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Tangential and normal conductivities of Nafion® membranes used in polymer electrolyte fuel cells

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Abstract

Conductivity measurements of Nafion® 112, 115 and 117 membranes in the normal direction are reported in this paper. The measurements were made by means of impedance spectroscopy as a function of temperature. The conductivity was measured directly on hot-pressed carbon paper/membrane/carbon paper samples fully immersed in deionized water. The data show that Nafion® membranes are really isotropic and that tangential and normal direction conductivity measurements gave the same results when the same hydration level was utilized.
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Keywords: Ion-exchange membranes; Nafion®; Conductivity; Polymer electrolyte fuel cells

1. Introduction

The knowledge of ion conductivity in ion-exchange membranes is required for the design of numerous devices that employ these materials. In particular, the proton conductivity plays a significant role in controlling the performance of polymer electrolyte fuel cells (PEFCs).

Many groups have previously studied the conductivity of Nafion® membranes [1–23] and a large quantity of data has been published. The main difficulty in the analysis and comparison of these works is related with the utilization of different measuring methods. It is very difficult to rationalize all these data, but it appears clear that conductivity measurements are influenced by a number of parameters such as: (a) cell geometry, (b) technique employed, (c) electrolyte and (d) sample preparation method.

Two kinds of cell geometry were cited in the literature regarding the direction of the conductivity measurements, i.e. tangential [1–5,15] and normal [4–14,16]. In this paper, we summarize in three tables the literature data on these measurements and, to better compare the results, the conductivities were always calculated from the area resistance with respect to Nafion® 117 nominal thickness (183 μm). The values presented between brackets in the tables are referred

to calculations using hydrated thicknesses, when they were reported by the authors. The tangential direction conductivity (TDC) method is known [4] to be relatively insensitive to the contact impedance at the current carrying electrodes, but does not resemble the normal direction ionic motion through a membrane inside a fuel cell. This observation implies that the normal direction conductivity (NDC) method is of paramount importance when an anisotropic membrane must be tested for use in fuel cells.

Table 1 shows the results of TDC of Nafion® obtained at room temperature by several researchers. Zawodzinski et al. [1] and Sone et al. [2] reported that conductivity measurements are strongly influenced by the water content of Nafion® membranes. The first three references in Table 1 are referred to a fully hydrated Nafion® 117 membrane with maximum number of water molecules per sulfonate group (λ) of 20–22. By using this procedure [1], lower values of conductivity were obtained when the membrane was not fully immersed in deionized water, but only settled in water vapor gas at different relative humidities (RH). The same authors [1,2] agreed that for Nafion® 117 the maximum number of water molecules per sulfonate group is 13–14 at 100% RH and 30 °C. At room temperature, Sumner et al. [4] presented a higher value (λ=19), which is probably overestimated. Considering only the measurements of a fully hydrated membrane in Table 1, we obtained an average TDC of $96 \pm 8 \, \mathrm{mS \, cm^{-1}}$ at room temperature. Lower values of area resistance and conductivity were registered [1–4] when

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Table 1
Tangential direction conductivity measurements of Nafion[®] 1100 EW membranes

$\lambda = n\mathrm{H_2O/SO_3H}$	Technique	σ (mS cm^{-1})	R (Ω cm^2)	T (°C)	Reference
22–23[a]	AC impedance (5 kHz)	102	0.180	30	[1]
22–23[a]	AC impedance (10 kHz)	91 (100)	0.200	25	[15]
Wet state	AC Coaxial Probe method	72 (86)	0.255	22	[6]
18–19[b]	AC impedance (100 kHz)	81	0.225	25	[3]
0–14[b]	AC impedance (5 kHz)	5–63	3.5–0.29	30	[1]
19[b]	AC impedance (100 kHz)	52	0.350	20	[4]
14[b]	AC 4 electrodes (20 kHz)	15–43 (17–47)	1.2–0.425	45	[2]

[a] Membrane fully immersed in water.
[b] Membrane in controlled relative humidity.

λ decreased. The data show that the control of this parameter is of great importance for this kind of measurement. Gardner and Anantaraman [6] stored Nafion[®] samples in distilled water and just before use wiped them quickly and inserted them in the measurement system at undefined RH. Due to this procedure and to the use of a different technique, the result is hardly comparable with those of other works.

Among the NDC measurements [8,11,12,14,15], we have found two different methods: (1) membrane fully immersed in the center of a cell containing an acid (sulfuric or chloridric) and not placed in contact between two electrodes and (2) membrane pressed directly between two electrodes.

