



How to improve Nafion with tailor made annealing†

Cite this: *RSC Adv.*, 2018, 8, 27268Riccardo Narducci,^a Philippe Knauth,^{b,c} Jean-François Chailan^d
and Maria Luisa Di Vona^{a,c}Received 5th June 2018
Accepted 23rd July 2018

DOI: 10.1039/c8ra04808h

rsc.li/rsc-advances

A tailor-made annealing procedure was developed for Nafion in order to avoid a critical degradation of the mechanical properties associated with a decrease of the ionic conductivity. The formation of layered morphologies, prevalently oriented in the direction parallel to the membrane surface, is responsible of the decay in fuel cell operation conditions. Nafion membranes are annealed at 140 °C over 7 days in the presence of dimethylsulfoxide (DMSO) as a proton-acceptor solvent. The important increase of mechanical stability is related to the formation of a crystalline phase, which acts as a physical cross-linker. The procedure is followed by hydrothermal annealing in liquid water in order to obtain an optimal water uptake at equilibrium (tailor made). To better understand the behavior of these polymers, we use the INCA method (Ionomer n_c Analysis) and compare with dynamic mechanical analysis (DMA). The stabilized materials are proposed for use in intermediate temperature fuel cells, where the mechanical stabilization by the annealing procedure plays a fundamental role.

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. In particular, polymer electrolyte fuel cells (PEMFCs) are preferred for automotive applications,^{1–7} but are also used for co-generation systems,^{8,9} and sometimes in combination with electrolyzers.¹⁰ Perfluorinated sulfonic acid (PFSA) membranes are characterized by excellent chemical inertness, high proton conductivity, and good mechanical and thermal stability.¹¹ However, the mechanical and thermal stability are not high enough for present needs.^{2,12–14}

When the relative humidity and temperature (RH/ T) exceed certain critical values, irreversible processes take place and provoke a severe decrease of the through-plane conductivity of membranes constrained between electrodes. Measurements of the frequency response show that the bulk-transport properties of the ionomer membrane are modified.¹⁵ The conductivity decay does not occur when the membrane is free to swell in all dimensions; an anisotropic deformation only occurs when the

membranes are forced to swell in the direction parallel to the electrodes.

A layered morphology has been hypothesized for Nafion more than 35 years ago, even if subject to debates still today.¹⁶ The presence of lamellar platelets in Nafion was initially proposed by Fujimura;¹⁷ one year later, a layered morphology was reported by Starkweather.¹⁸ Lamellar morphologies were described in 1997 by Litt,¹⁹ in 2001 by Haubold²⁰ and in 2013 by Kreuer.²¹ Ribbon morphologies were disclosed by Gebel,²² Rubatat,²³ Perrin²⁴ and Termonia.²⁵ The passage from random to in-plane oriented morphologies was assumed to explain the experimental behaviour of this ionomer. In our group, the Nafion conductivity was recorded in function of time for about 150 hours. The irreversible transition was affected by RH values between 95–100% in the temperature range of 70–130 °C; for RH = 100%, the instability begins near 80 °C.^{15,16,26} Large layered Nafion 117 membrane batches prevalently in-plane oriented and with decayed through-plane conductivity were prepared and characterized with a special device.¹⁶ Densities, proton conductivities and counter-osmotic pressure index (n_c) were determined *vs.* temperature (n_c/T plots) for the above samples. To avoid the formation of these harmful layered morphologies, we tried to use annealing procedures, well known in polymer technology.^{27–29} Many attempts for obtaining some mechanical stabilization by thermal procedures have been reported also for pre-formed ionomer membranes.^{30–32} The concept that the mechanical stabilization was due to a generic decrease of the free volume between ionomer chains when thermally treated^{33,34} was abandoned and replaced by the consideration that the mechanical stabilization was induced by an increased crystallization of a pre-existing semi-crystalline phase. A certain amount of molecular rearrangement must

^aUniversity of Rome Tor Vergata, Department of Industrial Engineering, Via del Politecnico 1, 00133 Roma, Italy. E-mail: riccardo.narducci@uniroma2.it

^bAix Marseille Univ, CNRS, Madiel (UMR 7246), Electrochemistry of Materials Group, Campus St Jérôme, 13397 Marseille, France

^cInternational Associated Laboratory (L.I.A.), Ionomer Materials for Energy, France and Italy

^dUniversité de Toulon, MAPIEM (EA 4323), CS 60584, 83041 Toulon Cedex 9, France

† In memoriam Prof. Giulio Alberti.



