Characterization of electrosprayed Nafion films

E.H. Sanders [a], K.A. McGrady [a,1], G.E. Wnek [a,*], C.A. Edmondson [b], J.M. Mueller [b],
J.J. Fontanella [b,2], S. Suarez [c], S.G. Greenbaum [c]

[a] *Department of Chemical Engineering, School of Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA*
[b] *Department of Physics, United States Naval Academy, Annapolis, MD 21402-5076, USA*
[c] *Department of Physics, Hunter College of CUNY, New York, NY 10021, USA*

Abstract

Nafion has long served as a benchmark material when evaluating the performance of proton conducting membranes used in PEM fuel cells. Traditionally, the membranes are either extruded from dry polymer or cast from a liquid polymer solvent solution. Recently, a different technique for fabricating membranes has been developed. The new approach exploits electrostatic spraying, or electrospraying, to deposit PEM films, with the longer-term goal of fabricating membrane-electrode assemblies using this technique. The focus of this paper is to compare the proton transport and physical properties of electrosprayed membranes with those of extruded Nafion.

Audio frequency complex impedance studies of the electrosprayed membranes were conducted at a variety of temperatures and pressures over a wide range of membrane water contents. The results are compared with similar data for Nafion 117 and for membranes cast from the electrosprayed solutions. Water uptake, dimensional changes, and electrical conductivity measurements indicate that extruded, cast, and electrosprayed Nafion films are similar, with the exception that the electrosprayed Nafion absorbs as much as 15 wt.% water more than the other two membranes with only a slight increase in conductivity. The activation volumes for electrosprayed Nafion are also consistent with those for Nafion 117 and concur with proposed mechanisms for proton transport in Nafion membranes. As in Nafion 117, a dielectric loss peak appeared in the electrosprayed Nafion at low temperatures after heating in vacuum at 380 K, further demonstrating the similarity between the two materials.

1. Introduction

Nafion has long served as a benchmark material when evaluating the performance of proton conducting membranes used in PEM fuel cells [1]. Traditionally, the membranes are either extruded from dry polymer or cast from polymer solutions in appropriate solvents. Recently, a new approach for fabricating membranes and catalyst layers has been proposed [2] that is based upon electrostatic polymer processing, namely electrospraying and electrospinning. A long-term goal is the fabrication of membrane-electrode assemblies (MEAs) using these techniques to control catalyst composition, porosity, and wettability within the MEA. Electrospraying and electrospinning can afford particles and fibers with diameters of 100 nm or less, suggesting that

nanostructured electrolytes and electrodes may be obtained by judicious choice of materials and electrostatic processing parameters. Moreover, these electrostatic processing approaches may have applicability to other polymer-based electrochemical devices including batteries, capacitors, and electrochromic and electroluminescent displays. The focus of the present paper is to compare the proton transport properties of electrosprayed Nafion membranes with those of cast films and commercial membranes [3]. Electrospraying of a PEM represents the first step toward the fabrication of an MEA using electrostatic processing. Also, characterization of electrosprayed Nafion itself is important for future work directed toward electroprocessing of electrode layers containing Nafion.

Electrospraying of polymer particles or films is typically accomplished by applying a strong electric field (ca. 1–3 kV/cm) to a polymer solution. By providing a small pressure at one end of a fluid reservoir and a small orifice at the other, a fine jet can be generated when the solution is charged beyond the Rayleigh limit [4]. This thin, unsupported liquid column will break up into small droplets due to a Rayleigh instability. (In the case of electrospinning,

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* Corresponding author. Tel.: +1-804-828-7789; fax: +1-804-828-3846.
E-mail address: gewnek@vcu.edu (G.E. Wnek).
[1] Present Address: NSWC Dahlgren Division, Dahlgren, VA 22448-5000, USA.
[2] Co-corresponding author. Tel.: +1-410-293-5507; fax: +1-410-293-3729. *E-mail address*: jjf@usna.edu (J.J Fontanella).

