ORIGINAL RESEARCH PAPER

Fuel Cells DOI: 10.1002/fuce.201200126

Annealing of Nafion 1100 in the Presence of an Annealing Agent: A Powerful Method for Increasing Ionomer Working Temperature in PEMFCs▲

G. Alberti[1]*, R. Narducci[2], M. L. Di Vona[2], S. Giancola[1]

[1] Dipartimento di Chimica, Università di Perugia,via Elce di Sotto 8, I-06123 Perugia, Italy
[2] Dipartimento di Scienze eTecnologie Chimiche, Università di Roma Tor Vergata, I-00133 Roma, Italy

Received July 16, 2012; accepted November 13, 2012; published online November 8, 2012

Abstract

The possibility of increasing the working temperature of fuel cells using Nafion as ionomer membranes by a new annealing procedure in the presence of dimethylsulfoxide or tributylphosphate as annealing agents has been investigated. The extent of annealing was derived by the shift of n_c/T plots of annealed membranes (n_c is the index of counter-elastic force) relatively to the plot of as received membranes. n_c/T plots can be used as a powerful analytical method useful for deriving quantitative information on the annealing extent and for obtaining information on the melting temperature of the semi-crystalline phase grown during annealing. It was found that, by using an annealing temperature of 140 °C in the presence of an annealing agent, an important effect on the thermal stability of Nafion membranes was obtained. The increased thermal stability was related to the increase of the original semi-crystalline phase which acts as a physical cross-linker so that the mechanical properties are no longer lost at the glass transition temperature but at the melting point of the semi-crystalline phase. The use of n_c/T plots as analytical tools for detecting and understanding important ionomer properties was denominated as "Ionomer n_c Analysis" (INCA).

Keywords: Fuell Cells, Nafion Membranes, Annealing Procedures, Semi-crystalline Phase, Thermal Stability

1 Introduction

Owing to their very good chemical inertness and high proton conductivity, perfluorinated ionomer membranes are till now the most popular ones for use in polymer electrolyte membrane fuel cells (PEMFCs) [1–7]. However, a dramatic decrease of the performance of these membranes at temperatures higher than 80–90 °C makes their use problematic for fuel cells operating at temperature near or little above 100 °C [8]. On the other hand, an increase in the working temperature of about 15–20 °C is expected to be very useful for solving cooling problems arising in PEMFCs for cars in tropical countries or in summer hot days in non-tropical countries. Fuel cell operating at temperatures little more than 100 °C are also useful in PEMFCs for co-generation use, because heat transport is facilitated and heat can also be used for thermal air-conditioners [9–12].

Various strategies are under investigation in our Laboratories in order to overcome PFSA membrane instability at temperatures higher than about 80–90 °C (depending also in the used relative hymidity, RH%). In this paper, some data on the stabilization of Nafion 1100 by annealing procedures in the presence of annealing agents will be reported and discussed.

Annealing procedures were already well known in the polymer technology [13–15] and therefore many attempts for obtaining some mechanical stabilization by thermal procedures also for pre-formed ionomer membranes have been

▲ *Paper presented at the E-MRS Spring Meeting 2012, Strasbourg, May 14–17, 2012*