take place during crystallization, but this rearrangement cannot arise through large-scale molecular diffusion as the process is occurring in the solid state.²⁹ The annealing temperature (T_{ann}) must be chosen between the glass transition temperature (T_g) and the melting temperature (T_m) of the crystalline phase.²⁹ In order to facilitate the crystallization process, the addition of small amounts of proton acceptor solvents with plasticizing effect was considered and experiments in the presence of these substances were carried out. Our choice was dimethyl sulfoxide (DMSO), which is an annealing agent used for the crosslinking of sulfonated poly(ether ether ketone) (SPEEK),^{35–42} a benchmark of sulfonated aromatic polymers (SAP); SAP are alternative materials to perfluorinated membranes in fuel cells at medium temperature (80–110 °C).^{42–44} During these studies, the effect of the thermal annealing was evaluated by the use of n_c/T plots (INCA method) described in ref. 12, 29, 45 and 46. The improved functional properties are of great interest in electrochemical applications (such as PEMFCs).

In this paper, we describe thermal treatments of Nafion 117 in DMSO to increase the crystallinity and the mechanical stability and allow a better control of the water uptake. The materials treated in this way are compared with the material as received, in various aspects such as water uptake, Young's modulus, DMA tests and with the INCA method (Ionomer n_c Analysis). The ionomer can be further processed in a home-made device to obtain the layered material and observe its stability in these critical conditions. Finally, an optimized treatment (tailor made) will be proposed for use in fuel cells.

2. Material and methods

2.1 Chemicals

Nafion 117 membranes (equivalent weight EW = 1100 g eq.⁻¹, thickness 180 μm) were supplied by Sigma-Aldrich. Dimethyl sulfoxide (DMSO) and all the other chemical reagents were Carlo Erba RP products.

2.2 Membrane preparations

As received Nafion. As received Nafion 117 membranes were treated according to the standard procedure (1 hour in boiling 3% solution of hydrogen peroxide; 1 hour in boiling 0.5 M sulfuric acid; 1 hour in boiling distilled water).

As received and annealed Nafion. “As received and annealed” Nafion 117 was prepared as follows:²⁹ a large batch of 1 M solution of DMSO in ethanol was prepared. One piece of 0.5 mEW anhydrous Nafion 117 was cut and weighed (*i.e.* 0.55 g of the above membrane). The membrane was then placed inside a Teflon bottle. Ethanol solution was added in the vessel to give a calculated value of $\lambda(\text{DMSO}) = 2.0 \pm 0.4$ (*i.e.* about 1 mL of the ethanol solution of DMSO), where $\lambda(\text{DMSO})$ are moles of DMSO per EW of ionomer. The vessel was closed and the solution was left to equilibrate with the ionomer membrane for about 1 h at room temperature. After evaporation of the ethanol solution under moderate agitation at 80 °C, the vessel was closed again and placed in an oven at 140 °C for 7 days. After cooling a 0.5 M sulfuric acid solution was introduced in the vessel for 1 h and

the membrane was washed with distilled water several times for 24 hours for DMSO removal.

Oriented Nafion. Small round pieces of “as received” and “as received and annealed” Nafion 117 were placed between the plaques of a special laboratory-made apparatus.¹⁶ The membrane diameter was larger (about 1–2 cm) than the metallic disc diameter (3–5 cm) to facilitate the hydration. The plates were covered with Teflon to avoid the direct contact between metal and membrane. The Nafion membrane was well-tightened in the laboratory-made apparatus, and placed inside an autoclave at 120 °C and RH = 100% for 48 hours. Given that the Nafion is tightened between rigid metal plaques, the membrane swelling perpendicular to its surface is not allowed, thus anisotropic swelling in the parallel direction was facilitated; in other words, the transition from the conductive to the low conductive state was forced. The whole system was then cooled quickly to room temperature. The samples obtained were called respectively “as received and oriented” and “annealed and oriented”, and maintained in closed vessels.

2.3. Characterization

Water uptake and n_c measurements. The previous materials were treated in liquid water for 600 hours at different temperatures inside a Teflon container to determine the n_c index.

After this equilibration, membranes were kept at 25 °C for 24 hours in a closed Teflon vessel.¹² The excess of water was carefully wiped off and the membrane mass was determined (m_{wet}); then the samples were dried over P₂O₅ for 3 days and weighed (m_{dry}). The water uptake (WU) was calculated according to eqn (1):

$$\text{WU} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \quad (1)$$

The hydration number was calculated as:

$$\lambda = \frac{n(\text{H}_2\text{O})}{n(\text{SO}_3\text{H})} = \frac{\text{WU}}{\text{IEC} \times M(\text{H}_2\text{O})} \times 10 \quad (2)$$

IEC is the ion exchange capacity of Nafion (0.909 meq. g⁻¹). The uncertainty is about 0.5.

