

Processing, Morphology, and Water Uptake of Nafion/Ex situ Stöber Silica Nanocomposite Membranes As a Function of Particle Size

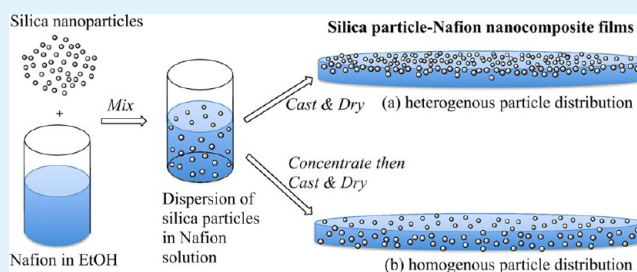
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S Supporting Information

ABSTRACT: Because of the bicontinuous phase structure of Nafion with small hydrophilic channels, formation of composites with silica colloids to improve thermal stability, hydration, and proton conductivity should be influenced by size and surface functionality of the colloids. To test this hypothesis, we prepared batches of silica particles between 20 and 400 nm in diameter with narrow polydispersities using a modified Stöber procedure. Some particles were subsequently surface-modified using mercaptopropyltriethoxysilane. Enough particles were mixed with Nafion in alcohols to achieve 5 wt % silica in the final membranes, which were made by casting and drying. Membrane top and bottom surface and cross-section morphologies were examined with AFM and SEM to determine how the particles were dispersed. We discovered that casting the membranes from dispersions with viscosities less than 65 cPs led to larger particles floating to the top surface of the membrane where they were easily dislodged from the dry membrane. Membranes cast from more viscous solutions exhibited homogeneous distributions of particles. Water uptake was over 60% higher in nanocomposites with unmodified silica particles than for Nafion and about 15% higher than for Nafion with in situ generated silica particles, but showed no trend in water uptake correlating with particle size. Surface silylated particles of all sizes appeared to have reduced water uptake relative to Nafion alone.

KEYWORDS: Nafion membrane, silica nanoparticles, water uptake, morphology



1. INTRODUCTION

Increasing the thermal operating range for perfluorosulfonic polymers, such as Nafion, to above 100 °C is desirable to allow polymer electrolyte membrane fuel cells to operate with technical grade hydrogen.^{1,2} Dehydration, mechanical failure, and even loss of the necessary bicontinuous phase structure of membranes at temperatures over 100 °C have led researchers to add inorganic, hydrophilic fillers (silica, zirconia, titanium dioxide) to Nafion so as to improve its water retention and mechanical properties.^{2–4} Although Nafion/silica composite membranes have been demonstrated to improve fuel cell performance,^{3,5–10} there has been less information on the effect of particle size on hydration and proton conductivity, and almost nothing on how the morphology of the membranes will affect these properties. For silica to improve the water uptake, it must be associated with the hydrophilic phase throughout the bicontinuous Nafion membrane. Because the hydrophilic phase is generally thought to consist of networks of channels that are several nanometers in diameter,¹¹ smaller particles should be easier to disperse into Nafion. Ultimately, these smaller particles should have greater influence on the ability of the membrane to retain or take up water. This has been corroborated in three studies that showed better membrane performance with small silica particles.^{4,5,12} Unfortunately, one study compared only the effects of two different sized metal oxide particles (20 nm and 200–300 nm)⁴ and the second

study looked only at particles that were larger than 120 nm in diameter.⁵ The third study looked at in situ generated particles less than 20 nm in diameter.¹² Equally important in the preparation of particle-filled polymer nanocomposites is the homogeneity of dispersion of the inorganic filler phase. Neither study^{4,5} included observations or discussion of the nanocomposite membranes' morphology and the distribution of the particles.

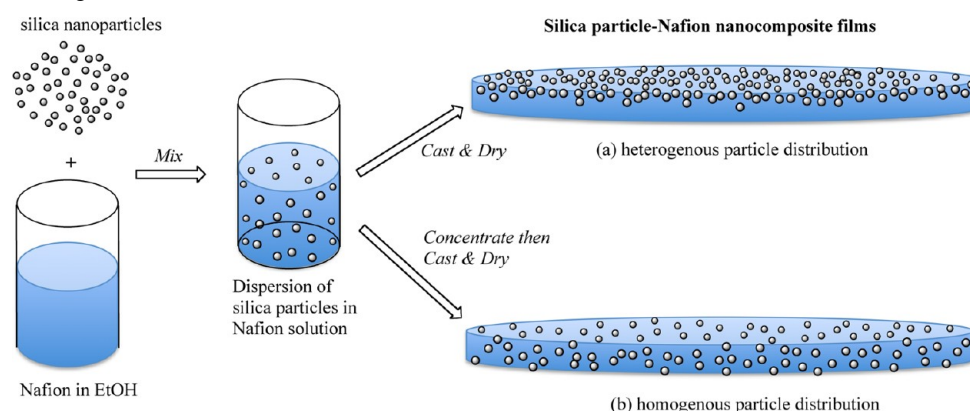
In this work, we looked at the effects of processing conditions, five different particle sizes between 20 and 300 nm, and particle surface modification on the preparation, morphology, and water uptake of Nafion/ex situ silica nanocomposite membranes. Because the focus of the project was on particle size rather than particle concentration, a loading of 5 wt % was used for all of the samples because water uptake and conductivities seem to be optimal at this loading with large silica particles.¹² The size of the nearly monodispersed silica particles, prepared from tetraethoxysilane using a modified Stöber process,¹³ was controlled by varying the concentration of ammonia used in the sol–gel reaction. By producing the particles separately (ex situ) from the Nafion, the size, distribution, and precise quantity of particle used to prepare

