Hybrid Polyelectrolyte Materials for Fuel Cell Applications: Design, Synthesis, and Evaluation of Proton-Conducting Bridged Polysilsesquioxanes

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A method for the synthesis of chemically and thermally robust sulfonic-acid-containing hybrid membrane materials has been established. These polyelectrolyte membranes are prepared by oxidation of the corresponding disulfide-bridged polysilsesquioxanes. This strategy allows for high acid-group loading. Their microstructure is determined by nitrogen adsorption porosimetry, solid-state NMR spectroscopy, and atomic force microscopy. Application of these hybrid materials as proton-exchange membranes for fuel cells is investigated by measuring their proton conductivity, which increases linearly with increasing sulfonic acid content to 6.2 mS/cm.

Introduction

The search for means of power generation alternatives to the combustion engine has become a pressing issue in the past few decades. The adverse environmental, economic, and political impact of using fossil fuels is becoming more apparent, prompting a significant amount of effort in the area of fuel-cell research.[1] Among the many different types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) are believed to be best suited for the automotive industry and portable devices; although the technology is at the point of implementation, commercialization of PEMFC is limited by high costs.[2] One of the contributing factors is the current state-of-the-art electrolyte membrane material, Nafion, a perfluorosulfonic acid-based polymer possessing high proton conductivity, processability, and good mechanical and chemical stability. [3] Fluorine-free materials with properties comparable to Nafion is one of the directions in the development of cheaper polyelectrolytes. In addition to hydrocarbon-based polymers such as sulfonated styrene−ethylene/butylene−styrene block copolymers,[4] which have limited chemical stability, sulfonated aromatic polymers based on poly(arylene ether)s and poly(imide)s have been studied. However, to achieve acceptable conductivities, a high degree of sulfonation is often required. This can impart considerable swelling of the membrane upon hydration.[5,6]

Bridged polysilsesquioxanes, a class of hybrid organic−inorganic materials, offer a different direction in polyelectrolyte research. Prepared by sol−gel polymerization of organo-bridged trialkoxysilane monomers (Figure 1), these materials allow for properties such as porosity, permeability, permselectivity, chemical functionality, and chemical, mechanical, and thermal stability to be fine-tuned because of the vast variety of synthetically available monomers.[7−11] Honma and co-workers reported on the synthesis of a protonic conductive polysilsesquioxane membrane containing poly(ethylene oxide), polypropylene oxide and polytetramethylene oxide organic bridging groups functionalized with isocyanotopropyltriethoxysilane and condensed in the presence of phosphotungstic acid or monododecyl phosphate. There materials were shown to function as proton carriers.[12,13] Such doping of functional molecules often limits the operational lifetime of a material because of leaching.[14] A material with covalently bound acidic groups would be desirable for preventing this phenomenon. In addition, under strong oxidative fuel-cell conditions, the stability of the

(5) Steele, B. C. H.; Heinzel, A. *Nature* **2001,** *414,* 345.
(6) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004,** *104,* 4587.
(7) Loy, D. A. *MRS Bull.* **2001,** *26,* 364.
(8) Oviatt, H. W.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993,** *5,* 943.
(9) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001,** *13,* 3306.
(10) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992,** *114,* 6700.
(11) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Man, M. W. C. *Chem. Mater.* **1992,** *4,* 1217.
(12) Honma, I.; Takeda, Y.; Bae, J. M. *Solid State Ionics* **1999,** *120,* 255.
(13) Honma, I.; Nishikawa, O.; Sugimoto, T.; Nomura, S.; Nakajima, H. *Fuel Cells* **2002,** *2,* 52.
(14) Stangar, U. L.; Orel, B.; Groselj, N.; Judeinstein, P.; Decker, F.; Lianos, P. *Monatsh. Chem.* **2001,** *132,* 103.
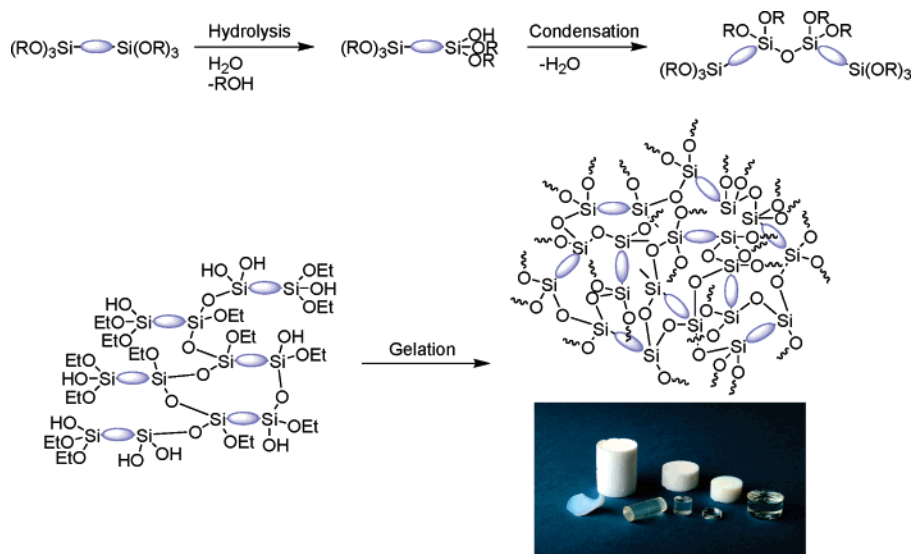
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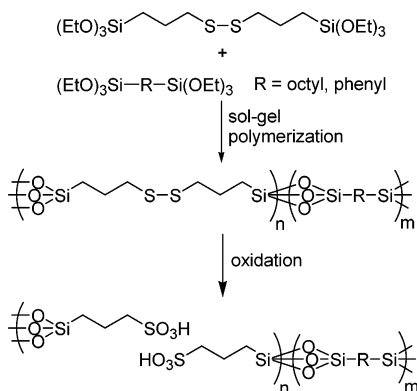† University of California, Irvine.
‡ University of Arizona.
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|| Sandia National Laboratories.

(1) Haile, S. M. *Mater. Today* **2003,** *6,* 24.
(2) Winter, M.; Brodd, R. J. *Chem. Rev.* **2004,** *104,* 4245.
(3) Carrette, L.; Friedrich, K. A.; Stimming, U. *Fuel Cells* **2001,** *1,* 5.
(4) Kim, J.; Kim, B.; Jung, B. *J. Membr. Sci.* **2002,** *207,* 129.