The λ values were converted into n_c values, as previously described,² by the eqn (3):

$$n_c = \frac{100}{\lambda - 6} \quad (3)$$

This equation is valid for $\lambda \geq 10$.

Density and molar volume. The density and molar volume were determined as previously described.^{13,16} A Nafion membrane (~20 × 20 mm) was first dried at room temperature for 24 hours with P₂O₅ and weighed using an analytical balance; the *a*, *b*, *c* sizes were determined with a micrometer. Then the membrane was equilibrated in bi-distilled water at 25 °C for 24 hours, wiped carefully with filter paper and the weight and *a*, *b*, *c* dimensions were again determined.



Conductivity. The proton conductivity was measured by impedance spectrometry (EG&G M6310) in through plane two point configuration. The amplitude of the applied voltage was 20 mV and the frequency range was between 100 kHz and 50 Hz. The measurements at full humidification were made at 25 °C in a Swagelok cell in presence of liquid water. The membrane resistance R was acquired from the intersection of the impedance arc with the real axis on a complex plane impedance plot (Nyquist plot).³⁶ The conductivity σ was quantified from eqn (4), where d is the membrane thickness and A the electrode area.

$$\sigma = d/R \times A \quad (4)$$

Mechanical tests. The experiments were made using an Adamel Lhomargy DY30 uniaxial tensile test machine at ambient temperature and humidity, determined using a humidity sensor (RH = 36 ± 3%). The constant crosshead speed was 5 mm min⁻¹ with aluminum sample holders. The measurement time was below 5 min. The thickness of the membranes was (206 ± 5) μm, the length of the samples between the clips was (26.0 ± 0.1) mm and their width 5 mm.

DMA. Dynamic Mechanical Analysis (DMA) was performed on a DMA Q 800 apparatus (TA Instruments) in extension mode with samples of approximately 15 mm × 7 mm size and 180 μm thickness. The DMA was operated in air at a fixed frequency of 1 Hz with 1 N initial static force, force track 125.0% and oscillation amplitude of 10 μm. This last value was chosen to keep the linear viscoelastic domain of samples during the experiments. The measurements were conducted with a 3 K min⁻¹ heating rate between 40 and 180 °C.^{43,47}

3. Results and discussion

3.1 Ionomer n_c analysis

The Ionomer n_c Analysis (INCA method) uses n_c/T plots to get some fundamental properties of an ionomer, such as the degree of crystallinity, Young's modulus¹² and the melting temperature. The use of the INCA method allows a quantitative and comparative evaluation of different materials.

Figure 1 shows the n_c/T plot in a large range of 50 °C to 140 °C for “as received and oriented” Nafion 117 (sample a),¹⁶ “as received” Nafion 117 (sample b)¹² and “as received and annealed” Nafion 117 (sample c).²⁹ For example, the “as received and annealed, H₂O 100 °C” sample corresponds to the sample c equilibrated 600 hours at 100 °C in liquid water. The hydrothermal treatment in liquid water is applied in order to obtain an optimal water uptake at equilibrium (tailor made sample). The formation of oriented ribbon-type phases is harmful in our application because of the low conductivity of such domains. In order to avoid or limit them, the goal is to reinforce the matrix by performing heat treatments in the presence of annealing agents that increase the crystallinity without sacrificing the conductivity. This is why we decided to test the “annealed” sample after orientation, this sample is called “annealed, H₂O 100 °C and oriented”.

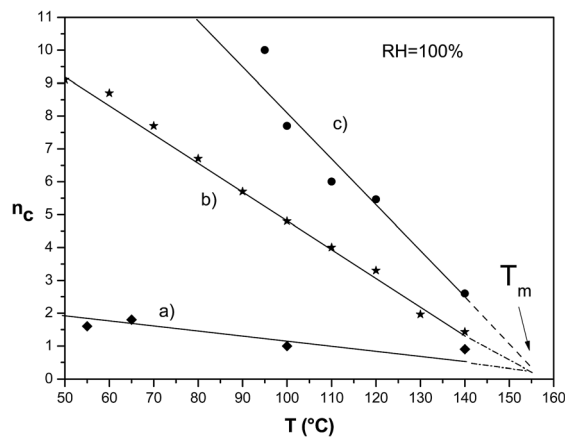


Fig. 1 Comparison between n_c/T plots for Nafion 117 “as received and oriented” (curve a), “as received” (curve b) and “as received and annealed” (curve c) in the range of temperature 50–140 °C.

