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Novel Organic−Inorganic Hybrids with Increased Water Retention for Elevated Temperature Proton Exchange Membrane Application

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A new class of proton-conducting hybrid membranes have been developed using a combination of a solvent-directed infiltration method and sol−gel chemistry with a range of organofunctional silane and phosphate precursors. The phase-separated morphology of Nafion is used as a structure-directing template, which drives the inorganic component into the ionic clusters of the Nafion membrane. The kinetics of the sol−gel reactions were monitored using spectroscopic techniques. Photoacoustic Fourier transform infrared spectroscopy (PA-FTIR) confirms formation of Si−O−Si and Si−O−P bridges in the hybrid membranes, indicating silicate and phosphosilicate structures. The presence of the silicate/phosphosilicate network in the hybrid membranes enhances their thermal stability, thermomechanical properties, water retention at elevated temperatures, and relaxation temperature T_c. Scanning electron microscopy (SEM) and small angle neutron scattering were used to determine the morphology and microstructure of these membranes. A structural model of the hybrids is proposed to describe the size and shape of the inorganic particles, which is consistent with the SEM observations. Proton conductivity measurements were made from 30 to 80 °C and at relative humidities ranging from 30% to 90%. The presence of inorganics in the polymer membrane has improved the water management in these new organic−inorganic hybrids at elevated temperatures above 100 °C, which is a key parameter when designing proton-exchange membranes for medium-temperature fuel cell application.

Introduction

Proton-exchange membrane (PEM) fuel cells are attracting enormous interest as one of the most promising clean power generation technologies for their potential use as an environmentally benign and a highly efficient electric power generation technology for various applications, particularly for low/zero-emission vehicles and utility sector including distributed home power generators, power source for small portable electronics, etc.[1,2] However, a profound drawback of current PEMs including the most commonly used membrane from Nafion is the low water retention at temperatures above 80 °C or inability to operate under lower humidity for extended periods.[3] Retention of water within the membrane at and above 80 °C is a key parameter to achieving high proton conductivity in these materials.[4] Proton conductivity of the polymeric membrane increases linearly with the water content of the membrane, achieving highest conductivity at a fully hydrated condition. At elevated temperature and low relative humidity the Nafion membrane tends to dehydrate, which drastically lowers the proton conductivity and reduces the overall performance of the fuel cell.[5] For this reason, current Nafion and other membranes cannot meet the requirements for practical PEMFC applications and thus impede commercial development of this technology.

It is well known that incorporating inorganic fillers into polymer membranes can alter and improve the physical and chemical properties of the polymer (such as hydrophilicity, thermal stability, mechanical strength, proton conductivity, glass transition temperature, and water retention) while retaining its important properties to enable operation in the fuel cell.[6] One approach to improve the performance of proton-exchange membranes is to increase the ion-exchange capacity (IEC) by adding ionic groups to the polymer. Membranes with high IEC can show higher proton conductivity, but they experience excess swelling, which leads to loss of the mechanical integrity. Another approach is to enhance the water retention of Nafion membranes by incorporating hygroscopic inorganic nanoparticles, which can promote interactions between the particles and water molecules, thus enhancing the hydration properties without loss of mechanical integrity. Previous efforts[7−14] to improve the water retention properties of Nafion and related membranes

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by addition of metal oxide particles have produced some very promising results. Jalani et al.[15] prepared Nafion−MO₂ (M = Zr, Si, Ti) nanocomposite membranes and examined the proton conductivity, water uptake, and thermomechanical properties. These hybrid membranes demonstrated higher water uptake than unmodified Nafion at 90 and 120 °C. The Nafion−ZrO₂ membranes exhibited a higher conductivity at 90 and 120 °C, which was attributed to the increase in acidity of zirconia-based membranes in comparison to other nanocomposites based on Ti and Si. Jiang et al.[16] also reported enhanced water uptake properties of their composite silica/Nafion membranes, which were prepared from tetraethylorthosilicate (TEOS). It was noted that at higher inorganic loadings between 10% and 15% the proton conductivity decreased due to a higher membrane resistance. Mauritz et al.[17−22] proposed a sol−gel approach to prepare organic−inorganic hybrids using Nafion membranes with enhanced performance. The inorganic nanoparticles produced via the sol−gel route are homogeneously distributed in an angstrom scale versus submicrometer length scales for the particle composites. Matsuda et al.[23−26] investigated phosphosilicate glasses as potential solid-state proton conductors for proton-exchange membrane fuel cells. These gels consist of thermally stable silica and phosphates, which have a strong affinity for adsorbed water molecules. The gels have been found to exhibit high conductivity at medium temperatures even at low relative humidity. Phosphosilicate gels prepared from TEOS and H_3PO_4 show conductivities of up to 1.5×10^{-2} S cm^{-1} at 130 °C and 0.7% relative humidity apart from good thermal stability, water retention at low relative

Table 1. Various Hybrid Membranes from Nafion 117

Membrane	Inorganic Component	Chemical Structure
Hybrid 1	TEOS / phytic acid	Phytic acid TEOS
Hybrid 2	imidazole	Imidazole
Hybrid 3	imidazole / phytic acid	
Hybrid 4	PHPS	PHPS
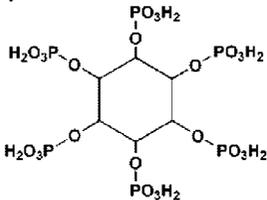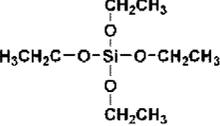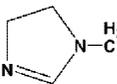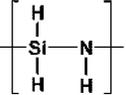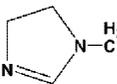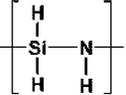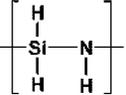
humidity. These gels show significant promise towards the development of self-humidifying membranes. The most common method for introducing such highly dispersed inorganic structures in a polymer is by the sol−gel process. In this work, we have chosen to prepare Nafion−silicate and −phosphosilicate hybrids using the sol−gel process and some novel precursors. We selected phytic acid, a novel phosphate precursor, to prepare phosphosilicate gels with various silanes using sol−gel chemistry. Phytic acid is chosen due to its multifunctional structure, so that the hydroxyl groups will allow strong bond formation with water molecules to help retain water at elevated temperature within the Nafion hybrid. Use of perhydropolysilazane (PHPS) as the starting material is advantageous for fabrication of the SiO₂ layer with a high rate and uniform chemical composition without extensive control of oxidation and hydrolysis processes.

Four different hybrid systems (Table 1) were prepared using Nafion 117 membrane and a combination of three silicon and one phosphorus precursors such as tetraethylorthosilicate (TEOS), perhydropolysilazane (PHPS), *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (imidazole), and phosphate precursor phytic acid, which are shown in Table 1. Nafion hybrid membranes were prepared by the solvent-directed infiltration method where hydrolysis and condensation reactions occurred in situ. The structure and morphology of the hybrids were characterized by thermal, spectroscopic, microscopic, and scattering techniques.

Experimental Section

Materials. Nafion 117 with an IEC of 0.91 meq/g[27] purchased from Sigma-Aldrich was cleaned by placing it in a 3% H_2O_2

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solution at 80 °C for 60 min, rinsing it with milli Q water, placing it in 1 M H_2SO_4 at 80 °C for 60 min, rinsing again in milli Q water, and then placing it in milli Q water at 80 °C for 60 min. Cleaned membranes were dried at 100 °C overnight before inorganic modification. Tetraethylorthosilicate (TEOS) and hydrated sodium phytate ($IP_6Na_{12}\cdot30H_2O$) were obtained from Aldrich and used as received. Phytic acid solutions were prepared from sodium phytate by ion exchange using Amberlyst resin according to a reported method.[28] *N*-(3-Triethoxysilylpropyl)-4,5-dihydroimidazole (imidazole) from Gelest and perhydropolysilazane (PHPS) from AZ Electronic Materials, Japan, were used without further purification. Ethanol, xylene, and milli Q water were used as solvents.

Phosphosilicate Gelation Studies. In order to examine the first stages of the sol−gel reaction between TEOS and phytic acid in solution, evolution of the sol to gel was followed by transmission FTIR spectroscopy. The sols were prepared at 0 °C in order to slow down the reaction, initiated by mixing 1.65 g of phytic acid dissolved in 3.6 mL of milli Q water, adjusted at 20 °C to pH = 3, and 11.2 mL of TEOS (P/Si = 0.05; H_2O/TEOS = 4). Infrared spectra were recorded at set time intervals. Aqueous phytic acid is not initially miscible with the TEOS, with the reaction starting at the interface. As the reaction proceeds, enough methanol is released to homogenize the mixture. The reaction between imidazole and phytic acid and imidazole was much the same except the ratio of H_2O/imidazole=3. Upon completion of the reaction, the final product was dried at 80 °C over several days to remove any residual solvent.