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Scheme 1. Preparation of Silica Particle–Nafion Nanocomposite Films Showing the (a) Undesirable Segregation of Particles and (b) Desired Homogeneous Distribution of Particles



the Nafion/silica composite membrane can be more easily controlled than with *in situ* methods (where the silica is generated in the Nafion from the hydrolysis and condensation of tetraalkoxysilanes¹⁴). The *ex situ* synthesized particles were mixed into a solution of Nafion, and the resulting mixture was cast to afford membranes for characterization with scanning electron microscopy (SEM) and atomic force microscopy to determine if the particles were uniformly distributed and then tested to determine how particle size affects water uptake (Scheme 1).

2. EXPERIMENTAL SECTION

2.1. Materials. Nafion (5 wt %) in aliphatic alcohol, tetraethoxysilane (TEOS), 3-mercaptopropyltrimethoxysilane, concentrated ammonium hydroxide, and anhydrous ethanol were obtained from Sigma Aldrich (St. Louis, MO). Aqueous ammonia hydroxide was titrated against 0.1 N HCl with methyl orange as indicator to determine its actual concentration (9M). TEOS was distilled from calcium hydride prior to use.

2.2. Preparation of Stöber Silica Particles (13). Silica nanoparticles were prepared by hydrolysis and condensation reactions of tetraethoxysilane in the presence of ammonium hydroxide according to the Stöber process.¹⁵ The size of the particles was best controlled by changing the concentration of the ammonium hydroxide. Examples of the volumes of ethanol, TEOS, aqueous ammonia (9M) used in making the particles with mean diameters ranging from 15 to 400 nm are given in Table 1 below. The narrow size dispersities of the samples are apparent from the small standard deviation values.

The particles were prepared by adding the aqueous ammonia to the anhydrous ethanol in a scintillation vial (20 mL) along with a magnetic

stir bar. After stirring the solution in the capped scintillation vial for 5 min, the TEOS was added in one quick aliquot with stirring at 600 rpm. The vial was tightly sealed, and the mixture was stirred for 24 h before analysis. Residual monomer and reactants were removed from the particles by rinsing with ethanol, centrifuging and decanting the solution from the particles. The particles were placed in fresh ethanol, sonicated at 25 ± 3 °C until redispersed then centrifuged again. After three repetitions, the particles were free of residual ammonia and TEOS. The particles were dried and weighed, then redispersed in ethanol, characterized by dynamic light scattering and atomic force microscopy before mixing with the Nafion solutions.

Surface modification of particles, to be used in preparing the PNSST nanocomposites, was achieved by adding about 3 wt % (relative to amount of TEOS used to prepare the particles) 3-mercaptopropyltrimethoxysilane in the preformed particle solution prior to washing. These wt% was based on calculations with total surface coverage of 100 nm diameter particles and assuming a particle density of 2.2 g/cm^3 . The samples were left stirring at 600 rpm and at room temperature for 12 h. After surface modification, the particles are washed as described earlier.

2.3. Preparation of Nafion Nanocomposite Membranes (NSS) Series. To prepare Nafion nanocomposite membranes, we added 6 mL of the Nafion solution (5 wt % in aliphatic alcohol) to a 20 mL scintillation vial equipped with a stir bar and placed on a magnetic stir plate. To this solution, was 400 μL of silica nanoparticles (4 wt %) in ethanol (enough to make 5 wt % silica in Nafion membranes) and the resulting mixture was stirred overnight. The dispersion was sonicated in a sonic bath at room temperature for 30 min to remove bubbles prior to casting. The membranes were cast on glass Petri dishes (60 mm \times 15 mm) at room temperature. Afterward, the temperature was raised gradually to 60 °C in an oven and the membranes were left to dry at 60 °C overnight. Afterward, the membranes were annealed at 90 °C for 30 min. This step was crucial to liberating the membranes from the glass surface of the Petri dish. Once dry, the membranes were removed from the Petri dish by soaking in deionized water for 2 min. At least three duplicate membranes were prepared for each formation. This technique was used to prepare a family of Nafion nanocomposite membranes with different particle size but same weight% particles (5 wt %) in Nafion. Nanocomposite membranes with functionalized particles were prepared in similar manners and are designated as shown in the Table 2. NSS stands for the Nafion Stöber silica, and the number indicates the size of the silica particles in nanometers; NSST refers to the Nafion membranes made with 3-mercaptopropyl-silylated particles. These procedures were adapted from literature procedures reported for preparation of Nafion composite membranes with commercial silica particles.^{4,15}

2.4. Preparation of Nafion/Stober Silica Nanoparticle Nanocomposite Membranes Cast from Viscous Solutions (PNSS Series Membranes). Nafion nanocomposite membranes (PNSS) were prepared as described for the NSS series, but with the addition of

Table 1. Stöber Silica Formulations and Corresponding Particle Sizes (hydrodynamic diameters) Determined by Dynamic Light Scattering (DLS)

anhydrous ethanol (mL)	titrated NH ₄ OH (mL)	distilled TEOS (mL)	DLS particle diameter (nm) \pm standard deviation
15.0	0.4	0.5	15 \pm 3
14.9	0.5	0.5	24 \pm 2
14.9	0.6	0.5	38 \pm 2
14.7	0.7	0.5	62 \pm 3
14.0	0.9	1.0	105 \pm 2
14.5	1.0	0.5	138 \pm 2
14.1	1.1	0.5	262 \pm 2
13.6	1.8	0.5	396 \pm 12

