

More on Nafion Conductivity Decay at Temperatures Higher than 80 °C: Preparation and First Characterization of In-Plane Oriented Layered Morphologies

Giulio Alberti,* Riccardo Narducci, Maria Luisa Di Vona, and Stefano Giancola

Dipartimento di Scienze e Tecnologie Chimiche, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma, Italy

ABSTRACT: In order to have a better understanding of Nafion behavior in fuel cells operating at temperatures higher than 80 °C, the preparation of membranes containing a large amount of layered morphologies prevalently oriented in the direction parallel to the membrane surface (hence of low through-plane conductivity) was attempted. Successful in-plane oriented samples were obtained by forced swelling of membranes between rigid planar constraints. Other than the expected low through-plane conductivity, a first characterization of these modified membranes clearly showed that the dimension change during processes of dehydration and successive hydration takes place essentially in the direction perpendicular to the membrane surface. It was furthermore found that the forced swelling was accompanied by a strong reduction of ionomer density (from an initial value of 2 to about 1.4 g/cm³). Finally, evident changes of the n_c/T plots were also found. A discussion on the formation of these in-plane oriented layered morphologies is reported, giving emphasis to the fact that their formation in working fuel cells is particularly dangerous when they are prevalently oriented in the direction parallel to the membrane surface (large extent of through-plane conductivity decay). Some practical expedients for avoiding the formation of these dangerous in-plane “oriented layered morphologies” under the operative conditions of relative humidity and temperature are also reported. The inter-relations between spectroscopic investigations, recent stochastic simulation processes, and our experimental results are finally discussed.

1. INTRODUCTION

Both the impelling need for a consistent reduction of pollution in large towns and carbon dioxide in the atmosphere, as well as the continuous increase in petrol cost, have reinforced the interest in efficient and clean systems such as fuel cells (FCs) for the conversion of fuels into electrical energy.^{1–3} Among them, polymeric electrolyte fuel cells (PEMFCs) using proton conducting membranes seem to be presently the FC type of higher interest for automotive applications.

Among the different kinds of ionomer membranes, perfluorinated sulfonic acid (PFSA) membranes are characterized by excellent chemical inertness, high proton conductivity, and good mechanical and thermal stability; however, the mechanical and thermal stability are sometime not high enough for present needs in automotive or cogeneration applications.

Since the greatest interest for PFSA ionomers in recent years derives from their application as proton conducting membranes in PEMFCs, research has been largely driven by this important technologic application.^{4,5} Although a lot of information on ionomer membranes, especially of Nafion type, has been acquired, it is widely accepted that much more remains to be learned even for this important ionomer.⁶ In the following, the present state of knowledge on conductivity decay and on possible layered morphologies of this ionomer will be briefly examined in order to understand better the investigation here performed for increasing the working temperature of Nafion membrane PEMFCs.

Nafion Conductivity Decay. In previous papers,^{7–9} it was reported that when the couple relative humidity–temperature (RH–T) exceeds certain critical values, ionomers can undergo some irreversible processes which provoke a dramatic decrease

of their through-plane conductivity. The analysis of the evolution of both frequency response and through-plane conductivity during the conductivity decay suggested that the above decay arises from changes in the bulk-transport properties of the ionomer membrane.¹⁰ Since it was observed that the decay does not occur when the membrane is free to swell, it was inferred that the decay transition is associated with the anisotropic deformation that is taking place, under certain conditions of RH and temperature, when the membrane is constrained between the electrodes and forced to swell only in the direction parallel to them. In this case, effects of the anisotropic swelling can be considered to be similar to those provoked by an applied stretching parallel to the membrane surface.

Due to the practical implication of conductivity decay in PEM fuel cells, systematic conductivity determinations of Nafion 1100 at controlled RH, temperature, and electrode pressure were carried out and results used to build up Nafion instability maps (i.e., plots providing the RH–T couples for which the conductivity was not stable). To define the instability domain, the conductivity was recorded as a function of time for a maximum of 150 h at controlled RH and temperature. The border of the instability domain was obtained as a line separating the RH–T couples for which the conductivity is stable for at least 150 h from those for which the conductivity

Special Issue: Enrico Drioli Festschrift

Received: December 29, 2012

Revised: March 11, 2013

Accepted: March 12, 2013

Published: March 14, 2013

decays within the same time. It was found that, in the temperature range 70–130 °C, the instability transition is essentially affected by high RH values and practically confined between 95 and 100% RH.

In particular, it was found^{11,12} that, for RH = 100%, some instability of Nafion conductivity begins already for temperatures near 80 °C.

Successes on the thermal stabilization of the Nafion matrix were recently obtained by thermal annealing in the presence of annealing agents.¹³ However, it was found that the thermal stabilization appreciably reduces the capability of the ionomer in taking up water from wet air at a given temperature. On the other hand, the FC temperature must be sufficiently elevated to allow the elimination of the heat generated in the fuel cell even for external temperatures of about 45 °C. The cell cooling is not an inconvenient for fixed cogeneration FCs but can be a serious problem for transport applications, where small radiators of similar size and weight of those presently used for internal combustion cars of comparable power are highly desirable.