The data collected in Table 2 show that the first kind of normal direction conductivity (NDC-1) measurement appears more scattered than those performed with the membrane in the same plane of the electrodes (TDC) (Table 1). To better compare the results, also in this case the conductivities were calculated from the area resistance values using the Nafion[®] 117 nominal thickness. As cited by Slade et al. [9] and Tricoli et al. [14], the obtained conductivities were affected by an error due to the background electrolyte resistance measurements, which represent 60–80% of the cell resistance. Moreover, an influence of absorbed acid on membrane conductivity has been hypothesized [9]. The average NDC-1 value is 92 ± 33 mS cm^{-1} and, because of this high error, this measurement cannot be used to demonstrate the equality between tangential and normal conductivities.

Table 3 summarizes the second method for measuring the normal direction conductivity (NDC-2), where Nafion[®] membranes were pressed directly between two electrodes. This type of measurement appears to be more related with a real fuel cell system, since the membrane is pressed between carbon electrodes and the active component of the conductivity is the normal one. However, the obtained values are lower than TDC and NDC-1 and this could be a consequence of a lower content of water molecules per sulfonate group in the membranes pressed between the electrodes ($\lambda < 22$). In fact, by using a cell designed with a variable number (2–10) of well-hydrated membranes ($\lambda = 23$), only Halim et al. [22] obtained a conductivity value comparable to the previous methods. This should demonstrate that when the water contents are similar, the tangential and normal conductivities should be in the same range. Contrasting this hypothesis and using both the tangential and normal configurations,

Table 2
Normal direction conductivity (NDC-1) measurements of Nafion[®] 1100 EW membranes in acidic electrolyte

Electrolyte	Technique	σ (mS cm^{-1})	R (Ω cm^2)	T (°C)	Reference
1 M $\mathrm{H_2SO_4}$	DC technique (4 point probe)	140 (160)	0.130	25	[9]
1 M $\mathrm{H_2SO_4}$	DC technique (4 point probe)	129 (140)	0.142	25	[15]
1 M $\mathrm{H_2SO_4}$	DC current pulse	70 (88)	0.260	20	[16]
10^{-5} M $\mathrm{H_2SO_4}$	DC technique (4 point probe)	55–85 (62–94)	0.327–0.215	20	[14]
1 M $\mathrm{H_2SO_4}$	AC impedance	71	0.259	25	[20]
2 M HCl	DC technique	61 (66)	0.300	25	[23]

Table 3
Normal direction conductivity (NDC-2) measurements of Nafion[®] 1100 EW membranes in direct contact with electrodes

$\lambda = n\mathrm{H_2O/SO_3H}$	Technique	σ (mS cm^{-1})	R (Ω cm^2)	T (°C)	Reference
Wet state	AC impedance	34	0.530	25	[13]
Wet state	AC coaxial probe	24	–	22	[6]
3	AC impedance	3–10	–	25	[7]
23	AC impedance	82 (90)	0.224	20	[22]
Wet state	AC impedance	83	0.220	30	[20]
12–13	AC impedance	49	0.375	25	This work

Gardner and Anantaraman [6] cited that the specific conductivity of Nafion® 117 is anisotropic and the tangential conductivity is almost 3.6 times higher than the normal conductivity. Differently, Nouel and Fedkiw [19] mentioned that the tangential and normal conductivities are essentially equal and obtained the same value (140 mS cm^{-1}) for both Nafion® 112 and 117 membranes, but only at 65 °C. The results of Zawodzinski et al. [21] agree with Nouel's tangential conductivity of Nafion® 117 at 65 °C. On the other hand, no works were found that confirm the high Nouel's normal direction conductivity. The question arises whether the NDC-2 measurements depends on the cell geometry, and more specifically on the capacity of fully hydrated membranes, or Nafion® is really anisotropic and the NDC measurements should be lower than the TDC ones.

In this work, we have measured the normal direction conductivities of Nafion® 112, 115 and 117 membranes using a new ex situ method where the samples inserted between two carbon paper (CP) porous disks were hot pressed in an analogous way as that of membrane electrode assemblies (MEAs). A control of humidification of the tested membranes was carried out for comparison with the literature data. The data show clearly that the same results can be obtained with the TDC and NDC-2 methods considering the same level of water molecules per sulfonate group. The presented method can be considered as a valid and simple alternative for the tangential direction measurements, and is able to give results similar to those obtained by in situ measurements.

In addition to the conductivity measurements, Nafion® samples were extensively characterized in order to verify some physicochemical data such as density, equivalent weight, water uptake and thickness that were poorly reported in the literature especially for Nafion® 112 and 115 membranes. These measurements showed unexpected differences as for the equivalent weight, and some explanations were proposed to justify them.

