Effects of hydrothermal/thermal treatments on the water-uptake of Nafion membranes and relations with changes of conformation, counter-elastic force and tensile modulus of the matrix

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Abstract

A kinetic investigation of the water-uptake of Nafion 117 membranes after different hydrothermal and thermal treatments was performed. Long equilibration times (150–225 h) and a decrease of kinetic rate with the increasing of temperature were found. This behaviour suggests that the kinetics of the water-uptake is the result of two distinct processes: one very fast that can be attributed to the time of osmotic equilibration necessary for the water diffusion within the thin membrane and the other, very slow, that has been associated with a slow modification of the Nafion conformation with the temperature.

The irreversibility of the hydration process with the temperature was related to the irreversibility of the conformational changes. The memory of the thermal treatment is due to the fact that ionomers are essentially constituted as an amorphous matrix in which some microcrystalline phases are embedded. All the amorphous ionomers can give metastable phases that can appear kinetically stable although, in fact, they are thermodynamically unstable.

Previous osmotic models for ionomers were re-visited in order to relate the water-uptake isotherms of the various treated samples to the counter-elastic force of their matrix. It was found that an index proportional to the counter-elastic force of the matrix can be simply derived by determining the water-uptake of the samples in liquid water at 20 °C. Furthermore, some useful relations between this index and tensile modulus and the shape of water-vapour sorption isotherm of the samples are reported and discussed.

We believe that the researches on the modifications of PFSA membranes by thermal and hydrothermal treatments are very important: (1) in order to have a better understanding of the fundamental properties of this important class of membranes; (2) for obtaining reliable comparisons between the properties of different PFSA membranes and (3) for improving the stabilization of the Nafion membranes at temperatures higher than 90 °C.
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1. Introduction

The perfluorosulfonic acid (PFSA) membranes are characterized by high mechanical stability, excellent chemical inertness, good thermal stability and high proton conductivity at high relative humidity [1,2]. Due to these peculiar properties, they have been, and till now are, the membranes of choice for automotive PEMFC working in the temperature range 60–80 °C. On the other hand, it is well known that the proton conductivity of PFSA membranes dramatically decreases at low relative humidity. This fact already seriously limits their use in medium temperature PEMFC since high pressures of the stacks are necessary for maintaining high relative humidity. Furthermore, it was found in our Laboratory [3] that an irreversible decay of the proton conductivity can take place at temperatures higher than about 80 °C in the presence of high relative humidity. This decay was recently associated with an anisotropic swelling of the membrane along the direction parallel to the electrode surface [4]. The anisotropic swelling takes place when the membrane is clamped between two electrodes, as in the usual MEA configuration, which prevents the swelling in the direction perpendicular to the membrane surface.

In conclusion, if a low relative humidity is used for avoiding cell pressurization at temperatures higher than 100 °C, too

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low proton conductivity is obtained. If high RH values are used, an anisotropic swelling accompanied by an irreversible decay of the proton conductivity can occur. The values of the couples T–RH at which the conductivity of Nafion is irreversibly decreased (instability maps) have been experimentally determined in our laboratory [5]. It was found that in the temperature range 80–130 °C the irreversible decay of the proton conductivity can be avoided by operating at RH values lower than about 75%. However, even a mistake of few minutes in this control can have serious consequences on the FC since the provoked decay of the conductivity is then irreversible.

In this situation, it was decided to investigate if PFSA membranes with improved characteristics for their use in medium temperature FC could be obtained after suitable thermal modifications.

Already in the beginning of this research on Nafion membranes it was well evident that this ionomer easily forms metastable phases. We realized also that the metastability of the Nafion conformations obtained after various thermal treatments (Nafion memory) was the main reason for the discrepancies found in the literature for many important properties of Nafion membranes.

It was therefore decided to re-investigate in detail the water-uptake isotherms of this ionomer after different thermal treatments. Previous osmotic models for ionomers were re-visited in order to relate the water-uptake isotherms of the various treated samples to the counter-elastic force of their matrix. It was found that an index proportional to the counter-elastic force of the matrix can be simply derived by determining the water-uptake of the samples in liquid water at 20 °C. Furthermore, some useful relations between this index, the tensile modulus and the shape of vapour water sorption isotherm of the examined samples will be reported and discussed.

2. Experimental

2.1. Membrane treatments

In all the treatments below described, the membranes are handled using tweezers with Teflon covered tips.

Standard treatment. Before thermal or hydrothermal treatments, as received Nafion 117 membranes were treated according to the standard procedure (1 h in boiling 3% solution of hydrogen peroxide; 1 h in boiling 0.5 M sulfuric acid; 1 h in boiling distilled water). Hereafter, the membranes of Nafion 117 obtained after the above standard treatment will be simply indicated as M samples.

Thermal treatments. M samples (dimensions 3 cm × 1 cm) were placed in an oven at the wished temperature for the wished time. The thermal treated M samples are therefore characterized by two numbers, the first referring to the temperature (°C) and the second to the time of treatment (h). For example, the M(120;15) sample is a Nafion 117 membrane that, after the standard treatment, has been heated at 120 °C for 15 h.

