbent paper before being inserted layer by layer in the middle of the hollow Teflon® tube. The duration of drying samples depends on the desired water content of samples we intended to prepare. A stack of 40 layers of membrane samples was then built inside the Teflon tube. Afterwards, a commercial GDE (gas diffusion electrode) and a home-made electrode with platinum wire were inserted together at each side of this membrane stack. The "filled tube" (composed of the Teflon® tube + 40 layers of Nafion® 117 + 2 GDEs + 2 electrodes) was then inserted in a Plexiglas® tube where one of the end points was sealed. At the other end point of this Plexiglas® tube, a screw cap allows us to close this tube and also to keep immobile all layers of the described assembly. The assembled home cell was afterwards inserted in a ^1H NMR commercial probe for ENMR experiments. The current is applied to the electrodes via a home-made control unit which was designed for this particular application. This unit possesses several ranges (mA to A) and, within each range, a fine potentiometric tuning. The necessary constant voltage is provided by a commercial power supply. The whole apparatus (home-made unit and power supply) are controlled by the NMR console. We underline that the experimental procedure was repeated for each new sample stack used in this study. Moreover, the water content of each membrane stack was calculated at the end of each ENMR experiment. The dry mass of the stack was obtained after drying in an oven overnight at 60°C. The water content of the stack was expressed by λ in equation 1.

$$\lambda = \frac{EW^+}{M_{H_2O}} \times \frac{m_{H_2O}}{m(dry)} + \lambda_0 \qquad (1)$$

where EW^+ is the equivalent weight of Nafion (EW = 1100 g.mol^{-1}) corrected for the exchanged cation C^+ [18] and expressed by equation (2) (below).

M_{H2O} = 18 g mol^{-1}

m_{H_2O} = m(wet sample) – m(dry)

m(dry) = mass of sample obtained at 60°C.

$$EW^+ = EW + (M_{C^+} - 1) \quad (2)$$

M_{C^+} is the molar mass of the cation C^+

λ_0 (= 1.2) refers to our previous work and it corresponds to the part of bound water non dryable at 60°C [19].

2.4. ENMR experiments

ENMR measurements were performed with a Bruker Avance III 600 MHz Wide Bore (vertical magnet) NMR spectrometer at ambient temperature (24°C). We used a commercial probe (MicWB57, with gradients of 45G/cm), designed for spectroscopy, microimaging, diffusion measurements… With this probe, we can check the position of the membrane stack and also measure the thickness of the stack. The latter depends on the hydration level of the membrane stack and, in this study, varies from 6.4 to 7.8 mm. The microimaging resolution is about ±0.2 mm (Fig. 1). Moreover, the image allows us to check the homogeneity of the membrane stack. This point is important to ensure a good cationic conduction within the stack and also reliable results. An example of homogeneous and inhomogeneous membrane stack is shown in Fig.1 (a) and (b). An artefact in the center of the figures is observed due to the presence of platinum wire (inside the home-made electrodes), which blinds the magnetic field. In the case of inhomogeneous membrane stack (Fig.1 (b)), results are not similar using the two current configurations. Therefore no measurement is done when membrane stacks are inhomogeneous.

2.5. K_{drag} calculation

The experimental set up consists of applying a PGSTE (Pulse Gradient Stimulated Echo) [20] sequence in the membrane stack (Fig. 2) and then measuring the phase of the NMR signal with and without electrical current imposition. Δ and τ were fixed at 1 and 10^{-3}s respectively. The difference between the phases of the two ^{1}H signals (with and without current), $d\varphi$, is given in equation (5) and is seen to be related to the mobility of charged species inside the membrane, this mobility being induced by an electric current.

In order to understand how this experiment works, let us suppose that the gradient acts along the *X* axis of the laboratory frame, defined as the axis joining the two electrodes of the ENMR cell. The first gradient pulse produces a phase change $\gamma\delta g a$ (γ being the proton gyromagnetic ratio and g the gradient magnitude) for the transverse magnetization at location *a* (transverse magnetization being created by the initial 90° pulse and then stored as longitudinal magnetization by the second 90° pulse). In the absence of electric current, this phase change is annihilated by the second gradient pulse (identical to the first one) preceded by the third 90° pulse. In that way, half of the magnetization is refocused independently of the spin location within the membrane and the phase of

the NMR spectrum is simply due to the spectrometer settings. The NMR spectrum or the echo attenuation E(g) is expressed as below:

$$E(g) = \frac{M_0}{2} \exp\left(\frac{-\Delta}{T_1}\right) \exp\left(-\gamma^2 g^2 \delta^2 D\Delta\right) \quad (3)$$

where M_0 is the magnetization, D is the self-diffusion coefficient, T_1 is the longitudinal relaxation time. They are all constant parameters during the course of an experiment at a given water content.

