

# Preparation and Characterization of Ball-Milled Nafion® Powders for Membrane Applications

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**ABSTRACT:** A method for producing Nafion® powder from commercially available pellets, and using this powder to produce membranes, is described. A description of particle size distribution, chemical composition, and thermal properties of Nafion® powders prepared by high-energy ball milling of pellets is given. Nafion® powders prepared in this manner exhibit thermal behavior similar to that of the precursor pellets; however, traces of iron from the milling materials are shown to be present through transmission

electron microscopy analysis of the particles. The membranes prepared by hot pressing of the Nafion® powders also show thermal behavior similar to that of the precursor pellet materials. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2275–2281, 2004

**Key words:** ionomers; membranes; processing; TEM; particle size distribution

## INTRODUCTION

Despite the advances made in fuel cell membrane materials, sparked by the renewed interest in fuel cells, the premier polymeric proton-exchange membranes continue to be made of Nafion®, which is manufactured in various forms by DuPont (Wilmington, DE). Nafion® is a perfluorinated polymer, with small amounts of sulfonic ( $\text{SO}^{3-}$ ) or carboxylic functional groups, which is available in sheet form for membrane applications in thicknesses of 50–250  $\mu\text{m}$ . It is also available in the form of pellets and as a solution. The microstructure of Nafion® is complex, and is the subject of numerous papers and several models,<sup>1–3</sup> as is the mechanism by which it conducts protons in membrane-type applications.<sup>4</sup>

Because of its fluorocarbon structure, Nafion® is also difficult to process into useful forms. Routine polymer-processing techniques such as solution casting and extrusion are not applicable. Hence, new processing routes must be investigated that will allow Nafion® to be molded not only into sheets of desired thicknesses, but into new geometries as well. Further-

more, new processing schemes are required that will allow other phases, such as ion-conducting ceramic phases, to be incorporated into Nafion®-based composites, which may ultimately lead to new properties and applications.

One such processing method is the two-step process of particle formation and hot pressing. This technique, in its various forms, has been successfully applied to metallic and ceramic systems for many years, but only recently has been used to process polymeric materials. In this method, the material (or materials) of interest is (are) reduced in size to powder form in a milling device. Although the types and sizes of mills can vary, the most common laboratory mill in use today is the high-energy ball mill. A description of high-energy ball mills for powder and nanoparticle formation can be found elsewhere.<sup>5</sup> The as-milled powders can then be consolidated and compacted using such techniques as mechanical pressing or hot isostatic pressing (HIP).

In this article, the application of high-energy ball milling, followed by mechanical pressing, to form a dense Nafion® membrane is described. Particular attention is paid to the formation and characterization of the powders obtained from high-energy ball milling of Nafion®.

## EXPERIMENTAL

The starting material was extruded Nafion® pellets obtained from Ion Power Inc. (Bear, DE), with a number-average molecular weight of  $M_n = 13,000$ . All handling of the polymer during and after milling was

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performed in a glove box under nitrogen to limit sample oxidation. High-energy ball milling was performed in a SPEX 8000 mixer/mill (Spex CertiPrep, Inc., Metuchen, NJ) in a temperature-controlled environment at 4°C. Two hardened steel vials and milling balls with a ball-to-polymer weight ratio of 10 : 1 were used for milling. Liquid nitrogen was added to the vials before milling to prevent chain mobility. Milling times of 50, 100, 200, and 400 min were used.

The as-milled polymer powders were analyzed for particle size by means of sieve analysis. For this method, the as-milled powders were sieved through a Bel-Art microsieve set (Bel-Art Products, Pequannock, NJ), and each fraction was weighed. A total of nine fractions were weighed for each sample, with the smallest fraction containing particles < 63  $\mu\text{m}$ , and the largest containing particles > 700  $\mu\text{m}$ .

The physical characteristics of the unmilled and milled polymers were compared using differential scanning calorimetry (DSC), simultaneous thermogravimetric (TGA) and mass spectrometric (MS) analysis (TGA-MS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses.