Nanocomposite Membrane Synthesis. The infiltration method was used to prepare the hybrid membranes.[29] First, Nafion membranes were preswollen in a H_2O/ethanol mixture for 60 min. In the case of the imidazole hybrid, the membrane was placed into a 1:9 (v/v) solution of imidazole/ethanol for 1 h. After removal from the silicon alkoxide solution, the membranes were rinsed thoroughly with ethanol to remove any residual reactants from the membrane surface and dried in an oven at 100 °C for 4 h. For imidazole/phytic acid and TEOS/phytic acid hybrids, the membranes were first soaked in the respective silane/ethanol solution for 1 h followed by washing in ethanol and subsequent immersion in an aqueous solution of phytic acid for 1 h. Finally, the membranes were removed from the phytic acid solution and again rinsed in ethanol before placing in the oven at 100 °C for 4 h. In the case of the PHPS hybrid, Nafion was preswollen in xylene for 1 h and then immersed in 1:9 PHPS/xylene (v/v) solution for 1 h. After removal from the PHPS solution, the membrane was rinsed thoroughly in xylene and then placed in an oven at 150 °C for 1 h for silica conversion.

Sample Characterization. *Spectroscopic Characterization.* Photoacoustic-Fourier transform infrared spectroscopy (PA-FTIR) was performed using a Nicolet Magna Spectrometer (model 750) equipped with a MTEC (model 300) photoacoustic cell. Carbon black was used as reference. Helium was used due to its high thermal conductivity. A gas flow rate of 10 cm^3/s was used. The resolution of 8 cm^{-1}, 256 scans, and mirror velocity of 0.158 cm/s were used for all measurements. Solid-state NMR spectra were recorded on a Bruker 300 spectrometer operating at 79.5 and 162 MHz for ^{29}Si and ^{31}P NMR spectra with a standard pulse sequence, and the samples were cut to small pieces and packed in an airtight rotor fitted with Kel-F cap. The rotor was spun at the magic angle at a frequency of 5 KHz.

Microscopic Characterization. Scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDAX) was used to study the structure and morphology of the hybrid material. The sample was coated with carbon coating before the test. The samples were examined using a Philips XL20 scanning electron microscope integrated with an energy dispersive X-ray analyzer to determine the elemental composition.

Thermal Analysis. TGA of the samples was conducted using a TGA 2950 thermal analyzer (TA Instruments) using a conventional (heating rate) mode under either a nitrogen or an oxygen atmosphere at a flow rate of 50 mL min^{-1}. The mass of samples was kept between 10 and 12 mg. The sample was heated from 30 to 900 °C at a heating rate of 10 °C min^{-1} up to 500 °C in nitrogen and between 500 and 900 °C in oxygen. The onset of degradation, weight loss, and residue remaining at 900 °C were evaluated.

DSC was performed using a TA 2920 DSC instrument (TA Instruments) with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The sample mass was kept between 5 and 10 mg. The unit was fitted with a liquid nitrogen cooling accessory (LNCA). Dry samples were cooled from room temperature down to −50 °C, kept at s^{-1} temperature isothermally for 5 min, and then heated up to 300 °C. Membranes swollen in water were heated up to 250 °C to determine the water uptake of the hybrid membranes.

Dynamic Mechanical Analysis. Dynamic mechanical properties of the samples were measured using a DMA 2980 (TA Instruments) in tension mode. Samples were heated from room temperature to 175 °C at a frequency of 1 Hz at 0.08% strain amplitude with a programmed heating rate of 3 °C min^{-1}.

Small-Angle Neutron Scattering (SANS). SANS studies were performed with the small-angle neutron scattering instrument at the Bragg Institute, Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney, using the AU-SANS facility. The neutron wavelength λ was 3.5 Å with a dispersion of $\Delta\lambda/\lambda$ 0.01. The sample to detector distance was fixed at 5 m. The q range of the instrument was 0.01−0.1, where q is the scattering vector, $q = [4\pi/\lambda]\sin(\theta/2)$. The two-dimensional scattering data were circularly averaged to produce one-dimensional scattering intensity $I(q)$ vs q. The data were corrected for background and pure solvent, and the scattering contributions from the empty cell were normalized to constant beam intensity. The measurements were made using quartz cells.

Proton Conductivity. An ESPEC SH-240 temperature/humidity chamber and a 2-probe conductivity cell were used for measurement of membrane in-plane conductivity (σ) under conditions of variable temperature and humidity. Each sample used was approximately 12 × 10 mm, and σ was calculated from eq 1

$$\sigma = \frac{l}{Rhw} \qquad (1)$$

where l is the distance (cm) between the two Pt electrodes, h and w are the thickness (cm) and width (cm) of the membrane, respectively, and R (Ω) is the resistance of the membrane obtained from the complex impedance plot measured by Solartron 1260.

Results and Discussion

Effect of the Sol−Gel Reaction on the Structure of Inorganic Gel. *Spectroscopic Studies.* In order to understand the kinetics of the sol−gel reaction between the inorganic precursors and monitor formation of the phosphosilicate network, infrared spectroscopy was monitored over a period of 48 h to determine completion of the hydrolysis and condensation reactions. Figure 1 shows the progress of the sol−gel reaction of the imidazole silane in presence of phytic acid at 0, 90, 160, 210, 270, and 330 min.

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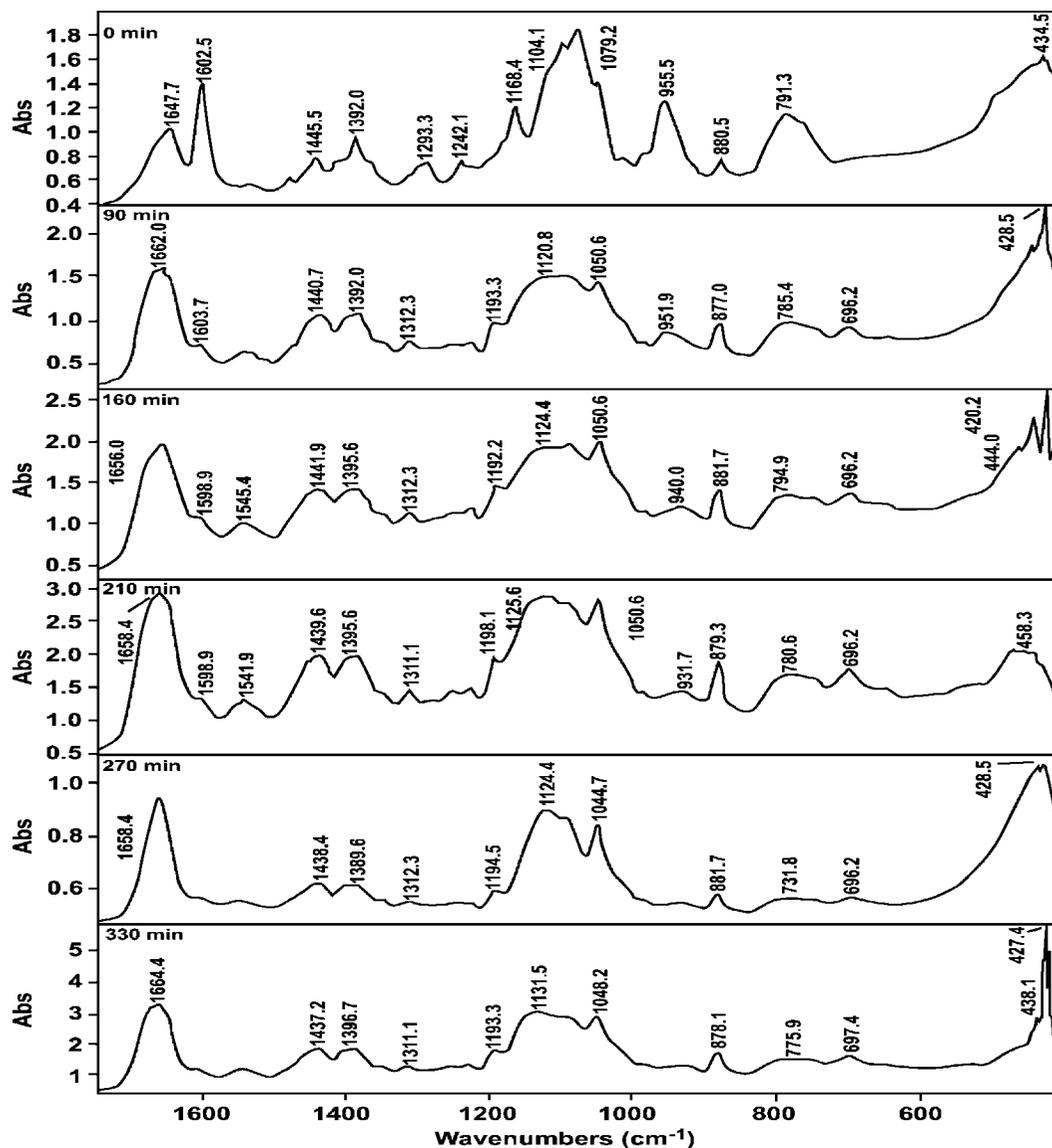
Figure 1. Infrared spectra showing the evolution of bonds formed during sol−gel reaction of imidazole silane and phytic acid.

