New results on the visco-elastic behaviour of ionomer membranes and relations between T−RH plots and proton conductivity decay of Nafion® 117 in the range 50−140 °C

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ABSTRACT

The colligative properties of acidic solution inside Nafion® 117 membranes have been investigated, in a large temperature range, by two different methods.

1) The matrix counter-pressure index of the ionomer, n_c, was first determined and then its relations with the molar fraction and molality of the inner proton solution were found.
2) In order to calculate the density of the inner proton solutions, a factor F_e proportional to the solution electro-restriction, was experimentally found. The molarity and molality of the inner proton solution, and hence the inner osmotic pressure, were then calculated.

The obtained data confirmed the viscous behaviour of Nafion® 117 membranes. Furthermore, the comparison between the molality of inner proton solution obtained with the above different methods showed that to consider a solvation shell for the protons (first method) is equivalent to consider an electro-restriction of the solutions (second method). In other words, hydration number and electro-restriction factor are strictly related and the equation relating them is reported.

Finally, T−RH plots at constant n_c values show that the believing concerning the inability of Nafion® membranes to be employed in fuel cells at temperature higher than about 80−90 °C is not completely true.

1. Introduction

Both in automotive and cogeneration applications of Polymer Electrolyte Membrane Fuel Cells (PEMFCs), a working temperature in the range 100°−130 °C is highly desirable [1−3].

Owing to their good mechanical properties, excellent chemical inertness, (due to the presence of fluorine atoms) as well as to their high super-acidity and very high proton conductivity, perfluorinated polymeric membranes containing sulfonic acid groups (PFSA membranes such as Nafion® and Aquivion®) are presently the most used membranes for PEMFCs [4−8].

However, it is today commonly accepted that, for automotive application (where PEMFCs able to operate at very high

current density are required), all the ionomer membranes exhibiting high proton conductivity (including PFSA membranes) are unable to operate at temperature higher than 80–90 °C because a dramatic decrease of their performance was found at higher temperatures [9,10]. We remember also that a special volume of Journal of Membrane Science has been dedicated to this important problem and that the possibility to find polymer electrolytes better than Nafion® was considered [11].

In order to overcome the ionomer instability in the range 90°–130 °C, we believed that to find new ionomer membranes more stable than perfluorinated ones could be very difficult. Therefore, we preferred the following strategies: 1) Research for a better understanding of the reasons provoking thermal instability of known ionomers [12–17]; 2) Research on the matrix reinforcement of known ionomers by new annealing and/or by new cross-linking procedures [18–20].

Concerning the research of the first type, we found that the difficulty for all known ionomers to operate at temperatures $\geq$100 °C it is due not only to the fact that high RH values are necessary in order to obtain high proton conduction (we remember that these high values can be only obtained in pressurized cells) but also due to a real thermal instability of the proton conducting ionomers. By studying the behaviour of annealed Nafion® 117 membranes, it was found that a strong decay of the proton conductivity perpendicular to the electrodes at temperatures higher than about 80 °C was essentially due to an anisotropic swelling of the ionomer parallel to the catalytic electrodes [12,13]. Furthermore, it was very recently found that this anisotropic swelling can lead to a change from the original ionomer conformation to a layered one exhibiting very low conductivity perpendicularly to the layers. This latter important result, together with first characterization of some properties of the layered conformation, will be reported elsewhere [17]. Concerning the research of the second type, we already reached results of interest on thermal annealing and cross-linking of sulfonated aromatic polymers (SAPs) in the presence of dimethyl sulfoxide (DMSO) solvent [18]. We are now studying more in depth the role played by DMSO in the thermal stabilization of SAPs. Furthermore, it was already reported that the stabilizing effect of thermal annealing on PFSA membranes can be quantitatively followed by determining the change of the so-called counter-pressure index (n_c) of the ionomer for the various thermal treatments [14–16]. For its importance, we remember here that this index is proportional to the permanent deformations provoked by the swelling (hence, also proportional to the ionomer memory of previous treatments). The obtained results made evident that also the conductivity decay must be related to the visco-elastic behaviour of the ionomer matrix, encouraging us to go on in this research.

We will report here the relations between n_c with the proton molar fraction (χ_s), molality (m) and molarity (M) of the inner proton solution of annealed Nafion® 117 membranes after thermal treatments at given RH% values. The inner osmotic pressure (π_i) calculated by the corresponding molarity values at the various water-uptakes, is also reported. By n_c–temperature plots at different RH values, we arrived also to the important conclusion that the decay of Nafion® proton conductivity in the range 100–120 °C can be avoided just by a small reduction (2–3 RH% units) of the RH% value provoking the conductivity decay.

