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Novel Polysilsesquioxane Hybrid Membranes for Proton Exchange Membrane Fuel Cell (PEMFC) Applications

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Abstract: Novel polysilsesquioxane (R–Si–$(O)_{1.5}$) PEMs with highly cross-linked Si–O backbones and pendant organic side chains comprising propylsulfonic or ethylphosphonic acid groups, were prepared via sol-gel polymerization. The inorganic component provides thermal/mechanical/chemical stability while the organic component gives flexibility and proton-conducting properties. The propylsulfonic acid membranes exhibited proton conductivities (σ) up to 10^{-2} S/cm cm at high relative humidities and temperatures, while the ethylphosphonic acid membranes showed lower proton conductivities but higher thermal stabilities. Preliminary results for the propylsulfonic acid membranes in direct methanol fuel cell (DMFC) performance are reported.

Keywords: Polysilsesquioxane, proton exchange membrane fuel cell

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are one of the most promising candidates for clean and renewable power sources for transportation, portable devices, and distributed power applications (1).

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In particular, the direct methanol-powered fuel cell (DMFC) has been gaining popularity due to the ease of fuel handling for these same applications. However, major technical challenges for DMFCs include high fuel crossover and low power densities (2). The technology has seen some implementation but high costs and membrane durability issues limit the commercialization of both PEMFCs and DMFCs.

PEMFCs consist of a membrane electrode assembly (MEA) and fuel/oxidant supply channels. The MEA is a key part in the PEMFC system and has a major impact on the system's overall power density, cost, efficiency, and control. For H_2/O_2 fuel cells, it is made up of two gas diffusion layers (GDLs), two carbon supported catalyst layers, and the PEM, which is sandwiched between coatings of catalyst layers (commonly Pt or Pt alloys). The PEM conducts protons from the anode to the cathode and separates the anode and the cathode reactants from each other.

Under operating conditions, a reductant, such as hydrogen or methanol, is fed into the anode side, and an oxidant, such as oxygen/air, is fed into the cathode side. In a DMFC, methanol is oxidized into carbon dioxide, protons, and electrons on the anode catalyst surface (Equation 1). The resulting protons diffuse through the membrane and reach the cathode. On the cathode side, oxygen is reduced to O^{2-}, which combines with the protons diffusing through the membrane to form water (Equation 2). The electrons generated at the anode pass to the cathode and supply power to the external circuit.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{1}$$

$$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \tag{2}$$

$$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O \tag{3}$$

There is a need to improve upon present-day sulfonated fluoropolymers such as Dupont's Nafion® membrane for PEMFC applications. These membranes rely on the presence of water to solvate and transport protons and, therefore, operate over a limited temperature range and can encounter water management problems. They also have a low glass transition temperature (T_g) that restricts their application to below 100°C, (3) relatively low proton conductivity at temperatures greater than 100°C and low relative humidity conditions, suffer from unacceptable fuel crossover, especially in DMFCs, can exhibit significant dimensional changes with water content, and have relatively high cost (4–10). These limitations have stimulated an intense interest in the development of new proton conducting membranes, including polymer proton electrolytes with nanometer-sized hygroscopic metal oxides (11,12), sulfonated aromatic polymer membranes, polymer-H_3PO_4 membranes (13–15), and hybrid inorganic-organic proton conducting membranes doped with proton-conductive components, including H_3PO_4, heteropolyacids, and grafted $-SO_3H$ groups (16–19).

Nano-ordered composites, comprising organic polymers and inorganic components, have attracted attention for their use as new high-performance materials. These hybrid compounds, made by the formation of siloxane (Si–O–Si) bonds, are an important body of materials, ranging from inorganic silicates to organically-modified polysiloxanes (20), and may serve as an alternative membrane material to reach higher fuel cell operation temperature. The inorganic component allows the thermal stability to be increased while capitalizing on the mechanical and proton conducting properties of the organic component. Similarly, the inorganic phase can improve chemical stability and high temperature proton conductivity of the membrane by increasing water retention at higher temperatures (21).

