



Impact of chemical treatments on the behavior of water in Nafion® NRE-212 by ^1H NMR: Self-diffusion measurements and proton quantization

Feina Xu, Sébastien Leclerc, Olivier Lottin, Daniel Canet

► To cite this version:

Feina Xu, Sébastien Leclerc, Olivier Lottin, Daniel Canet. Impact of chemical treatments on the behavior of water in Nafion® NRE-212 by ^1H NMR: Self-diffusion measurements and proton quantization. Journal of Membrane Science, 2011, 371 (1-2), pp.148 - 154. 10.1016/j.memsci.2011.01.038 . hal-01482010

HAL Id: hal-01482010

<https://hal.univ-lorraine.fr/hal-01482010>

Submitted on 3 Mar 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Impact of Chemical Treatments on the Behavior of Water in Nafion[®] NRE-212 by ¹H NMR: Self- Diffusion Measurements and Proton Quantization

Feina Xu^{,1}, Sébastien Leclerc¹, Olivier Lottin¹, Daniel Canet²*

¹ Laboratoire d'Energétique et de Mécanique Théorique et Appliquée (LEMTA), UMR 7563 Nancy
Université – CNRS, B.P. 160, F-54504 Vandoeuvre Cedex, France

² Méthodologie RMN (CRM2), UMR 7036 Nancy université – CNRS, B.P. 239, F-54506
Vandoeuvre-lès-Nancy Cedex, France

Feina.Xu@ensem.inpl-nancy.fr

* To whom correspondence should be addressed. Email: Feina.Xu@ensem.inpl-nancy.fr

Phone / Fax : (33) 3 83 59 55 59 / (33) 3 83 59 55 51

ABSTRACT

In this paper, we have studied by ^1H NMR the behavior of water in Nafion under acid, sodium and potassium forms which arises from different chemical treatments with or without EDTA. Self-diffusion coefficients were measured by PGSTE (Pulsed Gradient STimulated Echo) whereas integration of the proton spectrum provides a quantitative information about water content. Examination of the self-diffusion coefficients of water in Nafion shows clearly that: (i) in the acid form, the use of a chelating agent does not affect translational diffusion of water, (ii) regardless of sample conditioning, water within Nafion in acid form diffuses more rapidly than in sodium and potassium forms, in particular at low water content (at $\lambda = 3.4$, $D = 5.4 \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ vs. $7.2 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$), (iii) for a given water amount, water diffusion is identical in sodium and potassium forms. Point (ii) is due to the presence of oxonium ions within Nafion in acid form, favoring both vehicle and Grotthuss mechanisms. It is also due to a higher number of protons available for diffusion (we find an average value of 1.19 in acid form vs. 0.91 in sodium form). Our results suggest in the case of Nafion in acid form that, at low water content, diffusion occurs by jumps between different sites. Moreover, plotting self-diffusion coefficients vs. relative humidity leads to a clear differentiation between sodium and potassium cations, related to their respective solvation number.

KEYWORDS: NMR, self-diffusion coefficients, Nafion, chemical cleaning, counter-cations, protons transport.

1. Introduction

During the past decades, a lot of renewable and clean alternative energies has been envisaged in order to replace eventually fossil fuel energy. Among them, electrochemical devices like Proton Exchange Membrane Fuel cell (PEMFC) can be considered as a means to produce competitive and clean energy, since their by-products are only water and heat. The key element of this electrochemical cell is the polymer electrolyte, which ensures both gas separation and transport of protons from the anode to the cathode. Moreover, this electrolyte must possess good (electro)-chemical, mechanical and thermal stabilities.

Until now, perfluorosulfonated membranes like Nafion are the most used ionomers in PEMFC because they possess all these properties, and mostly important a high ionic conductivity when hydrated. These properties arise from their chemical structure: a hydrophobic matrix in teflon on which are grafted perfluorovinyl ether chains terminated by hydrophilic sulfonated groups. In general, the latter are compensated by cations to ensure the electroneutrality. As a result, Nafion can be in various cationic forms and the acid form $\text{-RSO}_3\text{H}$ is the most common. It is actually in the acid form that the ionic conductivity of Nafion is the most important, since protons can be transported via two mechanisms, vehicle and Grotthuss [1]. The former is proton diffusion through sulfonated sites and the latter is the transport of a proton from one water molecule to its neighbor by modification of the hydrogen bond network.

Although Nafion is the most studied membrane [2,3], results from literature cannot be compared without taking into account the history of the membrane. Indeed, thermal and chemical treatments on the one hand and conditioning on the other hand affect membrane swelling and performances [4,5]. In addition, as the hydration state of Nafion in a running fuel cell can vary, due to gas distribution, from almost dry to fully hydrated, this parameter has to be controlled. Since water plays a crucial role on ionomer performances, it seems important to determine its influence in the transport of protons at different scales, in particular for modeling purpose. Thus, an investigation of

water dynamics within Nafion should enable us to improve our understanding of the effect of water on the proton transport properties. Among all existing techniques, we have applied ^1H NMR for studying this membrane. ^1H NMR has the advantage to provide information on water dynamics in a confined medium at molecular and microscopic scales, and also, with some precautions, on the amount of water in the sample.

NMR experiments [6,7] for measuring either relaxation times (T_1 and T_2) or self-diffusion of water are well known to be reliable, although the preparation and conditioning of samples may considerably affect their results [8-11]. As ^1H NMR suffers from the presence of paramagnetic species which may entail ambiguous interpretation, some caution has to be exercised before NMR measurements, in particular about membrane cleanings. However, concerning this latter point, there is no standard protocol specifically designed prior to NMR measurements. As a result, some authors have preferred to use Nafion in its acid form as received [9,12], others have chosen to clean the membrane using either acid baths [8,10,13] or both acid and EDTA chelating agent baths [14]. Although Nafion was studied in acid form and in fully hydrated conditions, water self-diffusion coefficients varying from 6.1×10^{-6} to $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ have been reported in the literature [8-10,14]. In addition, the use of EDTA was suggested by Mac Millan et al. [11] in order to remove all paramagnetic cations within Nafion, since such species impart an additional relaxation mechanism which can become prominent. However, EDTA in acid form is not soluble in water even at a low concentration, contrary to its salted forms. This means that using EDTA in salted forms (e.g. sodium or potassium forms) provokes the exchange of counter-cations within Nafion with cations from the soaking solution.

