

# Nafion/sulfonated poly(indene) polyelectrolyte membranes for fuel cell application

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## Abstract

Sulfonated poly(indene) (SPInd), with 35% and 45% degree of sulfonation, was blended with Nafion to prepare blended membranes with 10, 15 and 20 wt.% of SPInd. Membranes were evaluated by infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, scanning electron microscopy and X-ray diffraction. Water uptake (WU), ion exchange capacity (IEC) and through-plane proton conductivity were measured. The membranes presented similar thermal stability to Nafion. WU was slightly higher for Nafion/SPInd membranes (19-21% at RT and 40-44% at 90 °C) compared with recast Nafion (16% and 34%, respectively), and IEC values showed a similar trend. Blended Nafion membranes had increased proton conductivity of  $2.41 \times 10^{-2}$  and  $2.37 \times 10^{-2} \text{ Scm}^{-1}$  (20 wt.% of SPInd 35% and 45%, respectively), compared with  $1.16 \times 10^{-2} \text{ Scm}^{-1}$  for recast Nafion. The results show that the addition of SPInd to Nafion is a potential route towards improving the performance of Nafion in proton conductivity for use in fuel cells devices.

**Keywords:** *blended membrane, Nafion, proton exchange membrane, sulfonated poly(indene).*

## 1. Introduction

Fuel cell technology has emerged in recent years as a keystone for future energy supply. Notably, proton exchange membrane fuel cells (PEMFCs), with high efficiency and high power density, are well suited to a variety of applications, including residential power generation, transport (mainly automobile industry) and portable electronics. Hydrogen powered vehicles using Polymer Electrolyte Membrane Fuel Cells (PEMFCs) have been demonstrated by a number of auto manufacturers and hydrogen powered buses are in service in several cities<sup>[1-3]</sup>. Basically, a PEMFC electrochemically converts hydrogen and oxygen into electrical power, heat, and water. In PEMFCs, the proton exchange membrane (PEM) conducts protons from the anode to the cathode, acts as a barrier to the fuel and separates the electrodes. Although PEMFCs offer several advantages, including the possibility of using renewable fuels and having minimal environmental impact, there are also several key shortcomings with current PEMs that hinder fuel cell efficiency. These shortcomings include low proton conductivity at higher temperatures, poor water management and high fuel crossover<sup>[4,5]</sup>.

Currently, the most popular PEMs used in fuel cells devices are Nafion membranes. The commercial polymer consists of a perfluorosulfonic acid-polytetrafluoroethylene ethylene (PFSA-PTFE) copolymer, with a tetrafluoroethylene backbone and perfluorinated vinyl ether side chains terminated with sulfonic acid groups. Nafion membranes are still quite expensive for large-scale application in PEMFCs<sup>[6,7]</sup> and although they offer high proton conductivity and good chemical, thermal, mechanical stability, an ideal PEM must be of low cost. Typically, they have micro- or nanophase

morphological structure comprised of a hydrophobic matrix and interconnected hydrophilic ionic clusters, called ionic channels<sup>[8]</sup>. Proton conduction occurs via the ionic channels in the hydrated membrane and has a strong dependence on the water content as well as the operating temperature, usually between 80 °C and 100 °C<sup>[9]</sup>. Nafion continues to be at the focus of research due to the superior performance, and hence, Nafion composites containing other polymers or inorganic compounds have been widely studied<sup>[8-10]</sup>. Great efforts have been made to prepare the composite membranes based on Nafion to improve the performance and reduce the cost of the membranes used for FCs. Liyanage et al. reported that Nafion membranes modified with sulfonated organosilicon dendrimers exhibited less swelling (despite a high number of sulfonic acid groups), and higher ion exchange capacity and water retention<sup>[10]</sup>. Liu et al.<sup>[11]</sup> reported that Nafion membranes with 0.05 wt.% of functionalized multiwalled carbon nanotubes (MWCNTs) showed a 1.5-fold increase in mechanical strength and a five-fold increase in proton conductivity.

In this work, membrane blends were produced to be applied in PEMFCs using hydrogen as fuel. Nafion was modified with sulfonated poly(indene) (SPInd) using a simple, inexpensive process, aiming to improve the membrane water content, while maintaining good proton conductivity. SPInd was obtained through the sulfonation of poly(indene) with chlorosulfonic acid, previously reported by our group as a potential polymer electrolyte<sup>[12]</sup>. The SPInd has a thermally stable cyclic backbone with sulfonic groups attached to phenylene groups, making it hydrophilic. Nafion/SPInd

membranes were prepared by solution casting, using different contents of SPInd with sulfonation degrees of both 35% and 45%. The thermal, physicochemical and morphological characteristics of these membranes were investigated.

## 2. Materials and Methods

### 2.1 Materials

Chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ ;  $\geq 98\%$ ) was purchased from Merck. 1, 2-dichloroethane (DCE, 99%), *n*-hexane (95%) and ethanol (96%) were purchased from Neon. Dimethylacetamide (DMAc; PA) was purchased from Sigma Aldrich. All reagents were used as received. The Nafion solution (Liquion™; 1100 EW, 15 wt. %) was purchased from Ion Power, Inc. Poly(indene) (PInd) ( $M_n = 45,000 \text{ g}\cdot\text{mol}^{-1}$ ) was synthesized by cationic polymerization of indene as described in a previous article published by our group<sup>[13]</sup>.