not discussed here, chain entanglements at higher polymer concentrations stabilize the jet and allow fiber formation.) The resulting droplets are charged and, as solvent evaporates, droplet diameter decreases and increasing charge repulsions lead to fragmentation into smaller droplets. The resulting droplet diameters can be quite small, frequently in the sub-micron regime. The charged droplets can be collected and, depending upon the solvent evaporation rate, dry particles or wet droplets can be deposited onto a grounded target. Electrospraying of a solution of Nafion in alcohols is an example of the latter, and leads to the deposition of free-standing films achieved by coalescence of wet droplets. Hence, proton exchange membranes can be directly deposited by this approach. Electrospraying of solutions is anticipated to facilitate bonding of the sprayed layer to a film on the target (e.g., catalyst on proton exchange membrane), affording good molecular adhesion at this critical interface. We use the phrase 'Nafion solution' rather loosely as such systems are believed to contain multi-chain aggregates rather than truly dissolved polymer chains [5].

2. Experimental

A solution of 5 wt.% Nafion in a mixture of lower aliphatic alcohols and water (Aldrich) was electrosprayed from a syringe using a blunted needle and an applied voltage of 20 kV and approximately 5 ml of solution delivered at a rate of 2 ml/h. The solution was deposited onto a rotating Teflon-coated mandrel which remained grounded at all times and was located approximately 7 cm from the needle tip (Fig. 1). Films with thicknesses of approximately 50–60 μm were removed from the mandrel.

Studies were carried out on commercially extruded Nafion 117 (E.I. DuPont de Nemours), electrosprayed Nafion and on cast Nafion membranes which were made from the same starting material as for the electrosprayed samples. The electrosprayed and cast membranes were approximately 0.05 mm thick and it was verified that the commercial Nafion 117 was approximately 0.18 mm (0.007 in.) thick. All samples used in the electrical conductivity and activation volume studies were approximately 10 mm in length and 6 to 8 mm in width. The samples used in the dilatation studies were approximately 20 mm long.

Samples were dried for several hours in vacuum and transferred to a room temperature, atmospheric pressure glove box with a water content of less than 1.0 ppm. Samples remained in the glove box for several days and the mass and dimensions were measured in situ. Samples used in the dielectric relaxation studies were loaded into the experimental cell while in the glove box. The cell was then transferred to a temperature controlled dewar and the samples were heat-treated under vacuum at approximately 380 K for an additional week. Materials used in the electrical conductivity and activation volume studies were transferred from the dry glove box to a chamber where the relative humidity was controlled by an ETS model 514 automatic humidity controller using an ETS 5612C ultrasonic humidification system. After allowing the samples to reach equilibrium, the mass and dimensions were again measured.

Electrosprayed Nafion samples with various water contents were sealed inside Viton tubing and transferred to a high-pressure vessel. Impedance arcs were measured at room temperature at various pressures ranging from atmospheric pressure to approximately 0.25 GPa (2500 bars).

While the samples remained in the chamber, the audio frequency complex impedance of the samples, $Z^* = Z' - jZ''$, was measured using a CGA-83 capacitance bridge, a Hewlett-Packard 4194A impedance/gain-phase analyzer or a 1255 Solatron frequency response analyzer connected to a Solatron 1296 dielectric interface.