All of these siloxane-based materials can be prepared by hydrolysis and condensation of sol–gel precursors. When the mechanical stability is an important parameter, as is the case for membranes with thicknesses between 100 and 200 μm, one or more additional polymerizable groups can be introduced to permit further cross-linking. The homogeneity of the inorganic and organic phases allows for molecular engineering of the bulk properties of the hybrid inorganic/organic materials with nano-scale phase separation. The organic group, covalently attached to the silicon atom, can be varied in length, rigidity, functionality, and geometry of substitution. This variability allows for tuning bulk properties such as porosity, thermal stability, chemical resistance, mechanical properties, permeability, and electrical properties (22).

The sol-gel process is a suitable method to generate not only the inorganic network through metal-oxygen-metal bonds, but also the incorporation of organic groups bonded to silicon atoms that can be susceptible to organic polymerization. This process includes two reactions: hydrolysis of the metal alkoxide followed by subsequent condensation producing alcohol, water, and the metal oxide network. Several parameters, such as solvent, H_2O/Si ratio, catalyst used, and postprocessing (such as drying and annealing) conditions can be adjusted to obtain membranes with the optimal thermal/mechanical/chemical stability and highest proton conductivity.

Promising research for the use of polysilsesquioxanes for PEMs has recently appeared (22). Khiterer, et al. (2006) prepared membranes by oxidation of the corresponding disulfide-bridged polysilsesquioxane and reported proton conductivity values of up to 6.2 mS/cm under fully humidified conditions. These membranes, with covalently bound sulfonic acid groups, exhibited both oxidative and thermal stability.

The proton conduction in these sulfonated polymers, including Nafion® membranes, follows both the vehicular and Grotthuss mechanisms, in which water plays a vital role at high humidification (23). Nafion® 117 membranes contain about 22% water and produce proton conductivities of ~0.08 S/cm at 100% relative humidity conditions (24), and proton conductivity is observed to decrease at lower humidification levels (25). The use of the hygroscopic sulfonic acid group in these membranes enhances their water uptake ability and increasing the density of sulfonic acid functional groups, covalently bonded to the network structure would be expected to enhance this effect. Nano-sized metal oxide particles, such as SiO_2 and TiO_2, can also be incorporated into these membranes, as they are known to enhance proton conductivity by providing more acidic sites for water uptake (26–28). Other additives, such as polymeric phthalocyanines (polyPc), have the potential of limiting fuel crossover and improving mechanical stability due to the network structure they can provide, similar to the effect of montmorillonite incorporation in the membranes (28).

In this study, three-dimensionally cross-linked polysilsesquioxanes, with covalently bound sulfonic acid functional groups, were prepared as novel PEM materials. Membranes were prepared with and without nanometer-sized metal oxide additives and polyPc, and exhibited proton conductivities ($\sim 10^{-3}$ to 10^{-2} S/cm) over a wide range of temperatures and relative humidity conditions. The polarization performance of these membranes in single fuel cells fed with methanol and O_2 at 50°C was investigated.

Similarly, phosphonic acid-grafted polysilsesquioxane membranes were also prepared and compared to results recently reported (29). Phosphonic acid groups have some advantages over sulfonic acid groups due to their greater stability in harsh environments and better water-holding ability (30). These materials were synthesized via sol-gel polymerization and were readily cast into membranes of various thicknesses. These membranes exhibited higher thermal stability than the sulfonic acid membranes and proton conductivities of 10^{-2} S/cm at 80°C under fully humidified conditions.