### 2.2 Poly(indene) sulfonation

The sulfonated poly(indene) (SPInd) was obtained by the sulfonation of PInd with chlorosulfonic acid. PInd (10g/0.086 mol) was dissolved in DCE (60 ml), under stirring, in a four-necked flask and then cooled at  $-2^\circ\text{C}$ . Chlorosulfonic acid (0.029 or 0.036 mol) was dissolved in DCE (10 ml) and was added dropwise in the PInd solution. The reactant mixture was stirred at 500 rpm for 2 h at  $-2^\circ\text{C}$ . The reaction was stopped by adding ethanol and the product was filtered and washed with hexane until the pH was between 6 and 7. The sulfonated poly(indene) (SPInd) was dried at  $60^\circ\text{C}$  for 24 h, and kept in a desiccator in the dark. Two samples of SPInd, with degree of sulfonation (DS) of 35% (SPInd35) and 45% (SPInd45), were prepared and both had a brownish color.

### 2.3 Membrane preparation

Nafion (15 wt. %) and SPInd (20 wt. %) were dissolved separately in DMAc at room temperature. Pre-determined volumes of SPInd and Nafion solutions were mixed under stirring at room temperature. The recast Nafion and Nafion/SPInd membranes were obtained by pouring the DMAc solutions onto a glass Petri dish and evaporating the solvent under vacuum at  $60^\circ\text{C}$  for 24 h. The membranes were removed from the Petri dishes by immersing them in water. Flexible and transparent yellowish membranes were obtained and after being dried at  $140^\circ\text{C}$  for 2 h, the thicknesses were around  $280 \pm 30 \mu\text{m}$ . Blended Nafion/SPInd membranes were prepared with 10, 15 and 20 wt. % of SPInd. More than 20% of SPInd lead to poor miscibility and water-soluble domains in the membrane. The Nafion/SPInd membranes were dipped in a 3 wt. %  $\text{H}_2\text{O}_2$  solution at  $80^\circ\text{C}$  for 1 h to oxidize the organic impurities. The membranes were immersed in DI water for 1 h and then activated with a 0.5M  $\text{H}_2\text{SO}_4$  solution at  $80^\circ\text{C}$  for 1 h. Finally, the membranes were rinsed with DI water until a neutral pH was measured in the water. All membranes were stored in DI water, at room temperature and in the dark until use.

### 2.4 Fourier Transform Infrared Spectroscopy (FT-IR)

The membranes were analyzed using a Perkin Elmer FT-IR spectrometer (Spectrum 1000) to identify the main groups present in the blended membranes. The analysis

was performed with KBr pellet over the wavelength range of  $400\text{-}4000 \text{ cm}^{-1}$ .

### 2.5 Thermal properties of the membranes

Thermogravimetric analysis (TGA) of the membranes was performed on a Shimadzu TGA-50 analyzer raising the temperature from  $25^\circ\text{C}$  to  $800^\circ\text{C}$  at a heating rate of  $20^\circ\text{C min}^{-1}$ , under nitrogen atmosphere. Prior to analysis, the membranes were heated at  $110^\circ\text{C}$  for 3 h in an oven to remove the moisture. Calorimetric analysis of the membranes was evaluated using a differential scanning calorimeter (DSC) (TA Instruments model 2910) raising the temperature from  $40^\circ\text{C}$  to  $240^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ , under nitrogen atmosphere. The membranes were heated to  $120^\circ\text{C}$  and kept at this temperature for 5 min to eliminate the water, cooled to  $20^\circ\text{C}$ , and then re-heated to  $200^\circ\text{C}$  (second run). The second endothermic curve was analyzed.

### 2.6 SEM and XRD analysis

The morphology of the cross-sectional area of the membranes was examined using a Jeol JSM 6060 field emission scanning electron microscope (SEM). The cryogenic fracture surface of the specimens was sputter coated with Au for 120 s. X-ray diffraction (XRD) analysis of the membranes was performed on a Philips diffractometer (X-Pert MPD) using a  $\text{Cu K}\alpha$  X-ray source (wavelength  $\lambda = 1.54056 \text{ \AA}$ ) and a  $2\theta$  range of  $5^\circ$  to  $50^\circ$  with a scanning rate of  $3^\circ \text{ min}^{-1}$  and scanning step of  $0.05^\circ/\text{s}$ , at 40mA and 40 kV. Before the measurements were taken, the membrane specimens were fixed on a glass sample holder and equilibrated under room temperature/pressure conditions for 24h.

### 2.7 Water uptake and ion exchange capacity of the membranes

The membranes were dried under vacuum at  $80^\circ\text{C}$  until a constant weight ( $W_{\text{dry}}$ ) was obtained. Pre-weighed dry membrane specimens of  $2 \text{ cm}^2$  were soaked in deionized water at room temperature for 24 h and then heated to  $90^\circ\text{C}$ . After 1 h the specimens were cooled to room temperature, removed from the water, wiped with tissue paper and weighed ( $W_{\text{wet}}$ ). The water uptake of the membranes was determined by correlating the weight differences of the hydrated ( $W_{\text{wet}}$ ) and dry ( $W_{\text{dry}}$ ) membrane according to Equation 1.

$$\text{Water Uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

The ion exchange capacity (IEC) of the membranes, expressed in mequiv.  $\text{g}^{-1}$ , was determined using acid-base titration. The membrane specimens ( $2 \text{ cm}^2$ ), dried under vacuum at  $80^\circ\text{C}$  to a constant weight, were soaked in a 1 M NaCl solution and equilibrated for at least 24 h to allow exchange between the  $\text{H}^+$  and  $\text{Na}^+$  ions. Aliquots of the solution, in duplicate, were titrated with a 0.01 M NaOH solution to determine the HCl concentration in the medium. The IEC was calculated as the milliequivalents of sulfonic groups per gram of dried sample.

