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Blends of Nafion and Dow Perfluorosulfonated Ionomer Membranes

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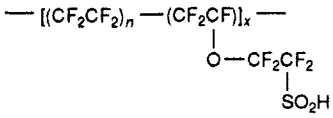
ABSTRACT: Solution-cast membranes from perfluorosulfonated ionomers (PFSI) and their blends were prepared from E. I. du Pont de Nemours's Nafion 117 and Dow Chemical's experimental membrane XUS. Water sorption and ac impedance measurements were performed on the solution-cast membranes in an attempt to characterize their electrical properties. Water uptake versus relative humidity for the solution-cast membranes was measured and it was observed that the solution-cast membranes imbibe less water than as-received membranes. The dc conductivity was extracted from the impedance measurements, and the room temperature dc conductivity of the solution-cast membranes was found to be approximately 10^{-7}–10^{-6} S/cm, $\approx 10^4$ times lower than the room temperature conductivity of the original PFSI membranes. Impedance analysis also revealed the existence of the γ-relaxation in the solution-cast membranes. The drastic drop in conductivity and the existence of the γ-relaxation are thought to be caused by structural changes in the solution-cast PFSI as is supported by high-resolution wide-angle X-ray diffraction (WAXD) measurements.

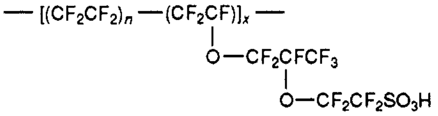
Introduction

The great success of the perfluorosulfonated ionomer (PFSI) cation conducting membranes stems from the unique properties that they possess. The fact that water and cation species may readily permeate the membrane while anions remain virtually impermeable, coupled with their excellent mechanical, chemical, and thermal stabilities, has allowed the PFSI membrane to find widespread use in many electrochemical applications.[1–3] The first commercially available PFSI, Nafion, was developed by E. I. du Pont de Nemours and Co. in the 1960s. More recently, although not commercially available yet, Dow Chemical Co. has introduced a similar product, the XUS experimental membrane. Both membranes incorporate poly(tetrafluoroethylene)-like backbones with perfluorocarbon sulfonate side chains that facilitate ionic conduction. However, the sulfonated side chains of the Dow XUS membrane (a) are much shorter than those of Nafion (b) and only contain a single ether group per sulfonated side chain.



$$\begin{array}{l} -[(CF_2CF_2)_n-(CF_2CF)]_x- \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad O-CF_2CF_2 \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad SO_2H \end{array}$$

a



$$\begin{array}{l} -[(CF_2CF_2)_n-(CF_2CF)]_x- \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad O-CF_2CFCF_3 \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad O-CF_2CF_2SO_3H \end{array}$$

b

In recent years much work has been performed on the two different membranes in an effort to identify the structure and morphology of these PFSI. Wide-angle X-ray diffraction indicates there is, at least, partial crystallinity in Nafion and XUS as witnessed by the Bragg peak superimposed on an amorphous halo at ca. $2\theta \approx 18°$.[4–7] This peak has been attributed to the partial crystallization of the poly(tetrafluoroethylene) (PTFE) backbones and is found to be relatively insensitive to both the cationic form and the moisture content of the PFSI membrane. It has also been demonstrated that the degree of crystallinity decreases with decreasing equivalent weight (EW) due to the increasing concentration of the side-chain material with decreasing EW. Also, small-angle X-ray scattering reveals evidence for the existence of ionic-rich domains, or "clusters", that are observed in both Nafion an XUS.[4,7] It has been proposed that these clusters, containing the majority of the ion pairs, act as multifunctional "electrostatic" cross-links due to their strong Coulombic nature.[8] Keeping the above morphological information in mind, it is not surprising that PFSI are so resilient in both very harsh acidic and basic enviroments and, in fact, will remain virtually insoluble in any solvent below 200 °C. While chemical stability and thermal stability are desirable properties for PFSI membranes, they do pose limitations on the number of useful applications for the PFSI. For example, the use of PFSI in chemically modified electrodes or as corrosion-resistant coatings was not possible until a dissolution procedure for PFSI was developed by Martin et al.[9] Even then, the physical and chemical proprties of the recast PFSI films were not suitable for many applications as they did not possess the original qualities of the as-received membranes. It was not until high-temperature solution processing techniques were developed[7,10] which produced PFSI films having comparable physical and chemical properties that the use of PFSI as useful coatings could be attained.

