

Mechanical and Hydration Properties of Nafion[®]/Ceramic Nanocomposite Membranes Produced by Mechanical Attrition

Amanda L. Moster, Brian S. Mitchell

Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA 70118

Received 12 October 2007; accepted 6 July 2008

DOI 10.1002/app.29177

Published online 17 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A solid state method of Nafion[®]/ceramic nanocomposite membrane preparation is described. A nanocomposite powder from Nafion pellets and a zirconium phosphate ceramic is formed by mechanical milling. The nanoparticles are then consolidated into membrane form by mechanical pressing. Cross-sectional analysis by scanning electron microscopy indicates that the ceramic particles exist in agglomerates that are evenly dispersed across the membrane. Dynamic mechanical analysis and tensile testing found the membranes to be mechanically equivalent, and in some cases superior, to a commercial extruded membrane. Increasing ceramic content is accompanied by an increase in

modulus and shift in the alpha peak to higher temperature. Maximum water uptake of the membranes, as measured by thermal gravimetric analysis, is double that of values reported for the commercial membrane, and complete dehydration is postponed to higher temperature. The proton conductivity of fully hydrated membranes, measured by the 4-probe method at 60°C in water, is comparable with that of the extruded membrane. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1144–1150, 2009

Key words: nafion; nanocomposites; membranes; mechanical properties; thermal properties

INTRODUCTION

Nafion[®] was first successfully used in a NASA fuel cell in 1966 and remains the foremost material used in polymer electrolyte membrane fuel cells today. Many of the ionomer's attributes—particularly proton conductivity, gas selectivity, and thermomechanical stability—arise directly from the morphology of the polymer. Modification of these properties can be achieved by making changes to the chemical structure,¹ by altering the membrane formation or processing procedures,¹ or by the addition of filler materials.² In this work, an alternate method of membrane formation is investigated: near net-shape manufacturing (NNSM). NNS refers to a manufacturing method that produces as-formed components with dimensions close to those of the final product; i.e., little dimensional change due to solvent evaporation from the polymeric component or sintering of the ceramic component. The process used herein begins with reduction of the material to nanoparticles via a mechanical milling device. The powder is

then consolidated by mechanical pressing and/or hot isostatic pressing (HIP).

This method has been applied successfully to metallic and ceramic systems, but has seen less use in the field of polymer science.³ As a solid state method, it provides several benefits over more typical polymer processing routes. The risk of thermal degradation of the polymer during melt processing is eliminated, as is the sometimes difficult task of solvent removal from a solution-cast piece. Another advantage of the process is the relative ease with which a composite material can be created; the desired materials can simply be comilled. The greater the interfacial interaction between the components, the greater the influence the filler will have on the properties of the polymer.²

In an effort to further improve the mechanical and thermal properties of NNSM Nafion membranes, an appropriate material for composite membrane formation is desirable. Inorganic additives to Nafion, specifically nonconductive ceramic oxides, such as silica,^{4,5} alumina,⁵ titania,⁶ and montmorillonite^{7,8} are common. Zirconium phosphates have also become popular not only because of their moderate to high proton conductivity,^{2,9} but also more importantly because of their ability to increase the waters of hydration around the sulfonic acid group¹⁰ which gives rise to the potential for operation at elevated temperatures and reduced humidity. For this reason,

This work has been supported by the Tulane Institute for Macromolecular Engineering and Science (TIMES) and NASA Grant NCC3-946.

Correspondence to: B. S. Mitchell (brian@tulane.edu).

Journal of Applied Polymer Science, Vol. 111, 1144–1150 (2009)
© 2008 Wiley Periodicals, Inc.

a zirconium phosphate-based ceramic was selected for this study.

The goal of this research, then, is to form nanocomposite membranes of Nafion and proton conducting ceramic using near net-shape manufacturing techniques, and compare the mechanical and thermal properties with those of a commercially available Nafion membrane.

EXPERIMENTAL

NR50 Nafion pellets (1100EW, sulfonic acid form) and N1110 Nafion membrane (1100EW, sulfonic acid form, 10-mil thickness) produced by DuPont Fluoropolymers were purchased from Ion Power (New Castle, DE). A zirconium phosphate proton conducting ceramic, known as PRONAS, was provided by Ceramtec (Salt Lake City, UT) in powder form. Tetrabutylammonium hydroxide (TBAOH) (1M in methanol) and methanol, obtained from Aldrich (St. Louis, MO), and sulfuric acid, obtained from Fisher Scientific (Pittsburgh, PA), were used without further purification. Deionized water (18 M Ω) was used throughout.

