

Short communication

Broadband dielectric spectroscopic characterization of Nafion[®] chemical degradation

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Abstract

H⁺-form Nafion 212 films were chemically degraded via Fenton's reagent and characteristic polymer chain motions were analyzed using broadband dielectric spectroscopy. The β -relaxation peak maximum frequency (f_{\max}) shifts to higher temperatures upon degradation, reflecting slower chain motions. Perhaps this is due to an upward shift in average molecular weight caused by low molecular weight fragments being leached out of the membrane during the degradation experiment. Permittivity data for degraded and undegraded materials were fitted to the Havriliak–Negami equation. The quantities extracted from these fits were the relaxation time (τ) and parameters that reflect the breadth and asymmetry of the distribution of τ . These parameters were also used in the Vogel–Fulcher–Tammann–Hesse (VFTH) equation which was well-fitted to relaxation time versus temperature data. The increase in the Vogel temperature with degradation reflects more restricted chains. The distribution of relaxation time curve shifts to longer times, broadens, and is transformed from being bi- to tri-modal which reflects an increase in microstructural heterogeneity after degradation. It is concluded that dielectric spectroscopy can be a powerful tool in assessing the chemical degradation of Nafion membranes in the fuel cell environment.

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1. Introduction

In the realm of fuel cell science and technology, Nafion perfluorosulfonic acid ionomers are considered the benchmark material for proton exchange membranes (PEM). To separate H₂ and O₂ gases in the anode and cathode regions a PEM must be mechanically, thermally and chemically stable. However, during operation, PEMs eventually fail often due to chemical degradation caused by OH radicals that result from the decomposition of generated H₂O₂ [1–4]. Although it is commonly accepted that these free radicals are the reason for failure, their specific mechanism of degrading the membrane is ill-understood. Recent research has focused on generating small molecule model compounds to simulate the complex polymer degradation process

[5]. Peroxide radical attack on the polymer endgroups with residual H-containing terminal bonds is believed by DuPont researchers to be the principal degradation mechanism [6,7]. Schlick et al. utilized electron spin resonance to study oxygen radicals that were generated via UV-irradiation of aqueous H₂O₂ solutions in the presence of model compounds that were chemically similar to the ether side chain or the backbone and their view is that Nafion can degrade along the chain and in side chains as well as at the chain ends [8–10]. Schiraldi reports in a review of this topic that the primary problem is the generation of H₂O₂ that breaks down forming peroxide radicals [11,12]. These peroxide radicals then abstract hydrogens from the carboxyl acid groups that are located at the polymer chain ends according to the DuPont view. Reducing the carboxylic acid groups by fluorination drastically reduces the degradation process and improves the PEM lifetime.

Recently, Mauritz et al. demonstrated that a similar hydrolytic degradation process that takes place in poly lactides can be characterized and tracked using dielectric relaxation spectroscopy (DRS) [13]. It was seen that there is a shift in the glass tran-

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sition, monitored in this way, due to increased chain mobility resulting from hydrolytic degradation. Motivated by the success in characterizing biodegradation in this way, DRS was chosen to track the chemical degradation process of Nafion.

1.1. Background

Modern broadband dielectric spectroscopy is, in a sense, the electrical counterpart to dynamic mechanical analysis (DMA). For a number of polymers, especially those having strong dipoles, DRS is superior to DMA in that it probes the molecular dynamics of polymers over a much broader frequency range, i.e., from the milli- to giga-Hertz region. This allows for the examination of motional processes which take place on vastly different time scales [14]. In the bulk entangled state, amorphous polymers are in fact heterogeneous and this heterogeneity gives rise to a distribution of relaxation times. The long and short range molecular motions in an array of amorphous entangled polymer chains can exist on very different time and length scales and the motional processes can depend on the morphology of the system. Thus, information on chemical structure, phase separation, molecular chain length and distribution, glass and sub-glass transitions, can be extracted using this sensitive probe [14].

As DRS is a relatively uncommon means of characterization, a brief background of the theory will be given here. At a fixed temperature, a dielectric relaxation is identified by a peak on a loss permittivity (ϵ'') versus f curve which corresponds to a step decrease on the storage permittivity (ϵ') versus f curve. In addition to the primary, long ranged α -relaxation (glass transition) amorphous polymers usually exhibit at least a secondary, short ranged sub- T_g β -relaxation.