Table 2. Nafion/Stöber Silica (NSS) Particle Nanocomposite Membranes

particle size (nm)	nanocomposite membranes with silica particles	nanocomposite membranes with thiol-terminated particles
20	NSS-20	NSST-20
40	NSS-40	NSST-40
68	NSS-70	NSST-70
90	NSS-90	NSST-90
100	NSS-100	NSST-100
136	NSS-136	NSST-136

solvent evaporation step to increase solution viscosity and permit homogeneous particle distribution in the final membranes. Nafion solution was mixed with enough Stöber silica nanoparticles (in ethanol) to make 5 wt % particles in the final Nafion membranes. Mixture was stirred for overnight as described earlier. Next the mixture was placed in a conventional oven at 70 °C for 2 h resulting in a 50% reduction in volume and an increase in solution viscosity from 14.5 ± 1.2 to 64.6 ± 1.4 cPs, or about the viscosity of SAE 10 motor oil. The mixture was then stirred at 600 rpm for 4 h to redisperse the particles in the polymer solution. Membranes were cast by pouring the viscous mixture in a glass Petri dish (60 mm \times 15 mm) at room temperature and the temperature raised gradually to 60 °C in the oven. The membranes were left to dry overnight at 60 °C, and finally annealed at 90 °C for 30 min. Once dry, the membranes were detached from the Petri dish by soaking in deionized water for about 2 min. This technique was used to prepare a second family of Nafion nanocomposites membranes with different particle sizes but same particles weight % (5 wt %) in Nafion as shown in Table 3. Nafion nanocomposite membranes with functionalized particles were prepared in a similar manner and are designated with the PNSST acronym.

Table 3. Nafion/Stöber Silica Particle Nanocomposite Membranes, the PNSS (Preconcentrated Nafion Stöber Silica) Series

particle size (nm)	nanocomposites membranes with silanol-terminated particles	nanocomposite membranes with thiol-modified particles
20	PNSS-20	PNSST-20
40	PNSS-40	PNSST-40
60	PNSS-60	PNSST-60
100	PNSS-100	PNSST-100
136	PNSS-136	PNSST-136

2.5. Preparation of Nafion/TEOS Nanocomposite Membranes (NTEOS Series Membranes). Nanocomposite membranes were prepared following the conventional sol–gel method used to prepare in situ Nafion silica composite membranes^{1,16} to compare with the ex situ silica filled membranes in both the NSS and PNSS series. These membranes were made by adding (15 μ L) TEOS to Nafion (5 wt %) solution in aliphatic alcohol with stirring for 24 h. Acidic sulfonic groups in the Nafion polymer catalyze the sol–gel reaction of TEOS with water in the polymer electrolyte to afford silica particulates.¹ The solutions were sonicated in a sonic bath for 30 min prior to casting to remove bubbles. This solution was cast on glass Petri (60 mm \times 15 mm) dishes at room temperature then dried by gradually heating to 60 °C in a conventional oven. This was followed by annealing at 90 °C for 30 min. The membranes were detached from the Petri dish by soaking in deionized water for 2 min. This technique was used to prepare membranes with the amount of TEOS added ranging from 1 to 10 wt % relative to the Nafion; the mass of fully condensed silica would be between 0.28 and 2.8 wt %. Nanocomposite membranes prepared following this technique are designated NTEOS-1, NTEOS-2, NTEOS-5 and NTEOS-10 where the NTEOS stands for Nafion/TEOS and the number at the end corresponds to the weight percent of TEOS added.

In this work, the thickness of all the nanocomposite membranes was controlled by the type and size of the Petri dish used, and the amount of Nafion solution (6 mL) used. The average thickness of the nanocomposite membranes was determined with micrometer measurements at five different locations. All membranes were found to have an average thickness of 90 ± 10 μ m.

2.6. Characterization of the Nafion/Ex situ Silica Nanocomposite Membranes. Distribution of the silica particle in Nafion nanocomposites was determined by morphological analysis of the membranes with both AFM and SEM. Samples were prepared by mounting the membrane on a sample holder using carbon adhesive stabs. Morphology of the samples was analyzed using tapping mode AFM without additional sample preparation. However, samples for SEM analysis were coated with platinum at 6 mA and 7 V for 90 s prior the experiments. Images were obtained at an accelerating voltage of 2KV and current 10 μ A or else samples would start burning. Although SEM is a good technique for morphological and microstructural analysis, it is very challenging to obtain adequate images when dealing with inorganic particle–polymer nanocomposite membranes. With exposure to the electron beam, the polymer starts to decompose faster than images can be captured making it difficult to get good images with smaller particles. Therefore, atomic force microscopy, a nondestructive technique, was preferred for the nanocomposites. In all of the nanocomposites, determination of the weight percent silica by thermal gravimetric analysis is prevented by the thermal generation of HF from the Nafion and its reaction with the silica to afford gaseous silicon tetrafluoride.¹⁷

Water-uptake measurements for all the membranes (NSS, PNSS, and NTEOS series) were used to examine the effect of membrane processing on their properties. This was achieved by first post-treating the membranes. Membranes were soaked in 3 wt % hydrogen peroxide at 80 °C for 1 h then rinsed with deionized water to remove organic impurities. Then, membranes were soaked in 0.5 M sulfuric acid at 80 °C for 1 h for acidification followed by rinsing with deionized water. Nanocomposite membranes were left in deionized water for 24 h before analysis. Pretreated membranes were dried at 100 °C for 2 h in a vacuum oven and weighed (dry weight), and then soaked in deionized water at 60 °C for 2 h, blotted dry and weighed (wet weight). Water-uptake values were calculated from eq 1 below.

$$\text{water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} * 100 \quad (1)$$

Here, W_{wet} is the weight of the wet membranes and W_{dry} the weight of the dry membranes.