[*] *Corresponding author, alberti@unipg.it*

reported [16, 17]. However, in many of these papers, thermal treatments were believed to be more and more efficacious as the temperature increases and therefore empirical short treatments were performed at high temperatures (in the range 160–200 °C, i.e., just a little lower than thermal ionomer decomposition). In any case, also our first attempts of Nafion annealing for long times at 140 °C gave modest results and were therefore mainly used to reduce or cancel the ionomer memory due to (permanent) deformation accumulated in previous ionomer history. On the basis of our first experience, it was decided to go on in these investigations but in less empirical and more quantitative manner. The previous researches on the annealing of polymers were carefully reconsidered [13, 18–21]. The concept that mechanical stabilization was due to a generic decrease of the free volume between ionomer chains when thermally treated was abandoned and replaced by the consideration that the mechanical stabilization was induced by an increased crystallization of a preexisting semi-crystalline phase. Thus, on the basis of the above consideration, the annealing temperature (T_{ann}) was connected with the crystallization temperature (T_c) and it became clear that the annealing temperature cannot be higher than the melting temperature (T_m) of the semi-crystalline phase. In our opinion, a certain amount of molecular rearrangement must take place during crystallization, but this rearrangement cannot arise through large scale molecular diffusion as the process is occurring in the solid state. Thus, in order to facilitate the above crystallization process, the addition of small amounts of proton acceptor solvents with plasticizing effect was considered and experiments in the presence of these substances (in the following called annealing agents) were carried out. Our first choice on DMSO as an annealing agent has surely been influenced by our knowledge on this solvent acquired during our investigations on the thermal formation of chemical cross-links in sulfonated aromatic ionomers [22, 23]. During these preliminary investigations, it was realized that the study of the effect of the thermal annealing was enormously facilitated by the use of n_c/T plots already described in Refs. [24, 25] and in a recent review [26]. We also recall that the relations between n_c and the water molar fraction, molality, and molarity of the inner proton solutions at given RH% values, as well as the inner osmotic pressure at various temperatures in the range 20–140 °C, have been recently reported and discussed [27].

In this paper, we report some preliminary annealing experiments of Nafion 1100 in the presence of annealing agents. The annealing effects were conveniently pointed out by n_c/T plots.

2 Materials and Methods

2.1 Chemicals

Dimethyl Sulfoxide (DMSO), Tributyl Phosphate (TBP), and all the other chemical reagents were Carlo Erba RP products.

2.2 Membrane Standard Treatment Procedure

Nafion 117 membranes (EW = 1100, thickness 180 μm) 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 sulfuric acid; 1 h in boiling distilled water).

2.3 Annealing Procedures in the Presence of An Annealing Agent

(a) **DMSO**: a large batch of 1 M solution of DMSO in ethanol (i.e., a solution containing 78 g of DMSO in a liter of solution) was prepared. One piece of anhydrous Nafion 117 membrane, equivalent to about 0.5 mEW, was cut and weighed (i.e., one piece of about 0.55 g of the above membrane).

The membrane was then placed inside a Teflon container. A volume of the above ethanol solution was added in the vessel to give a calculated value of $\lambda_{DMSO} = 2 \pm 0.4$ (i.e., about 1 mL of the ethanol solution of DMSO) where λ_{DMSO} are moles of DMSO for EW of ionomer. The vessel was closed and DMSO was left to equilibrate with the ionomer membrane for about 1 h at room temperature. The vessel was opened again and the ethanol was evaporated under a mild agitation at 80 °C. The vessel was then closed , placed in an oven at 140 °C and left for 4 days at the above T_c temperature. After cooling, 100 mL of a 0.1 N sulfuric acid solution were introduced in the vessel for eliminating residual DMSO present in the sample. The vessel was placed again in an oven at 95 °C for 1 h and then the sample was washed with distilled water. Finally, the hydrated Nafion sample was dehydrated at 140 °C for 3 days. The annealed sample was now ready for further investigation on its n_c value at the various temperatures in the range 20–120 °C.

(b) **TBP**: an annealing procedure quite similar to that described above for DMSO was used. A large batch of 1 M ethanol solution was prepared. Also in this case, a λ_{TBP} equal to 2 ± 0.4 was used as a standard amount of annealing agent inside the ionomer.

2.4 Determination of Equilibrium λ and Related n_c/T Plots

Equilibrium water-uptake, expressed as λ value (i.e., moles of water for EW of ionomer) are only obtained after ≥ 600 h of equilibrium at different temperatures [24]. The index n_c was obtained from water-uptake as previously described [24, 25] after equilibration 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 equation:

$$n_c = \frac{100}{\lambda - 6}$$

already derived in Ref. [25] and valid for $\lambda \geq 10$.

