Preparation and Characterization of Sulfonated Copolyamides Based on Poly(hexafluoroisopropylidene) Isophthalamides for Polymer Electrolytic Membranes

Yamile Pérez-Padilla,‡ Mascha. A. Smit,‡ and Manuel J. Aguilar-Vega*†

†Unidad de Materiales and ‡Unidad de Energías Renovables, Centro de Investigación Científica de Yucatán A.C., Calle 43 No. 130, Chuburná de Hidalgo, 97200, Mérida, Yuc. México

ABSTRACT: A series of sulfonated random copolyamides with increasing sulfonation degree were synthesized from the aromatic diamine 4,4'-[hexafluoroisopropylidene]dianiline, HFA, reacted with 2,4-diaminobenzensulfonic acid, DABS, by direct polycondensation using isophthalic diacid, ISO, as comonomer. Thin films of the sulfonated copolyamides were prepared by the solution-evaporation method using dimethylacetamide, DMAc. The structure of the resulting sulfonated copolyamides was confirmed by FTIR and 1H NMR which evidenced the presence of amide and sulfonic groups in the proposed concentrations. Thermal stabilities as characterized by TGA, showed the onset of decomposition at 320 °C for the iono moieties and above 600 °C for the nonsulfonated part of the copolymers. The values of water uptake and ion exchange capacity, IEC, at room temperature for 115 tested under the same conditions show superior performance, the application of these membranes is limited by their high cost, loss of proton conductivity at high temperature and loss of humidity and poor barrier properties to methanol crossover.1–6

The most successful alternative (PEM) membranes studied to date are based on high performance polymeric backbones containing sulfonic acid groups, such as polysulfones,2,5,7–9 polyimides,10–15 poly(arylene-ether)16–19 and poly (ether-ether-ketones).20,21 Sulfonation of these polymers is achieved by introducing sulfonic groups (–SO3H); either by treating an existing polymer with sulfonating agents (postsulfonation) or by synthesizing polymers with monomers containing sulfonated moieties, which render these polymers proton conductive. The hydrophobic backbones enhance physical properties and the sulfonic acid groups provide the ionic conductivity, and the resulting polymers exhibit high ionic conductivity, good mechanical strength, and high temperature resistance.1–5,8–11 Preparation of materials by postsulfonation procedures not only affects mechanical and thermal stability but also could make control of the sulfonation process difficult. On the other hand, when sulfonation is achieved by synthesis of the polymer with monomers bearing sulfonic groups, it is possible to control the concentration and position of the sulfonic group in the polymer structure. Moreover, it is important to control the sulfonation degree (SD); high sulfonation degrees generally lead to high swelling and even dissolution in water of the membranes, while low sulfonation degrees generally result in poor proton conductivity.22–24

Aromatic polyamides are considered a class of engineering polymers that are thermally stable, with excellent mechanical properties. The incorporation of ionic groups into the structure of these polymers could impart them with ion exchange properties.22 Because of the presence of amide groups, aromatic polyamides tend to retain water. Amorphous aromatic polyamides, particularly those containing fluorine groups such as poly(hexamersulfonicacid) isophthalamide, HFAISO, are reported to absorb 4 to 10% water; they are also reported to have a high fractional free volume due to the presence of the lateral −CF3 groups that hinder rotation and increase chain rigidity.22,23 Depending on their chemical composition, polyamides may show enhanced water absorption and proton conduction capacity by the introduction of sulfonic acid side groups.22,26,27 Since fluorinated polymers such as Nafion are known to be resistant to degradation in a PEM cell environment due to their perfluorinated hydrophobic backbone membranes, the possibility of sulfonating HFAISO to render it proton conductive should be explored to determine if it could reach acceptable properties for PEM cell applications. In this work, we report a series of sulfonated copolyamides, with sulfonation degrees, SD, between 20 and 50 mol % that are synthesized from the diamines 4,4′-[hexafluoroisopropylidene]dianiline, HFA, and 2,4-diaminobenzensulfonic acid.