Conversely, when an electric current is applied between the electrodes of the ENMR cell, it produces a displacement at velocity *v* of a given charged species. Therefore, transverse magnetization initially at location a, is located at $a + v\Delta$ at the moment of the application of the second gradient pulse. The echo attenuation (E(g)) in this case is a combination of diffusion and flow effects and it can be described as follow:

$$E(g) = \frac{M_0}{2} \exp\left(\frac{-\Delta}{T_1}\right) \exp\left(i\delta g\gamma\Delta v - \gamma^2 g^2 \delta^2 D\Delta\right) \quad (4)$$

The amplitude of E(g) depends on the self-diffusion D given by the term $\gamma^2 g^2 \delta^2 D\Delta$ and the difference of phase or the phase shift is given by the term $\delta g\gamma\Delta v$.

Thus, refocused magnetization is only affected by a phase change given by equation (5).

$$d\varphi = \gamma\delta\Delta g v \quad (5)$$

The velocity (v) expressed in equation (5) is related to mobile charged species, which move when a current is applied. Using ^{1}H NMR, we probe and measure all ^{1}H contained in the sample (mobile and immobile ^{1}H) because we are dealing here with a single signal, because of chemical exchange or because of similar chemical shifts. Thus, the velocity (v) of equation (5) is an average and is consequently proportional to the number of mobile species divided by the total number of ^{1}H nuclei contained in a sample. Therefore, v can be expressed according to equation (6).

$$v = v(mobile\ species)\frac{n(\,^1H, mobile\ species)}{n(\,^1H, total)} \quad (6)$$

In the case of Nafion in acid form, there is only H^+ as mobile species. Using ^{1}H NMR, we have only H^+ and H_2O as ^{1}H species within Nafion. So the velocity is given by equation (7).

$$v = v(\mathrm{H}^+)\frac{n(H^+)}{n(\,^1H, total)} \quad (7)$$

with $n(\,^1H, total) = n(H^+) + 2n(H_2O)$

As the current *I* is related to the velocity and the number of mobile species, we can expressed *I* according to the following equation where F is the Faraday constant (96500 C.mol^{-1}).

$$I = n(H^+)Fv(\mathrm{H}^+) \quad (8)$$

Then we obtain what will be called the theoretical velocity (v_{th}) if the electro-osmotic drag does not exist.

$$v_{th} = v(\mathrm{H}^+)\frac{n(H^+)}{n(\,^1H)} = \frac{I}{F}\frac{1}{n(\mathrm{H}^+) + 2n(\mathrm{H_2O})} \quad (9)$$

Now, if the electro-osmotic drag phenomenon takes place, protons and dragged water (H^+ and $(H_2O)_{drag}$) are considered as mobile species. As the velocity H^+ is identical to the velocity of $(H_2O)_{drag}$, the measured velocity (v_m) can be expressed as follows

$$v_m = v(\mathrm{H}^+)\frac{n(H^+,(H_2O)_{drag})}{n(\,^1H)} = \frac{I}{n(\mathrm{H}^+)F}\frac{n(\mathrm{H}^+)+2n((\mathrm{H_2O})_{\mathrm{drag}})}{n(\mathrm{H}^+)+2n(\mathrm{H_2O})} \tag{10}$$

Then the ratio of the measured velocity (v_m, given by equation (10)) to the theoretical velocity (given by equation (9)) allows us to access the electro-osmotic drag coefficient ($K_{drag}(\mathrm{H}^+)$) inside our sample.

$$\frac{v_m}{v_{th}} = \frac{d\varphi_m}{d\varphi_{th}} = \frac{n(\mathrm{H}^+)+2n((\mathrm{H_2O})_{\mathrm{drag}})}{n(\mathrm{H}^+)} = 1 + 2K_{drag}(\mathrm{H}^+) \tag{11}$$

In order to keep the same hydration level at each electrode of the membrane stack, the polarity of the electrodes is switched at each measurement as illustrated in Fig. 3. Depending on the chosen polarity, we have either a positive or a negative $d\varphi_{exp}$. However, the value of $|d\varphi_{exp}|$ is not expected to change much since the water content of the stack remains unchanged during the two measurements.

