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Advanced Mesostructured Hybrid Silica−Nafion Membranes for High-Performance PEM Fuel Cell

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Organic−inorganic hybrid membranes of Nafion and mesoporous silica containing sulfonic acid groups were synthesized using the sol−gel process with the goal of increasing the proton conductivity and water retention at higher temperatures and lowering relative humidities as well as improving the dimensional stability. These hybrid membranes were prepared via in situ co-condensation of tetraethoxysilane and chlorosulfonylphenethylsilane via self-assembly route using organic surfactants as templates for the tuning of the architecture of the silica or hybrid organosilica components. In this paper, we describe the elaboration and characterization of new hybrid membranes all the way from the precursor solution to the evaluation of the fuel cell performances. These hybrid materials were extensively characterized with the determination of their physicochemical and electrochemical properties. The membrane containing functionalized silica showed a higher ionic exchange capacity and greater water management than standard Nafion. The hybrid membranes showed improved proton conductivity at 95 °C and over the whole range of relative humidity in comparison to recast Nafion and Nafion 112 membranes.

Introduction

Fuel cell technology has emerged in recent years as a keystone for future energy supply. Proton exchange membrane fuel cells (PEMFCs) have attracted much attention as clean energy sources because of their high power density and efficiency with low emission levels for various applications such as electric vehicles, portable electronics, and residential power generation.[1] Up to now, perfluorosulfonic polymers such as Nafion have been the reference membrane for fuel cells because of their high electrochemical properties as well as excellent chemical resistance.[2] There is an extensive literature reporting physical, chemical, and operational data for these materials.[3–6] Nafion is usually made with a polytetrafluoroethylene backbone and perfluorinated vinyl ethers pendant side chains terminated by a sulfonate ionic group.[3,4] Because of this amphiphilic composition, a nanophase separation occurs between the hydrophobic matrix and hydrophilic ionic domains in hydrated Nafion.[4,7] Therefore, such a membrane must be fully hydrated for good proton conductivity and usually operates at temperatures below 80 °C.

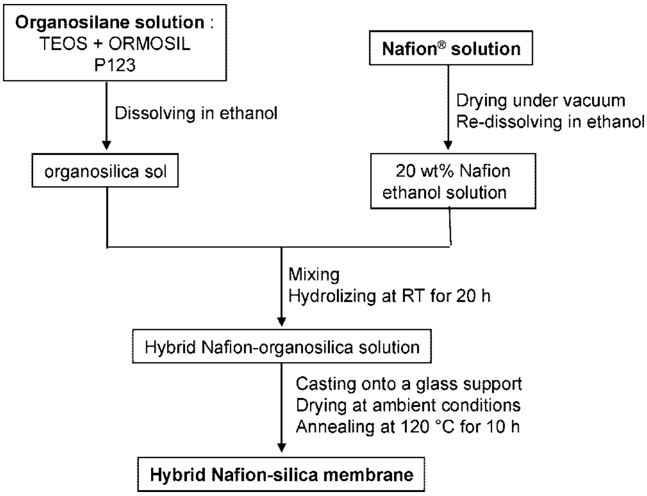

Figure 1. Preparation protocol of Nafion/mesoporous silica hybrid membranes.

To enable high-energy-consumption applications like transportation and to limit the poisoning of anode catalysts by trace amounts of CO, the operating temperature must be increased above 100 °C.[8–10] However, at these temperatures,

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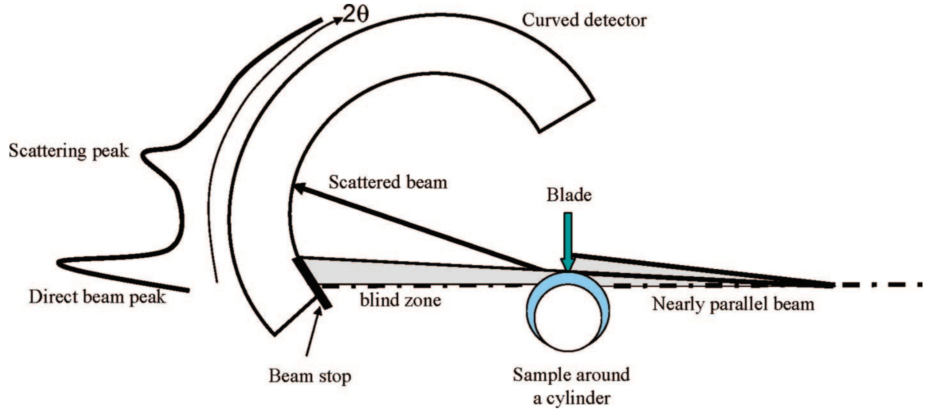

Figure 2. Schema of the X-ray measurements.

