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# Synthesis and characterization of hybrid membranes based on sulfonated poly (ether ether ketone) (SPEEK) and polysiloxane

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## ABSTRACT

Polymer electrolyte membrane fuel cells (PEMFC) for hydrogen and methanol have attracted the attention of research groups for many years mainly because they are promising candidates for clean and renewable power sources. The most common commercial product used as PEM is Nafion®. However, certain limitations and high production costs stimulate the research of new materials. In this work, new hybrid proton-conducting membranes for PEMFC based on sulfonated poly(ether ether ketone) and an inorganic–organic polysiloxane phase were obtained with the objective of improving its mechanical, thermal, and chemical resistance properties. The hybrid membranes were prepared by dissolving the base polymer in DMSO and adding different amounts of the polysiloxane phase previously obtained from polydimethylsiloxane and a cross-linking agent (tetraethyl orthosilicate or phenyltrimethoxysilane). Membranes were characterized using infrared spectroscopy and thermal analysis. Macroscopic properties as water uptake, ion-exchange capacity, and proton conductivity were determined. The methanol permeabilities were in the range of $5.53 \times 10^{-7} - 8.36 \times 10^{-7}$ cm$^2$/s, which is several times lower than that of Nafion® 117 ($1.55 \times 10^{-6}$ cm$^2$/s). The hybrid membranes with both cross-linkers also exhibited higher proton conductivity with respect to Nafion® 117 (40 mS/cm) at 80˚C and 90% relative humidity.

*Keywords:* Proton-conducting hybrid membranes; Sulfonated poly(ether ether ketone); Polysiloxane

## 1. Introduction

The direct methanol fuel cell (DMFC) is attracting much interest as an energy source for electric vehicles, residential power sources, and portable devices due to several properties such as high energy density, low pollution, and fast startup. One of the most important components in DMFC is the proton-exchange membrane (PEM) which provides ionic pathways for proton transfer, acts as separator between the electrodes

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and also as a barrier against fuel and oxidant permeation. The most common commercial product used as proton-exchange membrane is Nafion®, a perfluorosulfonic acid-based membrane that is composed of carbon–fluorine backbone chains with perfluoro side chains containing sulfonic acid groups. It is widely used in fuel cells, since it exhibits high proton conductivity under fully hydrated conditions, and good chemical and mechanical stabilities. However, these membranes suffer from a high methanol crossover rate, decrease of proton conductivity above 80˚C, and high production costs [1].

Recently, membranes based on sulfonated aromatic hydrocarbon ionomers have shown promising results as an interesting option of new chemically durable materials mainly in terms of proton conductivity, reactant permeability, and mechanical properties [2]. Among the ionomers most widely used are: polystyrene [3], polyether ether ketone [4,5], polysulfone [6], and polyimide [7].

Poly(ether ether ketone) (PEEK) is a low-cost polymer with excellent mechanical and thermal properties, and broad chemical resistance. Chemical modification, like sulfonation, makes this polymer suitable for applications in fuel cells. It is possible to achieve high proton conductivities with high sulfonation degrees (SD). However, methanol crossover and water uptake increase at higher SD and its mechanical properties progressively deteriorate with sulfonation [8]. To counter these negative effects, there are two approaches that are considered as the most effective ways to improve the performance of sulfonated poly(ether ether ketone) (SPEEK): increasing the cross-linking of the membranes (i.e. using polyatomic alcohols [9], amines) and formation of hybrid membranes [10]. As a consequence of this latter approach, recent developments are focused on new membrane systems based on hybrid inorganic–organic materials. Such materials are very attractive for membrane synthesis because they can combine the basic properties of organic and inorganic materials resulting in an improved kind of membranes with great potential because they show a positive synergistic effect when compared to the single materials used separately. Organic materials have important limitations associated with mechanical, chemical, and thermal stabilities; however, the flexibility and low cost of polymers make them highly interesting for many applications. Although inorganic materials do not usually form films, some other desirable membrane properties, such as mechanical or thermal resistances are ensured by the inorganic network formed throughout the material.