1. INTRODUCTION

The development of proton exchange membranes (PEM) for fuel cells has received extensive attention lately, because they are known to be one of the most promising clean energy conversion technologies. PEM fuel cells are regarded to be the next step into the evolution of fuel-cell technologies. PEM fuel cells are regarded to be the next step into

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DABS, as comonomer. The mixture of diamines is reacted by polycondensation with isophthalic diacid, ISO, in order to produce random copolymers poly(hexafluorosopropylidene-co-2,4-diaminobenzensulfonic) isophthalamides (HFA-co-DABS/ISO). Membranes from the sulfonated polyamides were prepared using solvent evaporation. Their structure is characterized by FTIR and $^1$H NMR spectroscopy. Their thermal stability was assessed as well as their ionic exchange capacity (IEC), water uptake, and proton conductivity in order to determine the effect of an increased concentration of sulfonic acid groups on these properties. At the same time, we would like to assess if sulfonated HFA-co-DABS/ISO as prepared membranes present characteristics similar to those membranes used in PEM cells.

2. EXPERIMENTAL SECTION

2.1. Materials. Monomers for sulfonated copolyamide preparation, 4,4’-(hexafluorosopropylidene)dianiline (HFA), 2,4-diaminobenzensulfonic acid (DABS), and isophthalic acid (ISO), were obtained from Aldrich Chemical Co. Solvents such as pyridine (Py), triphenyl phosphate (TPP), and dimethyl acetamide (DMAc) were used as received without further purification. Isophthalic acid (ISO) and DABS were dried at 100 °C for 24 h before used. N-Methyl-2-pyrrolidone, NMP, was stored over molecular sieves. Calcium chloride (CaCl$_2$) was dried at 180 °C under vacuum for 24 h before use. All reactants and solvents were purchased from Aldrich Chemical, Co.

2.2. Synthesis of Homopolyamides and Sulfonated Copolyamides. Polyamide poly(hexafluorosopropylidene)isophthalamide, HFA, and the sulfonated copolyamides were synthesized by direct polycondensation following a procedure described first by Yamazaki$^{28}$ with some small modifications due to the ionic nature of comonomer DABS. The polycondensation reaction was performed with equimolar amounts of the diamine, HFA, and diacid, ISO, for HFA preparation, or a controlled combination of nonsulfonated and sulfonated diamines, HFA and DABS with isophthalic diacid, ISO, for copolymers preparation, HFA-co-DABS/ISO, adjusting the concentration of diamine monomer HFA to monomer DABS (HFA/DABS) as shown in Table 1 which in turn adjusts the concentration of nonsulfonated and sulfonated comonomer, by the thermogravimetrical measurements repeated in the dried samples from 50 up to 800 °C.

Thermal decomposition of the as cast membranes was followed by thermogravimetric analysis in a TGA-7 Perkin-Elmer Inc. under nitrogen atmosphere. The scans for thermal decomposition were taken between 50 and 800 °C at a heating rate of 10 °C min$^{-1}$. To make sure that all the solvent was eliminated in the membrane, all polyamides were previously heated from 50 to 320 °C at a heating rate of 10 °C/min, if solvent presence was detected, they were further dried in a vacuum oven at 230 °C, and the thermogravimetric measurements repeated in the dried samples from 50 up to 800 °C.

The ability of the membranes to absorb water was estimated by gravimetric analysis. The membrane was dried under vacuum at 120 °C for 48 h to eliminate moisture content. Then, it was immersed in deionized water for 48 h at a fixed temperature (at 25, 45, 65, and 75 °C). At the end of this time the membrane was extracted, wiped with blotting paper, and immediately weighed to determine its wet membrane weight ($W_w$). The next step was to dry the membrane at 120 °C under vacuum for 48 h and weight it again to determine the dry membrane weight ($W_d$). The water uptake, $S$, was calculated according to the following equation:

$$S = \frac{W_w - W_d}{W_d} \times 100$$

Water uptake for polyamides and copolyamides is reported as the average value of at least two measurements. A potentiometric titration technique was used to determine the ion exchange capacity (IEC) of the membranes at room temperature. The dry membrane was weighed and immersed in 1 M HCl solution for 24 h and then washed with deionized water until the pH was neutral. The membrane in the acid form, H$^+$, was then converted to the sodium form, Na$^+$, by immersing the membrane in NaCl 2 M solution for