Nafion reference membranes commonly show a dramatic alteration on their conductivity performances that is due to water evaporation. Such an effect is assigned to the dehydration of the initial ionic domains. Consequently, today the commercial Nafion membranes do not carry out the requirement for fuel cell applications above 100 °C and hydrated swollen membranes are desirable at elevated temperature in order to maintain proton conductivity and mechanical properties.[8,11,12]

Sol−gel processing opens the possibility of tailoring new nanomaterials with versatile morphology control.[13] Attempts to prevent the loss of water through modification via sol−gel chemistry of the chemical composition of Nafion membranes have been performed by several groups.[8–17] Indeed, incorporations of hydrophilic inorganic phases such as silicon oxide,[8,10,12,14] ORMOSILs,[15,16] metal oxide,[17] metal phosphonate,[18] and heteropolyacids[19] were initiated in Nafion. These studies were carried out by dispersion of nanoparticles or by direct growth of inorganic phase using SO_3^- groups of Nafion to catalyze sol−gel polymerization of metal oxide precursor. Mauritz et al. have reported the fundamental data of Nafion/silica hybrid membrane, such material has been synthesized by sol-gel polycondensation of Tetraorthosilicate (TEOS) to form silica inside the swollen ionic domains of Nafion membrane.[15,16,20,21] At temperatures above 100 °C, their PEMFC performances were enhanced, compared with commercial Nafion reference.[8] However, because the inorganic polymerization was restricted to the cluster regions, small nanoparticles prevailed and the amount of incorporated inorganic component is limited.[22] Adjemian et al.[8,23] have recast hybrid membranes from a mixed Nafion−TEOS hybrid solution and tested them in a PEMFC. They found that the incorporation of silica into Nafion allows maintaining proton conductivity up to 140 °C in increasing water uptake at this temperature level.[22] However, these silica−Nafion membranes were not fully characterized and few fuel cell tests have been reported thus far.

In most of the previous studies, the condensation of the sol−gel precursors yields poorly ordered solids with amorphous structures and low specific surface areas. In the present study, we describe the synthesis of perfluorosulfonic acid mesoporous silica hybrid membranes using self-assembly silica phase growth in a Nafion matrix. The use of amphiphilic block copolymers[24] as structure-directing agents for the silica or organosilica-based framework enables the synthesis of mesoscopically ordered materials exhibiting a narrow pore size distribution after surfactant removal. In such a method, this mesoporous organization is obtained by evaporation-induced self-assembly (EISA) of inorganic or/and hybrid precursors in the presence of surfactant, water, solvent, and catalysts.[13] Moreover, the growth of high-surface-area silica embedded in an organic polymer should enhance water-uptake properties at higher temperature. Recently, we have demonstrated the possibility to develop transparent hierarchically structured hybrid functionalized membranes using in situ generation of mesostructured hybrid phases inside a nonporogenic polymeric host−matrix.[25] This new approach allows the growth of mesoporous silica in a polymeric host−matrix like Nafion to enhance water retention properties and resulting proton conductivity under tough operating conditions (high temperature or low relative humidity). Porous silica has been established to be a proton conductor,[26] even at elevated temperatures, and its surface proton mobility in many cases is well-known to exceed that

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Table 1. Determination of Ion Exchange Capacities of Native and Hybrid Nafion Membranes

	silica content (wt %)	ion exchange capacity (meq/g) calculated IEC_{th}	 titration IEC_{tit}	 elemental analysis IEC_{EA}	IEC_{tit}/IEC_{th} (%)
recast Nafion	0	0.91	0.79	1.0	87
NMS13	13	0.79	0.70	1.0	89
NSMS13	13	1.01	0.98	0.9	97
NMS19	19	0.74	0.64	0.9	86

Table 2. Water Uptakes of Native and Hybrid Nafion Membranes

	silica content (wt %)	water uptake (wt %)	IEC_{th} (meq/g)	moles of water molecules per sulfonic acid groups λ
Nafion 112	0	38	0.91	23
recast Nafion	0	39	0.91	24
NMS13	13	48	0.79	34
NSMS13	13	56	1.01	31
NMS19	19	54	0.74	40

Table 3. Size Expansions for Native and Hybrid Nafion Membranes

	silica content (wt %)	thickness (μm) dry state	 wet state	thickness expansion (%)
Nafion 112	0	50	59	18
recast Nafion	0	62	74	19
NMS13	13	51	59	16
NSMS13	13	90	104	16

of the bulk by orders of magnitude.[27] In the present work, we use this innovative procedure based on a one-step direct synthesis of hybrid inorganic−organic membranes from a mixed Nafion−TEOS-ORMOSIL−surfactant solution. In this work, specifically designed hybrid materials for high-temperature membranes have been prepared and evaluated. Preliminary results of solid-state NMR spectroscopy, scanning electron microscopy, X-ray diffraction, water uptake, proton conductivity, and fuel cell tests of these new Nafion−mesoporous silica hybrid membranes are reported.

Experimental section

Materials. A 20 wt % solution in water/alcohol mixture was supplied by Dupont Chemical. Tetraethoxysilane (TEOS, VWR) was used as the major silica source, Pluronic P123 was purchased from Aldrich and is employed to produce mesopores in the 8–10 nm range. 2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane (Gelest) was used to functionalize the inorganic network pore surface with proton conductive groups. Absolute ethanol obtained from VWR was used as the solvent. Hydrogen peroxide (30 wt %, Aldrich) and sulfuric acid (95%, PROLABO) were used during the membrane post-treatments. All chemicals were used without further purification.