Nafion pellets were cleaned by soaking in 4M methanolic H₂SO₄ at room temperature for 24 h followed by thorough rinsing with methanol to remove excess acid. Moore et al.¹ found that by exchanging the hydrogen of the sulfonic acid for a bulkier group, the electrostatic crosslinks formed between the sulfonic acid groups can be weakened and crystallinity of the backbone can be disrupted rendering the material melt-processable. Neutralization of the pellets to a melt-processable form was accomplished by soaking in TBAOH for 48 h at room temperature. After rinsing thoroughly with methanol to remove excess TBAOH, the pellets were dried in the fume hood overnight.

Gravimetric analysis was used to determine the conversion of the reaction. Before and after the neutralization, pellets were dried to constant weight over anhydrous calcium sulfate desiccant and their mass determined. Using the equivalent weight of the polymer, as well as the molecular weight of the H⁺ and TBA⁺ ions, the expected increase in mass was calculated. On comparing the calculated and measured changes in mass, conversion was found to be 100.6%.

Powders were created from the Nafion TBA⁺ pellets by mechanical milling at cryogenic temperature in the SPEX 6750 freezer mill (SPEX CertiPrep, Metuchen, NJ). Milling media used was the SPEX 6751 grinding vial set, which consists of a stainless steel impactor and two end plugs with a polycarbonate center cylinder. The milling cycle consisted of a 15 min precooling segment followed by three cycles of 2 min of milling (30 impacts/s) and 2 min of cooling resulting in a 6 min total milling time. Compos-

ite powders were created by adding ceramic to the milling vial in the desired weight percent.

Scanning electron microscopy (SEM, Hitachi S-4800) was performed on the Nafion TBA⁺, and Nafion TBA⁺/ceramic composite powders to determine particle size and shape. Samples were adhered to the SEM stub with Tissue-Tek O.C.TTM Compound 4583 (Agar Scientific, Stansted, UK) and platinum coated for viewing at an accelerating voltage of 3 kV.

Milled powder was consolidated into membrane form by mechanically pressing at 2000 psi and 190°C. A stainless steel mold in combination with a hydraulic platen press (Grimco Presses, Patterson, NJ) was used to produce 11.43 cm (4.5 in) square membranes. Membranes were converted back to hydrolyzed form by refluxing in 4M methanolic H₂SO₄ for 1 h. After a thorough rinse with deionized water, the samples were dried to constant weight over anhydrous calcium sulfate desiccant before further processing by hot isostatic pressing (American Isostatic Presses, Columbus, OH) at 310 MPa and 110°C in a nitrogen atmosphere. For consistency, commercial membrane samples were cleaned by refluxing in 4M methanolic H₂SO₄, thoroughly rinsed with deionized water and dried over desiccant. Samples were also HIPed at the conditions noted earlier.

SEM images were taken of the Nafion H⁺ and Nafion/PRONAS composite membranes. Following storage over anhydrous calcium sulfate desiccant, membrane samples were chilled in liquid nitrogen and fractured. Samples were mounted vertically using carbon tape for support so that the fractured cross-sections could be analyzed. A coating of gold and accelerating voltage of 3 kV were used.

Dynamic mechanical analysis (DMA) and tensile testing were conducted with a DMA 2980 (TA Instruments, New Castle, DE) to evaluate the mechanical properties of the NNSM membranes and compare with those of a commercially produced membrane. DMA was conducted in tensile mode with the tension film clamp. Samples were 0.0254–0.0305 cm (0.010–0.012 in) in thickness, 0.40 cm (0.157 in) in width, and 1.2 cm (0.472 in) in length (active length). Experimental parameters used were amplitude, 25 μ m; preload force, 0.010 N; force track, 125%; frequency, 1 Hz; and temperature was increased from 27°C to 160°C at a rate of 2°C/min. Tests were conducted in a nitrogen atmosphere. Tensile tests were performed in controlled force mode with the tension film clamp on samples of the same dimensions. Experimental parameters used were preload force, 0.005 N; force ramp rate, 0.5 N/min; upper force limit, 18 N; and isothermal temperature of 27°C.¹¹

Thermal gravimetric analysis (TGA) was conducted with a TGA 2950 (TA Instruments) to