Now in the case of Nafion in other cationic forms, we can envisioned a similar approach. The mobile species seen by ^{1}H NMR are the dragged water molecules when a cation moved with current. So the measured velocity can be expressed as

$$v_m = v(\mathrm{C}^+)\frac{2n((\mathrm{H_2O})_{\mathrm{drag}})}{2n(H_2O)} \tag{12}$$

As one have always

$$I = n(\mathrm{C}^+)Fv(\mathrm{C}^+) \tag{13}$$

And

$$K_{drag}(C^+) = \frac{n((\mathrm{H_2O})_{\mathrm{drag}})}{n(\mathrm{C}^+)} \tag{14}$$

One obtains finally

$$v_m = \frac{I}{Fn(H_2O)}K_{drag} \tag{15}$$

3. Results and Discussion

3.1. Results of the experimental phase ($d\varphi_{exp}$) of Nafion in H^+, Na^+ and K^+ forms

The described method was applied for the membrane stack of Nafion in acid, sodium and potassium forms. In the case of Nafion in acid form, we can see in Fig. 4(a) that $d\varphi_{exp}$ increases linearly with the current whatever the water content of Nafion. This result is expected since the electro-osmotic flux is proportional to the current intensity. However, the coefficient of determination (R^2) of the linear

regression of the curves from Fig. 4(a) is not so close to unity: R^2 is lower than 95%. Nevertheless this coefficient of determination is quite comparable with those reported by Ise et al. [15].

We repeated the same experiment with Nafion in sodium and potassium forms. As it is illustrated in Fig. 4(c) and 4(e), $d\varphi_{exp}$ does not vary linearly with the increase of the current intensity for the two cationic forms of Nafion, particularly at "high" currents (0.5 A for instance). This behavior was not expected when compared with Nafion in acid form.

To explain this result, we supposed that (i) the electro-osmostic flux of the samples in sodium and potassium forms should be the same whatever the chosen configuration of the electrodes and (ii) the peculiar behavior comes mainly from the experimental set up. To improve those results, we need to determine the cause of these apparent discrepancies.

It is well known that the ionic conductivity of Nafion in acid form is higher than in sodium or in potassium form: 90, 18 and 12 $mS.cm^{-1}$ for Nafion in H^+, Na^+ and K^+ forms respectively at 23°C [21]. In other words, the ionic resistance of Nafion membrane is lower in acid form than in other cationic forms. Using this approach, it is easy to understand that when applying a current, the voltage of the membrane stack in sodium and potassium forms is higher than the voltage of the Nafion stack in acid form. This is confirmed by the data of table 1. For a similar water content close to 7 and for the two current intensities (0.3 and 0.5 A), the voltage of the Nafion stack in potassium and sodium forms are respectively 6 and 4 times higher than the voltage of the Nafion stack in acid form. This ratio can also be translated as the ratio of membrane resistance when conditioned in sodium and potassium forms.

The increase of membrane resistance affects the temperature of the membrane stack, especially when Nafion is in neutral cationic forms (Na^+ and K^+). To avoid this consequence, we need to keep constant the temperature inside our home cell whatever the applied current. However, the regulation of temperature with any kind of systems is not as fast as the increase of temperature inside the stack when a current is applied. Therefore, we have to find out some method for circumventing the effect of temperature on the measured phases of the NMR signal. It turns out that the increase of temperature inside the membrane stack alters the performance of the NMR detector and leads to an additional dephasing of the NMR signal which, in our case, can be measured by running the PGSTE experiment without gradient (g=0). In fact, this additional phase (φ_{ad}) depends on the experimental conditions. When an imposition of current is coupled with PGSTE sequence with gradient, the phase is equal to:

$$d\varphi = \delta g \gamma \Delta v + \varphi_{ad} \tag{16}$$

When an imposition of current is coupled with PGSTE sequence without gradient (g=0), the measured phase is equal to:

$$d\varphi = \varphi_{ad} \tag{17}$$

Consequently, by subtracting φ_{ad} from the phase measured in the normal PGSTE experiment (with gradient), we can access indirectly the phase arising from the sole transport phenomena (equation (11) and (15)). As it is illustrated in Fig. 4, we have compared the measured phase without correction ((a), (c) and (e)) and the measured phase with correction ((b), (d) and (f)) respectively for the acid, sodium and potassium forms of Nafion. In the case of Nafion in sodium and potassium forms, the phase correction is crucial for actually observing a linear increase of $d\varphi_{exp}$ with the increase of the

current intensity. Conversely, the phase correction in the case of Nafion in the acid form seems not so necessary since the shape of the curves does not change significantly. Neverthless, this method allowed us to obtain some improvement on $d\varphi_{exp}$ particularly at high currents (>0.5A) where the increase of temperature is thought to especially disturb the measurements.