Important features of these spectra are the presence of significant peaks in the region 2000−400 cm^{-1} which are related to the inorganic structure. The sharp peak at 1602 cm^{-1} in the spectrum obtained at 0 min is ascribed to H−O−H bending of physisorbed water. As the hydrolysis progresses, this peak disappears and methanol is formed. The band at 791 cm^{-1} which is attributed to Si−O−C bonds disappears after 90 min of reaction, indicating that the silane has been completely hydrolyzed. The band at 1647 cm^{-1} is related to the C=N bond in imidazole; this peak has shifted to 1662 cm^{-1} and remains unchanged in all other spectra. The IR band at 1079 cm^{-1} corresponds to the O−Si−O bond present in the structure of the silane. As the reaction proceeds, this band broadens as Si−O−Si and Si−O−P bonds are formed between precursor materials. Si−OH groups in silica present a band at 955 cm^{-1}, and after 90 min we see this peak disappears as condensation occurs between the OH groups. Peaks at 1120 cm^{-1} are due to formation of Si−O−P bonds;[30] the presence of Si−O−P within the phosphosilicate

gels is expected to enhance retention of absorbed water in gels. The band at 427 cm^{-1} can be assigned to various vibration modes of Si−O−Si bonds which have been formed from the imidazole silane structure. The band at 1392 cm^{-1} corresponds to stretching of P=O from the structure of phytic acid and is present throughout all spectra with a slight shift in its position. The band at 880 cm^{-1} corresponds to the P−O−P linkages present in phytic acid. It is clear that Si−O−P bridges have been formed between silica and phosphate precursors via the sol−gel reaction as they can be found throughout all spectra and further confirmed by ^{29}Si and ^{31}P NMR spectroscopy.

FTIR Studies on Hybrid Membranes. The representative FTIR spectra for unmodified Nafion, imidazole/phytic acid hybrid, and PHPS hybrid after complete hydrolysis and condensation reactions are shown in Figure 2. The major vibrational bands associated with the Nafion membrane are found in all three samples. The C−F stretching vibrations of the PTFE backbone can be observed between 1000 and 1400 cm^{-1}. The peaks that are observed at 1056 and 978 cm^{-1} are attributed to the stretching vibrations of SO$_3^-$ and

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Novel Organic−Inorganic Hybrids

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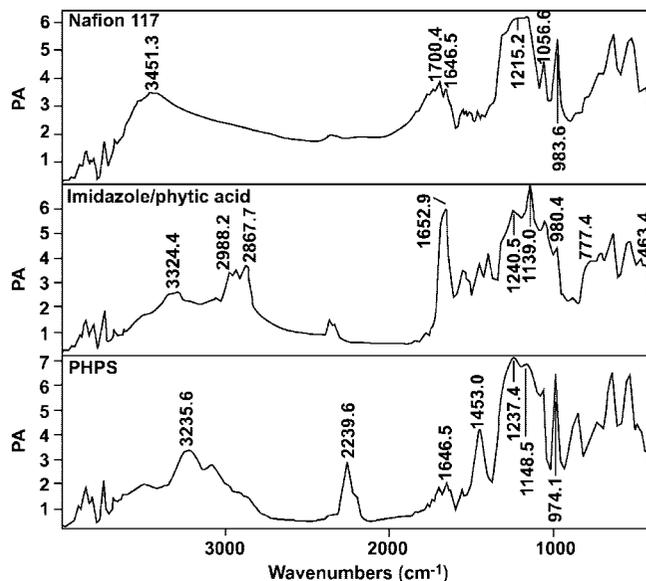
Figure 2. Representative spectra of unmodified Nafion 117, imidazole/phytic acid, and PHPS hybrid membranes.

C−O−C of Nafion, respectively. In the spectrum of imidazole/phytic acid hybrid, the band between 1000 and 1400 cm^{-1} has become broader due to the asymmetric stretching vibration of Si−O−Si groups.[31] This provides evidence of a successful polyfunctional condensation reaction between SiOR groups. It is clear that Si−O−Si groups are the result of the condensation reaction between the hydrolyzed silanol Si−OH groups. The IR band at ∼980 cm^{-1} has broadened in the spectrum of imidazole/phytic acid hybrid as it masks the band at 960 cm^{-1}, which is attributed to Si−OH stretching vibrations. This is related to uncondensed SiOH groups, and it is sometimes referred to as a 'defect band' within the context of network structure.[17] The spectrum of imidazole/phytic acid hybrid is different from the spectrum of the inorganic gel shown in Figure 1 due to the fact that the phosphosilicate gel has been incorporated into the Nafion membrane. In this spectrum there is formation of peaks at 2988, 2931, and 2867 cm^{-1} which are related to the stretching of C−H and Ar−H bonds due to the structure of imidazole. A strong sharp band is present at 1652 cm^{-1} which is related to the C=N bond present in the structure of the imidazole silane precursor. An important and significant peak at 1139 cm^{-1} is due to formation of Si−O−P[30] bonds between the silane and phosphorus precursors within the Nafion membrane. Vibrational bands at 777 and 463 are related to symmetric stretching and bending of Si−O−Si, repectively. In the spectrum of the PHPS hybrid membrane the peak at 1237 cm^{-1} has become much broader in comparison to unmodified Nafion, which is a result of Si−O−Si vibrations. Individual peaks in this region have been masked by the broad peak from 960 to 1380 cm^{-1}, which is attributed to various symmetric and asymmetric stretching bands of Si−O−Si. The above results indicate that Si−O−Si and Si−O−P groups are formed via the sol−gel reaction. The existence of the Si−OH group indicates that the condensation reaction was not completely finished.

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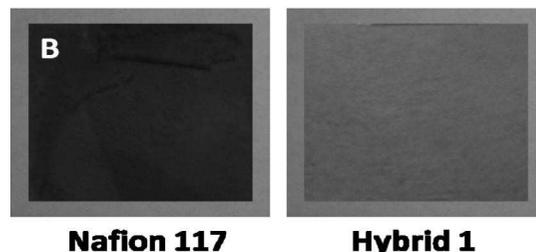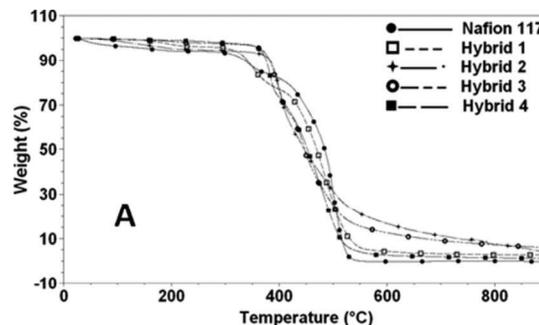
Figure 3. Thermogravimetric analysis (TGA) of Nafion 117 and hybrid membranes (A) and aging test (B).

NMR Study. Formation of phosphosilicate gel in the Nafion membrane was also confirmed by solid-state ^{29}Si and ^{31}P NMR spectroscopy. The ^{29}Si spectrum of the TEOS/phytic acid hybrid shows one peak at −102 ppm. This peak can be assigned to a Q^3 unit,[32] [Si(OSi)$_3$(OH)]. The presence of [Si(OSi)$_2$(OP)(OH)] appears in the range from −102 to −112 ppm; this peak has not been resolved and overlaps the peak corresponding to a Q^3 unit. There is no peak observed at −120 ppm, which is assignable to Q^4 units of Si bonded to four phosphate groups, Si(−O−P)$_4$. The dimensions and geometry of the phytic acid prevent the approach of four bulky groups around a single silicon atom. A major peak at 2.3 ppm and a minor one at −9 ppm is observed in the ^{31}P spectrum of the TEOS/phytic acid hybrid membrane. The major peak can be assigned to free phytic acid molecules, which have infiltrated the membrane but have not reacted with the silane. The minor peak at −9 ppm is assigned to singly bound Q^1 species: O=P(OH)$_2$(O−Si−O).[33] These results show that many phytic acid molecules are covalently bonded to the silica network, forming Si−O−P bonds. NMR spectra of other hybrid systems also confirm silicate and phosphosilicate structures present within the membrane.

