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# Synthesis and Characterization of Perfluorinated Carboxylate/Sulfonate Ionomer Membranes for Separation and Solid Electrolyte Applications

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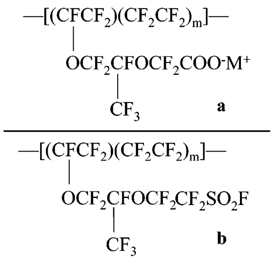
A synthesis procedure is given for mixed functionality carboxylate/sulfonate (c/s) perfluorinated ionomer membranes starting from sulfonyl fluoride-form Nafion precursor. The described method produces ionomers with up to 30% carboxylate-substituted equivalents. Attenuated total reflectance and transmission Fourier transform infrared analyses show that the c/s membranes have carboxylate-rich surfaces and a sulfonate-rich center. The surfaces of the c/s membranes are uniform in carboxylate content across the entire membrane areas. The c/s membranes show interesting transport characteristics when compared to Nafion, including proton conductivity that decreases moderately, and water permeability that decreases significantly with increased carboxylate content. As an example, an increase in carboxylate content from 2.4 to 7.5 and 11.4% results in a 26.9 and 32.7% drop in conductivity coupled with a 67.7 and 97% drop in permeability, respectively. Given the dehydration problem in modern $H_2$/air proton-exchange membrane (PEM) fuel cells and the methanol crossover problem in direct methanol PEM fuel cells, these c/s membranes may offer increased performance in fuel cell applications. The synthesis procedures can be used in general to attach functional molecules to the terminal sulfur atom on the ionomer side chains, creating a number of possibilities in forming dual-functionalized Nafion films.

## Introduction

Carboxylate-form perfluorinated ionomers such as those made by DuPont (Nafion CR), with the structure given in Figure 1a, have shown interesting properties compared to their sulfonate-form counterparts.[1−6] These properties arise from the weaker acidity of the carboxylic acid pendant group and the smaller size of the carboxylate anion. Carboxylate-form membranes have proven useful in the chlor-alkali process by providing increased exclusion of aqueous anions at the cell cathode and increased cell efficiency.[1,2,4] Recently, the Nafion sulfonate/carboxylate bilayer membranes (Nafion 90209) were shown to be potentially useful in the dehydration and concentration of mineral acids because of the increased anion exclusion capability of the carboxylate layer.[7,8] Given the improvements in cation/anion selectivity over sulfonate-form ionomers, it is clear that the carboxylate-form perfluorinated ionomers offer advantages where cation/anion separation is critical or where anion exclusion is sought in general. Unfortunately, carboxylic acid and carboxylic acid/sulfonic acid bilayer ionomer membranes exhibit unacceptable water permeability and proton conductivity, rendering them impractical in acid dehydration and fuel cell applications.[3,4,7]



$$\text{—[(CFCF}_2\text{)(CF}_2\text{CF}_2\text{)}_m\text{]— ; OCF}_2\text{CF(CF}_3\text{)OCF}_2\text{COO}^-\text{M}^+$$

$$\text{—[(CFCF}_2\text{)(CF}_2\text{CF}_2\text{)}_m\text{]— ; OCF}_2\text{CF(CF}_3\text{)OCF}_2\text{CF}_2\text{SO}_2\text{F}$$

**Figure 1.** Structure of (a) carboxylate and (b) sulfonyl fluoride-form Nafion. The average equivalent weight (EW) of the film is given by $EW = 100m + 446$.[3] $M^+$ can be any alkali metal or a proton.

One of the reasons for the low flux of water in acid-form carboxylate membranes is the physical thickness of the films; the permeance of solvents and ions is greatly reduced with increased thickness. A good way to circumvent this limitation is to decrease the thickness of the membrane. To make this resistive layer as thin as possible, the membrane should be attached to a support layer with lower resistance.[9] Because the sulfonic acid form of Nafion is highly permeable to water and ions, it is a logical support for a thin carboxylic acid-form membrane. The carboxylate layer could be cast or laminated onto a sulfonate layer (e.g., Nafion 90209), or

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10.1021/cm070138h CCC: $37.00