Additional samples of Nafion-117 (DuPont) and electrosprayed Nafion were allowed to dry under ambient conditions then cut into strips, packed parallel to each other
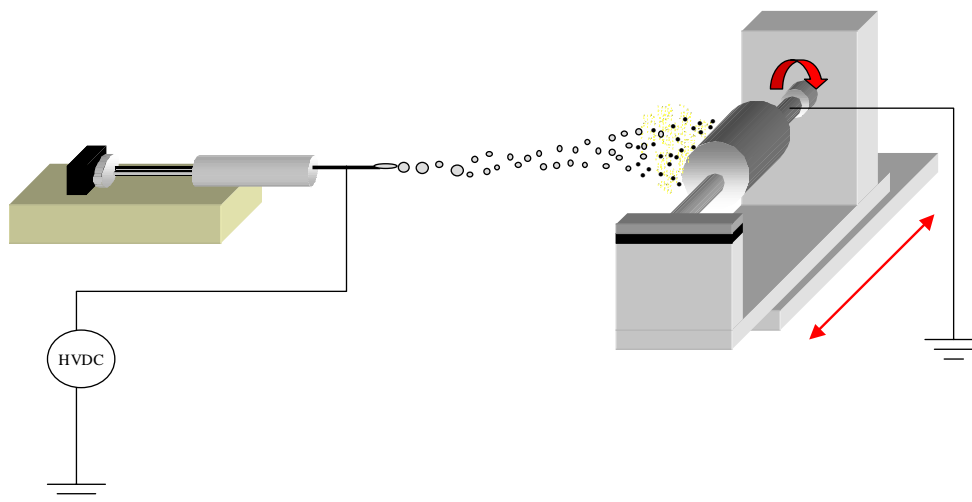

Fig. 1. Schematic representation of an electrospraying apparatus.

and placed into 5 mm NMR pyrex glass tubes containing 0.05 ml of distilled water. Extreme care was taken so that the membranes were suspended above the surface of the water, allowing clear separation between the membrane strips and the water surface. This was necessary so as to allow equilibration of the membrane by the water vapor and to ensure that the membranes were at 100% RH during the measurements. The sample tubes were sealed and allowed to stand upright for 14 h prior to the NMR measurements.

^{1}H NMR spectra, self-diffusion coefficients and spin-lattice relaxation times (T_1) were obtained on a Chemagnetics CMX-300 spectrometer in which the Larmor frequency for protons is 301.02 MHz. The temperature range investigated was 20–87 °C, with 20–25 min intervals between temperature changes. Pure distilled water was used as the proton reference, with a pulse width of 15 µs. Self-diffusion coefficients were obtained using the NMR-PGSE technique, which consists of the Hahn spin echo pulse sequence [6] ($\pi/2 - \tau - \pi$) with square shaped magnetic gradient pulses applied after each RF pulse [7], using a Nalorac Z-Spec gradient probe. The gradient strengths (g) ranged from 0.2 to 1.2 T/m, while the time interval between two gradient pulses (Δ) and the duration of a single gradient pulse (δ) ranged from 0.4 to 3 ms and 5 to 15 ms, respectively.

Gradient calibration was done on distilled water at 25 °C where the self-diffusion coefficient is known to be 2.29×10^{-5} cm²/s. Uncertainties in diffusion measurements are about 3–5%. Spectra were obtained by the Fourier transform of single pulse FIDs, with pulse delays of at least 5 T_1s. Spin-lattice relaxation times were obtained by inversion recovery, which involves a $\pi - \tau - \pi/2$ pulse sequence with about 12–15 τ values, again with a pulse delay greater than 5 T_1. T_1 was obtained by fitting the exponential recovery to $[A_\infty - A(t)]/A_\infty = C \exp(-\tau/T_1)$ where A_∞ and C are fitting constants. The uncertainty in the T_1 determinations is ~3%.

3. Results and discussion

3.1. Sample swelling with water uptake

Fig. 2 shows the observed percent change in length from the dry state as a function of wt.% water uptake. The percent change in length versus water content is essentially the same for all of the materials for water contents up to approximately 15 wt.%. The cast and electrosprayed Nafion samples show slightly less swelling at high water content than is observed for Nafion 117.