In order to extract the most information from spectra the data is commonly fitted to the phenomenological Havriliak–Negami (HN) equation [15–17]:

$$\begin{aligned} \epsilon * (\omega) &= \epsilon' - i\epsilon'' \\ &= -i \left(\frac{\sigma_0}{\epsilon_0 \omega} \right)^N + \sum_{k=1}^3 \left[\frac{\Delta \epsilon_k}{(1 + (i\omega\tau_{\text{HN}})^{\alpha_k})^{\beta_k}} + \epsilon_{\infty k} \right] \quad (1) \end{aligned}$$

Eq. (1) has three relaxation terms in the summation and the term on the left accounts for dc conductivity, when present. ϵ_0 is the vacuum permittivity and $\omega = 2\pi f$. For each relaxation term, $\Delta \epsilon_k = (\epsilon_R - \epsilon_{\infty})_k$, which is the difference between ϵ' at very low and very high frequencies, respectively. For the dc conductivity term, σ_0 is the conductivity in S cm^{-1} and the exponent N ($0 < N \leq 1$) characterizes the conduction process in terms of the nature of charge hopping pathways and mobility constraints. The parameters α and β ($0 < \alpha < 1$, $\alpha\beta \leq 1$) characterize the breadth and symmetry, respectively, of ϵ'' versus ω peaks. τ_{HN} is the Havriliak–Negami relaxation time and is related to τ_{max} by the following equation [Ref. 14, p. 64]:

$$\tau_{\text{max}} = \tau_{\text{HN}} \left[\frac{\sin((\pi\alpha\beta)/2(\beta + 1))}{\sin((\pi\alpha)/2(\beta + 1))} \right]^{1/\alpha} \quad (2)$$

$$\tau_{\text{HN}} = \tau_{\text{max}} \text{ when } \beta = 1 \text{ and } \alpha = 1.$$

For most polymers, the glass transition is usually the most prominent relaxation. τ_{max} versus $1/T$ plots for this relaxation often shows curvature that is non-Arrhenius in nature and is commonly modeled using the Vogel–Fulcher–Tammann–Hesse (VFTH) equation [18]:

$$\tau(T) = \tau_0 \exp \left(\frac{E_a}{k_B(T - T_V)} \right) \quad (3)$$

k_B is the Boltzmann constant and τ_0 , E_a , and T_V are treated as parameters obtained by fitting Eq. (3) to experimental DRS data. τ_0 is a hypothetical relaxation time at infinite temperature. E_a , while having units of energy, is a ubiquitous quantity that it is not associated with an activated process in the usual sense. T_V , the Vogel temperature, is the temperature at which chain segments become frozen in a hypothetical situation in which a polymer is cooled at a quasi-static rate from the rubbery state. T_V is expected to be lower than T_g [19].

Recently, Moore et al. [20,21] identified the molecular and morphological origins of the α - and β -relaxations of Nafion[®]. The high temperature α -relaxation was attributed to the onset of long range mobility of the backbone as coupled to the side chains that are aggregated through electrostatic interactions in a way that these interactions are weakened and significant ion-hopping occurs. The α peak temperature was shown to be greater than 100 °C for H-form.

On the other hand, the low temperature β -relaxation was attributed to a glass transition involving the backbone within the framework of a static electrostatic network. Here, the glass transition for Nafion will be regarded as the β -relaxation.

In this work, we report the use of broadband dielectric spectroscopy to investigate the shifts in this relaxation caused by chemical degradation.

2. Experimental

2.1. Materials

Cast Nafion[®] 212 films (2 mil thick, 1100 equivalent weight) were obtained from the E.I. DuPont Company. To remove impurities these as-received (AR) membranes were cleaned by refluxing in 8 M HNO₃ for 2 h, rinsing them three times with deionized water, and then boiling them in deionized water for 1 h. Chemical degradation was conducted in the usual way using Fenton's reagent (FeSO₄/H₂O₂) at room temperature for pre-specified times. The AR cleaned samples were dried at 70 °C for 12 h under vacuum and then kept in a vacuum oven at room temperature until tested.