**Table 1. Synthetic Routes to C/S Membranes**

| synthetic route | outcome |
|---|---|
| Step 1: Reduction of $R_f{-}SO_2F$ to $R_f{-}SO_2H$ | |
| contact with forming gas (3.5% $H_2$ in inerts) at 120 °C | $SO_2F$ not reduced |
| soak in dilute aqueous hydrazine, room temperature to 95 °C | $SO_2F$ not reduced |
| soak in concentrated hydrazine ($>$50% w/w), room temperature | $SO_2F$ rapidly reduced, no control over the extent of reduction, membrane damaged after short soak times |
| soak in concentrated or diluted hydrazine($>$20% w/w) in DMSO, room temperature | $SO_2F$ rapidly reduced, little control over the extent of reduction, membrane damaged after 1 h, maximum conversion 30% |
| soak in diluted hydrazine (20−50% w/w) with $Ca^{2+}$ added as a fluoride scavenger to increase conversion of $SO_2F$ | $SO_2F$ not reduced |
| soak in diluted hydrazine (20−50% w/w), room temperature | $SO_2F$ reduced, extent of reduction controlled by soak time, extensive soaks lead to membrane damage, maximum conversion 30% |
| soak in several fresh batches of diluted hydrazine (20−50% w/w), room temperature | $SO_2F$ reduced, additional soaks lead to membrane damage, maximum conversion 30 |
| Step 2: Hydrolysis of $R_f{-}SO_2F$ to $R_f{-}SO_3^-$ | |
| soak in hydrolysis mixture at ≥80 °C (usual route for hydrolysis of Nafion precursor[18]) | $SO_2F$ completely hydrolyzed in 20 min, loss of ion exchange capacity due to probable formation of disulfide bonds[19−21] between unstable $SO_2^-$ moieties,[22,23] large holes form in membrane sheets |
| soak in hydrolysis mixture at $<$80 °C | $SO_2F$ completely hydrolyzed in 20 min, no loss of ion-exchange capacity |
| Step 3: Oxidation of $R_f{-}F_2SO_2^-$ to $R_f{-}CO_2^-$ | |
| soak in hot concentrated $HNO_3$ (a typical reagent used to oxidize sulfinic acid to sulfonic acid[24]) | $SO_2^-$ not oxidized |
| soak in concentrated $H_2O_2$, room temperature to 90 °C | $SO_2^-$ not oxidized |
| heat in air in a salt ($K^+$ or $Na^+$) form up to 200 °C | $SO_2^-$ not oxidized |
| heat in air in acid form at $<$80 °C | $SO_2^-$ not oxidized |
| heat in air in acid form at ≥ 80 °C | $SO_2^-$ rapidly oxidized, loss of ion exchange capacity due to desulfinization,[22,23] loss of functional groups increases with increased temperature |
| reflux in water in a salt form | $SO_2^-$ not oxidized |
| reflux in water in acid form | $SO_2^-$ completely oxidized in 3 days |
| soak in water saturated with air or oxygen at $<$80 °C in acid form | $SO_2^-$ completely oxidized in several weeks |
| soak in water saturated with air or oxygen at ≥80 °C in acid form | $SO^-$ completely oxidized in 2−4 h |
| soak membranes in salts of Fe, V, U, Co, Ni, Cu, or Mn to speed oxidation in air, as suggested by Grot[10] | not considered, because multivalent cations are very difficult if not impossible to remove from Nafion and can cause significant reductions in performance in electrochemical cells[25,26] |
| Other Approaches Starting from Sulfonate-Form Nafion | |
| procedures described by Grot et al.[10] using pressurized fluorine/oxygen mixtures | not considered because of safety concerns |
| procedures described by Fujimura et al.[6] using aqueous reagents | procedures could not be reproduced accurately, extensive process times of weeks and months, use of halogenated reagents and creation of excessive amounts of waste, no control over extent of conversion to the $R_f{-}CO_2^-$ functional group |

alternatively, the carboxylate layer could be created by modifying the surfaces of a sulfonate-form membrane. Of these two approaches, surface modification is the better way to create very thin, defect-free carboxylate layers on already-thin starting materials. If such a thin "supported" carboxylate membrane can be made, it may be of particular use to the separations and electrochemical communities.

Although the syntheses of carboxylate-form Nafion membranes from materials with both nonionic and ionic materials have been shown in general,[6,10] few of the important procedural details have been disclosed. Furthermore, although it is known that membranes with both carboxylate and sulfonate functionality can be made from a monofunctional starting material, control over the ratios of ionic equivalents have not been demonstrated, nor have the distributions of functional groups through the film thickness been determined.[11,12]

This paper details a method for making bifunctional carboxylate/sulfonate perfluorinated ionomer membranes (hereafter called c/s membranes or c/s films) from a commercially available precursor film. The procedure is generalized to allow for application to any addition reactions between covalently bound sulfinic acids and other chemical moieties, or for chemical cross-linking reactions. Methods for characterizing the bifunctional membranes are discussed, including determination of the relative amounts and distribution of functional groups within the c/s membranes. Finally, some representative mass-transfer characteristics of the c/s membranes are discussed, with an emphasis on the films' potential uses in polymer electrolyte membrane (PEM) fuel cells.

## Experimental Section

**Materials**. Nafion 111-F precursor sheets (copolymer of tetrafluoroethylene and perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl

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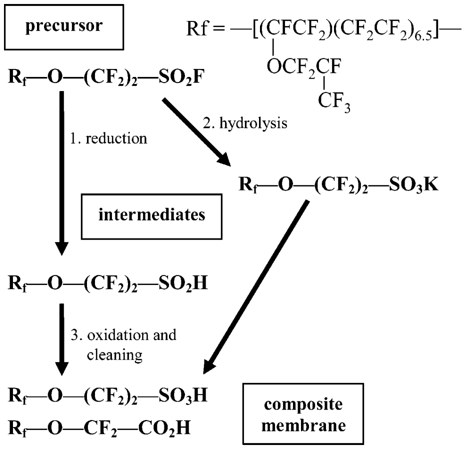

**Figure 2.** Flow diagram for the synthesis of c/s ionomer films.

fluoride)) were purchased from Ion Power, Inc. A second batch of precursor was provided by DuPont Fuel Cells. The repeat structure of the sulfonyl fluoride precursor is shown in Figure 1b. The films have a nominal equivalent weight (EW) of 1100 g of ionomer per mole of $SO_2F$ and a nominal thickness of 25 $\mu$m. Hydrazine monohydrate (100%) and triflic acid (99.9%) were purchased from Aldrich; nitric acid (67%), potassium chloride (KCl), and potassium hydroxide (KOH, 87.8%) were purchased from Mallinckrodt; dimethyl sulfoxide (DMSO, 99.9%) was purchased from Fisher; and hydrogen peroxide ($H_2O_2$, 3% USP) was purchased from a local drug store. All chemicals were used without further purification. Distilled water, further purified to a minimum resistivity of 18 MΩ cm, was used for all chemical dilutions, washing steps, and membrane storage. All vessels used in all experiments were of Teflon or glass construction, and all stainless steel forceps and cutting tools were used sparingly.