3.2. Electrical conductivity versus water content

All complex impedance diagrams were similar to those previously reported for Nafion [1]. An impedance arc is observed at high frequencies and is attributed to the bulk properties and a slanted line is observed at low frequencies
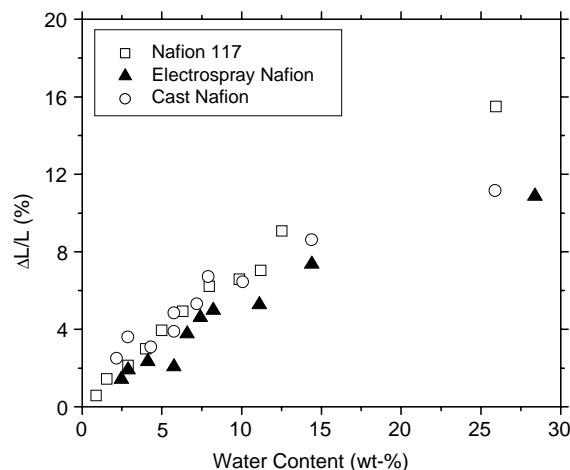

Fig. 2. Percent change in length vs. water content in wt.%. The open squares are for Nafion 117, the closed triangles are for electrosprayed Nafion and the open circles are for Nafion membranes cast from the same liquid Nafion solution as the electrosprayed membranes.

attributed to electrode effects. The nonzero intercept of the arc with Z' axis is taken to be the bulk resistance of the sample. The data were transformed to electrical conductivity, σ, using techniques described elsewhere [1]. For the calculation of the electrical conductivity, it was assumed that all dimensions changed in a fashion similar to that shown in Fig. 2.

The electrical conductivity results for various values of water content are shown in Fig. 3. The most striking feature of Fig. 3 is the similarity of Nafion 117, cast Nafion and electrosprayed Nafion in the region of typical water uptake by Nafion 117. The spread in the data is more representative of the uncertainty in the measurement than of any significant difference in the conductivity of the samples. Since the conductivity removes dimensional dependence, this figure adds confidence that the data are representative of the bulk properties of the material and are not controlled by surface effects.
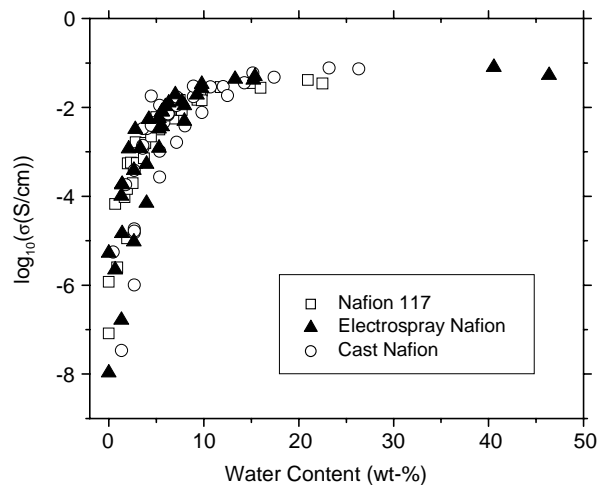

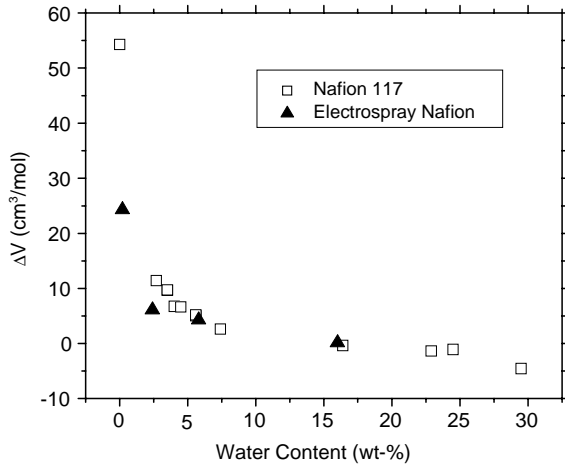Fig. 3. Electrical conductivity vs. water content in wt.% at room temperature.