2.5 Attempt to the T_m Determination of the Semi-Crystalline Phase by DSC

A Mettler-Toledo DSC 1 STARe system thermal analyzer was used for DSC determinations. The presence of the semi-crystalline phase in annealed Nafion samples (5 mg) were determined by the DSC curves after elimination of residual annealing agent and then dehydration at 140 °C for 3 days, as above reported. Information on T_m has been obtained by determining the quenching temperature of the semi-crystalline phase. In short, three separate portions of the same annealed Nafion were separately heated at 150, 160, and 170 °C, respectively for 5 h, then rapidly cooled at 100 °C and finally their DSC again examined.

3 Results and Discussion

(a) n_c/T plots

In Figure 1 (curve a), is reported the n_c/T plot (RH = 100%) of "as received Nafion 117" after dehydration at 120 °C for 15 h. In the same figure (plot b) is shown the evolution of the above plot after annealing treatment at 140 °C for 4 days. Finally, the plot (c) refers to the sample obtained after an annealing treatment in the presence of DMSO at 140 °C for 4 days.

If the shift of the n_c/T plot toward right is taken, for the moment, as an index for the annealing effect, it can be seen that very little effect is obtained for temperatures ≤ 140 °C, even for very long times of treatment (curve b). On the contrary, a large shift was obtained at 140 °C in the presence of DMSO, as described in the *Experimental* (curve c).

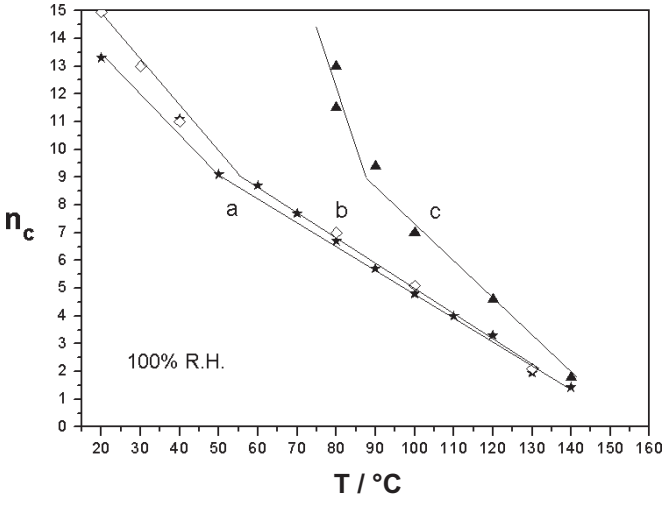

Fig. 1 A comparison of n_c/T plots (RH% = 100) for Nafion 1100 after thermal annealing without and in the presence of an annealing agent. Plot (a) refers to anhydrous "as received membrane", plot (b) refers to plot (a) after additional thermal annealing at 140 °C for 4 days, plot (c) refers to an annealing procedure performed at the same temperature and same time, but in the presence of DMSO.

Encouraged by this positive result, many other annealing experiments in the presence of annealing agents were performed and some results obtained in the presence of DMSO and TBP are reported in Figures 2 and 3, respectively.

From these data, the following general trends were observed:

i) The shifts of the plots increase with increasing time of thermal treatments at 140 °C;
ii) If the time is taken constant, the shift increases from 130 to 140 °C;
iii) All n_c values linearly decrease with temperature. However, an abrupt change of the slope can be observed at about a given n_c level that in the case of Nafion 1100 seems to be placed between 8.5 and 9.5.
iv) It is also evident that all extrapolations of n_c plots above the said n_c level converge at about 110 °C, in the while all