In this work, new hybrid proton-conducting membranes for PEMFC based on SPEEK and an inorganic–organic polysiloxane phase were prepared with the objective of improving its mechanical, thermal, and chemical resistance properties. The hybrid membranes were prepared by dissolving the base polymer in DMSO and adding different amounts (5, 10, 15, and 20% *w*/*w*) of the polysiloxane phase previously obtained from polydimethylsiloxane and a cross-linking agent (tetraethyl orthosilicate or phenyltrimetoxysilane). Membranes were characterized using infrared spectroscopy and thermal analysis. Macroscopic properties as water uptake, ion-exchange capacity, and proton conductivity were determined. The methanol permeability values of the hybrid membranes were in the range of $5.53 \times 10^{-7}$ to $8.36 \times 10^{-7}$ cm$^2$/s, which is several times lower than that of Nafion® 117 ($1.55 \times 10^{-6}$ cm$^2$/s). The hybrid membranes with both cross-linkers also exhibited higher proton conductivity with respect to Nafion® 117 (40 mS/cm) at 80˚C and 90% relative humidity.

## 2. Experimental

### 2.1. Materials

PEEK was obtained from Polysciences Inc, USA. Sulfuric acid (97.5%), tetrahydrofuran (THF, 100%), dimethyl sulfoxide (DMSO, 100%), and methanol (99.93%) were obtained from J. T. Baker. Hydrochloric acid (37%), 2-propanol (≥99.5%), polydimethylsiloxane hidroxy-terminated (PDMS, Mn~550), and Nafion® 117 solution were from Sigma–Aldrich. Tetraethyl orthosilicate (TEOS, 98%) and phenyltrimethoxysilane (PhTS, 97%) were purchased from ABCR Gmbh and Co. KG.

### 2.2. Sulfonation of PEEK

Ten grams of PEEK, dried overnight at 120˚C, was dissolved in 250 mL of concentrated sulfuric acid and vigorously stirred at room temperature. Then the polymer solution was gradually precipitated into ice-cold water under continuous agitation. The polymer precipitate was filtered and washed several times with distilled water until the pH was neutral and dried for 48 h at 80˚C. The sulfonation degree was determined by elemental analysis.

### 2.3. Synthesis of inorganic–organic network (polysiloxane phase)

For the polysiloxane phase preparation, 990 μL of 2-propanol, 240 μL of THF, 80 μL of distilled water, and 25 μL of HCl were first added to a round-bottomed flask. Then, 550 μL of tetraethoxysilane and 1 g of polydimethylsiloxane were simultaneously poured into the mixture. The flask was introduced into a water bath at 80°C and the reaction took place under reflux with vigorous agitation for 25 min. When phenyltrimethoxysilane was used as cross-linking agent, the same procedure was followed using 480 μL of this reagent and leaving the reaction to take place for 40 min.

### 2.4. Preparation of hybrid membranes

The hybrid membranes were prepared by the solution casting method. An amount of 550 milligrams of SPEEK sample was dissolved in 10 mL of DMSO at room temperature. The polysiloxane phase previously synthesized was added at different weight percents (5, 10, 15, and 20%) to the solution and stirred for about 1 h. The resulting solution was poured into a glass plate and heated at 60°C for solvent evaporation. For comparison, a Nafion® 117 membrane was prepared using 6 mL of a Nafion® 117 solution. In the following sections, the hybrid membranes will be described as X/Y/Z. “X” represents the polymer used (SPEEK), “Y” represents the cross-linking agent used in the synthesis of inorganic–organic network (TEOS or PhTS), and “Z” represents the weight percent of inorganic–organic network used.

### 2.5. Proton conductivity

Proton conductivity through-plane direction of membranes was determined using Scribner Membrane Test System (MTS-740) with a Solartron SI 1,260 Impedance/Gain Phase Analyzer. EIS was conducted by applying a small alternating voltage (10 mV) at 0 $V_{DC}$ and varying the frequency from $10^6$ to 1 Hz and 10 steps/decade. The membrane samples $3 \times 1$ cm were compressed between gas diffusion electrode layers (GDE) and attached to the platinum electrodes with conductive carbon paint. The sample compressive loading was kept at 2.1 MPa. A typical procedure for 30 and 80°C, and RH of 40–95% consists of preconditioning the sample at RH 95% for 120 min, followed by a RH step-decreasing program, conditioning for 30 min followed by EIS measurements at each step. The specific conductivity was obtained from Eq. (1), where $l$ is the membrane thickness, $A$ is the overlapping area of the electrodes, and $R$ is the resistance.