It is worth to underline that using the two configurations for applying the current (Fig.3), the values of current are for instance positives for the configuration 1 and are negatives for the configuration 2. This is the reason why the values of current can be positive and negative. When changing the direction of imposition of current, the sign of the measured phase changes also because of the change of the flow direction. However, the absolute value of the difference of phase ($d\varphi$) for a given current remains the same.

3.2. Electro-osmotic drag coefficients (K_{drag})

Here, we underline the fact that it is not so easy to prepare membrane stacks having exactly the same water content for each cationic form of Nafion. In fact, we had to prepare many samples with similar and hopefully identical water contents for comparison. Moreover, we repeated the phase measurement for each current at least two times in both configurations for checking the reproducibility and accuracy of our measurements.

The coefficients of electro-osmotic drag (K_{drag}) of the Nafion in acid, sodium and potassium forms for different amounts of water content are gathered in Fig. 5. As we can observe, K_{drag} depends on the counter-cation and on the water content of Nafion membrane. K_{drag} of Nafion in sodium form is the highest whatever the water content, followed by K_{drag} of Nafion in potassium form and then by k_{drag} of Nafion in acid form. For the three cationic forms of Nafion, K_{drag} increases linearly with the water content of Nafion, excepted for the Nafion in acid form when λ becomes higher than 12.

3.2.1. K_{drag} of Nafion in acid form

In the case of Nafion in acid form, when the water content of Nafion is between 12-22 molecules of water per sulfonate site, we found an almost constant electro-osmotic drag coefficient value (maximum around 1.6). At high water content (>12), this electro-osmotic drag coefficient value appears small in comparison with the data from the literature [9, 10, 15]. Indeed, most of the authors found values higher than 2. However, the conditions of measurement and the experimental methods are different. Usually, a high electro-osmotic drag coefficient is measured when Nafion membrane is kept in contact with liquid water or an electrolyte solution.

Ise et al. used ENMR to measure the electro-osmotic drag coefficients of Nafion and PEEKs membranes. They used a home-made cell with a thermoregulation system. The diameter of the membrane stack sample is around 7 mm as well as the thickness of the membrane stack. Concerning the results about Nafion® 117 membrane, the authors reported K_{drag} values around 2.7 for λ between 17 and 20. However, the uncertainty is rather important for each electro-osmotic drag coefficient (+/- 0.5) and for some nearby water contents, the reported K_{drag} varies significantly. For instance K_{drag} is 1.7 at λ = 16.5, 2.7 at λ =17 and 2.4 at λ =20 without taking into account the error bar attributed to

each value. Even if one plots K_{drag} as a function of the water content (λ = [11-20]), no clear trend is apparent. We can actually see two kinds of behavior in their results: (i) λ =11-16.5, K_{drag} is rather constant and its value is about 1.7 and (ii) λ =17-20, K_{drag} is also rather constant and the value is around 2.7. The question is about the difference of these two groups of K_{drag} values. Actually, the change of the K_{drag} value between these two ranges of water content is probably due to the difference in sample preparation. According to the authors' description, the highest water content samples were obtained by always keeping them in liquid water whereas the lowest water content samples were prepared by desorption with filter paper. As their sample surface is 5 times smaller than our sample surface, it means that the current density is about 5 times higher in their work for the same applied current (for instance for an applied current of 1A, it is equal to 260 A/cm^2 vs. 50 A/cm^2). With such high current density, liquid water contained in the highest water content samples can participate in the total amount of water flux. In other words, liquid water outside the membrane can be dragged when a current is applied. This possibility could explain the difference between the two mean values of K_{drag} and its non-linear increase with respect to the water content. Therefore, K_{drag} measured at the highest water content in our work cannot be compared with those reported in the literature because of the difference of membrane preparation and also because of the different experimental methods.

However, the K_{drag} values of Nafion in acid form in Fig. 5 are very similar of those obtained by Ise et al. at λ =11-16.5: 1.4-1.6 vs. 1.7 respectively. This comparison makes us confident in our experimental method, since the results of the ENMR technique appear especially reproducible. At higher water contents (λ>17), the two samples measured at λ>20 lead to a similar K_{drag} value around 1.6. In this study, we do not need to keep always samples in liquid water because the sample size is big enough to prevent any dehydration during measurements. Without the presence of liquid water outside of the membrane stack, K_{drag} remains unchanged with the increase of water content.