EXPERIMENTAL METHODS

Materials

The following chemicals were obtained from Gelest, Inc.: 3-(trihydroxysilyl)-1-propanesulfonic acid (A), (30–35% in water), bis[(3-methyldimethoxysilyl)propyl]-propylene oxide (B), bis(triethoxysilyl)octane (C), silanol-terminated polydimethylsiloxane (E), and diethylphosphatoethyltriethoxysilane (95%). Absolute ethanol, methanol (±99.8%), bis(triethoxysilylethyl)benzene (G) and 1,4-bis(triethoxysilyl)benzene (H) were purchased from Sigma-Aldrich and were used as received. The N_2 (99.995%) and O_2 (99.5%) gases were obtained from Air Liquide. Catalyst-coated bilayers containing 50:50 (% by weight) Pt on C were purchased from ELAT®, E-TEK Div. of De Nora, N.A., Inc. with the standard $4\,mg/cm^2$ loading using unsupported HP Pt black. Fumed SiO_2 (0.014 μm) and SiO_2 in surfactant solution were obtained from Sigma Aldrich and used as received. TiO_2 nanoparticles were synthesized according to a published literature (31). Polymeric phthalocyanine (polyPc) was synthesized according to published method (32).

Preparation of Silyl-Functionalized Sulfonic and Phosphonic Acid

Excess water from commercially available 3-(trihydroxysilyl)-1-propanesulfonic acid was removed by azeotropic distillation with absolute ethanol. The resulting viscous 3-(trihydroxysilyl)-1-propanesulfonic acid (A) (67–75% by weight in water) was used with different silane precursors for membrane preparation.

Trihydroxysilylethane phosphonic acid (D) was prepared by hydrolysis of diethylphosphatoethyltriethoxysilane (95%) by a method similar to published procedures (28). Diethylphosphatoethyltriethoxysilane (10 mmol) and 1646 mmol of 37% HCl are heated under reflux at 90°C for 24 h under a N_2 blanket. Unreacted hydrochloric acid was removed by vacuum distillation at 50–60°C resulting in 100% yield of hydrolyzed diethylphosphatoethyltriethoxysilane (D).

Membrane Preparation

The membranes were prepared by sol-gel polymerization of either silyl-functionalized sulfonic acid or phosphonic acid, with different silane precursors such as B, C, E, TEOS, G, and H (Fig. 1). The silane precursors were combined and stirred with absolute ethanol for 2 min. Into the resulting solution, the acid component was added dropwise, followed by the addition of an acid (typically concentrated HCl, 12 M) catalyst until the pH of the solution reached 2. The mixture was stirred for 1 to 24 h at room temperature. The resulting solutions were cast (pour-cast or drawn-cast) in polystyrene (PS) Petri plates or onto a Teflon® or Mylar® substrate. The membranes were allowed to air-dry for 3 d and annealed at 60°C for another 3 d. All draw-casting procedures were

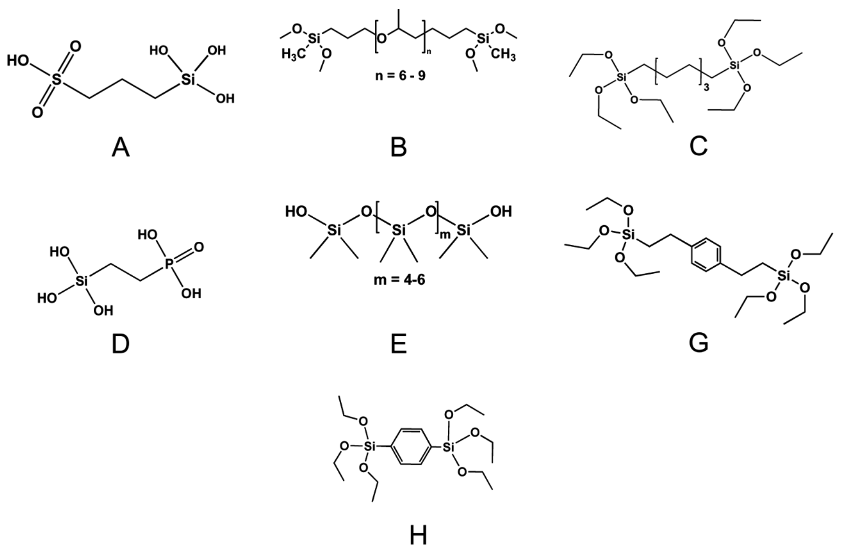

Figure 1. Chemical structures of silane precursors.

performed using the Acculab® Jr. Draw-Casting Table. The membrane thickness ranged from 10 to 800 µm as determined by using a digital micrometer, and further confirmed by scanning electron microscopy (SEM).