A TA Instruments (New Castle, DE) DSC 2920 was used to analyze the thermal behavior of the Nafion®. The samples were tested under nitrogen atmosphere at a heating rate of 10°C/min, from room temperature to 400°C. TGA-MS was performed in a high-resolution TA Instruments 2950 TGA, coupled to a Pfeiffer ThermoStar mass spectrometer (Pfeiffer Vacuum Technology AG, Asslar, Germany). Samples, with sizes ranging from 20.5 to 20.7 mg, were subjected to a temperature range of 20 to 800°C ramped at 10°C/min under flowing nitrogen of 90  $\mu\text{L}/\text{min}$ . The TGA off-gas was fed through a capillary to the mass spectrometer, where the composition was analyzed every 2 s.

SEM images were taken with a JEOL (Tokyo, Japan) electron microscope with accelerating voltage of 5 keV, and used to compare the particle size of the milled Nafion® powders. Each sample was sieved, and a small portion of each was allowed to adhere to a 9.5  $\times$  9.5 mm SEM stub (Ted Pella, Inc., Redding, CA). The polymers were then placed in an SCD 05 sputter coater (BAL-TEC AG, Balzers, Germany) and coated with platinum, then imaged.

TEM images were taken with a JEOL 2010 scanning transmission electron microscope with energy-dispersive spectroscopy (EDS) capability, operating at an acceleration voltage of 120 keV. TEM samples were prepared by suspending the milled polymer in an alcohol solution, which was then sonicated for 1 to 2 min to ensure that the particles were evenly dispersed. The polymer suspension was then placed on a carbon-coated TEM grid (Ted Pella, Inc.) by a transfer pipette. The sample was allowed to completely dry under ambient conditions before the TEM imaging was conducted. No staining method was applied.

Membrane disks of the Nafion® powders were made using a 20-ton specimen-mount press and a 3.8-cm (1.5-in.) diameter stainless steel ram-type mold (both from Buehler, Lake Bluff, IL), equipped with an external resistance heater. The inside of the stainless steel mold was coated with a thin layer of silicone mold release (Buehler). Next, a known amount of milled polymer powder was poured into the mold to create an even layer, the piston portion of the mold was inserted, and the entire mold compacted in the press at 20 MPa pressure. The external heater was activated and the sample and mold were heated to 140°C for 20 min. After 20 min, the temperature controller was turned off, allowing the mold to cool to room temperature. The disk was then released from the mold.

## RESULTS AND DISCUSSION

### Particle size

The distribution of particles for the various milling times, as obtained from sieve analysis, is shown graphically in Figure 1. For ease of visualization, data for several sieve fractions were grouped together: <63, 63–88, and 88–125 fractions (<125); fractions 125–177 and 177–250 (177–250); fractions 250–354 and 354–500 (250–500); and fraction 500–700 with fraction > 700 (>500). This plot clearly shows two important effects: the reduction in average particle size and elimination of Nafion® pellets with milling time (>500  $\mu\text{m}$  fraction); and the initial increase in small particles (<125  $\mu\text{m}$  fraction) up to 100 min milling time, followed by a decrease up to 200 min, during which time intermediate fractions (177–250 and 250–500) increase as the smaller particles agglomerate. Irreversible agglomeration of particles is well described in the literature,<sup>6</sup> and is the primary result of van der Waals attractions between the particles.

Even longer milling times cause a further increase in intermediate particle fractions. This is confirmed through SEM analysis. In Figure 2, the SEM photomicrograph shows secondary agglomerates < 100  $\mu\text{m}$  in size that are composed of much smaller primary particles. The presence of submicron particles, as small as several hundred nanometers in diameter, is confirmed by TEM analysis (Fig. 3). At 400 min of milling time (Fig. 4), the secondary agglomerates have grown in average size.