Thermal Analysis. *Thermogravimetric Analysis (TGA) of Dry Membranes.* Thermal analysis was used to determine the degradation temperature of the membranes as well as the ratio of inorganic residue within the membrane. Figure 3A shows the thermogravimetric analysis (TGA) results of Nafion and Nafion hybrid membranes. The unmodified Nafion membrane decomposes in three stages, which is clearly seen in Figure 3A. The small weight loss of about 6.15% on heating from 30 to 290 °C can be attributed mainly to loss of residual water within the membrane. The first stage (290−400 °C) is associated with the desulfonation process,[13]

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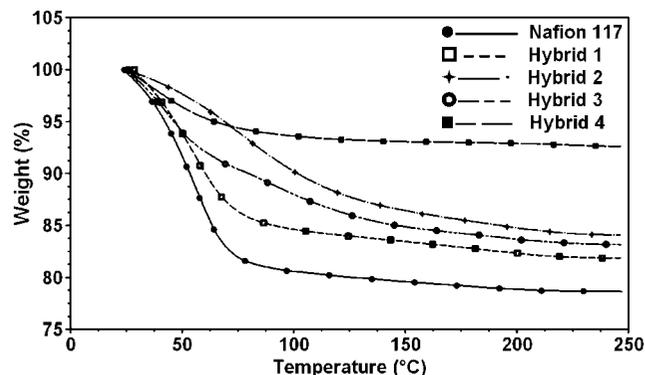
Figure 4. Status of water within membranes.

while the second stage (400−470 °C) may be related to side chain decomposition and the third stage (470−560 °C) to PTFE backbone decomposition.[34] The first stage of mass loss for unmodified Nafion occurs at a temperature of 290 °C.[16] This decomposition behavior can be attributed to desulfonation of sulfonic acid groups present in the unmodified Nafion membrane.[15] This feature shifts to higher temperatures with addition of inorganic particles within the Nafion membrane. All hybrid membranes show an increase in the onset of thermal decomposition in comparison to unmodified Nafion. The onset of thermal degradation has shifted from 290 °C in the unmodified Nafion to 355, 365, and 377 °C in hybrids 4, 3, and 2, respectively. This indicates that the in situ sol−gel reaction increases the thermal stability of the Nafion in the hybrid membrane. This is due to the presence of the inorganic phase and its interaction with sulfonic acid groups. Hybrid 1 shows only a small improvement in thermal degradation temperature as compared to Nafion. Elevation of the onset degradation temperature implies that the inorganic phase may increase the durability of Nafion membranes. At 800 °C, the residual weights are 7.5, 7.3, 2.9, and 1.4 wt % for imidazole, imidazole/phytic acid, TEOS/phytic acid, and PHPS hybrids, respectively. Below 310 °C for all samples there are only small weight changes corresponding to the low molecular weight byproducts, the solvents, and further condensation of silica. TGA results demonstrate that both imidazole and imidazole/phytic acid hybrids are thermally more stable than the unmodified Nafion restricting the desulfonation process due to specific interaction between the inorganic additives and ionic clusters. In addition, an aging test was carried out by placing both unmodified Nafion and Nafion hybrids in the oven at 100 °C for 72 h. After removing membranes from the oven it was observed that the unmodified Nafion membrane had turned dark brown in color whereas the Nafion hybrid membranes remained transparent (Figure 3B). These results also indicate that the presence of particles within the membranes has improved both the thermal and the chemical stability of these materials.

TGA of Swollen Membranes. TGA was also used to determine the status of water in the membranes as a function of temperature. Figure 4 shows the thermogram of Nafion and the hybrid membranes swollen in water for 2 days. Water

retention of proton-exchange membranes is a key parameter for these materials to be suitable for high-temperature fuel cell application. The major problem with the current proton-exchange membranes is that they tend to dehydrate at elevated temperatures, resulting in poor conductivity and cracking of the membrane. These results show that the water retention of the modified membranes has significantly increased compared with the unmodified Nafion membrane. At 70 °C, the unmodified Nafion loses most of the water contained within the membrane. This indicates that the swollen Nafion membrane contains mostly interfacial water, which is only weakly bound to the polymer. All hybrid membranes exhibit lower water uptake than the unmodified Nafion because the inorganic component decreases the elasticity of the ionomer matrix, which thus decreases the swelling of the membranes. The unmodified Nafion has a water uptake of 21%; all hybrid membranes show a lower uptake with 17.5%, 16.5%, 15%, and 7% for TEOS/phytic acid, imidazole/phytic acid, imidazole, and PHPS, respectively. Addition of inorganic particles also reduces the free volume in these membranes and, hence, a decrease in water uptake. Both imidazole and imidazole/phytic acid membranes show continual weight loss up to 200 °C. This indicates that these hybrid membranes contain a high ratio of strongly bound water, which remains within the system above 100 °C. PHPS hybrid membrane had the lowest water uptake due to the inorganic particles increasing the stiffness of the membrane significantly as shown by DMA (discussed later). This in effect reduces the elasticity of the polymer matrix and hence decreases the swelling behavior. Hybrid 1 had the highest water uptake in comparison to other hybrids even though inorganic content was low. TEOS has four alkoxy groups in its structure, which can be fully hydrolyzed and form an extensive phosphosilicate network with phytic acid, allowing more water to be bound to the inorganic network. Both imidazole-containing hybrid membranes show the best water retention properties as their weight loss profile is more gradual with temperature and occurs over a larger temperature range than unmodified Nafion and other hybrid membranes. The presence of phytic acid within the membrane helps contribute to the water uptake of the hybrid, which is due to the multifunctional hydroxyl groups present in the structure. There are 12 proton dissociation sites on the phytic acid molecule, six of which are strongly acidic with an approximate pK_a value of −1.5, which can form strong hydrogen bonds with water molecules. The enhanced water retention properties of these hybrids can be attributed to the hydrophilic nature of the inorganic additives within Nafion, which form strong hydrogen bonds with water molecules and require a higher temperature for dissociation of these bonds. Wang et al.[35] described the thermal dehydration of Nafion as a two-step process, which can be related to the two fundamentally distinctive structural regions of the polymer. The fast dehydration process is attributed to the high water content of Nafion, with percolation structure, where hydrated ionic clusters are interconnected by channels. The slow dehydration process is related to the low water

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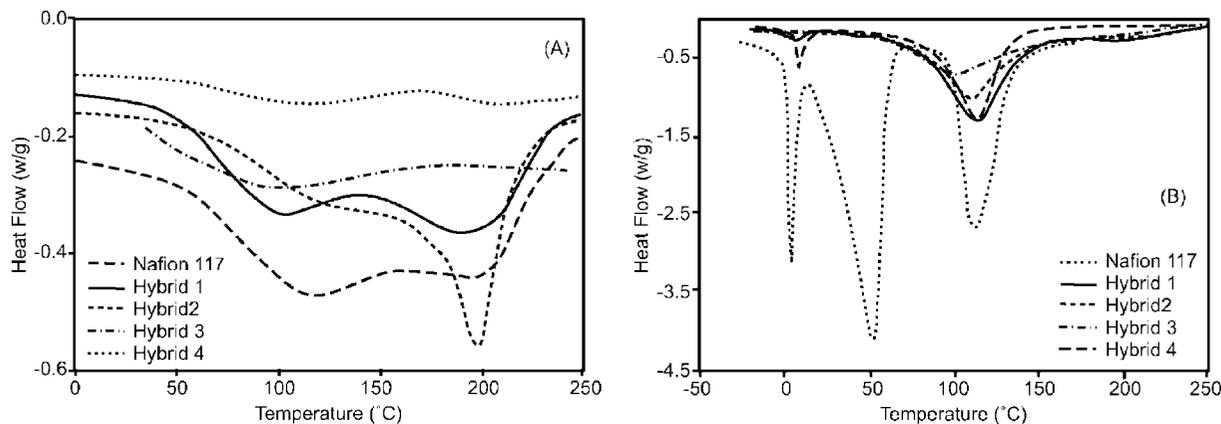
Figure 5. DSC curves of Nafion and the hybrids in dry (A) and swollen state (B).

content of Nafion 117 where ionic clusters are isolated with no interconnected water channels. Thermal dehydration of Nafion involves organization of microstructure from a percolation to isolated cluster structure. In ionic clusters, water molecules are found in the core and interact with the sulfonate groups through hydrogen bonding. These interconnected channels between clusters are formed by interfacial water, which is only loosely bound to the membrane. Unmodified Nafion shows a two-step water loss profile; weight loss up to 80 °C can be attributed to interfacial water within the interconnected channels between the ionic clusters. This is followed by a much slower weight loss profile as shown and is due to strongly bonded water within the ionic clusters. Modified hybrid membranes show a similar weight loss behavior to that of the unmodified membrane. However, the initial dehydration process of hybrid membranes shows a more gradual drop in weight loss. The slow dehydration process, which is correlated to low water content and isolated cluster morphology of Nafion, occurs over a larger temperature range for the hybrid membranes. This indicates inorganic moieties that reside within the ionic domains of Nafion increase the amount of hydrogen-bonded water in the ionic clusters. Bonded or nonfreezable water refers to water molecules embedded in the structure, bonding with inorganic and ionic moieties. It is clear that the hybrid membranes show enhanced water retention properties over unmodified Nafion, suggesting that hydrophilic inorganic additives can strongly bind water at elevated temperatures.