In the n_c/T plots, a shift towards right is linked to an increase of mechanical properties; from these plots, one can also get the glass transition (T_g) and melting temperature (T_m) of the material and decide which treatment to perform (tailor made annealing). We remember that one n_c unit is equivalent to an increase of Young's modulus by about 6.5 MPa;^{12,13,48} it is clear that the “as received and oriented” material has a low elastic modulus in the whole range of temperatures. The decrease with respect to the “as received” material (Fig. 1) is between 7 units of n_c for 50 °C and about 1 n_c unit for 140 °C. The “as received and annealed” Nafion presents instead high values of n_c due to the increased crystallinity of the material. However, all of them have a melting temperature of about 160 °C (see the extrapolated n_c plots);²⁹ obviously the crystalline phase is already present in the “as received” material, remains, but probably with a lower content, in the “as received and oriented” material and increases in “as received and annealed” samples.

The mechanical properties were measured for Nafion 117 “as received and annealed, H₂O 100 °C” to compare its properties with those of pristine Nafion (Table 1). In liquid water, the elastic modulus is higher for the annealed sample with respect to pristine Nafion due to the increase of the crystalline phase.²⁹ This stabilization is important for the application in FCs working in fully humidified conditions. In ambient humidity, the increase of the elastic modulus can be observed if the residual DMSO, which acts as plasticizer, is removed with concentrated sulfuric acid. The elongation at break after annealing increases compared to pristine Nafion especially when the residual DMSO was removed.

Recent DSC results confirm that thermal treatments in the presence of DMSO increase the amount of crystalline phase, which improves the Young's modulus, due to its greater compactness.²⁹

In Table 2 are shown data of various Nafion samples treated 600 h at 100 °C and kept at 25 °C for 24 hours in a closed Teflon vessel. From the conductivity data shown in Table 2, it can be noted that the annealing treatment does not affect the conductivity; the data are very close to that of as received



Table 1 Mechanical properties of Nafion 117. E is the elastic modulus, σ is the yield stress, σ_{\max} is the tensile strength and ϵ_{Break} is the elongation at break

Sample	Measurement conditions	E (MPa)	Sigma (MPa)	σ_{\max} (MPa)	ϵ_{Break} (%)
N117 “as received and annealed, H ₂ O 100 °C”	RH = 36 ± 3%, 20 °C	255 ± 20	10.7 ± 0.5	27 ± 3	230 ± 20
	Liquid water, 20 °C	190 ± 20	10.5 ± 0.5	31 ± 3	280 ± 20
	“Washed, RH = 36 ± 3%, 20 °C	290 ± 20	10.5 ± 0.5	36 ± 3	320 ± 20
N117 ^b	RH = 50%, 23 °C	249	—	43	225
N117 ^b	Liquid water, 23 °C	114	—	34–26	200

^a Washed: 2 h H₂SO₄ 1 M + 24 h H₂O; after washing, 3 days under P₂O₅ and then stabilized for 10 days at RH = 36 ± 3%. ^b https://www2.dupont.com/FuelCells/en_US/assets/downloads/dfc101.pdf.

samples, even if the water uptake has a lower value. We can assume that the increased crystallinity reduces the tortuosity of the material. From Table 2, the treatment with DMSO does not entirely prevent the formation of the low conductivity phase after orientation, checked by the density measurements, however, the conductivity decrease between “as received and annealed” and “annealed and oriented” samples is limited only to 15%.

The density changes in the dry state are lower when compared with the large change observed in Nafion 117 “as received and oriented” (Table 2), where the density reaches a very low value around 1.4 g cm⁻³ and the conductivity decreases by a factor 3, in spite of the large water uptake. We can therefore deduce that the thermal treatment in presence of DMSO reduces the formation of non-conductive oriented phases inside the membrane.

The hydration number of “as received and oriented” Nafion is much higher than the other data due to the conformational modifications that occur after orientation (density lowering, large equivalent volume, and swelling along the c axis, perpendicular to the plates of the device). One can observe that the annealing reduce the effect of the orientation.