In this situation of uncertainty, we decided a further investigation on the phenomenon of PFSA conductivity decay in order to be able to optimize the working temperature of car FCs at about 95 °C.

Nafion Layered Morphologies. The existence of an ionomer layered morphology has been already postulated for Nafion more than 30 years ago, although this idea has been subjected to many controversial debates.

On the basis of the existence of a low angle scattering maximum, the existence of lamellar platelets in Nafion was suggested already in 1981, by Fujimura.¹⁴ One year later, the formation of a layered Nafion morphology was reported also by Starkweather.¹⁵ Later, lamellar morphologies have been reported by Litt¹⁶ in 1997 and Haubold¹⁷ in 2001. More recently, ribbon morphologies have been reported by Gebel^{18,19} and Perrin²⁰ while Termonia confirmed the layered morphology by stochastic simulation.²¹ Finally, a Nafion layered morphology was expected to be present in membranes with decayed through-plane conductivity in order to explain the experimental behavior of this ionomer.²² Surely, a success in the preparation of a large amount of macroscopic Nafion samples prevalently constituted by in-plane oriented layered morphologies could be of great help since these samples allow experimental determination of their macroscopic properties.

In this paper, the first successful results in the preparation and characterization of large layered Nafion 1100 membrane batches prevalently in-plane oriented and with decayed through-plane conductivity are below presented and discussed.

Densities, proton conductivities, and counterosmotic pressure index (n_c) vs temperature (n_c/T) plots of the above samples were determined. Some considerations on a possible transition from conductive to through-plane low conductive Nafion morphologies are reported and the interconnection between spectroscopic investigations, recent stochastic simulation processes, and our present results are discussed.

2. EXPERIMENTAL SECTION

Treatment of “As Received” Nafion 1100 between Rigid Planar Constraints. Small round pieces of as received Nafion 1100 membranes were placed between the plaques of the apparatus shown in Figure 1.

To facilitate the hydration, the ionomer membrane diameter was larger (of about 1–2 cm) than the metallic disc diameter

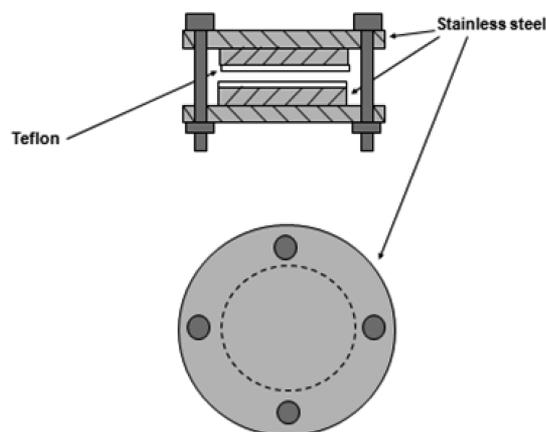


Figure 1. Schematic view of the apparatus used for facilitating the transformation of “as received” Nafion 1100 membranes into Nafion “treated” samples.

(3–5 cm). Furthermore, in order to avoid the direct contact metal-membrane, the metallic plates were suitably covered with a thin disk of Teflon. The ionomer membrane was first well tighten between the plaques, and then, the apparatus with the inserted membrane was placed inside a suitable autoclave at 120 °C at RH% = 100 for about 2 days. As it will be later discussed, under this RH–T couple and equilibration time, the expected water-uptake expressed as λ (moles of water for EW of ionomer) was equal to 32 which produces, as discussed later, a volume increase²² of $(32-4) \times 18 = 504 \text{ cm}^3$. Being the membrane tighten between rigid metal plaques, the membrane swelling perpendicular to its surface is not allowed, thus facilitating an anisotropic swelling in the parallel direction, i.e., in the direction that facilitates the ionomer transition from the conductive to the low conductive Nafion membrane.¹⁰ The autoclave was then cooled at room temperature and the ionomer samples so obtained were maintained in closed vessels.

In order to distinguish the samples obtained by the procedure above-described from those of as received, hereafter these former samples will be simply called “treated” Nafion.

Determination of Through-Plane Conductivity. Through-plane conductivity was determined as previously described.¹⁰

Determination of Membrane Swelling: In-Plane and Through-Plane Directions. A portion of treated Nafion membrane (usually 15 mm \times 15 mm) was first dried for one night over P_2O_5 , and then, its weight and its a , b , and c dimensions were accurately determined. The dried membrane was then dipped in bidistilled water at 20 °C and equilibrated for 1 day. Its a , b , and c dimensions were again determined. The membrane was finally dried again over P_2O_5 , and its weight again determined. Samples with different hydration (expressed as λ values) can be obtained by dipping the anhydrous samples in water at different temperatures for different times.

Determination of Water-Uptake (λ). Water-uptake (expressed as λ values) of treated Nafion samples were determined as previously described^{7,8,22} where similar investigations for as received Nafion samples are reported.