Longer milling times have other undesirable effects. First, polymer degradation can result, as indicated by a distinct color shift from yellow to dark green in the polymers milled for longer than 100 min.<sup>7</sup> Second, contamination from the milling media (ball and vial) can arise in the milled powders, even at shorter milling times. Contamination, too, can lead to color changes in the samples, attributed to reaction of the

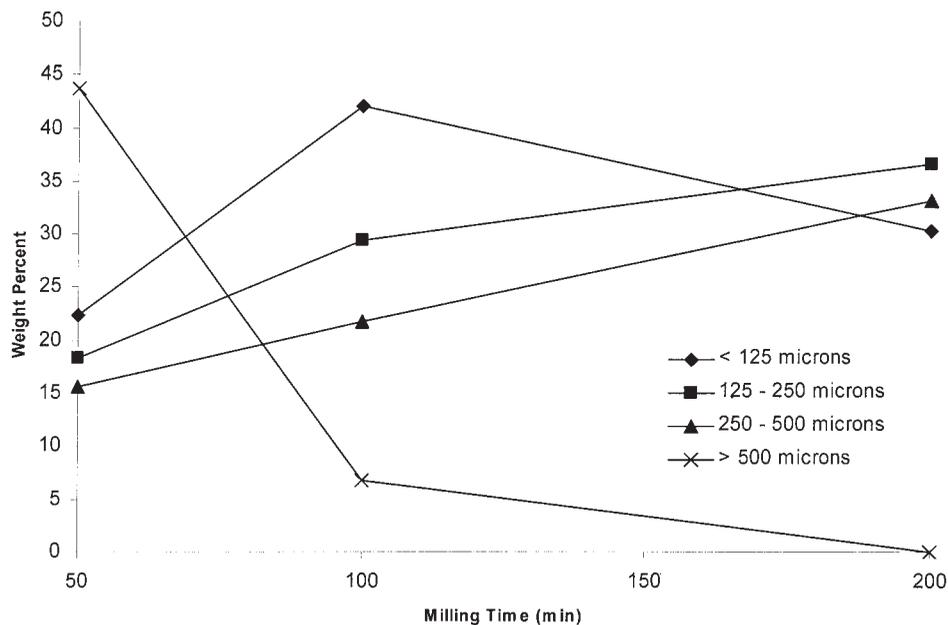


Figure 1 Agglomeration effect of Nafion® particles at longer milling times.

metal impurities with sulfonic acid groups in the polymer that lead to the formation of metal salts. An example of the contamination of polymer particles by metallic elements from the milling media is shown in Figure 5, which is an isolated area of the particle shown in Figure 3. This TEM image shows the presence of dark inclusions that are approximately 5 nm in size. The dark contrast of these inclusions, relative to the lighter regions of the polymer particle, indicates that the inclusions contain higher molecular weight species than the surrounding material. EDS analysis (Fig. 6) of a selected region confirms this result, and further identifies the primary contaminants as iron and chromium (copper is present as a result of the TEM grid). The presence of iron and chromium, in the proportions given by the relative peak heights in Figure 6, is attributed to the effects of milling with stain-

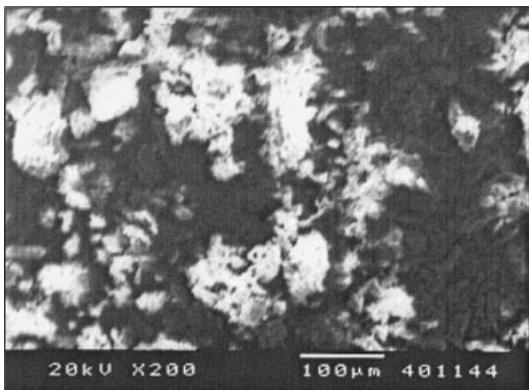


Figure 2 SEM photomicrograph of Nafion® milled for 100 min.

less steel media. The use of polymeric milling media, such as nylon, has been described to reduce the effects of contamination during mechanical attrition with metallic milling media.<sup>8</sup> However, those studies were performed with metallic and ceramic powders, from which polymeric contaminants are easily removed by thermal oxidative or dissolution methods. The separation of polymeric contaminants such as nylon from polymeric powders such as Nafion®, although possible, may prove to be more problematic than removing them from metallic or ceramic powders. This issue is the topic of continuing studies. The effect of milling time on molecular weight in the Nafion® samples was not determined in these studies because of the difficulty in finding a suitable solvent for molecular weight determinations, but it is expected that chain scission and molecular weight reduction occurred as a result of milling, as has been found in the high-energy ball milling of other polymers.<sup>7</sup>