Figure 1. Bridged silsesquioxane monomers are polymerized by a series of acid- or base-catalyzed hydrolysis and condensation reactions resulting in oligomeric silsesquioxanes, which eventually form an infinite network.
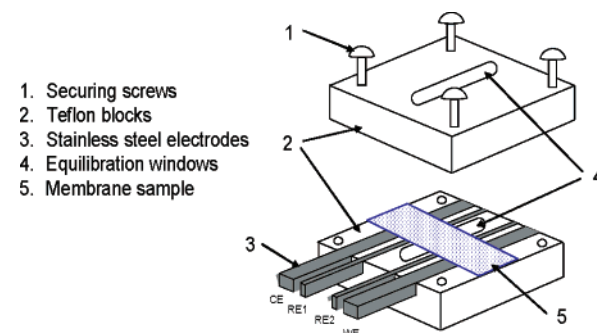

Figure 2. Overview of the preparation of conductive polysilsesquioxane materials that covalently bind proton carriers.

1. Securing screws
2. Teflon blocks
3. Stainless steel electrodes
4. Equilibration windows
5. Membrane sample

Figure 3. Test cell for proton-conductivity measurements.

Experimental Section

Instrumentation. Solution ^{1}H and ^{13}C NMR were recorded on 500 MHz spectrometers. ^{1}H NMR spectra were obtained at an operating frequency of 500 MHz, where chemical shifts are reported in parts per million with the indicated solvent as an internal reference. Coupling constants are reported in Hz. Splitting abbreviations are as follows: *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *m*, multiplet. ^{13}C NMR spectra were obtained at an operating frequency of 125.8 MHz, where the chemical shifts are reported in parts per million with the indicated solvent as an internal reference.

Solid-state NMR spectra were obtained with sample spinning rates of 7.5 kHz. ^{13}C NMR spectra were obtained at 75.5 MHz. ^{29}Si NMR spectra were obtained at 59.6 MHz.

Proton conductivity of the membranes was measured by four-probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260 frequency response analyzer coupled with a Solartron 1287 potentiostat. EIS was performed on water-immersed samples by imposing a relatively small (10 mV amplitude) sinusoidal (AC signal) voltage across the membrane sample at frequencies between 100 kHz and 100 Hz (scanning from high to low frequencies); the resulting current response was measured. A schematic diagram of the membrane conductivity cell is shown below (Figure 3).

The outer electrodes are connected to the working and counter electrodes on the 1287 potentiostat, and the two inner electrodes are connected to the reference electrodes. From the amplitude and phase lag of the current response, we computed a complex number,

carbamate linkages present in the membrane is uncertain, and thus more chemically inert bridged triethoxysilane precursors could improve stability.

In the following text, we describe the preparation of proton-conductive polysilsesquioxane materials with covalently bound sulfonic acid functional groups. These groups are introduced in latent form as bis(triethoxysilyl)propyl disulfides, where the disulfides maximize sulfur loading compared to a mercapto-containing silane monomer. The propyl group introduces a degree of mobility, allowing for the possibility of sulfonic acid cluster formation, which would enhance proton conductivity. Monomers 1,4-bis-(triethoxysilyl)benzene and 1,8-bis(triethoxysilyl)octane were utilized as network-supporting functionalities, whose content is varied to optimize the mechanical properties of the membrane materials (Figure 2). This is the degree of control that sets polysilsesquioxanes apart from T-resins, which can only be prepared as dense, highly brittle materials.

Following sol−gel polymerization and processing, the materials were characterized by solid-state NMR spectroscopy, IR spectroscopy, TGA, nitrogen adsorption porosimetry, and AFM spectroscopy. Proton conductivity is measured by impedance spectroscopy.

called the impedance, composed of a real component, Z', and an imaginary component, Z''. To compute the membrane proton conductivity from the complex impedance response, we extrapolated the impedance line to the x axis. The extrapolated value of the real impedance where the imaginary response is zero (Z' at $Z'' = 0$) is then taken as the resistance of the membrane and the membrane proton conductivity is computed according to the following equation

$$\kappa = \frac{L}{Z'A}$$

where L is the length between the sense electrodes, Z' is the real part of the impedance response (extrapolated to $Z'' = 0$), and A is the area available for proton conduction (width x thickness). All proton conductivities reported here were measured with the film immersed in liquid water at 30 °C during the measurement time.[15,16]

Intermittent contact mode AFM images were obtained in air at ambient pressure and humidity using an AutoProbe CP-Research scanning probe microscope. The piezoelectric scanner was calibrated using a 5.0 μm grating in the xy and z directions using an AFM reference (Pacific Nanotechnology, Santa Clara, CA; model P-000-0004-0). The tips were silicon (Ultrasharp cantilevers, model NSC11, MikroMasch, Wilsonville, OR). Topographs were obtained as 256 × 256 pixels, flattened line by line, and analyzed using the AutoProbe image processing software supplied by the manufacturer of the AFM. The root-mean-square (RMS) surface roughness over selected scanned areas was calculated from $R_{RMS} = [\sum^N (z_n - \bar{z})^2/(N - 1)]^{1/2}$, where $\bar{z}$ is the average z height, z_n is the height at each point on the sample and N is the number of points sampled.

Monomers. *General Procedures.* All solvents were purified by fractional distillation from the appropriate drying agents or dried by filtration through appropriate drying agents prior to use. 1,8-Bis(triethoxysilyl)octane **6** and 3-mercaptopropyltriethoxysilane were purchased from Gelest Inc. and used as received. 1,4-Bis-(triethoxysilyl)benzene **3** was prepared according to a literature procedure.[10] 1,4-Dibromobenzene was purchased from Aldrich Chemical Co. and used as received. Tetraethyl orthosilicate was purchased from Aldrich Chemical Co. and fractionally distilled prior to use.

Bis(triethoxysilyl)propyl Disulfide (2). To a 100 mL three-neck flask equipped with a condenser and a Tygon tubing outlet for HCl gas, bubbled through a saturated solution of $NaHCO_3$, were added 1,2-dichloroethane (7.0 mL) and 3-mercaptopropyltriethoxysilane **1** (5.09 mL, 0.021 mol). To the solution was added freshly purified sulfuryl chloride (0.88 mL, 0.011 mol) over a period of 7 min. The solution was stirred for 15 min at room temperature and then heated at reflux (70 °C) for 2 h. During the first hour, the colorless solution became yellow, and it turned orange toward the end of the heating period. Upon the reaction mixture being cooled to room temperature, THF (10 mL) was added, followed by the addition of a mixture of ethanol (8.1 mL, 0.14 mol) and triethylamine (2.5 mL, 0.018 mol) over a period of 15 min. White precipitates formed immediately. The condenser and the HCl gas outlet were removed, and the reaction was stirred at room temperature under a steady flow of N_2 for 16 h. Hexanes (50 mL) were added to precipitate any additional amine salts, which were removed by vacuum filtration under N_2. The filtrate was concentrated in vacuo to remove hexanes and THF. Product **2** was obtained without further purifica-

tion as a clear, yellow oil (4.03 g, 80.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.80 (q, $J = 7.0$ Hz, 12H), 2.68 (t, $J = 7.1$ Hz, 4H), 1.79 (m, 4H), 1.21 (t, $J = 7.0$ Hz, 18H), 0.71 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 58.6, 42.1, 22.9, 18.5, 10.0. HRMS (CI) *m/e*: calcd for [M] $C_{18}H_{42}O_6S_2$, 474.1961; found, 474.1760.