Preparation of Hybrid Membranes. The preparation protocol of Nafion−mesoporous silica hybrid membranes is shown in Figure 1. A first sol is prepared using absolute ethanol, Pluronic P123, and TEOS. In an attempt to increase the conductivity of the silica phase and the film flexibility, part of the TEOS (10% molar) is substituted by organo-alkoxysilane (2-(4-chlorosulfonylphenyl) ethylsilane) in some cases. The organosilane solution is added drop by drop continuously in a stirred Nafion alcoholic solution containing 20 wt % water. The resulting homogeneous sol is then stirred at room temperature (20 °C) for 20 h. The hybrid membranes are obtained by pouring the mother solution onto a glass support using a hand-coater (Unicoater 409 Erichsen equipped with an Autonics temperature controller TZ4SP Series) followed by drying at 30 °C for 10 h through laminar flow. During slow solvent evaporation, a polymeric mesoporous silicon oxide phase is grown by the sol−gel process. In the typical method previously reported,[25] the surfactant can be organized as micelles in the hydrophilic domains of Nafion where the growth of silica network occurs via hydrolysis and condensation of inorganic precursors. Through this procedure, organic segments could be introduced and grafted in situ onto the mesopores surface using an ORMOSIL. The condensation reactions and cooperative self-assembly organization take place during solvent evaporation like in an EISA process.[13] The hybrid-cast membranes are dried at 120 °C for 10 h to remove trapped volatiles and promote further inorganic condensation inside the Nafion network. The hybrid membranes are then separated from the glass plate by dipping them in deionized water. Finally, the membranes are purified by boiling in deionized water for 1 h, subsequently boiling in 3% by volume H_2O_2 solution for 1 h to remove surfactant and residual organic impurities, and washing in boiling deionized water for 1 h, boiling in 0.5 M sulfuric acid solution for 1 h to remove any possible inorganic contaminants, and finally rinsing in deionized water for over an 1 h. The activated membranes in their acid form are stored in deionized water before use. As a comparison, pure Nafion membranes (called recast-Nafion membranes) are prepared using the above procedure without the addition of inorganic precursors or any surfactant.

In this work, the SiO_2 weight proportions n are given assuming total conversion of TEOS to silicon oxide. The Nafion−mesoporous silica *n* wt % membrane is named NMS*n* and the sulfonated one is named NSMS*n*. Membrane thickness is measured with a micrometer at several locations of the membrane sample to determine an average value.

Characterization. *Solid-State NMR Spectroscopy.* ^{29}Si-NMR provides the mean condensation degree of silica network. The hybrid films are cut into small fragments which are loaded into a 4 mm rotor. The solid-state NMR spectra are recorded on a Bruker avance spectrometer-300 MHz operating at a frequency of 79.5 MHz for the ^{29}Si nucleus and using the magic angle spinning technique. The sample spinning rate is 10 kHz. Spectra are acquired using a HPDEC sequence and the acquisition time is 90 s. The chemical shifts are given with reference to tetramethylsilane.

Scanning and Transmission Electron Microscopy. To investigate the morphology of films, we probed surface and side views from embedded samples by classical and field-emission scanning electron microscopes (Jeol LEO 435VP model with a tungsten filament). This microscope is equipped with an energy-dispersive spectrometer which allows evaluating the silicon and sulphur profile amount across fields of view on surface and cross-sections. A more detailed structural study is carried out with TEM characterization for the hybrid materials.

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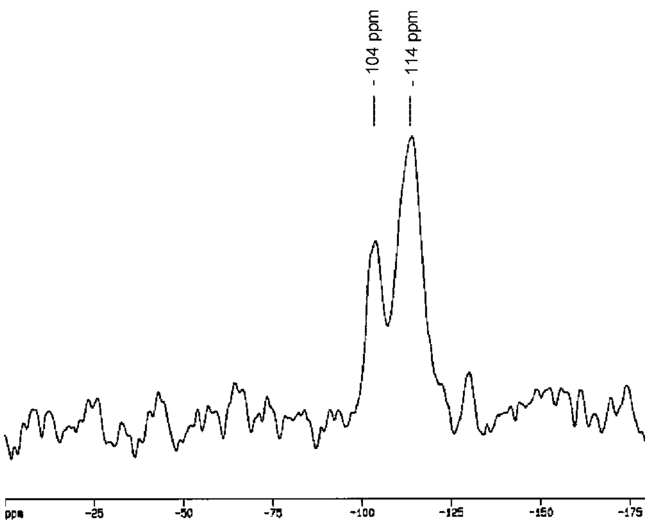

Figure 3. ^{29}Si solid-state MAS NMR spectra of a NMS17 membrane.

X-ray Diffraction. Small angle X-ray scattering measurements are performed on an INEL G3000 powder diffractometer, equipped with a flat Ge(111) monochromator and a CPS590 detector. The X-ray beam is nearly parallel after monochromatization ($K\alpha_{1,Cu}$, $\lambda = 1.54056$ Å). All the measurements are performed at room temperature at angular 2θ between 0.4 and 5°. To maximize the thickness of material traversed by X-rays, the membrane samples are wrapped around a 2.5 mm diameter cylinder using adhesive tape. Unwanted radiation coming from beam divergence is blocked by a blade mounted on top of the sample so that it rests lightly on its surface. The sample height is then increased until it obscures the whole of the incident beam. This procedure ensures that the beam traverses the top of the cylinder shaped membrane, thus maximizing the volume probed by the X-rays (Figure 2). The blade makes it possible to reach an angular detection threshold of 0.4° in 2θ ($d < 25$ nm).

Ion Exchange Capacity. Ion exchange capacity (IEC) is defined as the ratio between the number of sulfonic groups (in mmol) and the weight of the dry membrane.