Thermogravimetric analysis (see Fig. 7) of the powders indicates that milling has little effect on the overall weight loss of Nafion®: effectively all of the polymer decomposes by 500°C. However, the effect of particle size can be seen in the onset temperature of the decomposition. The weight loss occurs at a lower temperature as milling time increases. This is attributed to a decrease in particle size, which increases the relative surface area of the sample. Previous studies<sup>9</sup> have shown that transition temperatures such as those exhibited in TGA and DSC occur at lower temperatures as the surface area of the samples increases because of an increase in heat transfer area. The increased heat transfer rate allows

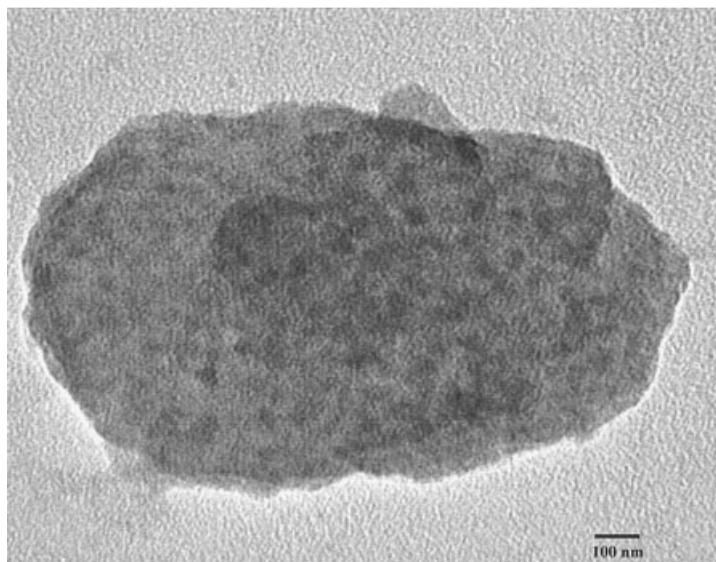


Figure 3 TEM image of Nafion® milled for 100 min.

the individual particles to achieve the furnace temperature more rapidly than for larger particles. In decomposition reactions, the increased surface area also facilitates removal of gaseous decomposition products from the powder, such that the overall decomposition proceeds more rapidly and is completed at a lower effective temperature. Mass spectrometry data (not shown) indicate little difference in the decomposition products from the milled Nafion® powders as a result of increased milling time. In all cases, the appearance of decomposition products coincides with the weight losses in the TGA plots, and are composed of (in increasing order of molecular weight)  $\text{H}_2\text{O}$ , F, HF, S,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ . The presence of all decomposition fragments can be attributed to the structure of Nafion®.

The thermal behavior of the milled powder is shown with a representative plot in Figure 8. At 100

min of milling time, the powder exhibits a single endothermic transition at  $138^\circ\text{C}$ , followed by a weak exothermic event at  $308^\circ\text{C}$  and a strong exothermic event at  $411^\circ\text{C}$ . The exothermic events agree well with thermogravimetric analysis (see Fig. 7) that shows the onset of weight loss around  $300^\circ\text{C}$ , which levels off slightly, followed by the majority of weight loss around  $400^\circ\text{C}$ . Derivative traces of the TGA plots for powders (not shown) show two distinct weight loss peaks, at approximately  $300$  and  $400^\circ\text{C}$ , which correspond to the exothermic events in the DSC curves. Mass spectrographic analysis of the off-gases from these exothermic events indicates that the first peak is attributable to loss of HF, whereas the remaining components ( $\text{H}_2\text{O}$ , F, S,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ ) evolve during the primary weight loss at  $411^\circ\text{C}$ .