2. Material and methods

2.1. Chemical and membrane standard treatment procedure

Nafion® 117 membranes (EW = 1100, thickness 180 μm) and all other reagents were supplied by Aldrich. As received membranes were treated according to the standard procedure (1 h in boiling 3% solution of hydrogen peroxide; 1 h in boiling 0.5 M sulphuric acid; 1 h in boiling distilled water).

2.2. Annealing procedure

The membranes obtained by the standard treatment procedure were annealed in an oven at 120 °C for 15 h to provide the same memory to all the examined samples.

2.3. Determination of the counter-pressure index of the ionomer matrix

The index (n_c) was determined as described in Ref. [14]. In short, the samples were equilibrated in distilled liquid water at room temperature for 24 h. The memory water-uptake values (λ_m) were then obtained. The λ_m values were finally converted into n_c values by the Eq. (1):

$$n_c = 100/(\lambda_m - 6) \tag{1}$$

already derived in Ref. [15] and valid for $\lambda_m \geq 10$.

2.4. Thermal treatments at known RH values

These treatments were performed as described in Ref. [14].

2.5. Determination of equilibrium λ_e values

For each thermal treatment at known RH values, true equilibrium water-uptake values (λ_e) are only obtained after $\geq$500 h of treatment. It can be pointed out that while λ is related to the temperature and time of equilibration, λ_e is only related to the temperature.

2.6. Determination of the equivalent volume of anhydrous Nafion®

A portion of Nafion® 117 membrane (usually 5 × 5 cm) was dried in an oven at 120 °C for 15 h and the placed into a desiccator. After cooling, its weight and a, b, and c dimension were determined. The equivalent volume was then calculated taking into account the equivalent weight (1100) of this membrane.

3. Results and discussion

3.1. Determination of the proton molar fractions (χ_s) and molalities (m) of the inner proton solutions, after various equilibrium treatments, by n_c values

If we assume that the protons, for $\lambda_e \geq 10$ in liquid water at room temperature, have a hydration number of 7 [14], the index (n_c) can be obtained by:

$$n_c = 100/(\lambda_e - 6) \tag{2}$$

It is also easy to demonstrate that:

$$m = 55.55/(\lambda_e - 7) \tag{3}$$

$$n_c = \%\chi_s = 100m/(m + 55.55) \tag{4}$$

Thus, since the equilibrium λ_e values of annealed Nafion® 1100 in liquid water at different temperatures are already known (see [14]), m, % χ_s and n_c values can be calculated. These calculated values are reported and compared in Table 1.

Note that molarity values were not obtained by n_c values because the densities of the inner proton solutions were not known.

3.2. Determination of the proton molar fractions (χ_s) and molalities (m) of the inner proton solutions, after various equilibrium treatments, by the densities of the inner proton solutions

In order to have some information on the densities of the inner solutions, the following experiments were performed: A large numbers of samples exhibiting various λ values were prepared and the volumes of the membrane samples were

accurately estimated by measuring their a, b and c dimensions. The results so obtained were referred to 1 equivalent of proton and plotted in Fig. 1.

It can be easily seen that, for values $\lambda > 10$, all the obtained volumes are related to water-uptake values by the relation:

$$V_t = V_r + 18(\lambda - 4) \tag{5}$$

Where V_t is the total equivalent volume and V_r is the relative equivalent volume of the ionomer for $\lambda = 10$.

From this simple Eq., it is easy to deduce that, for values $\lambda > 10$, the difference $V_t - V_r$ is the volume due to the water-uptake. Since the weight of the water taken-up must be equal to 18λ, the density ρ of the proton solution must be:

$$\rho = \lambda/(\lambda - 4) \tag{6}$$

Without to enter in detailed calculations for the electro-restriction of water due to the effect of 1 equivalent of dissociated protons, we underline the fact that, for all the λ values > 10, the total aqueous inner volume is reduced, for the electro-restriction, of about $4 \times 18 = 72$ mL. Of course, the decreased volume could be in part due also to an electro-restriction of the polymeric matrix. However, it must be considered that the electro-restriction of the matrix is expected to decrease with the dilution of the proton solution while the experimental volume contraction was found to remain about constant with dilution (for λ value > 10). In any case, we tried to use the density values obtained by the Eq. (6) for density calculations of the inner proton solutions. Taking into account that all these solutions contain 1 equivalent of protons, the inner proton molarities of these solutions can be simply obtained be the Eq:

$$M_i = 1000/V_i \tag{7}$$

where V_i is the inner equivalent volume of the solution:

$$V_i = (\lambda - 4) \times 18 \text{ mL} \tag{8}$$

The molality of the inner solutions can be then obtained by the relation:

$$m_i = M_i \rho \tag{9}$$

All the above amounts were calculated for the same λ values of Table 1 and the results reported in Table 2.