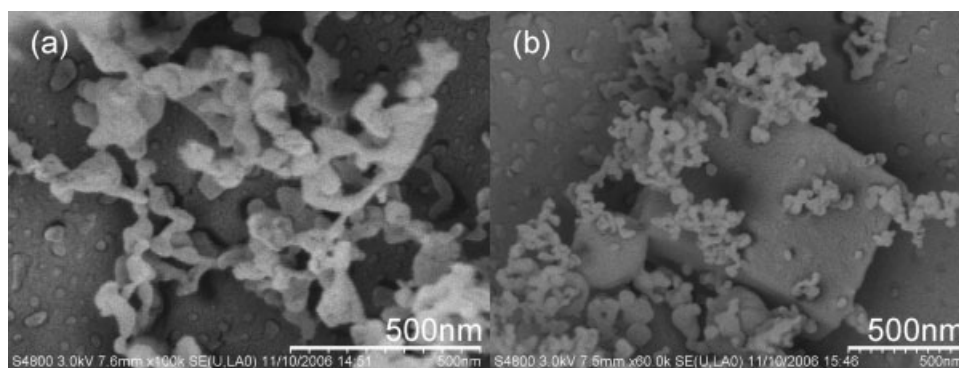


Figure 1 SEM photomicrographs of (a) Nafion TBA+ and (b) Nafion TBA+/PRONAS cryomilled powders.

evaluate membrane water uptake. Samples of 20 mg in mass were cut from membranes that had been dried over anhydrous calcium sulfate desiccant. The samples were boiled in deionized water for 60 min then stored in water at room temperature until use. At test time, a sample was removed from the water and blotted dry. The sample was placed vertically into an aluminum oxide sample pan so that both sides of the membrane would be exposed to the heated purge gas. The total time from removal from water to the start of data collection was not more than 2 min. Temperature was increased at a rate of 5°C/min to 120°C, then held at 120°C for 30 min. The percent water uptake of the membranes was calculated with eq. (1)¹ using the hydrated (initial) and dry (final) masses as measured by the TGA. The temperature at which 90 wt % of the total water absorbed is lost was selected as a basis for comparison of dehydration properties, and was determined by eq. (2) from TGA data.

$$\text{percent water uptake} = \frac{\text{mass hydrated} - \text{mass dry}}{\text{mass dry}} \times 100\% \quad (1)$$

$$\text{mass at 90 wt \% water lost} = 0.1(\text{mass hydrated} - \text{mass dry}) + \text{mass dry} \quad (2)$$

Proton conductivity of the membranes was determined with the 4-probe method¹² using a commercial conductivity cell (Bekktech LLC, Loveland, CO) and ZPlot[®] software (Scribner Associates, Southern Pines, NC). The impedance measurements were conducted in the frequency range of 0.8 MHz to 0.1 Hz and with ac current amplitude of 20 mV using a frequency response analyzer (Solartron 1255) and electrochemical interface (Solartron 1286). Measurements were taken in the longitudinal direction at 60°C in deionized water. Before testing, membranes were hydrated by boiling in deionized water for 60 min then stored in water at test temperature until use. Once loaded in the test cell, samples were allowed

to equilibrate at test conditions for 30 min before data collection began. Conductivity was determined with eq. (3), where σ is the conductivity in Scm^{-1} , L is the fixed distance between the two voltage sensing electrodes (0.425 cm), R is the resistance in Ω , W is the width of the membrane (0.5 cm), and T is the membrane thickness expressed in centimeter.

$$\sigma = \frac{L}{R \times W \times T} \quad (3)$$

RESULTS AND DISCUSSION

An SEM photomicrograph of Nafion TBA+ cryomilled powder appears in Figure 1(a). Nafion TBA+ pellets have been reduced to elongated, agglomerated particles with an average minor axis dimension in the 50–100 nm range. Investigations into the morphology of commercial Nafion membranes have shown aggregation of sulfonic acid end groups into clusters ranging in size from 5 to 30 nm.^{13,14} Additionally, super nodular aggregates comprised of spherical domains have been identified by tapping mode atomic force microscopy.¹⁵ The domains were found to have an average diameter of 45 nm and to be composed of spherical grains with an 11 nm mean diameter. The mechanically milled particles created here have dimensions that are approaching the domain size of the ionomer. The high surface-to-volume ratio created during the milling process facilitates intimate mixing of the ionomer with a second component, in this case a proton conducting ceramic [Fig. 1(b)].