**C/S Membrane Synthesis**. All c/s films were produced using the following procedure. Variations of the procedure were considered and are included in Table 1. The general reaction scheme is shown in Figure 2 and includes four primary steps: reduction of sulfonyl fluoride to sulfinic acid, hydrolysis of residual sulfonyl fluoride to sulfonate, oxidation of sulfinic acid to carboxylic acid, and cleaning of the resultant ionomer. Note that although Nafion 111-F was used in this study, these procedures can be applied to thicker Nafion precursor films, or to other sulfonyl fluoride-form fluoropolymers.

Precursor samples approximately 155 $cm^2$ in size were carefully laid in the bottom of Pyrex baking dishes. Special care was taken when transferring the precursor to the glass dishes, as the films developed a significant static “cling” and folded onto themselves and the glass. Once the precursor stuck to itself, it was extremely difficult to separate without tearing or stretching. A mixture of 45 mL of hydrazine monohydrate and 15 mL of water (48.4% hydrazine w/w) was poured over each precursor sheet, a timer was started, and the reaction vessels were covered with plate glass. Gas bubbles formed during the reaction, floating the precursor sheets to the surfaces of the hydrazine mixtures, so the films were frequently tapped below the free surface of the hydrazine solution to ensure that membrane surfaces were always in contact with liquid. After predetermined periods, the precursor sheets were removed from the dishes, thoroughly rinsed with water, and submerged in concentrated nitric acid for 20 min to quench the reduction reaction and remove residual hydrazine. The films were then removed from the acid, rinsed with water, and soaked in water for 20 min to remove excess acid.

Following the water soak, membranes were rinsed and soaked in a hydrolysis solution of 13% KOH, 30% DMSO, and water for 2 h at 70 °C. The films were then rinsed with water and soaked in 1 M nitric acid for 12 h at room temperature. To produce a Nafion 111 film, virgin precursor was hydrolyzed and annealed as outlined below.

To oxidize the resultant sulfinic acid groups, films were preheated in 1 M nitric acid solution to 95 °C and transferred, without rinsing, to a large beaker of water at 80 °C. Next, filtered air was bubbled into the water through a stainless steel frit, and the membranes were allowed to soak in the oxygen-enriched water for 8 h. Finally, the c/s films were rinsed, patted dry with Kimwipes, placed on glass plates, and annealed for 3 h at 165 °C under filtered air. The benefits of this annealing procedure are explained elsewhere.[13]

After heat treatment, membranes were loosened from the glass plates with water and soaked in water for several hours. The annealed films developed an amber tint due to adsorbed organics from the annealing oven. To remove this discoloration and fully protonate the films (termed H-form films hereafter), we refluxed the c/s films for 2 h in 3% $H_2O_2$, rinsed in water, refluxed 4 h in 10% nitric acid, and refluxed in three fresh charges of water for 80 min each. Finally, the c/s membranes were checked for full conversion with Fourier transform infrared spectroscopy (FTIR) and stored in water.

**Instrumental Analysis**. X-ray fluorescence spectroscopy (XRF) measurements were performed with an EDAX Eagle II XLP micro-XRF system equipped with a polycapillary focusing optic Rh target excitation source and a SiLi detector. FTIR measurements were performed with a Thermo-Nicolet Nexus 870 FTIR, the sample chamber of which was purged with $CO_2$- and $H_2O$-free air. Transmission FTIR measurements were made with a deuterated triglycine sulfate detector. Attenuated total reflectance (FTIR-ATR) measurements were made with a mercury cadmium telluride detector. A Specac ATR cell with a KRS-5 crystal was used for all ATR measurements, and resultant spectra were put though an ATR correction using Thermo Nicolet Omnic software to account for the different penetration depths of the different wavelengths of infrared light. All samples were vacuum-dried for 24 h at room temperature before FTIR analysis.

$^{19}F$ magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained with a Chemagnetics Infinity 400 NMR spectrometer operating at 376.2 MHz for $^{19}F$. The spectra were recorded at 310 K using DEPTH[14] pulse-sequence in order to suppress $^{19}F$ background signals from some of the probe materials. Ninety degree pulse lengths of 5 $\mu$s, relaxation delays of 5 s, and MAS speeds of 11.2 kHz were used. The chemical shift reference was a sample of external polytetrafluoroethylene, which was assigned a chemical shift of −123.3 ppm.[15] The NMR spectrometer was equipped with Chemagnetics speed and temperature controllers.

Membrane samples were tested for EW using a titration method discussed elsewhere.[16]

## Results and Discussion

**C/S Film Synthesis**. In developing a standard procedure for the synthesis of c/s membranes, we established six primary goals. These are outlined in Figure 3, and their fulfillment is explained in the discussion that follows. Although conceptually simple, the task of converting sulfonyl

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1. Create carboxylate-rich ‘skins’ on membrane surfaces
2. Maintain control over the extent of conversion of sulfonyl fluoride groups to carboxylate anions
3. Minimize safety hazards and waste generation
    - Minimal use of chemicals
    - Conduct all procedures at mild temperatures and pressures
4. Minimize reaction times
5. Maintain a uniform ion exchange capacity among films
6. Develop repeatable procedures