$$\sigma = \frac{l}{AR} \tag{1}$$

### 2.6. Methanol permeability

Methanol permeability was measured using a two-compartment transport cell provided with a circular window ($r = 1.2$ cm). The membrane was clamped between the two compartments; one was loaded with 90 mL of a 2.47 mol dm$^{-3}$ methanol solution and the other with 90 mL of deionized water. Both compartments were mechanically stirred at room temperature (20°C) with the aid of two motors located on the upper part of the cell to ensure uniform mixing during the experiment. The concentration of the permeating methanol was measured by refractive index [11] (Abbemat 350, Anton Paar). The reported results correspond to the average of two replicates.

### 2.7. Water uptake

The water uptake of membranes was calculated by measuring the change in the weight between the dry and wet membranes. The membranes were dried at room temperature under vacuum for a week. To obtain the wet weight, a dried membrane sample was equilibrated with distilled water until constant weight was obtained. Water uptake (WU) of the membranes was calculated from Eq. (2):

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{2}$$

where $W_{dry}$ and $W_{wet}$ are the weight of dry and wet membranes, respectively.

### 2.8. Thermal analysis

Thermogravimetric analysis (TGA/SDTA 851e, Mettler Toledo) measurements were performed between 25 and 700°C at a heating rate of 10°C/min under nitrogen in platinum sample holders, containing approximately 10 mg of dried membrane sample.

Two types of water, freezing water and non-freezing water, were determined in the membranes by melting transitions in differential scanning calorimetry (DSC) measurements (Mettler DSCI STARe System). The samples were first cooled to −50°C during 3 min and then heated up to 40°C at a rate of 5°C/min. Calculation of the amount of freezing water in the samples was done by integrating the peak area of the melt endotherm ($Q$). The melting enthalpy of this type of confined water in the polymer was assumed to be the same as that of bulk water ($\Delta H = 334$ J/g). The mass of freezable water was obtained with Eq. (3)

$$W = \frac{Q}{\Delta H} \tag{3}$$

The non-freezing water was calculated by subtracting the freezing water from total water content.

### 2.9. Fourier transform infrared

Attenuated total reflectance Fourier transform infrared (ATR/FTIR) spectra were collected in the 4,000–580 $\text{cm}^{-1}$ range using a Perkin Elmer Spectrum GX FTIR spectrometer together with an ATR accessory (DuraSampl IR II from SensIR Technologies) and analyzed with commercial software. Spectra were recorded by positioning the samples on a cell platform operating at room temperature (25 scans).

## 3. Results and discussion

### 3.1. Sulfonation of PEEK

Based on the procedure described above, samples of SPEEK with two sulfonation degrees were obtained. The sulfonation degree and IEC were determined from data obtained by elemental sulfur analysis. Results obtained are shown in Table 1. Materials with a relatively high sulfonation degree (>70% SD) show a high hydrophilicity that consequently leads to an elevated interaction with water, and a resulting poor membrane mechanical strength that hinders the use of such materials towards obtaining mechanically resistant homogeneous membranes [12]. Conversely, materials with a lower sulfonation degree are characterized by low proton conductivity. In this work, since the aim was to evaluate the introduction of a polysiloxane phase in the performance characteristics of SPEEK, the polymer with 70.7% SD was chosen for characterization and subsequent preparation of hybrid membranes.

From the FTIR spectra of the pristine polymer and the sulfonated polymer, the characteristic vibrations of PEEK were observed: in 1,649 $\text{cm}^{-1}$ $\nu_{\text{C=O}}$, 1,595 and 1,488 $\text{cm}^{-1}$ $\nu_{\text{C=C}}$, 1,221 $\text{cm}^{-1}$ $\nu_{\text{as C–O}}$, and 1,099 $\text{cm}^{-1}$ $\nu_{\text{s C–O}}$ y 927 $\text{cm}^{-1}$ $\nu_{\text{s pH-(C=O)-Ph}}$. The appearance of a broad band around 3,392 $\text{cm}^{-1}$ in the sulfonated samples was assigned to O–H vibration from sulfonic acid groups interacting with water molecules. The absorptions at 1,250, 1,079, and 1,022 $\text{cm}^{-1}$, which appeared upon sulfonation, were assigned to the sulfonic acid groups in SPEEK.