Membranes created from the milled powders are homogenous in appearance. The pure Nafion membranes are transparent and colorless, whereas nanocomposite membranes are translucent and white because of the addition of the opaque white ceramic. The cross-sections of membranes converted back to the acid form were analyzed by SEM for the presence of void space, ceramic distribution, and to visually compare the morphology of the NNSM

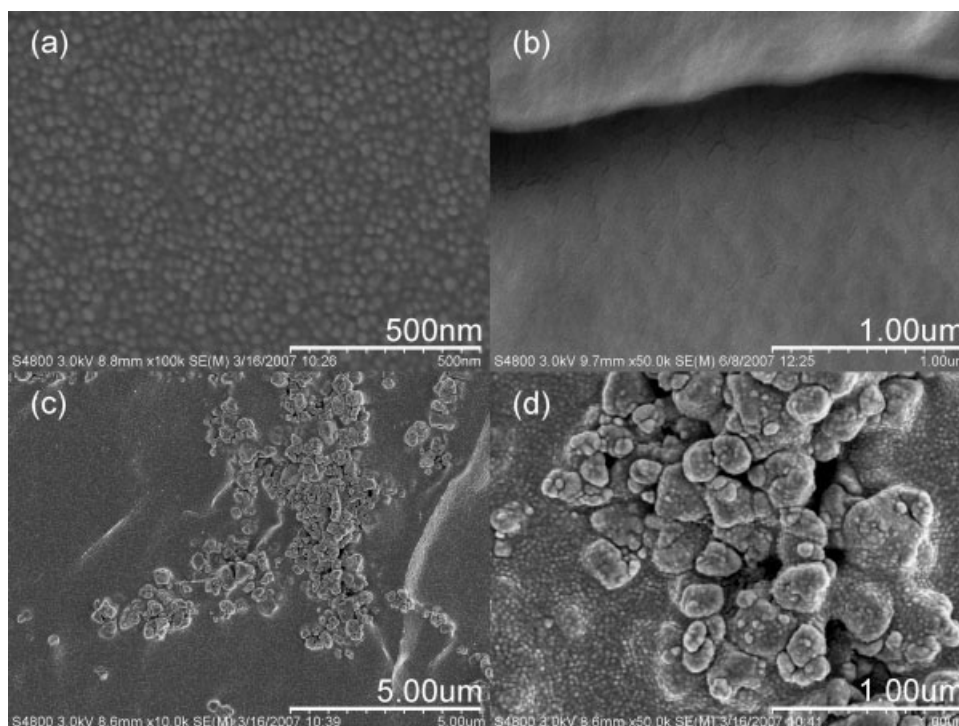


Figure 2 SEM photomicrographs of membrane cross-sections (a) NNSM Nafion membrane, (b) commercial membrane (c) and (d) 95-5 wt % Nafion/ceramic composite membrane.

membrane Nafion with that of the commercial membrane. Images of a NNSM Nafion, commercial Nafion, and 95-5 wt % Nafion/ceramic composite membrane appear in Figure 2. The NNSM Nafion membrane is homogeneous in appearance and although manufactured from particles 50–100 nm in size, has a distinct lack of void space. The membrane is found to be comprised of spherical domains 20–50 nm in diameter. These domains are not seen in the commercial membrane and arise due to consolidation of the polymer particle morphology shown in Figure 1(a). Composite membranes are characterized by homogeneous Nafion regions interrupted by pockets and “veins” of agglomerated ceramic particles. The agglomerates vary greatly in size and create void space within their structure. Although local concentrations of ceramic exist, the ceramic agglomerates are evenly dispersed across the thickness of the membrane. Analysis of all membranes before and after HIPing shows no obvious effect of this step of the procedure on the morphology of the membranes.

To explore the relationship between processing method and material properties, DMA, tensile testing, and TGA were conducted on the NNSM membranes as well as a commercial membrane of similar thickness. Membranes were tested both before and after the HIP procedure.