Before being placed between the electrodes in the dielectric spectrometer, the films were preconditioned in a moisture chamber with controlled 6.4% relative humidity for 4 days. Upon removing the specimens from the chamber, the specimens were immediately loaded into the spectrometer. The loading process took less than 2 min. Quick sample transference is critical because it was determined that slight variations in atmospheric RH and loading times significantly altered the β (high temperature) relaxation of the AR sample. To enhance sample reproducibility, the moisture content of the AR sam-

ples was further conditioned in the instrument by drying each specimen therein until the β -relaxation had an f_{\max} (frequency at loss peak maximum) value of approximately 5100 Hz. The degraded films did not require this later in situ conditioning step. Rather, after the Fenton's degradation process the degraded samples were simply dried under vacuum at room temperature. Due to their fragile nature and temperature sensitivity, the additional cleaning and drying at 70°C was not used on the degraded samples. The ramifications of this are discussed later.

2.2. Dielectric spectroscopy measurements

Dielectric relaxation spectra were collected using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer over the frequency (f) range 0.01 Hz to 3 MHz and over the temperature range of -130 to 200 °C. The temperature stability of the instrument was controlled to within ± 0.2 °C. Two samples were tested for each type of material. Samples were cut to a diameter of 2 cm and placed between two 2 cm diameter gold coated copper electrodes. Aluminum foil was sandwiched between the specimen and the electrode to prevent the polymer from adhering to the gold coating of the electrode. Verification tests were conducted to ensure that the aluminum foil did not alter the dielectric spectra of Nafion.

Curve fitting to dielectric permittivity data was performed using the Novocontrol WinFit program. The parameters σ_0 , N , τ_{HN} , $\Delta\epsilon$, α , and β seen in Eq. (1) were obtained by best-fitting the HN equation to the loss (ϵ'' versus f) spectra for each specimen.

3. Results and discussion

A broad view of an ϵ'' versus f and T response surface of a cleaned as-received Nafion sample is seen in Fig. 1. There is a ridge on this surface that is the locus of points that are peaks, located at respective values of f_{\max} , over the range of tested temperatures. This ridge is taken to correspond to the β -relaxation. The peak emerges at approximately -80 °C although

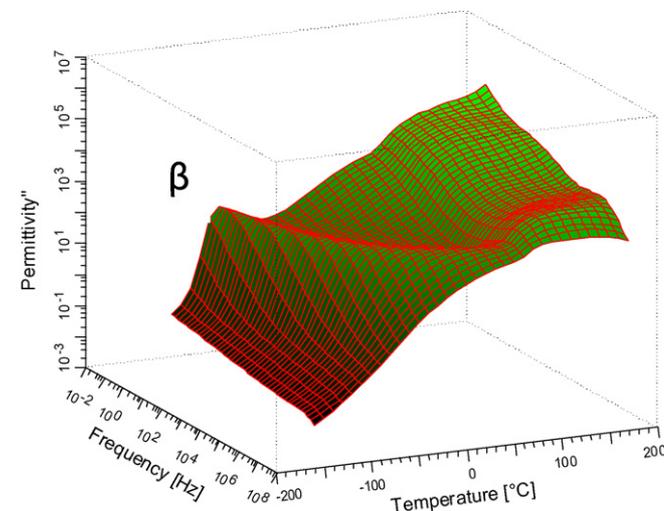


Fig. 1. 3D ϵ'' - f - T plot for cleaned as received Nafion 212 acid films.

its high frequency tail is already visible at temperatures as low as -100 °C.

This peak shifts to having higher f_{\max} values in the usual non-Arrhenius fashion as for glassy materials according to the VFTH equation from approximately -80 to 60 °C. However, at ~ 70 °C the peak deviates from VFTH behavior by shifting to lower frequencies with increasing T and this opposite trend continues until 200 °C [21].

A cut through this surface, i.e., a graph of ϵ'' versus for a fixed T , provides a more clear examination of this relaxation. An example is seen in Fig. 2 for $T = 10$ °C. The data is best fitted using three HN relaxation terms and a dc conductivity term to account for the upswing in ϵ'' at low f . The presence of two-relaxations, with a major and minor peak for the glass transition (β -relaxation), is similar to the behavior described by Yeo and Eisenberg who also determined that the two peaks shift to higher temperatures with the desorption of water [22,23]. The sensitivity of relaxations to residual water has been studied and will be described in a future report. The temperature behavior of τ_{\max} for the major, rightmost peak for both specimens confirms that the β -relaxation obeys the VFTH equation until approximately 70 °C but not at higher temperatures.