Hydrothermal treatments. M samples were placed in a closed vessel, schematically shown in Fig. 1, in which temperature and relative humidity can be controlled. The hydrothermal treated
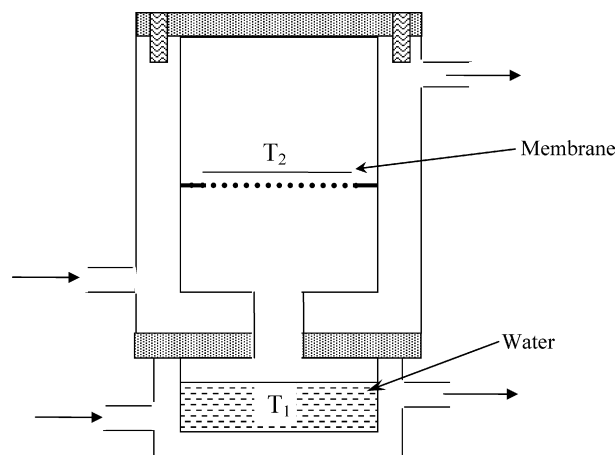

Fig. 1. A schematic view of the vessel used for hydrothermal treatments at known relative humidity. The temperature T_2 at which the membrane must be heated is obtained by circulation of a warm fluid and controlled by a thermocouple near the membrane. The wished RH is obtained by warming the water at the right temperature T_1.

samples are therefore characterized by three numbers. For example, the M(110;200;50) sample is a Nafion 117 membrane that, after the standard treatment, has been heated at 110 °C for 200 h at 50% relative humidity. In the simple case of equilibration in warm water, the samples are immersed in distilled water contained in closed vessel of Teflon (thickness: 2 mm, 5 mm and 20 mm for temperatures in the range 20–100 °C; 100–110 °C and 110–140 °C, respectively). The containers are then placed in a thermostat at the wished temperature. In this case, the last number is replaced by lw. The M(130;15;lw) sample is therefore a membrane heated at 130 °C for 15 h in liquid water.

Finally, the samples to which two sequential treatments are applied will be indicated by M(·) + (·).

For example, a thermally treated sample M(120;15) to which also a hydrothermal treatment in liquid water at 120 °C for 48 h has been then applied will be written as M(120;15) + (120; 48;lw).

2.2. Water-uptake determinations

After the thermal or hydrothermal treatment, the membrane is equilibrated in distilled water at 20 ± 1 °C for 24 h. The membrane is then separated from liquid water and the excess of external liquid water is removed (inside a box or a small room where the relative humidity can be maintained at values ≥95%) by placing the membrane between two foils of filter paper and pressing lightly. This drying procedure is repeated, as fast as possible, for three times. The membrane is then immediately placed in a weighing glass container, closed and weighed. The membrane is finally dried at 140 °C for 5 h, placed still warm in the same weighing container, closed and weighed again at room temperature. The hydration number λ (moles of water for equiv. –SO₃H), is then calculated by the weight differences between hydrated and anhydrous samples.
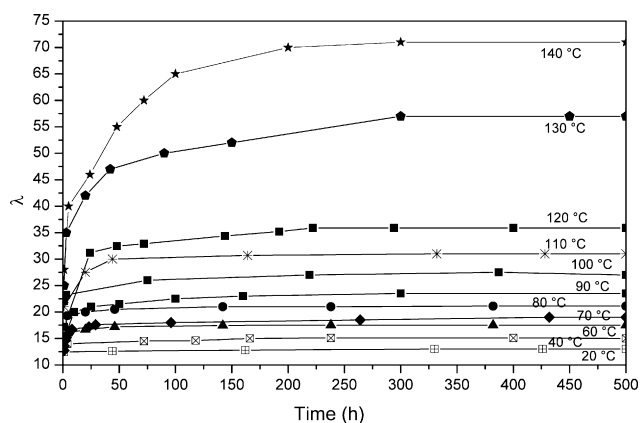
Fig. 2. Water-uptake as a function of equilibration time for M(120;15) sample when immersed in water at different temperatures.

2.3. Tensile modulus determinations

The mechanical properties of the membranes were investigated by stress–strain static tests with a Zwick Roell Z1.0 testing machine, and the data were elaborated by the TestXpert V11.0 Master Software; the test speed was of 2 mm min^{-1}. A punch cutter cut the sample and the size of specimen was of 100 mm × 5 mm. Before the measurements, the samples were conditioned in liquid water at 20 °C for 24 h. To assure that water was not lost during the determination of tensile modulus, the excess of water was eliminated with filter paper and the measurements immediately performed in room conditioned at 20 °C and in which the relative humidity was maintained ≥95%.

3. Results and discussion

3.1. Effects of hydrothermal/thermal treatments on the water-uptake of Nafion membranes

The water-uptake of Nafion 117 immersed in water at different temperatures has been already reported by Hinatsu et al. [6] and Zawodzinsky et al. [7]. Because equilibration times at the various temperatures were not determined, we preliminarily performed a detailed kinetic investigation on the water-uptake (λ) of M(120;15) samples. The water-uptakes as a function of equilibration time over a large range of temperature (20–140 °C) are shown in Fig. 2.

Table 1 reports the times necessary for the equilibrium, λ values at the equilibrium and the percentages of equilibrium reached after 1 h of equilibration. Note that the times necessary for equilibrium (150–225 h) are longer than expected for the hydration of thin Nafion membranes. Furthermore, the percentage of equilibrium after 1 h is enough high at low temperature but appreciably decreases with increasing the temperature of the liquid water. Both the long equilibration times and the decrease of kinetic rate with the temperature can be explained if the total water-uptake is the results of two distinct processes, the first very fast and the second very slow. Reasonably, the fast process can be attributed to the equilibration necessary for the water dif-

Table 1
Equilibrium times and equilibrium values of water-uptake at the various temperatures for Nafion 117 membranes

T (°C)	Equilibrium time (h)	λ (equilibrium values)	λ (1 h of equilibration)	Equilibrium% (1 h)
20	170	13.0	12.4	95.4
40	160	15.0	13.2	88
60	150	17.5	14.0	80
70	200	19.0	12.7	67
80	150	21.0	15.4	73
90	160	23.5	15.0	64
100	150	27.5	21.5	78
110	165	31.0	21.0	68
120	220	35.9	17.2	48
130	225	57.0	25.0	44
140	200	71.0	28.0	39

λ values and percentage of the equilibrium after 1 h are also reported.

fusion within the thin membrane while the slow process can be associated with a modification of the Nafion conformation with the temperature (see later).