Table 1 — Some colligative properties of inner proton solutions for annealed Nafion® 117 after equilibration in water at different temperatures (range 60—140 °C). The membranes were annealed at 120 °C for 15 h and the colligative properties deduced on the basis of λ_e values, by taking into account that the protons are hepta-hydrated (at room temperature and for $\lambda_e > 10$) [14]. Thus, appropriate Eqs. have been used (see text).

T(°C)	T(K)	λ_e	m	% χ_s	n_c
60	333	17.5	5	9	9
70	343	19	4.5	8	8
80	353	21	4	7	7
90	363	23.5	3.5	6	6
100	373	27	3	5	5
110	383	31	2.5	4	4
120	393	36	2	3	3
130	403	57	1.1	2	2
140	413	76	0.8	1.4	1.4
≈150	≈423	106	0.56	1.0	1.0

λ_e = equilibrium values of water-uptake (data from Refs. [14,15]).
m = molality of the inner proton solution, calculated using Eq. (3).
% χ_s = percentage of the inner molar fraction of protons, calculated by Eq. (4).
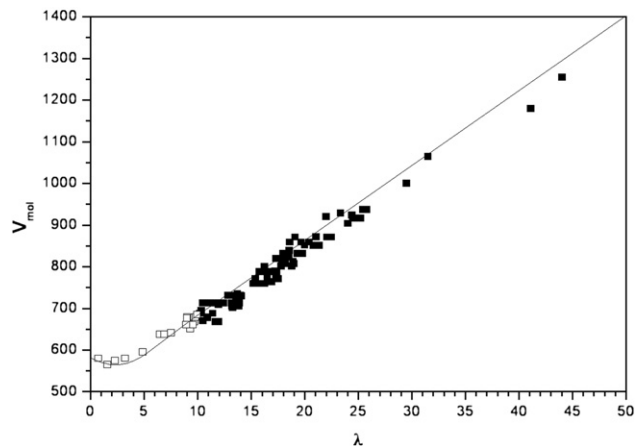n_c = index of the matrix counter-osmotic pressure, calculated by Eq. (2).

Fig. 1 — Equivalent volume of Nafion® 1100 annealed at 120 °C for 15 h. For λ values > 10, the experimental points fit a straight line (Eq. (5)).

Table 2 – Some colligative properties of inner proton solutions for annealed Nafion® 117 (120 °C for 15 h) after equilibration in water at different temperatures (range 60–140 °C). Properties were deduced on the basis of λ_e values, taking into account the experimental Eq. (14) for the density of the inner proton solutions.

$T(°C)$	$T(K)$	λ_e	n_c	ρ_i	V_i	M_i	m_i	$\% \chi_s$
60	333	17.5	9	1.3	243	4	5	9
70	343	19	8	1.3	270	3.5	4.5	8
80	353	21	7	1.2	306	3.5	4	7
90	363	23.5	6	1.2	351	3	3.5	6
100	373	27	5	1.2	414	2.5	3	5
110	383	31	4	1.1	486	2.0	2	4
120	393	36	3	1.1	576	1.7	2	3
130	403	57	2	1.07	954	1.0	1.1	2
140	413	76	1.4	1.06	1296	0.77	0.8	1.4
≈ 150	≈ 423	106	1.0	1.04	1836	0.54	0.56	1.0

λ_e and n_c as in Table 1.
ρ_i = density of the inner proton solution (g/mL), calculated by Eq. (6).
V_i = volume of the inner liquid pore (mL) at 293 K for equivalent of protons, calculated by Eq. (8).
M_i = molarity of the inner proton solutions, calculated by Eq. (7).
m_i = molality of the inner proton solution, calculated by Eq. (9).
$\% \chi_s$ = percentage of the inner molar fraction of protons, calculated by Eq. (4).

Table 3 – Inner osmotic pressures for annealed Nafion® 117 membrane at various temperatures (same conditions of Table 2).