Several additives, including nano-sized metal oxides and polyphthalocyanine, were incorporated into the membranes. Silicon dioxide nanoparticles (fumed or in surfactant solution) and titanium oxide were suspended in absolute ethanol and sonicated for 15 to 30 min to obtain a homogeneous dispersion prior to combining with other membrane components. Particle sizes of the prepared polyPc ranged from 50–150 µm as determined by SEM.

Characterization of PEMs

Scanning electron microscopy (SEM) images of the membrane samples were acquired using a Zeiss-LEO Model 1530 Variable Pressure Scanning Electron Microscope using a 10 kV electron beam. The membrane samples were fractured under cryogenic conditions and sputter-coated with a thin layer of Au/Pd. The mechanical strength and flexibility of the membranes were evaluated under ambient conditions by tensile test using an Instron 5848 MicroTester with 10 mm gauge length and 0.10 mm/min extension speed. The results were the average of at least three measurements. Those membranes exhibiting sufficient flexibility and strength to allow them to be easily peeled from the substrate were further characterized. Thermogravimetric analysis (TGA) of the membranes was carried out using a Perkin Elmer Pyris 1 TGA under N_2 atmosphere, heating from 90 to 800°C at a rate of 10°C/min. The ionic exchange capacity (IEC) was measured by potentiometric titration using a 0.1 N HCl solution obtained by soaking membranes in a 0.1 N NaOH solution for 2 d. The 0.1 N NaOH solution was standardized against potassium acid phthalate before use. Hydrolytic stability of the membranes was measured by boiling in water for 5 to 10 h while monitoring the membrane's flexibility and integrity. Only the membranes that displayed no physical degradation after boiling for up to 10 h, were considered hydrolytically stable for our tests. Water uptake ability and the degree of membrane swelling (measured as changes in area, A) was obtained by soaking previously dried and weighed membranes in deionized water for 24 h at room temperature, blotting external water, and then reweighing the membranes. Water uptake ability and swelling ratio were computed using equations (4) and (5).

$$\%\ \text{water uptake} = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \times 100 \tag{4}$$

$$\%\ \text{swelling ratio} = \frac{(A_{wet} - A_{dry})}{A_{dry}} \times 100 \tag{5}$$

where membrane area, A (cm^2) was calculated by multiplying the membrane length and width.

Membrane Electrode Assembly (MEA) Fabrication

Before the fabrication of an MEA, the thickness of the composite membrane was measured using a Mitutoyo IP 54 digimatic micrometer and confirmed by taking images of membrane cross-sections using SEM. MEAs were prepared by hot-pressing a 3.5 cm × 3.5 cm area of membrane between two catalyst-coated bilayers (active surface area of 4.84 cm^2, E-tek® Division of De Nora N.A., Inc.) at a temperature of 80–85°C and a pressure of ~300 psig for 2 min. The MEAs were assembled in a 5 cm^2 single cell (Fig. 2a and c, Fuel Cell Technologies Inc.) with PTFE films (1 mil or 5 mils) used to shim the thickness of the membranes and bilayers during the assembly. The eight bolts of single cells were tightened with a uniform torque of 20 inch pounds.