It is the purpose of this report to investigate the electrical properties of solution-cast PFSI membranes. To do so PFSI were dissolved using the previously reported techniques.[7,10] More importantly, blends of Nafion and XUS were produced via mixing the two solutions to produce a third 1:1 by volume of XUS + Nafion solution. These solutoins were then cast onto metal-coated glass slides, the metal layer serving as an electrode. Aluminum was vacuum coated on the upper side of the PFSI film to serve as the other blocking electrode. Impedance measurements were then performed on various solution-cast PFSI films. The analysis of the dielectric spectroscopy and the extraction of the dc conductivity were performed as outlined in previous reports.[11,12] As well, wide-angle X-ray diffraciton will be performed in an attempt to elucidate morphology and structure of the solution-cast PFSI films.

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Experimental Section

Materials. Nafion 117 (1100 EW in the acid form) was obtained from E. I. du Pont de Nemours. Dow Chemical provided the Dow PFSI (membrane XUS 13204.10). The XUS membrane, received in the acid form, was 0.127 mm thick and approximately 800 EW. Chemicals used including dimethyl sulfoxide (DMSO), 1-propanol, and absolute ethanol (EtOH) were obtained from commerical sources.

Dissolution Procedure. The dissolution procedures as outlined in refs 7 and 10 were followed. However, prior to dissoluton both the Nafion and XUS PFSI were refluxed in 15 M HNO_3 to remove the discoloration of the as-received membranes. After refluxing, the membranes were vacuum-dried for 24 h at 100 °C. A 1% w/v solution of Nafion was prepared in the following manner. One gram of the refluxed vacuum-dried membrane was placed in a high-pressure reaction vessel with 100 mL of a 1:1 EtOH/deionized water (DI) solution. The vessel was purged with N_2, sealed, heated to 250 °C, and held at that temperature for at least 1 h. A similar 1% w/v solution of XUS was prepared by placing 1 g of the refluxed vacuum-dried XUS in 100 mL of a 1:1 propanol/DI solution, purging with N_2, and heating to 250 °C. However, for the XUS solution it was necessary to hold the temperature at 250 °C for at least 3 h to completely dissolve the membrane. After preparation both solutions were vacuum filtered with #1 Whatman filter paper. Blends of Nafion and XUS were produced by mixing equal volumes of the two solutions together. During the mixing of the two PFSI solutions, there was no evidence of any phase separation or precipitates forming and the solution remained optically clear.

Film-Casting Procedure. To produce solutions that were suitable for casting sound films, the following procedure was employed. Twenty-five milliliters of the PFSI solution was placed in an oil bath and held at a constant temperature of 80 °C in an effort to remove the majority of the alcohol. After the majority of the alcohol was removed, 10 mL of DMSO was added and the temperature of the oil bath was raised to 135 °C. The solution was then placed under vacuum to remove any remaining alcohol/DI solution as well as to boil off some of the high boiling point DMSO. The remaining solution could then be used to cast films onto the glass slides. Once the solution was cast onto the slides, they were placed in a vacuum oven at 130 °C. The oven was purged with N_2 and subsequently pumped down to 20 in. of Hg and held for 2 h. After 2 h the oven was completely evacuated and held for 24 h. After cooling to room temperature, Al electrodes were coated on the exposed side of the solution-cast films to facilitate impedance measurements.

Instrumental Methods. Wide-angle X-ray diffraction (WAXD) was performed on the solution-cast PFSI samples with a conventional wide-angle X-ray diffractometer (Philips Electronics) using a Cu Kα source. To achieve high resolution on the scattering intensity, a slow scan, up to 60 s per 0.04° angular step, as compared to the usual 1 s per step, was employed so that smooth, precise data curves were obtained. The WAXD samples were all conditioned at room temperature and 40% relative humidity. Impedance measurements were performed as outlined in previous reports,[11,12] and again a Hewlett-Packard HP4284A impedance analyzer was employed.