DMA was used to examine mechanical properties as a function of increasing temperature. Storage

modulus curves (not shown) were found to be similar in shape, indicating that the NNSM processing route produced a membrane with dynamic mechanical properties similar to those of the extruded commercial membrane. Examination of the storage modulus values with increasing temperature (Table I) reveals that the NNSM Nafion pre-HIP samples consistently possess the lowest values. The three remaining pure Nafion membranes: NNSM Nafion post-HIP and pre-HIP and post-HIP commercial product have moduli that are comparable and often within one standard deviation of each other. The HIPing procedure has little, if any effect on the commercial product, but consistently produces an increase in membrane stiffness in the NNSM Nafion membrane. The principal dynamic mechanical relaxations in Nafion are dependent on the strength of the interactions between the side-chain terminal SO_3X groups.^{1,16,17} These interactions are primarily those of hydrogen bonding in the H^+ form of the ionomer. It is likely that the temperature and extreme pressure of the HIP encourage further development of such interactions between the terminal SO_3H groups of the polymer thereby strengthening the bonds between the consolidated particles.

Values of $\tan \delta$ also appear in Table I. The α -relaxation of Nafion is related to the onset of main chain and side chain long range mobility. This mobility is facilitated by the weakening of electrostatic interactions within the ionic aggregates.¹⁷ NNSM and

TABLE I
Results of DMA and Tensile Testing

Membrane	Storage modulus			tan δ ($^{\circ}$ C)	Tensile modulus
	50 $^{\circ}$ C (MPa)	80 $^{\circ}$ C (MPa)	110 $^{\circ}$ C (MPa)		27 $^{\circ}$ C (MPa)
Commercial					
Pre-HIP	330 \pm 10	150 \pm 23	23.1 \pm 2.9	114 \pm 1.3	195 \pm 16
Post-HIP	322 \pm 32	158 \pm 5.9	22.5 \pm 1.4	113 \pm 0.9	237 \pm 24
NNSM Nafion					
Pre-HIP	313 \pm 16	128 \pm 2.2	15.2 \pm 0.2	113 \pm 0.8	198 \pm 70
Post-HIP	347 \pm 5.3	157 \pm 0.9	18.5 \pm 0.7	114 \pm 0.7	233 \pm 29
95-5 wt % comp.					
Post-HIP	337 \pm 0.4	175 \pm 5.7	23.9 \pm 0.7	115 \pm 0.7	252 \pm 35
90-10 wt % comp.					
Post-HIP	454 \pm 18	290 \pm 26	89.1 \pm 26	129 \pm 6.9	340 \pm 25

commercial Nafion membranes show little difference in α peak position. Peak temperatures, ranging from 111.8 $^{\circ}$ C to 114.8 $^{\circ}$ C, are consistent with values found in literature.¹⁶ A small difference in peak height was noted in the plots. Peak height is proportional to the number of chains that have entered the mobile state.^{10,17} The taller peaks associated with the NNSM membranes suggest that a greater number of chains have become mobile as a result of solid-state processing.

DMA of composite membranes reveals an increase in storage modulus with increasing ceramic content (Table I). A shift in the α -relaxation peak to higher temperature is also observed. In both cases the change associated with the addition of 5 wt % ceramic is minimal, but becomes more pronounced in the 10 wt % ceramic membranes. Both of these effects have been previously noted in Nafion zirconium phosphate composite membranes.¹⁰ As mentioned earlier, many of the desirable properties of Nafion arise from the morphology of the membrane. The ability to add a second component to the membrane without undermining the inherent mechanical properties of the material is an advantage of the NNSM technique.

To further compare mechanical properties of the membranes, tensile testing was conducted on the membranes at room temperature (Table I). NNSM Nafion and the commercial membrane were found to have comparable moduli both before and after HIPing. The NNSM membrane modulus increased from 197.7 to 233.3 MPa, whereas the commercial sample had a modulus of 194.7 MPa before HIPing and 237.2 MPa after the procedure. As was found in the dynamic testing, an increase in modulus was seen with the addition of the ceramic. At 5 wt % the effect was modest, producing a modulus of 252.1 MPa. The 10 wt % addition results a substantial increase to 339.5 MPa.

TGA was used to determine the hydration properties of the HIPed membranes. The results of the test-

ing are shown in Figure 3. The wt % water contained in the fully hydrated membranes was found with eq. (1). Nafion product information supplied by Dupont indicates the maximum water uptake of a membrane soaked in water at 100 $^{\circ}$ C for 60 min to be 38%.¹⁸ The water uptake of the commercial membrane in this work was found to be 46%. The increase is likely due to the pretreatment of the membrane in the 4M methanolic H₂SO₄. Pretreatment conditions have been found to induce microstructural changes in Nafion that remain after the membrane is dried and later affect sorption behavior upon rehydration.^{19,20} NNSM membranes have a significantly higher level of maximum hydration than commercial membranes. Water uptake of the NNSM Nafion was found to be 76%. Membranes with 5 wt % PRONAS content show a level of maximum hydration similar to that of the pure NNSM Nafion. At 10 wt % the maximum water content