Due to the importance of this procedure, some details for equilibrium water-uptake determination in samples equilibrated in liquid water (i.e., RH = 100%) in the temperature range 20–105 °C will be here shortly remembered: a membrane sample (usually 5–10 mg) is first equilibrated in bidistilled water in a closed container at the wished temperature for at least 150 h.

The closed container is then cooled at room temperature and the water can be changed, especially in presence of doubts about release of some substance by the used ionomer sample. When the room temperature is appreciably different than 20 °C, a further equilibration in a thermostatic bath at 20 °C ± 1 for at least 10 h could be necessary for more precise comparisons.

The membrane is then separated from liquid water and the excess of external liquid water is removed by placing the membrane between two foils of filter paper and pressing lightly. This drying procedure is repeated 2–3 times. The samples are then placed in a weighing container, closed and weighed. The sample is finally dried at 130–140 °C for at least 4–5 h and again weighed. The hydration number λ is obtained by the weight differences between hydrated and anhydrous samples. The error on λ determination decreases with increasing λ value. As an example, the error percentages in the ranges 30–20 and 30–50 are $\leq \pm 3$ –5% and $\leq \pm 3$ –2%, respectively. For more details in the errors, see ref 8.

Determination of the Equivalent Volume of Hydrated Treated Nafion Samples and Their Densities. The determination of the equivalent volumes (EV) for many treated Nafion hydrated samples has been carried out as previously described for as received Nafion.²²

As already found for as received Nafion,²² when these equivalent volumes are plotted as a function of λ , a linear plot is obtained for $\lambda \geq 4$.

The density (ρ) of hydrated samples can be directly obtained by the relation: $\rho = EV/EW = EV/(1100 + \lambda)$.

EV values are obtained by the average of many samples which fit a linear EV/ λ plot for $\lambda \geq 4$; the error in their density determination can be estimated to be <5%. In agreement with what previously reported,²² the density of the anhydrous treated Nafion is assumed to be very near to that of the hydrated sample with $\lambda = 4$.

Plots n_c/T . The n_c/T plots were determined as previously described for as received Nafion.^{8,13}

We remember that n_c can be obtained from equilibrium λ values at the various temperatures (i.e., for at least 150 h of equilibrium when the samples equilibrated in liquid water). We remember also that (for RH = 100%) n_c can be calculated by the simple relation: $n_c = 100/(\lambda - 6)$.

3. RESULTS

Directional Swelling Experiments. Table I shows a comparison among density, water-uptake, and through-plane conductivity of as received and treated Nafion samples. Table II shows directional swelling experiments.

The obtained results clearly show that the swelling of treated samples takes essentially place in the c direction i.e., in the direction perpendicular to the membrane surface. An expected decrease of the through-plane conductivity can be clearly seen

Table I. Comparison among Density, Water-Uptake, and Through-Plane Conductivity for as Received and Treated Nafion Samples

ionomer	density (ρ) (g/cm ³)	water-uptake (λ) (mol/equiv)	σ (S/cm) [RH = 100%; $T = 100$ °C]
Nafion 117 as received	2.00	25.0	1.1×10^{-1}
Nafion 117 treated	1.46	≈ 70	$\approx 4 \times 10^{-2}$

but this decrease is also accompanied by an appreciable unexpected decrease of the ionomer density.

Through-Plane Conductivity and Changes in the Ionomer Density. The decay determination of proton conductivity has initially been used as an experimental proof that Nafion samples of low through-plane conductivity can be obtained when the membrane is used between rigid electrodes.¹⁰ After the discovery that treated Nafion also exhibits much lower density than that of as received one, the ionomer density values may be used to determine the extent of the transformation of as received Nafion into treated samples of low through-plane conductivity.

EV/ λ Plots. A comparison between EV/ λ plots of treated and as received Nafion is shown in Figure 2.

n_c/T Plots. In Figure 3 is shown the n_c/T plot of treated Nafion sample (obtained by the INCA method¹³). In the same figure is also shown the n_c/T plot of as received Nafion samples. We remember that n_c is a dimensionless index proportional to the ionomer mechanical properties^{7–9} and that, at 20 °C, one n_c unit corresponds to a Young's modulus of about 6.5 MPa.

Morphological Models. On the basis of the previous results some morphological layered models are schematized in Figures 4 and 5. Note that the reported models are only hypothetical, and schematic ones and are here illustrated only for showing that it is possible the existence of more than one subtype of layered morphology. Furthermore, the side view is also giving a better view of the ionic clusters in the interlayer region. Note also that, due to the extended shape of the main chain, the formation of intrachain clusters (i.e., clustering of $-\text{SO}_3^-$ polar heads belonging to same main chains) is highly unlikely.