Owing to the fact that the nature and size of cations affect Nafion hydration [15], we have to check, via NMR measurements, the effects of EDTA and of counter-cations on the behavior of water in Nafion. In such a complex environment, the main question that we wish to answer is: can ^1H NMR spectroscopy make the difference between water in acid form, in sodium and potassium forms in a confined medium like Nafion? Moreover, can ^1H -NMR techniques distinguish water

surrounding sodium and potassium cations? Answering those questions would allow us to select the more suitable cleaning protocol and also to have a better understanding of protons transport through Nafion in various cationic forms.

In this report, we focus on the dynamics of water within Nafion[®] NRE 212, by taking into account different parameters such as the type of counter-cations, the use of a chelating agent, **the way of conditioning and preparing samples**. For this purpose, we have prepared five series of samples in acid, sodium and potassium forms and possibly treated with EDTA. The samples are studied over a wide range of water content varying from almost dry to fully hydrated by means of self-diffusion coefficient measurements and proton **quantization** through ¹H NMR. As membrane history is important for understanding the results of this study, we report with some details in the following sections the different chemical treatments of the membrane, the method for determining the drying mass and the hydration time.

2. Experimental Section

2.1 Materials and Sample Preparation

The materials used throughout this work were (a) Nafion[®] NRE-212 from Ion Power, (b) salts with purity superior to 99%: LiCl, MgCl₂, Mg(NO₃),H₂O, NaCl, KClO₃, EDTA (Ethylenediaminetetraacetic acid – C₁₀H₁₆N₂O₈ or EDTA-H₄), EDTA disodium salt dehydrate (C₁₀H₁₄Na₂N₂O₈ or EDTA-Na₂), EDTA dipotassium salt dehydrate (C₁₀H₁₄K₂N₂O₈ or EDTA-K₂), (c) HCl (37% wt), H₂SO₄ (95-97% wt) and HNO₃ (65 % wt) acids with quality upgraded, (d) NaOH 1 mol L⁻¹ with reagent quality, (e) D₂O with 99.9 % enrichment of D, and (f) pure water produced by a reverse-osmosis apparatus (Purite 1 Select) from Onda. All chemical products (salts, acids, caustic soda and D₂O) were purchased from Aldrich and they were used as received.

In order to remove possible metallic cations present within 5 mm NMR tubes (with screw cap from New Era), the latter were cleaned using a protocol similar to the one described by MacMillan [11]. All tubes were filled with a mixture of acid solutions (50% of H_2SO_4 + 50% of HNO_3 , 1 mol L^{-1}) for 24h. They were rinsed at least 4 times with distilled water before being immersed in an ultrasound bath in order to remove any trace of impurities. They were then soaked in a solution of EDTA-H_4 (0.015 mol L^{-1}) neutralized by NaOH 1 mol L^{-1} for at least 24h. After that, all tubes were rinsed thoroughly with distilled water before immersing them again in an ultrasound bath. Thereafter, they were rinsed again and dried in an oven at 60°C overnight.

The membrane Nafion[®] NRE-212 is a non-reinforced dispersion-cast film and it can be considered as a new generation of Nafion[®] 112. Thus, its EW (Equivalent Weight) is 1100 g equiv⁻¹ and its mean thickness is 50 μm . The membrane sheets, as received, were cut into pieces of 1.1 x 9 cm^2 prior to preparing them for the chemical treatments. All the strips were boiled in H_2O_2 , 3% wt for 1h in order to remove organics impurities that could come from Nafion synthesis. They were then rinsed in pure water at room temperature before being boiled again in pure water for 1h. After that, all strips were arranged in five groups for being prepared in the following forms: H^+ , $\text{Na}^+(\text{M1})$, $\text{H}^+-\text{Na}^+(\text{M1})-\text{H}^+$, $\text{Na}^+(\text{M2})$ and $\text{K}^+(\text{M2})$.

(1) *Samples in acid form: H^+* . The pieces of Nafion were prepared in acid form by soaking in a 2 mol L^{-1} of HCl solution for 2h at 80°C. They were then rinsed several times with pure water at room temperature prior to immersion in demineralized water for 2h at 80°C. Thereafter, they were acidified again in a 1 mol L^{-1} of HNO_3 solution for 2h at 80°C. After this last step of acidification, all samples were rinsed thoroughly in pure water at room temperature and all excess of acid within the samples were removed by cleaning twice in distilled water at 80°C for 2h.

(2) *Samples in sodium form: $\text{Na}^+(\text{M1})$ and $\text{Na}^+(\text{M2})$* . Both samples $\text{Na}^+(\text{M1})$ and $\text{Na}^+(\text{M2})$ were prepared according to methods 1 and 2 described below. The only difference between these two methods is the choice of EDTA salts. Method 1 makes use of a solution of EDTA-H_4 neutralized with caustic soda. This is because EDTA in the acid form (EDTA-H_4) is not soluble in water. Using

this method, the soaking solution is generally basic with a pH around 11. Method 2 consists in soaking membranes in an EDTA-Na₂ solution, leading to a pH around 5. With these two solutions, one should be able to detect the influence of pH on self-diffusion coefficients. For both methods, the next steps are similar to the procedure of Mac Millan [11]. The samples were first acidified according to subsection (1). Then, they were soaked in a solution at 0.015 mol L⁻¹ for more than 3 days, either of EDTA-H₄ + NaOH (Method 1) or EDTA-Na₂ (Method 2). *Note that the soaking solutions were changed at least 5 times during the complexation step and at each time a large amount of solutions was used (at least 500 mL).* Finally, they were thoroughly rinsed with pure water before cleaning them twice in demineralized water at 80°C for 2h.

(3) *Samples in acid form and treated with EDTA: H⁺-Na⁺(M1)-H⁺.* The samples H⁺-Na⁺(M1)-H⁺ were prepared in the same way as samples Na⁺(M1). They were then acidified with a solution of HNO₃ at 1 mol L⁻¹, 80°C for 2h and rinsed twice in pure water at 80°C for 2h. At each step, samples were thoroughly rinsed in distilled water at room temperature.

(4) *Samples in potassium form: K⁺(M2).* The set up was the same as for the samples Na⁺(M2), with EDTA-K₂ in place of EDTA-Na₂.

Following the above described treatments, all samples were dried in an oven overnight at 60°C before being introduced in a rolled form at the bottom of NMR tubes. To prevent a possible humidification of the rolled membranes within NMR tubes during the insertion step, they were dried again at 60°C overnight prior to equilibration at a desired humidity. After that, the dry mass of each piece of membrane was weighed (typical weight for a sample is around 0.1g).