Loosely bound particles on the surfaces of the nanocomposite membranes were easily removed with mechanical stirring or sonicating resulting in membranes with lower loadings of particles than intended. To determine how much of the particles could be lost during processing we used simple gravimetric analyses. Newly prepared nanocomposite membranes were dried under vacuum at 100 °C for 24 h to remove any residue solvent. After cooling, the membranes initial dry weight was measured. Then the membranes were placed in stirred water for 2 h, dried under vacuum at 100 °C for 24 h and reweighed to determine how much mass was lost with simple washing. The size of particles dislodged from the nanocomposites was measured by dynamic light scattering (DLS). Total change in membranes weight was attributed to loss of particles because no polymeric species were detected in the aqueous wash nor was there any significant change in the mass of Nafion membranes made without particles taken through the same processing.

Percentage weight loss of particles after stirring was calculated from eq 2 below

$$\% \text{loss} = \frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

Where W_1 is the weight of the dry membranes before stirring and W_2 is the weight of the membranes after stirring.

3. RESULTS AND DISCUSSION

Our basic objective was to prepare silica nanoparticle (5 wt %)-Nafion composite membranes then evaluate the effects of particle size on water uptake. However, it quickly became evident that the conditions used in making the membranes had remarkable consequences on their morphology. In particular, the silica particles were discovered to float to the surface of the cast membranes during drying, resulting in heterogeneous distributions of silica particles.

3.1. Floating Particles with the NSS Nanocomposite Membranes Series. The original series of Nafion/Stöber silica (NSS) nanocomposite membranes were prepared by casting a dispersion of 5 wt % silica nanoparticles in ethanol with 95 wt % Nafion in ethanol, then drying. The silica particles were prepared by ammonia-catalyzed polymerization of tetraethoxysilane. Stöber conditions allow the particles to be made with narrow size distributions and varying the ammonia concentration permits the average size of the particles to be controlled.¹³ Upon casting the first series of nanocomposite membranes (NSS) we observed that the membranes made with particles 90 nm or larger in diameter appeared translucent (Figure 1). SEM and AFM imaging revealed that the silica

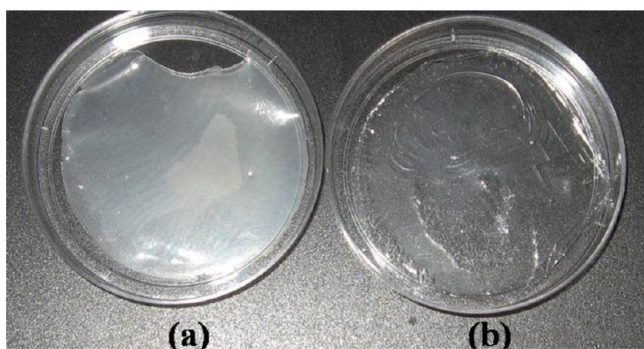


Figure 1. Comparison of Nafion/silica nanocomposite membranes (a) NSS-90 membrane (b) PNSS-120 membranes. NSS-90 membrane is opaque because of scattering of the phase-separated or agglomerated silica particles on the membrane surface.

particles were not homogeneously distributed through the membrane, but had aggregated to the top surface of the membrane. Figure 2 shows the SEM of the surface of a nanocomposite membrane with 70 nm diameter silica particles concentrated on the surface. Examination of the bottom surface of the membrane showed relatively small numbers of particles dispersed in the polymer matrix. Comparison of the top and bottom of the membranes as a function of particle size shows that floatation occurred with particles larger than 40 nm in diameter, but was not apparent with smaller particles (Figure 3). One important consequence of the particle segregation is that the particles on the top of the membrane can be dislodged mechanically or with washing. Figure 4 shows the AFM images of a NSS-136 nm nanocomposite membrane before and after washing. In contrast, the population of particles on the bottom of the membranes did not change suggesting that particles at the bottom side of the membrane are trapped in the polymer matrix. Gravimetric analysis of washed NSS-series nanocomposite membranes with 5 wt % particles shows that it is possible to lose between 0.5 to 2 wt % particles during the membrane processing thus interfering with the nanocomposite membrane composition. This will in turn affect the properties

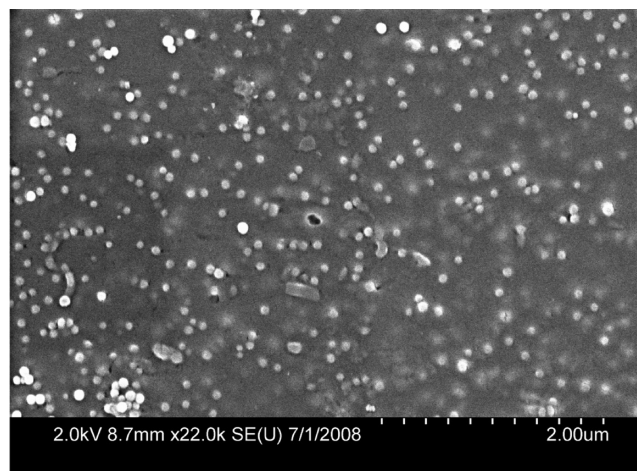


Figure 2. SEM image of top surface of NSS-70 nanocomposite membranes showing a high concentration of the silica particles on the membrane surface.

of the nanocomposite membranes observed as will be described later. Examination of the particles washed from the surface by dynamic light scattering indicates essentially the same particle size distribution used to prepare the membrane indicating no significant size sieving was occurring with the relatively narrow particle size distributions used.