4. DISCUSSION

As reported in the Introduction, the recent stochastic investigations of Termonia²¹ seem to be a definitive demonstration that the Nafion morphology is of layered type. Now, taking into account that the swelling of a layered compound takes place in the direction perpendicular to the planar layers and that the swelling of as received Nafion is isotropic (i.e., the swelling occurs in all space directions), we can conclude that the layered morphologies in as received Nafion must be randomly oriented. On the other hand, the dimensional swelling experiments (Table I) clearly show that the treated Nafion samples essentially swell in the direction perpendicular to the membrane surface. Since layered morphologies are expected to be already present in as received Nafion membranes^{15–21} and since the experimental swelling behavior of treated Nafion membranes can be predicted for the swelling of layered morphologies, in which all the layers planes are parallel to the membrane surface, it can be concluded that Nafion treatment essentially induces changes in the orientation of the layered morphologies by increasing the amount of morphologies oriented parallel to the membrane plane. However, since a stretching effect of the ionomer chains parallel to the membrane surface is very likely induced in treated samples, the formation of an additional amount of layered morphologies during the samples treatment cannot be excluded. Furthermore, taking into account the present and previous experimental results on the through-plane conductivity decay,^{10,22} it can be also concluded that the formation of in plane oriented layered morphologies can be formed when the ionomer swelling perpendicular to the membrane surface is

Table II. Swelling Data for Three Samples of Treated Nafion

	weight (g)	dimension (cm)			V (cm ³)	ρ (g/cm ³)	λ (mol/equiv)	EV (cm ³ /equiv)
		a	b	c				
sample 1								
P ₂ O ₅ 24 h	0.045	1.55	1.25	0.016	0.031	1.45	≈0	760
H ₂ O 20 °C 24 h	0.065	1.70	1.35	0.020	0.046	1.41	27.1	1176
sample 2								
P ₂ O ₅ 24 h	0.022	1.50	1.40	0.007	0.015	1.47	≈0	750
H ₂ O 20 °C 24 h	0.039	1.65	1.50	0.012	0.030	1.30	47.2	1528
sample 3								
P ₂ O ₅ 24 h	0.040	1.30	1.20	0.017	0.027	1.48	≈0	743
H ₂ O 20 °C 24 h	0.058	1.50	1.40	0.020	0.042	1.38	27.5	1166

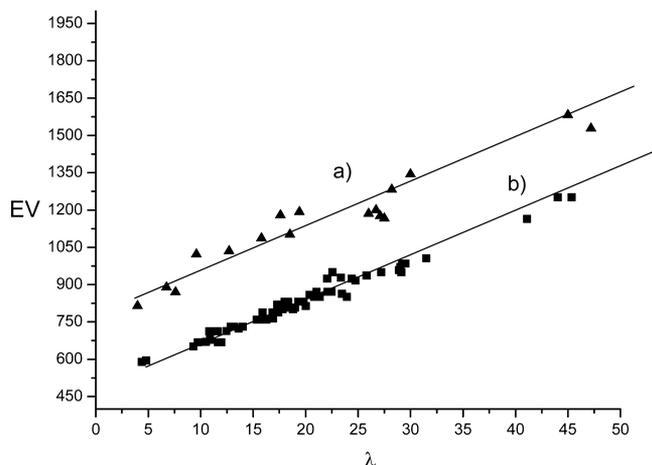


Figure 2. Comparison between equivalent volumes of treated (curve a) and as received (curve b) Nafion samples as function of λ . Curve b is adapted from ref 22.

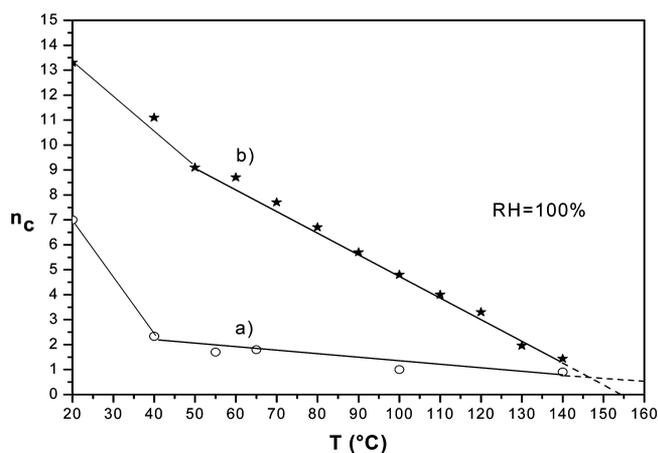


Figure 3. Comparison between n_c/T plots for a Nafion treated sample (curve a) and the as received sample (curve b).

impeded by rigid planar constraints, including the catalytic electrodes.

It could be of interest to know if the total effect provoked by rigid planar constraints is only limited to a simple orientation of pre-existing ribbon morphologies or are occurring also some changes in the subtype of the original morphology present in as received Nafion samples.