In this work, we had recourse to two methods (dubbed “vapor phase” and “liquid phase”) for equilibrating samples. The first one (vapor phase) makes use of water vapor pressure P/P_0 (P_0 : atmospheric pressure) of a hygroscopic solution for hydrating Nafion at room temperature. Each sample in its NMR tube is placed in a sealed jar containing the saturated salt solution. In order to cover a large range of water relative humidity - 11, 32, 53, 75 and 98% respectively, we have used the following salts: LiCl, MgCl₂, Mg(NO₃)₂·H₂O, NaCl and KClO₃. Thus, knowing the relative

humidity imposed by the hygrostatic solutions, we were able to prepare a series of samples at different water contents. These water contents can be converted into λ parameters by means of the sorption isotherm curves. This parameter is defined as the number of water molecules per number of SO₃-cation pairs and is calculated according to (1) [17]:

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

With $M_{H_2O} = 18 \text{ g mol}^{-1}$

$$m_{H_2O} = m(\text{wet sample}) - m(\text{dry})$$

$m(\text{dry})$ = mass of the sample obtained at 60°C.

and where EW^+ is the Nafion Equivalent Weight (EW) corrected for the exchanged cation C^+ as expressed below.

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

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

Since conditioning samples in vapor phase limits λ to 14 due to Schroeder's paradox [2,16], we had to resort to the second method (liquid phase) which consists in swelling membranes with liquid water so as to go beyond this limit. For obtaining a given water content, the excess of liquid was removed from hydrated samples by condensing water at the upper part of the NMR tube with the help of a water bath at 70°C. Water droplets were progressively removed with a soft paper until the desired value of λ is reached.

2.2 Chemical characterizations

The thermo-gravimetric analysis was performed using a TGA 2950 High Resolution from TA Instruments. The samples were heated in nitrogen atmosphere from 25°C to 600°C with a scanning rate of $10 \text{ }^\circ\text{C min}^{-1}$. In order to distinguish between free and non-free water in the Nafion matrix, all samples were immersed in liquid water overnight prior to the analysis.

The Infra-red spectra were recorded using an FTIR-ATR from Bruker, equipped with a ZnSe crystal. Before recording an FTIR-ATR spectrum, all samples were dried in an oven at 60°C overnight in order to get rid of water absorption bands.

2.3 NMR measurements

Diffusion experiments were performed at ambient temperature on a Bruker Avance DRX-600 spectrometer equipped with a cryogenic probe. The pulse-gradient stimulated echo sequence (PGSTE) method was applied throughout this work, with bipolar sine-shaped gradient pulses [6,7]. As longitudinal (T_1) and transverse (T_2) relaxation times vary with the water content in the polymer, the duration of each sine-shaped gradient pulse ($\delta/2$) and of the diffusion interval (Δ) were chosen according to the relaxation time values: a range of 5 to 10 ms for δ and a range of 60 to 150 ms for Δ . The gradient strength, with a maximum of 50 G cm⁻¹, was incremented in 32 steps between 2 % and 95 % of this maximum value, each step corresponding to a separate experiment.

Standard proton spectra have been obtained at room temperature on a homemade 200 MHz spectrometer equipped with a 4.7 Tesla Oxford magnet. The same experimental set-up was maintained throughout all experiments. The recycle time (between two consecutive experiments) has been set to five times the longest T_1 (or longer). Moreover, all samples correspond to the same membrane roll height, matched to the receiver coil height. These precautions ensure quantitative comparison.

3. Characterization of samples prior to NMR measurements

As NMR results depend strongly on the history of the sample, they have to be characterized prior to NMR measurements by the drying temperature, the possible presence of EDTA and the equilibration time of membranes in rolled form.

3.1. Choice of the drying temperature

Before hydrating samples, drying mass must be determined in order to calculate the water content or the number of H₂O molecules per sulfonated groups. A number of methods has been reported for getting a dry mass of Nafion, like drying over P₂O₅ at room temperature [8], drying under vacuum for a long period at different pressure (for example 10⁻⁵ torr or 1 torr) either at room temperature [18] or at a temperature higher than 105°C [18]. Other authors have mixed both methods by drying theirs samples under vacuum at 50°C in presence of P₂O₅ [19]. One molecule of water per sulfonated group was found by drying under vacuum at room temperature, whereas a value of λ close to zero was calculated by dehydrating Nafion under vacuum at 105°C or over P₂O₅ at room temperature. However, Yeo et al. [20] have demonstrated that there is a residual water of 0.2 wt. % even after drying Nafion under vacuum at 170°C. According to literature data, it seems that reaching an “absolute” drying mass is difficult and depends on experimenters and mostly on the homogeneity of the polymer.

Thermo-gravimetric analysis enables us, on the one hand, to apprehend the decomposition of hydrated Nafion through a range of temperature (25-600°C) and, on the other hand, to select the temperature for drying Nafion. Data from thermo-gravimetric analysis (Figure 1) show four regions of Nafion degradation. The first two regions can be described as the release of two kinds of water: free water released between 25°C and 60°C, non-free water released between 60°C and 260°C. Non-free water is strongly bound to the ionomer matrix and cannot be released at low temperature. By increasing temperature, sulfonated groups disappear from 260°C to 360°C and perfluoroether side chains from 360°C up to more than 600°C [21]. From data in Figure 1, we notice that 60°C is high enough to remove almost all free water, the remaining amount (non-free water) being not totally negligible. Indeed, depending on the sample, the latter part represents only 1.8 to 2.1 wt %, thus leading to a λ value which lies between 1.1 and 1.3. Owing to Nafion inhomogeneity, we shall

retain $\lambda = 1.2$ for all samples which have been dried at 60°C. Thus, for all results given later, the non-free water will be taken into account for the calculation of λ .

3.2. Effect of EDTA on Nafion[®] membrane

EDTA-H⁴⁺ is a large anion which cannot penetrate into Nafion because of the repulsion from SO₃⁻ groupings. However, it may interact with the membrane surface leading to a possible poisoning of the membrane. In order to check this eventuality, FTIR-ATR of Na⁺(M1) and H⁺ membranes (the latter being devoid of EDTA) were compared. As shown in Figure 2, both spectra are quite similar except in the 1600-1800 cm⁻¹ region and exhibit features due to vibrations of C-F (1202 and 1144 cm⁻¹), SO₃⁻ (1052 cm⁻¹) and COC (980 cm⁻¹) groups. The peak around 1730 cm⁻¹ observed in the spectrum of sample H⁺ confirms the acid form of the membrane (HOH deformation in oxonium ions), while this band shifts to 1650 cm⁻¹ for the Na⁺(M1) sample, this latter frequency corresponding to the deformation of water [22]. As no characteristic band of C=O in the carboxylate COO⁻ grouping (expected around 1800 cm⁻¹) is visible, we can conclude that EDTA is not present in the sample Na⁺(M1).