Fig. 3 shows ϵ'' versus $\log f$ curves, also at 10 °C, for Nafion films degraded in Fenton's reagent for 75 h along with non-degraded films for a control. Degradation shifts f_{\max} to lower values in such a way that $\tau_{\max} = (2\pi f_{\max})^{-1}$ increases by decades, reflecting significantly slower chain motions. This may seem counterintuitive as it is expected that chain segmental motion would increase due to the generation of shorter, degraded chain lengths [13]. While not understood at this time, the following explanations are offered, the first is the notion that the morphology of Nafion is fundamentally altered.

The second explanation is linked to the idea that sulfonic acid groups coordinate with Fe^{2+} ions that enter the membrane during the Fenton reagent degradation process. If so, these coordinations might prevent smaller chains from leaching out of the 75 h degraded samples because the samples were tested after degradation without further cleaning with HNO_3 . To clar-

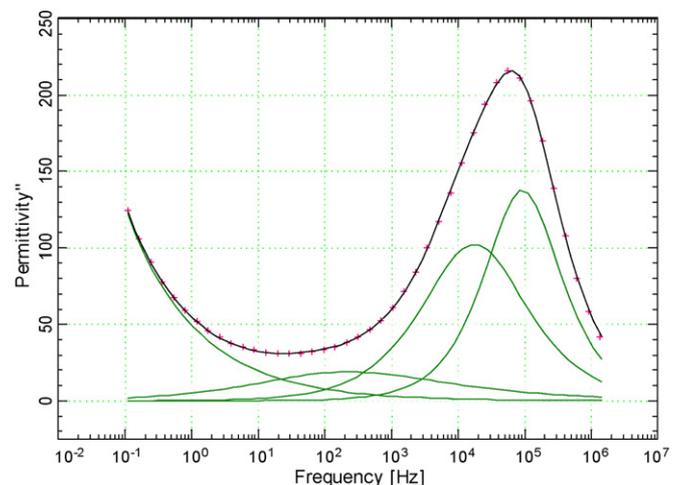


Fig. 2. ϵ'' vs. f for cleaned as-received Nafion at 10 °C. The data is well-fitted with three HN terms and a dc conductivity term at low f .

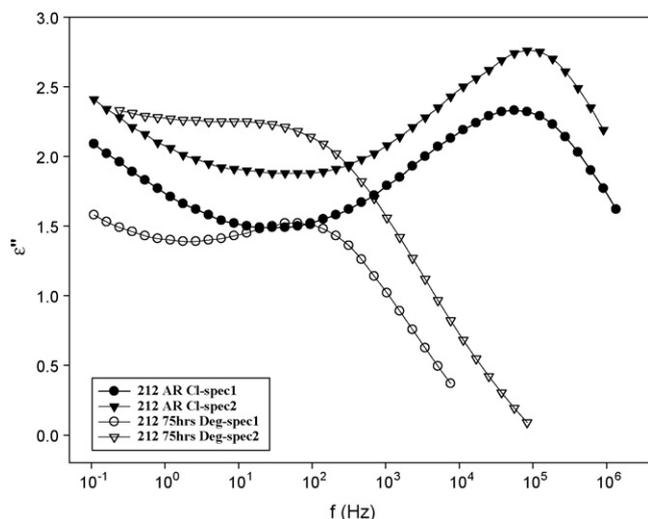


Fig. 3. ϵ'' vs. $\log_{10} f$ plots, at 10°C , for Nafion 212 acid films degraded in Fenton's reagent for 75 h as well as the curve for a non-degraded as-received sample. Two separate data sets for each sample are presented to illustrate reproducibility of the relaxation peak position.