$\mathrm{IEC_{tit}}$ is measured by titration after ion exchange of the counter ions following a procedure already described.[28] Thus, $\mathrm{IEC_{tit}}$,is calculated as the total proton charge divided by the weight of the dry membrane after the following steps: protonation by immersing the membrane in 0.5 M hydrochloric acid, then by cation-exchange by immersion in 2 M NaCl solution and titration of the collected solutions with sodium hydroxide solution.

$\mathrm{IEC_{EA}}$ is calculated from the sulfur content obtained by elemental analysis and the theoretical $\mathrm{IEC_{th}}$is determined from IEC of Nafion solution and the silica amount (wt %), using the following equations

$$\mathrm{IEC_{EA}} = 1000S/\mathrm{MW}$$

S corresponds to the sulfur content determined by elemental analysis, MW corresponds to the sulfur molecular weigh (32 g/mol), and 1000 is the multiplying factor to obtain an IEC value in mmol g^{-1}.

$$\mathrm{IEC_{th}} = (100 - \mathrm{wt\ \%\ Si})\mathrm{IEC_{Nafion}}$$

wt % Si corresponds to the silica amount in weight and $\mathrm{IEC_{Nafion}}$ corresponds to the IEC of Nafion solution (equal to 0.91).

Water Uptake. Water uptake (*W*) is determined by calculating the difference between wet weight (W_{wet}) and dry weight (W_{dry}) of the membrane using the following equation

$$W = (W_{\mathrm{wet}} - W_{\mathrm{dry}})/W_{\mathrm{dry}} \times 100$$

To obtain the weight of the wet membrane, we equilibrated the latter with deionized water at room temperature overnight after the activation treatments described above. The wet sample was then removed and blotted dry with a Lym-Tech C6 (Conformat) and weighed immediately. The weight of the dry membrane was measured after drying the sample in an oven at 100 °C for 1 day.

Ionic Conductivity. Membranes' proton conductivity is measured by an AC impedance spectroscopy method. The hybrid films are placed between two platinum electrodes of 0.5 cm in diameter under a constant pressure supporting by two springs. Impedance measurements are performed using a Solartron SI 1260 impedance/gain phase analyser which is interfaced to a computer. The experimental setup used consists of a conductivity cell placed in a Weiss WK 11180 environmental chamber where temperature and moisture can be controlled. All membranes are in their acid-protonated state and immersed in deionized water at room temperature overnight prior to conductivity measurement. Impedance spectra are recorded between 10 Mhz and 100 Hz with perturbation voltage amplitude of 10 mV. The conductivity of the membrane is calculated using the following equation

$$\sigma = 1/RS$$

where σ is the ionic conductivity (S/cm), 1 is the membrane thickness (cm) measured with a Mitutoyo digital micrometer, *R* is the resistance (Ω) corresponding to the intersection point with the real axis, and *S* is the contact area between the electrodes and the membrane (cm^2).

Results and Discussion

Physicochemical Properties. *Solid-State NMR Spectroscopy.* Figure 3 shows the representative ^{29}Si solid-state MAS NMR spectrum for a NMS*17* material. Such spectrum can yield quantitative information on the condensation state of silica network. During the hydrolysis and condensation process, Si atoms can present five possible coordination states on the NMR spectra, each state designated using the Q_n notation.[20] The relative population of a given Q_n coordination state is obtained by determining the relative area under the Q_n peak. Typical chemical shifts ranges in the *Q* region are: Q_0, −72 to −82 ppm; Q_1, −82 to −89 ppm; Q_2, −92 to −96 ppm; Q_3, −100 to −104 ppm; and Q_4, −110 ppm.[29] The spectrum represented in Figure 3 has a low signal-to-noise ratio because the Si nuclei are diluted throughout the polymer since the Nafion−SiO_2 weight proportion is only 83/17 in this case. Nonetheless, the spectral quality is quite adequate to determine the global condensation state of the inorganic network.

The ^{29}Si NMR spectrum clearly shows two peaks at −104 and −114 ppm, which are somewhat close to the data from literature corresponding to Q_3 and Q_4 species. The presence of only two peaks is relevant of an advanced condensation state of the silica network. Thus, this establishes the important fact that an in situ sol−gel reaction has occurred to form well-condensed silica network inside the Nafion matrix. For Nafion−silica hybrid materials, the percentage of Q_3 and Q_4 species is calculated to be 30% and 70% respectively which

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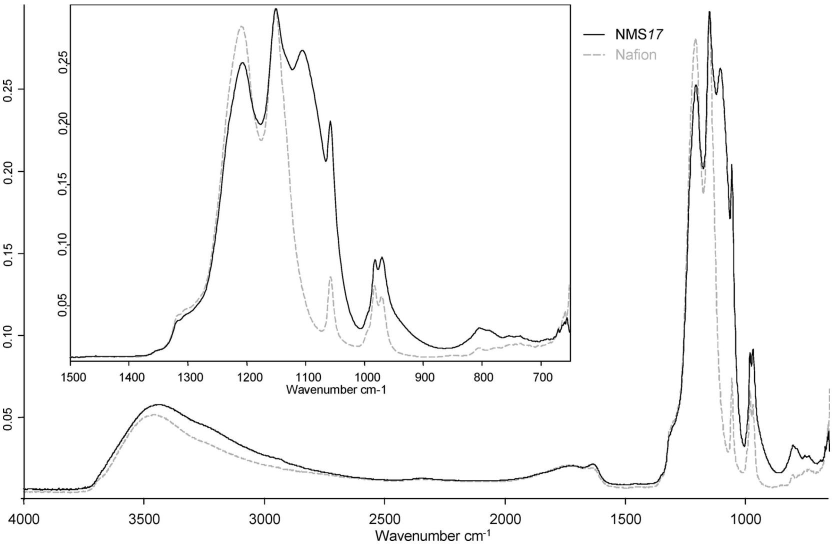

Figure 4. FTIR spectra of Nafion (dotted line) and NMS17 (dark line) membranes.