The endothermic event in the DSC trace for milled Nafion® is attributable to a glass transition in the ionic

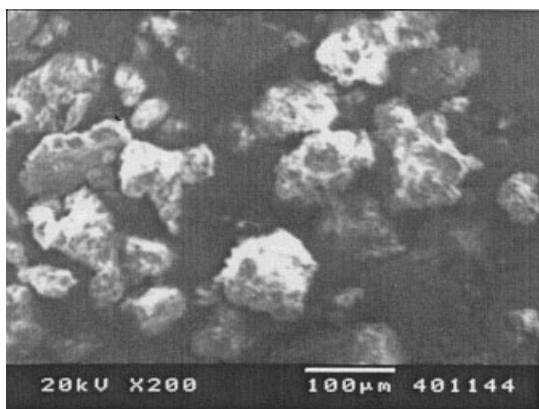


Figure 4 SEM photomicrograph of Nafion® milled for 400 min.

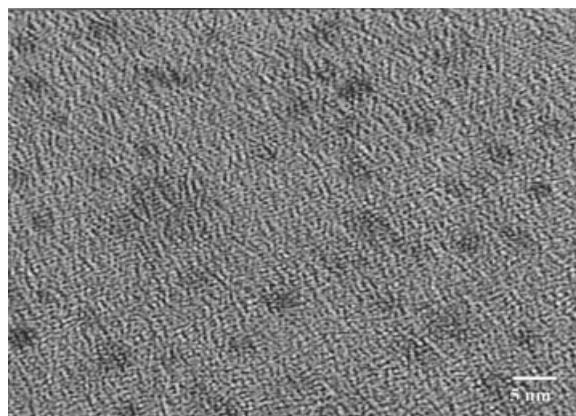


Figure 5 TEM image of Nafion® showing metallic inclusions.

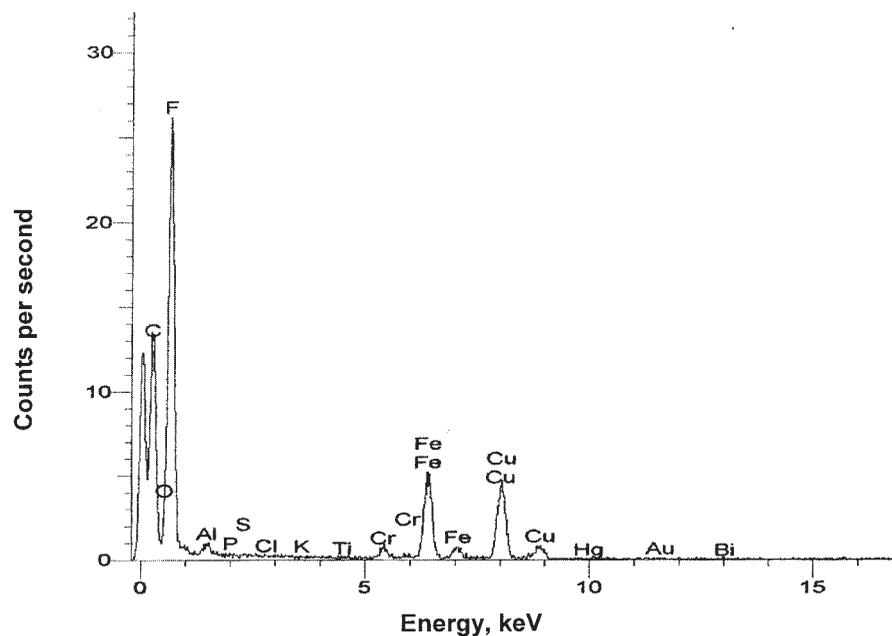


Figure 6 Typical EDS spectrum of Nafion® milled for 100 min.

clusters<sup>1,10</sup> and is in excellent agreement with previous thermal studies of Nafion®. This is evidence that the ionic clusters are not destroyed during the ball milling operation. However, previous studies have also shown a second endothermic peak at around 230–250°C, which is attributable to the melting of crystalline domains in Nafion®. No such peak is evi-

dent in the DSC trace for the powdered sample (Fig. 8), indicating that amorphization of the Nafion® sample has occurred. This is consistent with previous studies in which the crystallinity of high-crystallinity PET decreased with milling time.<sup>7</sup> The effect of hot pressing on the thermal properties of the Nafion® is described in the next section.