Synthesis of Bis-2-phenylethyl Disulfide (8). To a 100 mL three-neck flask equipped with a condenser and a Tygon tubing outlet for HCl gas, bubbled through a saturated solution of $NaHCO_3$, were added 3.2 mL (0.024 mol) of 2-phenylethylthiol and 1,2-dichloro-ethane (7.0 mL). Under a steady flow of N_2, freshly purified sulfuryl chloride (1.0 mL, 0.012 mol) was added over a period of 7 min. The solution was stirred for 15 min at room temperature and then heated at reflux (70 °C) for 2 h. During the first hour, the colorless solution became yellow. Upon the reaction mixture being cooled to 0 °C, a mixture of ethanol (9.2 mL) and triethylamine (3.8 mL, 0.028 mol) was added dropwise over a period of 15 min. The reaction mixture was stirred at room temperature under a steady flow of N_2 for an additional 16 h. Hexanes (50 mL) were added to precipitate any remaining amine salts, which were removed by vacuum filtration in air. The filtrate was concentrated in vacuo to remove hexanes. The residue was purified by flash column chromatography in hexanes to yield the product as a colorless oil (2.9 g, 87.9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30−7.18 (m, 5H), 2.99−2.90 (ddt, $J = 21.9, 5.9, 2.6$ Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.2, 128.9, 128.7, 126.6, 40.3, 35.9.

Synthesis of Sodium 2-Phenylethylsulfonate (9). To a solution of bis(2-phenylethyl) disulfide (0.186 g, 0. 679 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added concentrated (69.8%) HNO_3 (0.252 mL, 0.0041 mol) dropwise. Brown gas began evolving immediately. The reaction mixture was allowed to warm to room temperature and stirred in air until gas evolution was no longer observed (12 h). H_2O (5 mL) was added to the mixture; the aqueous layer was extracted, washed with diethyl ether, and extracted again. The aqueous layer was treated with a stoichiometric amount of 1N NaOH (1.3 mL, 1.3 mmol) to convert the sulfonic acid to the sodium salt. Water was removed in vacuo to yield an off-white solid (0.3974 g, 116%). ^{1}H NMR (500 MHz, D_2O): δ 7.38−7.26 (m, 5H), 3.18−3.03 (m, 4H). ^{13}C NMR (125 MHz, D_2O): δ 139.5, 128.9, 128.6, 126.7, 52.4, 30.4. IR (KBr) 3418, 2924, 1656, 1453, 1190, 621 cm^{-1}. HRMS (ESI) *m/z*: calcd for [2M + Na]$^+$ $C_8H_9O_3$-SNa, 439.0238; found, 439.0237.

Sol−Gel Processing. *General Polymerization Procedure.* All polymerizations were carried out in polyethylene membrane polymerization containers (vide infra). Monomers **1**−**3** were added to absolute ethanol in various ratios to result in a final total monomer concentration of 0.4 M. The solution was vigorously shaken for 30 s. To this solution was added 1 M NaOH. The solution was shaken for 30 s, injected into a polymerization container, and allowed to stand at room temperature. Gelation was determined by the point at which the solution stopped flowing.

Gel Processing: Xerogels. Once gelation occurred, the gel was allowed to age for an additional 48 h at room temperature. During this period, the gel decreased slightly in volume and expelled a small amount of solvent due to syneresis. At the end of the curing period, the gel was washed in ethanol for 2 h to remove unreacted monomer, followed by four washes in distilled water, 2 h each. Finally, after the gel was stored in freshwater overnight, it was broken up into smaller pieces and filtered. For purposes of analysis, the gel was allowed to dry under ambient conditions for 3 days. It was then ground to a fine white powder and dried in a vacuum oven (40 mmHg, 80 °C) for 24 h to remove residual water.

Material Synthesis: 20SS-80Ph (4). 1,4-Bis(triethoxysilyl)-benzene **3** (1.749 g, 4.502 mmol) and bis(triethoxysilyl)propyl disulfide **2** (0.5153 g, 1.1 mmol) were combined with ethanol to

(15) Fujimoto, C. H.; Hicknert, M. A.; Cornelius, C. J.; Loy, D. A. *Macromolecules* **2005**, *38*, 5010.
(16) Zawodzinski, T. A.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, *140*, 1041.

afford a 0.4 M solution. NaOH (1N, 0.629 mL, 6.2 equiv of H_2O water to monomer, 10.8% mol NaOH) was added. Gelation occurred after 1.5 h, and the gel was aged for 48 h. The resulting gel was crushed with a spatula and washed with ethanol (25 mL). The slightly yellow gel was soaked in H_2O. It was collected by vacuum filtration and allowed to air-dry in a Petri dish for 72 h. It was then ground to a fine powder and dried under vacuum for 24 h to yield an off-white xerogel (1.1237 g, 103.2%). IR (KBr): ν 3450, 1170, 1071, 920, 526 cm^{-1}. Nitrogen adsorption porosimetry: BET surface area 520 m^2/g, BJH pore diameter 23 Å. ^{29}Si CP MAS NMR (59.6 MHz): δ −60, −70, −82. ^{13}C CP MAS NMR (75.5 MHz): δ 59 (OCH_2CH_3), 42 (SSCH_2CH_2), 23, 17 (OCH_2CH_3), 12.

30SS-70C8 (5). Bis(triethoxysilyl)propyl disulfide **2** (0.5687 g, 1.2 mmol) and 1,8-bis(triethoxysilyl)octane **6** (1.265 g, 2.8 mmol) were added to ethanol to result in a 0.4 M monomer solution. The mixture was shaken for 30 s, and 1N NaOH (0.435 mL, 10.8 mol % NaOH, 6.2 equiv of H_2O) was added. Gelation occurred after 2 h, and the gel was aged for 48 h. The resulting gel was crushed with a spatula and washed with ethanol (25 mL). The white gel was soaked in H_2O. It was collected by vacuum filtration and allowed to air-dry in a Petri dish for 72 h. It was then ground to a fine powder and dried under vacuum for 24 h to yield a white xerogel (0.922 g, 101.6%). IR (KBr): 3425, 2929, 2860, 1123, 957 cm^{-1}. Nitrogen adsorption porosimetry: BET surface area 319 m^2/g, BJH pore diameter 91 Å. ^{29}Si CP MAS NMR (59.6 MHz): δ −48, −58, −48. ^{13}C CP MAS NMR (75.5 MHz): δ 58 (OCH_2CH_3), 42 (SSCH_2CH_2), 30, 24, 19 (OCH_2CH_3), 13.