2. Experimental

2.1. Membrane pretreatment and hot pressing

Commercially available Nafion® 112, 115 and 117 membranes were used as reference materials. The membranes were pretreated in boiling 3 wt.% H$_2$O$_2$ for organic residue elimination followed by rinsing in boiling water. To assure the complete H$^+$ form of the membranes, the samples were treated in boiling 20 wt.% HNO$_3$ followed by rinsing twice in boiling water (at least 1 h for each step).

The membranes (14 mm diameter) were hot pressed between two Toray TGPH090 carbon paper disks (11 mm diameter, 0.27 mm thickness) with 46.5 kg cm^{-2} at 130 °C for 5 min in an analogous way as MEAs are usually assembled. The hot-pressed membranes were stored in deionized water prior to the conductivity measurements.

2.2. Ion-exchange capacity and equivalent weight measurements

Ion-exchange capacities (equivalent weights, EW) were measured by titration [24]. The samples were immersed in 0.1 M NaCl solution for 24 h under continuous stirring. To assure complete ion-exchange, the samples were immersed again in another 0.1 M NaCl solution for additional 24 h. The two solutions were mixed and the displaced H$^+$ ions were titrated with 0.1 M NaOH solution using phenolphthalein indicator. The NaOH titrant was standardized against dried reagent grade benzoic acid (Rudi Pont).

2.3. Water uptake

The water uptake and the number of water molecules per sulfonate group were calculated for both the free membranes and the membranes in the hot-pressed samples. Some membrane samples (1.5 cm^2 area) were weighed in the hydrated and dehydrated forms before the CP/membrane/CP sample preparation. The procedure of weighing hydrated membranes implied surface water elimination by carefully pressing the samples with a wet cotton cloth followed by quick drying with a kimwipe. The weight of the fully hydrated samples was obtained by extrapolating to zero the weight loss as a function of time. The number of water molecules per sulfonate group was calculated using the following equation:

$$\lambda = \text{EW} \left(\frac{(m_{\text{wet}} - m_{\text{dry}})/m_{\text{dry}}}{18} \right) \tag{1}$$

where m_{wet} and m_{dry} are the weights of the fully hydrated and dried membranes, respectively. The water uptake is the term between brackets reported in percent. The term λ of the membrane in the hot-pressed sample was obtained considering the weight of the carbon paper disks using the following equation:

$$\lambda = \text{EW} \left(\frac{(m'_{\text{wet}} - m_{\text{dry}})/m_{\text{dry}}}{18} \right) \tag{2}$$

where m'_{wet} is the weight of the membrane obtained by the difference between the weight of the wet CP/membrane/CP sample and the weight of the two carbon paper disks hydrated in the same conditions.

2.4. Density measurements

Wet membrane densities were determined using the hydrostatic weighing method [25] as follows. Membrane circles (3 cm diameter) were rinsed in water, and the surface water was blotted with kimwipes. The samples were weighed in a Gibertini E42-B balance. The rinsing, blotting and weighing procedures of the membranes were repeated 10 times to obtain an average sample weight, defined as air mass, m, and standard deviation. The same procedure was done for weight measurements performed in water with a Sartorius BP 210 S balance. The samples were put on a

weighing pan hung to a support and immersed in the center of a beaker half-filled with distilled water. The average value was recorded as the wet mass, m_w, and the membrane density was calculated using the following equation:

$$d = \frac{m(\rho_{\text{water}} - \rho_{\text{air}})}{m - m_w} + \rho_{\text{air}} \tag{3}$$

where ρ_{water} is the water density ($0.9982\,\text{g cm}^{-3}$) and ρ_{air} the air density ($0.00129\,\text{g cm}^{-3}$) at room temperature and 760 mmHg.

2.5. Thickness measurements

Membrane thicknesses were measured with an ATS FAAR digital micrometer at several points of the samples. After equilibrating the membranes with distilled water followed by careful surface drying with kimwipes, the average wet thicknesses were measured at room temperature. The dry thicknesses were measured either after keeping the samples in a dry room for 24 h or after drying them in a furnace at 110 °C for 1 h.

2.6. Proton conductivity measurements

The conductivity measurements were performed in the two-electrode AC impedance mode using a Solartron 1260 frequency response analyzer (Schlumberger). The spectra were recorded between 100 and 1 kHz with 10 points per decade at a maximum perturbation amplitude of 10 mV.