The equilibrium λ values obtained at the various temperatures of the water are plotted in Fig. 3. As indicated by the arrows, the hydration changes are not reversible and large hysteresis loops in the hydration, as before said, are obtained. Note that, in the examined temperature range 20–140 °C, the equilibrium hydration attained at a given temperature T tends to be maintained at lower temperatures. For example, if $T = 100$ °C, no apparent changes in the hydration are then observed at temperatures lower than 100 °C. Similar observations were already reported [6,7]. The reasons of this irreversibility (or memory of the previous treatments) will be discussed later.

Similar experiments were performed with other thermally and hydrothermally treated samples. The results, compared in Fig. 4, shows that similar, but shifted curves are obtained with the different thermally treated samples, thus demonstrating that the original memory of different thermal treatments is maintained even when hydrothermal treatments are then applied. The curve
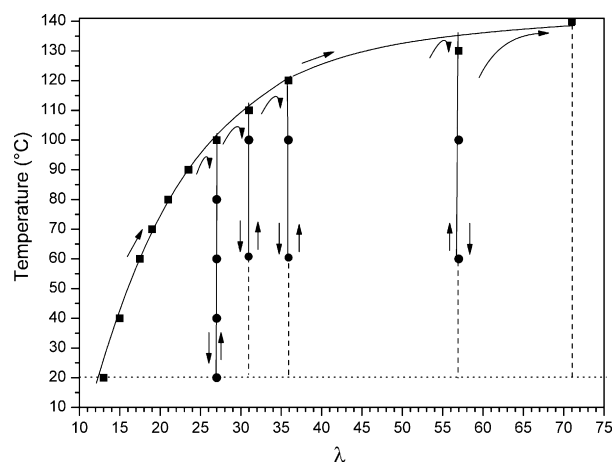

Fig. 3. Plot of the equilibrium values of the hydration number for the sample M(120;15) obtained after immersion in water at different temperatures for 500 h. Note that the water-uptake considerably increases with the temperature. As indicated by the arrows, the process of hydration is not reversible (see text).
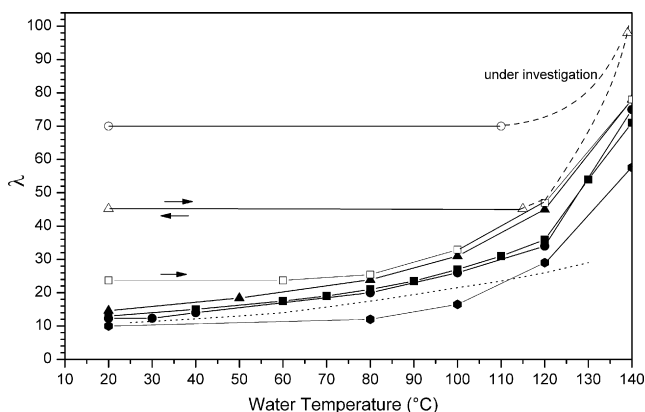
Fig. 4. Hydration numbers of different hydrothermally and thermally treated samples as a function of water temperature. The curve obtained by Hinatsu et al. is also reported for comparison (dotted curve) (●) M(100;360); (●) M(140;672); (■) M(120;15); (▲) as received; (□) M; (△) M(120;72;lw); (○) M(140;96;lw).

obtained by Hinatsu et al. is also reported for comparison in Fig. 4 (dotted curve).

3.2. Water-vapour sorption isotherms for solutions of dissociate and indissociate solutes with an applied external pressure

It is well known that many properties of an ionomer membrane strongly depend on the pre-treatment procedures (ionomer memory) [8]. Because the pre-treatments performed in various laboratories can be considerably different, a large discrepancy of values can be found even in recent literature. Concerning vapour sorption isotherms, Fig. 5 shows a comparison of some curves obtained by various authors for Nafion 117 membranes [6,7,9,10]. In our opinion, the large discrepancies between these curves cannot be attributed to experimental errors but they are reasonably due to different initial conformations of Nafion samples used in the various laboratories (see later). Thus, to avoid these disagreements, all the results on PFSA or similar ionomers
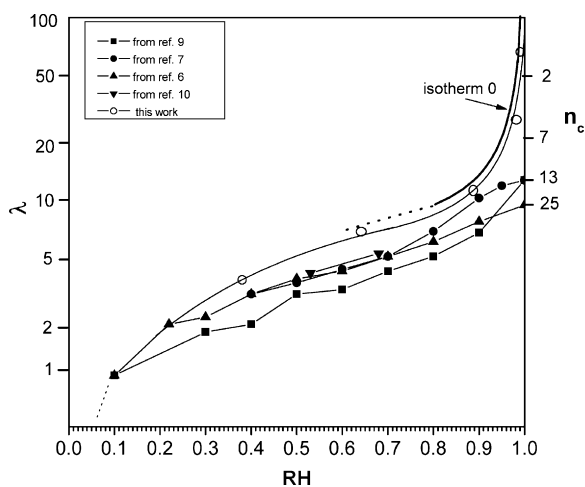

Fig. 5. A comparison between some water-vapour sorption isotherms obtained by different authors. The meaning of isotherm 0 and n_c index is explained in the text.
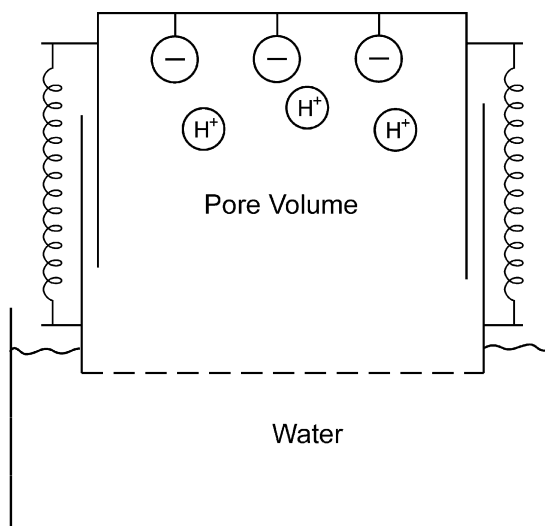

Fig. 6. A schematic view of the Gregor' model (redrawn from Ref. [11]). Fixed charges and dissociated protons are shown.

must be accompanied by complete information of the previous history of the samples which determines the actual Nafion conformation of the examined sample. If the history of the sample is unknown, before to make comparisons with the results of other laboratories, an index of the actual conformation reassuming all the previous history of the Nafion membrane used must be estimated.