### 2.8 Proton conductivity

The proton conductivity of the membrane specimens was measured in the transversal direction in a proton conductivity cell, immersed in deionized water at room temperature.

The stainless-steel electrode of the cell, with an area of 1.77cm<sup>2</sup>, was connected to an AC impedance analyzer (PGSTAT 30/FRA 2, Autolab). In the frequency response analysis (FRA) software, an oscillation potential of 10 mV, from 1 MHz to 1 Hz, was used. The proton conductivity ( $\sigma$ ) was calculated by applying Equation 2:

$$\sigma = \frac{l}{RA} \quad (2)$$

where:  $\sigma$  is the proton conductivity (S/cm),  $l$  is the thickness of the membrane (cm) or the distance between the electrodes,  $R$  is the ohmic resistance of the membrane ( $\Omega$ ), obtained by impedance analysis, and  $A$  is the cross-sectional area of the membrane (cm<sup>2</sup>). The membrane thickness was determined with a Byko-test 7500 (BYK GARDNER) gage. The resistance ( $R$ ) was obtained at the high frequency intercept on the real axis ( $Z'$ ) of the impedance spectrum.

### 3. Results and Discussions

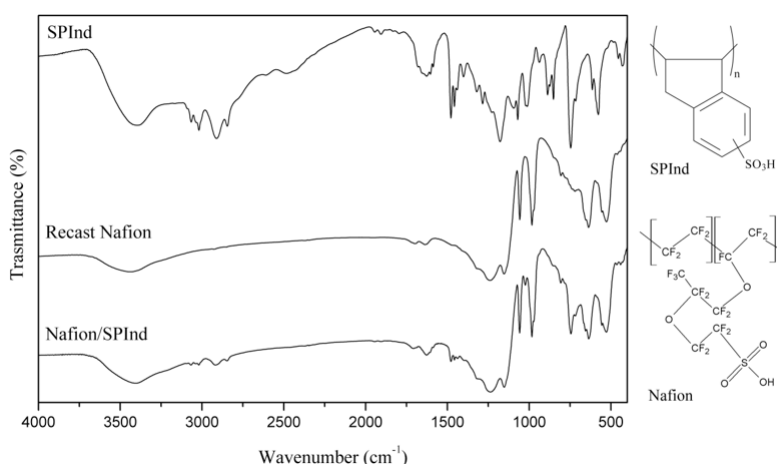
Poly(indene) (PInd) has a repeating unit comprised of a five-membered ring with an aromatic ring attached to it, which easily undergoes electrophilic substitution with a sulfonic acid (-SO<sub>3</sub>H) group. Sulfonated poly(indene) (SPInd) shows thermal stability up to 200 °C and good proton conductivity<sup>[12]</sup>. SPInd with DS 35 or 45% (SPInd35 and SPInd45, respectively) was used to prepare blended Nafion/SPInd membranes with 10, 15 or 20 wt.% SPInd.

Figure 1 shows the FT-IR spectra for the SPInd35, recast Nafion and Nafion/SPInd35 membranes. All spectra show a broad band at 3450 cm<sup>-1</sup> arising from the -OH vibration of water linked to the hydrophilic -SO<sub>3</sub>H groups<sup>[14]</sup>. On the SPInd spectrum the aromatic C-C band is split into two peaks, at 1470cm<sup>-1</sup> and 1493cm<sup>-1</sup>, due to the presence of sulfonated and non-sulfonated rings. The absorption peak at 1022cm<sup>-1</sup> was associated with the S=O stretching vibration. The absorption peaks at 1080cm<sup>-1</sup> and 1250cm<sup>-1</sup> were associated with the symmetrical O=S=O stretching vibration, and the asymmetric stretching vibration of the sulfonic groups, respectively. The absorption at 1650cm<sup>-1</sup> was attributed to the backbone carbonyl-stretching band<sup>[15]</sup>.

The spectrum also showed peaks at 1200cm<sup>-1</sup> and 1144cm<sup>-1</sup> associated with the asymmetric and symmetric F-C-F stretching vibrations, respectively. The bands at 1410cm<sup>-1</sup> and 850cm<sup>-1</sup> correspond to S=O and S-OH stretching of the SO<sub>3</sub>H group and the band at 1052cm<sup>-1</sup> was related to the symmetric SO<sub>3</sub><sup>-</sup> stretching vibration<sup>[16]</sup>. For comparison, the FT-IR and NMR spectra for PInd and SPInd20 were reported in previous publications from our group<sup>[12,13]</sup>.

Figure 2 shows the thermogravimetric (TG) and derivative (DTG) curves of recast Nafion and blended Nafion/SPInd membranes. A modification of the Nafion degradation curve profile is observed due to the SPInd incorporation in the membrane and a lower chain degradation maximum temperature. The membranes degradation under nitrogen may be analyzed in relation to three distinct temperature ranges: (I) 50 to 200 °C due to a gradual loss of water; (II) 200 to 425 °C due to the desulfonation process and side chain decomposition; (III) 425 to 600 °C due to the PTFE and SPInd backbone degradation. The apex temperature ( $T_{max}$ ) in each range and the correspondent mass loss, as well as the residue at 800 °C are shown in Table 1. The water content of the membranes depends on the water uptake and linked water retained in it. The water mass loss of the Nafion blended membranes remained at the same order of magnitude, since previously the analyses were heated in an oven at 110 °C for 3 h. The water content in the Nafion/SPInd membranes is higher than in recast Nafion due to a higher content of -SO<sub>3</sub>H group in the membrane. The high mass loss of the Nafion/SPInd45-10 can be due to a non-homogeneous specimen.