The membrane resistance, R_m, was obtained by the difference between the measured resistance, R_{total}, and the contribution of the empty and short-circuited cells, R_{short}. Both values were obtained by intercepting the impedance curve to the real axis. For instance, Fig. 1 illustrates the contribution of R$_{\text{short}}$ in a measurement done for a CP/Nafion® 117/CP

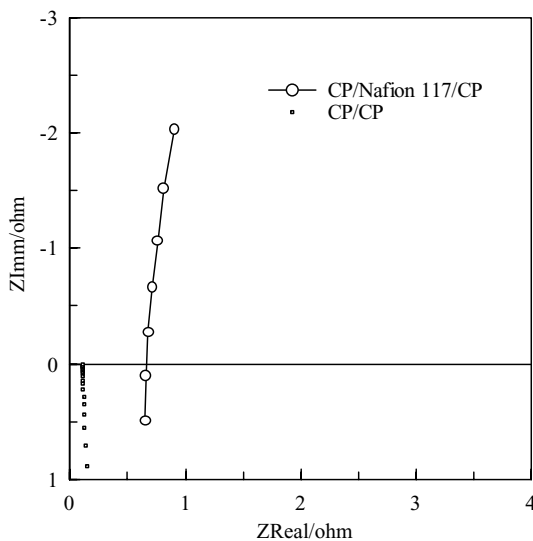
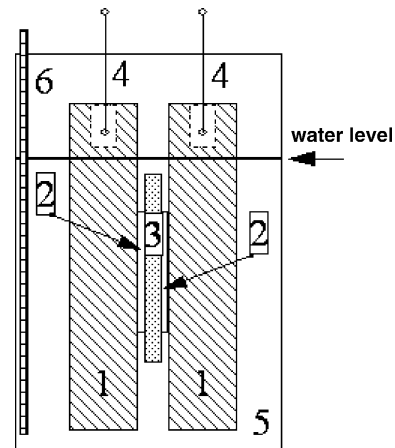Fig. 1. Nyquist plots of conductivity cell with CP/Nafion® 117/CP sample or CP/CP short-circuited at 25 °C.

Fig. 2. Schematic illustration of a conductivity cell for Nafion® membranes: (1) graphite current collectors; (2) carbon paper electrodes; (3) membrane; (4) electric connection; (5) beaker filled with deionized water and (6) thermocouple.

sample. The Zview 2.1b software by Scribner Associates Inc. was used for the impedance data analyses.

The measurements were carried out in a conductivity cell (Fig. 2) consisting of two XM9612 current collector graphite disks (35 mm diameter, 5 mm thickness) produced by SGL Carbon Group (Germany). The electrical contacts were made by two gold jacks plugged into holes at the top of the graphite electrodes.

The CP/membrane/CP samples were contacted between the two graphite electrodes that were pressed together with a peg at 1.37–$1.47\,\text{kg cm}^{-2}$. By using this pressure range, the area resistance was found to be independent of the pressure applied by the peg if the CP/membrane/CP sample was previously hot pressed. The system was partially immersed in a beaker filled with deionized water and only the electric connections in the graphite collector were kept outside (Fig. 2). In this configuration, the active area of the electrodes was $0.95\,\text{cm}^2$ with membrane exceeding area of about $0.59\,\text{cm}^2$. The membrane exceeding parts fully immersed in deionized guaranteed a constant hydration level and did not make electric contact with the graphite current collectors.

The beaker in Fig. 2 was fully immersed in a Haake thermostatic bath for temperature control by means of a thermocouple placed also inside the beaker.

To ensure the reproducibility of our measurements, six different CP/Nafion® 112/CP samples were prepared as described above. The samples were inserted in the cell at 25 °C and the conductivity was measured three consecutive times for each sample. The conductivity was $23\,\text{mS cm}^{-1}$ with a standard deviation of about ± 1.

3. Results and discussion

3.1. Density and water uptake measurements

The density value found for the Nafion® 112, 115, 117 series in the wet state was practically the same, i.e.

Table 4
Water uptake, λ, and EW of Nafion® 112, 115 and 117 (E-Form)

Nafion®	%$_{water}$	$\lambda = n\text{H}_2\text{O}/\text{SO}_3\text{H}$	EW
117	35 ± 1	22.6 ± 0.9	1100 ± 15
115	39 ± 2	22.1 ± 1.5	1075 ± 15
112	36 ± 4	20.9 ± 2.6	1020 ± 15

Table 5
Nafion® thickness: nominal [32], wet and dried at $110\,^{\circ}\text{C}$ for 1 h

Sample	$d_{nominal}$ (µc)	d_{wet} (µc)	d_{dry} (µc)	%
117	183	203 ± 2	177 ± 4	-12.8
115	127	149 ± 9	124 ± 2	-16.7
112	51	55 ± 3	39 ± 5	-20.0