$T(K)$	λ_e	V_i	M_i	π_m	π_T	$\pi_m \times V_i$ [a]
333	17.5	243	4	96	109	23.3
343	19	270	3.5	84	98	22.7
353	21	306	3.5	84	101	25.7
363	23.5	351	3	72	89	25.3
373	27	414	2.5	60	74	24.8
383	31	486	2	48	63	23.3
393	36	576	1.7	41	55	23.6
403	57	954	1.0	24	33	23.8
413	76	1296	0.77	18.5	26	24.0
≈ 423	106	1836	0.54	12.9	19	23.7

V_i = volume of the inner proton solution (mL) at 293 K for equivalent of protons calculated by Eq. (8).
π_m = inner osmotic pressure (atm.) after cooling at 293 K, calculated by Eq. (10).
π_T = inner osmotic pressure (atm.) calculated at the temperature T.
a The product $\pi_m \times V_i$ (l atm mol^{-1} at 20 °C) was calculated for comparison with the Eq. of ideal gases at 20 °C: we remember that $PV = n \cdot R \cdot 293 = 24.0$ (l atm mol^{-1}).

3.3. A comparison among the proton molar fractions (χ_s) and molalities (m) of the inner proton solutions, after various equilibrium treatments obtained by the two different methods reported in Sections 3.1 and 3.2

It is now of interest to compare the m values reported in Tables 1 and 2 because they have been obtained by two different methods. This comparison shows that there is a very good agreement between these values. In our opinion this is a demonstration that the densities of the inner solutions can be evaluated by Eq. (3). Thus, the molarities of the inner solutions reported in Table 2 can be considered also very near to true values. We tried therefore to use these values for the calculation of the inner osmotic pressures at 20 °C. In order to obtain the inner osmotic pressures at the other temperatures, the relation:

$$JI_i = M_i RT \tag{10}$$

where R is the gas constant while T is the temperature (K).

The calculated values are reported in Table 3. Note that the inner osmotic pressures of the ionomer decreases with increasing temperatures. This fact, in apparent contrast with Eq. (6), can be easily explained if a prevalent viscous behaviour of the ionomer, especially at temperatures higher than 80 °C, is also taken into account.

3.4. Some considerations on the proton solvation shell and its relation with the electro-restriction of the inner solvent

In the method based on n_c index, the inner molality of the proton solution was derived by considering a part of the water-uptake as solvation shell of protons. In particular, the total water-uptake, λ_{tot}, was defined in Ref. [14] as:

$$\lambda_{tot} = \lambda_{hyd} + \lambda_{OS}. \tag{11}$$

and $\lambda_{hyd} = 7$ was used for λ values > 10.

Electrostatic effect of the protons are therefore not explicitly included in this model.

In the second method, the solvation shell was not considered as belonging to protons, but the effect of the electro-restriction of the total solvent under the electric field of the protons was considered by introducing a factor of electro-restriction F_e.

Taking into account the experimental results before reported, it was of interest to find if λ_{hyd} and F_e are related among them.

Considering the Eqs. (7)–(9), respectively, we can write:

$$V_i = (\lambda - F_e) \times 18 \tag{12}$$

$$M_i = 1000/[(\lambda - F_e) \times 18] \tag{13}$$

$$\rho_i = 18\lambda/[(\lambda - F_e) \times 18] \tag{14}$$

By introducing Eqs. (13) and (14) in Eq. (9) we obtain:

$$m_i = 55.55\lambda/(\lambda - F_e)^2 \tag{15}$$

Finally, by recalling Eq. (3), we can write:

$$\frac{55.55\lambda}{(\lambda - F_e)^2} = \frac{55.55}{(\lambda_e - \lambda_{hyd})}$$

Thus,

$$(\lambda - F_e)^2 = \lambda(\lambda - \lambda_{hyd}) \quad \text{and} \quad \lambda - F_e = (\lambda \times \lambda_{OS})^{1/2}$$