The high mass loss of the blended membranes in the range II is a consequence of the higher decomposition of -SO<sub>3</sub>H groups<sup>[17,18]</sup> present in these membranes. In the range III, the lower mass loss of the blended membranes is because the SPInd has an aromatic hydrocarbon main chain that undergoes carbonization during the -SO<sub>3</sub>H groups decomposition. This process is corroborated by a higher residue content at 800 °C. The low residue (0.6%) of recast-Nafion at 800 °C indicates a better oxidation and degradation process of a fluorocarbon backbone compared to an aromatic one. Usually hydrocarbons with an aromatic or



**Figure 1.** FT-IR spectra of recast Nafion, SPInd35 and Nafion/SPInd35 membranes.

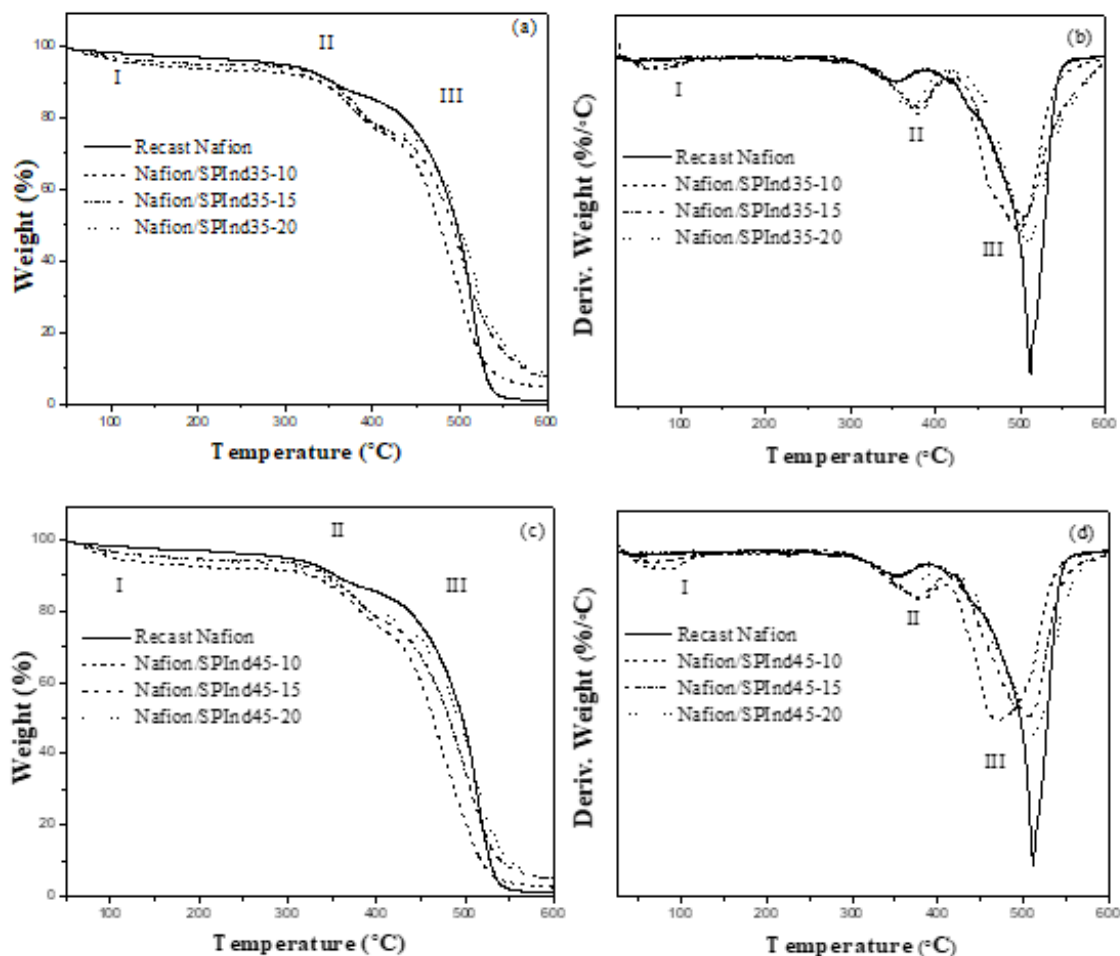


Figure 2. TG and DTG curves of Nafion/SPInd35 (a,b) and Nafion/SPInd45 (c,d) membranes comparatively to recast Nafion.

Table 1. Maximum temperature and mass loss in the degradation ranges and residue at 800 °C of recast and blended Nafion/SPInd membranes.