For the determination of this index, we re-visited old osmotic models for ionomers and attempts for deriving simple equations relating this index to vapour sorption isotherms and tensile modulus of Nafion membranes were made. Many similar models are available [1,11,12]. For its simplicity, the Gregor's model [11], schematically shown in Fig. 6, was chosen as a starting model. In this model, fixed ionized groups and dissociated protons are considered as hydrated species, while the counter-elastic force of the ionomer matrix is represented as a spring which counteracts the volume expansion due to water-uptake.

To account the possibility of anisotropic swelling, the counter-elastic forces in the three directions have been introduced in the original model. Furthermore, by eliminating fixed ionized groups and dissociated protons, a simple three-dimensional model for the study of water-vapour sorption isotherms of solutions under different applied pressures can be also obtained (Fig. 7a). In these models, the external surface of the solute container is considered as a semipermeable membrane which allows free passage of water but prevents solute molecules or ions from passing through.

Let us suppose that inside the three-dimensional model without any applied external pressure (Fig. 7b) there is initially a solution of a not dissociate solute which does not appreciably interact with water. We can write:

$$X_s = 1 - X_w \tag{1}$$

where X_s and X_w are the molar fraction of the solute and of the water, respectively.
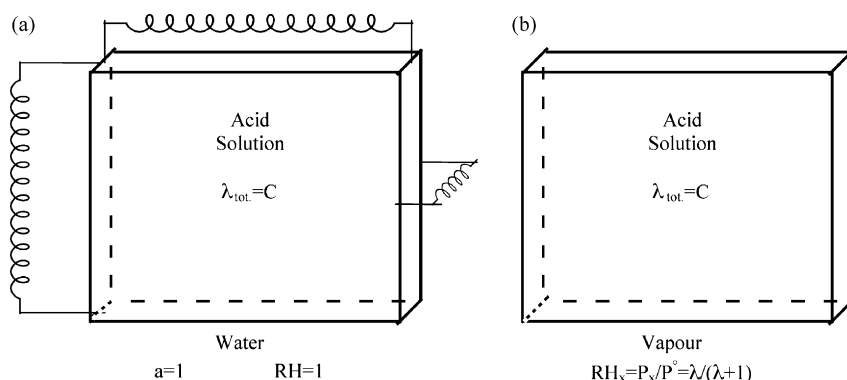
Fig. 7. (a) A simplified model of a three-dimensional cell filled with acid solutions. The surface of the cell is considered as a semipermeable membrane. The cell is immersed in liquid water. An equilibrium between the external and inner water is reached when the osmotic pressure is balanced by the counter-elastic force of the springs (in absence of anisotropic swelling, the counter-elastic force is the same in the three directions). (b) The cell (a), without any applied counter-elastic force, is equilibrated with an external atmosphere of known RH.

Taking into account the Raoult low, we can also write:

$$X_w = \frac{P}{P^0} = RH \tag{2}$$

Finally, by remembering that:

$X_w = n_w/(n_w + n_s)$ (where n_w and n_s are the number of water and solute molecules, respectively), by dividing numerator and denominator by n_s we obtain

$$X_w = \frac{\lambda}{\lambda + 1} \tag{3}$$

where λ is the number of water moles for mol of solute or hydration number of the solute.

Taking into account Eq. (1), we can also write:

$$RH = \frac{\lambda}{\lambda + 1} \tag{4}$$

When this three-dimensional model is equilibrated with external vapour at different RH values, water is exchanged through the semipermeable surface. The ideal vapour sorption isotherm of the solution can be obtained by plotting λ against $\lambda/(\lambda + 1)$ (dotted curve of Fig. 8). Hereafter, the isotherm curves without any applied external or inner pressure will be indicated as isotherm 0.

Fortunately, this isotherm can be compared with that obtained using experimental values found in old tables [13] for lowering of vapour pressure at $100\,^\circ C$ of phosphoric acid solutions of different concentrations (first two columns of Table 2). The hydration numbers (λ) corresponding to the various concentration can be calculated (column 3) while RH values can be easily derived by the lowering of the vapour pressure (column 4). By reporting the experimental data of Table 2 in Fig. 8, it can be seen that they fit very well the isotherm 0 derived for an ideal not dissociate solute. The phosphoric acid, due to the low values of its first dissociation constant ($K_1 = 7.5 \times 10^{-3}$) can be indeed considered as a not dissociated solute. However, the ideal behaviour even for concentration as high as 5–10 M indicates that no strong interactions between phosphoric acid and water take place at $100\,^\circ C$. In other words, phosphoric acid behaves as an anhydrous molecule at $100\,^\circ C$.
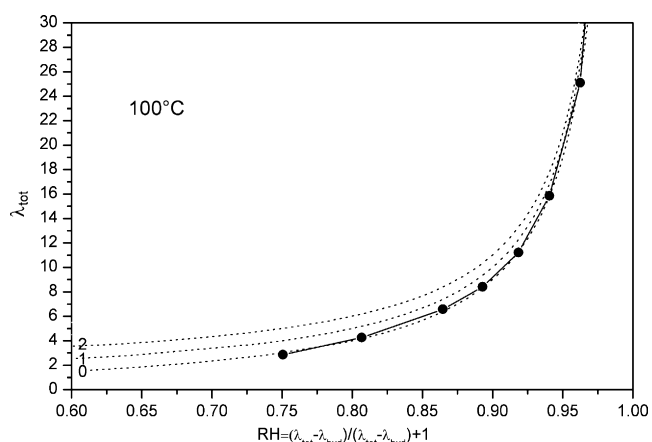

Fig. 8. Calculated water-vapour sorption isotherms for a solution of phosphoric acid at various degrees of hydration. Experimental values for phosphoric acid solutions at $100\,^\circ C$ (see Table 2) are inserted. Note the good fit of these points with the isotherm derived for anhydrous phosphoric acid.