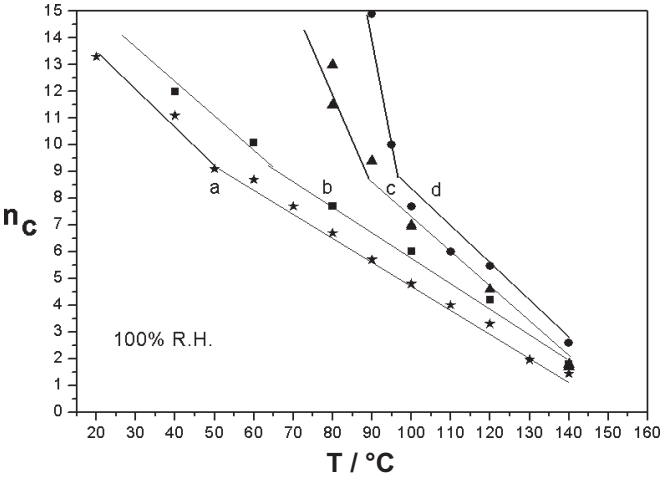

Fig. 2 n_c/T plots (RH% = 100) for Nafion 1100 after thermal annealing for different times in the presence of DMSO. (a) "as received membrane"; (b) sample annealed at 130 °C for 4 days; (c) sample annealed at 140 °C for 4 days; (d) sample annealed at 140 °C for 7 days.

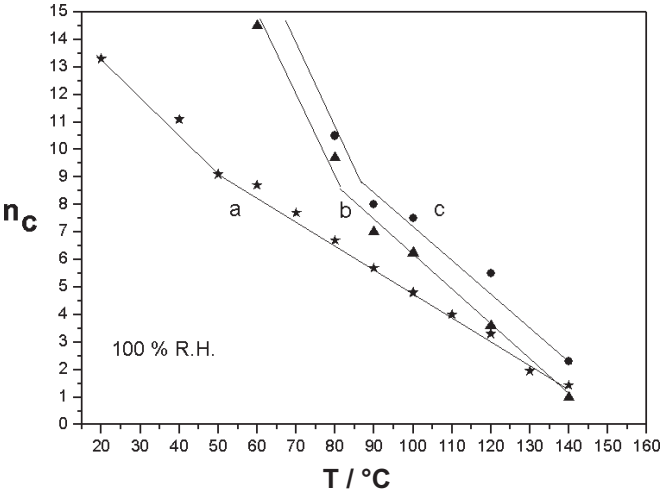

Fig. 3 n_c/T plots (RH% = 100) for Nafion 1100 after thermal annealing for different times in the presence of TBP. (a) "as received membrane"; (b) sample annealed at 140 °C for 4 days; (c) sample annealed at 140 °C for 7 days.

extrapolations of n_c plots under the said n_c level converge at about 155 °C. Because of the convergence at 110 °C seems to correspond to the glass transition of Nafion, the convergence at about 155 °C was associated to the melting temperature of the semi-crystalline phase created during the annealing process.

The obtained experimental data seem to indicate that n_c values (hence the mechanical properties of the Nafion matrix [26]) are shifted towards higher temperatures with increasing degree of annealing. In other words, the ionomer matrix increases its thermal stabilization with increasing degree of annealing.

A plausible explanation of the above strong stabilization could be related to the formation of a semi-crystalline phase giving rise to a physical cross-linking of the remaining amorphous ionomer part (Figure 4). The above hypothesis explains well because mechanical properties are completely lost (i.e., n_c tends to zero) to a certain temperature that corresponds to the melting temperature of the formed semi-crystalline phase.

It can be noted that the idea of an increasing amount of semi-crystalline ionomer phase associated to annealing processes is not new. To our knowledge, it was shown for the first time by Gebel et al. [28] by wide- and small-angle X-ray scattering patterns, that thermal treatments of Nafion 117 improve the degree of crystallinity of the ionomer. Improving of polymer semi-crystallinity by annealing is also well described in Ref. [29].