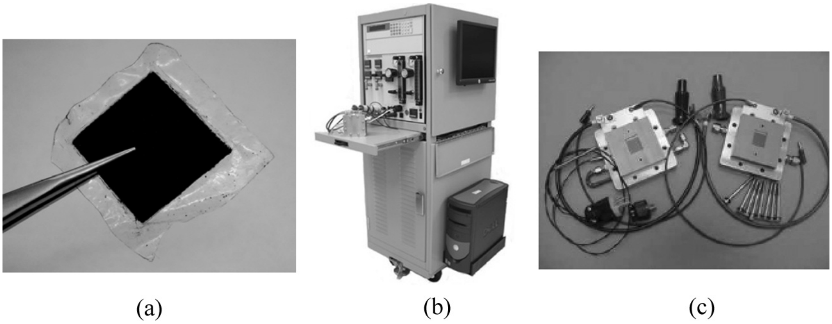
(a) (b) (c)

Figure 2. Fuel cell hardware and components: (a) Hot-pressed MEA, (b) Fuel Cell Testing Station, and (c) 5 cm^2 single cell (Fuel Cell Technologies, Inc.).

Proton Conductivity Measurements

Through-plane measurements were used to evaluate the membranes for proton conductivity since this represents the conductivity direction in an operating fuel cell (33). Catalyst-coated bilayers with the standard 4 mg/cm^2 loading using unsupported HP Pt black were hot-pressed on both sides of the membranes as cathode and anode to maximize contact area between the membrane and the catalyst. A PC-controlled frequency response analyzer (PARSTAT® 2273 Advanced Electrochemical System) was used to record the membrane's complex impedance over a frequency range of 100 MHz to 100 mHz at an AC voltage amplitude of 10 mV. All measurements were carried out under ambient pressure and well-controlled humidity conditions and temperatures using a 5 cm^2 single cell in a fuel cell testing station (Fig. 2b, Fuel Cell Technologies Inc.) with 5 h equilibration for each temperature and relative humidity condition. The error of the proton conductivity measurement was typically less than 10%. The resistance value (in ohms) of the membranes was determined from the intercept point where the Nyquist (or its graphically extended) curve intersects the real axis. The proton conductivity, σ, in S/cm was calculated using the following equation:

$$\sigma = L/(R^*A) \tag{6}$$

where L is the membrane thickness (cm), A is the cathode surface area (cm^2), and R is the measured membrane resistance (ohms). The typical complex impedance spectra (Nyquist plot) presents a semi-circle through the origin at high frequencies with samples measured at temperatures up to 80°C, and additional 45° inclined lines at low frequencies when samples are measured at temperatures greater than 80°C. The semi-circle represents a typical equivalent circuit of a resistor and capacitor connected in parallel corresponding to the bulk electrical properties, and the line is the Warburg impedance caused by the diffusion process of protons. The increase in temperature leads to smaller semi-circles (resistance reduction) because proton conductivity is in general a thermally stimulated process (39).

Single Cell-Performance Characterization

A fuel cell test station (Fig. 2b, Fuel Cell Technologies, Inc.) was used to measure fuel cell (FC) performances. Before the measurements, the cell was stabilized at open circuit potential for ~3 h. The polarization (I–V) curves were recorded by cycling the cell voltage between 0.8 and 0.2 V in ±0.1 V increments and 60-s delay. All experiments were carried out by feeding the anode 8% (w/w) aqueous methanol and the cathode O_2 at flow rates of either 0.33 mL/min or 100 mL/min, respectively, under ambient pressure conditions.

RESULTS AND DISCUSSION

The performance of nano-composite membranes depends both on the properties of the individual components and their morphology, and interfacial characteristics. The sol–gel process is a versatile method for preparing well-controlled composites due to its unique mild synthesis conditions and flexibility (26).

Propyl-Sulfonic-Polysilsesquioxane Hybrid Membranes

Sulfonic acid functionalized polysilsesquioxane membranes were synthesized from 3-trihydroxysilyl-1-propanesulfonic acid (A) via the sol-gel process using different ratios of A with several bridging organic (aliphatic/aromatic) and siloxane components were used as cross-linking agents (B, C, E, G, H, Fig. 1) for the inorganic-organic polysilsesquioxane structures with three-dimensionally cross-linked Si–O networks.