Membrane Preparation. A polymerization container was prepared by puncturing a hole in the bottom of a plastic cup and covering the top (8 cm in diameter) with stretched poly(vinylidene chloride) film. The container was turned upside down, and the thoroughly mixed polymerization solution (as described in the general polymerization procedure) was injected through the hole. The injection opening was sealed to prevent solvent evaporation and the solution was allowed to gel, then age for an additional 48 h. The membrane, still attached to the poly(vinylidene chloride) film, was carefully taken out of the plastic container and peeled off. The membrane was solvent processed as described above, foregoing the drying steps and stored in H_2O if it is to be followed by oxidation (vide infra) and proton-conductivity measurements or processed further to obtain a xerogel for full characterization.

Membrane Oxidation: Typical Procedure. To a beaker containing the fully hydrated polymer membrane was added concentrated (69.8%) HNO_3 (10 mL). Evolution of a brown gas was observed immediately. The beaker was agitated for 24 h, upon which gas evolution subsided. The membrane was removed from the solution and soaked in H_2O (100 mL) four times for 12 h each and subsequently stored in water. No visible mechanical membrane degradation was observed (with the exception of 60SS-40C8, in which very small cracks were visible after 24 h in HNO_3).

46SO3H-54C8. IR (KBr): 3424, 2927, 2857, 1107, 1010 cm^{-1}. Nitrogen adsorption porosimetry: BET surface area 322 m^2/g, BJH pore diameter 51 Å. ^{29}Si CP MAS NMR (59.6 MHz): δ −48, −57, −66. ^{13}C CP MAS NMR (75.5 MHz): δ 53 (HO$_3$S$CH2CH2$), 30, 23, 18, 13.

Ion-Exchange Capacity (IEC). Membranes 46SO3H-54C8, 57SO3H-43C8, 67SO3H-33C8, and 75SO3H-25C8 were prepared by refluxing in 2 M H_2SO_4 for 1.5 h to ensure full protonation of the sulfonic acid groups. They were then washed with H_2O for 12 h, followed by refluxing in H_2O for 1.5 h. After an additional 3 h of washing in H_2O, the membrane samples were patted dry and added to vials containing NaOH (20 mL, 1 M). The vials were agitated for 24 h. Aliquots (3 × 5 mL) were taken out of the

Scheme 1. Monomer Syntheses
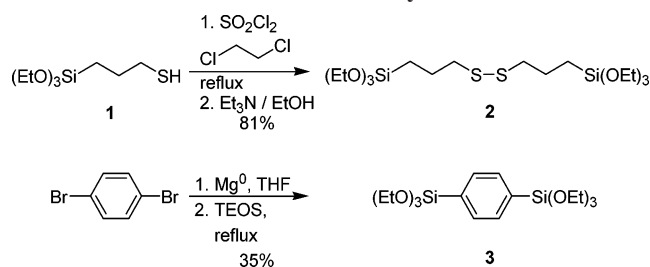
aqueous solution and titrated with 0.1 M HCl. The IEC (equiv/g) was calculated according to the following equation

$$IEC = \frac{4[(0.005 \text{ mol NaOH}) - (\# \text{ of moles of HCl required to reach end point of titration})]}{\text{weight of dry polymer (g)}}$$

The dry polymer weight was obtained by re-treating the samples with H_2SO_4 and H_2O, as described above, and drying them in a vacuum oven for 24 h (40 mmHg, 80 °C). The final IEC was obtained as the average of the three aliquots used in titrations.

Results and Discussion

Monomer Synthesis. Synthesis of the bis(triethoxysilyl)-propyl disulfide and 1,4-bis(triethoxysilyl)benzene monomers is outlined in Scheme 1.

Monomer **2** was prepared via oxidative coupling of 3-mercaptopropyltriethoxysilane with sulfuryl chloride. Because of the conversion of some triethoxysilyl groups to the corresponding chlorosilanes under the reaction conditions, the reaction mixture was subjected to an ethanolic work up. The disulfide was isolated by filtration. Monomer **3** was synthesized following a literature procedure, in which 1,4-dibromobenzene and TEOS were subjected to Barbier−Grignard conditions.[10] The product was purified by fractional distillation to isolate it from higher-molecular-weight byproducts. 1,8-Bis(triethoxysilyl)octane was obtained from a commercial source.

Polymer Preparation and Oxidation. Polysilsesquioxane polymers **4** and **5** were prepared by the hydrolytic condensation of bis(triethoxysilyl)propyl disulfide (**2**) and 1,4-bis(triethoxysilyl)benzene (**3**) and/or 1,8-bis(triethoxysilyl)-octane (**6**), respectively (Scheme 2).

The relative quantities of the monomers were varied to optimize the mechanical stability and investigate the dependence of proton conductivity on sulfonic acid content. All polymerizations were carried out in 0.4 M ethanolic solutions with 10.8 mol % NaOH catalyst and 6 equiv of water. The obtained gels were allowed to age for 48 h. They were then solvent-processed by soaking with ethanol and water and dried to afford glassy xerogels, which were ground to fine powders for oxidation and characterization.

To determine optimal conditions for complete disulfide oxidation within the polymer material, we carried out a model study for converting an organic disulfide to the corresponding sulfonic acid. Bis-2-phenylethyl disulfide (**8**) was prepared in 89% yield by the oxidative coupling of 2-phenylethylthiol (**7**) with sulfuryl chloride. The product was purified by flash column chromatography. The disulfide was oxidized to the sulfonic acid by treatment with 6.1 equiv of concentrated

Scheme 2. Synthesis of Disulfide-Containing Polysilsesquioxanes
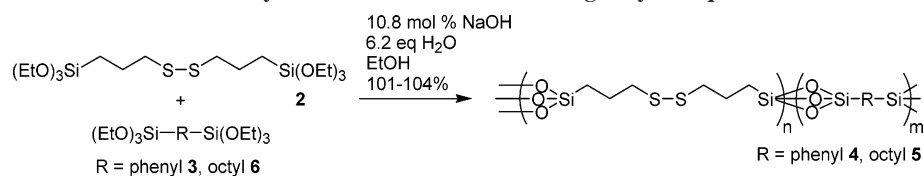
**Scheme 3. Synthesis and Oxidation of the Disulfide Model Compound**
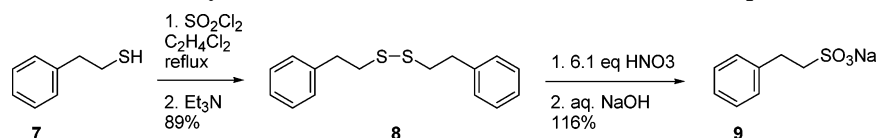
nitric acid. The product was isolated as the sodium salt (**9**) (Scheme 3).