F_e and λ_{hyd} are therefore related by the Eq:

$$F_e = \lambda - [\lambda \times (\lambda - \lambda_{hyd})]^{1/2} \tag{16}$$
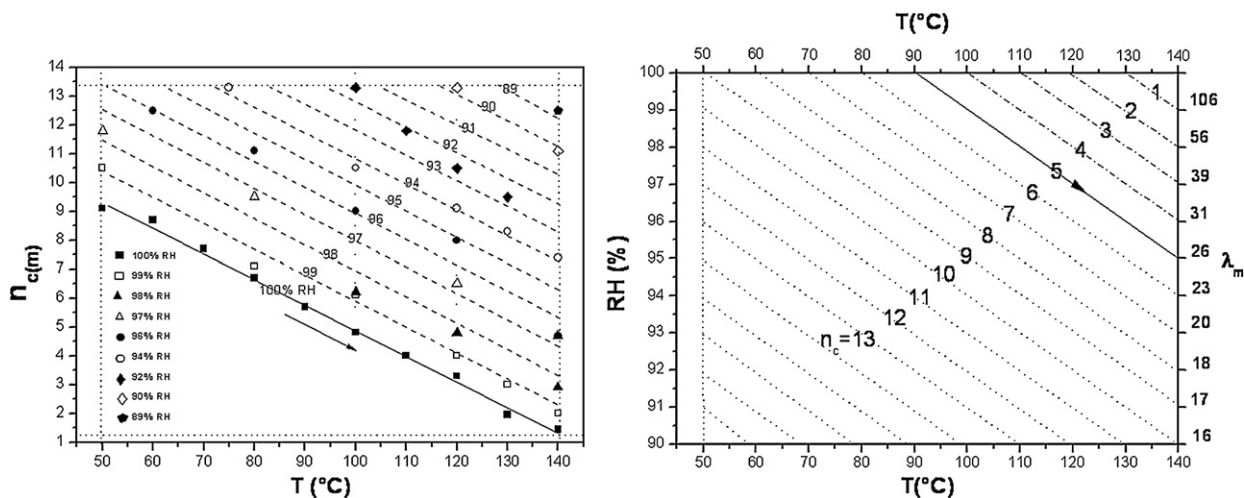
Fig. 2 − Left: n_c−T plots at constant RH% values for Nafion® 117 membrane (annealed at 120 °C for 15 h; data from Ref. [14]). Right: Conversion of the left plots in T−RH% plots for constant n_c values. The zone with n_c values <6 represents an instability zone for temperatures >80 °C when RH% = 100.

If, for example, we assume that, for $\lambda_{tot} = 47$, the hydration number is 7, the corresponding F_e factor is:

$F_e = 47 − (47 \times 40)^{1/2} = 3.6$, in good agreement with the average value of 4 in Eq. (8).

In conclusion, to consider a solvation shell of seven waters for the proton is equivalent to consider an electro-restriction factor of about 4. In other words, to consider a solvation shell for the proton is equivalent to insert an electro-restriction factor in the method based on the use of n_c.

3.5.   T−RH plots at constant n_c values and their relation with thermal ionomer instability of the proton conductivity

n_c-Temperature plots at constant RH values have already reported and discussed in Ref. [15]. In Fig. 2 (left) are shown the plots for annealed Nafion® 117 membrane while in Fig. 2 (right) are shown the related T−RH plots at constant n_c values.

Note that the non-equilibrium value of $\lambda = 22$, obtained by the standard procedure, corresponds to the equilibrium λ_e value at about 80 °C. When this hydrated membrane is placed in an FC working at 100 °C, its hydration increases to an equilibrium λ_e value corresponding to this latter temperature (i.e., $\lambda_e = 27$). An asymmetric swelling of the Nafion® membrane can therefore take place (parallel to the catalytic electrodes) with consequent decay of proton conductivity. Note that it is sufficient to increase the n_c value of just 2 units for avoiding the conductivity decay of the membrane. In fact, the increasing of two n_c unit is equivalent to decrease the temperature of about 22 °C (i.e., a decrease from 100° to 78 °C, where we already know that Nafion® membranes can work even for very long times).

4.   Conclusions

For the first time, the inner colligative properties of an ionomer in a large range of temperatures (50°−140 °C) have been determined and their relation with the visco-elastic properties

of the ionomer has been shown. From the trend of the inner osmotic pressure with the temperature, it can be deduced that, especially at temperatures higher than about 80 °C, Nafion® 1100 must be considered as an ionomer with a prevalent viscous behaviour.

In addition, T−RH plots for constant n_c values showed that, for Nafion® 1100 annealed at 120 °C for 15 h, it is sufficient to work at RH values ≤96% for avoiding the decay of its proton conductivity in the temperature range 100−120 °C.

Thus, the present believing that the known ionomers cannot be employed at temperatures higher than 80−90 °C is not completely true. New prospects are therefore open for the use of already known ionomers in PEMFCs at medium temperatures, especially if we will be able in the near future to increase their stability of some n_c unit by new annealing procedures or by introduction of stable cross-link bonds. We are presently involved in both these researches.

Acknowledgements

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