3.3. Equilibration time

Samples were conditioned in 5 mm NMR tubes at room temperature with different relative humidity (RH - %). The water content of the samples H⁺, Na⁺(M1), Na⁺(M2) and K⁺(M2) was determined by weighing after 3 weeks and after 3 months (Figure 3). The comparison of these two curves show that membranes in rolls form require quite a long time to be hydrated properly if placed in NMR tubes. 3 weeks for conditioning the membranes are actually not enough to reach a fully hydrated membrane, in particular at 98% RH. By increasing the equilibration time, we can notice that results in term of water uptake for the acid form are in good agreement with the literature

[8,15]. Although, as reported by Zawodzinski et al. [8], the equilibration time for Nafion 117 in flat form is around 4 days, it turns out that, for our samples, a much longer time is necessary (hence the three months to make sure that full hydration has been reached). It was indeed reported that several weeks are necessary for hydrating samples in rolled form inserted into 10 mm diameter NMR tubes [23]. This is not surprising since water must penetrate by the membrane thickness rather than by its surface. Even though this method is time consuming, samples in rolled form lead to a better NMR signal/noise ratio, in particular with thin membranes. In addition, from the isotherm curves given in Figure 3(b), it is confirmed that water uptake is related to cation solvation number [2,15]. Indeed, the solvation number is 5 ± 1 , 4 ± 1 and 3 ± 2 for H^+ , Na^+ and K^+ , respectively [15]. Moreover, it seems that the pH of the soaking solutions does not affect the sorption of Nafion in sodium form, regardless of the sample preparation ($Na^+(M1)$ and $Na^+(M2)$). Thus, hydration of Nafion depends essentially on the type of cation.

4. Results and Discussion

4.1 Water self-diffusion coefficient measurements

The water self-diffusion coefficient (D) of each sample was measured by the PGSTE method (see the experimental section) [6,7]. The results shown in Figure 4 exhibit two major trends. The first one, as expected, is that water self-diffusion coefficients depend on the membrane hydration. It actually varies by two orders of magnitude between the lower and the higher water content (λ) for all series studied here. Our results with Nafion in acid form (samples H^+ and $H^+-Na^+(M1)-H^+$) can be compared to those of literature [8,13]. However the literature water self-diffusion coefficients are scattered, in particular at the lower and higher λ values and therefore seem to depend to a large extent on the sample preparation. For example, Nicotera et al [10] reported an increase of D at $20^\circ C$ from 0.5 to $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for extruded Nafion 112 with a water content ranging from 14% to

37% (obtained by weighing). These samples were prepared by immersion in distilled water for 2h to 2 days at room temperature. After removing water droplets on their surface, membranes were inserted into 5 mm NMR Pyrex tube and hermetically sealed. For the sake of comparison with our samples in acid form H^+ for the same water uptake (28% or $\lambda = 18$), we find a D value of $6.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ instead of $1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [10]. By contrast, at $\lambda = 2$, a value of $6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ was reported for a flat Nafion 117 [8] while a value of $8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ is obtained here. This comparison emphasizes that both sample preparation and the method of insertion into the NMR tube (in flat or rolled form) have a considerable impact on water uptake and also on the self-diffusion coefficient.

The second trend is that, for a given water content, protons from samples in acid form (the series H^+ and $H^+-Na^+(M1)-H^+$) diffuse more rapidly than those from samples treated with EDTA salts (Na and K). It can be noticed that this behavior is more pronounced when λ is lower than 11.

These experimental observations can be rationalized on the following basis: when the counter-cation is H^+ , **proton hopping occurs via two mechanisms, vehicle (using sulfonated sites) and Grotthuss (using water network)**; this feature does not evidently exist when the counter-cation is Na^+ or K^+ . Indeed, translational diffusion is favored by **proton hopping** and this explains why, for a given water content (λ), diffusion coefficients of water in the acid form are systematically higher (by an order of magnitude at low λ) than in sodium or potassium forms. In fact, a similar explanation has been proposed for explaining the evolution of the water self-diffusion coefficients of Nafion 117 in acid and sodium forms, equilibrated in a fully hydrated state [17]. Now, **in the case of Nafion in acid form**, the very small values found for self-diffusion coefficients at low λ can be explained by the ability for a water molecule (or an oxonium ion) to jump from one sulfonated site to another (vehicle mechanism) and/or to proton exchange between water molecules. This latter possibility will become more important at higher λ values, in addition to normal molecular diffusion of water. This explains the increase of D with λ . **Concerning water diffusion in Nafion in sodium and potassium forms at low water content, it can be supposed that water is transported by solvation sites, considering that sulfonated groupings make a pair with Na^+ and K^+ cations. For a given self-**

diffusion coefficient of water, Nafion is more hydrated in sodium form than in acid form: for instance, for $D \sim 8.10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $\lambda = 3.5$ in the sodium form and drops to 2 in the acid form.

Moreover, from the λ values of Figure 4, it is seen that (i) sodium and potassium behave similarly, (ii) pH has no significantly effect ($\text{Na}^+(\text{M1})$ and $\text{Na}^+(\text{M2})$), (iii) in the acid form, there is no difference between the two treatments (with or without EDTA).