$1.6 \pm 0.1\,\text{g}\,\text{cm}^{-3}$. Within the error uncertainty, this result well fits with those obtained by other authors [25,33] for Nafion® 117. As shown by several authors [1,2,7,26], the water uptake plays a determining role in the conductivity measurements. Table 4 shows the water uptake and the relative λ values found for Nafion® 112, 115 and 117 as well as the EWs measured by titration. Eq. (1) correlates all these parameters and the results show that for thinner membranes the water uptake and λ remains constant and EW decreases. Anyway, the evaluation of water uptake was very difficult due to the measuring procedure required to eliminate the surface water before weighing the wet samples. This methodology is, however, very much influenced by the carrier of the measurements who macroscopically establishes the complete elimination of surface water. Moreover, the influence of temperature, relative humidity and the time employed between the water elimination and the weight measurement were observed. The sample thickness can also play a relevant role. As cited in Section 2.3, the use of the extrapolation method for small area samples showed to minimize the error in the weighing of the wet samples (Fig. 3). However, we emphasize that, independently of the pretreatment imposed to the samples, only an average value of water uptake for the Nafion® 112, 115, 117 series can be given.

Most of the literature data regard Nafion® 117, whilst the 112 and 115 membranes are generally considered as having the same equivalent weight (1100) and water uptake (35–38%$_{water}$) [32]. We have found a decrease of EW and, within the error limit, a constant value (average of $37 \pm 2\%_{water}$) for the water uptake and λ, as reported in Table 4. This result seems to be in contrast with the semi-empirical equation proposed by Yeager et al. [27], %$_{water} = A \exp(B/\text{EW})$, and the results obtained by Hinatsu et al. [24] who observed an increase of water uptake
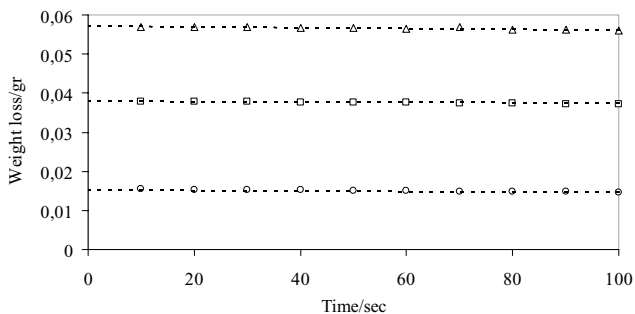
with decreasing EW. However, the error inherent in the water uptake results does not allows us to further conclude about this point.

3.2. Thickness measurements

Table 5 shows the thickness of Nafion® 1100 membranes in the dry and hydrated forms and the % reduction from wet to dry states. Thinner membranes showed higher percentage of thickness reduction between the wet and dry forms. We can rationalize the results considering that a lower EW means a higher acid capacity. In consequence of the higher number of sulfonate groups, more water molecules are supposed to be absorbed, thus increasing the water uptake.

In contrast with our results, Slade et al. [9] did not find a tendency in EW for Nafion® 1100 (112, 115, 117), giving very scattered values (1010–1075). In addition, they measured a slight decrease of water uptake (from 39 to 36%) for the 117, 115, 112 series. Besides, the same authors measured an almost constant thickness reduction from wet to dry states in the range 10–14%.

The water uptake is affected by many variables. As reported above, it is known [22,24,26,27] that for fully immersed samples the water uptake increases with decreasing EW. In addition, for a fixed EW, it increases with increasing bath temperature. Moreover, it depends on the polymer activation process, and thus the protocol treatment of the samples is relevant for a correct comparison of the conductivity data. In particular, the temperature of the thermal treatment and the subsequent rehydration process are fundamental. Normally, heat treatments in the temperature range 80–$130\,^{\circ}\text{C}$ produce a reduction of water uptake (%$_{water}$) and, consequently, a reduction of λ. This effect is due to a change in the membrane structure as the temperature reaches the glass transition temperature (T_g), i.e. 120–$130\,^{\circ}\text{C}$ [28]. When the membrane is well hydrated, the hydrophilic clusters in Nafion® contain dissociated sulfonate groups that help maintain the backbone structure through coulombic repulsion. When the membrane becomes dry, the sulfonate groups are not dissociated and the clusters collapse. The situation gets worse if a dry membrane is heated, as in the hot-pressing process. In this situation, the rehydration process must be done at high temperature. Four forms of Nafion® have been detected as a function of the thermal treatment [1,2,24,29]: membrane without heat treatment or the expanded form (E-Form), membrane heat treated at $80\,^{\circ}\text{C}$ or the normal form (N-Form), membrane heat treated at $105\,^{\circ}\text{C}$ or the shrunken form (S-Form), and membrane

Fig. 3. Weight loss vs. time of wet Nafion® 112 (○), 115 (□) and 117 (△) samples.