Let us now to examine the effect of an applied external pressure on the isotherm 0. For simplicity we assume that springs of same elastic force are applied to the three-dimensional model of Fig. 7a. The applied springs will counteract the inner osmotic pressure and the water content inside the osmotic cell will be decreased. Note that the pressure exerted by the springs can

Table 2
Lowering of vapour pressure for H_3PO_4 solutions at $100\,^\circ C$ (data from Ref. [13])

M	Lowering of vapour pressure (mmHg)	λ	RH
0.5	6.6	108.30	0.9913
1.0	14.0	52.84	0.9816
2.0	28.6	25.11	0.9624
3.0	45.2	15.85	0.9405
4.0	62.0	11.21	0.9184
5.0	81.5	8.41	0.8928
6.0	103.0	6.57	0.8645
8.0	146.9	4.26	0.8067
10.0	189.5	2.86	0.7506

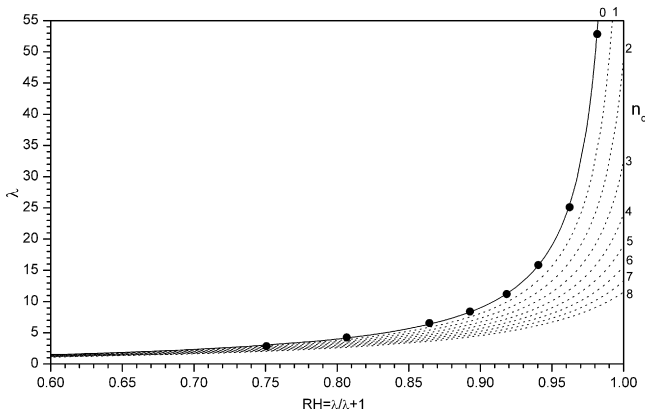Original data were converted into λ and RH values.

Fig. 9. Calculated water-vapour sorption isotherms for a solution of phosphoric acid at $100\,°C$ under different applied pressures. The original isotherm 0 is shifted towards right and cut the abscissa axis at RH = 1. For each λ value corresponding to the cut, the difference $(1 - RH) \times 100$ is called n_c index. The meaning of this index is explained in the text.

be calculated by the following ideal experiment. Suppose that the model is first equilibrated in water (100% RH). A given λ value, depending on the strength of the springs, is obtained at the equilibrium (see Fig. 7a). The springs are then removed and the tendency of the water to enter in the osmotic cell is now balanced by decreasing the water activity. This can be obtained by equilibrating the cell at a certain external RH value where the same λ value is obtained (Fig. 7b).

Since λ is not changed, the shift $(1 - RH)$ corresponds to the pressure exerted on the osmotic cell by the applied springs. The value $(1 - RH)$ can be therefore taken as an index of this pressure. We called index of counter-elastic force (n_c) the shift in RH% unit:

$$n_c = 100(1 - RH) \tag{5}$$

In Fig. 9 are shown the vapour sorption isotherms for phosphoric acid under different pressures corresponding to different shift of the RH% of the isotherm 0. Further discussion on the index of counter-elasticity will be made later when the vapour sorption isotherms of Nafion will be discussed.

Let us now to examine the ideal vapour sorption isotherms for an acid solute HA which in water is completely dissociated in two particles: $HA + nH_2O \rightarrow H_{n'H_2O}^+ + A_{mH_2O}^-$. Triflic acid can be taken as an example of this solute. However, sulfuric acid was chosen because the relative humidity of H_2SO_4 solutions of various molar concentrations at $20\,°C$ [14], $25\,°C$ [15] and $100\,°C$ [13] were found in old literature. Furthermore, scattered data for some solutions at $110\,°C$, $120\,°C$ and even higher temperatures were also found. This acid has been considered as completely dissociated: $H_2SO_4 + nH_2O \rightarrow H_{n'H_2O}^+ + HSO_{4\,mH_2O}^-$, while the contribution of the dissociation of HSO_4^-, being K′ [H_2O] = K = 1.2×10^{-2}, was considered negligible for the examined concentrations. A treatment similar to that before described for phosphoric acid can be therefore made taking into account the dissociation in two particles and their hydration.

Eq. (4) for solutions of sulfuric acid of hydration = 0 becomes:

$$RH = \frac{\lambda}{\lambda + 2} \tag{6}$$

By defining the total hydration ($\lambda_{hyd.}$) as the sum of the hydration numbers of protons and HSO_4^- anions we have

$$\lambda_{tot.} = \lambda_{hyd.}^+ + \lambda_{hyd.}^- \tag{7}$$

Furthermore, by considering that

$$\lambda_{tot.} = \lambda_{os.} + \lambda_{hyd.} \tag{8}$$

Eq. (6) can be written as

$$RH = \frac{\lambda_{tot.} - \lambda_{hyd.}}{(\lambda_{tot.} - \lambda_{hyd.}) + 2} \tag{9}$$

Eq. (9) contains the hydration of the ions. It must be recalled that the ion solvation is thermodynamically not well defined, so that the distinction between free solvent and solvation shells is, to a certain extent, arbitrary. Nevertheless, the hydration of the ions is largely accepted since greatly helps in understanding and explain in simple manner quite a number of phenomena, at least in a semi-quantitative way.