Table 4. Proton Conductivities of Native and Hybrid Nafion Membranes Measured at Room Temperature

	silica content (wt %)	thickness (μm)	ion conductivity σ (mS/cm)
Nafion 112	0	65	9.0 ± 0.5
recast Nafion®	0	52	8.5 ± 0.9
NMS 13	13	70	5.9 ± 0.9
NSMS 13	13	73	22 ± 5

Table 5. Activation Energies at 98% and 80% RH for Nafion 112 and Nafion−mesoporous Silica Hybrid Membranes Calculated in the Range 20–95 °C According To the Arrhenius Equation

	activation energy E (kJ mol^{-1})	
	at 98% RH	at 80% RH
Nafion 112	9.1 ± 0.2	18.2 ± 0.8
NMS13	11.5 ± 0.5	12.1 ± 0.4
NSMS13	7.1 ± 0.2	7.6 ± 0.9

corresponds to a mean degree of condensation[30] around 93%. The inorganic network seems to be more polymerised in our case than Maciel et al.[31] reporting results concerning a close acid-catalyzed TEOS gel which contained approximately equal amounts of Q_3 and Q_4 species. Because the pH of hybrid solution is very low and in the presence of excess of water, it can be expected that mainly all the Si-ethoxy groups have been hydrolyzed.[32] Consequently, the 30% uncondensed siloxane bounds (Si-OX) corresponding to ^{29}Si NMR Q_3species can be mainly assigned to silanol groups Si-OH. These silanol groups, also visible by infrared spectroscopy (around 3300 cm^{-1}) should highly enhance the hygroscopy of the inorganic phase. These residual Si-OH groups are very important because they are necessary to retain water via hydrogen bonds and to ensure good phase compatibility between Nafion and the inorganic network.

Scanning and Transmission Electron Microscopy. SEM analyses of surface and cross-section of the hybrid membranes have been performed. The surface is smooth and similar to that of recast-Nafion. The control of drying conditions during recasting is very important to avoid surface defects. All the hybrid membranes show a great homogeneity at the micronic scale confirming that no micronic phase separation has occurred during the drying process. From SEM images, the hybrid membrane presents similar homogeneity as standard Nafion and cross-section do not reveal any macroporosity or segregation and sedimentation of the inorganic network. This is presumably due to the in situ growth of the inorganic phase entrapped in the polymeric network and well-dispersed at submicronic level creating strong interaction with Nafion. Figure 5 shows a transmission electron microscopy image for a NMS*13* membrane. This provides evidence that these hybrid membranes have nano-sized silica particles homogeneously dispersed within the polymer. The main advantage of preparing hybrid membranes from solution instead of swelling a Nafion membrane with TEOS[15] is the possibility to obtain larger silica particles. The inorganic polymerization is not restricted to the sulfonic acid clusters of Nafion because these clusters are formed simultaneously to the inorganic network growth during solvent evaporation.

The silica content is confirmed by EDX, which gives a constant Si/S ratio. Since the sulfur peak intensity is taken as an internal standard, the peak intensity ratio Si/S corresponds to a relative measure of silica content. All the hybrid membranes exhibit uniform intensity profiles across the membrane thickness and the same intensity ratio on both surface and cross-section. These results suggest that the polymer/silica phase is uniform and homogeneous at the micrometer scale.

X-ray Diffraction. The XRD patterns recorded in the low angle range exhibit scattering peaks with weak intensities. The background contribution is removed and the peaks are then fitted using a gaussian profile. The peak located at $2\theta = 2.4°$ ($3 < d < 4$ nm) is always observed and exhibits an intensity which varies with relative humidity ratio. This peak can be assigned to the Nafion® polymer.[33] For the

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Nafion−SiO_2 sample, without the use of any surfactant, no extra scattering peak is detected. When the surfactant is added to the organosilane solution, a new peak located at $2\theta = 1°$ ($d = 9$ nm) is systematically observed on the pattern. This suggests that the inorganic network embedded in the Nafion has a mesoscopically ordered structure characteristic of the surfactant used. The XRD pattern of the surfactant-extracted material also reveals the presence of a peak with a d-spacing position remaining unchanged, suggesting that the meso-ordered structure of the material is conserved after template removal.