Alberti and coworkers¹⁶ demonstrated that the swelling of the oriented materials takes place along the c direction, perpendicular to the surface. The conductivity decrease can be observed in Table 2, which is accompanied by a dramatic decrease of the ionomer density (1.4 g cm⁻³). We concluded that lamellar morphologies are present in “oriented” Nafion samples. This ionomer presents a low degree of crystallinity and low Young's modulus; a consequence is the large water uptake across the temperature range (Fig. 1). The changes in density are very likely due to a disordered packing of in-plane oriented morphologies.¹⁶ To prevent the formation of these

non-conductive phases, we treated the Nafion 117 membranes at an annealing temperature $T_{\text{ann}} = 140$ °C with a small amount of DMSO, a proton acceptor solvent with plasticizing effect to increase the amount and/or the size of the preexisting semicrystalline phase.²⁹ Gebel has shown with wide-angle (WAXS) and small angle X-ray scattering (SAXS)⁴⁹ that the heat treatment increases the degree of crystallinity of Nafion.⁵⁰

3.2 Dynamic mechanical analysis (DMA)

Using sinusoidal solicitations of the sample, DMA analysis allows a separation of the storage modulus E' , describing the elastic response of the polymer, and the loss modulus E'' , related to the viscous response of the polymer. Given that in most cases the viscous part of the polymer modulus is much lower than the elastic part, the storage modulus is very close to the static elastic modulus obtained from mechanical measurements. The damping ($\tan \delta$), which is defined as the ratio of the loss modulus and the storage modulus E' , is a good parameter to evidence dynamic mechanical relaxations and especially the glass transition of the polymer T_g . Those phenomena appear as damping peaks during temperature ramp experiments. In an earlier publication, Kyu and Eisenberg⁵¹ discussed such relaxations for the acid form of Nafion and assigned greek letters based on the sequence of observation from low to high temperature. The first relaxation γ (around -100 °C) was assigned to short-range molecular motions in the tetrafluoroethylene backbone (crankshaft motions). The second one β around 20 °C was assigned to large chain motions of amorphous fluorocarbon units separated from the ionic aggregates. Finally, the largest peak α around 110 °C was assigned to the main relaxation process, which is associated to the glass transition, as in most polymers. In the Nafion case, this relaxation

Table 2 Conductivity, hydration number λ , n_c index, density of dry and wet membranes at 25 °C of Nafion 117 “as received”, “as received and oriented”, “as received and annealed, H₂O 100 °C” and “annealed, H₂O 100 °C and oriented”. All samples were treated for 600 h at 100 °C in water. The dry data were measured after 24 h over P₂O₅ and all other data after 24 h in H₂O

Sample	σ (mS cm ⁻¹)	λ	n_c	d_{wet} (g cm ⁻³)	d_{dry} (g cm ⁻³)
As received	30	25	5.3	—	2.0 ± 0.1
As received and annealed, H ₂ O 100 °C	31	18	8.3	1.7 ± 0.1	2.0 ± 0.1
As received and oriented	10	70	1.6	—	1.4 ± 0.1
Annealed H ₂ O 100 °C and oriented	26	17	9.1	1.6 ± 0.1	1.7 ± 0.1



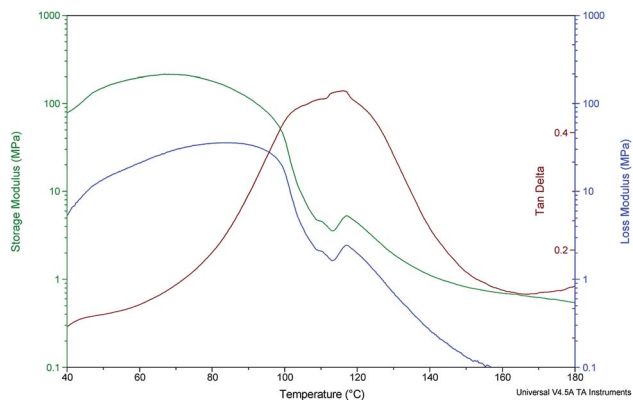


Fig. 2 DMA analysis for Nafion 117 “as received and oriented”. The brown line refers to $\tan \delta$, the green line refers to the storage modulus ($\log E'$) and the blue line refers to the loss modulus ($\log E''$). Sample parameters: length 8.95 mm, width 6.62 mm, thickness 0.18 mm.

mainly takes place in the polar regions, because it is sensitive to the ion type (in Na^+ form the α peak is around 250 °C), the degree of neutralization, and the water content. It is due to chain motions within or near the ion-rich domains.^{52,53} More recently, correlations of DMA data with molecular dynamics studies and morphological relaxations observed using variable temperature solid state NMR and SAXS experiments, allows attributing the α relaxation to the onset of long-range mobility of both the main and side chains as a result of a destabilization of the electrostatic network of ion-rich domains.¹ Fig. 2 presents the DMA results for “as received and oriented” Nafion 117 in the 40–180 °C temperature range. The $\tan \delta$ curve shows a main peak around 110 °C attributed to the α relaxation phenomenon. Although the arrangement is probably different (the ribbons are present both in the “as received” and “as received and oriented” Nafion), this result indicates that the ionic interactions are similar in the layered and in the as received sample. This main relaxation process of the polymer is in line with that reported in the literature.¹ One can see a shoulder probably due to the loss of water during the temperature ramp. This last phenomenon can also explain the increase in storage modulus below 60 °C, which is compensated above this temperature by the decrease of modulus during the α relaxation process. Most likely, the decrease in proton conductivity is due to a lower percolation also attributable to the new matrix arrangements. The question still deserves further study.