Results and Discussion

Solution-cast films of both the 1% w/v solution of XUS and Nafion were prepared as described previously in this report. A third solution-cast film consisting of a 1:1 mixture of the 1% w/v solutions of XUS and Nafion was also prepared. The water uptake of all three films under various relative humidities (RH) was measured and is presented in Table 1. It is observed from Table 1 that the ability for the solution-cast membranes to imbibe moisture was drastically reduced in comparison to the as-received Nafion 117 membranes. In particular, the water sorption behavior of the PFSI blend seems to lie closer to that of the solution-cast Nafion membrane than to the solution-cast XUS membrane. Since water sorption is intimately linked with the ionic groupings or clusters within the membranes, one can conceive that the solution-cast membranes do not possess the fully developed cluster morphology thought to be present in the as-received membranes. It may be possible that not enough time was allowed for the formation of clusters during the casting of the films. However, a more plausible explanation is that, due to the extremely dehydrated state of the ionomer during the casting procedure, there was insufficient thermal energy provided to overcome the activation energy of formation. This explanation is in agreement with the concepts proposed by Eisenberg,[13] who suggests that cluster formation is a balance between the opposing forces of the dipole–dipole interactions that favor formation and the elastic forces that oppose clustering. Accordingly, with very low moisture content in the cast membrane, the favorable dipole–dipole interactions will be highly suppressed and cluster formation will not readily occur.

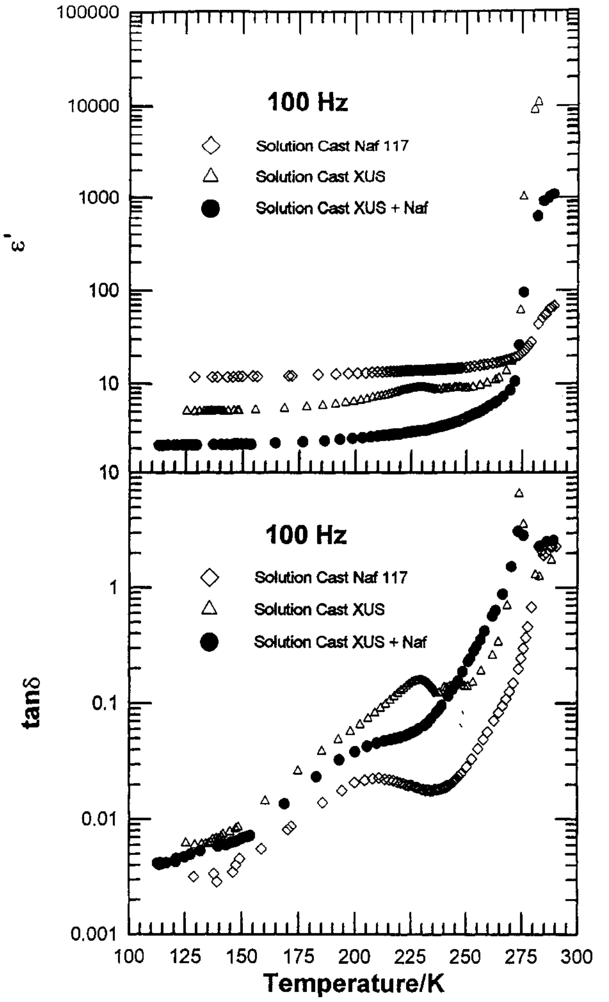

Figure 1. ϵ' and $\tan\delta$ for various solution-cast membranes (100 Hz).

Table 1. Weight Percent Water Uptake for Various Membrane Types

% RH	solution-cast XUS	solution-cast Nafion	solution-cast 1:1 mixture of XUS + Nafion	as-received Nafion 117
0	0	0	0	0
40	5.4	1.4	1.2	11
100	19.4	9.2	11.2	24

The dielectric analysis of the three solution-cast membranes also presents evidence that the cluster morphology may not be fully developed within the membranes. Figures 1–4 display the experimentally measured values of both ϵ' and $\tan\delta$ versus temperature for various frequencies. It is obvious that the values of ϵ' do not undergo a large