Table 6
Dependence of the thermal treatment of Nafion® 117 (E-Form) on the water uptake (%$_{water}$) and conductivity measured at 45 °C [2,24]

	%$_{water}$	$\lambda = n\text{H}_2\text{O}/\text{SO}_3\text{H}$	Heat treatment (°C)	σ (mS cm^{-1})[a]
E-Form	37	23	–	47
N-Form	22	13	80	35
S-Form[a]	18	11	105	22
FS-Form	–	–	120	17

[a] Using TDC at 100% RH corresponding to $\lambda \approx 13$–14.

Table 7
Dependence of the rehydration temperature on the water uptake of Nafion® 117 (E-Form) dried at 105 °C (S-Form) [1]

	E-Form	S-Form rehydration temperature		
		27 °C	65 °C	80 °C
%$_{water}$	34.3	19.6	22.9	26.2
λ	21	12	14	16

heat treated at 120–130 °C or the further shrunken form (FS-Form). Table 6 summarizes the results of Sone et al. [2] and Hinatsu et al. [24] showing the water uptake for these four forms upon immersion in water at 25 °C, and also the conductivities measured at 45 °C. As shown by Zawodzinski et al. [1], the effect is partially reversible for S-Form samples as the water uptake can be increased again by rehydrating the membrane in a water bath. Table 7 shows the dependence of the hydration level on the bath temperature only for the S-Form. We verified through our measurements that the rehydration of the S-Form samples immersed in water at 80 °C does not restore the previous E-Form water uptake. We also studied the S-Form/E-Form hydration process and, in addition to the results of Table 7, we observed that the as-received Nafion® 117 membranes cannot be considered as E-Form samples. In fact, these membranes showed a lower water uptake (27%) than the same sample subjected to purification and acidification pre-treatments described in Section 2.1. Moreover, we boiled a S-Form sample and we verified that at least 2 h are needed to obtain the full hydration of the membrane up to the original E-Form water uptake.

3.3. Proton conductivity measurements

In view of these results, the first effort was to consider the thermal treatment applied and to control and evaluate the water uptake and λ of the samples utilized in the NCD-2 measurement. In addition to a short thermal treatment at 130 °C for 5 min (similar to the above-cited FS-Form), we also have a hot-pressing stage that could have an influence on the water uptake. Using a gold/membrane/gold configuration with 7 cm^2 area hot pressed at 130 °C for 5 min with 140 kgf/cm^2, Cappadonia et al. [7] obtained a λ of about 3 after storing the samples in water at room temperature for 72 h, and found very small conductivities. In this sense, we can presume that the hot-pressing procedure reduces the membrane volume promoting a further decrease of the water amount in the membrane. In this work, to increase the water amount in the CP/membrane/CP sample, the gold disks were substituted for porous carbon papers and, in addition, a smaller membrane area (0.95 cm^2) was used.

The results in Table 8 confirm that for an-unpressed Nafion® 117 sample the heat treatment at 130 °C effectively reduces λ from 22 to 15 water molecules per sulfonate group and the rehydration process at 65 °C for 2 h increases λ up to 17. Moreover, when the same membrane was hot pressed between two carbon paper disks, the reduction of λ reached 7.5. The rehydration of the Nafion® membrane in the hot-pressed sample at 65 °C increased again its λ level to 13, but the value did not reach that of the unpressed membrane. These results were also verified by Slade et al. [9] who measured a decrease of λ from 23.2 to 16.3 of hot-pressed Nafion® 117 membranes after reimmersion in water at 80 °C.

Fig. 4 shows an Arrhenius plot of conductivity as a function of temperature of Nafion® 112, 115 and 117 membranes. The data were obtained by means of Eq. (4), where σ is the conductivity (S cm^{-1}), R the measured resistance (Ω), l the membrane nominal thickness (cm) and S the membrane area (cm^2)

$$\sigma = \frac{l}{R \times S} \tag{4}$$

From the slope of the linear regression, the activation energy (E) for the proton conduction was obtained for

Table 8
Dependence of the thermal treatment and rehydration temperature on the water uptake of Nafion® 117 (E-Form) free or hot pressed at 130 °C between carbon papers