ify whether Fe^{2+} ions coordinate with $-\text{SO}_3^-$ groups, samples degraded for 60 h were cleaned and dried as described in the experimental section. These 60 h degraded and cleaned samples were seen to have the same spectroscopic signature as those that were degraded for 60 h and not cleaned as well as the as received samples. Thus, after 60 h of degradation, any coordination of Fe^{2+} ions with sulfonic acid groups does not appear to affect dielectric spectra in a way that is associated with molecular weight fragments that are present or not. To further understand the situation, both the cleaned as-received and degraded films were fully converted to the organic, less hydrophilic TBA⁺ Nafion form. It was observed that there are no spectroscopic differences in the TBA⁺-exchanged degraded films from that of the TBA⁺ converted as-received-cleaned films which suggests that interactions between side chains are not involved in this phenomenon, i.e. the β -relaxation. Studies have shown that the water absorption/desorption properties are drastically altered between as-received and degraded 75 h films. Specifically, the water uptake significantly changes between 60 and 75 h of degradation. τ_{\max} for the β -relaxation was not affected by moisture as was the case for the cleaned as-received samples. This might imply that a catastrophic molecular degradation occurs between 60 and 75 h of degradation.

The third explanation for the increase in relaxation time involves an upward shift in average molecular weight caused by low molecular weight fragments that were leached out of the membrane into the external electrolyte during the degradation experiment. Longer chains will have longer relaxation times.

Fig. 4 shows relaxation time vs. temperature plots for the untreated and 75 h degraded samples. The plots with T^{-1} are nonlinear which implies that this is not a relaxation that can be described in terms of conventional activated rate theory. The degraded sample curves are significantly vertically shifted up

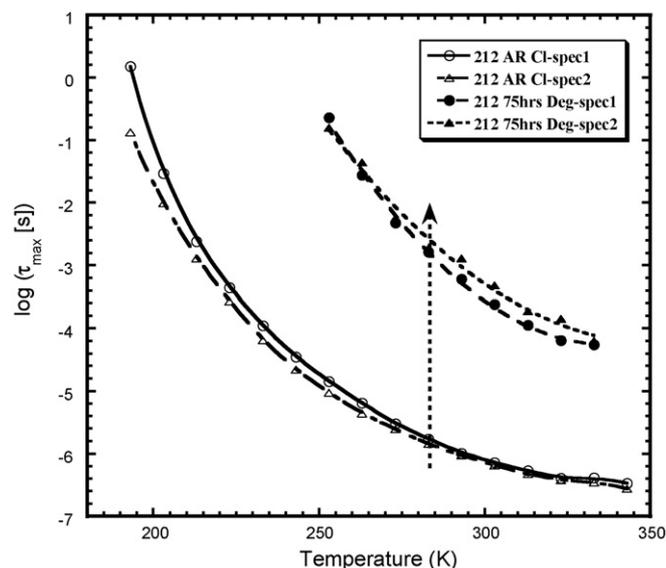


Fig. 4. Relaxation time vs. T plots for Nafion 212 acid films degraded in Fenton's reagent for 75 h as well as for an untreated sample control. Two specimens from the same film are plotted in each case to show data reproducibility.

from those of the cleaned as-received control sample. Values of τ_{\max} for the 75 h degraded samples are significantly higher than the as-received-cleaned samples, again demonstrating that the degraded samples have slower, more restricted chain motions. Curve-fitted VFTH equation parameters for these samples are listed in Table 1. It is seen that while τ_{\max} increases by three orders of magnitude, T_V increases with degradation which suggests more restrictive chain mobility. This increase in T_V is in harmony with an upward shift in polymer molecular weight due to low molecular weight fragments leaching out of the membrane during the degradation experiment. Shorter chains have higher free volume per mass because of the higher density of chain ends which act as packing defects. Further studies are underway to better understand this behavior.

In the Havriliak–Negami equation α and β determine the distribution of relaxation times, $G(\tau)$ such that α characterizes the distribution breadth and β , by its deviation from unity, characterizes the degree of curve asymmetry [16]. $G(\tau)$ is given by the following equation [16]:

$$G(\tau) = \frac{(\tau/\tau_{0i})^{\beta_i\alpha_i} \sin(\beta_i\Theta_i)}{\pi\tau((\tau/\tau_{0i})^{2\alpha_i} + 2(\tau/\tau_{0i})^{\alpha_i} \cos(\pi\alpha_i) + 1)^{\beta_i/2}} \quad (4)$$

Table 1

Relaxation times at 10°C obtained from fitting the Havriliak–Negami equation to the data, and the Vogel temperature obtained from fitting the VFTH equation to relaxation time vs. temperature data, for dielectric spectra of samples degraded for 75 h as well as for an undegraded control

Sample	Relaxation time (s) ^a	T_V (K)
212 AR Cl-spec1	1.72×10^{-6}	153
212 AR Cl-spec2	1.42×10^{-6}	135
212 75 h Deg-spec1	1.26×10^{-3}	192
212 75 h Deg-spec2	1.85×10^{-3}	172

^a As calculated by Eq. (2).