It appears that the segregation of the particles to the surface of the membrane occurs through floatation of porous silica particles larger than 40 nm in diameter in the 5 wt % Nafion solution. In ethanol solution, Nafion is known to assume rigid rod conformations with sulfonic groups on the surfaces.^{11,18,19} Homogeneous dispersion of the smaller silica particles likely relies on strong nonbonding interactions between the polar macromolecular surface and the surface silanols on the particles. We found silica particles that were surface modified with mercaptopropyltriethoxysilane or decafluorooctyltriethoxysilane similarly segregated when the particles were greater than 50 nm in diameter. This is not the first time that this phenomenon has been observed, similar aggregation was reported previously with fluoroalkyl, surface-modified silica particles in Nafion, but the cause was not discussed.²⁰ Clearly, the size rather than the functionality of the silica particles is the critical parameter for keeping the particles homogeneously dispersed.

The fact that the particles segregated to the top of the membranes in every case, suggested that the driving force for floatation was the relative density of the particles compared with the Nafion solution. As purchased, the Nafion solution used to prepare the composites is 5 wt % polymer in aliphatic alcohol and has a density of 0.874 g/mL. The silica particles were dispersed in ethanol and so were very easy to mix in the Nafion solution. As the solvent evaporates, the solution viscosity increases and the solution density increases toward the density of dry Nafion (2.2 g/mL).¹¹ Amorphous nonporous silica has a density between 2 and 2.3 g/mL²¹ and thus nonporous silica particles should remain dispersed in the polymer matrix even after drying all the solvent. There has been a lack of consensus on whether or not Stober silica particles are porous or not. However, nitrogen sorption porosimetry revealed that the silica particles used in this study were in fact porous (Table 4) and of lower density than nonporous amorphous silica.

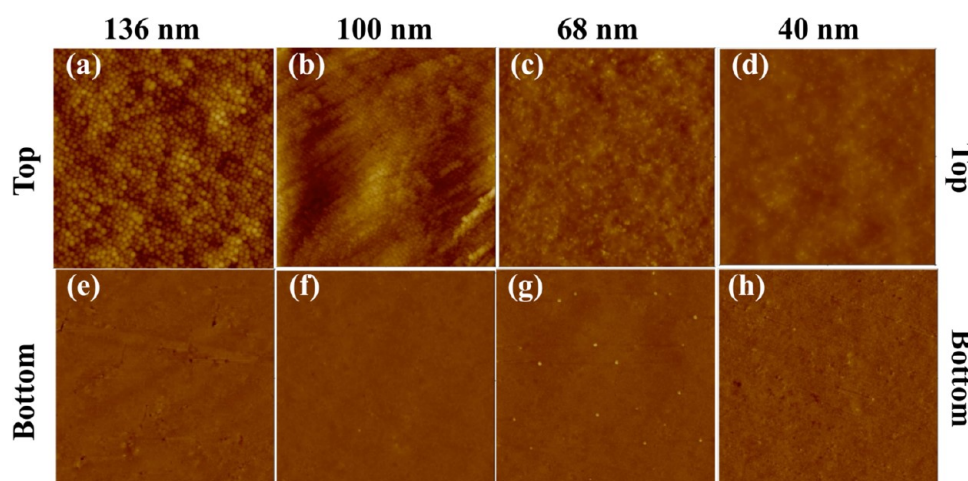


Figure 3. Tapping mode AFM height images ($5 \mu\text{m} \times 5 \mu\text{m}$) of NSS series nanocomposite membranes showing the top and bottom surfaces with (a, e) 136, (b, f) 100, (c, g) 70, and (d, h) 40 nm diameter silica particles.

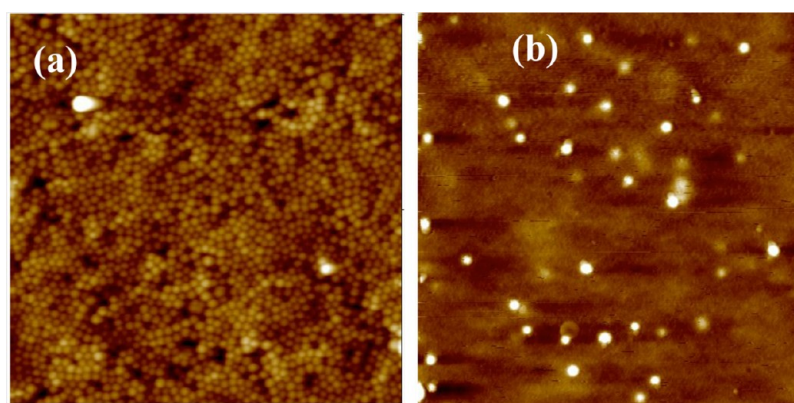


Figure 4. Tapping mode AFM height images ($5 \mu\text{m} \times 5 \mu\text{m}$) NSS-136 nanocomposite membranes (a) before and (b) after washing to dislodge particles.