Since information on the change of mechanical properties of the ionomer matrix can be obtained by ionomer n_c/T plots, a simple comparison between the plots of as received and treated

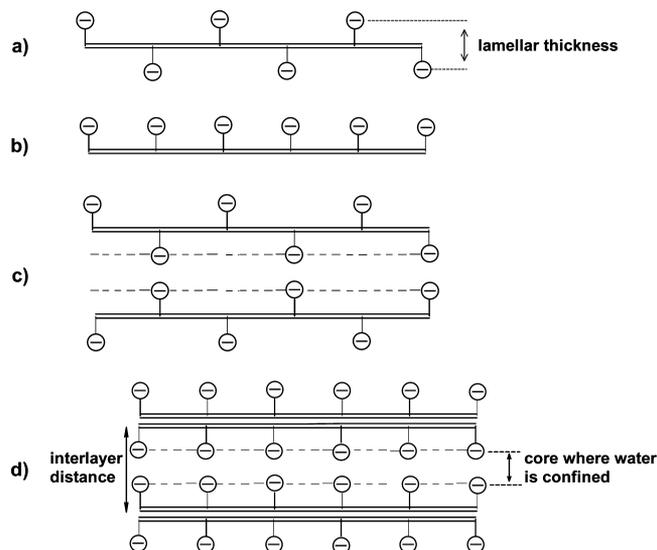


Figure 4. (a) Schematic representation of an elongated main chain of Nafion with side chains carrying $-\text{SO}_3\text{H}$ groups all in trans positions. (b) Same elongated main chain with all side chains in cis positions. (c) One possible subtype of bidimensional morphology formed by two layers of a subtype (front view). (d) Another hypothetical subtype of bidimensional morphology, formed by two layers of b subtype (front view).

Nafion samples already shows that the Nafion mechanical properties are greatly modified by the treatment between rigid planar constraints. Thus, these experiments could suggest that an “in plane orientation process” also induces some changes on the counterelastic properties of the ionomer. At the present, other experiments are in progress to give a more exhaustive answer to the above question, but surely spectroscopic investigations on treated samples could be of great value, especially to obtain detailed structural information.

Although already discussed¹⁴ for as received Nafion, it is of some interest to clarify the meaning of the Figure 2, where the equivalent volumes (EV) of treated Nafion samples are reported as a function of λ . For this plot, it is assumed that the equivalent volume of one hydrated ionomer sample $(\text{EV})_h$ is equal to the sum of the equivalent volume of the anhydrous ionomer $(\text{EV})_a$ and the equivalent volume of the water solution $(\text{EV})_w$. This latter volume (cm³), is obtained by the relation:¹⁴

$$\text{EV}_w = (\lambda - 4) \times 18$$

Therefore, we can write the following:

$$(\text{EV})_h = (\text{EV})_a + (\lambda - 4) \times 18$$

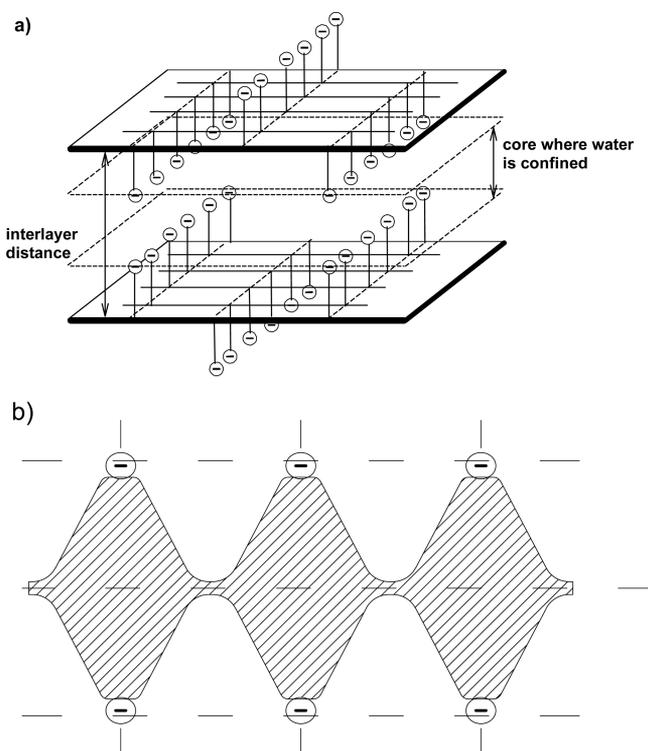


Figure 5. (a) Side view of the subtype morphology showed in Figure 4c. (b) Schematic representation of the expected qualitative shape of the proton solution in the inner “core” region (front view). Note that the specific surface area of each polar head does not depend on λ while the interlayer distance is expected to increase with increasing λ since the thickness of the core region increases with the proton dilution. In each aqueous task are contained two protons.