<table>
<thead>
<tr>
<th>Polymer</th>
<th>mmol of HFA</th>
<th>mmol of DABS</th>
<th>mmol of Diacid ISO</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFA</td>
<td>1.25</td>
<td>-</td>
<td>1.25</td>
</tr>
<tr>
<td>HFA582</td>
<td>1.00</td>
<td>0.25</td>
<td>1.25</td>
</tr>
<tr>
<td>HFA573</td>
<td>0.875</td>
<td>0.375</td>
<td>1.25</td>
</tr>
<tr>
<td>HFA564</td>
<td>0.75</td>
<td>0.5</td>
<td>1.25</td>
</tr>
<tr>
<td>HFA555</td>
<td>0.625</td>
<td>0.625</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Scheme 1. Schematic Reaction to Obtain the HFA-co-DABS/ISO Sulfonated Copolymides

24 h. The exchanged H$^+$ ions were titrated using NaOH 0.01 M solution. The IEC of the membranes was determined by\(^2\)

\[
eq \frac{C \times V}{W}
\]

where \(C\) (M) and \(V\) (mL) are the concentration and volume of NaOH, respectively. \(W\) (g) is the weight of the dry membrane. IEC is reported as the average of at least two measurements.

Mechanical properties under uniaxial tension for wet membranes were determined at 25 °C in a microtensile machine Minimat (Rheometrics Inc.) at a testing speed of 1 mm min\(^{-1}\) with a 100 N load cell. The samples were cut into strips 6.5 mm long \(\times 3.2\) mm wide with a thickness between 0.08 and 0.15 mm. The strips were dried under vacuum at 120 °C for 48 h. Then the dried strips were immersed in deionized water at 25 °C for 48 h prior to testing. For each homopolymer and copolymer sample the average value is reported for at least three measurements.

Proton conductivity was measured by electrochemical impedance spectroscopy using a potentiostat-galvanostat AUTOLAB model PGSTAT12/30/302 with the EIS module over a frequency range of 10\(^{-2}\) to 1 Hz with oscillating voltages of 50 mV. Prior to the measurement, and in order to test their stability, the membranes were immersed in water for 96 h, then they were immersed in deionized water at 25 °C for 48 h prior to testing. For each homopolymer and copolymer the average value is reported for at least three measurements.

Mechanical properties under uniaxial tension for wet membranes were determined at 25 °C in a microtensile machine Minimat (Rheometrics Inc.) at a testing speed of 1 mm min\(^{-1}\) with a 100 N load cell. The samples were cut into strips 6.5 mm long \(\times 3.2\) mm wide with a thickness between 0.08 and 0.15 mm. The strips were dried under vacuum at 120 °C for 48 h. Then the dried strips were immersed in deionized water at 25 °C for 48 h prior to testing. For each homopolymer and copolymer sample the average value is reported for at least three measurements.

In Figure 1 the IR spectra of the synthesized HFA polyamide and HFA-co-DABS/ISO copolymers obtained were white rigid fibers. The fiber size increased with decreasing concentration of sulfonated diamine in the copolymer. In contrast, the fibers tend to swell in water with increasing concentration of sulfonic acid groups.

The amount of CaCl\(_2\) used in the reaction had a great effect on the polymerization, as it was necessary to add a larger amount (8 to 10% more) of CaCl\(_2\) as the amount of sulfonated diamine increases in the copolymer polymerization reaction. It was also necessary to increase the reaction times described in the literature,\(^2\) during the synthesis of sulfonated copolymides; otherwise a yield reduction in the reaction or low molecular weight products were obtained. The resulting polyamides showed moderated inherent viscosities which decrease with increasing concentration of sulfonated monomer and they are in the range of 0.35—0.18 dL/g in DMAC with \(\eta_{inh}\) being quite similar for the copolyamides with the highest concentration of sulfonic acid groups HFA\(_{84}\) (40 mol % of sulfonic acid groups) and HFA\(_{85}\) (50 mol % of sulfonic acid groups). As can be observed in the Table 2, in general, as the degree of sulfonation increased, the inherent viscosity decreased. This effect had been observed in several sulfonated polymers.\(^2\)

Films of copolymers elaborated using the solution evaporation method were translucent with a yellowish coloration that intensified as SD increased. The rigidity of the films also increased with increasing sulfonation degree. The thickness of all membrane films was in the range 0.08—0.15 mm.