### 3.2. Methanol permeability

The MeOH permeability values for SPEEK and SPEEK hybrid membranes are presented in Table 2. It is observed in all cases that the MeOH permeability is lower for the SPEEK hybrid membranes when compared with Nafion® 117. Furthermore, methanol permeability is slightly higher when PhTS is used as cross-linker.

### 3.3. Water uptake

It was observed that for the hybrid SPEEK/TEOS and SPEEK/PhTS membranes, the addition of the polysiloxane phase diminished the amount of water uptake in about 4 and 5%, respectively, when compared to the sulfonated polymer. In general, for hybrid membranes, the total amount of water absorbed remains unchanged with the amount of polysiloxane phase added.

### 3.4. Thermal analysis

The TGA thermograms for SPEEK/TEOS and SPEEK/PhTS hybrid membranes indicate they are stable up to 322 and 312°C, respectively, where a loss is observed probably due to the splitting-off of the sulfonic acid groups. A second degradation step starts at 477°C for SPEEK/TEOS and at 487°C for SPEEK/PhTS. As for the SPEEK membrane, the first loss starts also at 322°C and the second loss at 483°C.

Three states of water are found in the polymer matrix: freezing bound water, non-freezing water (bound water), and free water (unbound water) [13]. The freezing bound water has a phase transition temperature lower than free water due to the weak interaction with the polymer matrix. The non-freezing water is strongly associated with the polymer matrix, mainly with the hydrophilic groups, and is not observed calorimetrically. The free water is characterized calorimetrically and its transition enthalpies are equal to those of pure water.

Table 1
Characteristics of SPEEK samples obtained

| Reaction time (h) | % S | IEC | Sulfonation degree (%) |
|---|---|---|---|
| 1 | 5.82 ± 0.19 | 1.82 ± 0.06 | 61.4 ± 2.36 |
| 2 | 6.55 ± 0.21 | 2.05 ± 0.07 | 70.7 ± 2.70 |

Table 2
Methanol permeability and water uptake values for SPEEK and SPEEK hybrid membranes

| Membrane | Permeability (cm$^2$/s) × 10$^{-7}$ | Water uptake (%) | Freezable water (%) | Non-freezable water (%) |
|---|---|---|---|---|
| Nafion® 117 | 15.0 ± 0.50 | 25.00 ± 1.86 | ND | ND |
| SPEEK | 5.80 ± 0.17 | 45.26 ± 1.03 | ND | ND |
| SPEEK/TEOS/5 | 5.58 ± 0.13 | 41.95 ± 1.67 | 4.59 ± 0.55 | 37.36 ± 0.55 |
| SPEEK/PhTS/5 | 6.10 ± 0.12 | 43.37 ± 2.99 | 5.21 ± 0.42 | 38.16 ± 0.42 |
| SPEEK/TEOS/10 | 5.53 ± 0.11 | 40.49 ± 0.04 | 2.36 ± 0.78 | 38.13 ± 0.78 |
| SPEEK/PhTS/10 | 6.52 ± 0.18 | 37.68 ± 0.17 | 3.60 ± 0.43 | 34.07 ± 0.43 |
| SPEEK/TEOS/15 | 7.54 ± 0.14 | 40.78 ± 1.53 | 2.69 ± 1.32 | 38.08 ± 1.32 |
| SPEEK/PhTS/15 | 7.69 ± 0.18 | 39.99 ± 0.79 | 4.75 ± 0.94 | 35.24 ± 0.94 |
| SPEEK/TEOS/20 | 7.64 ± 0.15 | 41.13 ± 1.95 | 2.42 ± 1.50 | 38.71 ± 1.50 |
| SPEEK/PhTS/20 | 8.36 ± 0.06 | 40.51 ± 0.90 | 4.67 ± 1.01 | 35.83 ± 1.01 |

Note: ND—Not determined.