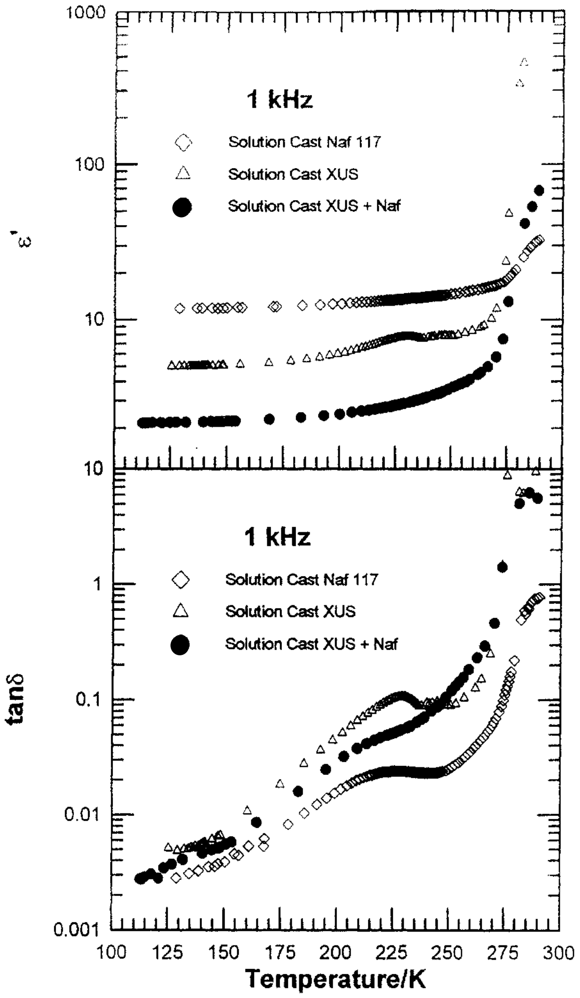

Figure 2. ϵ' and $\tan \delta$ for various solution-cast membranes (1 kHz).

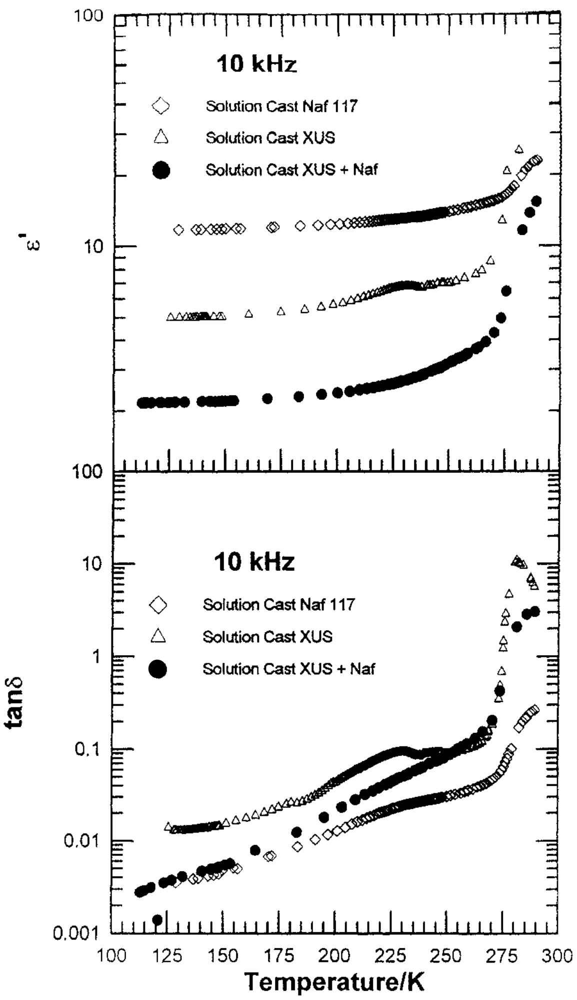

Figure 3. ϵ' and $\tan \delta$ for various solution-cast membranes (10 kHz).