In Figure 1 the IR spectra of the synthesized HFA polyamide and HFA-co-DABS/ISO copolymides are shown. These spectra were used to analyze characteristic bands of the —SO\(_3\)H group in the polymer chains. There are several bands present that are expected for the formation of the sulfonated polyamides. The characteristic broad bands for the amide group between 3270 and 3310 cm\(^{-1}\) (N—H), the amide carbonyl groups at 1660 cm\(^{-1}\). On the other hand, the bands at 1077, 1020, and 690 cm\(^{-1}\) appeared only in sulfonated copolymers. The absorption band at 690 cm\(^{-1}\) is assigned to C—S stretching vibration and those at 1077 cm\(^{-1}\) and 1020 cm\(^{-1}\) are characteristic of the symmetric and asymmetric O==S==O stretching vibrations of the sulfonic acid group, respectively. These three characteristic bands

### Table 2. Sulfonation Degree Determined by \(^1\)H NMR and Inherent Viscosity of Polyamide and Sulfonated Copolymides HFA-co-DABS/ISO

<table>
<thead>
<tr>
<th>polymer</th>
<th>theoretical SD (%)</th>
<th>(^1)H RMN</th>
<th>(\eta_{inh})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFA</td>
<td>-</td>
<td>18.00</td>
<td>0.35</td>
</tr>
<tr>
<td>HFAS82</td>
<td>20</td>
<td>39.71</td>
<td>0.27</td>
</tr>
<tr>
<td>HFAS73</td>
<td>30</td>
<td>39.71</td>
<td>0.25</td>
</tr>
<tr>
<td>HFAS64</td>
<td>40</td>
<td>49.26</td>
<td>0.18</td>
</tr>
<tr>
<td>HFAS55</td>
<td>50</td>
<td>49.26</td>
<td>0.19</td>
</tr>
</tbody>
</table>

\(\eta_{inh}\) = inherent viscosity at a polymer concentration of 0.2 g/dL.
have a gradual increase with an increase in the content of sulfonated diamine, SD, in the copolymer.

Figure 2 shows the \(^1\)H NMR spectra of (a) HFA polyamide, and (b) HFA-co-DABS/ISO sulfonated copolyamides respectively. The integration area ratio of each proton agrees with the structure of HFA polyamide, Figure 2a, and HFA-co-DABS/ISO copolyamides, Figure 2b. Initially there appear two new proton interactions when the sulfonic acid groups are introduced to the polyamide, the peak at 8.95 ppm only appears in the spectra of sulfonated copolymers. This signal corresponds to the ortho proton \(H_g\) with respect to the sulfonic acid group, appearing at downfield due to the electron-withdrawing effect of the sulfonic acid group. The aromatic hydrogen atoms \(H_b\) and \(H_h\) near the \(-SO_3H\) group were detected at 8.63 and 7.54 ppm, respectively. We also observed that with an increasing amount of sulfonated monomer there is an increase in the intensity of the signal of these protons. All the other peaks correspond to other aromatic hydrogen atoms of the chemical structure of the sulfonated copolyamides that are also present in the homopolyamide HFA.

To determine the sulfonation degree, from Figure 2 (b) the relationship between the areas of protons which does not change in HFA or the copolymers, \(H_f\), and the proton ortho to the \(-SO_3H\) group in the copolymer \(H_g\), was calculated. The resulting concentration of sulfonated moieties using the ratio of the areas for protons \(H_f\) and \(H_g\) for sulfonated copolyamides agrees well with the concentration of sulfonated monomer initially charged for the synthesis, with a minimum drift, indicating that the structures proposed with different sulfonation degrees, SD, were obtained, as described in Table 2.