In order to experimentally confirm by another independent method that the convergence point at 155 °C was really the melting point of the Nafion semi-crystalline phase created by the annealing process in the presence of DMSO at 140 °C, DSC analysis of annealed Nafion was attempted.

(b) DSC results

Figure 5, curve a, shows the DSC obtained from a sample annealed for 7 days at 140 °C after elimination of DMSO and dehydration at 140 °C, as described in *Experimental*. In the same figure, curve b, is also shown with the result obtained with another portion of the same annealed sample that, after DMSO elimination and its dehydration at 140 °C, was also heated for 3 h at 160 °C directly inside the DSC apparatus, then cooled rapidly at 140 °C and DSC in the temperature range 80–210 °C determined.

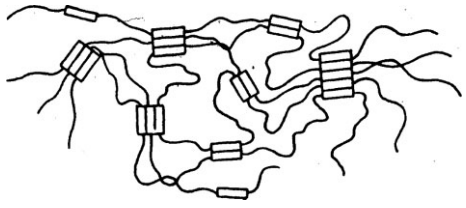

Fig. 4 A schematic representation of semi-crystalline phase in annealed ionomers. The presence of this phase induces physical cross-link of the ionomer chains. Note that each ionomer chain can be incorporated in different adjacent crystals and that inter-crystalline chain links can be therefore formed.

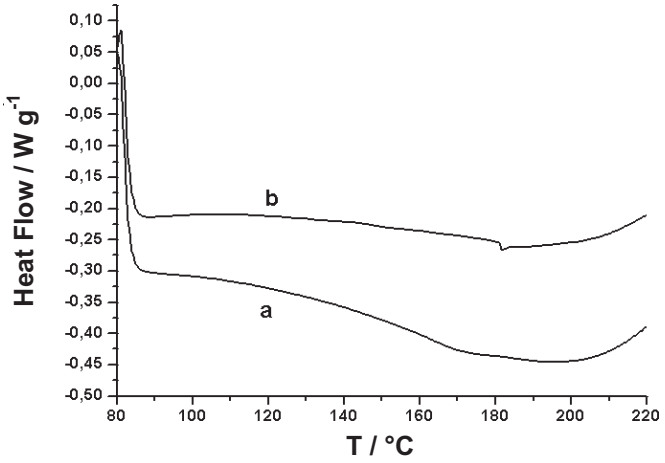

Fig. 5 DSC curves. (a) sample annealed for 7 days at 140 °C after elimination of DMSO and dehydration at 140 °C; b) the same annealed sample heated for 3 h at 160 °C directly inside the DSC apparatus and cooled at 140 °C.

The direct comparison of DSC obtained curves, shows that a thermal treatment at 160 °C eliminates all the irreversible endothermic transitions occurring at temperature range <160 °C. If the endothermic process found in curve a was due to the formation of the semi-crystalline phase, it can be concluded that the T_m value of this phase is ≤ 160 °C, i.e., in good agreement with the convergence point found in n_c/T plots (155 °C) of annealed Nafion samples.

The detection of the small percentage of the semi-crystalline phase eventually present in as received Nafion samples by DSC experiments resulted very difficult especially for the presence of small endothermic processes in the temperature range 150–170 °C, probably related to the presence of low percentages of the low melting temperature of E-crystalline phase (see later).

It can be noted that although many DSC investigations on Nafion have been reported [30–32], endothermic processes in the temperature range 150–160 °C have been observed only by Moore and Martin [31] and generically attributed to a transition related to ionic clusters.

In our case, after elimination of endothermic processes, such as water evaporation, in the range 50–140 °C, an endothermic process in the range 150–160 °C was found (Figure 5, curve a). Because this endothermic process is not detectable in "as received Nafion", it can be concluded that the shift observed in the n_c/T plot of annealed Nafion as well as the endothermic process found at about 155 °C are related to each other, so strongly reinforcing the idea that ionomer annealing in the presence of an annealing agent is an useful method for increasing the amount (and/or the crystal size) of a semi-crystalline phase.