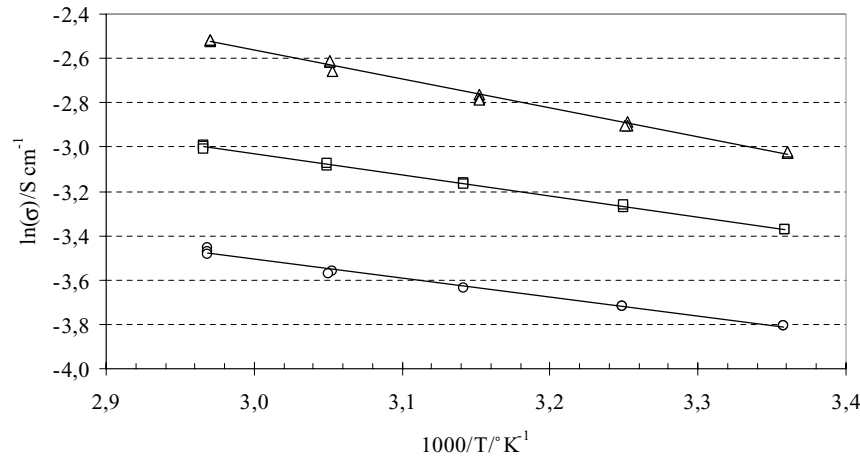| Sample	Treatment	%$_{water}$	λ
N117[a]	E-Form before heating at 130 °C for 5 min	36 ± 1	22
N117	Heated at 130 °C and rehydrated in H$_2$O at 25 °C for 2 days	25 ± 1	15
N117	Rehydrated in H$_2$O at 65 °C for 2 h	28 ± 1	17
CP/N117/CP	Hot pressed at 130 °C for 5 min	–	–
CP/N117/CP	Rehydrated in H$_2$O at 25 °C for 2 days	18 ± 2	11
CP/N117/CP	Rehydrated in H$_2$O at 65 °C for 2 h	22 ± 2	13

[a] N: Nafion®.

Fig. 4. Temperature dependence of Nafion® 112 (○), 115 (□) and 117 (△) membranes on conductivity.

the three samples and the data of Nafion® 112, 115 and 117 are presented in Table 9. The activation energy decreases with the membrane thickness showing that proton migration in thinner membranes is less influenced by the temperature variation. The value obtained for Nafion® 117 (10.9 kJ mol^{-1}) is similar to that found by Tricoli et al. [14] (11 kJ mol^{-1}) using the NCD-1 measurement. Cappadonia et al. [7] also found comparable values (9.6–10.6 kJ mol^{-1}) for Nafion® 117 with $12 > \lambda > 15$ using the NCD-2 technique. On the opposite, Halim et al. [22] noted a higher value (13.5 kJ mol^{-1}) using the NCD-2 technique, but with $\lambda = 23$. It must be emphasized that Halim's results are an average of 2–10 cells mounted in series.

As shown clearly in Table 9, the Nafion® membranes do not show independence of conductivity with sample thickness, as predicted for an ohmic conductor. These results well agree with those of Slade et al. [9] who found the same tendency in NCD-1 measurements of Nafion® in 1 M H$_2$SO$_4$ solution at 25 °C and in in situ measurements with single cell at 80 °C using the current interruption technique. The authors [9] excluded that their results could be due to uneven water distribution or inhomogeneities in the density distribution of sulfonic acid groups. Their opinion was based on the statement that all the membranes showed approximately the same EWs and were fully hydrated. However, the author's results showed to contradict their statements, since they measured an evident water uptake decrease (from 39 to 36%) with decreasing membrane thickness and the EW was found to be quite scattered (1010–1075). According to the

same authors [9], the decrease in conductivity with thickness should be attributed mainly to the membrane extrusion production process, where pressure and temperature should have a pronounced effect on the surface structure of the materials, and differences in water uptake were excluded. The hypothesis of Slade et al. [9] is that thinner membranes may have been produced with a higher roller pressure resulting in a structural change. Buchi and Scherer [30] also found the same tendency using in situ measurements for Nafion® membranes at 60 °C. Finally, Dimitrova et al. [31] reported the same results at 15 and 80 °C using a configuration quite similar to that of the present work (membrane samples inserted between two gold disks and fully immersed in deionized water). The authors [31] excluded transient dry effects as an explanation for this dependence because the measurements were performed in cells fully immersed in water. On the other hand, however, they observed a clear decrease in λ with decreasing thickness of Nafion® membranes. As hypothesis, the same authors [31] justified the dependence of conductivity on thickness in consequence of a layered structure of the membranes, showing that the experimental results of Nafion® 112, 115, 117 can be explained if membrane surface layers have lower conductivity than that of the membrane bulk.