Table 4. Surface Area and Water Uptake of Stöber Silica Particles of Different Sizes

DLS (nm)	calcd ^a surface area (m ² /g)	BET surface area (m ² /g)	pore volume (cc/g)	water uptake (%)
41 ± 2	66	84	0.49	13.9
69 ± 2	40	95	0.48	8.4
134 ± 3	20	381	1.46	13.6
200 ± 17	14	264	0.84	9.0
300 ± 10	9	297	0.57	10.2

^aSurface areas were calculated for spherical, nonporous silica particles with a density of 2.26 g/cm^3 .

3.2. Evenly Distributed Silica Particles in PNSS Nanocomposite Membranes. Because it was apparent that the particles were floating to the top of the membrane during drying, we decided to slow segregation by evaporating solvent before casting in order to increase the viscosity while keeping the particles dispersed. Concentrating the Nafion solution before adding the silica particles made dispersion difficult. Instead, after combining the silica particle suspension and Nafion solution in ethanol together, the resulting mixture was placed in an oven until sufficient ethanol had evaporated to increase the viscosity before casting. Once the mixture was stirred to ensure homogeneous dispersion, membranes were

cast and the homogeneity of silica particle dispersion was evaluated with SEM or AFM. Ultimately, we found that evaporating ethanol from the mixture until the viscosity increased from 14 cPs to 65 cPs gave membranes with no apparent segregation of particles. The combination of having less ethanol to evaporate and higher viscosity to impede particle movement allowed uniform membranes to be fabricated. In appearance, the PNSS series membranes look transparent (Figure 1b) even with the 120 nm particles because of the absence of particle aggregates on the membrane surface. Figure 5 shows AFM images of the top and bottom surfaces of the PNSS series membranes with different particle sizes. The bright spots on the image represent the particles while the brown regions are the polymer matrix. The cross-section SEM images also show a satisfactory distribution of the particles throughout the entire thickness (Figure 6). The particulates observed on the top and bottom surfaces and in the cross-sections analyses are in the same size range as the particles used to prepare the membranes. Few if any particles appear to be dislodged with washing or mechanical abuse. Furthermore, preconcentration also works with homogeneously dispersing surface modified silica particles into Nafion (PNSST series).

3.3. Conventional Nafion–TEOS Nanocomposite Membranes. The NTEOS series membranes, prepared by polymerizing TEOS in the Nafion solution, show good distribution of particles on both sides as shown in the AFM

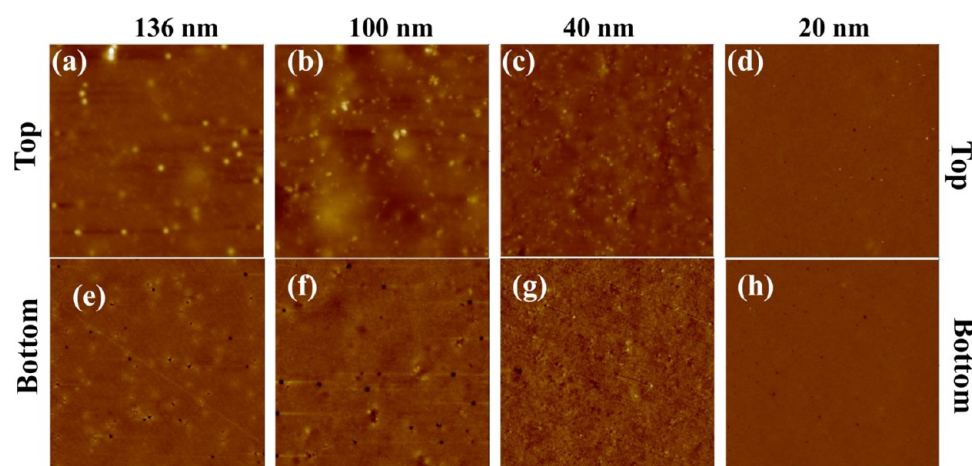


Figure 5. Tapping mode AFM height images ($5 \mu\text{m} \times 5 \mu\text{m}$) of PNSS nanocomposite membranes showing top and bottom surfaces with (a, e) 136, (b, f) 100, (c, g) 40, and (d, h) 20 nm diameter silica particles.