Differential Scanning Calorimetry (DSC) of Dry Membranes. DSC was used to determine the influence of inorganic particles on the thermal transition behavior of the membranes as a function of temperature. DSC curves for dry unmodified Nafion membrane and hybrid membranes under nitrogen in the range from −50 to 250 °C are shown in Figure 5A. The unmodified Nafion membrane shows a large endothermic peak at 125 °C. This peak is related to the T_g of Nafion as observed by DMA also (discussed later). This endothermic peak can also be attributed to structural changes in ionic clusters, which is associated with the order destruction in these domains. Tadano et al.[36,37] assigned this

endothermic peak to an order−disorder transition inside the ionic clusters. According to Mauritz et al.,[38] this behavior is associated with the molecular rearrangements inside the polar phase of the base polymer. Hybrid membranes show a different behavior to that of the Nafion membrane due to incorporation of inorganic additives. Both TEOS/phytic acid and imidazole/phytic acid hybrids (hybrids 1 and 3) show a very similar DSC profile. The first endothermic peak is similar to that of the Nafion membrane, which is related to changes in ionic clusters and release of water. There is another endothermic peak present in these two hybrids at 200 °C, which is attributed to release of hydrogen-bonded water within the membrane.[19] In the imidazole hybrid (hybrid 2) condensation is not complete and the sharp endothermic peak at 200 °C can be related to release of water and alcohol as condensation occurs between the silanol groups. There are 12 proton dissociation sites on the phytic acid molecule, six of which are strongly acidic, three sites are weakly acidic, and the remaining three are very weakly acidic. The first peak in both TEOS/phytic acid and imidazole/phytic acid is related to loss of water from the weakly and very weakly acidic sites of phytic acid, while the peak at ∼200 °C corresponds to loss of water from the six strongly acidic sites. Incorporation of inorganic additives introduces strong hydrogen-bonding sites within Nafion in the form of Si−OH and P−OH groups. FTIR in Figure 2 confirms the presence of strongly bound water in these membranes due to the broad band present between 3000 and 4000 cm^{-1}. TGA of the hydrated membranes also shows that these membranes continue to lose bound water up to 220 °C. The imidazole hybrid shows a different behavior to that of Nafion and phytic acid containing hybrids. There is a major sharp endothermic peak at 200 °C with a shoulder present at 125 °C. The peak at 200 °C is due to release of strongly bound water, as evidenced by TGA results. The PHPS hybrid membrane shows a completely different pattern to all other membranes with two very small peaks: one at 125 °C and the other just above 200 °C, which are attributed to the same phenomena as in other hybrid membranes. However, due to the small inorganic content, the amount of bonded water is relatively small. Endothermic peaks are very small due to the very small amount of inorganic component in this hybrid. Table

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Table 2. DSC Data Showing Temperature and ΔH Changes for Endothermic Peaks in Nafion 117 and Hybrid Membranes

membrane	T_1 (°C)	ΔH_1 (J/g)	T_2 (°C)	ΔH_2 (J/g)
Nafion 117	125	28.7		
hybrid 1	104	82.8	193	91.4
hybrid 2	134	67.1	198	100.7
hybrid 3	120	143.3	194	80.9
hybrid 4	100	21.7	215	5

2 shows the endothermic peak temperatures for Nafion and hybrid membranes with the corresponding enthalpy values. The blank Nafion membrane shows only one major endothermic peak at 125 °C, while in the hybrid membranes (except the imidazole hybrid) the first endothermic peak shifts to lower temperature; this can be associated with a water plasticizing effect in the membrane. Since the inorganic component is hydrophilic it can absorb a greater content of water molecules; this absorbed water increases the free volume, increasing the chain mobility and decreasing temperature T_1. All hybrids have higher enthalpy values than blank Nafion for the first endothermic peak. This is due to water being bound to the hydrophilic inorganic component, which requires more energy to release. In hybrid membranes there is a second endothermic peak, which is attributed to tightly bound water within the hybrid membranes. Enthalpy values for the second endothermic peak show more energy is required to release the nonfreezable water contained within these hybrid systems. The imidazole/phytic acid hybrid contains the most bound water with enthalpy 224 J/g followed by TEOS/phytic acid and imidazole systems (hybrids 1 and 2).

DSC of Swollen Membranes. DSC analysis was used to determine the states of water present within the unmodified and inorganic modified membranes in the hydrated state. Figure 5B shows the DSC curves of unmodified Nafion and hybrid membranes in a hydrated state. The structure and organization of water within hybrid membranes is a key factor when preparing a proton-exchange membrane. Water can exist in a number of different states ranging from normal bulk water to water molecules hydrogen bonded to hydrophilic parts of the hybrid membrane. This behavior is usually approximated by a three-state model[39] which hypothesizes the existence of three different types of water in the polymer membrane; they are free water, interfacial water, and bound water. The free water consists of molecules not bound to the polymer and is characterized by melt temperature and enthalpy data similar to that of pure water.[40,41] The bound water strongly interacts with the polymer chain, and no detectable transition is observed in the −70 to 0 °C temperature range which is usually associated with water freezing/melting transitions.[40,42] The interfacial water weakly interacts with the polymer and is characterized by a phase transition temperature significantly lower than 0 °C. The unmodified Nafion membrane shows a number of different peaks related to water and cluster transitions of the polymer. The endothermic peak at 0 °C corresponds to the melting of ice of absorbed water. The larger broad peak at about 50 °C is due to the release and vaporization of water and is consistent with TGA results. The presence of the inorganic component has had an effect on the ionic aggregation within the membranes, and thus, the endothermic peak at 110 °C due to cluster transitions[43] is not seen in hybrid membranes. Therefore, the small endothermic peaks seen in hybrid membranes in the same temperature range can be attributed to release of bound or nonfreezable water. This can be explained in terms of increased hydrogen bonding between the hydrophilic inorganic phase and water, which shows strong bonding interactions. From the results obtained it can be concluded that incorporation of inorganics enhances the water retention properties of Nafion membrane at temperatures above 100 °C.

Dynamic Mechanical Analysis. DMA was used to determine the cluster relaxation T_c and the influence of inorganic content on the mechanical strength of the membrane. The tan δ curves for the hybrid membranes and Nafion are shown in Figure 6. For all the membranes the ionic cluster transition T_c was obtained from the peak of the tan delta (δ) curve. Nafion has a T_c of 116.8 °C, and it can be seen that the T_cs of all hybrid membranes are very broad and shift to higher temperatures. It is widely known that above 115 °C the network of hydrophilic clusters, made up from sulfonic groups, is becoming extremely mobile before the clustered structure finally collapses.[44] This can be due to either loss of water under dry and hot conditions or further uptake of solvents if exposed to saturated solvent/water vapor. This high mobility of the backbone and cluster network is shown by a higher value of loss tangent for unmodified Nafion in comparison to hybrid membranes. Further, we see that the T_c increases for the hybrid membranes, which implies that they are thermomechanically more stable than unmodified Nafion membrane. This increase in T_c results in a decrease in the free volume of Nafion, which is also seen by a lower water uptake of the hybrids by TGA of swollen membranes. For hybrids 2, 3, and 4 the onset of the T_c peak starts at 150, 130, and 140 °C, respectively. Incorporation of particles within the membrane has formed strong interaction between the inorganic component and polymer matrix and increases rigidity in the membrane. However, the T_c of the hybrid membranes appears to be very broad over a higher temperature range. This indicates that the segmental mobility in hybrid membranes occurs over a very broad temperature range. The hybrid membranes thus become more stable in nature and can withstand higher temperatures due to the presence of the inorganic additives within the pores of unmodified Nafion 117.[15] These results are also in agreement with the TGA results, which show an increase in the degradation temperatures for the hybrid membranes.

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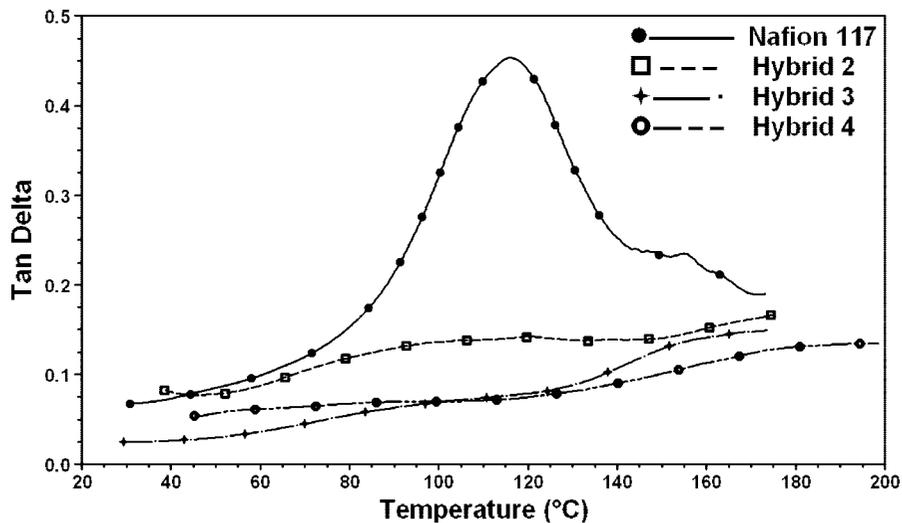
**Figure 6.** Tan delta curves of selected hybrid membranes.
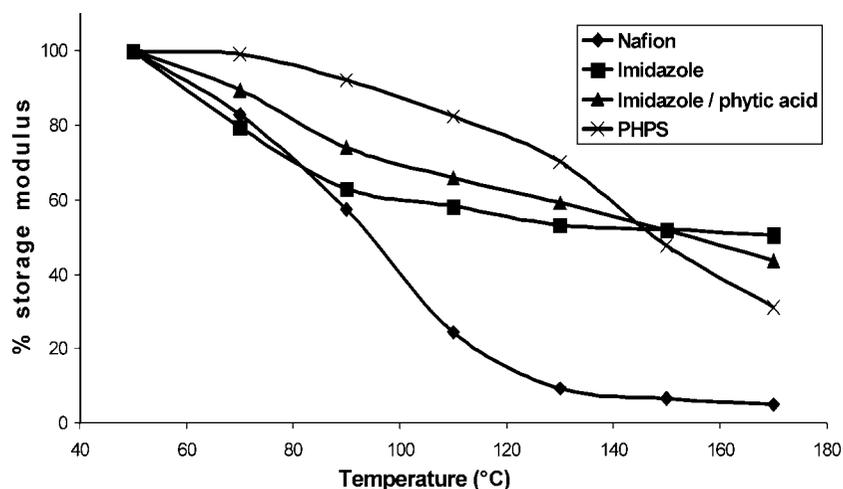
Figure 7. Storage modulus vs temperature plots for the hybrids.