Judging by the absence of any impurities in the ^{1}H and ^{13}C NMR spectra, the yield of 116% can be explained by the presence of NaNO$_3$. Complete oxidation of the disulfide to the sulfonic acid was confirmed by ES mass spectrometry.

Subsequently, oxidation of xerogel **5**, in which monomers **2** and **6** were present in a 3:7 molar ratio, was carried out by treatment with a large excess of concentrated nitric acid. The reaction was judged to reach completion within 24 h when evolution of brown N$_2$O$_5$ gas subsided. The degree of oxidation and integrity of the network were analyzed by solid state ^{13}C and ^{29}Si NMR, and the data were compared to the model study (Figure 4).

The model compounds allowed us to conclude that oxidation of the disulfide linkage to yield sulfonic acid

groups was represented by a 12 ppm downfield shift from 40 to 52 ppm of the ^{13}C peak corresponding to the carbon α to sulfur. The xerogel materials exhibited a similar shift, indicating complete disulfide oxidation, in which the ^{13}C peak at 42 ppm (Figure 4C) disappears upon oxidation and a new peak at 54 ppm is seen (Figure 4D). It was also noted that the polysilsesquioxanes are chemically stable to the harsh oxidative and acidic conditions. Neither cleavage of the C–Si bond occurred, as evidenced by both ^{13}C NMR and the absence of Q resonances[17] in the ^{29}Si spectra, nor were there any other signs of degradation. In addition, judging by a decrease in Q$_1$ and Q$_2$ peak areas and an increase in the Q$_3$ peak area in the ^{29}Si NMR spectra, the degree of condensation[18] of the polymer matrix increases from 84 to 88% upon treatment with HNO$_3$.
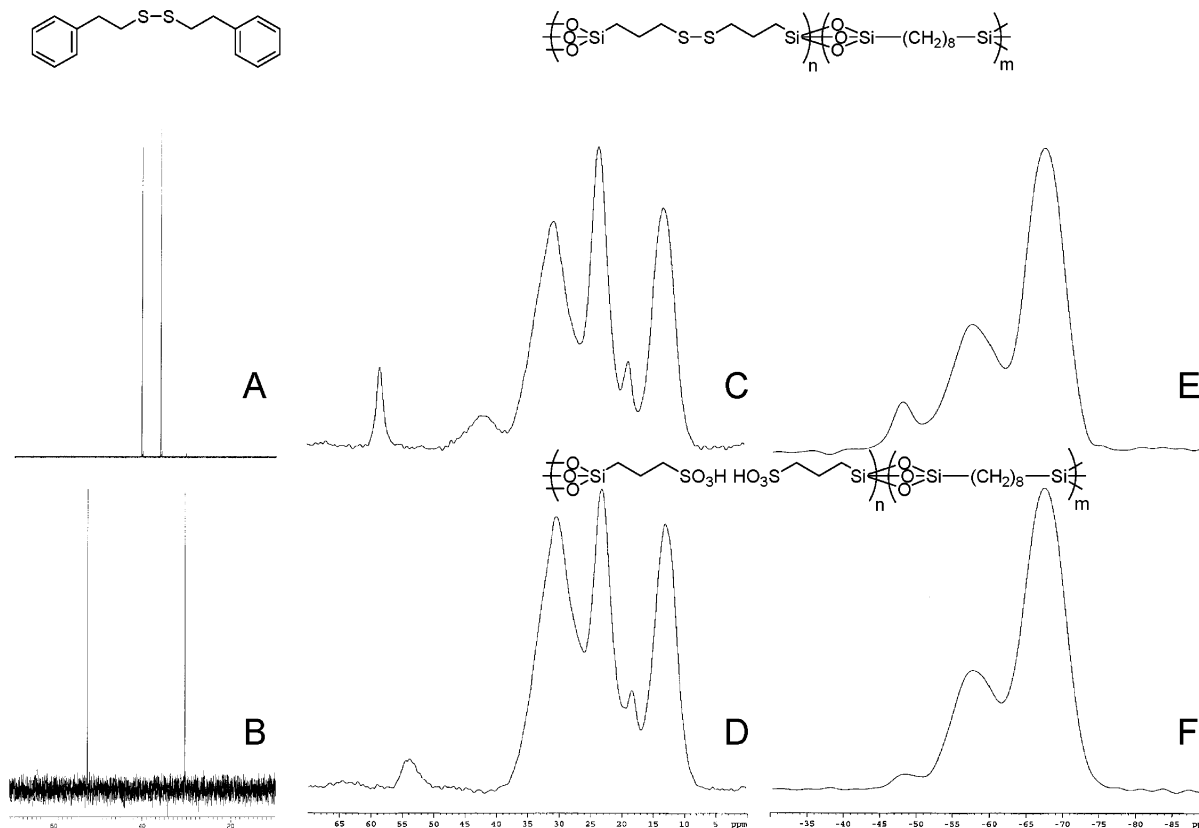
Figure 4. Selected regions of the ^{13}C and ^{29}Si NMR spectra before and after oxidation of the disulfide bond. (A) ^{13}C NMR (CD$_3$Cl) of bis(2-phenylethyl) disulfide (**8**). (B) ^{13}C NMR (D$_2$O) of sodium 2-phenylethylsulfonate (**9**). (C and D) ^{13}C SS MAS NMR of xerogels derived from bis(triethoxysilyl)propyl disulfide (**2**) and 1,8-bis(triethoxysilyl)octane monomers (**5**). (E and F) ^{29}Si SS MAS NMR of xerogels derived from 1-bis(triethoxysilyl)propyl disulfide and 1,8-bis(triethoxysilyl)octane monomers (**5**).