Fig. 4. Activation volume vs. water content in wt.% at room temperature. The open squares are for Nafion 117 and the closed triangles are for electrosprayed Nafion. The data for Nafion 117 are previously published.[1]

However, the electrosprayed sample exhibits one important difference. Under normal conditions (room temperature and pressure), the electrosprayed Nafion absorbs as much as 15 wt.% water more than the other two membranes with only a slight increase in conductivity. The reason for this additional water uptake is not clear at the present time.

3.3. Electrical conductivity versus pressure

The water content of each sample was determined by comparing the low-pressure conductivity with the results from Fig. 3. The pressure derivative of conductance was converted to the pressure derivative of conductivity using the equations and the estimates of the compressibility given elsewhere [1]. The apparent activation volume, ΔV, was calculated using

$$\Delta V = -kT \left[\frac{\mathrm{d} \ln \sigma}{\mathrm{d} p} \right]_T \tag{1}$$

Fig. 4 is a plot of ΔV versus water content for electrosprayed Nafion and Nafion 117. The data for Nafion 117 are those previously reported [1]. At a water content of approximately 0.2 wt.% electrosprayed Nafion has an activation volume of 24.3 cm^3/mole. This is consistent with the Nafion 117 data and is consistent with segmental motion playing a large part in electrical conductivity at low water content. The smaller values of ΔV observed at higher water contents are consistent with water-like proton transport as is the case, for example, in the Grotthus or vehicular mechanisms.

3.4. Electrical relaxation in electrosprayed nafion heated under vacuum

Impedance data can be transformed into the apparent complex dielectric constant, ε^*, given by
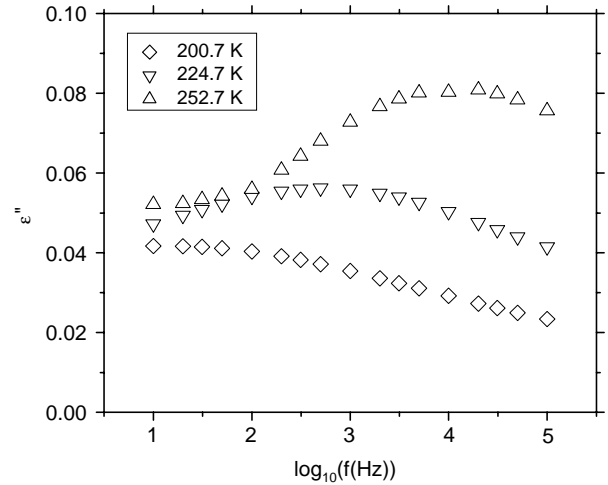
$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{2}$$

The imaginary part of the dielectric constant, ε'', can be expressed in term of the conductivity, σ:

$$\varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega} \tag{3}$$

where ω is the angular frequency and ε_0 is the permittivity of free space.

While no special features were observed in the electrosprayed Nafion prior to heating, a new feature (dielectric loss peak) appeared in the electrosprayed Nafion at low temperatures after heating in vacuum at 380 K. Fig. 5 shows the imaginary part of the dielectric constant plotted versus frequency for three temperatures in the vicinity of the dielectric loss peak. This is consistent with data observed for Nafion 117 that had been treated in a similar fashion [8].

The peak positions were determined from figures similar to Fig. 5 at various temperatures. The peak positions are plotted versus reciprocal temperature in Fig. 6. The line
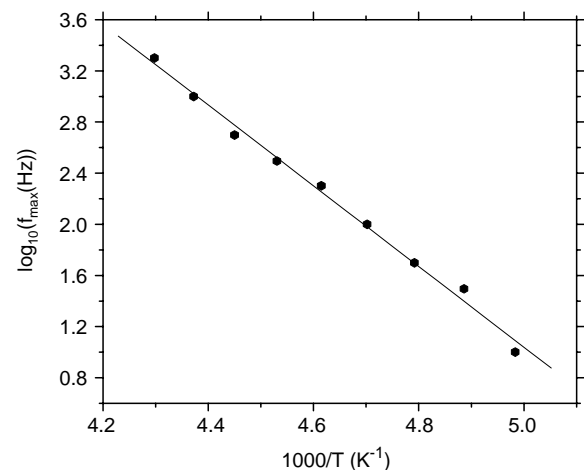
Fig. 5. Imaginary part of the dielectric constant vs. frequency at three temperatures for electrospray Nafion dried in situ.