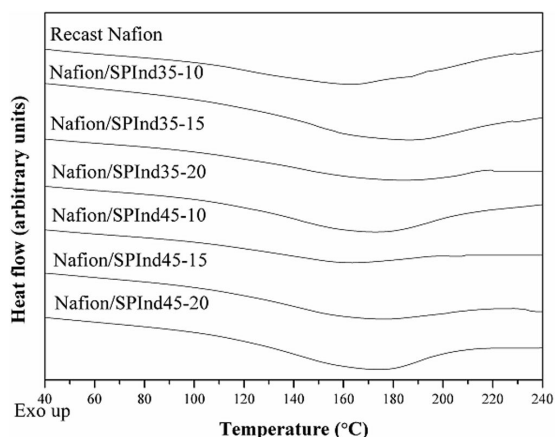
Membrane	I T < 200 °C		II 200 to 425 °C		III 425 to 600 °C		Residue at 800 °C (%)
	T <sub>max</sub> (°C)	Mass loss (%)	T <sub>max</sub> (°C)	Mass loss (%)	T <sub>max</sub> (°C)	Mass loss (%)	
Recast Nafion	No observed	1.6	350	10.4	512	87.4	0.6
Nafion/SPInd35-10	86	4.6	379	20.5	498	70.2	4.7
Nafion/SPInd35-15	85	4.0	379	20.4	504	70.0	5.6
Nafion/SPInd35-20	85	4.9	370	18.2	509	69.3	7.6
Nafion/SPInd45-10	85	6.5	380	19.9	472	71.1	2.5
Nafion/SPInd45-15	87	4.4	376	19.4	506	71.9	4.3
Nafion/SPInd45-20	82	4.5	362	16.5	512	73.7	5.3

cyclic backbone undergo ring condensation and carbonization at high temperature and inert conditions resulting in high residue content (2.5-7.6%).

Figure 3 shows endothermic curves of the second DSC run for recast and blended Nafion membranes in the range of 40 to 240 °C, after annealing at 120 °C (1<sup>st</sup> run) for 5 min to eliminate the water. The short broad endothermic peak with the apex at around 160 °C is due water evaporation and

shows that the membranes have water molecules strongly bound into -SO<sub>3</sub>H groups. Thus, the membranes contain some highly stable hydrophilic clusters. The SPInd content seems to have a variable effect on the endothermic peak and apex temperature, which may result from variations in the dryness of the sample analyzed. It was observed that the membranes can retain water molecules even when maintained at temperatures higher than 100 °C.

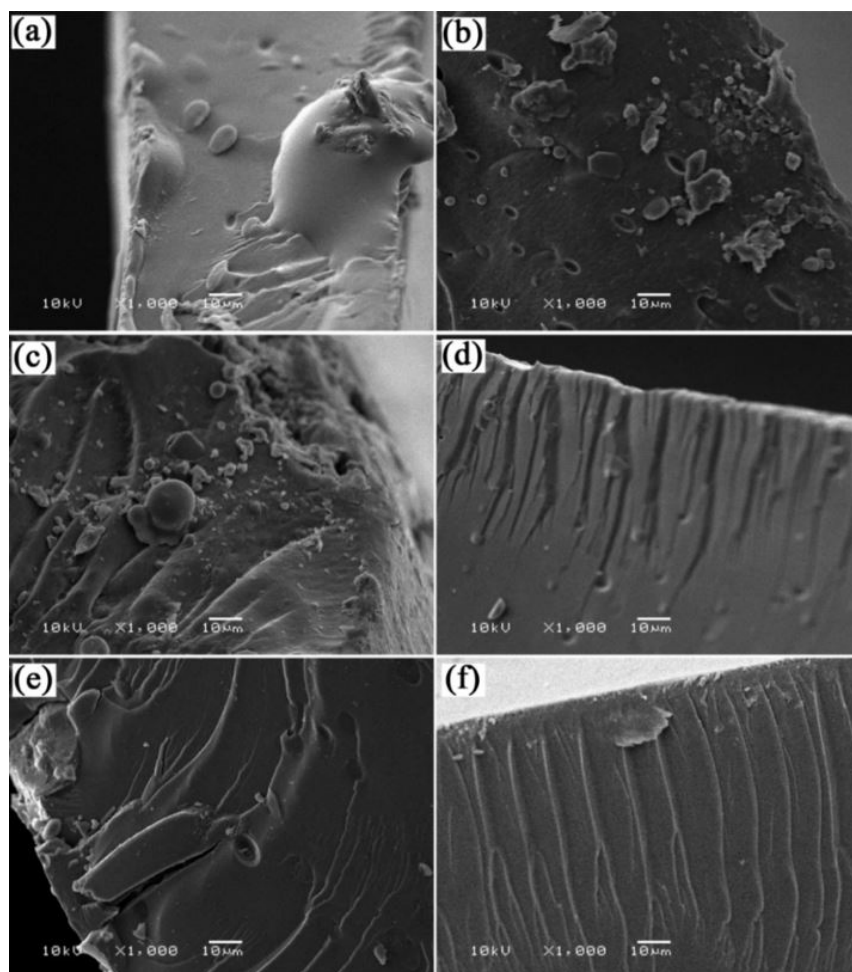
Similarly, to Nafion, SPInd is polymer with hydrophobic and hydrophilic domains, and when these polymers are blended chain molecules are reorganized per the affinity of domains. Water uptake plays an important role in the proton



**Figure 3.** Second run DSC endo/thermic curves of recast and blended Nafion/SPInd membranes.

transport and mechanical properties of a polymer electrolyte membrane (PEM)<sup>[19]</sup>. At temperatures below 100 °C, the water molecules facilitate the proton movement through the PEM membrane. The translocation of protons occurs via chemical exchange through a mechanism involving the reorganization of the hydrogen bonded water network, which provides sufficient ionic diffusivity<sup>[20]</sup>. Thus, an adequate level of water molecules is necessary to maintain a good level of proton conductivity. On the other hand, the water content should be optimized to ensure low fuel permeability.