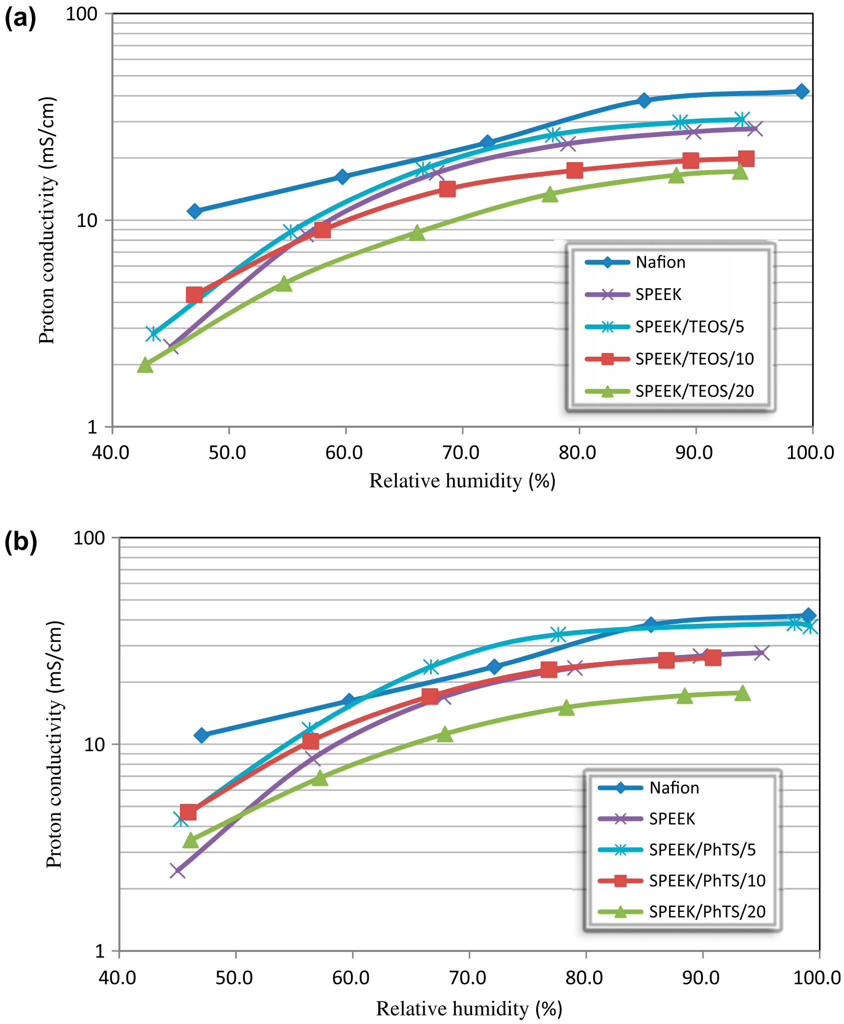

Fig. 1. Proton conductivity of the SPEEK hybrid membranes at 30°C: (a) with inorganic–organic TEOS matrix and (b) with inorganic–organic PhTS matrix.

The amount of polysiloxane phase added to SPEEK/TEOS hybrid membranes does not change the non-freezable water; however, there is a small decrease in freezable water. The SPEEK/PhTS hybrid membranes present a decrease in non-freezable water from 10% onward of polysiloxane phase added (Table 2).

### 3.5. Proton conductivity

The proton conductivities of the prepared membranes were estimated from AC impedance spectroscopy data in the range of 40–95% RH. The results for SPEEK hybrid membranes, SPEEK membranes, and Nafion® 117 and at 30 and 80°C are presented in Figs. 1 and 2, respectively. At both temperatures and under conditions of variable humidity, the proton conductivities of all the samples increased as the humidity increased. At 30°C, the Nafion® membrane has higher conductivity than the SPEEK hybrid membranes in all the range of relative humidity. The only membrane that has a performance comparable to Nafion® over 60% HR is SPEEK/PhTS/5. At 80°C and 80% onward of RH, the proton conductivity was greater for SPEEK, SPEEK/TEOS/10 (Fig. 2(a)) and all hybrid SPEEK/PhTS membranes (Fig. 2(b)). However, SPEEK/TEOS/20 (Fig. 2(b)) presents a higher conductivity with respect to Nafion® 117 at 80°C and 65% onward of RH. At 80°C, the best proton conductivity performance is for the SPEEK/PhTS/ hybrid membranes.