Concerning now the range of low water content (6<λ<12), we can see that K_{drag} increases linearly according to water content from 0.4 to 1.4. The low value of K_{drag} <1 is not a surprise since some authors in literature have already reported similar results obtained by different methods. Usually, K_{drag} measured with a membrane equilibrated in a water vapor system (i.e. low water content) is lower than K_{drag} measured in a liquid water system. Indeed, using a hydrogen pump, Peng et al. [12] reported that K_{drag} varies from 0.1 to 0.8 depending on their experimental conditions. Other authors used the method of activity gradient (chemical potential) to measure K_{drag} of a Nafion membrane [9, 22]. Fuller and Newmann [22] reported that k_{drag} is constant at a value of 1.4 when λ is higher than 4. This value of K_{drag} is comparable to our limit of K_{drag} (1.6) at high water content. Nevertheless, the fact that K_{drag} can be lower than 1 means that every proton does not drag one water molecule when they moved through Nafion. We will try to propose a plausible explanation later in this paper after discussing K_{drag} of Nafion in sodium and potassium forms.

3.2.2. K_{drag} of Nafion in sodium and potassium forms

We can observe on Fig. 5 that the K_{drag} of Nafion in sodium and potassium forms increases monotically as function of the water content. Here, it is worth noticing that the range of water content is different for both cationic forms even if sample preparation remains unchanged. In fact, it turns out that the sorption of Nafion depends on the type of counter-cation and particularly on the

number of solvation of three cations investigated here ($n_s(K^+)$=3±2; $n_s(Na^+)$=4±1; $n_s(H^+)$=5±1 [23]), the hydration of the Nafion membrane is thus limited by its presence. In a general way, the range of water content varies according to the nature of counter-cation within the Nafion membrane.

Furthermore, the results show that, depending on the water content, the K_{drag} of Nafion in sodium and potassium forms varies from 2.5 to 5.3 and from 1.5 to 3.5, respectively. Even if, for the sake of comparison, we do not have many data from the literature concerning K_{drag} of Nafion in these two cationic forms, we are confident in our results because our method was validated with the Nafion in acid form. In fact, K_{drag} values of Nafion in sodium form ranging from 3.7 to 6.4 were measured using a scanning electrochemical microscopy [24]. The reported values are close to the results of the present work.

Comparing the K_{drag} values at λ near 7 for the three cationic forms of Nafion (Fig.5), we have 2.6, 2.1 and 0.7 for Nafion in sodium, potassium and acid forms, respectively. Based on this comparison, we can stress that K_{drag} of Nafion in sodium and potassium forms behaves differently than K_{drag} of Nafion in acid form. Indeed, (i) the minimum value of K_{drag} for both cationic forms (Na^+ and K^+) is higher than 1 at low water content and (ii) K_{drag} of Nafion in sodium and potassium forms tends respectively toward the solvation number of these cations at high water content. Point (i) suggests that in a dehydrated medium, sodium and potassium cations are always surrounded by a minimum of water molecules, which constitutes its core of solvation and for which the bond between surrounding water molecules and cation might be strong and might seem unbreakable. Moreover, the size of the cations should also favor the transport of water molecules through the Nafion membrane. However, the most important criterium remains the solvation number. Even though the size of the sodium cation is smaller than that of the potassium cation, it is able to drag up to 5 molecules of water when it moves through hydrated Nafion. Indeed, 5.3 and 3.5 molecules dragged by the sodium and potassium cations, respectively, are in accord with their solvation numbers.

Now, the question is why K_{drag} of Nafion in acid form does not follow the same trend than K_{drag} of Nafion in neutral cations. Actually, several arguments could be put forward to explain this behavior: (i) the lability of proton, (ii) the small size and weight of proton, (iii) steric effects with its environment and (iv) possibly charge transfer between water molecules when a current is applied. It is well known that proton is a particular cation which is able to make inter and intra bonds with different water molecules because of its lability. Consequently, H^+ can be linked to different water structures like simple forms such as OH^-, H_2O or water molecules aggregates (H_4O_2, H_8O_4...). In other terms, H^+ can take different forms with short lifetimes due to its lability. Hence the two mechanisms of transport within a Nafion membrane: vehicular via sulfonated sites (SO_3^-) and by hopping via water molecules (Grotthuss mechanism). These two mechanisms favor a low K_{drag} value for a Nafion membrane. On the other hand, it appears that the results point out that the K_{drag} of Nafion in acid form is far lower than the proton solvation number (i.e. 1.6 vs. 5) at high water content. This suggests that a proton does not transport all its surrounding water molecules when it moves through a Nafion membrane because of the weak interaction with these water molecules (solvation core). When K_{drag} is lower than 1, it means that most protons cross the Nafion membrane without any water molecule. In our previous work dealing with the water behavior within Nafion in acid, sodium and potassium forms studied by NMR relaxometry, we concluded to two types of bound water within Nafion for the 3 cationic forms of Nafion at low water content [17]. These two kinds of population could be ascribed to the solvation core of sulfonated ions and cations, respectively. It could be thought that, in