4.2 Water quantization from proton NMR spectra

In order to make sure that diffusion measurements are meaningful, it appears interesting to measure the amount of protons in a given sample. For that purpose, the signal intensity of standard ^1H spectra should be the proper tool. The NMR signal includes protons from H_2O , H^+ , H_3O^+ , aqueous complexes of water and possibly OH^- (from the other form of water), which usually are in rapid exchange. The intensity of the NMR signal was deduced from the integral of each spectrum, eventually corrected by means of a calibration curve. The latter was obtained with a series of $\text{H}_2\text{O}/\text{D}_2\text{O}$ samples containing a known amount of H_2O . Furthermore, the liquid contained in these samples has the same height as the membranes in the samples under investigation so that the measurement should provide a reliable value for the water content. Standard precautions regarding quantization by NMR were taken (repetition time between scans, identical spectrometer settings...). Results of NMR measurements and those obtained by the weighing procedure described above are gathered in Figure 5. These results can be summarized by the ratio of the number of protons determined by NMR to the number of protons as obtained by weighing (that is the protons from water molecules). In table 1, we have reported the average of these ratios for the two ways of sample equilibration used in this work and for the different forms (acid, sodium and potassium). At low water content for Na^+ and K^+ forms, the uncertainty of NMR measurements renders meaningless the comparison between the two methods (NMR and weighing). Still for Na^+ and K^+ forms, at higher water content, we do not observe any significant variation. Conversely, in the acid

form, NMR measurements provide systematically higher values. Evidently, this increase is due to the counter-cation H^+ which is not detected by the weighing method. These counter-cations are in fact chemically equivalent to the oxonium ion and are probably involved in the increase of the **proton hopping process**, thus in the increase of the diffusion coefficient. Notice that more H^+ cations seem to appear for “Vapor phase” samples than for “Liquid phase” samples. This can be understood on the following basis: as we are dealing with a ratio and as the amount of H^+ is constant, the ratio is necessarily larger at small water amount.

4.3 Impact of counter-cations on the self-diffusion measurements

Owing to **the fact (i) that the** number of solvation between sodium and potassium is different; **(ii) that the difference between cations is not visible** in the **usual** representation of the water self-diffusion coefficient vs. water content cannot make, we propose in Figure 6 **a different** representation (diffusion coefficient vs. relative humidity) which highlights the importance of counter-cations. **In contrast with** Figure 4, we clearly observe here a specific behavior for each counter-cation. This behavior is simply related to the affinity of cations for water (solvation number) and to the increase of the number of protons involved in the diffusion process.

5. Conclusion

Water translational diffusion in cation exchange membranes is one of the key parameters as far as the properties of these membranes are concerned. Here we have dealt with the influence of chemical treatments to which Nafion membranes can be subjected. If an EDTA salt is used, this induces an exchange of cations inside the membrane; Na^+ or K^+ (according to the nature of the EDTA salt) are substituted to protons of the acid form. Owing to well established properties (confirmed here in Figure 3), the water uptake depends strongly on the nature of the counter-cation. Indeed the main results of this study can be formulated as follows:

- 1) Diffusion is the same for Na^+ and K^+ forms for a given water content.
- 2) At a given water content, diffusion is faster in the acid form as compared with diffusion in sodium or potassium forms. This feature is noticeably accentuated at low water contents.
- 3) The quantity of protons has been measured by NMR and compared with the quantity of water obtained by weighing. As H^+ cations are not seen by the latter method, the NMR method is fully justified in order to emphasize the importance of H^+ as far as measured diffusions are concerned.

The interpretation of all these data rests on the ability for a water molecule to jump from one site to other **and/or** for a proton to exchange with another neighboring proton, in addition to the classical molecular diffusion at high water content. The lability of water in the acid form (oxonium ion) is more effective than in Na^+ or K^+ forms.

Finally, it turns out that the original representation of figure 6 summarizes well the essential findings of this study and, moreover, emphasizes the importance of counter-cations.

Tables

Table 1

Average ratio of the number of protons determined by NMR and weighing for the 5 Series (see text).

Samples	Vapor phase	Liquid phase
H^+	1.19	1.15
$\text{H}^+ - \text{Na}^+(\text{M1}) - \text{H}^+$	1.35	1.09
$\text{Na}^+(\text{M1})$	0.96	1.02
$\text{Na}^+(\text{M2})$	0.91	0.99
$\text{K}^+(\text{M2})$	0.68	1.00

Figure Captions

Figure 1. Thermo-gravimetric analysis (TGA) of a sample of Nafion[®] NRE- 212 in acid form.

Figure 2. ATR-FTIR spectra of Nafion: (a) H⁺ sample, (b) Na⁺(M1) sample.

Figure 3. Water content of Nafion[®] NRE 212 expressed by λ after 3 weeks (a) and 3 months (b) of equilibration as a function of relative humidity (vapor phase).

Figure 4. Evolution of the water self-diffusion coefficients of Nafion of the five different pre-treatments as function of λ .

Figure 5. Water content determined by NMR (dots) and weighing (grey) for acid, sodium and potassium forms. Percentage indicates the relative humidity for “vapor phase”. LW stands for samples humidified with liquid water (“liquid phase”).

Figure 6. Evolution of the water self-diffusion coefficients of Nafion with relative humidity (RH %).

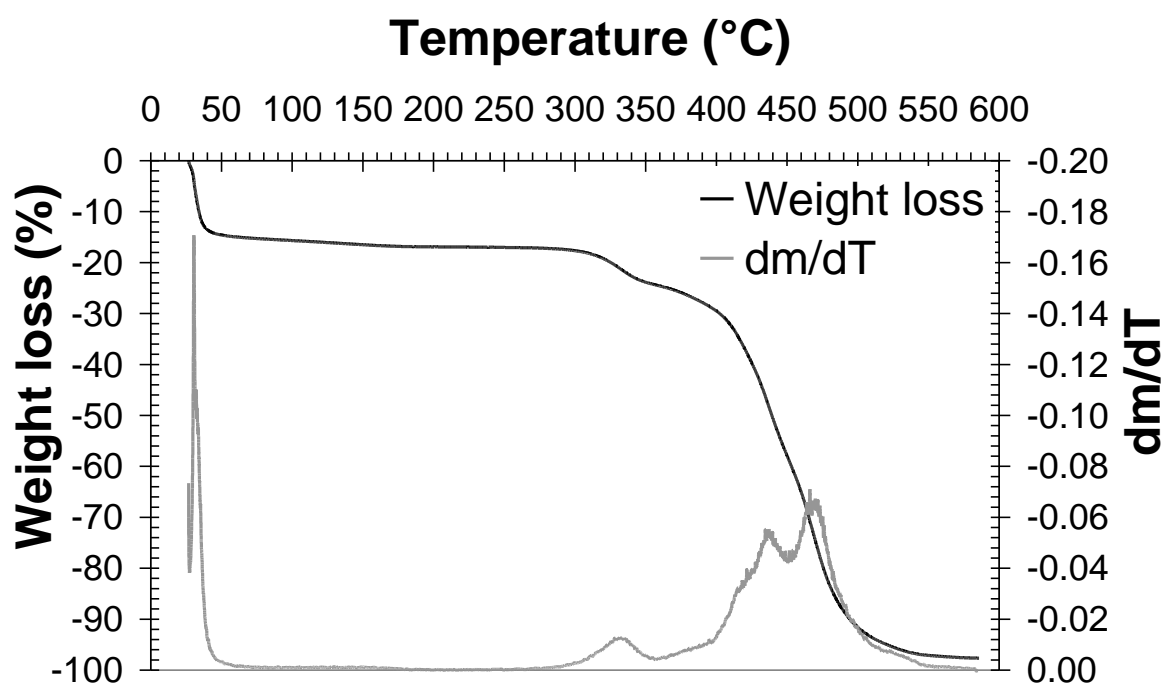


Figure 1.