The presence of sulfonic acid groups ( $-\text{SO}_3\text{H}$ ), further increased by the SPInd polymer, makes the hydrocarbon resin hydrophilic. Due to the interaction with water molecules via intermolecular hydrogen bonding, the hydrophilic channel volume and the size of the ionic domains in the microstructure is enhanced<sup>[21]</sup>. The performance of the membrane is also dependent on its morphological structure and hydrophilic and hydrophobic phase segregation, both of which strongly affect the proton conductivity of the membrane. Figure 4 shows SEM micrographs of the cross-sectional fractured surfaces of the membranes prepared with 10 to 20% of SPInd35 (a-c), 10 and 15% of SPInd45 (d and e), and recast Nafion (f). Comparison of Nafion/SPInd35-15 and



**Figure 4.** SEM images of the fractured surfaces of the blended membranes with 10 (a), 15 (b) and 20 wt. % (c) of SPInd35; and 10 (d) and 15 wt. % (e) of SPInd45; and recast Nafion (f).

Nafion/SPInd45-15 (b and e) shows that phase segregation occurred for the membranes when SPInd with a lower degree of sulfonation was used. It is apparent that if the SPInd contains fewer polar groups that the affinity with the perfluorosulfonated polymer is lower, evidenced by the formation of particles in the fractured surface (a-c). A slightly higher degree of sulfonation (SPInd45) changes the polymer polarity and a more compatible blend with the perfluorosulfonated polymer was possible. It can be seen in Figures 4d,e that the blended Nafion/SPInd morphology resembled recast Nafion (f). Thus, the dispersion of SPInd45 in the Nafion matrix produced a more homogeneous blend with no aggregation or domains of the sulfonated polymer. Blended Nafion/SPInd membranes resulted in uniform membranes but some fragile while handling.

Figure 5 shows the XRD spectra for the recast and blended Nafion/SPInd membranes. Nafion membranes are made from the copolymers of long branching perfluoro sulfonic acid monomers (PFSA) and long sequences of tetrafluoroethylene (PTFE) that may crystallize and presents a weak XRD reflection at  $2\theta$  equal to  $18^\circ$  due to the (1 0 0) plane. The peak at  $2\theta$  of  $39^\circ$  is of the order of the distance between the nearest neighboring  $\text{CF}_2$  units<sup>[22]</sup>. The recast Nafion and blended Nafion/SPInd membranes showed the characteristic XRD reflection at  $2\theta$  ( $=18^\circ$ ), superimposed as a shoulder on a large amorphous halo. For blended membranes, the full width at half maximum (FWHM) decreased with an increase in the SPInd content, due to the degree of crystallite perfection which gradually improved<sup>[23]</sup>. The XRD peak pattern profile variation shows that the structure in the membranes was slightly changed by the introduction of SPInd. The shift in the peak to a higher  $2\theta$  angle indicates that the inter-planar spacing in the blended membrane was reduced with the introduction of the SPInd relative to that of the recast Nafion. By applying Bragg's law ( $\lambda=2d \sin \theta$ ), it was estimated that the distance between the planes of the recast Nafion (0.520 nm) was slightly reduced to 0.506 nm and 0.499 nm for Nafion/SPInd35 and Nafion/SPInd45, respectively. A similar trend was observed by Rhee et al. for Nafion/sulfonated montmorillonite composite membranes<sup>[24]</sup>.

Figure 6 shows the water uptake of the Nafion/SPInd membranes after being soaked in water at room temperature ( $30^\circ\text{C}$ ). The SPInd increased the membrane water uptake due to increased sulfonic acid content, compared to the pristine Nafion membrane. Water uptake for SPInd35 was slightly higher than for SPInd45. Whereas the sulfonation degree (SD) of 45% was determinant for a morphology more like to the Nafion, SD of 35% or 45% did not have significance on water uptake at room temperature.

Figure 7 shows the Nafion/SPInd membranes' water uptake as a function of temperature. At room temperature, the water uptake of the blended membranes was of 19 to 21%, compared to 16% for the recast Nafion. As expected, water uptake increased with the temperature increasing, and as higher the temperature more significant was the sulfonation degree and SPInd content, due to a higher concentration of  $-\text{SO}_3\text{H}$  groups in the membranes<sup>[13]</sup>. At  $90^\circ\text{C}$ , the water uptake of the membranes Nafion/SPInd35 and Nafion/SPInd45 increased to 40-44% and 38-43%, respectively.

In agreement with these results, Amjadi et al. reported similar trends for the water uptake of composite membranes prepared from Nafion and  $\text{SiO}_2$ <sup>[25]</sup>. It was reported that water sorption of Nafion membranes increases with temperature due to an increase in the specific volume, and as well as a

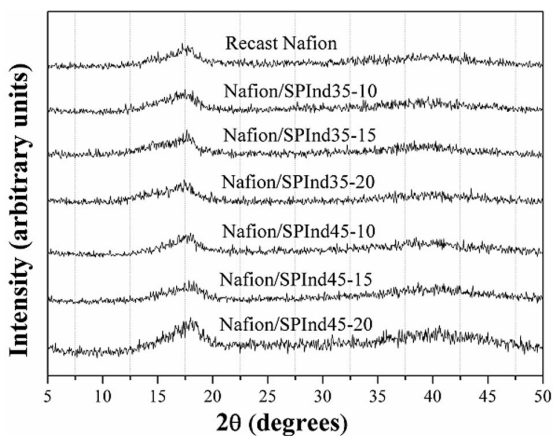


Figure 5. XRD spectra of recast and Nafion/SPInd membranes.