Freestanding membranes of various area were obtained by drop casting in polystyrene (PS) Petri dishes or onto Teflon® or Mylar® substrates. This procedure resulted in homogeneous, transparent membranes with thicknesses ranging from 50 to 800 μm. Thinner membranes (<50 μm) were obtained by draw-casting the membrane solutions onto a flat Teflon® or Mylar® substrate. These inorganic-organic hybrid membranes are clear and colorless, suggesting the absence of phase separation beyond the optical wavelength (33).

Sol–gel synthesis of silicate gels involves the hydrolysis of the alkoxide groups (–OR) into hydroxyl groups (–OH) and subsequent condensation of the silanol groups to siloxane bonds (–Si–O–Si–) and by-products of alcohol or water (34). Because water and alkoxysilanes are immiscible, ethanol, which is the by-product from the hydrolysis of the precursor molecules, was used as a homogenizing agent (35,36).

The H_2O/Si ratio affects the rate of the hydrolysis reaction. In theory, the H_2O/Si mole ratio in the reaction mixture is 4 for complete hydrolysis. If a large excess of water is present in the mixture, complete hydrolysis of silicon alkoxide takes place before significant condensation occurs, and the completion of this reaction is delayed due to the formation of a variety of intermediate species ($[SiO_x(OH)_y(OR)_z)]_n$; where $2x+y+z=4$) (35). When using the as-received 3-trihydroxysilyl-1-propanesulfonic acid, the large amount of water present in the casting solutions (H_2O/Si ratio $=22$) gave sticky membranes, which may be attributed to the incomplete or partial condensation of the silanol groups.

To facilitate complete condensation, the membranes were annealed at 50–60°C for 3 d. In addition, the use of a second crosslinker, bis(triethoxysilyl)-1,8-octane (C) afforded membranes with much improved mechanical properties (37). We determined empirically that adding 1.5% w/w to the membrane casting solutions resulted in flexible, nonsticky membranes, whereas incorporation of greater amounts produced brittle membranes. Addition of the bis(triethoxysilyl)-1,8-octane may be serving a second purpose other than crosslinking (33) since the bridged bis(triethoxysilyl)-1,8-octane is amphiphilic after hydrolysis of the trifunctional alkoxysilanes, due to its hydrophobic organic part and hydrophilic inorganic part at the same time. Nano-phase separated structures are thus possible which might help not only in additional cross-linking, but also in the formation of ion-conduction pathways that could improve proton transport (33).

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analyses of 60%: 40% (w/w) ABC membranes containing 1.5% (w/w) of C was performed with and without annealing. The intensity of the water absorption peak, observed at around $\sim 3500\,cm^{-1}$ decreased as the annealing temperature increased. The increased oxidizing effect of the sulfonic acid groups upon removal of water led to discoloration at annealing temperatures $>70°C$ (19). Hybrid membrane systems with sulfonated phenyl rings and condensed with 3-methacryloxypropyltrimethoxysilane also exhibited a color change upon thermal treatment at 120°C (33).

Several membrane systems consisting of propyl sulfonic polysilsesquioxanes were prepared and tested. The relative quantities of each of the components were varied to optimize mechanical stability and to investigate the dependence of proton conductivity on sulfonic acid content. The amount of A was limited to a maximum of 70% by weight of the membrane, because higher compositions of A resulted in weak or hydrolytically unstable membranes. Membranes with only 40% A did not show proton conductivities above 10^{-3} S/cm, so further investigation and characterization of those systems were not performed. All of the resulting membranes formed were transparent, optically homogeneous, yellowish to brown in color, hygroscopic, and hydrolytically stable in boiling water for more than 5 h.