Figure 3 shows the thermal decomposition thermograms of HFA and HFA-co-DABS/ISO sulfonated copolyamides. The thermograms have been shifted by 2% from each other starting from the one corresponding to HFA to make it easier to follow their decomposition. All polymers show an initial weight loss up to 100 °C that is associated with the loss of absorbed water. The mass loss of the nonsulfonated polyamide, HFA, is 2% at around 100 °C, as was expected from other similar aromatic polyamides found in the literature, while that of the sulfonated copolyamides could reach up to 5%. The initial weight loss of the sulfonated copolyamides is related to desorption of moisture bound by the polymer that increases with the presence of the hydrophilic sulfonic group. The polyamide HFA presents the highest thermal stability as compared with the sulfonated polyamides since it shows the onset of decomposition temperature, \(T_d\), at around 480 °C which is attributed to the onset of the aromatic polymer chain degradation. The resulting high decomposition temperature is due to the large number of aromatic groups as well as \(-CF_3\) groups present in the structure that results in a high thermal stability. On the other hand, all the thermograms for the sulfonated copolymers HFA-co-DABS/ISO show similar profiles which include two decompositions at different temperatures from that presented in the nonsulfonated HFA, one of them below 320 °C and a slope change above 550 °C up to 600 °C. The initial weight loss starting just below 320 °C, is attributed to the onset of sulfonic acid group, \(-SO_3H\), decomposition. The weight loss that occurs in HFA-co-DABS/ISO starting at around 320 and up to 550 °C until ∼600 °C
increases with increased concentration of sulfonic moieties in the copolymer. At 580 °C there is a change of slope in the ionic copolymers which is attributed to thermal decomposition of HFA aromatic moieties on the copolymer main chain since it follows closely the decomposition thermogram of HFA. The thermograms clearly indicate that the sulfonated copolymer onset of thermal stability is situated at around 320 °C, where the sulfonated moieties onset of thermal decomposition occurs, well above the servicing temperature for a PEM cell application. It is also clear in Figure 3 that all HFA-co-DABS/ISO membranes. As a reference, Na polyamide and HFA-co-DABS/ISO sulfonated copolyamides.

The hydrolytic stability of the membranes was determined by subjecting them to four cycles of 48 h immersion in deionized water and drying in a vacuum oven at 120 °C. The cycles were performed at four different temperatures of 25, 45, 65, and 75 °C, reported in Table 4 as water stability at 75 °C for 48 h, or up to 120 h at 25 °C. Under this conditions they did not dissolve and were observed only slightly bent and with a little stiffness but not broken. It is also expected that membranes with lower mechanical tensile modulus and strength. It is also found that the values for tensile strength and Young’s modulus are at least 2 times larger than those found in Naflon 115 at the same testing conditions.

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The amount of water uptake of polyamide HFA and copolyamide HFA-co-DABS/ISO membranes at different temperatures (25°, 45°, 65° and 75 °C) is shown in Figure 4. A commercial Naflon 115 membrane was also tested at the same conditions.

As can be seen in Figure 4, HFA-co-DABS/ISO membranes with higher sulfonation degree values, HFA564 and HFA555, tended to have larger water uptake at all temperatures and the water uptakes increase with increasing SD. It is also seen that the hydrophilicity in HFA564 and HFA555 is larger than the one observed in Naflon 115 which is attributed to a larger free volume due to the presence of −CF₃ groups and swelling of the membrane due to the water bonded by the −SO₃H groups. Those two effects combined are credited for the increase in water uptake at 25 °C. Since water uptake at 25 °C is already equilibrated at 48 h in the membranes, the mechanical tests values dispersion is attributed to differences in the plasticization of the test samples particularly for HFA555, which shows higher mechanical tensile modulus and strength. It is also found that the values for tensile strength and Young’s modulus are at least 2 times larger than those found in Naflon 115 at the same testing conditions. The mechanical tensile modulus and strength but not Young’s modulus are at least 2 times larger than those found in Naflon 115 at the same testing conditions.