**Figure 3.** Primary goals for the conversion of sulfonyl fluoride Nafion precursor to a c/s membrane.

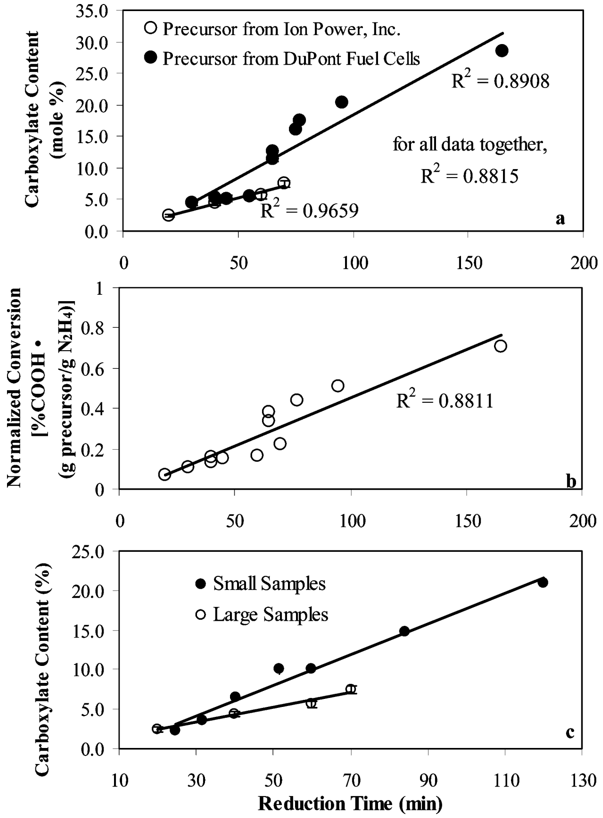

**Figure 4.** Relationships between reduction time and conversion to carboxylic acid moieties for (a) two lots of precursor material, (b) all samples normalized by precursor and reactant mass, and (c) different size sheets from the same batch of precursor, contacted with the same volume of hydrazine. Solid lines are linear least-squared fits of the data. Correlation coefficients are provided to compare the goodness-of-fit of each of the regressions.

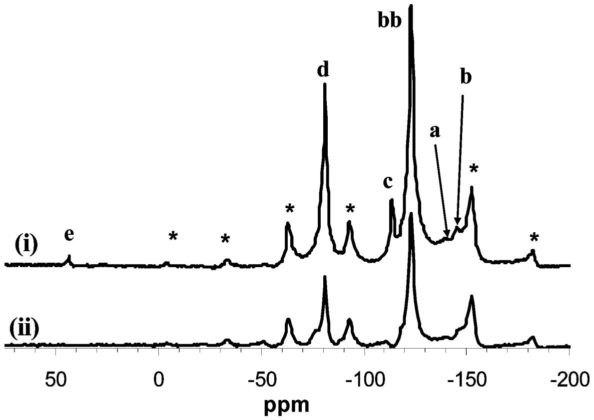

**Figure 5.** $^{19}$F NMR data for (i) sulfonyl fluoride precursor and (ii) a c/s film, stacked for comparison. The c/s film was reduced for 24 h in concentrated hydrazine and further converted to the c/s form. Peaks marked with an * are spinning sidebands. Peaks bb, a, b, c, d, and e, correspond to $CF_2$ in the polytetrafluoroethylene (PTFE) backbone, CF in the PTFE backbone, CF in the side chain, $CF_2S$ in the side chain, a combination of $OCF_2$ and $CF_3$ in the side chain, and SF in the sulfonyl fluoride precursor, respectively.

fluoride precursor to a dual-functional membrane is nontrivial. It took considerable time to develop repeatable and nondestructive conversion techniques, even with the various conversion procedures suggested by Grot,[10] and some preliminary c/s membrane synthesis work by Ames et al.[11] as guidelines. A summary of the synthetic routes we have explored along with their outcomes is provided in Table 1.

The reduction of sulfonyl fluoride was sensitive to reaction conditions, as shown in Table 1. Control of the reduction reaction was achieved by using moderately concentrated hydrazine and monitoring the reaction time, the results of which are shown in Figure 4. Using a mixture of 50% hydrazine in water, the total conversion of sulfonyl fluoride was proportional to reaction time. Different batches of precursor material showed different reaction rates, as shown in Figure 4a. This difference could not be explained by normalizing the extent of conversion by precursor mass (Figure 4b), or by precursor thickness or volume (not shown). Furthermore, within the same batch of precursor, there was variability in the reaction rate when different amounts of precursor were used. Figure 4c shows data for 155 and 19 cm$^2$ samples soaked in 60 mL of identical hydrazine solutions. Even though reactant hydrazine was present in excess for both samples, the reaction rate was considerably higher for the smaller samples indicating that reaction is favored in large excesses of hydrazine.

Steps 2 and 3 in the conversion process (hydrolysis of sulfonyl fluoride and oxidation of sulfinic acid, respectively) were also sensitive to reaction conditions, as indicated in Table 1. Ultimately, it was determined that the sulfinate intermediate is unstable at temperatures above 80 °C, and that a combination of heat, protons, water, and molecular oxygen are necessary to oxidize the perfluorinated sulfinic acid to a perfluorinated carboxylic acid without loss of ion-exchange capacity. The presence of water is especially important, as it appears to stabilize the reactive sulfinic acid group so that cleavage of the C−S bond, leading to increased EW, is hindered.