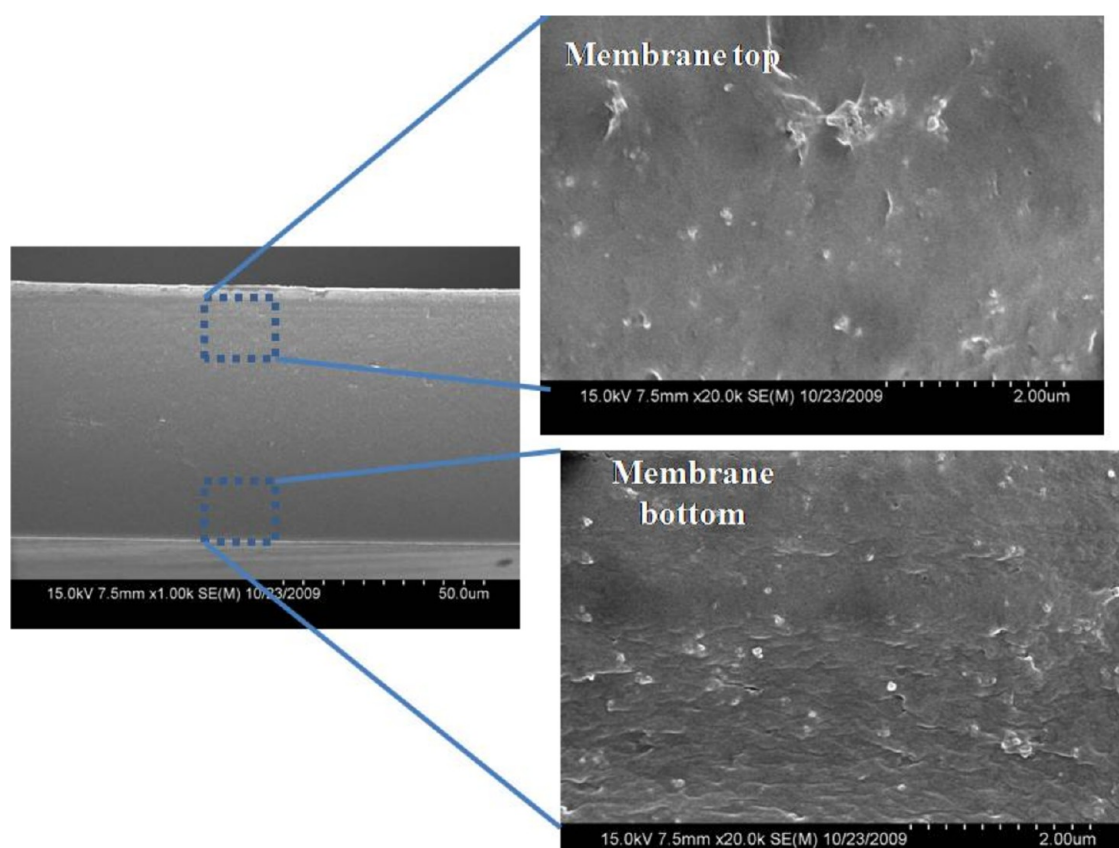


Figure 6. Cross-section analysis of PNSS-136 showing the distribution of the particles on the top and bottom section of the membrane. The white small dots are the particles distributed in the nanocomposite membranes.

images in Figure 7. All of the nanocomposite membranes appeared transparent indicating no significant aggregation. However, the size and shape of the silica particulates changes with changes in the amount of TEOS added with 1 wt % having the smallest particulates and 10 wt % having the largest particulates. NTEOS-10 nanocomposite membranes have silica particulates that are bigger than silica particles used in NSS and PNSS series membranes and would be expected to scatter more light than PNSS series membranes. However, silica particles in NTEOS-10 membranes are all different sizes and the final condensed silica is (2.8 wt %) much less than the amount of

particles added into Nafion (5 wt %). The technique used to prepare the NTEOS series permits preparation of transparent nanocomposite membranes, but does not allow for control of particle size making it inappropriate to use in analyzing the effect of particle size on the nanocomposite membranes properties.

3.4. Impact of Processing Conditions on Nanocomposite Membrane Water Uptake. Water uptake of Nafion, an important metric for fuel cell membrane performance, has been shown to increase when silica is added.³ In light of how silica particles can segregate during nanocomposite

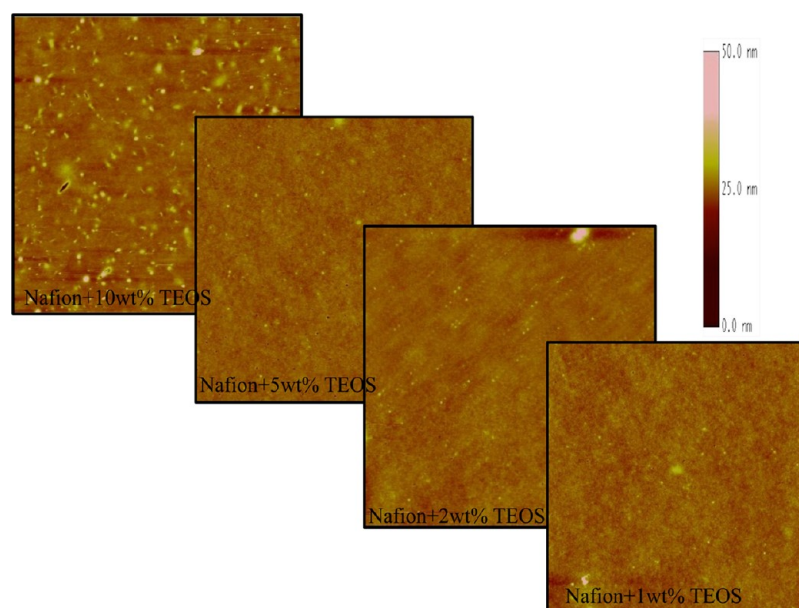


Figure 7. Tapping mode AFM height images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of NTEOS series nanocomposite membranes prepared with conventional sol–gel. Bright spots indicate the silica particulates in the membranes.

membrane formation, it is important to ascertain how membrane processing and homogeneity of silica in the nanocomposite influence water uptake. Figure 8 shows a