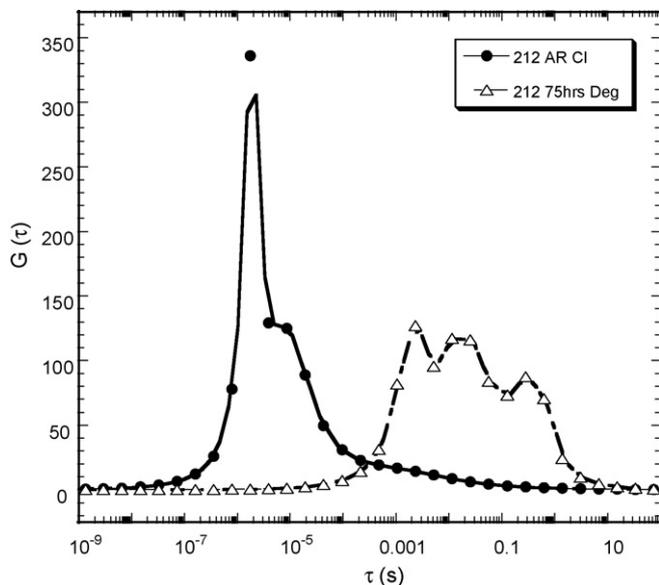


Fig. 5. Distribution of relaxation times, $G(\tau)$ at 10°C for Nafion 212 acid films degraded in Fenton's reagent for 75 h as well as for an untreated sample. The overall shift to the right reflects slower motions.

where

$$\Theta_i = \arctan \left(\frac{\sin(\pi\alpha_i)}{(\tau/\tau_{0i})^{\alpha_i} + \cos(\pi\alpha_i)} \right)$$

The angular quantity Θ_i has units in radians such that ($0 \leq \Theta_i \leq \pi$).

$G(\tau)$ plots for 75 h degraded versus non-degraded samples are shown in Fig. 5. It is seen in Fig. 5 that degradation not only broadens the distribution and shifts it to a region of longer relaxation times (slower chain motions) but a bimodal curve is transformed to a trimodal curve. This, in a general way, might be interpreted in terms of molecular weight distribution broadening with degradation.

In polymer blends, relaxation peak broadening is usually attributed to concentration fluctuation or intrinsic mobility differences between the blend components [24]. Within the context of Nafion, at some degradation stage, one can consider a 'blend' of chains of lengths that are so diverse as to create microstructural heterogeneity, in part because the solubility of chains depends on molecular weight and the effect is more pronounced for shorter chains. Thus, given the validity of this view, there will be a distribution in chain dynamics, i.e. relaxation times.

4. Conclusions

A study of Nafion samples that were degraded in Fenton's reagent was made using broadband dielectric spectroscopy for the purpose of identifying changes in characteristic chain molecular motions. The β -relaxation peak maximum (f_{max}) was seen to shift to lower values with degradation, reflecting slower chain motions. A plausible explanation is that, during the degradation experiment, soluble short chain fractions in the molecular weight distribution leach out, thereby increasing the average molecular weight, which, in turn, causes the relaxation time to increase.

The data for degraded and non-degraded materials were fitted to the Havriliak–Negami equation to extract not only relaxation times, but parameters that reflect the breadth and asymmetry of the distribution of relaxation times. These parameters were inserted in the Vogel–Fulcher–Tammann–Hesse equation which represented the temperature dependence of relaxation time very well for the β -transition in both degraded and undegraded samples. The Vogel temperature increased with degradation reflecting more restricted chain motions and decreased excess free volume which might be due to the out-leaching of low molecular weight fragments.

The distribution of relaxation time curve not only broadened with degradation and shifted to a range of longer times, but was transformed from being bimodal to trimodal. This can be partially explained in a general way in terms of a broadening of molecular weight distribution within the degraded samples and related microstructural heterogeneity. It is concluded that the technique of modern broadband dielectric spectroscopy can be a powerful tool in assessing the fundamental molecular events underlying Nafion degradation.

Acknowledgements

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