Fig. 6. Arrhenius plot of the frequency peak maximum for the γ-relaxation in electrospray Nafion dried in situ. The solid line represents a best fit Arrhenius expression.
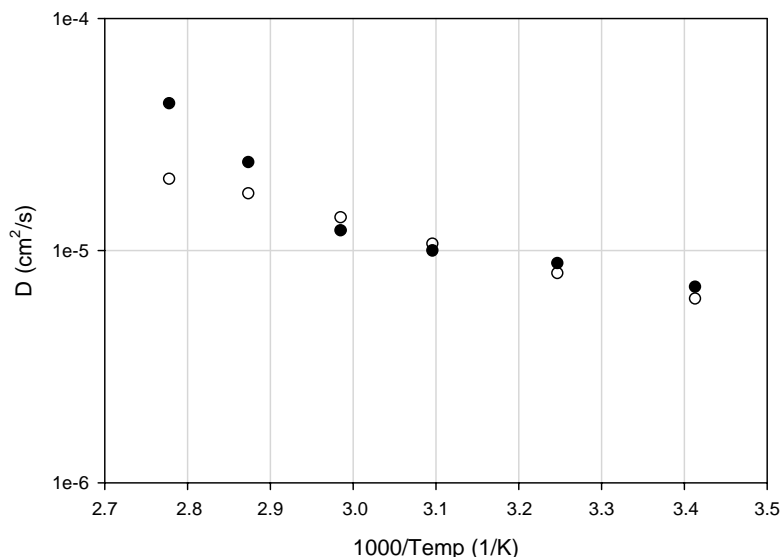
Fig. 7. [1]H self-diffusion coefficients vs. temperature of Nafion-117 (empty symbols) and electrosprayed Nafion (solid symbols).

shows a best-fit Arrhenius expression

$$f_{\max}(\mathrm{Hz}) = f_0 \exp\left(\frac{-E}{kT}\right) \tag{4}$$

The results of the best-fit, $\log_{10} f_0 = 16.8$ and $E = 0.63\,\mathrm{eV}$, are close to the values of $\log_{10} f_0 = 15.9$ and $E = 0.57\,\mathrm{eV}$ observed for Nafion 117. These values are similar to that observed for the γ relaxation mechanical loss peak observed by Yeo and Eisenberg [9] and Starkweather and Chang [10].

The results of the heating experiment further demonstrate the similarity between the electrical properties of electrosprayed Nafion and Nafion 117.

3.5. NMR

For a diffusing specie in the presence of a magnetic field, the application of square-shaped magnetic gradient pulses of magnitude g results in an attenuation of the resulting echo profile that may be fitted to the following gaussian equation:

$$A(g) = \exp\left[-\gamma^2 \, D \, g^2 \, \delta^2 \left(\Delta - \left(\frac{\delta}{3}\right)\right)\right]^2 \tag{5}$$

The self-diffusion coefficient, D, is the only unknown in this expression and can be extracted directly from the attenuation. Self-diffusion coefficients for both Nafion-117 and the electrosprayed Nafion are shown in Fig. 7. Both membranes gave comparable results from 20 to 62 °C. Above this range however, the electrosprayed Nafion exhibits diffusion coefficients higher by about 30 and 70% at 75 and 87 °C, respectively. This may be due to the greater water uptake of the electrosprayed Nafion versus Nafion-117 at 100% RH, especially at higher temperatures, as shown in Fig. 8.