Table 3. Comparison of Storage Modulus (E') Values of the Membranes at Different Temperatures

sample	E'/MPa at 50 °C	E'/MPa at 70 °C	E'/MPa at 90 °C	E'/MPa at 110 °C	E'/MPa at 130 °C	E'/MPa at 150 °C	E'/MPa at 170 °C
Nafion 117	146	121	83.8	35.6	13.6	9.63	7.13
hybrid 3	114	102	84.4	75.1	67.5	59	49.8
hybrid 4	115	114	106	94.8	80.7	54.9	35.8

Figure 7 shows the normalized plot of storage modulus as a function of temperature for selected hybrid membranes. The values of storage modulus for the membranes are listed in Table 3. The moduli for all samples decrease with temperature as the samples pass from the glassy to rubbery state. Unmodified Nafion shows the highest decrease in storage modulus from room temperature up to 170 °C. The imidazole hybrid shows the lowest decrease in modulus but remains more mechanically stable at temperatures above 130 °C than the unmodified Nafion. Imidazole/phytic acid hybrid displays a steady decrease in its elastic modulus, whereas PHPS hybrid shows higher strength below 150 °C but decreases rapidly once it passes from the glassy to the rubbery state. The T_c of PHPS hybrid has increased significantly over unmodified Nafion by incorporation of silica within the membrane. Even though this hybrid membrane has the lowest inorganic content, it shows the highest storage modulus. In this hybrid, the particle size is much smaller

than other systems, and there is an even distribution of silica throughout the membrane. Smaller particles enhance the effect of the filler on the stiffness of the material as there is greater interaction between inorganic component and polymer. Other composite membranes such as imidazole and imidazole/phytic acid also show an increase in their T_cs in comparison to neat Nafion. At 170 °C all hybrid membranes exhibit higher stiffness than Nafion, indicating that the inorganic additives contribute significantly to the materials mechanical strength. The inorganic component also contributes to a decrease in segmental mobility of polymer chains, which results in an increase in rigidity of composite membranes. In addition, the free volume in Nafion decreases by uptake of inorganic moieties and is seen by an increase in their storage modulus. Increase in T_c of composite membranes has considerably improved the thermomechanical properties of these membranes at temperatures up to 170 °C.
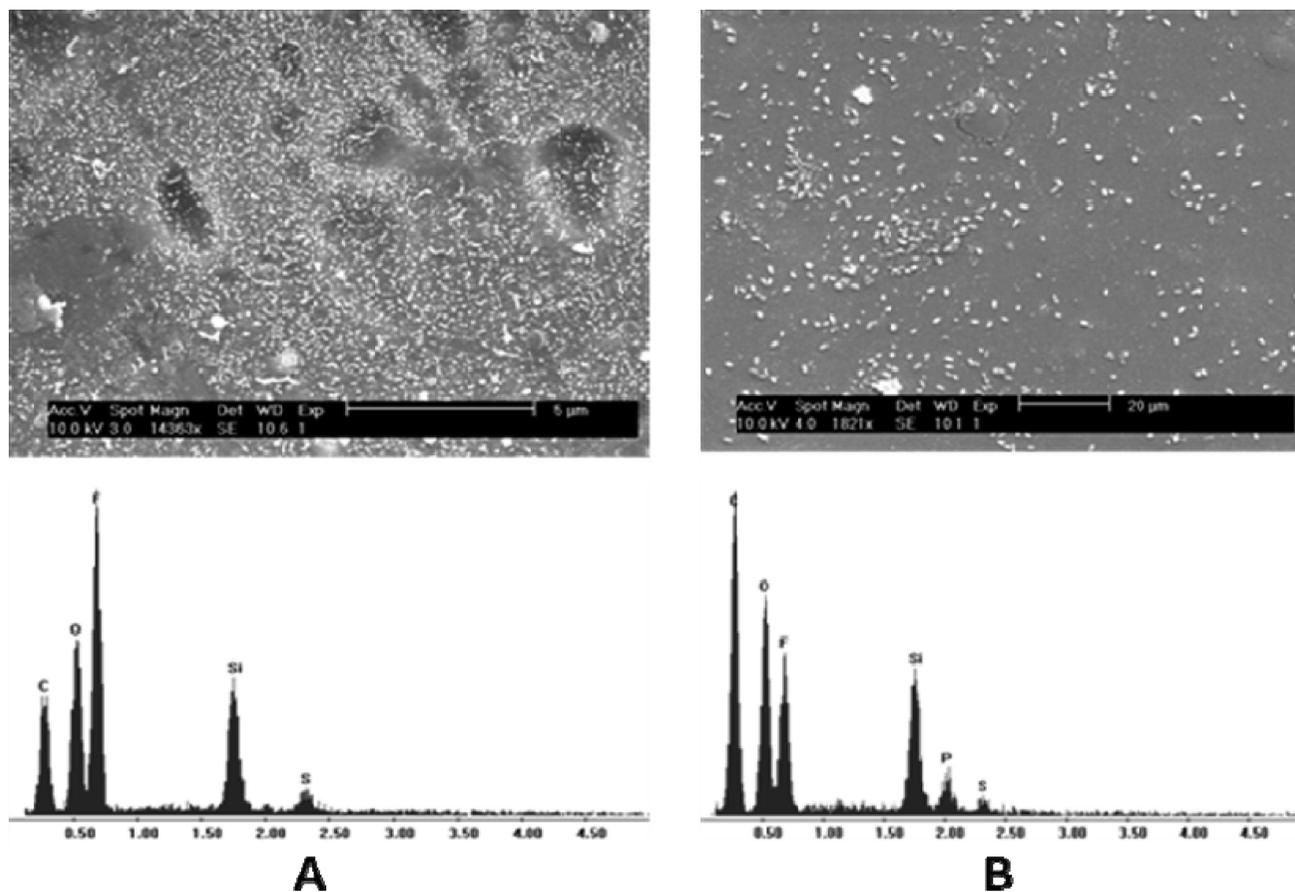
Figure 8. SEM-EDX of PHPS (A) and imidazole/ phytic acid (B) hybrid membrane.

Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX). SEM-EDX was performed to determine the morphology of the membrane and the elemental composition on a micrometer scale. Figure 8A shows representative SEM images and compositional analysis by EDX of PHPS hybrid membrane. It can be seen that there is a distribution of particles present in the membrane. The micrograph shows that these silica particles are distributed with a particle size between 40 and 100 nm. Incorporation of these silica particles significantly changed the properties of the Nafion membrane as shown by thermal analysis. T_c and thermal stability also increase due to the presence of these particles within the membrane. In contrast, the imidazole/phytic acid hybrid shows a very different morphology to that of the PHPS hybrid, which is clearly seen in Figure 8B. These particles are elongated in shape as opposed to spherical particles in PHPS hybrid, and some particles are shown to have agglomerated to form larger structures. The size of these ellipsoid particles has been calculated to be 900 nm in length and 200 nm in width. The difference in particle size and shape between PHPS and imidazole/phytic acid hybrids is due to the stabilization effects of phytic acid. Because of its structure, phytic acid is a good catalyst for hydrolysis of alkoxysilanes and a condensation center for subsequent gel growth.[45] The hydroxyl functionality in the phytic acid structure allows growth of a network structure and hence larger aggregation and particle size in the imidazole/phytic acid hybrid. Elemental analysis on particles shows the presence of both silica and phosphorus, confirming that phosphosilicate gels have formed inside the hybrid

membrane. The difference in the morphology between these two systems can be attributed to sample preparation in different solvents, as solvent can play a significant role in determining the final morphology. In the case of the PHPS hybrid, xylene was used as the solvent for directing inorganic particles within the membrane. Xylene is a hydrophobic organic solvent, so silica particles are directed to the hydrophobic fluorinated backbone of the polymer with even distribution in the matrix. This is reflected by the high storage modulus values from DMA. The imidazole/phytic acid hybrid was prepared using ethanol which is a polar solvent. In this case inorganic networks are more directed toward the ionic clusters of the polymer annd hence the resulting morphology. The EDX spectrum of the PHPS hybrid shows a F/Si ratio of 2:1 and a C/Si ratio of 1:1; due to inorganic particles being directed to the hydrophobic part of the membrane, fluorine content is much higher on the surface. In the case of the imidazole/phytic acid hybrid the F/Si ratio is 1:1 and the C/Si ratio is 2:1. In this hybrid system ethanol was used to prepare the membrane, which directs inorganics to the hydrophilic part of the membrane, bringing carbon to the surface of the membrane. The TEOS/phytic acid and imidazole hybrid membranes both show ellipsoid particles due to the network structure formed.