As reported above, we observed that when the membranes were hot pressed and the CP/membrane/CP samples were rehydrated in water at 65 °C, a decrease of water uptake and λ with thickness and EW was observed (Table 10). These results agree with those of Dimitrova et al. [31] who

Table 9
Conductivity at 25 and 65 °C and activation energy of proton migrations

	σ (mS cm^{-1}, 25 °C)	σ (mS cm^{-1}, 65 °C)	E_m (kJ mol^{-1})
Nafion® 117	48 ± 1	79 ± 3	10.9 ± 0.2
Nafion® 115	33 ± 2	45 ± 4	7.9 ± 0.1
Nafion® 112	23 ± 1	31 ± 1	7.1 ± 0.2

Table 10
Water uptake and λ of hot-pressed Nafion® 112, 115 and 117 samples after heat treatment in water at 65 °C for 3 h

Sample	%$_{water}$	λ
CP/N112/CP[a]	15 ± 4	8
CP/N115/CP	17 ± 2	10
CP/N117/CP	22 ± 1	13

[a] N: Nafion®.
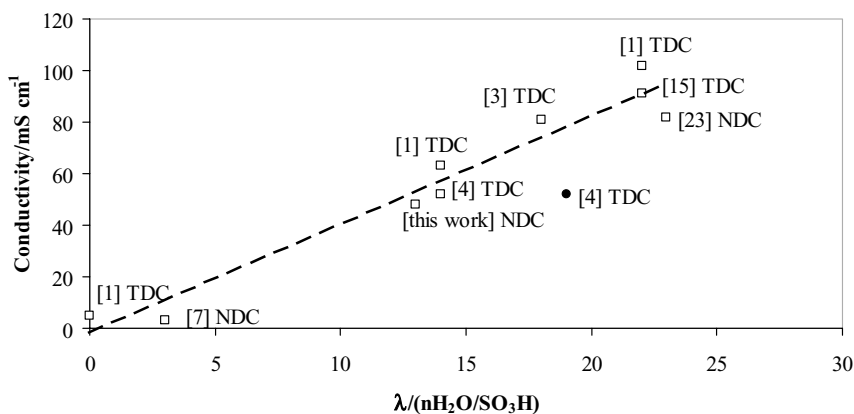
Fig. 5. Conductivity of Nafion® 117 vs. λ from different authors using the TDC and NDC-2 techniques. The data from [4] (●) were corrected from λ = 19 to 14 corresponding to 100% RH at 25 °C.

found the same tendency for samples heat treated at 90 °C for 5 h and immersed in water at 25 °C for 3 days. In particular, we observed that the slightly lower values founded by these authors depend on the room temperature rehydration treatment. In fact, our hot-pressed Nafion® 117 sample rehydrated in water at room temperature for 2 days showed exactly the same water amount of about 18 (see Table 3 and [31]).

Summarizing, three different hypotheses have been suggested to explain the decrease of conductivity with thickness: (a) differences in the water uptake, (b) structural changes due to the production process and (c) layered structure of the membranes. It is very difficult to establish which of these effects is predominant or if there is a contribution among them. However, our experiments demonstrated that the water uptake of thinner membranes is strongly influenced by the hot-pressing step with a higher reduction of water molecules per sulfonate group in comparison to thicker membranes. Besides, the lower EWs of thinner membranes suggest a difference in the structure probably due to the production process.

Fig. 5 presents the conductivity of Nafion® 117 obtained by several authors using the TDC and NDC-2 techniques as a function of the number of water molecules per sulfonate group. Only conductivity measurements taking into account the exact λ values were considered. The values reported by Sumner et al. [4] at 100% RH were presented versus λ = 19 (probably overestimated) and versus λ = 14 (corrected), as experimentally verified [1,2] for these humidification levels. The conductivity measured in the tangential or normal directions appears to be well fitted by a linear regression and the differences observed seem to be only a consequence of different water uptakes. The plot revealed that Nafion® membranes are really isotropic regarding the conductivity and can be used to better compare the conductivity data. In fact, by using a calculated linear regression equation ($\sigma = 4.2054 \times \lambda - 1.722$) for Nafion® 117, it is possible to correlate the data obtained for Nafion® 112 and 115 samples. For example, we calculated the conductivity of Nafion® 117 using the same λ levels found for our

Nafion® 112 and 115 samples (Table 9). We estimated conductivities of 24 mS cm^{-1} for λ = 8 and 33 mS cm^{-1} for λ = 10, which are close to the values found experimentally for Nafion® 112 and 115 (Table 9).

The measurements obtained directly in a single cell can be considered as a third kind of normal direction measurement (NDC-3) useful to establish the good quality of our ex situ method. Our measurements [17] in a 50 cm^2 single cell using Nafion® 115 membranes in the temperature range 25–70 °C showed a conductivity of 30–50 mS cm^{-1} by means of current interruption or AC impedance methods. The in situ experimental data well fit with those obtained by means of our ex situ measurements (34–50 mS cm^{-1}) in the same temperature range.

4. Conclusions

Evidences for conductivity isotropy of hydrated Nafion® membranes were found. The obtained values showed clearly that with tangential or normal conductivity measurements the same results can be obtained considering the same level of water molecules per sulfonate group. Our method can be considered as a valid and simple alternative for tangential measurements, and is able to give indications and results similar to those obtained with in situ measurements where the hot-pressing treatment must be applied.

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