The plots of Eq. (9) for hydration numbers 0–7 in the RH range 0.5–1 are reported in Fig. 10. The experimental values of the literature for the various temperatures are inserted. Note that, from the fit of the experimental points with isotherms calculated for different $\lambda_{hyd.}$ values can be estimated that total ion hydration of sulfuric acid at the temperatures $25\,°C$, $100\,°C$ and $\geq 110\,°C$ are between 6–7, about 3 and 1, respectively.

3.3. Nafion water-vapour isotherms and counter-elasticity force of the matrix

Let us now to apply to Nafion the relations before found for simple solutions of not dissociated and dissociated solutes.

In this treatment, $-SO_3H$ groups are considered as completely dissociated when $\lambda_{tot.}$ is ≥ 3 [16]. However, differently from sul-
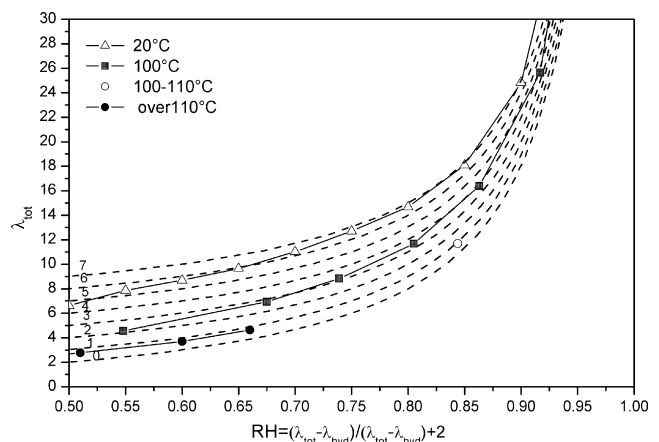

Fig. 10. Calculated water-vapour sorption isotherms for a solution of sulfuric acid at various degrees of hydration. The equation for RH is derived in the text. Experimental values taken from the literature for sulfuric acid solutions at various temperatures (see text) are also reported in order to have information on the hydration of this acid.
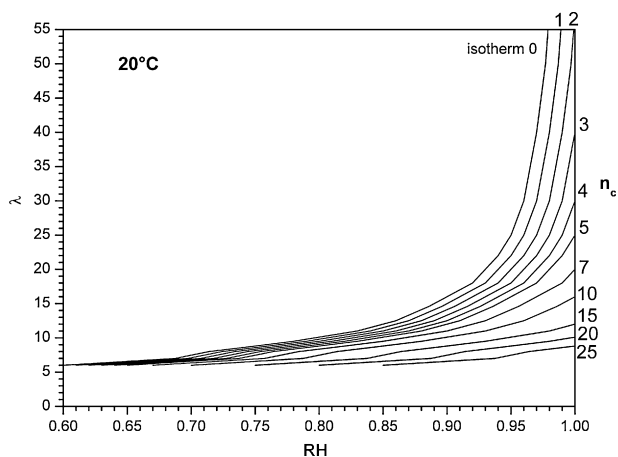
Fig. 11. Calculated isotherm 0 at 20 °C for an ideal Nafion without any applied counter-elastic force of the matrix and related shifted isotherms obtained when increasing counter-elastic forces, expressed as n_c indexes, are applied as in real Nafion. Each n_c unit at 20 °C corresponds to an applied pressure of 1.35 MPa.

furic acid, only dissociated protons contribute to the osmotic pressure while the dissociated $-SO_3^-$ groups contribute only to the total hydration at temperatures ≤ 110 °C. Thus, the osmotic behaviour of Nafion can be described in Eq. (4), derived for anhydrous phosphoric acid, by inserting the hydrations of protons and fixed charges, as in Eq. (9).

The equation is therefore of the type:

$$RH = \frac{\lambda_{tot.} - \lambda_{hyd.}}{(\lambda_{tot.} - \lambda_{hyd.}) + 1} \tag{10}$$

A water-vapour sorption isotherm for Nafion at 20 °C without any applied external or inner counter-elasticity force can be obtained by plotting Eq. (10). The values of $\lambda_{hyd.}$ at the different RH are assumed to be equal to those found for the isotherm 0 of sulfuric acid at 20 °C. This curve, shown in Fig. 11, can be considered as an ideal isotherm 0 for Nafion.

Now we can apply different counter-elastic forces to the Nafion matrix, thus obtaining the shifts of the isotherm 0, just as before described for solutions of phosphoric acid.

The inner counter-elasticity force of Nafion can be therefore estimated by Eq. (5), by replacing RH values of Eq. (10): $n_c = 100(1 - RH) = 100 - ((\lambda_{tot.} - \lambda_{hyd.})/((\lambda_{tot.} - \lambda_{hyd.}) + 1))$. This equation, after simple rearrangements, becomes:

$$n_c = \frac{100}{(\lambda_{tot.} - \lambda_{hyd.}) + 1} \tag{11}$$

Finally, by assuming that, as in the case of for sulfuric acid, $\lambda_{hyd.}$ for Nafion equilibrated in liquid water at 20 °C is equal to 7, we can write:

$$n_c = \frac{100}{\lambda_{tot} - 6} \tag{12}$$

Note that the experimental determination of n_c for Nafion is therefore very simple. It is sufficient to determine $\lambda_{tot.}$ in liquid water at 20 °C and apply Eq. (12).

The expected water-vapour sorption isotherm at 20 °C of a given sample M will be that obtained by shifting towards right

the isotherm 0 of a number of RH% units equal to the n_c value found for the examined sample.