Proton Conductivity Measurements. Proton conductivity of unmodified Nafion and hybrid membranes was measured at various temperatures and relative humidities, and results

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Table 4. Inorganic Content, IEC, λ Values, and Proton Conductivity of Nafion 117 and the Hybrids

sample	inorganic composition (%)	λ	proton conductivity (mS/cm)			
			30 °C/30% RH	30 °C/90% RH	80 °C/30% RH	80 °C/90% RH
Nafion 117	0	5.1	4.5	80.1	8	99
hybrid 1	2.9	9.9	4	26	7.2	89
hybrid 2	7.5	10.3	1	12.5	1.3	26
hybrid 3	7.3	5	0.31	1.2	0.012	2.7
hybrid 4	1.4	6.5		3.5	0.11	10

are shown in Table 4. The results in Table 4 show that the conductivity decreases as relative humidity decreases due to a decrease in water content. The general trend for unmodified Nafion is that conductivity increases with both an increase in temperature and relative humidity with the highest conductivity of 99 mS cm^{-1} at 80 °C and 90% RH. Incorporation of the inorganic additives to the polymer matrix has resulted in a decrease in conductivity compared to that of the unmodified membrane. Such low conductivities in the organic−inorganic hybrid membranes could be ascribed to a number of factors,[46,47] such as restricted proton mobility due to an increase in rigidity and decrease in free volume, which result in a decrease in water uptake. The TEOS/phytic acid hybrid shows the highest conductivity for composite membranes due to high water uptake in comparison to other hybrid systems. At 80 °C and 90% RH, this hybrid shows conductivities of 89 mS cm^{-1}, similar to that of Nafion at the same conditions (10% drop). At 80 °C and 30% RH, it shows only 10% drop in conductivity from that of unmodified Nafion. Imidazole/phytic acid hybrid shows unusually low conductivity values at all experimental conditions. This indicates that the presence of inorganic component has disrupted the proton-transfer pathway in this particular system. The imidazole hybrid performed much better than the imidazole/phytic acid system, and the conductivity of this membrane follows the same trend as Nafion but shows much lower values at different temperatures and humidities. This can be attributed to the increase in T_g, which restricts proton transfer and segmental mobility. At low temperature and RH, the PHPS hybrid was resistive and conductivity could not be obtained at 30 °C and 30% RH. SEM-EDX results show that this hybrid has more hydrophobic fluoro component and silica on the surface, which lowers the free volume within the membrane and explains low conductivity results. However, at higher temperature conductivity increases significantly from 3.5 mS cm^{-1} at 30 °C to 10 mS cm^{-1} at 90 °C due to the enhanced mobility within the membrane. Conductivity is primarily determined by the content of the inorganics, hydroxyl bonds, and water molecules within the membrane, and hence, water management is essential to maintain the conductivity.[15] Incorporation of silica and phosphosilicates inside the membrane was envisaged to aid water retention at high temperatures due to their hydrophilic nature. The number of water molecules per sulfonic acid group (λ) is listed in Table 4 for both unmodified Nafion and hybrids. Both TEOS/phytic acid and imidazole hybrid membranes show a considerable increase

in λ values and are around double the value of Nafion. However, this did not improve the conductivity over Nafion as the excess water molecules are likely to be involved in hydrating the incorporated silica and phosphosilicates rather than sulfonic acid groups. λ values for hybrid membranes are well below the required number for proton transfer. Hence, water available for either the hopping mechanism or solvating protons for migration purposes may be lower in a high-density medium, resulting in a decreased proton diffusion and conductivity.[16] All proton conductivity measurements show considerably lower conductivity values than that of the unmodified Nafion. In Nafion-based membranes, the proton migration is primarily by the Grotthuss mechanism.[48] In this mechanism, the proton which forms H_3O^+ ion jumps to the neighboring lone pair of electrons of a water molecule. The proton conduction in these membranes is an intimate function of crystallinity, equivalent weight (EW), RH (water content), and IEC. In hybrid membranes inorganic moieties have restricted diffusion and permeability of water in hybrids, which play a key role in the conductivity of membranes. It was envisaged that modifying Nafion to make an organic−inorganic hybrid would increase conductivity values above the Nafion 117 membrane. However, TGA of these samples confirms the presence of inorganics within the film which is incorporated in the membrane to retain water at higher temperatures. This is also verified by DSC analysis, which confirms that the presence of inorganics within the membrane help the hybrids to retain water above 100 °C. Thus, the major component in the hybrid membranes is actually bound water, while DMA demonstrates the shift in T_c of the hybrid membranes to a higher temperature. The cluster transition temperature of Nafion is between 110 and 115 °C; below this temperature molecules are not very mobile. The osmotic pressure in the membranes is significantly higher below this transition temperature, which prevents the mobility of protons within the membrane, and hence, conductivity is reduced. Several studies have reported that modifying Nafion with inorganics has resulted in decreased proton conductivity of the sample.[11] This is partly because (1) the relatively low conductivity of organosilica (2) and the slightly tortuous path through the membrane which is caused by the embedding of the organosilica into hydrophilic clusters.[46] Early work by Alberti et al.[44] shows that modification of polymers decreases the mobility and/or effective concentration of the charge carriers, which are responsible for proton conduction.

Structure Analysis by Small Angle Neutron Scattering. Structure analysis by small-angle neutron scattering. Small-angle neutron scattering (SANS) is a powerful tech-

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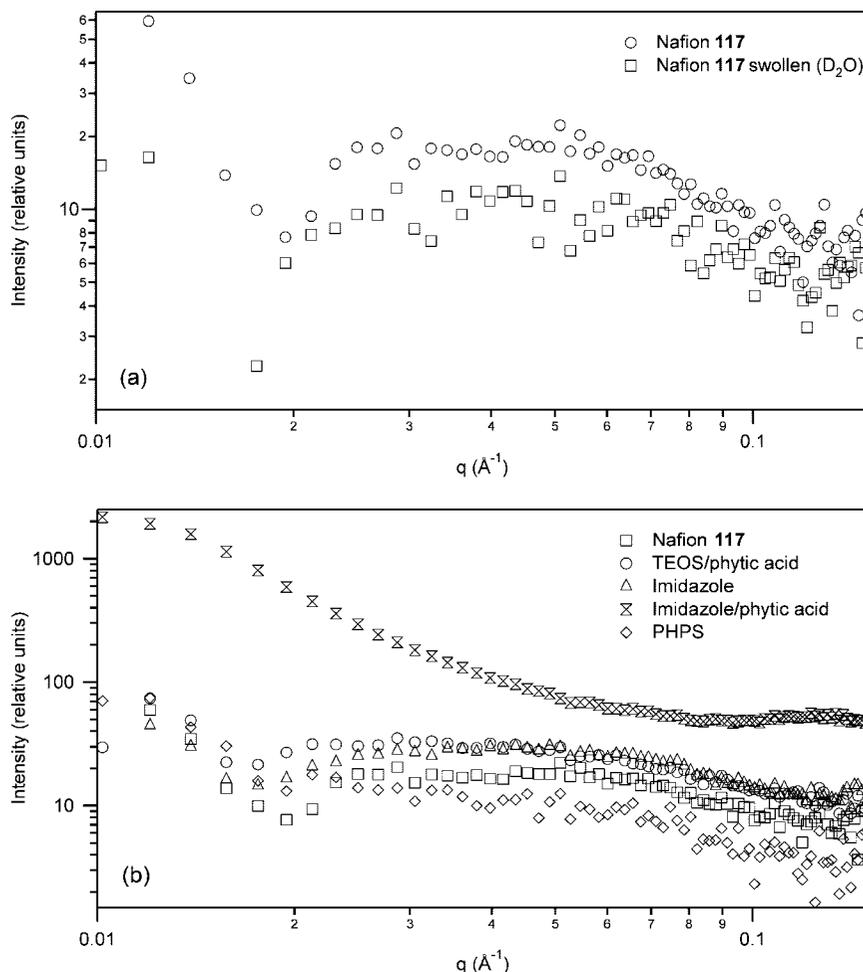
Figure 9. SANS spectra of Nafion 117 and the hybrids in dry (top) and swollen (bottom) state.

nique to identify structural organization within polymer systems and has been used extensively to study the nano-structure of Nafion membranes.[49-52] The random ionic clusters in Nafion act as a local cross-link and give rise to a local variation in cross-link density. Such network, on swelling in a low molecular weight solvent, exhibits competition between the osmotic pressure and the local elastic junction, resulting in local variation in polymer concentration. Depending on the size range of such variations, they can be well studied by SANS. Additionally, the proton conductivity and membrane performance are directly related to its ionic conductivity and subsequently to the ionic and water content. A number of small-angle scattering studies (both SAXS and SANS) have been done on perfluorosulfonate ionomer membranes which consistently show characteristic profiles of these membranes with three basic features: (1) a peak at approximately $q \approx 0.2$ Å^{-1} which is attributed to the clustering of acidic groups (ionomer peak), (2) a broad peak at $q \approx 0.04$ Å^{-1} which is related to crystalline regions within the membrane, and (3) an increase in intensity in the very low q region ($q < 0.01$ Å^{-1}) which is due to large-scale

heterogeneities. SANS was performed in the q range $0.01-0.1$ Å^{-1} to probe the structure of Nafion hybrids at molecular length scale. Figure 9a shows the SANS profiles of unmodified Nafion membranes in dry and swollen states. Due to the limitations of the SANS instrument used in this work (e.g., medium q instrument with relatively low neutron flux), the shape, size, and structure of larger features that appear in the region of $q < 0.01$ Å^{-1} cannot be seen.