Using any combination of synthesis routes, the total conversion of sulfonyl fluoride to carboxylate was limited to ∼30% of all functional groups. With reaction mixtures of 50% hydrazine (w/w), conversion to 30% $SO_2H$ (later oxidized to $CO_2H$) rarely required more than 1.5 h, and the resultant membranes retained an EW near 1100 g mol$^{-1}$. If membranes were reduced for longer periods, however, they retained their maximal 30% $SO_2H$ content and had significantly elevated EW values, indicating loss of functional groups. The loss of ion exchange capacity was explored with $^{19}$F NMR, shown in Figure 5. In the figure, a sulfonyl fluoride precursor membrane is compared to a c/s membrane that was initially reduced in concentrated hydrazine for 24 h. Peak assignments were obtained from a recent paper by Chen and

**Table 2. $^{19}$F NMR Peak Intensities and Ratio Analyses**

| peak | integrated intensity precursor | integrated intensity c/s membrane |
|---|---|---|
| bb | 181.5 | 215.9 |
| a | 13.3 | 6.9 |
| b | 14.6 | 15.9 |
| c | 18.5 | 4.8 |
| d | 63.0 | 55.6 |
| total (less $CF_2S$) | 272.4 | 294.3 |
| total side chain (less $CF_2S$) | 77.6 | 71.5 |
| ratios | | |
| total side chain to total (less $CF_2S$) (%) | 28.5 | 24.3 |
| $CF_2S$ to total side chain (%) | 19.3 | 6.3 |

Schmidt-Rohr,[17] and the peaks are labeled with letters. A few differences can be noted in the NMR spectra. First, the c/s film shows an absence of the peak at 43.4 ppm, indicating that all sulfonyl fluoride was either reduced or hydrolyzed in the conversion process. Second, the c/s film shows a drastically reduced peak at ~118 ppm, indicating that a significant portion of the distal $CF_2$ group on the polymer side chain (see Figure 1b) was removed upon conversion. The removal of this $CF_2$ is expected, at least partially, because the side chain is shortened upon oxidation of sulfinic acid to carboxylic acid (compare parts a and b in Figure 1). Still, FTIR analysis of this c/s membrane (explained later) showed a carboxylate content of ~30%, which means that a significant number of side chains should have retained the distal $CF_2S$ group. For such a large reduction in peak intensity, it is expected that a significant amount of side chain destruction near the ends of the chains occurred. This notion is supported by the c/s membrane's measured EW of 1731 g mol$^{-1}$, indicating that about 36% of all ionic groups were removed in the conversion process. Third, the c/s film shows a shoulder on the left side of peak d, whereas the sulfonyl fluoride film does not. According to Chen,[17] this peak is a superposition of peaks at $-80.4$, $-80.1$, and $-79.9$ ppm, corresponding to the side chain $CF_3$, proximal $OCF_2$, and distal $OCF_2$, respectively. The formation of this shoulder is likely due to a loss of distal $OCF_2$ or a loss of all groups associated with peak d with extra loss of distal $OCF_2$, which would reduce the shape of the left side of the peak. Again, this supports the suggested side chain degradation and the observed increase in EW. Fourth, the small peak at $-143.8$ ppm is diminished upon conversion to the mixed ionic form. Because this peak corresponds to side-chain CF groups, the reduction in peak intensity is further evidence of side-chain degradation. Finally, upon integration of the peaks in Figure 5 and subsequent ratio analysis, we find that, excluding intensities from peak c (which should be reduced upon oxidation of sulfinic acid), a lower percentage of total fluorine lies in the side chains of the c/s film than in the precursor film (see Table 2). Unlike other c/s membranes considered in this study, the c/s membrane shown in Figure 5 was reduced for a significantly longer period than other samples with all other conversion procedures remaining the same. Because the film showed an increased EW whereas other c/s films did not, we suggest that degradation occurs only in the reduction step. Therefore, it is not recommended that precursor films be reduced for longer periods than needed to achieve the 30% equilibrium limit.

**Table 3. Carboxylate Content and EW of Several C/S Membranes from Two Lots of Precursor Material**

| membrane | carboxylate content (mol of $CO_2H$/mol of equivalents) | equivalent weight (g mol$^{-1}$) |
|---|---|---|
| S020.75w.i | 2.4 ± 0.3 | 1140 ± 25 |
| S030.75w.d | 4.4 ± 0.4 | 1134 ± 15 |
| S040.75w.i | 4.4 ± 0.4 | 1112 ± 24 |
| S040.75w.d | 5.3 ± 0.4 | 1094 ± 11 |
| S045.75w.d | 5.1 ± 0.4 | 1158 ± 15 |
| S055.75w.d | 5.5 ± 0.4 | 1137 ± 11 |
| S060.75w.i | 5.6 ± 0.4 | 1110 ± 24 |
| S065.75w.d | 11.4 ± 0.5 | 1128 ± 24 |
| S065.75w.d (repeat) | 12.7 ± 0.4 | 1111 ± 11 |
| S070.75w.i | 7.5 ± 0.4 | 1126 ± 24 |
| S075.75w.d | 16.1 ± 0.4 | 1357 ± 14 |
| S077.75w.d | 17.6 ± 0.4 | 1144 ± 14 |
| S090.100.i | 30.0 ± 0.2 | 1011 ± 12 |
| S095.75w.d | 20.4 ± 0.3 | 1170 ± 17 |
| S165.75w.d | 28.4 ± 0.1 | 3953 ± 500 |

After oxidation of the sulfinic acid intermediates, the c/s membranes were stable in harsh chemical environments including peroxides and concentrated mineral acids and bases. Cleaned c/s films were transparent, flexible, and tough; resisted tearing; and had densities and thicknesses similar to those of Nafion 111. The EW of a number of c/s films was measured and is shown in Table 3. The naming convention for the sample membranes is as follows: S indicates that the film is symmetric (contacted on both sides with hydrazine), the next three numbers indicate the reduction time in minutes, the next two numbers indicate the volume fraction of hydrazine used in the reduction reaction (%), w indicates that water was used as a diluent, and i or d indicates that the precursor came from Ion Power, Inc., or DuPont Fuel Cells, respectively. The data in the table show that our conversion procedures do not cause a significant loss of ion exchange sites, unless the films are reduced for significantly long periods. As noted previously, it does not appear that greater than 30% conversion to carboxylate can be achieved using our procedures. Fortunately, membranes with carboxylate contents higher than 30% have poor electrical and transport properties (shown later), so this conversion limitation should not prevent the synthesis of useful ionomer films.