A/B membranes with 1.5% (w/w) C are superior in terms of their flexibility and toughness, among all membranes prepared without any additives, having toughness values up to 0.282 MPa (Table 1). The toughness of the various membranes was calculated from the total area under the stress-strain curve up to the point of failure (37). Incorporation of less amounts of B and increased amounts of the acidic component A reduced the corresponding overall toughness of the membrane. The decrease may be attributed to the presence of free silanol groups formed in the extremely acidic environment, resulting in only partial condensation. A digital image of this membrane is shown in Fig. 3. ATR-FTIR analysis of membranes with varying amounts of acid shown in Fig. 4 shows that the Si–O–Si peak at ~1100 cm^{-1} is present, indicating the formation of the inorganic backbone. A significant increase in toughness was observed for the 60:40% (w/w) A/B membranes (containing 1.5% (w/w) C) with polyPc compared to those without. This may indicate that the addition of polyPc particles into the membranes reinforces the mechanical

Table 1. Mechanical strength testing for polysilsesquioxane membranes

Membrane composition (thickness)	Tensile stress (MPa) vs. strain (%)		Toughness (MPa)
% (w/w) A/B/C			
60:40 (10 μm)	8.31	5.90	0.282
65:35 (25 μm)	12.23	12.25	0.062
70:30 (10 μm)	21.38	0.26	0.005
% (w/w) A/B/C with polyPc			
60:40 (279 μm)	2.50	45.00	0.379
% (w/w) D/B/C			
60:40 (150 μm)	1.66	5.64	0.041
% (w/w) D/B/C with polyPc			
60:40 (200 μm)	3.78	38.70	0.983

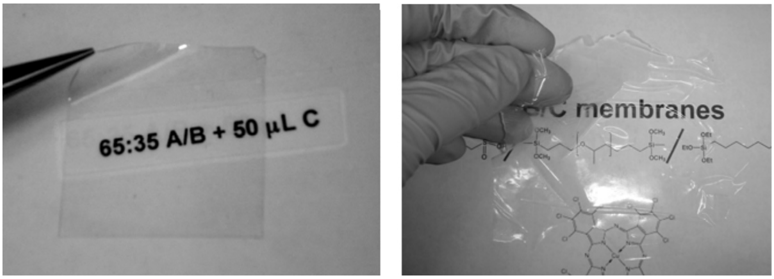

Figure 3. Digital images of 3-trihydroxysilyl-1-propane-sulfonic acid/bis[(3-methyldimethoxy-silyl)propyl]-propylene oxide/bis(triethoxysilyl)octane (A/B/C) membrane.

strength of the materials due to the formation of a network structure. SEM images of these membranes show the absence of pinholes or cracks on the surface (Fig. 5a) and in the cross-section (Fig. 5b).

When A/B membranes are prepared with tetraethoxysilane (TEOS) instead of C, the membranes are brittle. A/C and A/H (3-trihydroxysilyl-1-propanesulfonic acid/bis(trimethoxy-silyl)benzene) membranes were also brittle and A/G membranes (3-trihydroxysilyl-1-propanesulfonic acid/bis(trimethoxy-silylethyl)benzene), similar to the A/C system, formed cracks when A was below 60% (w/w). The 60:40% (w/w) A/G composition did, however, produce a membrane of sufficient strength to be measured in a FC configuration.

Membranes with nanometer-sized silicon dioxide particles as additives were also prepared with the aim of improving water retention as well

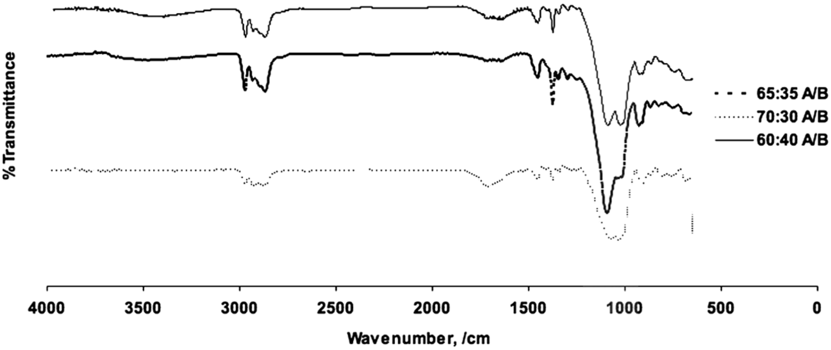

Figure 4. Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) analysis of A/B membranes with 1.5% (w/w) C.