Table 1. Conductivities and Ion-Exchange Capacities of Membrane Materials Derived from Bis(triethoxysilyl)Propyl Disulfide (2) and 1,8-bis(triethoxysilyl)Octane (5) Monomers

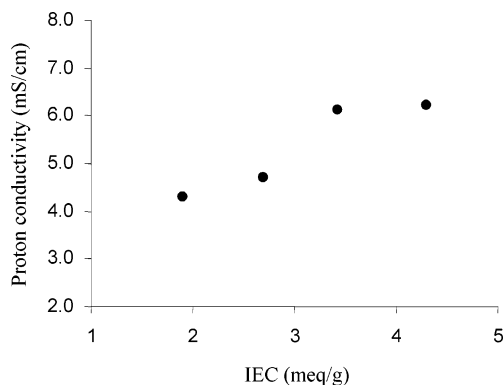| material formulation[a]	bis(triethoxysilyl)propyl disulfide (2) mol %[b]	1,8-(triethoxysilyl)octane (5) mol %[c]	ion-exchange capacity (meq/g)	proton conductivity (mS/cm)
20SS80C8	20	80	0.66	2.8[d]
46SO3H54C8	30 (46)	70 (54)	1.9	4.3
57SO3H43C8	40 (57)	60 (43)	2.7	4.7
67SO3H33C8	50 (67)	50 (33)	3.4	6.1
75SO3H25C8	60 (75)	40 (25)	4.3	6.2

[a] The formulations are abbreviated as follows, XXSSYYC8, where XX is the mol % disulfide and YY is the mol % octyl-bridged silane monomers used in membrane preparation; ZZSO3HYYC8, where ZZ is the mol % sulfonic acid, which is determined on the basis of the original disulfide monomer concentration, assuming complete oxidation, thus yielding 2 moles of sulfonic acid per 1 mole of disulfide (e.g., $30SS70C8 \rightarrow [(2\cdot30)/(2\cdot30 + 70)]SO3H[100 - (2\cdot30)/(2\cdot30 + 70)]C8 \rightarrow 46SO3H54C8$). [b] With the exception of the first entry, all data were collected on materials that had been oxidized completely. Numbers in parentheses refer to the mol % sulfonic acid. [c] Numbers in parentheses refer to mol % with respect to sulfonic acid. [d] Initial conductivity (conductivity decreases over time to 1.3 mS/cm after 30 min).

Membrane Preparation. Proton conductivities and ion-exchange capacities of the sulfonic-acid-containing polysilsesquioxanes were measured at 100% humidity utilizing fully hydrated monolithic samples. These membranes were prepared by injecting the polymerization solution into an up-turned plastic container covered by stretched poly(vinylidene chloride) film and allowing gelation to take place. Aged materials were peeled away from the film, resulting in uniform membranes of 1−2 mm thickness. The mechanical strength of the materials was fine-tuned by changes in composition of the three monomers. It was observed that materials containing exclusively monomer **2** and **3** and those containing **2**, **3**, and **6** were very brittle, whereas those comprising **2** and the octyl-bridged monomer **6** were more flexible. These were used for conductivity measurements. Oxidation of the hydrated monoliths was carried out according to the conditions described for dried xerogel powders. For further characterization, both the disulfide- and sulfonic-acid-containing membranes were solvent-processed and dried to yield monolithic (utilized in the AFM studies) and powder xerogels (utilized in solid-state NMR, IR, and TGA analyses).

Proton Conductivity Measurements. Conductivities of fully hydrated monolithic gels were measured using impedance spectroscopy with a two-electrode configuration at ambient temperature and 100% humidity. The obtained data (Table 1) were plotted as a function of ion-exchange capacity (Figure 5). The conductivities of sulfonic-acid-containing membranes did not exhibit significant fluctuations over a period of 30 min.

However, the unoxidized, disulfide-containing gel showed a continuing decrease in conductivity over time. This trend can be attributed to a lower degree of condensation of the unoxidized hybrid materials (vide supra), where there are a number of Si−OH groups. Silanols have a relatively low pK_a of 4.3 and can participate as proton carriers.[19] Under acidic conditions, such as those present during conductivity measurements, further sol−gel condensation can take place, converting silanol groups into Si−O−Si bonds and decreasing the ion-exchange capacity of the membrane.

The increasing trend of proton conductivity with increasing sulfonic acid concentration indicates that the proton-carrier

Figure 5. Proton conductivity measured by impedance spectroscopy as a function of ion-exchange capacity of oxidized membrane materials derived from bis(triethoxysilyl)propyl disulfide (**2**) and 1,8-bis(triethoxysilyl)octane (**5**) monomers.
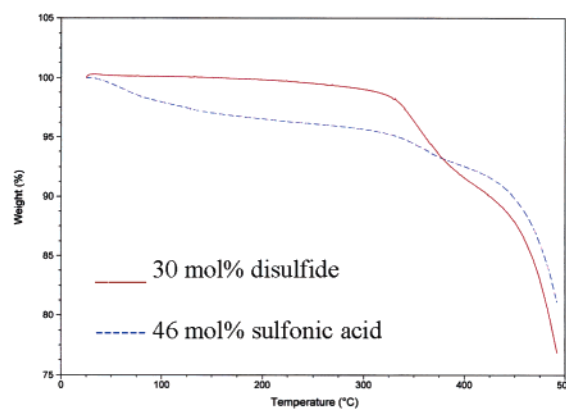
Figure 6. TGA of xerogels 30SS70C8 and 46SO3H54C8.

density is directly associated with these covalently linked groups. This trend is linear with respect to the ion-exchange capacity, reaching a plateau at 67 mol % sulfonic acid content (75SO3H25C8).

TGA. Thermal behavior of dried membranes was measured via TGA. The TGA traces of dry xerogel powders of both oxidized (46SO3H54C8) and disulfide-containing (30SS70C8) polysilsesquioxanes are represented in Figure 6.

The disulfide-containing material, 30SS70C8, exhibits very little loss of mass (2%) up to a temperature of 333 °C. This slight decrease in weight has been attributed to a loss of water and ethanol as further condensation takes place.[10] At 333 °C, the onset of organic decomposition takes place. However, more than half of the organic component remains, with an overall mass loss of 23% when the material is heated to 500

(17) Q resonances correspond to Si(OH)₄.

(18) Degree of condensation is calculated according to the equation {(0.5)[area Q₁] + (1.0)[area Q₂] + (1.5)[area Q₃]}/1.5.