### Table 3. Thickness and Mechanical Properties under Tension of HFA, Naflon 115, and Sulfonated Copolymides HFA-co-DABS/ISO

<table>
<thead>
<tr>
<th>polymer</th>
<th>thickness (mm)</th>
<th>tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFA</td>
<td>0.08</td>
<td>27.4 ± 8.6</td>
<td>494.3 ± 23.4</td>
<td>6.5 ± 3.4</td>
</tr>
<tr>
<td>HFAS82</td>
<td>0.11</td>
<td>34.8 ± 8.0</td>
<td>427.1 ± 38.2</td>
<td>11.9 ± 5.7</td>
</tr>
<tr>
<td>HFAS73</td>
<td>0.15</td>
<td>20.0 ± 5.6</td>
<td>277.5 ± 13.6</td>
<td>10.9 ± 1.6</td>
</tr>
<tr>
<td>HFAS64</td>
<td>0.12</td>
<td>21.0 ± 9.9</td>
<td>286.8 ± 11.8</td>
<td>9.1 ± 3.5</td>
</tr>
<tr>
<td>HFAS55</td>
<td>0.14</td>
<td>29.7 ± 1.5</td>
<td>410.8 ± 11.8</td>
<td>12.6 ± 1.7</td>
</tr>
<tr>
<td>Naflon 115</td>
<td>0.12</td>
<td>13.2 ± 0.1</td>
<td>89.3 ± 11.6</td>
<td>181 ± 54.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>polymer</th>
<th>IEC (mmol/g)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>water stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFA</td>
<td>0.15</td>
<td>25</td>
<td>120</td>
<td>O</td>
</tr>
<tr>
<td>HFAS82</td>
<td>0.59</td>
<td>75</td>
<td>48</td>
<td>O</td>
</tr>
<tr>
<td>HFAS73</td>
<td>0.87</td>
<td>25</td>
<td>120</td>
<td>O</td>
</tr>
<tr>
<td>HFAS64</td>
<td>1.02</td>
<td>75</td>
<td>48</td>
<td>O</td>
</tr>
<tr>
<td>HFAS55</td>
<td>1.39</td>
<td>25</td>
<td>120</td>
<td>O</td>
</tr>
<tr>
<td>Naflon 115</td>
<td>1.28</td>
<td>75</td>
<td>48</td>
<td>O</td>
</tr>
</tbody>
</table>

*Theoretical IEC values were obtained as in ref 1; IEC = (SD × 1000)/(318 + 80SD). Experimental measured by titration; T, temperature; t, time. (O) Mechanical strength maintained; (×) somewhat brittle.
uptake even though the aramide polymer backbone is less flexible than that of the Naion 115. It also seen that at low temperatures (25 °C), there is a jump in the water uptake between copolymers containing 30 and 40 mol % sulfonic acid groups, it is taken as an indication that there is a critical concentration of –SO₃H groups that given the opening of the structure and vicinity of them allows for an increase in water uptake, as have been reported in other similar polyamides.22 The water uptake of HFA is the lowest observed and it does not change appreciably with temperature. The sulfonated membranes with high concentrations of sulfonic acid groups, HFAS55 and HFAS64, present water uptake values that increase between 25 and 75 °C while membranes HFA and HFAS82, present water uptake values below those presented by Naion 115, and HFAS73 presented water absorption values that run close to those found for Naion 115 for the temperature interval evaluated. At elevated temperatures, the polymer chain mobility increases and the free volume in these copolymers could increase leading to the water adsorption increment in the membranes for all rigid membrane copolyamides.18,21 If only based on water absorption characteristic membranes HFAS64 and HFAS55 present the best characteristics of water uptake, even above those of Naion 115.

It has been reported in the literature that the water up-take and ion exchange capacity, IEC, play important roles in the conductivity of a sulfonated polymer. In fact, both IEC and water uptake contribute to the proton transport through the dense membrane. Therefore, it is important to consider how ion transport performance of the membrane correlates to its water retention capacity and also to the IEC value.8,14,18,19,21,30,31

Table 4 shows theoretical ion exchange capacity, IEC, values for the synthesized copolymers and they are compared to experimentally obtained values of IEC for HFA-co-DABS/ISO membranes with different sulfonation degrees evaluated by titration. The theoretical IEC values are higher than those found experimentally with the exception of the ones for HFAS55 which presents an IEC value that is larger than the theoretical one. There is also a lower than expected value of IEC for HFAS73 which is the lowest of all measured values. The low IEC for HFAS73 seem to correlate well with a low water uptake at 25 °C and also a lower proton conductivity which is discussed later.