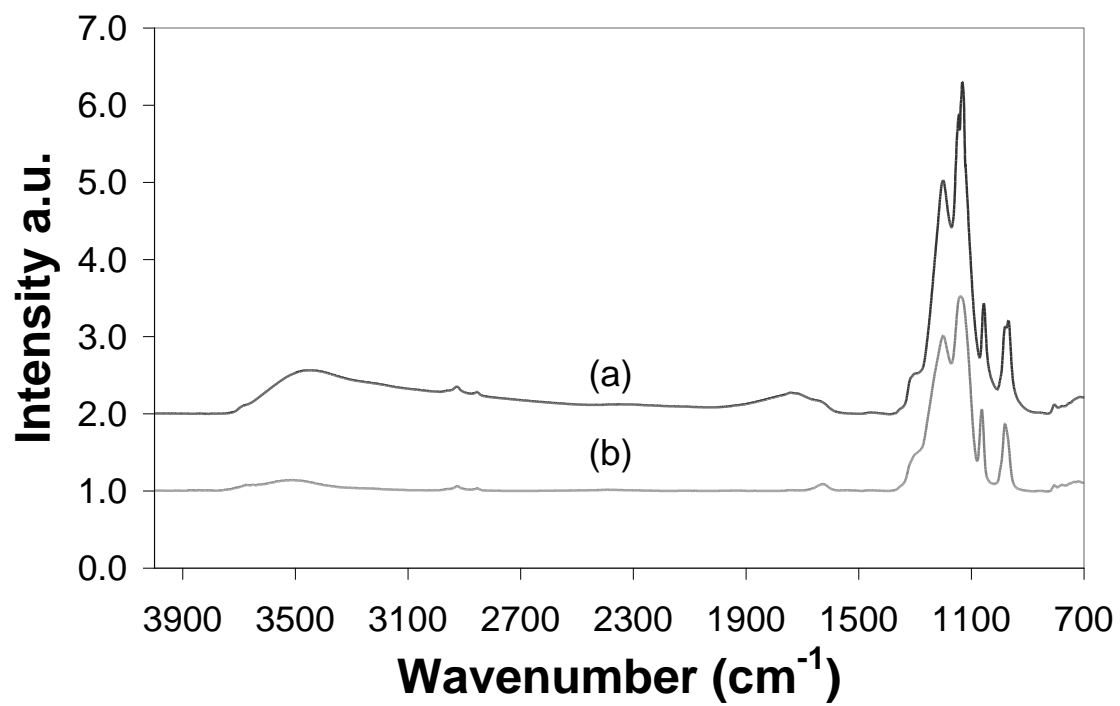


Figure 2.

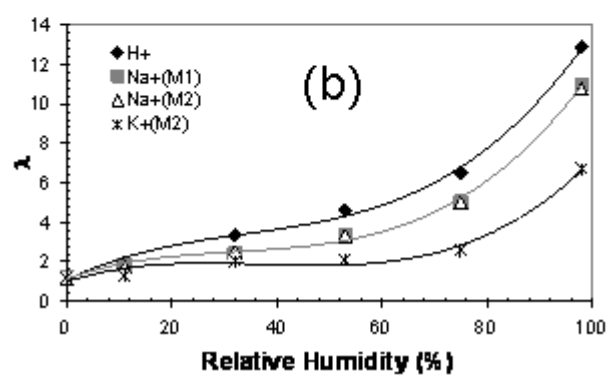
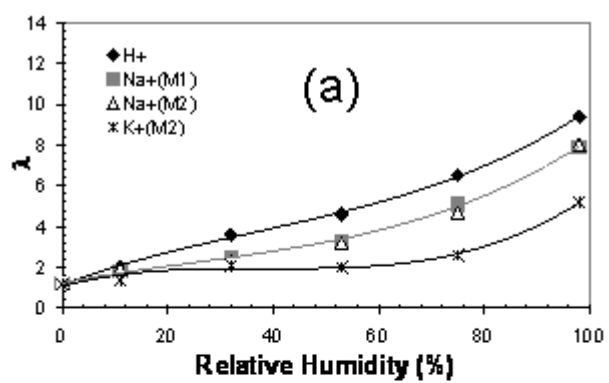


Figure 3.