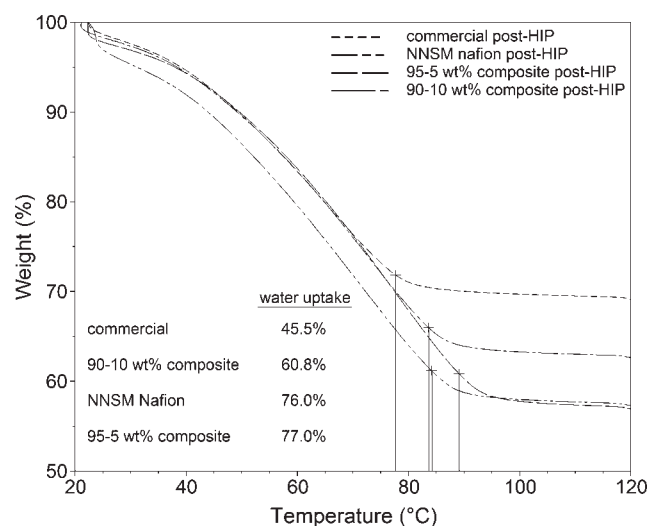


Figure 3 TGA of hydrated membranes. Vertical lines indicate the temperature at which 90% of the water absorbed by the membrane has been lost.

TABLE II
Proton Conductivity of Membranes Tested at 60°C in Liquid Water

Membrane	Conductivity (S/cm)
Commercial	
Pre-HIP	0.134 ± 0.001
Post-HIP	0.136 ± 0.001
NNSM Nafion	
Pre-HIP	0.116 ± 0.001
Post-HIP	0.124 ± 0.003
95-5 wt % composite	
Post-HIP	0.116 ± 0.005
90-10 wt % composite	
Post-HIP	0.115 ± 0.000

decreases significantly but does remain greater than that of the commercial membrane.

As was discussed earlier, cross-sectional analysis of the NNSM membranes by SEM showed no macroscopic void space. It is possible that porosity may exist on a smaller scale than can be visually detected with SEM. Such microscopic porosity may contribute to the increased water uptake of the NNSM samples. The addition of a zirconium phosphate ceramic to Nafion has been found to increase water uptake of the ionomer.¹⁰ In this work, a significant increase in water uptake was seen for all NNSM membranes, pure ionomer and composite alike. The increased membrane hydration is the result of the membrane fabrication technique rather than the addition of the PRONAS ceramic. It is possible that mechanical milling induces structural change in the polymer. Such change may alter the distribution of the ionic phase or reduce the crystallinity that exists in the hydrophobic domains comprised of the tetrafluoroethylene backbone segments. Further analysis is needed to evaluate this possibility.

The dehydration properties of the membranes were further analyzed by determining the temperature at which 90% of the total water absorbed is lost by the membrane. This was accomplished with eq. (2) described earlier. Dehydration occurs at higher temperatures for the NNSM membranes than for the commercial membrane. Water loss of 90% occurs at 84°C in the NNSM Nafion membrane as opposed to 78°C for the commercial membrane and is further extended to 89°C in the 5 wt % composite. This increase in dehydration temperature may be beneficial for high-temperature conductivity properties.

Preliminary proton conductivity test results of membranes tested at 60°C in liquid water appear in Table II. NNSM Nafion HIPed membranes were found to have an average proton conductivity of 0.124 S/cm, whereas the commercial HIPed membranes averaged 0.136 S/cm. Addition of ceramic to the NNSM membrane resulted in a slight decrease in the conductivity to 0.116 and 0.115 S/cm in the

95-5 wt % and 90-10 wt % composites, respectively. These results are consistent with the conductivity values of Nafion membranes at similar conditions as determined by others using the 4-probe method.¹² Comparison of pre-HIP and post-HIP samples showed a small increase in the NNSM Nafion conductivity with HIPing, but the procedure was found to have no effect on the conductivity of the commercial and composite samples. Membrane conductivity at elevated temperatures and reduced relative humidity is the subject of ongoing work.