dehydrated Nafion, sulfonated ions retain a certain amount of water molecules which constitutes its solvation core. Thus, in such a dehydrated medium, protons move through Nafion without dragging water molecules because water molecules are more tightly linked to sulfonated ions than to protons. Consequently, in that case, the hopping mechanism would be favored.

4. Conclusion

This paper focuses on an original method based on Electrophoresis NMR for measuring the electro-osmotic drag coefficients of water (K_{drag}) within Nafion in acid, sodium and potassium forms. Although this method has already been applied to the measurement of K_{drag} of Nafion in acid form, we have succeeded to extend it towards other cationic forms of Nafion. The comparison of the coefficients of electro-osmotic drag within Nafion in different cationic forms is certainly more reliable when a single method is employed (contrary to data found in the literature which have been obtained through different experimental methods).

Indeed, the results reveals that electro-osmotic drag coefficient depends on the type of counter-cation within Nafion and also on the hydration level of the membrane. In the case of Nafion in sodium and potassium forms, K_{drag} is higher than 1 even at low water content of Nafion. This result indicates that both cations are always solvated, but that the solvation layer depends on the water content of Nafion. Therefore at high water content, K_{drag} of these two forms of Nafion tends towards their own solvation number, i.e. 5 and 3 respectively for sodium and potassium forms.

Unexpectedly, K_{drag} of Nafion in acid form is the lowest among the three studied cationic forms of Nafion. Contrary to K_{drag} of Nafion in sodium and potassium forms, K_{drag} of Nafion in acid form goes from 0.4 to 1.6 in the investigated range of water content (λ= 6-22). The fact that K_{drag} is below 1 suggests that proton can be non-solvated within a dehydrated Nafion membrane. This result can be explained by (i) the variable ability of proton to link to water molecules in different structural states and (ii) the very probable existence of strong interactions between water molecules and sulfonated ions within Nafion. This fact could favor the hopping mechanism instead of the vehicular mechanism and also the transfer of charge. Finally, K_{drag} of Nafion in acid form at high water content does not tend towards its solvation number (i.e. 5±1). This is related to the lability of proton and to the weak interactions between the proton and its solvated water molecules.

Figure 1: Stack of 40 layers of Nafion membrane observed by NMR microimaging: (a) homogeneous membrane stack and (b) inhomogeneous membrane stack

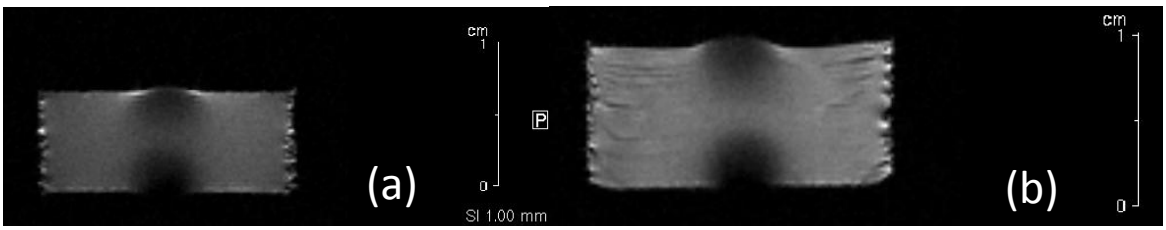

Figure 2: ENMR experiment with a PGSTE sequence coupled with possibly the application of an electric current at the electrodes of the ENMR cell. δ and the thin rectangles (in black) correspond to gradient pulses and to classical radio-frequency pulses respectively.