(19) Chaiyasut, C.; Takatsu, Y.; Kitagawa, S.; Tsuda, T. *Electrophoresis* **2001**, *22*, 1267.
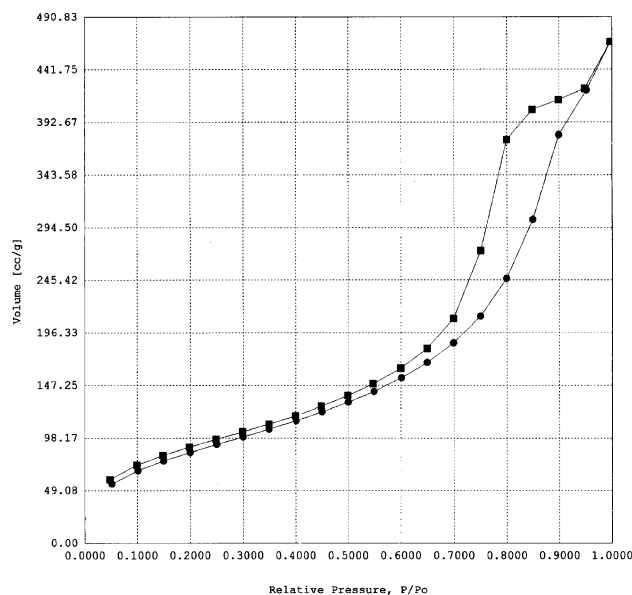
Table 2. Nitrogen Adsorption Porosimetry Data for Both Oxidized and Disulfide-Containing Xerogels Derived from Bis(triethoxysilyl)propyl Disulfide (2) and 1,8-bis(Triethoxysilyl)octane (5) Monomers

| material	BET surface area (m^2/g)	average pore diameter (Å)	total pore volume (cm^3/g)
30SS70C8	319	91	0.72
40SS60C8	335	67	0.64
50SS50C8	307	57	0.54
60SS40C8	311	72	0.55
46SO3H54C8	322	51	0.40
57SO3H43C8	220	34	0.19
67SO3H33C8	50	29	0.040
75SO3H25C8	9	113	0.025

°C; this confirms the high thermal stability inherent to organic-bridged polysilsesquioxanes. The oxidized xerogel, 46SO3H54C8, exhibits similar behavior, with the exception of higher initial mass loss of 5%, suggesting the presence of tightly bound water molecules associated with the sulfonic acid groups.

Nitrogen Adsorption Porosimetry of Disulfide and Sulfonic Acid Containing Xerogels. A summary of surface areas, pore volumes, and mean pore diameters is given in Table 2.

A representative type IV adsorption isotherm of the 30SS70C8 xerogel is shown in Figure 7. The isotherm, similar to that of silica gel, contains a type 2 hysteresis loop indicative of ink-bottle-shaped mesopores.[20] In addition, surface areas and total pore volumes were plotted as a function of disulfide and sulfonic acid concentration (Figure 8). It is immediately apparent that there are significant structural differences between the disulfide-containing and oxidized xerogels. The surface areas of the disulfide-containing gels remain relatively constant, fluctuating only between 311 and 335 m^2/g with increased sulfur content, and are similar to reported values of base-catalyzed materials derived from exclusively 1,8-bis(triethoxysilyl)octane.[8] This result is not surprising, as the organic bridge in the bis(triethoxysilyl)propyl disulfide monomer is an eight-atom linear chain that is similar in rigidity to the eight-carbon chain in 1,8-bis(triethoxysilyl)octane. In contrast, surface areas of the oxidized xerogels exhibit a sharp decline as sulfur content is increased beyond 46 mol %, decreasing to a fully collapsed, nonporous 9 m^2/g for the material containing 75 mol % sulfonic acid (75SO3H25C8). This suggests a reorganization of the molecular structure of the cross-linked network once a significant number of organic bridges are severed, where chain movement, arising from the cleavage of the disulfide bond, allows for a closely packed arrangement, which reduces total pore volume. In addition, this may allow the sulfonic acids to form ionic clusters, facilitating proton transduction through the membrane, which is the suggested mode of proton conductivity in Nafion.[21] Furthermore, the average pore diameter seems to decrease by a factor of 2 as each sample is oxidized, with the exception of the 65SO3H25C8/75SO3H25C8 pair, in which the pore diameter increases significantly upon cleavage of the disulfide bond. This perhaps can be attributed to a partial network

Figure 7. Adsorption isotherm for 30SS70C8 xerogel.
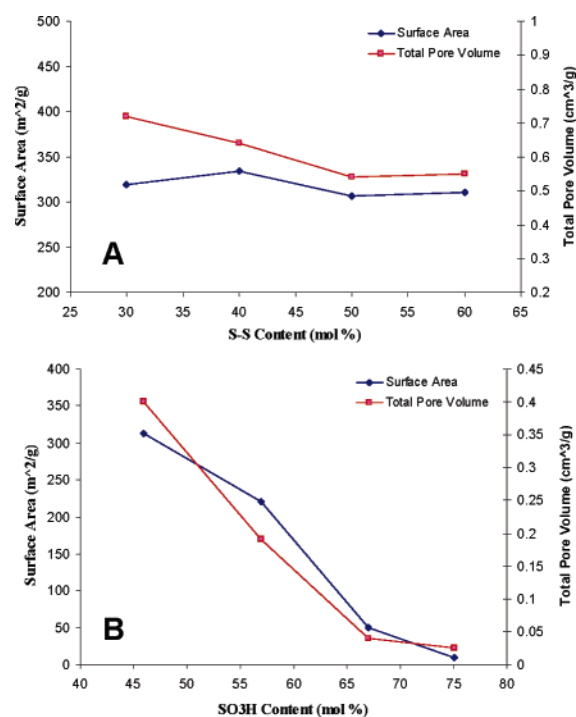
Figure 8. Surface area and total pore volume as a function of disulfide (A) and sulfonic acid (B) content in xerogel materials derived from bis-(triethoxysilyl)propyl disulfide (**2**) and 1,8-bis(triethoxysilyl)octane (**5**) monomers.

degeneration, as a large percentage of the organic bridges is cleaved.

Atomic Force Microscopy. Tapping mode AFM has been used to study surface morphology and image ionic domains in Nafion.[22–25] As in Nafion, the hybrid materials described herein contain sulfonic acid groups as the main proton carriers. Thus, the gels were analyzed by tapping mode AFM