CONCLUSIONS

Near net-shape manufacturing was shown to be a viable method for Nafion nanocomposite membrane formation. The technique allows for the production of nanoparticles possessing a high surface to volume ratio which enables the components to be intimately mixed at the scale of the ionomer structure. NNSM Nafion membranes were found to be mechanically comparable to the extruded membrane. Addition of the zirconium phosphate ceramic resulted in an increase in the membrane's modulus as well as a shift of the alpha transition to higher temperature. Water uptake of the NNSM Nafion membrane was found to be twice that of the literature value for the commercial product. In addition, membrane dehydration occurred at a higher temperature. These effects have been attributed to Nafion pretreatment procedure, as well as the likely increased exposure of sulfonic acid functional groups during the reduction to nanoparticles. Incorporation of 5 wt % ceramic had little effect on the water uptake; however, the 10 wt % addition resulted in a reduction of the total water uptake by half in comparison with the NNSM Nafion membrane. Preliminary proton conductivity results indicate the NNSM Nafion membranes have a slightly lower conductivity than the commercial sample. Addition of ceramic has a negligible effect on the conductivity. Although the ceramic particles were found to be larger than desired and agglomerated, small modifications to the method can improve the size and dispersion and are the subject of ongoing research.

The authors are grateful to Ceramtec Inc. of Salt Lake City, UT for supplying the PRONAS ceramic and to Shekar Balagopal of Ceramtec Inc. for technical discussions.

References

1. Moore, R. B.; Cable, K. M.; Croley, T. L. *J Membrane Sci* 1992, 75, 7.
2. Alberti, G.; Casciola, M. *Annu Rev Mater Res* 2003, 33, 129.
3. Haynes, S. D.; Mitchell, B. S. *J Appl Polym Sci* 2004, 93, 2275.
4. Jiang, R.; Kunz, H. R.; Fenton, J. M. *J Membrane Sci* 2006, 272, 116.

5. Arico, A. S.; Baglio, V.; Antonucci, V.; Nicotera, I.; Oliviero, C.; Coppola, L.; Antonucci, P. L. *J Membrane Sci* 2006, 270, 221.
6. Sacca, A.; Carbone, A.; Passalacqua, E.; D'Epifanio, A.; Licocchia, S.; Traversa, E.; Sala, E.; Traini, F.; Ornelas, R. *J Power Sources* 2005, 152, 16.
7. Jung, D. H.; Cho, S. Y.; Peck, D. H.; Shin, D. R.; Kim, J. S. *J Power Sources* 2003, 118, 205.
8. Song, M.-K.; Park, S.-B.; Kim, Y.-T.; Kim, K.-H.; Min, S.-K.; Rhee, H.-W. *Electrochimica Acta* 2004, 50, 639.
9. Bauer, F.; Willert-Porada, M. *Fuel Cells* 2006, 3-4, 261.
10. Bauer, F.; Willert-Porada, M. *J Membrane Sci* 2004, 233, 141.
11. Kawano, Y.; Wang, Y.; Palmer, R. A.; Aubuchon, S. R. *Polimeros: Ciencia e Tecnologia* 2002, 12, 96.
12. Lee, C. H.; Park, H. B.; Lee, Y. M.; Lee, R. D. *Ind Eng Chem Res* 2005, 44, 7617.
13. James, P. J.; Elliott, J. A.; McMaster, T. J.; Newton, J. M.; Elliott, A. M. S.; Hanna, S.; Miles, M. J. *J Mater Sci* 2000, 35, 5111.
14. Zhang, J. Z.; Wu, Q. M. J.; Shi, Z.; Holdcroft, S. *IEEE Trans Nanotechnol* 2005, 4, 616.
15. Lehmani, A.; Durand-Vidal, S.; Turq, P. *J Appl Polym Sci* 1998, 68, 503.
16. Osborn, S. J.; Hassan, M. K.; Divoux, G. M.; Rhoades, D. W.; Mauritz, K. A.; Moore, R. B. *Macromolecules* 2007, 40, 3886.
17. Page, K. A.; Cable, K. M.; Moore, R. B. *Macromolecules* 2005, 38, 6472.
18. DuPontTM Nafion[®] PFSA membranes. Revised: 2006. Accessed: October 2007. Available at: http://www2.dupont.com/Fuel_Cells/en_US/assets/downloads/dfc101.pdf.
19. Jalani, N. H.; Choi, P.; Datta, R. *J Membrane Sci* 2005, 254, 31.
20. Jalani, N. H.; Datta, R. *J Membrane Sci* 2005, 264, 167.