dispersion until ca. 260 K. Even then the magnitude of ϵ' only exceeds 1000 in the case of the 100 Hz measurements. This value is at least an order of magnitude lower in comparison to similar studies on the other as-received PFSI membranes[11,12] where $\epsilon' \geq 10^4$. The fact that the magnitude of ϵ' remains relatively low for the solution-cast membranes, as compared to as-received PFSI membranes of comparable RH, signifies that electrode effects and space charge are not dominating the ionomer response. This indicates that there is very low ionic mobility in the solution-cast membranes and, in fact, the conductivity is low enough that extreme polarization is only observed for the 100 Hz measurements presented in Figure 1. A second outstanding feature present in the $\tan \delta$ measurements in Figures 1–4 is the existence of a low-temperature γ-relaxation peak that resides between 200 and 235 K depending on the frequency of measurement. Historically, this peak has only been observed in dynamical mechanical analysis and was unable to be measured by electric measurements. However, in a recent report Fontanella et al.[14] have also observed the γ-relaxation peak in a dielectric study on acid form dried Nafion 117 membranes. The fact that the γ-relaxation peak is dielectrically active contradicts the prediction of Yeo and Eisenberg,[15] who have measured this peak via dynamic mechanical methods and predict the γ-relaxation to be dielectrically inactive. However, to date the γ-relaxation has only been observed to be active in dry PFSI membranes and has not been observed by either Fontanella's or this group's previous works on hydrated PFSI membranes.[11,12,16] The reason for not observing the γ-relaxation in hydrated PFSI is most probably due to the strong water relaxation, associated with hydrated clusters, eclipsing the response. Clearly, for our hydrated solution-cast membranes to exhibit the γ-relaxation signifies that the cluster formation associated with as-received PFSI must not be present or, if present, is not fully developed so as to provide a large enough region for massive water relaxation to occur. It should also be noted that the γ-relaxation is indeed electrically active and present for the solution-cast XUS + Nafion membrane. However, the γ-peak in the XUS membrane appears to possess only a relatively weak frequency dependence and may be an artifact. At present, further investigation is required to fully characterize the peak.

The dc conductivity has been extracted, as outlined in previous reports,[11,12] from the dielectric measurements for both the solution-cast XUS and the solution-cast XUS + Nafion membrane. The dc conductivity versus reciprocal temperature is presented in Figure 5. Immediately one notices that the dc conductivity of both of the solution-cast membranes has diminished considerably in comparison to be as-received PFSI, which ranges from 10^{-3} to 10^{-1} S/cm.[11,12] In fact, the room temperature conductivity of the solution-cast membranes has decreased by 4 orders of magnitude. Again, it is widely accepted that the ionic clustering within PFSI membranes plays an important role in ionic transport through the membrane. Bearing this in mind, possible explanations for the extreme drop in conductivity may be (i) that there are no clusters present within the membrane or (ii) that there are clusters present within the membrane but they are not fully developed. explanation i does not seem plausible as it contradicts

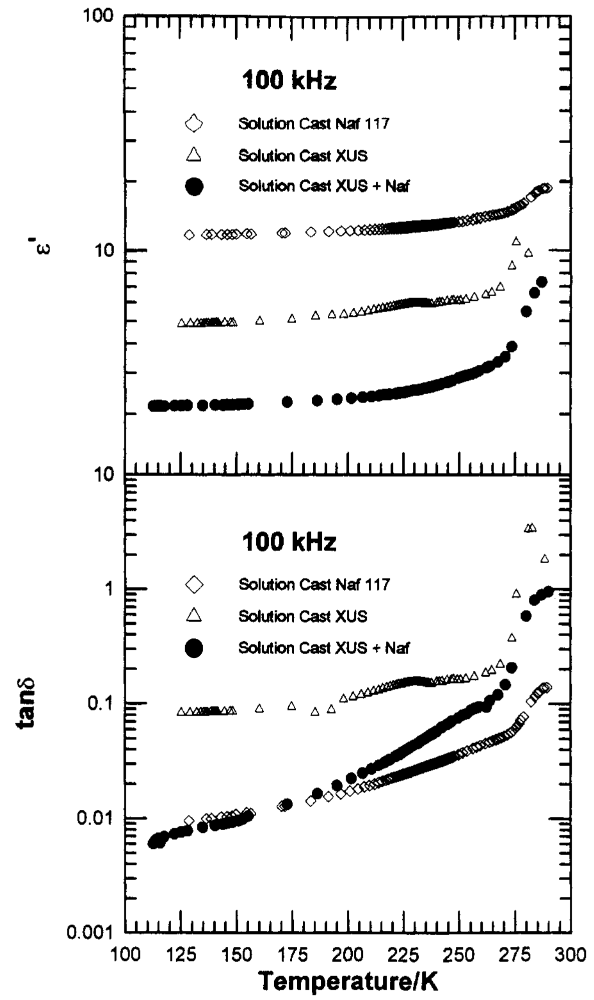

Figure 4. ε′ and tan δ for various solution-cast membranes (100 kHz).