**Determination of Carboxylate Content**. The bulk carboxylate content (mole percentage of carboxylate anionic sites) was measured using FTIR or XRF. To quantify carboxylate content via XRF, c/s films were first soaked in hot 1 M KOH for 4 h to exchange protons for potassium counterions (hereafter termed K-form films), then rinsed with water to remove residual KOH. Second, a series of potassium triflate ($CF_3SO_3K$) salt solutions were prepared from triflic acid, KOH, and KCl to mimic S and K atoms in c/s films.

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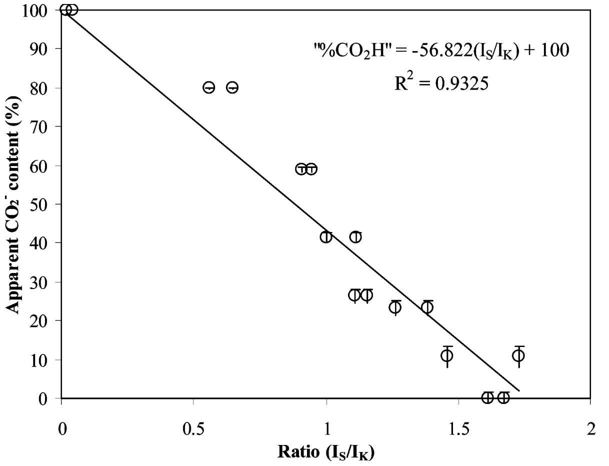

**Figure 6.** Simulated carboxylate contents from potassium triflate and KCl salts correlated with ratios of XRF intensities for S and K atoms. The solid line is a linear least-squares fit of the data. $I_s$ and $I_K$ are the XRF intensities of S and K atoms, respectively.

A salt ratio of zero S to finite K mimics a membrane with 100% carboxylate functional groups (no S from $SO_3^-$), and a ratio of 1 mimics a membrane with 100% sulfonate functional groups (one $K^+$ for each $SO_3^-$ and no excess $K^+$ associated with $CO_2^-$). Ratios between 0 and 1 mimic mixed carboxylate/sulfonate samples. Triflic acid was chosen so that the S and K atoms would reside in a fluorinated environment, similar to the ionomer. Third, the salt solutions were placed onto glass slides with Pasteur pipettes, evaporated to dryness, and analyzed for S and K content with XRF (scan area 1 cm$^2$). Fourth, a calibration curve was generated from the XRF data, correlating the actual ratios of S and K in the salt samples to the relative intensities of S and K obtained from XRF. This calibration is shown in Figure 6. Finally, the K-form c/s membranes were analyzed for S and K atoms, and the carboxylate contents obtained from the calibration.

Because the XRF instrument used in this study had very limited availability, a second method was devised to measure carboxylate content in the films via transmission FTIR. The same samples used in XRF analysis were acidified, rinsed, and vacuum-dried at room temperature for 24 h. Next, transmission FTIR spectra were collected at 6 different locations across a film area of 3 cm$^2$. Each collected spectrum was normalized and baseline-corrected using Thermo-Nicolet Omnic software. First- and second-derivative peaks were then generated to find the inflection points in characteristic $SO_3H$ and $CO_2H$ peaks (~1060 and ~1785 cm$^{-1}$, respectively), as demonstrated in Figure 7. Next, nine peak areas were calculated for both $CO_2H$ and $SO_3H$ peaks, corresponding to measured data lying at, just above, and just below the peak inflections. Peak area averages and standard deviations were then determined and the ratios of $SO_3H/CO_2H$ peak areas were calculated. Peak area ratios were used because samples inevitably vary in thickness and hence absorbance intensity. These steps were then repeated for all other sample spectra. When all peak area ratios and their uncertainties had been determined, a weighted average peak area ratio was calculated and plotted against the carboxylate content obtained via XRF. This correlation is shown in Figure 8.

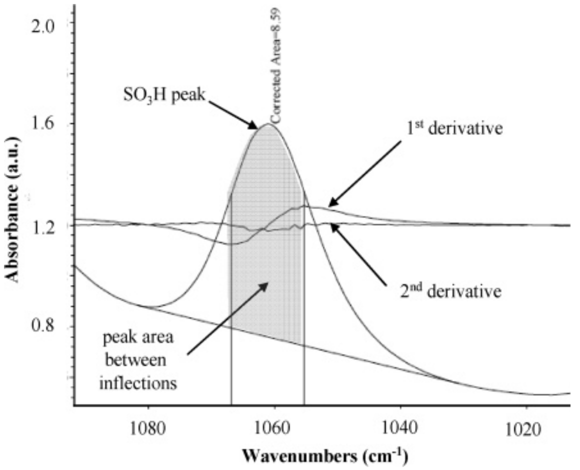

**Figure 7.** Determination of FTIR peak areas between peak inflection points. The shaded region is the area used for peak area ratios.