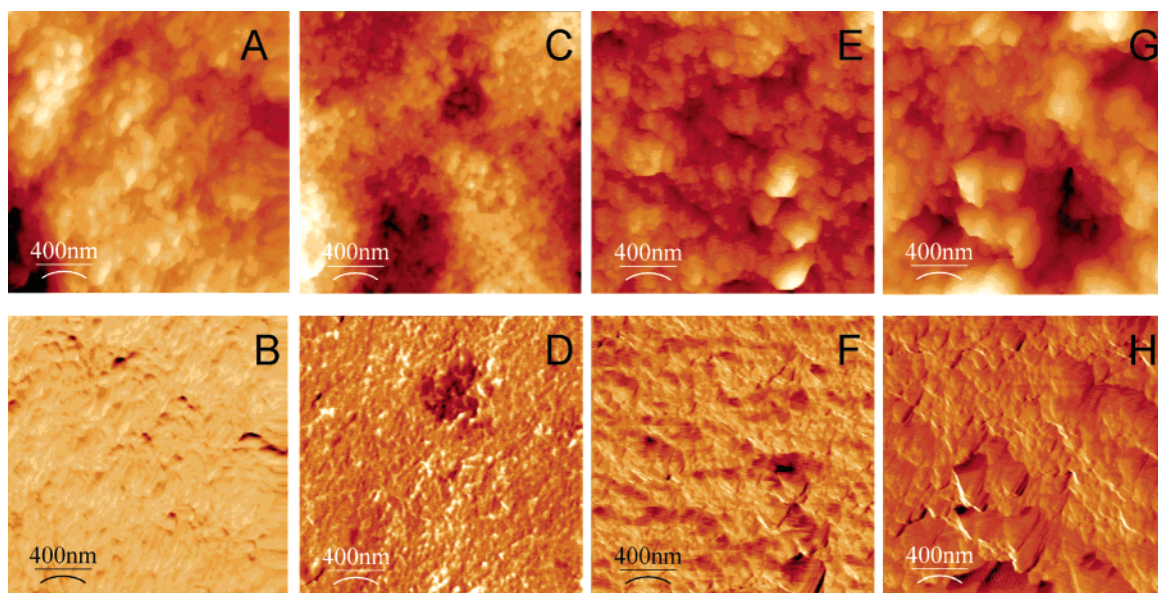(20) Kaneko, K. *J. Membr. Sci.* **1994**, *96*, 59.
(21) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535.
(22) McLean, R. S.; Doyle, M.; Sauer, B. B. *Macromolecules* **2000**, *33*, 6541.
(23) James, P. J.; Antognozzi, M.; Tamayo, J.; McMaster, T. J.; Newton, J. M.; Miles, M. J. *Langmuir* **2001**, *17*, 349.
(24) Lehmani, A. D.-V. S.; Turq, P. *J. Appl. Polym. Sci.* **1998**, *68*, 503.
(25) James, P. J.; Elliott, J. A.; McMaster, T. J.; Newton, J. M.; Elliott, A. M. S.; Hanna, S.; Miles, M. J. *J. Mater. Sci.* **2000**, *35*, 5111.

Figure 9. AFM topographic and phase images (2 mm × 2 mm) of 30SS70C8 ((A) topographic, (B) phase), 46SO3H54C8 ((C) topographic, (D) phase), 60SS40C8 ((E) topographic, (F) phase), and 75SO3H25C8 ((G) topographic, (H), phase) monolithic xerogels.

Table 3. AFM Parameters for Both Oxidized and Disulfide-Containing Monolithic Xerogels Derived from Bis(triethoxysilyl)propyl Disulfide (2) and 1,8-Bis(triethoxysilyl)octane (5)

material	surface roughness (RMS) (Å)	surface area (μm^2)
30SS70C8	420	4.8
46SO3H54C8	167	4.2
60SS40C8	268	5.4
75SO3H25C8	435	4.6

to investigate the possibility of phase separation, which would facilitate proton hopping in the electrolyte. The AFM topographic and phase images are summarized in Figure 9, and the AFM parameters are summarized in Table 3.

We chose dry monolithic samples with 30 mol % (30SS70C8) and 60 mol % (60SS40C8) disulfide content and the respective oxidized materials 46SO3H54C8 and 75SO3H25C8. The topographic images of 30SS70C8 and 46SO3H54C8 monoliths exhibit a rough surface with spherical features of relatively uniform size and shape. The root-mean-square (RMS) surface roughness of sample 30SS70C8 decreases significantly upon oxidation, which may be attributed to free movement associated with the sulfonic acid pendant arms following disulfide cleavage and thus some network reorganization.

There is a marked change in the phase images, taken simultaneously with the topographic images, between the 30 mol % disulfide material and the corresponding oxidized sample. Whereas the image corresponding to 30SS70C8 is relatively featureless, the 46SO3H54C8 image contains areas of high contrast. It is accepted that phase data obtained under tapping mode conditions sense differences in mechanical modulus down to 5−10 nm from the surface of a material. Thus, lighter regions of an image correspond to areas of greater stiffness.[26] Published AFM studies of Nafion 117 reveal very similar phase data with areas of light and dark domains.[22] The light areas are believed to correspond to

aggregates of sulfonic acid moieties, which aid proton movement through the membrane and may also be present in our oxidized 30 mol % disulfide polysilsesquioxanes as the phase images reveal. The phase images of 60SO3H40C8 and 75SO3H25C8 samples do not show similar changes in contrast. However, because of a large sulfur content (75 mol %) in the oxidized samples, the surface may simply be saturated with ionic domains, thus appearing uniform in the phase images.

Analysis of the topographic images of the 60SO3H40C8 and 75SO3H25C8 reveals an opposite trend in RMS surface roughness, which decreases with cleavage of the disulfide bond. This can be attributed to some network degradation, because a significant percentage of the links is severed.

The surface areas calculated from the topographic images correlate with the trend observed in measured BET surface areas (vide supra). The lower-disulfide-content material, 30SS70C8, shows a smaller change in topographic surface area upon oxidation (4.8 to 4.2 mm^2) compared to 60SO3H40C8 (5.4 to 4.6 mm^2), which exhibits a collapse in BET surface area.

In summary, we have developed a method for the preparation of bridged polysilsesquioxane materials containing covalently bound sulfonic acid groups. The precursors to these group are the corresponding disulfides. These organic−inorganic hybrid materials integrate a network-supporting component that can be systematically changed to fine tune their physical properties. The materials were utilized to prepare mechanically stable gel membranes. The application of these membranes as a PEMFC electrolyte was investigated, and it was found that they exhibited good proton conductivity at room temperature and 100% humidity. Conductivity increased with increasing sulfonic acid content and compares well with that of other proton-exchange materials.[6] In addition, the gels exhibit very high chemical stability. No degradation was observed under highly acidic and oxidative conditions employed for disulfide oxidation, as confirmed by solid-state NMR. This is a significant

(26) McLean, R. S.; Sauer, B. B. *Macromolecules* **1997**, *30*, 8314.

advantage for membrane materials used for fuel cells, for which such harsh conditions often lead to a decrease in electrolyte performance. The materials were also analyzed by TGA to confirm their high thermal stability. The morphology of the polysilsesquioxanes was investigated by nitrogen adsorption porosimetry and AFM. The studies revealed the possibility of molecular reorganization of sulfonic-acid-containing chains upon oxidation of the disulfide bridge. The performance of these hybrids at higher temperatures and reduced humidity remains to be tested with the current target operating conditions established by the DOE for electrolyte materials for the automotive industry as 120 °C and 50% relative humidity.

CM060440A