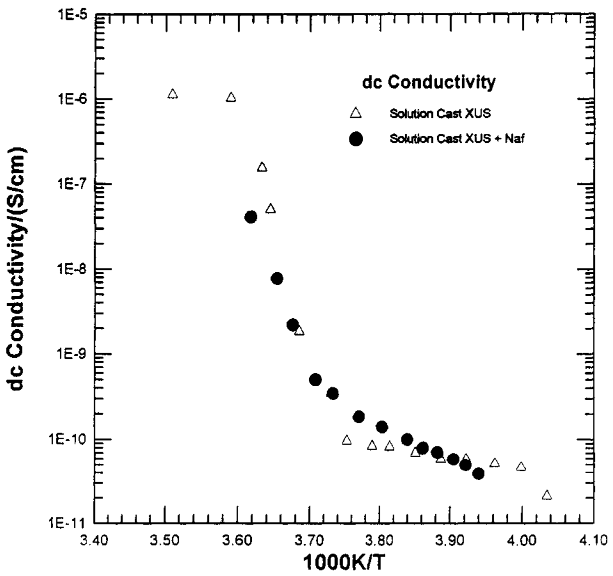

Figure 5. Temperature behavior of dc conductivity for various solution-cast membranes.

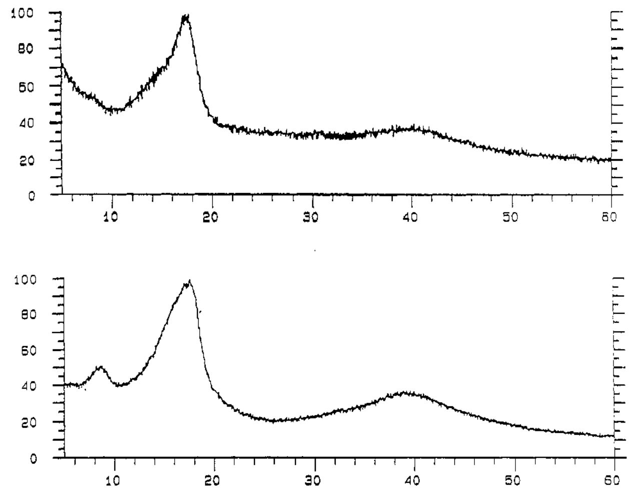

Figure 6. WAXD scans of Nafion 117: top, solution cast; bottom, as received.

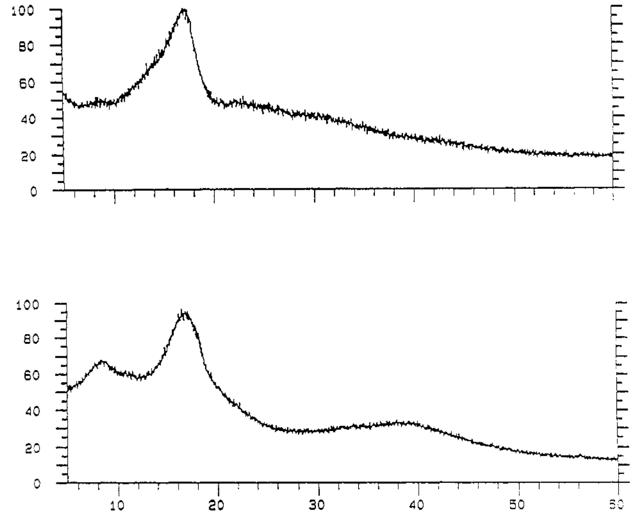

Figure 7. WAXD scans of XUS: top, solution cast; bottom, as received.