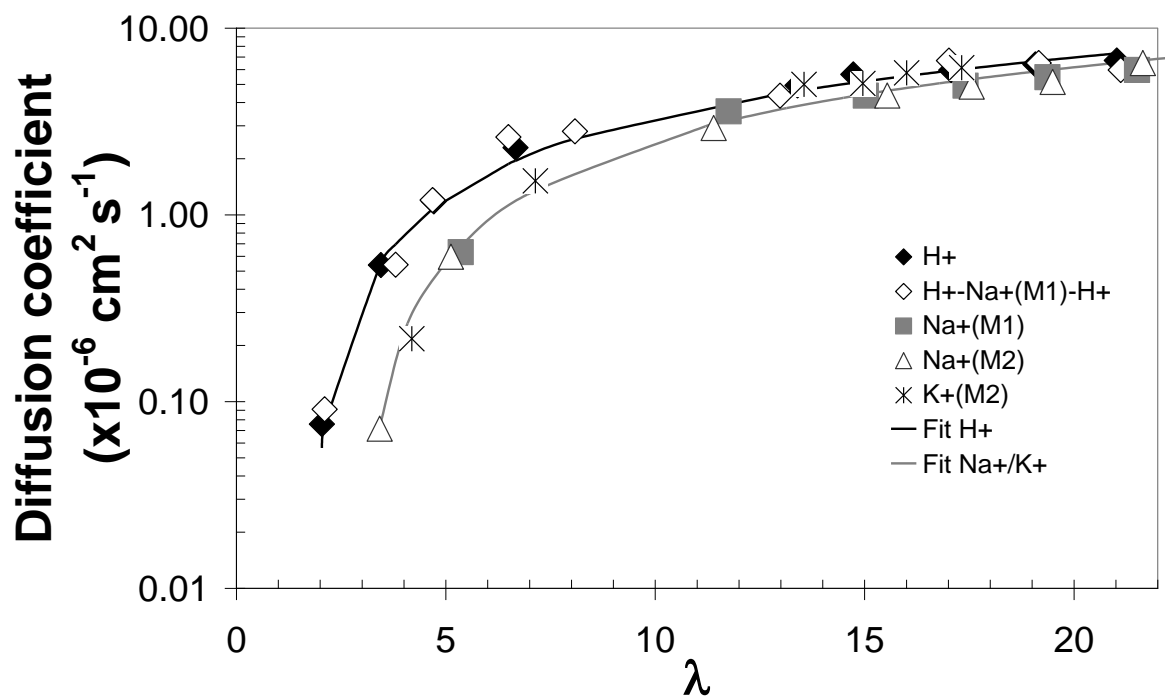


Figure 4.

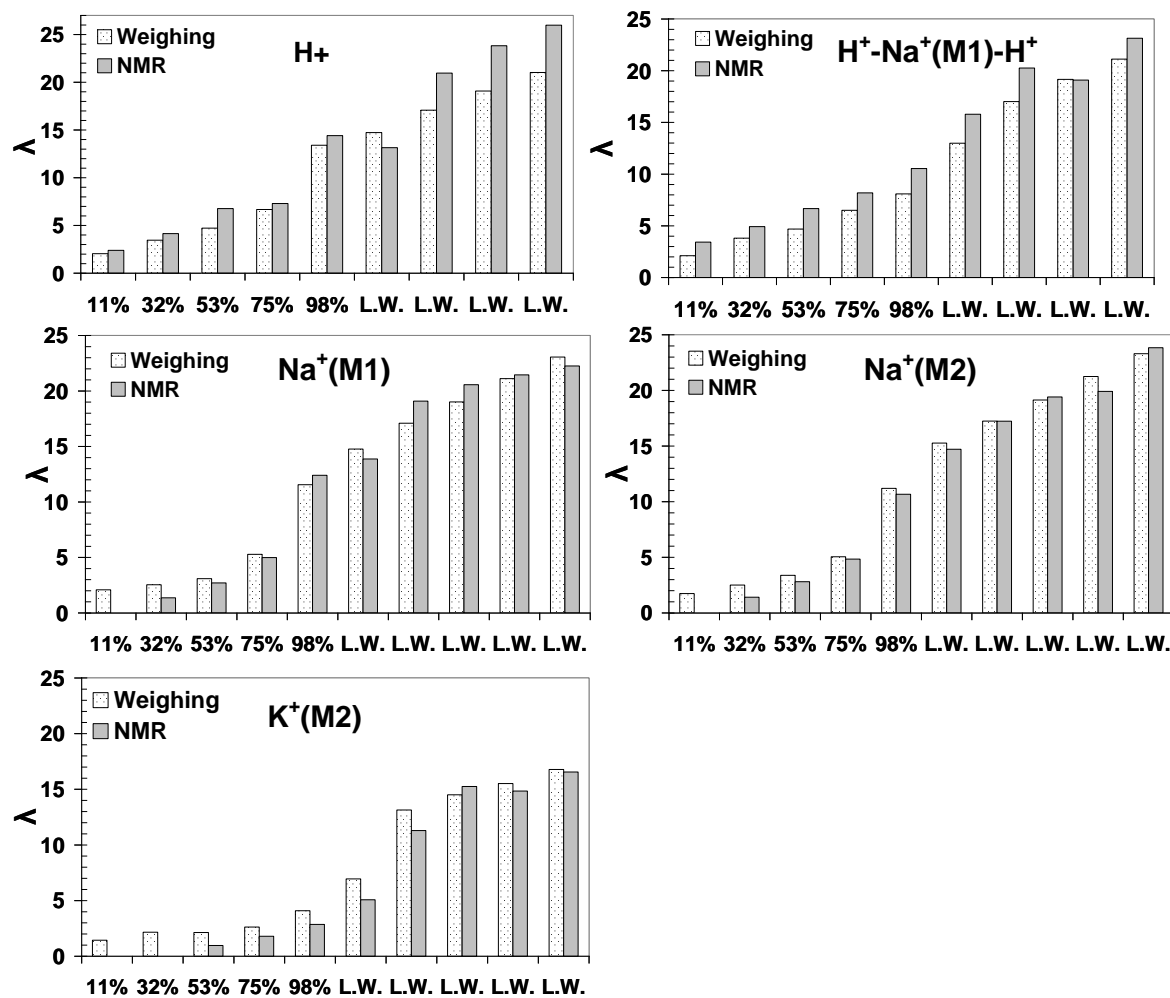


Figure 5.