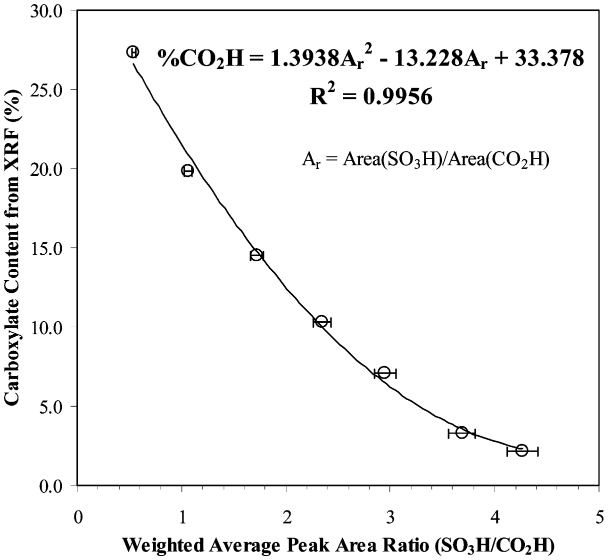

**Figure 8.** Correlation between peak area ratios from FTIR, and bulk carboxylate content from XRF.

Figure 8 can be used to determine carboxylate content in any c/s film as long as the film is thin enough to allow transmission FTIR measurement (<60 $\mu$m) and as long as the sample has been converted to the H-form and vacuum-dried. The drying step is particularly important because the carboxylic acid is resonance stabilized and easily solvated, which leads to an effective lowering of the carbonyl stretch intensity at ~1785 cm$^{-1}$,[12] and because the $SO_3H$ peak increases in intensity upon hydration.[27] The only way to

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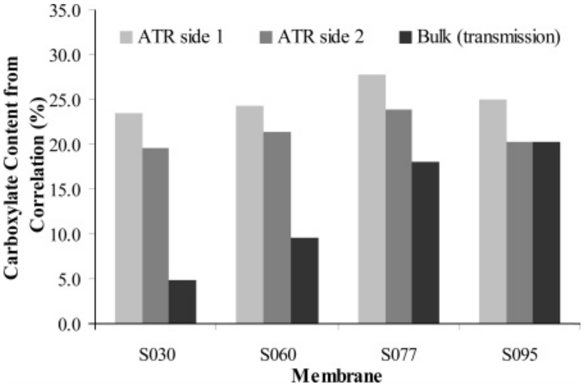

**Figure 9.** Carboxylate contents in c/s films at the surfaces and in bulk as measured by ATR and transmission FTIR.

ensure repeatable and comparable results is to analyze dry membranes. Determination of carboxylate content at different locations across membrane areas using FTIR showed that the conversion procedure produces films of uniform ionic composition. For thicker films (>60 μm up to 1 mm), the XRF method is recommended.

**Distribution of $CO_2H$ Groups through the Thickness of the Membrane.** It is of fundamental interest to know how the carboxylic acid moieties are distributed throughout the converted polymer, both for design of membrane separators and to help explain experimental results. Conceptually, there are three possible locations where the carboxylate functional groups can reside: as thin carboxylate-rich "skins: on the membrane surfaces, as homogenously dispersed entities surrounded by sulfonic acid groups, or as a mixture of the two.

ATR and transmission FTIR data, shown in Figure 9, suggest that the surfaces of the c/s films are enriched with carboxylic acid equivalents. For both measurements, carboxylate content was measured as described above. ATR data shows that among different films, the carboxylate contents at the films' surfaces (to a depth of about 1 μm) is uniformly high, with values between 20 and 28%. Each film has one surface with slightly higher carboxylate content, which may be due to the fact that the upper surface of the precursor film periodically dried out during the reduction process before being resubmerged in hydrazine. Transmission data show that as reduction time is increased, the average or bulk carboxylate content increases. This suggests that the penetration depth of hydrazine increases with reduction time, and that the c/s membranes consist of carboxylate-rich surfaces and a sulfonate-rich core.

In addition to FTIR analysis, two other instrumental methods were explored in an attempt to quantify further the distribution of $CO_2H$ groups through the film thickness. First, $^1$H self-diffusion coefficients were measured by NMR (method described elsewhere[13]) in an attempt to isolate different proton mobilities in carboxylate-rich and carboxylate-poor regions of the films. Second, films were ion-exchanged to the K-form and energy-dispersive X-ray analysis (EDAX) was used to measure the relative abundances of K and S atoms across the film thicknesses. Unfortunately, neither method provided conclusive evidence of symmetric or asymmetric distributions of carboxylate groups.

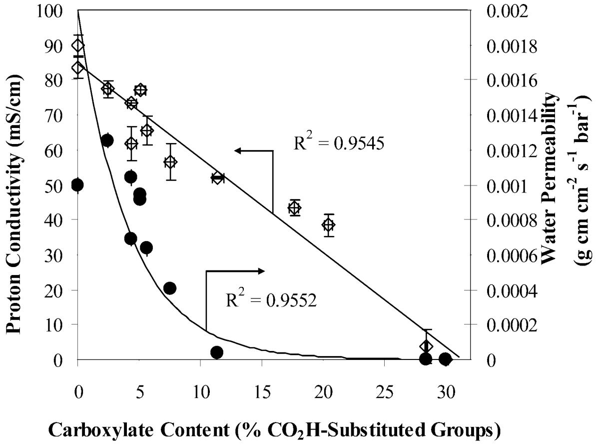

**Figure 10.** Water permeability at 35 °C and proton conductivity at room temperature and 100% relative humidity in c/s films. All measurements were taken with films in the acid form. Solid lines are least-squares fits of linear and exponential functions for conductivity and permeability data, respectively. Reprinted with permission from ref 16. Copyright 2007 Elsevier.