Spin-lattice relaxation times are shown in Fig. 9. The electrosprayed Nafion has shorter T_1s than Nafion-117. In the temperature range of the measurements (i.e. above the T_1 minimum), shorter T_1s are associated with more restricted motion and somewhat broader spectra, which is what was observed for the electrosprayed Nafion as shown in Fig. 10. Both ^{1}H NMR spectra in Fig. 10 exhibit a sharp component at 0 ppm attributed to the liquid water in the bottom of the sample tube, though care was taken to keep the bottom as far away from the RF coil as possible. At temperatures up to 62 °C, Nafion-117 and the electrosprayed sample give nearly identical Ds but different T_1s, reflecting high similarity between the two materials in long range water transport, but some difference in short range molecular motions.
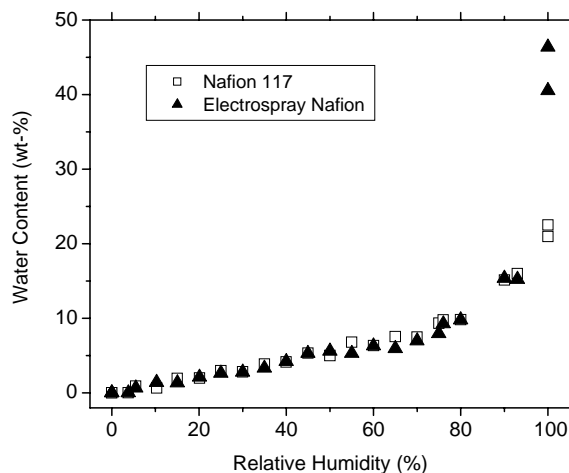

Fig. 8. Water uptake measurements. This is also comparable with ionic conductivity results obtained at higher levels of water uptake. The data at 100% RH is for wetted samples.
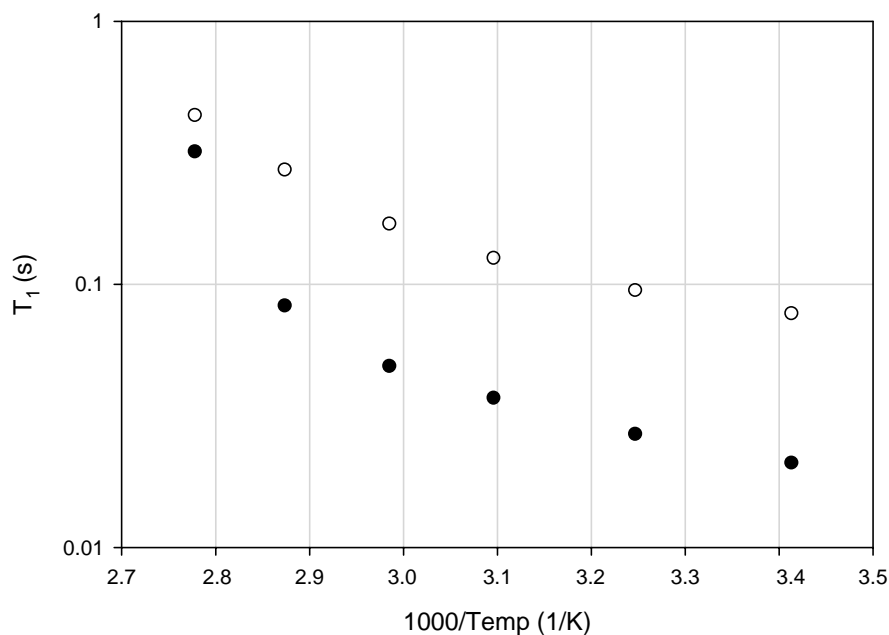
Fig. 9. Spin-lattice relaxation times vs. temperature of Nafion-117 (empty symbols) and electrosprayed Nafion (solid symbols).
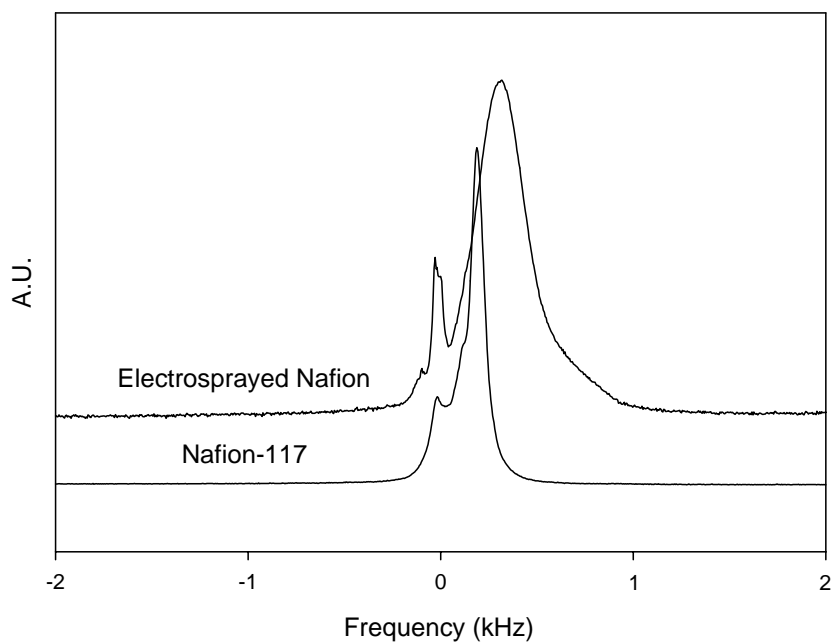