The membranes obtained from copolymides HFA-co-DABS/ISO showed an increase in IEC with increasing degree of sulfonation; this is attributed to the increase on water concentration and retention of sulfonated polyamides due to the increased concentration of sulfonic groups, which in turn opens the sites available for ionic exchange in the structure, and increases the possibilities of an enhanced proton transfer capacity. This behavior is better illustrated by Figure 5, where the proton conductivity and the relationship between –SO₃H group concentration and IEC are depicted. There is a clear indication that an increase in IEC and sulfonation degree in HFA-co-DABS/ISO membranes provides an increase in conductivity. It is also seen that proton conductivity in membranes HFAS82 and HFAS73 remains below or at 0.04 mS cm⁻¹, while there is a marginal increase to 0.09 mS cm⁻¹ for HFAS64. The best proton conductivity is found for the HFAS55 membrane which shows a value of 3.3 mS cm⁻¹ quite close to that found for Naion 115 (6.6 mS cm⁻¹) which goes hand-in-hand with increases in IEC.

The proton conductivity, σ, for membranes at 25 °C is shown in Figure 5. Naion 115 was used for comparison with the membranes synthesized in this work. Following the trend observed for ion exchange capacity, the proton conductivity of the copolyamides membranes shows a trend, of increasing proton conductivity with increasing SD as in other reports,4,31 see Figure 5. Membranes with higher IEC tend to have higher proton conductivity although differences for HFA-co-DABS/ISO copolymers are small (0.04 to 0.09 mS cm⁻¹) up to 40 - SO₃H mol % with a marked increase for HFAS55. The explanation of this behavior is related to a threshold in which, based on a gradual growth of SD domains, water clusters are formed in close proximity and once formed they give rise to an increase in proton conductivity. This mechanism seems to be followed closely by the sulfonated HFA copolyamide membranes and has been reported for other sulfonated polymers.5,23 The membrane HFAS55 had the highest IEC value and therefore greater proton conductivity compared to other membranes synthesized. In addition, although HFAS55 presents slightly larger IEC values than Naion 115, its proton conductivity is roughly in the same level as the Naion 115, tested under the same conditions. As shown in Figure 5, an increase in SD from 20 to 50% results in an increase of up to 2 orders of magnitude in proton conductivity values. These results indicate that it is possible to render proton conductive copolymers based on fluorinated polyamides such as those prepared in this work. By controlling the sulfonation degree, it is possible to obtain IEC and proton conductivities similar to those presented by standard ionic membranes of Naion 115, with better thermal stability. Further tests should be performed, in particular oxidative stability, to determine if HFAS55 is a suitable candidate for proton exchange membranes with improved thermal stability as compared to the ones now being used.

4. CONCLUSIONS

Membranes based on rigid fluorinated copolyamides, HFA, and a sulfonated monomer DABS were obtained with increasing degree of sulfonation by direct polycondensation, the resulting poly(hexafluoroisopropylidene-co-diaminobenzensulfonic) isophthalic copolyamide, HFA-co-DABS/ISO, was cast from DMAc; the thicknesses of all membrane films were in the range 0.08–0.15 mm, and the rigidity of the films increased with increasing sulfonation degree. Sulfonated copolyamides showed good thermal stability up to 320 °C which is attributed to the onset of sulfonic acid groups decomposition. The mechanical

Figure 5. Proton conductivity and IEC of HFA and HFA-co-DABS/ISO membranes as SD increases.
tests showed larger Young’s modules and tensile strength as compared to those presented by Nafton 115. The analysis of water uptake, IEC, and proton conductivity, generally show that they increase with increasing concentration of sulfonated diamine in the copolymides, although there is a threshold where the water uptake and IEC jump to higher values at a concentration between 30 and 40 mol % of sulfonic acid groups. The membranes HFAS55 show values of water uptake and IEC higher than that of Nafton 115 at room temperature. Proton conductivity values at room temperature obtained with the membrane HFAS55 are in the same order of magnitude as those obtained for Nafton 115. Overall membranes prepared from HFAS55 should be considered good candidates for proton exchange membranes with improved thermal stability as compared to the ones currently in use, although further testing for oxidative and acid stability should be made.

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: mjav@cicy.mx.

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