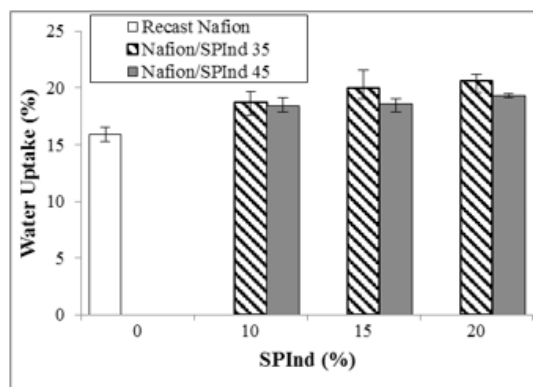


Figure 6. Water uptake at room temperature of recast and blended Nafion/SPInd membranes as a function of SPInd content.

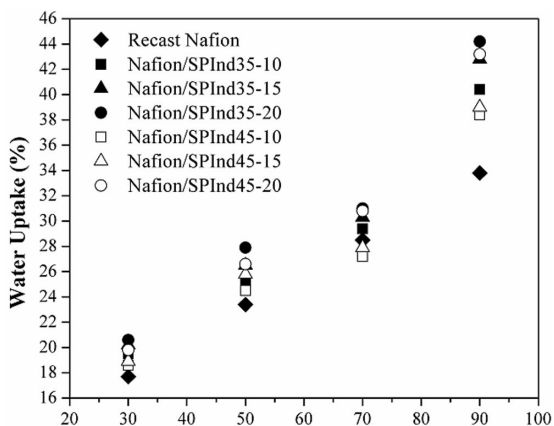


Figure 7. Water uptake of the Nafion/SPInd membranes as a function of temperature.

drop-in Young's Modulus<sup>[26,27]</sup>. In amorphous polymers, the free volume has great influence in the specific volume mainly in temperatures closer and above the polymer glass transition ( $T_g$ ). Higher free volume allows greater water sorption.

The Nafion's  $T_g$  is around 120 °C and the SPInd's  $T_g$  is above 200 °C<sup>[11]</sup>. In the glass state, the free volume remains constant and increases as the temperature approaches to  $T_g$ 's interval. The increasing of Nafion water uptake with the temperature is linear and is driven by the increase of the free volume fraction or specific volume below the  $T_g$ . The water uptake of the blended Nafion/SPInd besides the Nafion free volume contribution is influenced by the  $-SO_3H$  concentration in the membrane. There is no contribution of the free volume fraction of the SPInd since the highest temperature evaluated is quite far of its  $T_g$ . It is known that higher temperatures facilitate the fuel cross-over through the free volume of a membrane. Thus, hypothetically the SPInd domains with high  $T_g$  may help to depress the cross-over in the blended Nafion/SPInd membrane.

Values obtained for the membrane ion exchange capacity (IEC) as a function of SPInd content can be seen in Figure 8. The IEC value for recast Nafion was 0.93 mequiv.g<sup>-1</sup> and the membrane IEC increased as the SPInd content was increased.

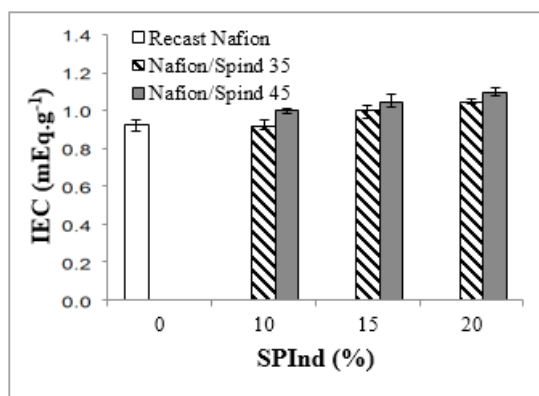
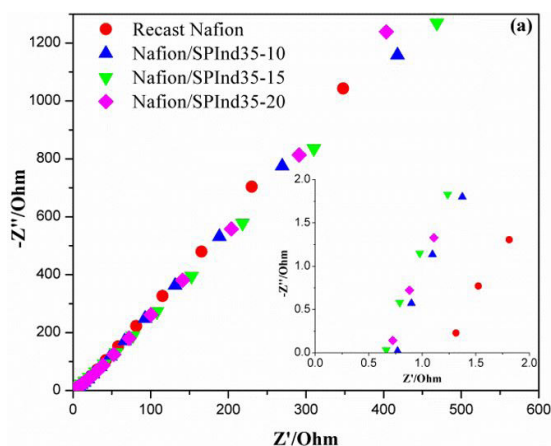


Figure 8. Ion exchange capacity of the Nafion/SPInd membranes as a function of the SPInd35 and SPInd45 content.



Moreover, the Nafion/SPInd membranes showed higher IEC values with increasing DS (1.05 and 1.10 mequiv.g<sup>-1</sup> for Nafion/SPInd35-20 and Nafion/SPInd45-20, respectively). However, it should be noted that the IEC for membranes with the same concentration of SPInd, but different DS values was not significant, indicating that the 10% variation in the DS caused no significant change in the ion exchange capacity. The water uptake values mirror this finding to some extent, as the SPInd with the higher DS did not result higher WU values.