Ion Exchange Capacity. Ion exchange capacities of recast and hybrid Nafion membranes, as measured by titration (IEC_{Tit}) and elemental analysis (IEC_{EA}), are shown in Table 1. The calculated IEC_{th} is based on 1100 Equivalent Weight for Nafion. The elemental analysis provides the global number of sulfonic sites which are susceptible to participate to proton transport. For recast Nafion, the result is somewhat close to literature data.[34] The density of sulfonic groups measured via titration is lower than the one determined by elemental analysis. This is probably because the titration method provides only the number of accessible acidic groups. Elemental analysis gives roughly the same IEC_{EA} for all the membranes, whereas the addition of non-sulfonated silica should decrease the IEC. This is presumably due to the accuracy of elemental analysis. However, IEC_{Tit} values are in good agreement with the calculated values (IEC_{th}). The density number of sulfonic groups decreases significantly from 0.79 to 0.64 mmol/g with increasing the incorporated silica. On the other hand, it increases significantly from 0.79 to 0.98 mmol/g when functionalized silica is grown inside the perfluorinated polymer. Approximately 87% of sulfonic groups are accessible in both recast Nafion and NMS hybrid membranes cases suggesting that mesoporous silica does not hinder proton transport between sulfonic groups of Nafion. This behavior is consistent with the good compatibility of SiOH groups and Nafion that avoid micronic phase separations as shown by SEM analysis. The hybrid NSMS*13* membrane provides a higher ratio of accessible sulfonic groups. This is an indication that the SO_3H groups of the hybrid silica phase, introduced with the organosilica precursor, are probably located inside open mesopores that are easily accessible.

Water Uptake. Water uptake of hybrid membranes, recast and commercial Nafion are gathered in Table 2. The thickness expansion of each membrane (calculated between wet and dry state thickness) is also presented in Table 3. Recast Nafion membrane has a high water uptake compared with the commercial one. A similar result was also reported in the literature,[10,35] indicating that the membrane properties (structural properties, ionic-domain organization, etc.) may be modified by the recasting procedure which is different from the extrusion process of commercial Nafion. From Table 2, it is observed that all of the hybrid membranes absorb more water than unmodified Nafion. Moreover, the thickness expansion of the hybrid membranes is smaller. This interesting result is due to the hygroscopic affinity of the incorporated silica and its high water absorption capacity.[7,10] The highly hydrophilic character of the SiOH groups, the high surface area of mesoporous silica, and the stronger interactions between the absorbed water and the modified matrix contribute to increase the water uptake. Moreover, higher silica loadings in the membrane matrix increase the relative water content suggesting that the number of silanol groups, which are thought to absorb water in the pores, also increase slightly with increasing silica content. Moreover, the NSMS*13* membrane seems to be optimum because it exhibits a high water uptake likely thanks to the combined presence of hydrophilic sulfonic and silanol groups inside the mesopores.

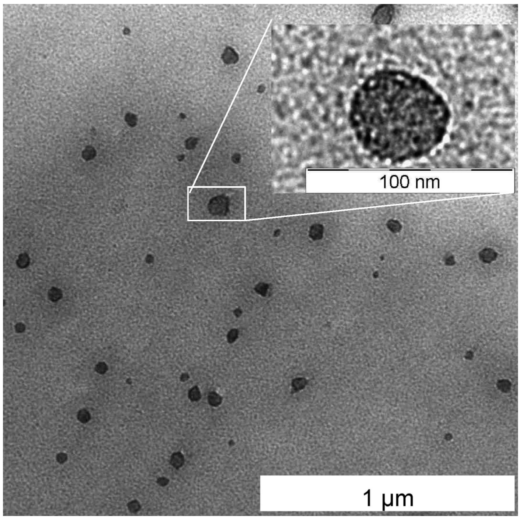

Figure 5. TEM micrograph of a NMS13 membrane showing silica nanoparticles within Nafion.

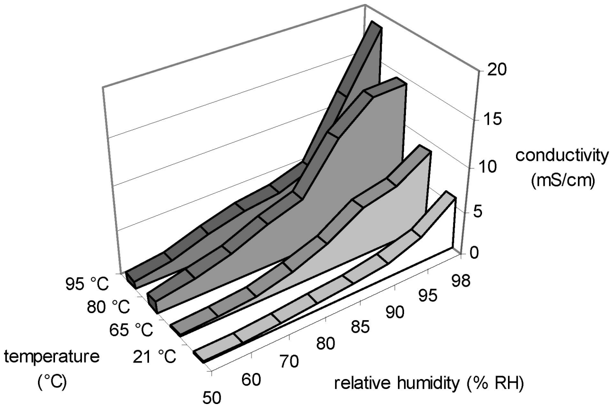

Figure 6. Proton conductivity of Nafion 112 versus relative humidity at several temperatures.

It is important to point out that an increase in silicon oxide content into the hybrid membrane leads to a substantial decrease in the ionic exchange capacity while water uptake is enhanced. Thus high silicon oxide content involves an elevated number of water molecules per acid site (λ) that reduce proton conductivity efficiency. The optimal percentage of silicon oxide for the recast membranes was then determined to be close to 13% by weight. Our results are in agreement with those reported by Adjemian et al.[23] The

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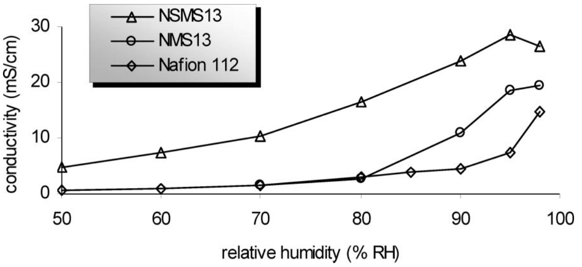

Figure 7. Proton conductivities versus relative humidity for Nafion 112 (square), NMS13 (circle), and NSMS13 (triangle) membranes measured at 95 °C.

NSMS*13* membrane shows the closest degree of hydration 31 to the value of 24 obtained from Nafion by assuming complete sulfonation of phenethyl groups.