Fig. 10. ^{1}H NMR spectra of Nafion-117 and electrosprayed Nafion at 20 °C.

4. Conclusions

Water uptake, dimensional changes and electrical conductivity measurements indicate that extruded, cast and electrosprayed Nafion films are similar, with the exception that the electrosprayed Nafion absorbs as much as 15 wt.% water more that the other two membranes with only a slight increase in conductivity. The activation volumes of electrosprayed Nafion are also consistent with those for Nafion 117 and concur with proposed mechanisms for proton transport in membranes. As in Nafion 117, a dielectric loss peak

appeared in the electrosprayed Nafion at low temperatures after heating in vacuum at 380 K, further demonstrating the similarity between the two materials. The NMR data also show similarity between the two materials in long range water transport, but some difference in short-range molecular motions. Further investigation is needed to determine the reasons for differences seen in NMR spectra and water absorption in electrosprayed Nafion membranes with respect to Nafion 117. Nonetheless, the results support the use of electrosprayed Nafion membranes for use in polymer electrolyte membrane assemblies.

Acknowledgements

References

[1] J.J. Fontanella, C.A. Edmondson, M.C. Wintersgill, Y. Wu, S.G. Greenbaum, Macromolecules 29 (1996) 4944.

[2] E.H. Sanders, J.A. Regrut, J. Bennett, T. Latham, W.D. Bates, G.E. Wnek, Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, Poster presentation abstract, Asilomar, CA, February 2003.

[3] C.A. Edmondson, P.E. Stallworth, M.E. Chapman, J.J. Fontanella, M.C. Wintersgill, S.H. Chung, S.G. Greenbaum, Solid State Ionics 135 (2000) 419.

[4] L. Rayleigh, Phil. Mag. 14 (1882) 184.

[5] G. Gebel, Polymer 41 (2000) 5829.

[6] E.L. Hahn, Phys. Rev. 80 (1950) 580.

[7] E.O. Stejskal, J.E. Tunner, J. Chem. Phys. 42 (1965) 288.

[8] J.J. Fontanella, M.G. McLin, M.C. Wintersgill, J. Polym. Sci. B: Polym. Phys. 32 (1994) 501.

[9] S.C. Yeo, A. Eisenberg, J. Appl. Polym. Sci. 21 (1977) 875.

[10] H.W. Starkweather, J.J. Chang, Macromolecules 15 (1982) 752.