Note that in the above equation, it is assumed that $(EV)_a$ remains constant in the hydration range $\lambda = 1-4$. If our initial assumption was exact, a linear plot was expected starting from $\lambda = 4$. It can be seen (Figure 2) that the experimental points fit the expected straight line well enough, thus confirming our initial hypothesis. Note that, for $\lambda \leq 4$, an average EV value of about 800 cm^3 is obtained. Furthermore, the average EV density of anhydrous treated Nafion can be calculated:

$$\rho = EW/EV = 1100/800 = 1.4 \text{ g/cm}^3$$

For a comparison, we remember²² that $(EV)_a$ and ρ of as received Nafion 117 are 550 cm^3 and 2 g/cm^3 , respectively. This experimental result is very surprising and shows that the transition:

as received \rightarrow treated Nafion samples

produces a drastic decrease of both through-plane conductivity and ionomer density.

In conclusion, since the interlayer free volume of layered ionomers could depend on the subtype of ribbon morphologies, the density determinations could be a useful method for obtaining information if two samples have or not the same layered morphology. However, since the crystallization degree of this ionomer is very low, the observed changes in density are very likely due to a disordered packing of in-plane oriented layer morphologies in which free volumes are very likely present

Coming back to the presence of large free volumes, where inner liquid water cannot be accommodated, we note that this

peculiar characteristic is due to the presence of acid groups in a polymeric matrix. In consideration of many potential technological applications of this peculiar property, experimental determinations of porosity in layered ionomers are of high interest since the free volumes are expected to be filled by gases. Finally, we note that the fast hydration of Nafion membranes is very likely related to the fact that water vapor can easily diffuse in the porous interlayer domains.

The interlayer “free” volume is an important key for understanding the influence of both length of side chains and ionomer EW on mechanical and conductive properties of ionomer membranes. For this reason, we are presently investigating the influence of the above macroscopic properties on short side chains PFSA of different EW by our INCA method recently described.¹³

The concept of the free volume is also strictly related to the fraction of ionomer volume (ϕ), and in the case of lamellar morphologies, the relation between ϕ and free volume must be clarified since ϕ is often used in ionomers investigations. If we admit that the liquid proton solution is filling all the free volume present in the interlayer regions, the ionomer volume should be equal to the total interlayer volume (V_{tot}) minus the aqueous volume (V_{w}). In our opinion the above assumption is however not correct. Since the proton solution is positively charged, it is very likely that, in agreement with Haubold model,¹⁷ it is confined between charged heads (i.e., within the dashed “core” region, shown in Figure 4). As a consequence of this confinement, it could remain a large free volume among pendant side chains. Later we will come back again to the presence of free volume in the interlayer domain.

At the present, we have scarce knowledge on the shape of the proton solution inside the layered morphology. We can only assume that protons are very likely located somewhere in the central part of the “core” region (shown as a dashed zone in Figures 4 and 5). As a consequence of protons localization, a larger amount of water is expected to be present at the center of the core region. It is also likely that the amount of water decrease with increasing distance from the central interlayer domain until the size corresponding to the specific area of each polar head is reached, as schematically shown in Figure 5. Further investigation will be necessary to support the above hypothesis.

Due to the fact that the proton conduction is experimentally found, we have to admit that protons are able to percolate from a given aqueous cluster zone to an adjacent one. Therefore, at least at the center of the interlayer distance, the thermal motion of hydrated protons makes some connection among adjacent aqueous clusters which permits the proton percolation. Note that the said hypothetical connection in the interlayer domain is similar to the hypothetical connection through very small channels in the Gierke model, although the explanations for the formations of these channels in a layered morphology are completely different.

The macroscopic properties of Nafion derive from the microscopic arrangement of the main polymeric chain and its side groups carrying the fixed $-\text{SO}_3\text{H}$ moieties; in other words, the various experimental conditions used in operating PEMFCs affect Nafion macroscopic properties influencing the arrangements of its polymeric chains and then its morphology.

Due to the presence of $-\text{SO}_3\text{H}$ moieties, some clustering of these groups must be expected and the cluster arrangement could play an important role also in main chain arrangements since side chains are covalently bonded to the main chain.

Furthermore, the morphology of the liquid water (present in Nafion as an immiscible, hence separated phase) is, in turn, not independent from the cluster morphologies formed because Coulomb attractions among negative fixed charge, $-\text{SO}_3^-$ groups, and protons dissolved in the aqueous phase are established.

Another important question is that experiences accumulated after many years of experimental research on polymers indicates that main chains with stiffer backbone usually adopt an elongated wormlike shape and ultimately become rodlike.²³ It is of interest to know if this simple experimental rule, valid for uncharged polymers, can be also applied to ionomers. In our opinion, its application to ionomers is presently doubtful because the tendency to the cluster formation could contrast the chain stiffness, thus inducing some chain coiling. In other words, the rigid fibrillar organization implicates that the ionomer macromolecules are in their fully extended shape; therefore, the possibility of formation of clusters between side chains of the same main chain is not very probable. This point deserves further attention because fully extended main chains giving rise to fibrillar (and/or ribbon) morphologies could depend on both water uptake and temperature. High λ and T values could induce the destruction of the interchain clusters which, as stated before, favor the extended shape of the main chains (i.e., the formation of fibrillar and ribbon morphologies). As a consequence, when a structural investigation is reported, it is essential to give also the full history of the examined sample (e.g., drying temperature, used solvent in the casting preparation procedure, previous treatments, final temperature used in the membrane extrusion, eventual exposition to wet atmosphere, etc.).