**Conductivity and Water Permeability in C/S Films.** The bulk (average) water permeabilities and proton conductivities in the c/s films were measured in a previous study,[16] and are reprinted in Figure 10. The figure shows that the replacement of sulfonic acid with carboxylic acid alters the transport properties of the membranes, effectively lowering the proton and water mobility in the films. Such a result is not surprising, because it is known that the carboxylate form of Nafion has very low proton conductivity.[4] The figure shows that the transport characteristics of the films are uninteresting at carboxylate contents higher than 30%. The c/s films are especially interesting, however, because the bulk transport of protons stays reasonably high as carboxylate content is increased, whereas the bulk transport of water drops significantly. For example, by increasing the carboxylate content from 2.4 to 7.5 and 11.4%, proton conductivity decreases by 26.9 and 32.7%, whereas water permeability decreases by 67.7 and 97.0%, respectively. Proton conductivity typically scales with water content (amount of sorbed water) in perfluorinated sulfonic acid membranes,[28,29] as does water permeability.[29−33] Therefore, at a given carboxylate content and water sorption, water permeability is expected to scale with proton conductivity, which it does not. This may be due to in part to the asymmetric structure of the c/s membranes, a hypothesis that has been mentioned in a previous paper[16] and is still under investigation.

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Previous work in our group has shown that the c/s films absorb nearly the same mass percentage of water as Nafion, up to a carboxylate content of 20%.[16] Therefore, it is apparent that the c/s membranes have proton and water transport mechanisms that differ from those observed in Nafion, with similar polymer makeup and water content. For fuel cell uses, such an observation is particularly attractive. One of the largest problems facing the application of low-temperature $H_2$/air fuel cells is that the electrolyte membrane (usually Nafion) dries because of high temperature and electroosmotic drag, causing a precipitous drop in proton conductivity and an increase in ohmic overpotential.[34−36] The observation that water is less permeable in the c/s films, a sign of decreased water mobility in the films, may indicate that water is more "bound' in the hydrophilic domains of the polymer and less apt to leave the film under hot and dry conditions. If this is the case, the c/s films may show improved performance over Nafion under higher temperature conditions.

One of the largest obstacles facing direct methanol fuel cell (DMFC) development is that no electrolyte material is available, which allows high proton conductivity and no methanol crossover. When methanol diffuses from anode to cathode in the DMFC, it effectively "shorts out" the cathode by using active catalyst sites and/or reactant $O_2$ for oxidation to $CO_2$, poisons the Pt catalyst by leaving adsorbed CO (because of incomplete oxidation), slows the kinetics of the oxygen reduction reaction, and lowers fuel utilization.[4,37−40] Attempts at lowering this methanol crossover have usually been met with a large decrease in proton conductivity.[38,41] Work in our lab has shown that c/s membranes have a decreased methanol permeabilities, both at room temperature and 50 °C, while conductivities remain high.[16] If these films have similar performances in operating DMFCs, the result will be a decrease in cathodic overpotentials and an increase in cell performance.

**Other Applications for C/S Membranes.** Aside from fuel-cell uses, the c/s membranes may have utility in membrane separation applications, especially electrically driven applications like electrodialysis and the chlor-alkali process. The carboxylate regions of the ionomer are, as mentioned in the introduction, more cation/anion-selective than sulfonate regions, with the caveat that they also show increased mass transfer resistance over perfluorosulfonate ionomers. Because the carboxylate regions can be formed as thin layers, the c/s membranes should provide improved separation characteristics and higher process rates than the commercially available sulfonate/carboxylate bilayer membranes. Further, the fluoropolymers' chemical stability makes them useful in a range of harsh environments. Research is currently underway at our laboratory to test the c/s films' performance in the removal of water from concentrated inorganic acids.

In addition to producing mixed carboxylate/sulfonate membranes, the conversion procedure outlined above might be adapted to produce other mixed-functionality ionomer films. This is possible because of the reactive nature of the sulfinic acid intermediate. We are unaware of studies that have compared the reactivity of sulfinic acids in a perfluorinated environment to those in a hydrogenated environment. However, it is known in general that sulfinic acids disproportionate to form disulfide and S−O−S linkages,[42] which may be useful in the cross-linking of ionomer materials to reduce swelling. In fact, Kerres et al. have shown the ability to make cross-linked polyethersulfone Udel membranes by using sulfinic acids as chemical cross-linkers.[23] Sulfinic acids readily undergo nucleophilic attack by halogens, giving the interested researcher a number of options for additions to the polymer side chains. Because of the unique chemistry of sulfinic acids, they are able to undergo reaction at the S or O atom, yielding sulfone and/or ester products. Sulfinic acids can react with unsaturated hydrocarbons to form sulfones and sulfinic salts can react with iodides or carbonyl halides to form esters.[42] The result is that many modifications to the perfluorinated ionomer precursor should be possible. Alternatively, multifunctional films can be made through a combination of procedures outlined in this work and methods developed by others. For example, Greso et al. have shown that additions to the side chain can be achieved by reaction of the sulfonyl fluoride group with organoalkoxysilanes.[43] Therefore, there are many routes for the modification of Nafion or other perfluorosulfonated ionomers at the terminal side-chain sulfur atom, once a reactive form of the ionomer is obtained.

The procedures outlined above can also be extended to make membranes with different distributions of functional groups. For instance, a single side of the precursor film could be reduced to form an asymmetric membrane, or a converted film could be solution processed using a technique such as that developed by Moore and Martin[44] to form a film with evenly dispersed sulfonate and carboxylate or other moieties.

As a final note, upon completion of this manuscript, we found two additional literature methods for producing sulfinic acid from sulfonyl halide that were not explored in this study. These methods included reaction with sodium sulfite and water to form the sulfinic acid, sodium fluoride, and sodium bisulfate, and reaction with aluminum hydrides to form sulfinate and hydrogen gas.[45] It was also noted in the literature, however, that extreme care must be taken to maintain low temperatures in the aluminum hydride reaction

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(to prevent further reduction of sulfinate). These methods should certainly be explored as alternatives to reduction with hydrazine, but it is unclear at this time if the fluorinated environment will affect these reagents' reactivity with sulfonyl fluoride, as it does the oxidizability of sulfinic acid.

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