Coming back to vapour sorption isotherms reported for Nafion in Fig. 5, our previous considerations clearly show that the differences are not due to experimental errors but to the different initial conformations of Nafion (very likely due to different history of the examined samples) to which different n_c values can be associated. These values have been therefore reported in the right ordinate of Fig. 5.

It is of interest to note that the shape changes of isotherms obtained with samples of increasing counter-elastic index recall the behaviour of sulfonated styrene of increasing degrees of cross-linking reported in the old literature [17]. We can conclude that the thermal treatments reinforce the morphological stability of the Nafion matrix as the degree of cross-linking does for styrene cation exchangers.

3.4. Hydration numbers and mechanical properties after different treatments

The water-uptake also influences the mechanical properties of Nafion membranes [18–20].

In order to find simple relations between mechanical properties and thermal treatments (hence relations between tensile modulus, water-uptake and index of counter-elasticity), the tensile modulus of thermally and hydrothermally treated samples was investigated.

The water-uptake in liquid water at 20 °C and the values of the tensile modulus and elongation at break of the four different series of thermally treated samples are reported in Table 3. The value obtained with as received Nafion 117 after the standard treatment is also reported for comparison. Note that the memory of the different thermal treatments is very strong at room temperature and large differences in the water-uptake are therefore obtained. Note also that the thermal treatment has a deep influence on the tensile modulus.

To better clarify this influence, the modulus E (in MPa) of a large number of M samples with different thermal or hydrothermal treatments in liquid water at 20 °C was thus determined and the obtained values are reported in Table 4.

A plot of all the values of Tables 3 and 4 as function of the hydration number is shown in Fig. 12. It was found that the experimental points fit a curve of equation:

$$E = \frac{500}{\lambda_{tot.} - 6} \tag{13}$$

Table 3
Hydration numbers and corresponding tensile modulus and elongation at break at 20 °C of some thermally and hydrothermally treated Nafion membranes

Sample	Hydration number (λ) (liquid water)	Tensile modulus (MPa) (RH 100%)	Elongation at break (%) (RH 100%)
M(100;360)	10.0	125.0	530
M(140;672)	12.2	115.0	661
M	21.2	33.0	507
M(120;15)	12.6	90.0	584
M(140;48;lw)	74.0	4.0	113

Table 4
Hydration numbers and corresponding tensile modulus (20 °C) of a large number of thermally and hydrothermally treated Nafion membranes

Sample	Hydration number (λ) (liquid water)	Tensile modulus (MPa) (RH 100%)
M(60;672)	17.4	50.5
M(80;672)	14.5	59.0
M(100;672)	12.0	111.0
M(120;672)	9.0	114.0
M(140;672)	9.4	107.0
M(140;15)	13.2	100.0
M(140;24)	13.8	103.0
M(140;168)	13.0	104.5
M(140;336)	13.0	111.0
M(140;504)	11.8	111.0
M(50;15)	21.0	40.0
M(80;15)	13.4	76.5
M(100;15)	12.8	82.0
M(140;15)	12.4	89.0
M(140;72;lw)	79.0	4.0
M(140;96;lw)	82.7	4.0
M(120;15) + (120;48;lw)	36.0	18.0
M(120;15) + (120;96;lw)	40.5	19.0
M(120;15) + (120;120;lw)	42.4	17.0
M(120;15) + (140;48;lw)	55.0	10.0
M(120;15) + (140;72;lw)	65.5	5.0

Note that this equation, apart the constant, is identical to that previously found for n_c (Eq. (12)). The ratio between Eqs. (13) and (12) is: $E/n_c = 5$.

Let us calculate the value of the pressure which provokes a shift of the RH of 1% of the isotherm 0 of the Nafion. By remembering Eqs. (1) and (2), we can write: $1 - RH = X_s = 0.01$ where X_s is the molar fraction of protons. It can be calculated that to a molar fraction 0.01 of protons corresponds a solution very near to 0.56 M to which, at 20 °C, corresponds an osmotic pressure $\pi = 0.56RT = 13.5$ atm. ~ 1.35 MPa.

Thus, the ratio E/n_c: becomes $5/1.35 = 3.7$. Apart for this factor, both n_c and E can be also considered as indexes of the ionomer conformation and, in this sense, they are equivalent.
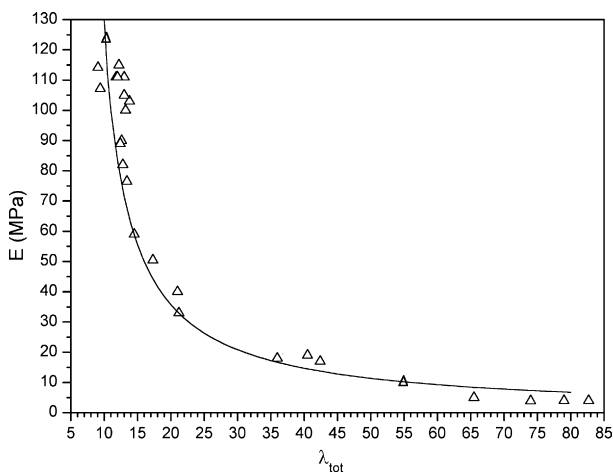

Fig. 12. A plot of tensile modulus values reported in Tables 3 and 4 as a function of the water-uptake ($\lambda_{tot.}$) when the Nafion samples is equilibrated in liquid water at 20 °C. The experimental points fit the curve of Eq. (13).
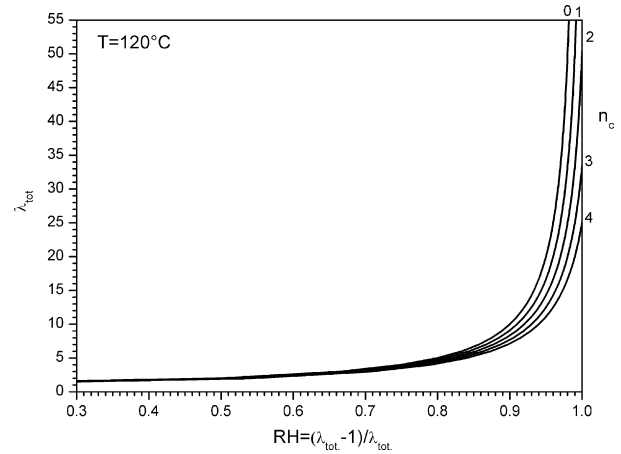

Fig. 13. Ideal isotherm 0 for Nafion at 120 °C and related shifted isotherms for various values of the index of counter-elasticity.