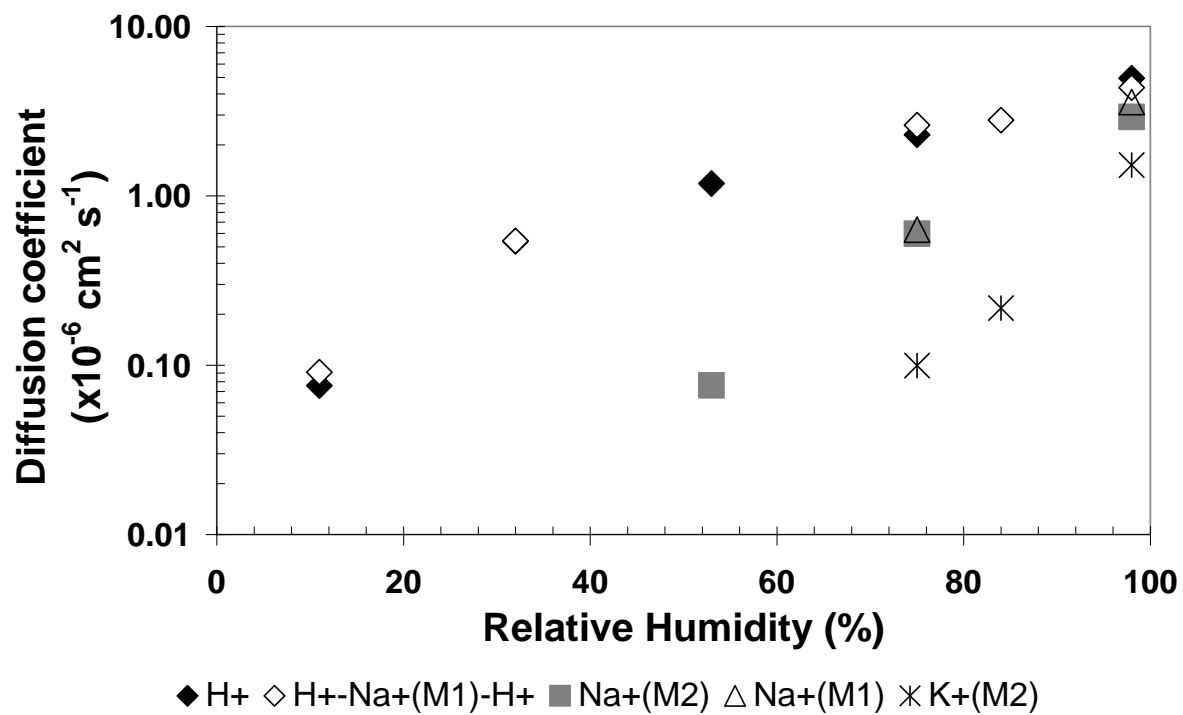


Figure 6.

References

- [1] S. Cukierman, Et tu, Grotthus! and other unfinished stories, *Biochim. Biophys Acta* 1757 (2006) 876-885.
- [2] K. A. Mauritz, R. B. Moore, State of understanding of Nafion, *Chem. Rev.* 104 (2004) 4535-4585.
- [3] M.A. Hickner, H. Ghassemi, Y. S. Kim, B.R. Einsla, J. E. McGrath, Alternative polymer systems for proton exchange membranes (PEMs), *Chem. Rev.* 104 (2004) 4587-4612.
- [4] C. E. Evans, R. D. Noble, S. Nazeri-Thompson, B. Nazeri, C. A. Koval, Role of conditioning on water uptake and hydraulic permeability of Nafion membranes, *J. Memb. Sci.* 279 (2006) 521-528.
- [5] S. Slade, S.A. Campbell, T.R. Ralph, F.C. Walsh, Ionic conductivity of an extruded Nafion 1100 EW series of membranes, *J. Electrochem. Soc.* 149 (2002) A1556-A1564.
- [6] E. O. Stejskal, J. E. Tanner, Spin-diffusion measurements: spin-echoes in the presence of a time-dependent field gradient, *J. Chem. Phys.* 42 (1965) 288-292.
- [7] T.E. Tanner, Use of the Stimulated Echo in NMR Diffusion Studies, *J. Chem. Phys.* 52 (1970) 2523-2526.
- [8] T.A. Zawodzinski, M. Neeman, L.O. Sillerud, S. Gottesfeld, Determination of water diffusion coefficients in perfluorosulfonate ionomeric membranes, *J. Phys. Chem.* 95 (1991) 6040-6044.
- [9] X. Gong, A. Bandis, A. Tao, G. Meresi, Y. Wang, P.T. Inglefield, A.A. Jones, W.-Y. Wen, Self-diffusion of water, ethanol and decafluoropentane in perfluorosulfonate ionomer by pulse field gradient NMR, *Polym.* 42 (2001) 6485-6492.
- [10] I. Nicotera, T. Zhang, A. Bocarsly, S. Greenbaum, NMR characterisation of composite polymer membranes for low-humidity PEM fuel cells, *J. Electrochem. Soc.* 154 (2007) B466-B473.

- [11] B. MacMillan, A. R. Sharp, R. L. Armstrong, An n.m.r. investigation of the dynamical characteristics of water absorbed in Nafion, *Polym.* 40 (1999) 2471-2480.
- [12] A. Y. Nosaka, Y. Nosaka, Slow morphological change of perfluorinated ionomer as deduced from ¹H NMR spectra of confined water, *J. Pow. Sour.* 180 (2008) 733-737.
- [13] S. Ochi, O. Kamishima, J. Mizusaki, J. Kawawura, Investigation of proton diffusion in Nafion 117 membrane by electrical conductivity and NMR, *Solid State Ionics* 180 (2009) 580-584.
- [14] S.L. Codd, D.T. Howe, J.D. Seymour, E.H. Werre, S.C. Busse, E.S. Peterson, Magnetic resonance microscopy of heterogeneity in polymer electrolyte membranes, *Appl. Magn. Reson.* 32 (2007) 13-24.
- [15] N. H. Jalani, R. Datta, The effect of equivalent weight, temperature, cationic forms, sorbates, and nanoinorganic additives on the sorption behavior of Nafion, *J. Memb. Sci.* 264 (2005) 167-175.
- [16] M. Bass, V. Freger, Hydration of Nafion and Dowex in liquid and vapor environment: Shroeder's paradox and microstructure, *Polym.* 49 (2008) 497-506.
- [17] M. Saito, N. Arimura, K. Hayamizu, T. Okada, Mechanims of ion and water transport in perfluorosulfonated ionomer membranes for fuel cells, *J. Phys. Chem. B* 108 (2004) 16064-16070.
- [18] N.J. Bunce, S. J. S., C. A. Fyfe, Proton NMR method for the quantitative determination of the water content of the polymeric fluorosulfonic acid Nafion-H, *Macromol.* 19 (1986) 333-339.
- [19] J. Zhang, M.V. Giotto, W.-Y. Wen, A. A. Jones, An NMR study of the state of ions and diffusion in perfluorosulfonate ionomer, *J. Memb. Sci.* 269 (2006) 118-125.
- [20] S. C. Yeo, A. Eisenberg, Physical properties and supermolecular structure of perfluorinated ion-containing (nafion) polymers, *J. Appl. Polym. Sci.* 21 (1977) 875-898.

- [21] M. Lavorgna, M. Gilbert, L. Mascia, G. Mensitieri, G. Scherillo, G. Ercolano, Hybridization of Nafion membranes with an acid functionalised polysiloxane: Effect of morphology on water sorption and proton conductivity, *J. Memb. Sci.* 330 (2009) 214-226.
- [22] F. Xu, C. Innocent, B. Bonnet, D. J. Jones, J. Rozière, Chemical modification of perfluorosulfonated membrane with pyrrole for fuel cell application: preparation, characterisation and methanol transports, *Fuel Cells* 5 (2005) 398-405.
- [23] J.-C. Perrin, S. Lyonnard, A. Guillermo, P. Levitz, Water dynamics in ionomer membranes by field-cycling NMR relaxometry, *J. Phys. Chem. B* 110 (2006) 5439-5444.