From Table 3, mesoporous silica can prevent Nafion from swelling by providing a more rigid material architecture and absorbed water can be trapped efficiently into the porosity. Hybrid membranes show restricted dimensional changes (16%), whereas recast Nafion membrane expands 19% of its initial size. From these results, the hybrid membranes appear more stable in dimension than the native Nafion membrane for higher water-absorption properties.

Electrochemical Properties. *Ionic Conductivity.* Typical membranes for PEMFC are made of organic polymers containing acidic functions such as sulfonic groups which dissociate when they are solvated with water allowing H_3O^+ hydrated proton transport. Therefore, the membrane performance is dependent on the number of ionic groups and on the hydration rate. As is shown in Figure 6, the proton conduction process of Nafion is directly dependent on the water content, which is associated with the environment conditions such as temperature and relative humidity. Proton conductivity of Nafion decreases with decreasing relative humidity and this is more significant at higher temperature. A first explanation for this dramatic conductivity drop due to loss of water under severe conditions can be a change in proton conduction mechanism from a vehicle process (the proton diffuses together with a water molecule) in the hydrated membrane to a hopping mode (frequently termed the Grotthuss mechanism) when water content decreases.[36] As previously reported,[33] Nafion is characterized by a microphase separation between ionic domains and perfluorinated matrix. The structure and the size of the ionic domains depend on the hydration state of the membrane and thus swelling modification induces an important structural re-organization of the intrinsic structure of Nafion, which can change percolation path and proton conductivity.

Thus, to evaluate our materials, we measured the ionic conductivity of recast and commercial Nafion 112 and hybrid membranes at different temperatures (from RT to 95 °C) for several relative humidities (from 50 to 98% RH). The proton conductivities obtained at room temperature and at fully hydrated state (measurements performed in deionized water) are given in Table 4. It clearly shows that the proton conductivity decreases with the incorporation of pure silica. This observation is in agreement with the work previously reported.[10,37] Studies[38] showed that proton conductivity is directly correlated with sulfonic number density (IEC) and degree of hydration. The NMS*13* membrane has a lower number density of sulfonic groups due to incorporation of non-sulfonated silica. Even though its water uptake is higher thanks to the presence of highly hydrophilic SiOH groups, a lower IEC leads to a decrease in proton conductivity. Beside, the NSMS*13* membrane possesses the highest IEC and an elevated water uptake that leads to an outstanding improvement in conductivity. It is highlighted that the performance of the membrane increases with the growth of a functionalized silica.

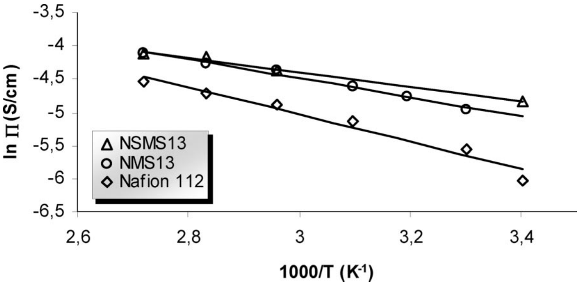

Figure 8. Regression curves of proton conductivity versus T^{-1} for Nafion 112 (square), NMS13 (circle), and NSMS13 (triangle) membranes under 80% RH environment.

Figure 7 represents the evolution of proton conductivity versus relative humidity at 95 °C, a temperature of practical interest in PEMFC. Hybrid membranes clearly possess higher values than Nafion membrane over the whole RH range and this improvement of ion conductivity is more significant at higher RH. At 95 °C, the performance of the NMS*13* membrane becomes higher than that of pure Nafion. This is presumably due to the inclusion of hygroscopic mesoporous silica within recast Nafion that helps water management and decreases the hybrid membrane's resistance. The NSMS*13* membrane has much higher conductivity than Nafion 112. This is probably because the functionalized hybrid membrane has a higher ion exchange capacity due to the in situ growth of sulfonated organo-silica. This fonctionalization yields decreased resistance even though the degree of hydration of this hybrid membrane is slightly higher than that of standard Nafion. Figure 7 clearly indicates that the growth of a sulfonated mesoporous silica within the Nafion leads to a more efficient material with improved proton conductivity.

The effect of temperature upon conductivity of the membranes is also studied at different humidification levels. Figure 8 shows the proton conductivity of Nafion 112 and hybrid membranes as a function of temperature under 80% RH environment. At this low hydration level, the performance of the hybrid membrane is much higher than that of commercial Nafion whatever the temperature. Both commercial and hybrid Nafion membranes show a significant increase in conductivity with increasing temperature. According to an Arrhenius law, the temperature dependence of conductivity can be associated with the activation process of proton conduction. These activation energies, which

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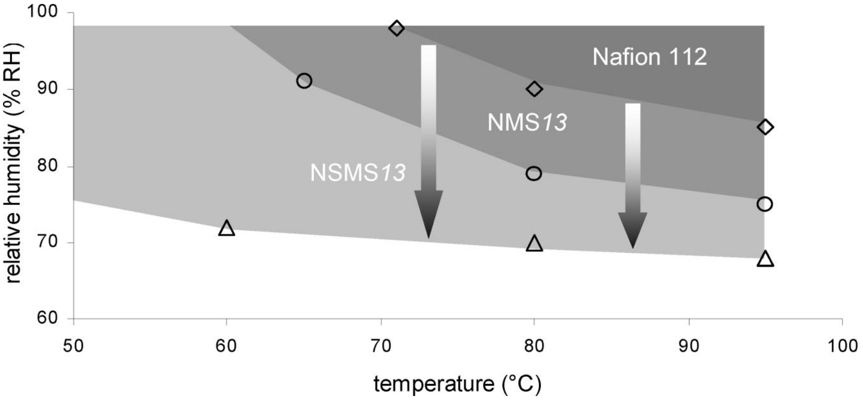