From the comparison of n_c/T plots of as received and treated Nafion (see Figure 3), it is possible to observe that mechanical properties of treated Nafion rapidly decay already at moderate temperatures, after that the slope of the linear n_c decay decreases. This result seems to be in agreement with a layered morphology in which the mechanical properties in the plane are almost independent from λ .

Because we are continuing our researches on Nafion with low through-plane conductivity, a deeper discussion on its chain conformation will be reported only when additional experimental data will be available.

From the experimental ionomer density values, it is possible to calculate that the difference $(\text{EV})_t - (\text{EV})_a$ (i.e., the difference between the equivalent volume of treated and as received Nafion) is about $250 \text{ cm}^3/\text{EW}$. Now, if we assume that in as received Nafion the layered crystallites represent only a small fraction of the total ionomer, the above large difference in EV must be essentially due to the free volume differences of the amorphous layered part of Nafion samples or to differences on the percentages of layered crystallites. Although to understand better this point other research is necessary, it is already very important, for the use of Nafion in PEMFCs, to know that the formation of in-plane oriented layer morphologies can compromise its performance. Thus, it is of a particular importance to identify how to avoid the said morphology. Some practical suggestions are reported below.

Some Practical Expedients for Avoiding the Formations of Dangerous In-Plane Oriented Layered Morphologies. Before we conclude, we believe it is useful to report some expedients for avoiding the above inconveniences:

- (i) The electrodes should be controlled so that they are not a complete rigid impediment to the membrane swelling in the perpendicular direction to its surface.
- (ii) Too drastic and fast hydration–dehydration processes must be avoided, especially at temperatures $>100^\circ\text{C}$.
- (iii) If it is possible to control the working RH, we advise to avoid RH% values greater than 98%.

5. CONCLUSION

From the reported data it can be concluded that the through-plane conductivity decay is accompanied by an important matrix rearrangement with a considerable increase of the equivalent volume (hence, a consistent decrease of the ionomer density). The counter-osmotic pressure index of the ionomer (n_c) decreases appreciably, thus indicating that the transition is accompanied by a decrease of mechanical properties. In our opinion, the transition is due to the formation of “oriented ribbon-type” morphologies with semicrystalline and amorphous layers parallel for the most part to the membrane surface. This hypothesis is in agreement with the anisotropic conductivity, with density decrement, and with the shape of n_c/T plots of Nafion treated samples. We note that the extended shapes of the main chain (schematized in Figure 4) are the bricks with which the bidimensional layered morphologies can be built. Note that the bidimensional morphologies obtained by their combination could be very similar to the sandwichlike morphologies proposed by Haubold.¹⁷ We also remember that the same structural bricks can be used to form the rod-like structures more recently described by Gebel,^{18,19} Perrin,²⁰ and Termonia.²¹

We outline the fact that these oriented morphologies can be formed during the permanence of a Nafion membrane in an operating PEMFC and that, once formed, they are stable enough. Especially, the formation of the in-plane-oriented layered morphologies must be avoided for membrane uses as proton conductors, due to their low through-plane conductivity.

Our experimental data seem to support the Nafion model in nanometric scale, recently proposed by Termonia.²¹ It was furthermore found that mechanical and other macroscopic properties are directly related to the nanoscale morphologies of PFSA ionomers. Therefore, we do not agree with Termonia's belief²¹ that “mechanical properties of Nafion are related to the formation of a Nafion super-molecular structure”. In our opinion, if this hypothetical superstructure really exists, the effect on many macroscopic Nafion properties could be of modest extent, unless it is the result of the packing of in-plane oriented ribbons.

Our experimental results are also in agreement with that reported by Termonia²¹ that the specific surface (i.e., the surface bound to each ionic head) does not change with dilution etc. In fact the ribbon thickness, at least for semicrystalline ribbons, is independent of the degree of dilution.

However, we note that from our experiments it is not possible to derive any direct information on the exact shape of the cluster water present in the inner core regions.

At the present stage of our research we think that the strong decrease of the through-plane conductivity is essentially due to a scarce connection between aqueous pools of the inner proton solution in the above-mentioned direction, as a consequence of the formation of in-plane ordered layered morphologies. Since

our present investigations are mainly devoted to the PEMFC development, hence essentially dedicated to the effect of working temperature and RH on the mechanical and conductive properties of the membranes presently used, we can affirm that, at the least for temperature less than 150 °C, (sufficiently higher than the wished optimal working temperature of 90–110 °C), the Nafion 1100 membranes do not reach a value of $\varphi > 0.5$. Thus, according to Termonia,²¹ the transition from ribbon to rodlike morphology (very likely of low conductivity) does not occur even for the maximum RH% value (i.e., 100%). However, we remember that, in order to avoid through-plane low conductivity, the formation of in-plane oriented lamellar morphologies must be avoided.