both the DSC and SAXS data presented in ref 10 which states that ionic domains are present in recast PFSI. Explanation ii, however, is plausible since ionic domains may be present in these solution-cast PFSI but they may not exist in the morphology usually associated with as-received PFSI membranes. It may be feasible that cluster formation is not complete and that only ion pairs or multiplets have formed due to the fact that the casting temperatures are below T_g and therefore the backbones of the polymer remain rigid and hamper the formation of clusters. It may also be possible that the actual number of ionic domains has decreased or that clusters have formed but are much smaller than in as-received PFSI, or both. A decreased number of clusters would certainly affect the conductivity of the solution-cast membranes by creating a much more tortuous path for ionic transport. Smaller sized clusters would decrease the volume needed for hydration and could therefore impede the mobility of ionic species. This would also be in agreement with the observed water sorption data of the solution-cast membranes. Regardless of the exact cause of the decreased conductivity it is, nevertheless, clear that the morphology, and hence properties, of the solution-cast PFSI are different for those of the as-received PFSI membranes. Another interesting feature of Figure 5 is that the conductivity of the solution-cast membranes exhibits a transition at ca. 265 K. The reason for this transitional behavior is not understood at present.

To further study the structural differences between the solution-cast membranes and the as-received PFSI, high-resolution WAXD spectra of both the solution-cast XUS and solution-cast Nafion are presented in Figures 6 and 7 along with, for comparison, the WAXD spectra of as-received XUS and Nafion 117. The large amorphous halo at ca. $2\theta = 18°$, associated with PTFE backbones, is still present in the solution-cast membranes. However, the peak at $2\theta = 8.5°$ has been diminished and/or eclipsed by a peak at much lower 2θ, as can be witnessed by the upturn in intensity for $2\theta < 8°$ in both of the solution-cast membranes. According to diffraction theory, the qualitative information of the radial distribution function, $\rho(r)$, which presents the areas where nearest neighboring atoms are concentrated, can be estimated by[17,18]

$$\lambda = \frac{8}{5} r_m \sin \theta_m \tag{1}$$

Therefore the peak at $2\theta = 8.5°$ for the as-received PFSI would correspond to a maximum in the radial distribution function at ≈14 Å. Extrapolating the shifted peak, it appears that the maximum may occur at $2\theta = 4$ or 5°. This would correspond to a maximum in the radial distribution function at ≈20–30 Å. The peak at $2\theta = 39°$ for the solution-cast PFSI has also been broadened in comparison to the same peak in the as-received PFSI. This peak at $2\theta = 39°$ would correspond to a maximum in the redial distribution function at ≈2.9 Å. This is on the order of the distance between nearest neighbor CF_2 units. The shift to lower 2θ for the peak at 8.5° and the broadening of the peak at $2\theta = 39°$ can be associated with some morphology change that is causing the solution-cast membranes to be more disoriented, thus affecting the formability of the ionic domains and, ultimately, the hydration and conduction of ions through the membranes.

Conclusions

Solution-cast membranes of XUS and Nafion 117, as well as a membrane of the blend of the two PFSI, were prepared utilizing the dissolution procedures developed by Martin et al.[9] Water sorption measurements at various RH indicate that the solution-cast membranes do not imbibe as much water as the as-received PFSI membranes. Impedance measurements performed on the solution-cast membranes indicate the existence of the γ-relaxation, residing between 200 and 235 K depending on the frequency of measurement, in all three types of solution-cast membranes. This is the first time that the γ-relaxation has been observed for hydrated PFSI, and which in fact is usually not observable due to massive water relaxation obscuring it. The temperature behavior of the dc conductivity of the membranes has been extracted from the impedance measurements. The room temperature conductivity of the solution-cast membranes was found to be on the order of 10^{-6} S/cm, which is 4 orders of magnitude less than the value for as-received PFSI ($\approx 10^{-2}$ S/cm). High-resolution WAXD of the solution-cast membranes reveals the existence of the amorphous halo at $2\theta = 18°$, associated with the PTFE backbone. However, the peak at $2\theta = 8.5°$, corresponding to a maximum in the radial distribution function at ≈14 Å, has been diminished and/or eclipsed by a peak that has shifted to lower 2θ. The peak at $2\theta = 39°$, corresponding to a radial distribution function maximum at ≈2.9 Å, has broadened in comparison to the as-received membranes. Given the drastic drop in conductivity, the observance of the γ-relaxation, and the changes in the WAXD, it is clear that there are distinct differences in morphology between the solution-cast PFSI and as-received PFSI membranes.

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