The SANS profile of the unmodified Nafion membrane shows a higher intensity in the low q region and a lower intensity in the high q range. The low q contribution reflects the presence of large-scale heterogeneities, and the higher q region shows the presence of smaller form factors due to short-range ordered structure. The high q region exhibits a broad maximum centered on $q \approx 0.04$ Å^{-1} and is attributed to the crystalline region of Nafion. This broad crystalline peak is due to the stress induced and/or nonisothermal crystallization during membrane fabrication and is affected by membrane thickness during processing.[53] The increase in intensity below $q = 0.02$ Å^{-1} is likely to originate from clustering of the crystalline phase, forming larger scale structures. The SANS profile of the D$_2$O swollen Nafion membrane shows a very similar trend to that of the dry membrane but a slightly lower intensity. This indicates that

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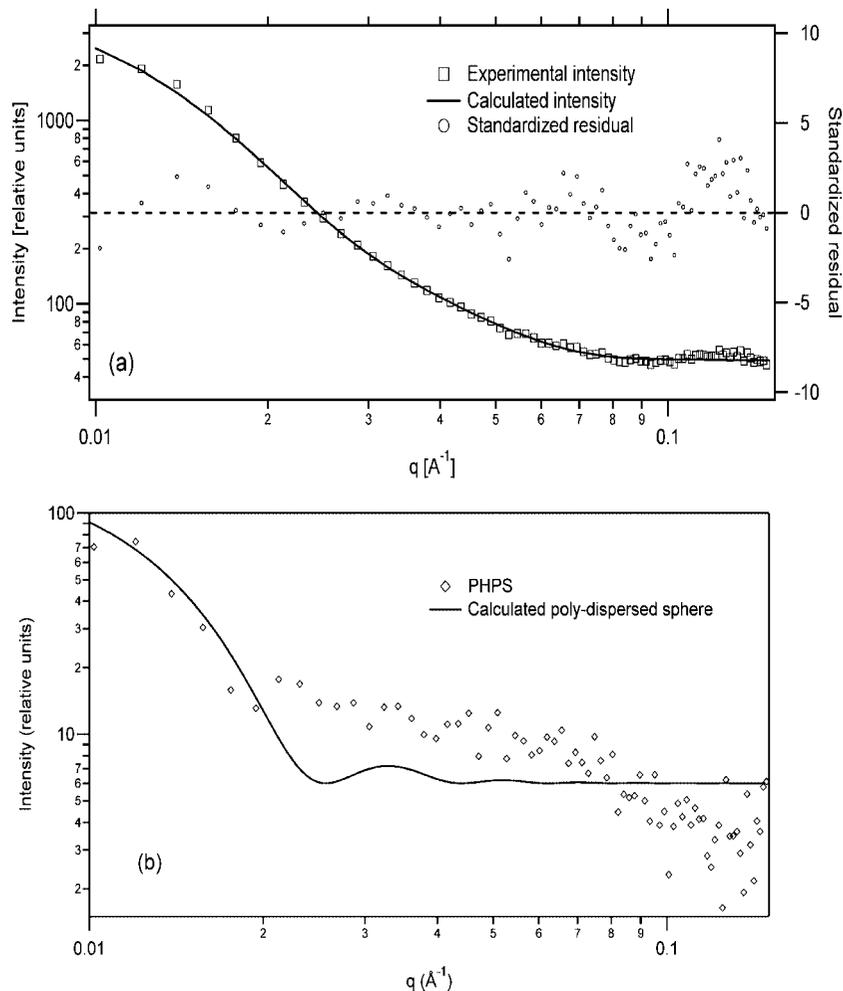
Figure 10. SANS model fitting: (top) imidazole/phytic acid hybrid and (bottom) PHPS hybrid.

the crystalline region of Nafion is unaffected by water uptake due to its hydrophobic nature. Previous studies have reported that the ionic peak shifts to lower q values (higher d spacing) as the volume fraction of solvent in the membrane increases due to expansion of the distance between the ionic domains.[52] Because the broad peak at $q \approx 0.04$ Å^{-1} represents correlation between crystalline regions within the membrane, its position yields information about the nature of swelling within the ionic regions of Nafion separating the crystalline regions.

Figure 9b shows the SANS profiles of the different hybrid systems prepared from Nafion. TEOS/phytic acid, imidazole, and PHPS hybrid membranes show a very similar SANS profile to that of the unmodified Nafion membrane. From these results it is suggested that addition of the inorganic additive to the polymer matrix has no effect on the crystalline region. The inorganic phase, therefore, resides within the ionic domains of Nafion except in the PHPS hybrid where inorganic particles are directed to the fluoro matrix. The imidazole/phytic acid hybrid shows a much different SANS profile compared to that of the unmodified Nafion membrane. The SANS profile for this hybrid shows a nice, evenly distributed scattering dependence on q. A high scattering intensity is shown in the low q region relating to growth of larger inorganic aggregates and decreases monotonically to the higher q region. The broad crystalline peak observed in

other membranes is not seen in the profile of the imidazole/ phytic acid system. This suggests that the inorganic phase in this hybrid system has disrupted the crystalline domains within the membrane. The intensity scale shows high intensity in comparison to other systems as there is good contrast in this sample. The high intensity seen in the imidazole/phytic acid hybrid is due to the increased number of particles within the system.

Model Development. Plausible models were developed for the SANS profiles for two representative solvent-directed systems: the imidazole/phytic acid and PHPS systems. Because of the limited q range (only one decade) and the limited signal-to-noise (low neutron flux) it was not possible to rigorously fit mathematical models to the experimental data. However, it was possible to select a model using all the data obtained from other techniques and explore the agreement between the model and the experimental SANS data. The SANS profile for the imidazole/phytic acid hybrid membrane was fitted to a prolate ellipsoid model, and the results are shown in Figure 10a (mean radius 91.1 Å and axial ratio 1:4). It was not possible to fit a spherical model to the SANS profile. These results are consistent with the morphology of this hybrid membrane shown by SEM.

The SANS profile for the PHPS hybrid shows a different q dependence than that of the imidazole/phytic acid hybrid, and a polydispersed spherical model was manually matched

to the experimental data (Figure 10b). The mean size of the spherical particles from this model was estimated to be ~400 Å diameter, and similar values were obtained from the SEM images. From SEM it was shown there was considerable variation in the size of particles with a range of ~400−1000 Å; therefore, the SANS profile is only due to the smallest particles. Due primarily to the experimental data (limited q range and very low signal to noise) and polydispersity, clearly the agreement between the experimental data and the calculated form factor is indicative. Nevertheless, the poly-dispersed spherical model suggests agreement between the SANS profile obtained from a bulk sample and a SEM image obtained from a sample cross-section.

Conclusion

In summary, we demonstrated formation of hybrid Nafion membranes with silica and phosphosilicates via the sol−gel process. Using different solvents, we can direct the inorganic component to a specific phase of the membrane. PA-FTIR results demonstrate formation of Si−O−Si and Si−O−P bridges within the membrane structure. Incorporation of functional inorganic additives within the membranes has enhanced the water retention properties up to 200 °C over unmodified Nafion, suggesting that the inorganic component can bind and hold water at elevated temperatures. The hybrid membranes show an increase in their thermal stability and increase in T_c due to interactions between the inorganic component and the polymer membrane. Morphological evidence shows an even distribution of inorganic particles throughout the membrane in most cases. SANS study reveals differences in scattering behavior between the hybrid mem-branes. Scattering data for the TEOS/phytic acid and imidazole hybrids suggest that inorganic additives have not disrupted the ionic cluster within the membrane. However,

the imidazole/phytic acid hybrid shows a very different scattering pattern, indicating that the inorganic phase has disrupted the orderly formation of ionic domains and disrupted the proton-transfer pathway. Model fitting of the PHPS and imidazole/phytic acid systems shows sphere and ellipsoid models, respectively, to describe best the shape and size of inorganic particles in these systems. These results were consistent with the morphology as shown by SEM. Proton conductivity results of hybrid membranes show a decrease in conductivity values of all the samples in comparison to that of unmodified Nafion membranes, indicating that the presence of inorganic particles has influenced the proton-transfer pathways. Below the T_c the ionic clusters of the hybrid membranes are in a state where their mobility is restricted causing a decrease in proton conduction. However, conductivity values were only margin-ally lower than that of unmodified Nafion at low humidity and elevated temperature. Further conductivity measurements at high temperature are required to determine the true performance of these materials as a high-temperature proton-exchange membrane. From this study it can be concluded that the imidazole- and TEOS-based hybrid membranes show promise for fuel cell application.