We remember that a similar behavior to that described above for annealed ionomers was already known for semi-crystalline polymers where the yield stress is found to lin-

early decay at the melting temperature of the semi-crystalline phase [33].

It can be noted that the type of semi-crystallinity here discussed (T_m at about 155–165 °C) is not in contrast with the type of crystallinity already observed in old papers on Nafion (T_m about 220–240 °C) [34]. This crystallinity will be discussed in detail in a separate paper [35]. It can be here anticipated that this last crystallinity can be assigned to crystals formed by extended ionomer chains (E-type crystals); no formation of useful physical cross-linking can be therefore expected from the presence of this type of crystallinity. The semi-crystallinity formed during annealing processes here described seems to be a type of crystallinity in which only small portions (segments) of the total ionomer chain are involved (S-type crystals). A large part of un-crystallized chains remains, therefore, connected to the crystalline part and crystalline links, as discussed before and schematically illustrated in Figure 4. In semi-crystalline Nafion, both crystalline and amorphous components of ionomer chains are contained. Since crystalline components are joined between them by the amorphous portions of ionomer chains, it can be concluded that, if the total system is considered as a bi-phasic system, mechanical separation becomes only possible after the melting of the crystalline component. Therefore, we think that the melting temperature can be detected in n_c/T plots from the linear extrapolation to zero of the n_c values at the melting temperature.

During the annealing process, especially in the presence of an annealing agent, the disordered and small crystals of E-type are transformed into more ordered and/or larger crystals. The endothermic processes due to their melting is therefore expected to be shifted to higher temperatures, thus facilitating the detections of S-type crystals by DSC method.

Further research on S- and E-type ionomer crystals will be necessary before definitive conclusions on ionomer types of crystallinity. Presently, a research on the stabilization of Aquivion series of ionomers by annealing is in an advanced stage (in the frame of EU-FP7, FCH-JU, Project Maestro) and the results by Alberti et al. will be reported elsewhere.

4 Conclusion

First results on ionomers stabilization by annealing procedures in the presence of annealing agents seem to be a very promising method and therefore we are presently involved in studying the annealing of different side-chain length perfluorinated polymers in order to see the side chain and branching percentages effects on the melting point of the semi-crystalline formed phases.

Although, additional investigations will be necessary in order to better clarify the role played by the nature and amount of annealing agents, some first conclusion on the annealing process can already be drawn out.

1) In the absence of annealing agents, no appreciable annealing effect can be obtained even for very long thermal treatments at 140 °C;
2) The annealing effect is strongly influenced by the chosen annealing temperature. In our opinion, the annealing temperature must be considered as a crystallization temperature and therefore all the present understanding on the crystal grow from molten polymer crystals must be taken into account;
3) It is very plausible to hypothesize that the reinforcement of the mechanical properties at temperatures higher than the ionomer T_g are due to the formation of a larger amount of this semi-crystalline phase, in agreement with what found for polymers where, a small percentage of this phase can give rise to a strong effect on the polymer mechanical properties [35];
4) n_c/T plots seem to be a very powerful method for studying annealing effect giving information both on the melting point and on the amount of the formed semi-crystalline phase.

Independent characterization by DSC method of annealed samples only show that an increased amount of endothermic processes takes place in annealed Nafion samples. Our hypothesis that the linear n_c/T plots converge at the melting point of the semi-crystalline phase remain very plausible, although other research will be necessary for definitive conclusions.

The use of n_c/T plots as analytical tools for detecting and understanding important ionomer properties such as T_g, T_m, and λ as a function of temperature and RH, mechanical properties, etc, was denominated in our Laboratories as "Ionomer n_c Analysis " (INCA) and it was found that this method, specific for ionomers can be used alone or in connection with other known methods for polymers such as DSC and DMA.

Acknowledgements

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.

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