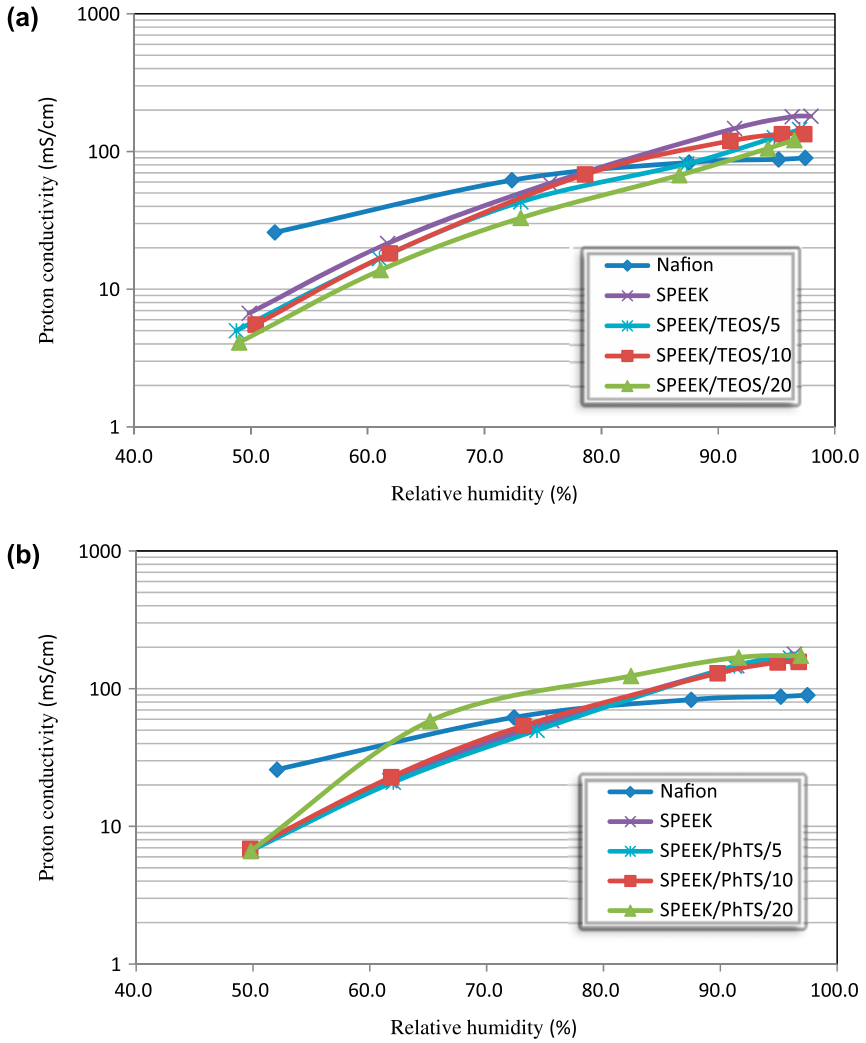

Fig. 2. Proton conductivity of SPEEK hybrid membranes at 80°C: (a) with inorganic–organic TEOS matrix and (b) with inorganic–organic PhTS matrix.

## 4. Conclusions

Hybrid membranes containing SPEEK and a polysiloxane phase were successfully prepared and tested for proton conduction. The results show that the proton conductivity of the hybrid membranes is dependent of the % RH and temperature. The best performance of the hybrid membranes were at a temperature of 80˚C. One membrane that exhibited a good behavior was SPEEK/PhTS/5 since at 80˚C and 65% of RH it presented higher conductivity than Nafion® 117 under the same conditions. The permeability of SPEEK/TEOS hybrid membranes to MeOH decreased when 5 and 10% of polysiloxane phase was added and increased when 15 and 20% of polysiloxane phase was employed. For SPEEK/PhTS hybrid membranes, the permeability for MeOH increased as polysiloxane phase increased. In all cases, the permeability to methanol of the hybrid membranes was lower than for Nafion® 117.

The addition of polysiloxane phase to SPEEK/TEOS and SPEEK/PhTS membranes does not change significantly the total amount of water content. All hybrid membranes present lower percent of total water uptake than the SPEEK membrane, but higher than Nafion® 117 membrane. The freezable water decreases in the SPEEK/TEOS hybrid membranes when the amount of polysiloxane phase added is 10% and over; however, the non-freezable water in these membranes remains unchanged. The non-freezable water decreases for SPEEK/PhTS hybrid membranes when the polysiloxane phase reaches a 10%. The SPEEK/PhTS/10 membrane has the lowest percent of freezable water.

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