Fig. 3 shows the DMA results for Nafion 117 “as received and annealed” after washing in sulfuric acid and water. The T_{α} value of 110 °C is the same as for oriented samples. A small shoulder is also visible around 40–50 °C leading to a non-symmetric α peak and probably due again to some water loss. Given that the DMA technique is very sensitive to local hindrance of macromolecular chains, further studies will be performed to understand how the increased crystallinity affects the position of this peak.

Fig. 4 presents the DMA results for Nafion 117 “annealed and oriented”. The main $\tan \delta$ peak attributed to the α relaxation phenomenon is around 130 °C, 20 °C higher compared to literature data and previous oriented or crystallised samples. In

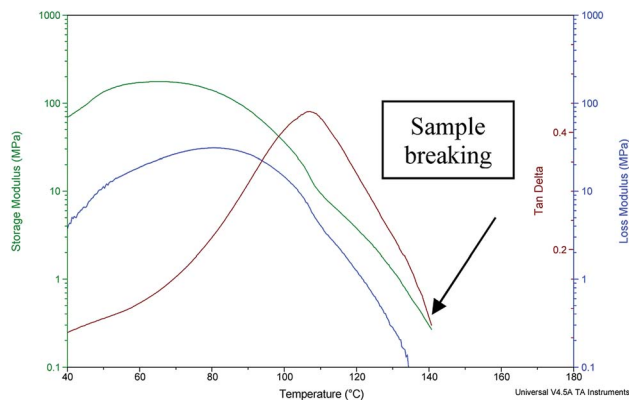


Fig. 3 DMA analysis for “as received and annealed” Nafion 117. Sample parameters: length 18.51 mm, width 5.24 mm, thickness 0.18 mm. This sample broke at 140 °C.

this case, orientation and crystallisation are combined and strongly hinder chains, which need more energy to move, leading to a higher relaxation temperature.⁵⁴ In addition, one can note that at 160 °C, in the rubbery state, the storage modulus is higher for the “annealed and oriented” sample than for the “as received and oriented” one.

A limitation of the DMA technique is the drying of the samples, which levels the effect on the main relaxation process due to its temperature close to 100 °C. The INCA method measures the mechanical properties at the working temperature and in liquid H_2O and can be a valid complement to DMA analysis in order to distinguish different ionomer samples.

Summarizing these results, we can say that the treatment at 140 °C in the presence of dimethyl sulfoxide is effectively limiting the formation of low conductivity oriented ribbon-type phases. The resulting formation of semi-crystalline phases with physical crosslinking increases the thermal stability. Then, the mechanical properties do not collapse at T_g , but at the melting temperature of the semi-crystalline phase (T_m). We remember that the knowledge of T_m is essential for using the appropriate annealing temperature to increase the crystallinity of ionomers, especially those having a low EW.⁴⁶ The “annealed” samples are

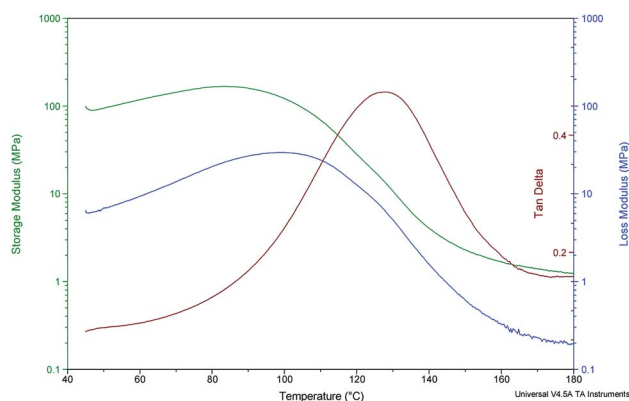


Fig. 4 DMA analysis for Nafion 117 “annealed, H_2O 100 °C and oriented”. Sample parameters: length 13.47 mm, width 5.75 mm, thickness 0.20 mm.



useful for applications in fuel cells with operating temperatures close to 100 °C. At such temperature, it is not necessary to pressurize the system and increase the cooling equipment for vehicles, which would lead to greater weight and greater use of energy. The increase of the working temperature of PEMFC by 15–20 °C can significantly improve their efficiency.