The determination of the counter-elastic index is however, very simple and does not require expensive apparatus. Note that an evaluation of the index of counter-elasticity can be also estimated at temperatures higher than 100 °C even for high relative humidities, where the determination of the tensile modulus is difficult for corrosion problems. As an example in Fig. 13 is reported the isotherm 0 for Nafion at 120 °C. This isotherm has been calculated using the equation:

$$n_c = \frac{100}{\lambda_{tot.}} \tag{14}$$

which has been obtained by Eq. (11), by considering the Nafion as monohydrated to this temperature. It can be reasonably assumed that this hydration number can be attributed to belong only to protons. By applying different n_c values, the shifted isotherms of samples with different tensile modulus are then obtained.

In Fig. 14 is reported the classic representation of the conformations proposed by Gebels [21] for the various water contents. To make clear the correspondence between the counter-elastic index (or tensile modulus) with Nafion conformation at various hydration, the water volume fraction has been converted into λ values and the corresponding n_c and E values are also reported.

Because the water-uptake and tensile modulus depend on the Nafion conformation, it can be deduced that different Nafion conformations are obtained by thermal treatments. Thus, we can say that n_c is also an index of the conformation obtained by a given thermal/hydrothermal treatment.

Note that the index n_c can replace, in a more quantitative way, the qualitative nomenclature introduced by Yeo and Yeager [8] who, on the basis of the thermal treatments, classified the membranes in "E form" (Expanded form), N form (Normal form) and "S form" (Shrunken form); a further shrunken form (FS form) was then introduced by Sone et al. [22]. Note also that, in the case of anisotropic swelling, three different n_c values could be obtained by measuring the swelling in the three directions.

The evolution of the Nafion conformation with thermal treatments is gradual and samples with n_c values in the range 1–30 can be obtained by appropriate treatments.
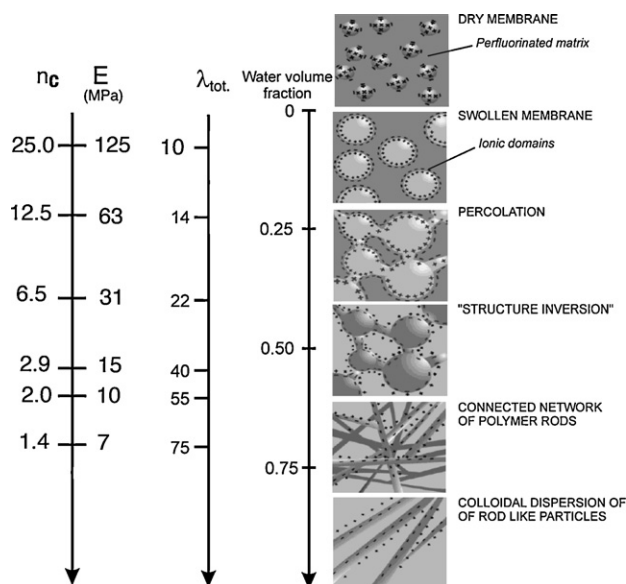
Fig. 14. Representation of the Nafion conformations proposed by Gebels [21]. The values of $\lambda_{tot.}$, tensile modulus and index of counter-elasticity corresponding to the various conformations are also reported.

This work confirms that the ionomer memory is due to the fact that these materials are essentially constituted as an amorphous matrix in which some microcrystalline phases are embedded. All the amorphous materials can give metastable phases that can appear kinetically stable although in fact are thermodynamically unstable. It was found in our laboratory that hysteresis loops in the water-uptake can be found when dehydrated samples obtained by thermal treatments and hydrated samples obtained by hydrothermal treatments are then equilibrated at the same relative humidity [23]. These loops, particular large at room temperature, decrease at increasing temperature and completely disappear at about 140 °C. Since the same value of the water-uptake was reached from two opposite directions, it can be concluded that memory effects due to previous treatments are in large part cancelled at temperatures higher than 140 °C.

4. Conclusions

Deep modifications of the conformation of as received Nafion 117 commercial membranes have been obtained by suitable combinations of hydrothermal/thermal treatments. The overall effect of a given thermal treatment on Nafion membranes can be evaluated by the variation of their index of counter-elastic force.

We believe that the researches on the modifications of PFSA membranes by thermal and hydrothermal treatments are very important: (1) in order to have a better understanding of the fundamental properties of this important class of membranes; (2) for obtaining reliable comparisons between the properties of different PFSA membranes; (3) for improving the stabilization of the Nafion membranes at temperatures higher than 90 °C. Being reasonable that similar stabilizations are also obtained in the

case of very thin membranes, we are now investigating Nafion 112 membranes. The higher current intensity obtained with thin membranes could partially compensate the low conductivity at relative humidity lower than 50%.

A fourth point that must be still clarified is the following: by suitable treatments is it or not possible to obtain an improvement of the Nafion conformation that, due to a better orientation of ionic clusters and/or to a better connection between them, may confer to Nafion membranes higher proton conductivity in the direction perpendicular to the membrane surface?

We are now engaged to give a definitive answer to this point.

Acknowledgements

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