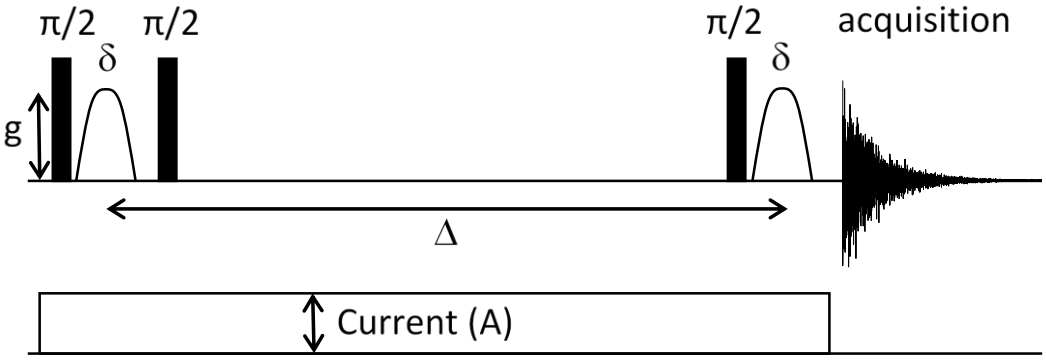

Figure 3: Configuration of the imposed electrodes polarity

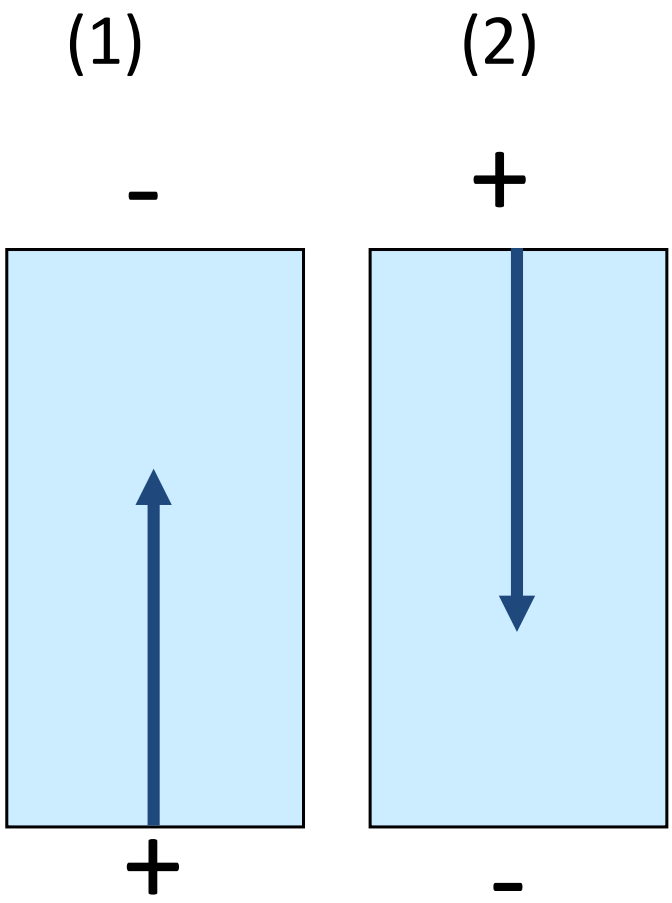

Figure 4: Experimental phases ($d\varphi_{exp}$) of Nafion respectively without and with correction phase (see text) in: (a) and (b) acid form at λ = 10; (c) and (d) sodium form at λ = 7; (e) and (f) potassium form at λ = 7