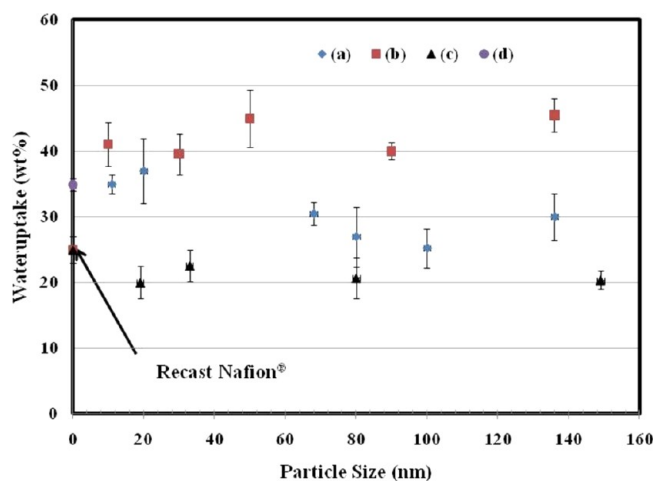


Figure 8. Comparison of the water uptake of the NSS, PNSS, and NTEOS series nanocomposite membranes. (a) NSS series nanocomposite membranes, (b) PNSS series nanocomposite membranes, (c) PNSST series nanocomposite membranes, and (d) NTEOS-5 nanocomposite membranes, where recast Nafion is indicated with the arrow.

comparison of water uptake measured for NSS, PNSS, NTEOS, and PNSST series membranes. All of the nanocomposites with unmodified silica particles show greater water uptake than recast Nafion, which is in agreement with the literature.³ The rationale for the increase is that the additional silanols on the silica surface expand the polar environment in the membranes for retaining water. However, with the NSS series nanocomposite membranes, water-uptake is highest with small particles, close to values obtained with PNSS series nanocomposite membranes with similar sized particles, and decreases with increasing particle size close to values with

recast Nafion. The decrease in the water uptake values with large particle sizes is attributed to the loss of loosely bound particles from the membrane surface during processing. Because small particles are retained during membrane casting, drying, and processing, the amount of silica in the nanocomposites and the resulting water uptake values are comparable to the analogous PNSS membranes.

Overall, the PNSS series membranes have higher water-uptake than NSS series and NTEOS series, which clearly shows that preparation and processing of the nanocomposite membranes has an impact on the properties. In addition, water-uptake values for PNSS series membranes are almost independent of the size of the particles. Assuming that all of particles are nonporous, the total surface area (Table 4) and total number of silanol groups decreases with increasing particle size. This, coupled with the relatively small size of the water bearing channels, would lead to the expectation that the water uptake should decrease as the particles get larger. Nitrogen sorption and BET²² surface areas reveal significantly higher surface areas, particularly for the larger particles. Particle porosity explains why the water uptake does not correlate to the geometric surface area of the particles in membranes. High uptakes with small particles are probably more significantly influenced by the fact that the particles can better fit into the polar channels, whereas high uptakes with the larger particles are due to their higher surface areas and porosity that would permit adsorption of water even if the particles were mostly outside of the hydrophilic domains. We believe that the NTEOS series nanocomposite membranes have lower water uptake than NSS or PNSS membranes because first, they have less condensed silica, and second in situ chemistry used to prepare the particles in the NTEOS yields broad size distributions of relatively hydrophobic particles.

NTEOS membranes are prepared via a one-step process, which is easy and saves time, but limits control over particle size and, most definitely, has an impact on the properties of the resulting nanocomposite membranes. In addition, it has been shown that the in situ produced silica phase in Nafion is partially condensed with the presence of surface ethoxide

groups.²³ The presence of the residue ethoxide group on the surface of silica lowers its hydrophilicity and thus lower water uptake of the nanocomposite membranes. Finally, the PNSST membranes have the lowest water uptake values because of the hydrophobicity of the mercaptopropylsilane side chains that blocks the silica from holding water in the membranes.

4. CONCLUSION

Nanocomposite membranes based on Nafion and silica nanoparticles were prepared and their morphology, and water-uptake evaluated as a function of silica particle size and surface functionalization, and membrane preparation and processing. Membranes were formed by casting mixtures of ex situ generated silica particles dispersed in ethanolic Nafion solutions. The size and dispersity of the silica particles was controlled between 20 and 300 nm by varying the ammonia concentration in a modified Stöber procedure. This ex situ method for introducing silica particles afforded greater control over particle size and dispersity than particle formation from the in situ sol-gel polymerization of tetraethoxysilane in Nafion (NTEOS). Using AFM and SEM analyses of membrane morphologies, we discovered that silica particles floated to the surface of cast ethanolic Nafion solutions of lower viscosity, resulting in heterogeneous distribution of silica particles in the dry membranes. Not only did this unfortunate distribution of silica particles make them more susceptible to displacement due to poor integration into the matrix, it made water-uptake measurements meaningless. Fortunately, homogeneous distribution of the particles in the polymer matrix was possible by casting higher viscosity (65 cP) solutions. The influence of the particle homogeneity in the nanocomposites is clear from the greater water-uptake observed with the homogeneous (PNSS) membranes when compared with the heterogeneous (NSS) membranes. The size of the silica particles had surprisingly little effect on the water-uptake of the membranes. In situ Nafion/silica nanocomposite membranes are easy to prepare, but they have lower water-uptake than the nanocomposite membranes prepared with ex situ silica particles. This may be due to less hydrophilic silica surfaces as a result of residual ethoxide groups on the particles' surfaces. Therefore, Nafion/ex situ remains the only way to monitor the effect of silica particle size on the properties of the nanocomposite membranes, but great care has to be taken in their preparation.

■ ASSOCIATED CONTENT

Supporting Information

Additional figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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