4. Conclusions

The through-plane conductivity decay, accompanied by an important matrix rearrangement with a consistent decrease of the ionomer density and n_c , is due to the formation of “oriented ribbon-type” morphologies with semi-crystalline and amorphous layers parallel for the most part to the membrane surface. The formation of the in-plane-oriented layered morphologies must be avoided for membranes used as proton conductors, due to their low through-plane conductivity essentially due to a scarce connection between aqueous pools of the inner proton solution. Annealing in the presence of DMSO is a promising method for the stabilization of membranes under the operating conditions of fuel cells, preventing the formation of low conductive phases. With the INCA method it is easy to find important properties of the material such as the T_g , also verified by DMA, and T_m ; moreover it is possible to establish the most suitable treatment of Nafion 117 (tailor made annealing). These results are promising for the use of these treated ionomers in a highly efficient medium temperature fuel cell.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are indebted to the late Prof. G. Alberti (May 1930–October 2017) for having initiated this work. The authors thank Dr A. Fahs for his help for the DMA measurements.

References

- 1 K. A. Mauritz and R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535–4585.
- 2 G. Alberti, R. Narducci and M. L. Di Vona, *Solid State Proton Conductors: Properties and Applications in Fuel Cells*, Wiley, 2012.
- 3 A. Paciaroni, M. Casciola, E. Cornicchi, M. Marconi, G. Onori, M. Pica and R. Narducci, *J. Phys. Chem. B*, 2006, **110**, 13769–13776.
- 4 A. Paciaroni, M. Casciola, E. Cornicchi, M. Marconi, G. Onori, M. Pica, R. Narducci, A. De Francesco and A. Orecchini, *J. Phys.: Condens. Matter*, 2006, **18**, S2029–S2038.
- 5 E. Roberti, G. Carlotti, S. Cinelli, G. Onori, A. Donnadio, R. Narducci, M. Casciola and M. Sganappa, *J. Power Sources*, 2010, **195**, 7761–7764.
- 6 G. Napoli, S. Micari, G. Dispenza, S. Di Novo, V. Antonucci and L. Andaloro, *Int. J. Hydrogen Energy*, 2017, **42**, 28034–28047.
- 7 J. Yuan, L. Yang and Q. Chen, *Int. J. Hydrogen Energy*, 2018, **43**, 8063–8078.
- 8 S. Bose, T. Kuila, X. L. N. Thi, N. H. Kim, K. T. Lau and J. H. Lee, *Prog. Polym. Sci.*, 2011, **36**, 813–843.
- 9 Z. B. Wang, G. P. Yin, Y. Y. Shao, B. Q. Yang, P. F. Shi and P. X. Feng, *J. Power Sources*, 2007, **165**, 9–15.
- 10 H. Ito, T. Maeda, A. Nakano and H. Takenaka, *Int. J. Hydrogen Energy*, 2011, **36**, 10527–10540.
- 11 A. Kusoglu and A. Z. Weber, *Chem. Rev.*, 2017, **117**, 987–1104.
- 12 G. Alberti, R. Narducci and M. Sganappa, *J. Power Sources*, 2008, **178**, 575–583.
- 13 G. Alberti and R. Narducci, *Fuel Cells*, 2009, **9**, 410–420.
- 14 M. Haghayegh, M. H. Eikani and S. Rowshanzamir, *Int. J. Hydrogen Energy*, 2017, **42**, 21944–21954.
- 15 M. Casciola, G. Alberti, M. Sganappa and R. Narducci, *J. Power Sources*, 2006, **162**, 141–145.
- 16 G. Alberti, R. Narducci, M. L. Di Vona and S. Giancola, *Ind. Eng. Chem. Res.*, 2013, **52**, 10418–10424.
- 17 M. Fujimura, T. Hashimoto and H. Kawai, *Macromolecules*, 1981, **14**, 1309–1315.
- 18 H. W. Starkweather, *Macromolecules*, 1982, **15**, 320–323.
- 19 M. H. Litt, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1997, **38**, 80–81.
- 20 H. G. Haubold, T. Vad, H. Jungbluth and P. Hiller, *Electrochim. Acta*, 2001, **46**, 1559–1563.
- 21 K. D. Kreuer, *Solid State Ionics*, 2013, **252**, 93–101.
- 22 G. Gebel, *Polymer*, 2000, **41**, 5829–5838.
- 23 L. Rubatat, G. Gebel and O. Diat, *Macromolecules*, 2004, **37**, 7772–7783.
- 24 J. C. Perrin, S. Lyonard, A. Guillermo and P. Levitz, *J. Phys. Chem. B*, 2006, **110**, 5439–5444.
- 25 Y. Termonia, *Polymer*, 2007, **48**, 1435–1440.
- 26 K. V. Peinemann and S. P. Nunes, *Membranes for Energy Conversion*, Wiley, 2008.
- 27 J. E. Hensley, J. D. Way, S. F. Dec and K. D. Abney, *J. Membr. Sci.*, 2007, **298**, 190–201.
- 28 Z. Y. Zhang and H. M. Zeng, *Polymer*, 1993, **34**, 3648–3652.
- 29 G. Alberti, R. Narducci, M. L. Di Vona and S. Giancola, *Fuel Cells*, 2013, **13**, 42–47.
- 30 X. Y. Ding, S. Didari, T. F. Fuller and T. A. L. Harris, *J. Electrochem. Soc.*, 2013, **160**, F793–F797.
- 31 Y. Xiao, K. K. Poornesh, L. Wendling and C. Cho, *Mater. Lett.*, 2014, **124**, 293–295.
- 32 H. B. Park, H. S. Shin, Y. M. Lee and J. W. Rhim, *J. Membr. Sci.*, 2005, **247**, 103–110.
- 33 M. K. Hassan, A. Abukmail and K. A. Mauritz, *Eur. Polym. J.*, 2012, **48**, 789–802.
- 34 L. A. Zook and J. Leddy, *Anal. Chem.*, 1996, **68**, 3793–3796.
- 35 B. Maranesi, H. Hou, R. Polini, E. Sgreccia, G. Alberti, R. Narducci, P. Knauth and M. L. Di Vona, *Fuel Cells*, 2013, **13**, 107–117.
- 36 M. L. Di Vona, L. Pasquini, R. Narducci, K. Pelzer, A. Donnadio, M. Casciola and P. Knauth, *J. Power Sources*, 2013, **243**, 488–493.