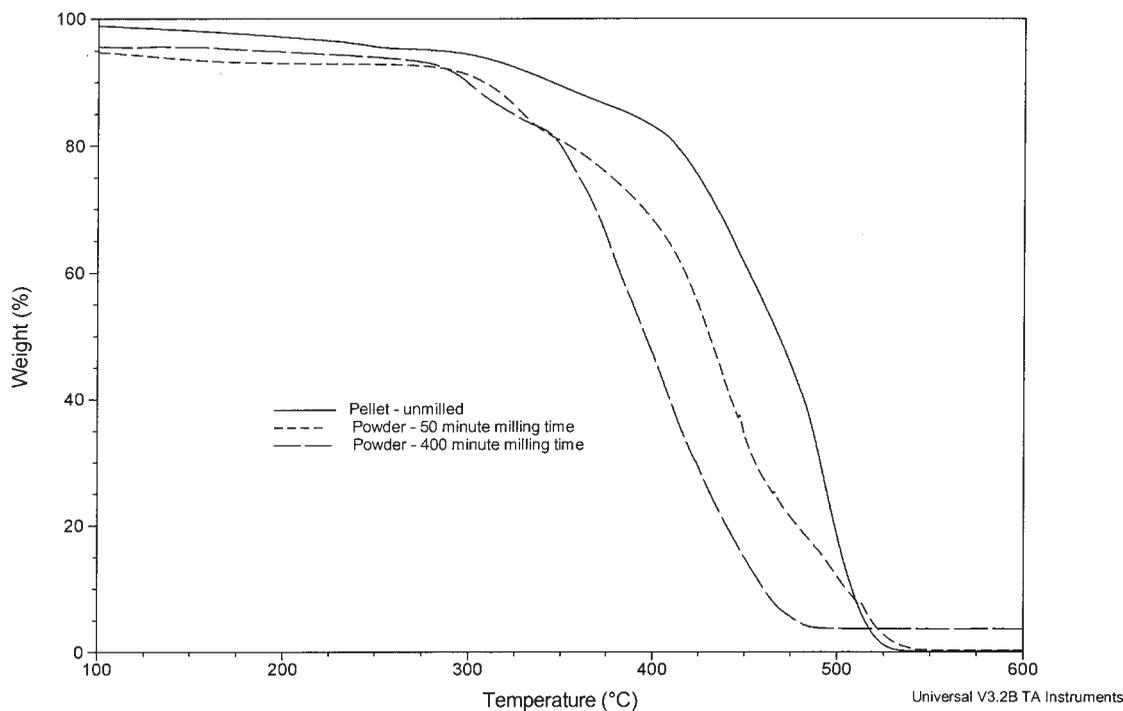


Figure 7 TGA plots of unmilled pellets, and powders milled for 50 and 400 min.