Figure 9. Environmental conditions (temperature and relative humidity) that allow a proton conductivity of 1 × 10^{-2} S cm^{-1} for Nafion 112 (square), NMS13 (circle), and NSMS13 (triangle) membranes.

correspond to the energy barrier for carrier transfer from one free site to another one, can be calculated from the slopes of the linear dependency ln σ versus T^{-1} reported in Figure 8. These activation energies are found to be 18, 12, and 8 kJ.mol^{-1} for Nafion 112, NMS*13*, and NSMS*13* membranes respectively. Table 5 reports the activation energies of commercial Nafion and hybrid membranes at 98% and 80% RH.

In the Nafion-based membranes, the proton migration of the highly hydrated state (98% RH) is primarily assumed by a vehicular mechanism.[36] When the relative humidity decreases from 98 to 80%, the activation energy E for native Nafion doubles, reaching 18.2 kJ mol^{-1}. Such a modification of the activation energy (E being in the 14–40 kJ mol^{-1} range) is characteristic of an evolution of the conductivity mechanism, which shifted from a vehicular mechanism to a Grotthuss type mechanism.[10] In this latter mechanism, the proton carriers reside on their sites, the protons being transferred by hopping from one site to the neighboring one. Decreasing the relative humidity in the Nafion membrane reduces the water content and so the number of hydrated proton carriers responsible for the vehicular mechanism; consequently with minimum water content the Grotthuss mechanism starts to be a preferential pathway for conductivity. On the contrary, for the hybrid membranes, the activation energy (E is in the 8–12 kJ mol^{-1} range) remains somewhat constant even at 80% RH. This is presumably because silanols and sulfonic acid groups of the mesoporous silicon oxide network have a higher propensity to retain water[39] and then to limit the dependence of the proton conductivity on hydration. Therefore, the proton migration in the hybrid membranes seems to occur by the vehicular mechanism even at higher temperatures.

Figure 9 shows the working operation conditions that allowed reaching conductivity farther than 10^{-2} S cm^{-1}, which is the usual value corresponding to good fuel cell performances. The graph clearly shows an enlargement of the working humidity level for the mesoporous silica hybrid membranes. As an instance, at 80 °C the relative humidity corresponding to a conductivity of 1 × 10^{-2} S cm^{-1} evolves from 90 to 70% with the inclusion of the sulfonated high surface area inorganic phase in the recast Nafion. This improvement in water management should have an enhancement on high temperature fuel cell operations. To corroborate these results, some fuel cell tests were performed using a NSMS*13* Nafion−mesoporous silica hybrid membrane and commercial Nafion 112. The first polarization curves are promising but an extended study is necessary to optimize the electrode membrane assembly because at the moment the gas diffusion layer still contains neat Nafion that limits performances at high temperature.

Conclusion

Organic−inorganic hybrid membranes based on Nafion−mesoporous silica materials were prepared via in situ generation of inorganic silica or hybrid silica networks using the sol−gel process. The mesostructuration proceeds through surfactant templated growth of inorganic or hybrid networks from silica and organosilica precursors in a non porogenic organic polymeric matrix. This strategy allows better definition of the pore dimension and the material architecture. This new method where mesoporous organosilica is formed during the recasting procedure leads to the formation of homogeneous efficient hybrid membranes. The solid state NMR analysis confirmed the advanced condensation state of the silica and scanning electron microscopy showed great homogeneity of the membranes at the micron scale. Small-angle X-ray diffraction experiments suggest the presence of ordered silica mesoporous networks inside the hybrid membranes.

Water uptake of the hybrid membranes increases with the amount of silica incorporated. In particular, the inclusion of sulfonated organosilica at the optimal rate of 13% in weight with respect to the silica content allows conserving a high degree of hydration at high temperature, close to those of Nafion at room temperature.

Moreover, we demonstrate that the presence of mesoporous silica has a great effect on dimensional stability of the hybrid membranes and improves water management. At high temperature these Nafion−mesoporous silica hybrid membranes have much better conductivity than conventional Nafion membranes. Indeed, the proton conductivity measured at 95 °C and 90% RH for the NSMS*13* membrane is 5 times higher than the Nafion 112 membrane. Moreover, the first

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fuel cell tests performed with these hybrid membranes show promising results compared to standard Nafion® 112. Under tough operating conditions, high temperature or low humidity level, the hybrid membrane shows slightly higher performances than native Nafion with a current density gain of about 60 mA/cm^2 corresponding to a 16% improvement in power density at 700 mV. This improvement at a cell temperature of 120 °C and reduced relative humidity can be attributed to the presence of the hygroscopic inorganic phase inside the polymer as mentioned previously with the ex situ characterizations. Nevertheless, fuel cell tests need an extended optimization of the electrode membrane assembly in order to precisely determine performances of such hybrid membranes. The present approach offers a new dimension for the preparation of organic−inorganic hybrid membranes, in which the porosity and pores functionality can be tailored. Furthermore, this kind of membranes with improved water management will be suitable for high-temperature operation fuel cell application.

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Supporting Information Available: XRD scattering pattern and polarization curves (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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