- 37 J. A. Kerres, *Fuel Cells*, 2005, **5**, 230–247.
- 38 J. A. Kerres, D. M. Xing and F. Schonberger, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 2311–2326.
- 39 A. Bhattacharya, J. W. Rawlins and P. Ray, *Polymer Grafting and Crosslinking*, Wiley, 2008.
- 40 R. Y. M. Huang, P. H. Shao, C. M. Burns and X. Feng, *J. Appl. Polym. Sci.*, 2001, **82**, 2651–2660.
- 41 P. Knauth, E. Sgreccia and M. L. Di Vona, *J. Power Sources*, 2014, **267**, 692–699.
- 42 R. Narducci, M. L. Di Vona and P. Knauth, *J. Membr. Sci.*, 2014, **465**, 185–192.
- 43 M. L. Di Vona, E. Sgreccia, R. Narducci, L. Pasquini, H. Hou and P. Knauth, *Front. Energy Res.*, 2014, **2**, 1–7.
- 44 M. L. Di Vona and P. Knauth, *Z. Phys. Chem.*, 2013, **227**, 595–614.
- 45 G. Alberti, M. L. Di Vona and R. Narducci, *Int. J. Hydrogen Energy*, 2012, **37**, 6302–6307.
- 46 G. Alberti, R. Narducci, M. L. Di Vona and S. Giancola, *Int. J. Hydrogen Energy*, 2017, **42**, 15908–15912.
- 47 R. Narducci, J. F. Chailan, A. Fahs, L. Pasquini, M. L. Di Vona and P. Knauth, *J. Polym. Sci., Part B: Polym. Phys.*, 2016, **54**, 1180–1187.
- 48 R. Narducci, G. Alberti and M. L. Di Vona, *Solid State Proton Conductors*, Wiley, New York, 2012.
- 49 G. Gebel, P. Aldebert and M. Pineri, *Macromolecules*, 1987, **20**, 1425–1428.
- 50 R. J. Young and P. A. Lovell, *Introduction to Polymers, Third Edition*, Taylor & Francis, 2011.
- 51 T. Kyu and A. Eisenberg, *Perfluorinated Ionomer Membranes*, American Chemical Society, 1982, vol. 180, pp. 79–112.
- 52 S. J. Osborn, M. K. Hassan, G. M. Divoux, D. W. Rhoades, K. A. Mauritz and R. B. Moore, *Macromolecules*, 2007, **40**, 3886–3890.
- 53 K. A. Page, K. M. Cable and R. B. Moore, *Macromolecules*, 2005, **38**, 6472–6484.
- 54 A. N. Frone, S. Berlioz, J. F. Chailan, D. M. Panaitescu and D. Donescu, *Polym. Compos.*, 2011, **32**, 976–985.