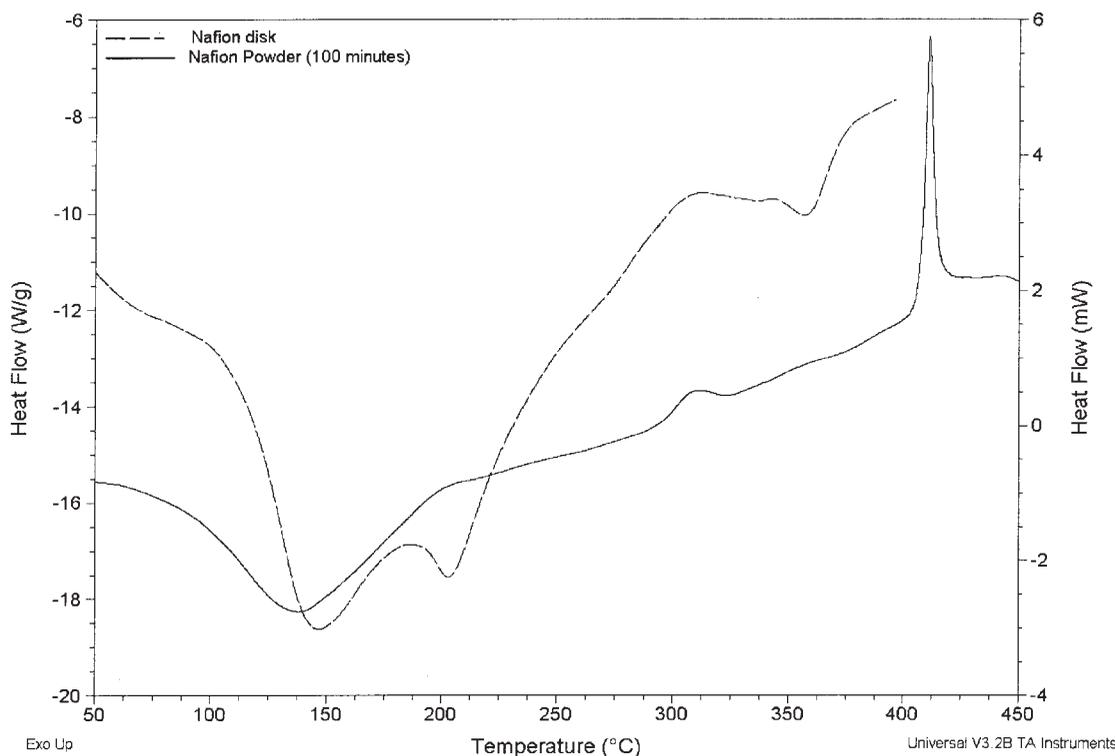


Figure 8 DSC traces of Nafion® powder and disk.

### Particle pressing and disk formation

The Nafion® powders milled for 100 min were selected for use in the formation of pressed membranes. The pressing process, as described in the experimental section, resulted in a dense, transparent disk (see Fig. 9), with an average thickness of 0.36 mm and density 1.61 g/cm<sup>3</sup>. The density is approximately 23% less than that of the precursor pellets, and 18% lower than that of most commercially available Nafion® membranes. The difference is attributed to the incorporation of pores and voids in the milling processes that are not completely removed during hot pressing. The use of HIP is being explored to further densify the membranes. The membrane color, similar to that of the precursor pellets, indicates minimal polymer degradation. Subsequent studies will characterize these

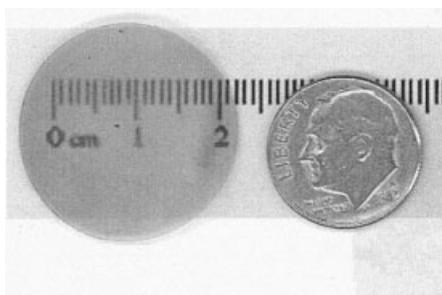


Figure 9 Hot-pressed Nafion® membrane.

membranes for hydrogen diffusivity and conductivity properties.

Thermal analysis of the pressed disk (dashed line in Fig. 8) shows two primary endothermic events and one broadly exothermic event, although the disk was not raised to the decomposition temperature (400°C) to preserve its mechanical integrity. The DSC traces of the disk indicate that hot pressing not only maintained the ionic clustering, as evidenced by the transition at 148°C, but also allowed some crystallization in the polymer to occur, as indicated by the second endothermic event at 203°C. This thermal behavior is similar to that observed by previous investigators on unmilled Nafion®.<sup>1,10</sup>

### CONCLUSIONS

The use of high-energy ball milling, followed by hot pressing, has been shown to be an effective method for producing Nafion® membranes. Milling times of less than 100 min are optimal to prevent particle agglomeration. The milled powders undergo some amorphization during milling, but otherwise possess thermal properties similar to those of unmilled Nafion®. The presence of metallic elements, specifically iron and chromium, as a result of milling in metallic media, is indicated. A membrane disk pressed from the milled powders shows thermal behavior similar to that of commercially available membranes.

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