AUTHOR INFORMATION

Corresponding Author

*E-mail: alberti@unipg.it.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The EU-FP7 (FCH-JU) project “LoLiPEM - Long-life PEM-FCH & CHP systems at temperatures higher than 100°C” (GA 245339) is gratefully acknowledged for funding this work. We also thank Professor M. Casciola for useful discussions and Ph.D. A. Donnadio for through-plane conductivity measurements.

REFERENCES

- (1) Doyle, M.; Rajendran, G. *Handbook of Fuel Cells*; Vielstich, W., Lamm, A., Gasteiger, H. A., Eds.; Wiley & Sons: Chichester, England, 2003; Vol. 3, pp 351–95.
- (2) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. Approaches and recent development of polymer electrolyte membranes for FC operating above 100 °C. *Chem. Mater.* **2003**, *15*, 4896.
- (3) Savogado, O. Emerging membranes for electrochemical systems; Part II high temperature composite materials for FC applications. *J. Power Sources* **2004**, *127*, 135.
- (4) Appleby, A. J. Electrochemical energy-progress towards a cleaner future. *J. Power Sources* **1995**, *53*, 187.
- (5) Zawodzinsky, T.; Derouin, C.; Radzinsky, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. J. Water uptake by and transport through Nafion 117 membranes. *Electrochem. Soc.* **1993**, *140*, 1041.
- (6) Mauritz, K. A.; Moore, R. B. State of understanding of Nafion. *Chem. Rev.* **2004**, *104*, 4335.
- (7) Alberti, G.; Narducci, R.; Sganappa, M. Effect of hydrothermal treatments on the water uptake of Nafion and relations with changes of counter-elastic force of the matrix. *J. Power Sources* **2008**, *145*, 108.
- (8) Alberti, G.; Narducci, R. Evolution of permanent deformations (or memory) in Nafion 117 membranes with changes in temperature, relative humidity and time. *Fuel Cells* **2009**, *4*, 410.
- (9) Alberti, G.; Narducci, R.; Di Vona, M. L. Perfluorinated sulfonic acids as proton conductor membranes. In *Solid State Proton Conductors*; Knauth, P., Di Vona, M. L., Eds.; Wiley: New York, 2012; Chapter 8.
- (10) Casciola, M.; Alberti, G.; Sganappa, M.; Narducci, R. On the decay of Nafion proton conductivity at high temperature and relative humidity. *J. Power Sources* **2006**, *162*, 141.
- (11) Alberti, G.; Casciola, M. Membranes for medium temperature PEFC based on Nafion filled metal phosphates and phosphonates. In *Membrane Technology*; Peinemann, K. V., Nunes, S. P., Eds.; Wiley-VCH: Weinheim, 2008; Vol. 2, Chapter 4, p 97.
- (12) Alberti, G.; Casciola, M. Composite membranes for medium temperature PEMFCs. *Ann. Rev. Mater. Res.* **2003**, *33*, 129.

(13) Alberti, G.; Narducci, R.; Di Vona, M. L.; Giancola, S. Annealing of Nafion 1100 in the presence of an annealing agent: a powerful method for increasing ionomer working temperature on PEMFCs. *Fuel Cells* **2013**, *13*, 42.

(14) Fujimura, M.; Hashimoto, T.; Kawai, H. Small-angle X-ray scattering study of perfluorinated ionomer membranes. I: origin of two scattering maxima. *Macromolecules* **1981**, *14*, 309.

(15) Starkweather, H. W. Crystallinity in perfluorosulfonic acid ionomers and related polymers. *Macromolecules* **1982**, *15*, 320.

(16) Litt, M. H. A reevaluation of Nafion morphology. *Polym. Prep.* **1997**, *38*, 80.

(17) Haubold, H. G.; Vad, T.; Jungbluth, H.; Hiller, P. Nano structure of Nafion; a SAXS study. *Electrochim. Acta* **2001**, *46*, 1559.

(18) Gebel, G. Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution. *Polymer* **2000**, *41*, 5829.

(19) Rubat, L.; Gebel, G.; Diat, O. Fibrillar structure of Nafion; matching fourier and real space studies of corresponding films and solutions. *Macromolecules* **2004**, *37*, 7772.

(20) Perrin, J. C.; Lyonnard, S.; Guillermo, A.; Levitz, P. Water dynamics in ionomer membranes by field-cycling NMR relaxometry. *J. Chem. B* **2006**, *110*, 5439.

(21) Termonia, Y. Nanoscale modeling of the structure of perfluorosulfonated ionomer membranes at varying degrees of swelling. *Polymer* **2007**, *48*, 1435.

(22) Alberti, G.; Di Vona, M. L.; Narducci, R. 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. *Int. J. Hydrogen Energy* **2012**, *37*, 6302.

(23) Young, R. J.; Lovel, P. A. *Introduction to Polymers*, 2nd ed.; CRC Press: Boca Raton, FL, 1991; p 152.