The electrochemical experiments for conductivity measurements at 100% RH at room temperature were carried out with membranes soaked for seven days in DI water. The Nyquist plots of the Nafion/SPInd35 and Nafion/SPInd45 membranes shown in Figures 9a,b, respectively, exemplify as the membrane ohmic resistance was taken.

The inset in both figures shows an enlargement of the high frequency area of the plot, in which by convention, the membrane ohmic resistance is taken to be represented by the high frequency intercept of the modeled Nyquist plot to the real axis ( $Z'$ )<sup>[28,29]</sup>. The ionic conductivity and thickness of the recast and blended Nafion membranes are indicated in Table 2. Blended Nafion/SPInd membranes had higher conductivity, which increased as the SPInd content increased, when compared with Nafion. The highest ionic conductivities ( $2.41 \times 10^{-2}$  and  $2.37 \times 10^{-2}$  S cm<sup>-1</sup>) were observed for Nafion/SPInd35-20 and Nafion/SPInd45-20, respectively. Thus, the proton conductivity increases as the SPInd content increases. As found in other measurements, the DS did not result in significantly different values. The maximum sulfonation degree of SPInd and percentage in the blend

Table 2. Thickness, resistance and conductivity of recast and blended Nafion membranes.

Membrane	$l$ ( $\mu$ m)	$R$ ( $\Omega$ )	$\delta$ ( $\times 10^{-2}$ S cm <sup>-1</sup> )
Recast Nafion	255	1.24	1.16
Nafion/SPInd35-10	300	0.78	2.17
Nafion/SPInd35-15	269	0.65	2.34
Nafion/SPInd35-20	294	0.69	2.41
Nafion/SPInd45-10	302	0.98	1.74
Nafion/SPInd45-15	307	0.81	2.14
Nafion/SPInd45-20	281	0.67	2.37

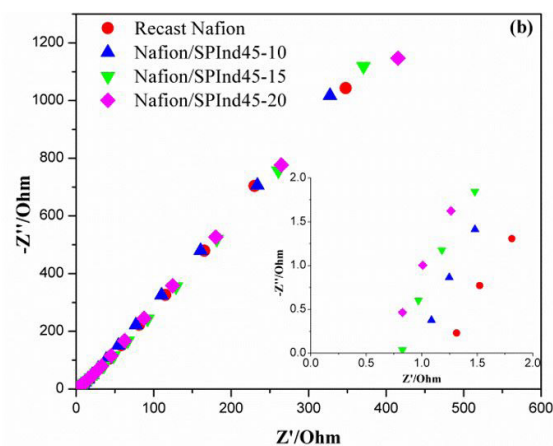


Figure 9. Nyquist plots of the Nafion/SPInd35 (a) and Nafion/SPInd45 (b) membranes.

is only limited by the SPInd water solubility. Sulfonation degree higher than 45% turn the SPInd totally water soluble, and higher percentage of it in the blend harder the sample solubility in the Nafion matrix.

Proton transport in the membrane relies on the presence of well-connected hydrophilic channels through the membrane, thus the water uptake and morphology of the membrane are crucial factors between others. The sulfonic groups of the SPInd positively contributed to the increased water uptake that enhanced this hydrated pathway. Increased water content in membranes is thought to lead to increased structural diffusion of water resulting in higher proton conductivity<sup>[30]</sup>. Furthermore, swelling of the ionic domains of the Nafion and SPInd improves the channel connectivity and extension through the membrane. Finally, the addition of extra sulfonated functional groups ( $-\text{SO}_3\text{H}$ ) via the SPInd blending provided additional protons to the hydrophilic channels, leading to increased transport via the high water content ( $(\text{H}_2\text{O})_n\text{H}^+$ ). Investigation of the mechanical stability, proton conductivity at increased temperature and single cell performance is required, and under way in our group.

#### 4. Conclusions

Blended Nafion/SPInd membranes could be prepared by casting from DMAc solution. Sulfonation degree higher than 45% turn the SPInd totally water soluble, and higher percentage of it in the blend harder the sample solubility in the Nafion matrix. Blended Nafion/SPInd membranes resulted in uniform membranes but some fragile while handling, however showed good proton conductivity. The SPInd slightly increased the water uptake of blended Nafion membranes and the ion exchange capacity at room temperature, and as expected, water uptake increased with the temperature. The higher the temperature more significative the sulfonation degree and the SPInd content were, due to a higher concentration of  $-\text{SO}_3\text{H}$  groups in the membranes, while maintaining good thermal properties. The membrane water uptake reduction can be related to the decreasing of free volume in the Nafion matrix and presence of hydrophobic SPInd domains in the blended Nafion/SPInd membranes. The ionic conductivity of the blended membranes was slightly higher compared with the recast-Nafion membrane prepared under the same conditions. Increased water content in membranes is thought to lead to increased structural diffusion of water resulting in higher proton conductivity. Proton transport in the membrane relies on the presence of well-connected hydrophilic channels through the membrane, thus the water uptake and morphology of the membrane are crucial factors between others. The sulfonic groups of the SPInd positively contributed to the increased water uptake that enhanced this hydrated pathway. The maintaining IEC and proton conductivity values observed for the blended Nafion/SPInd membranes, indicate promising potential for fuel cell application. Thus, Nafion membranes can be modified with SPInd, a lowest cost polymer, by replacing part of it without loss of conductivity and efficiency.

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