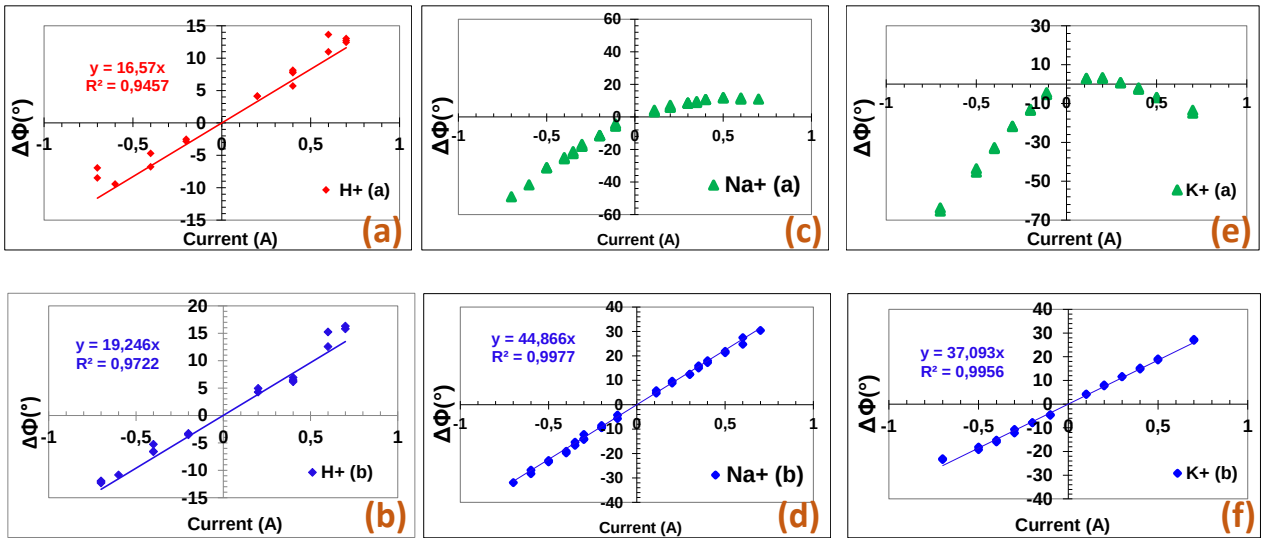

Figure 5: Coefficients of electro-osmotic drag of Nafion in acid, sodium and potassium forms vs. the water content expressed by λ (in fact $\lambda - \lambda_0$; see equation (1))

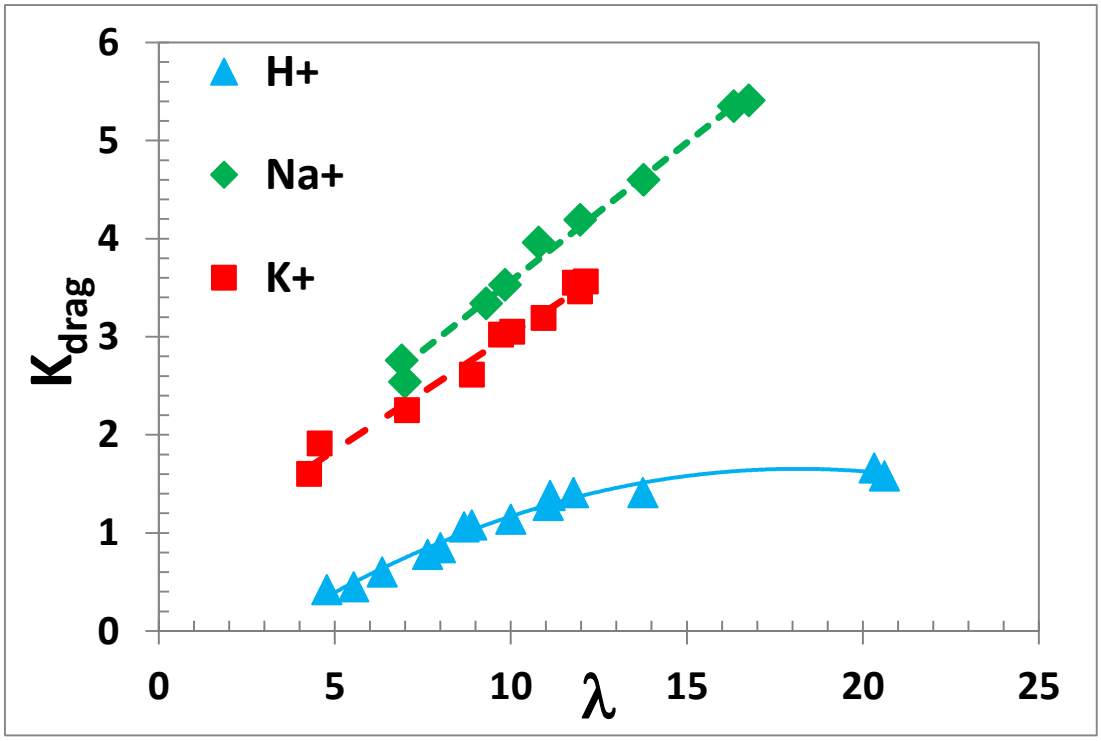

Table 1: Thickness and voltage of Nafion® membrane stack with different counter-cations for a similar water content and two applied currents (0.3 and 0.5 A).

Cation		H^+	Na^+	K^+
λ		7.6	6.9	7.0
Stack thickness (± 0.2mm)		7.4	7.0	6.8
Voltage (V)	0.3 A	3.9-4.2	15.0-15.5	25-26
	0.5 A	6.1-6.5	23-24	39-40

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Figures Captions

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