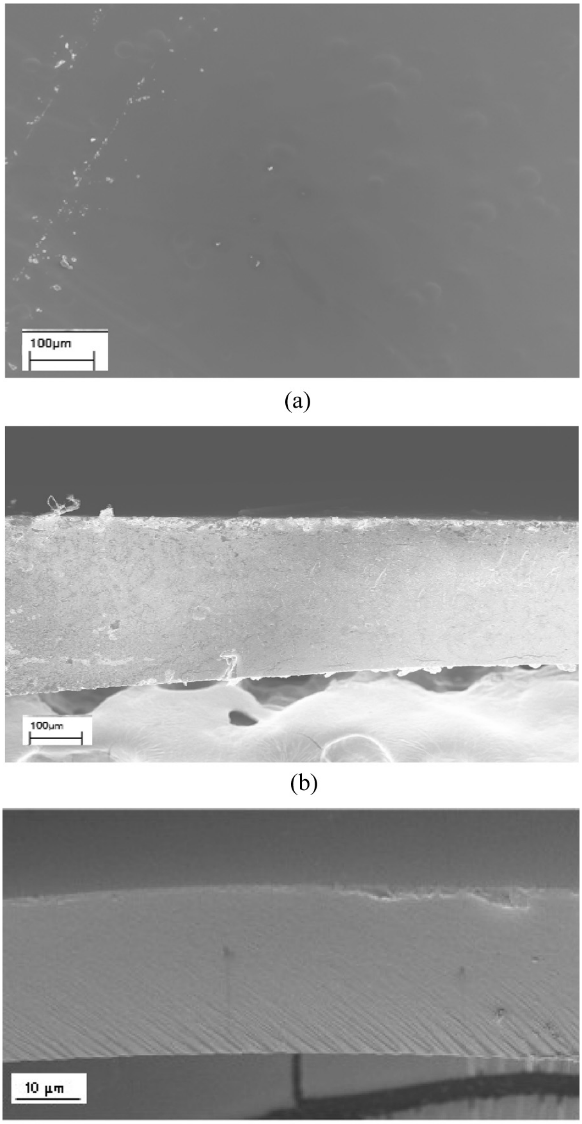

Figure 5. SEM images of 60:40% (w/w) + 10 mmol 3-trihydroxysilyl-1-propanesulfonic acid/bis[(3-methyldimethoxy-silyl)propyl]-propylene oxide/bis(triethoxysilyl)octane (A/B/C) membranes (a) surface, (b) cross-section (bottom part of the cross-section image is magnetic carbon tape), and (c) cross-section (25 µm).

as potentially providing additional acidic sites (38). The filler's surface area becomes prevailing in determining the water retention properties of the composite membranes at high temperature, with the surface properties playing a more important role than its crystalline structure. Particles of fumed SiO_2 and SiO_2 in surfactant, with sizes ranging from 0.014 to 5 μm, were dispersed in absolute ethanol via sonication prior to the preparation of the membrane. Membranes containing SiO_2 in surfactant formed white, translucent films, while those with fumed silica exhibited rough surfaces and an uneven distribution of the silica aggregates. Adding 2% (w/w) polyPc to the 60:40% (A/B) membranes containing 1.5% (w/w) C resulted in a significant increase in toughness compared to those membranes without this additive suggesting that the polyPc particles reinforce the mechanical strength of the materials due to the formation of a network structure. A dark green powder (average particle size $<50\,\mu m$) was obtained by grinding with a ball-mill. This powder was dispersed in concentrated sulfuric acid (18 M) and added to the rest of the membrane components at various levels. A 2% (w/w) polyPc for a 3.5 g membrane gave the most uniform distribution whereas greater concentrations manifested severe aggregation. A/B/C membranes containing a uniform distribution of 2% (w/w) polyPc were studied. The dark green membranes had glossy surfaces and were tough (Table 1). A digital image of a 60:40% A/B membrane with 1.5% C and 2% (w/w) polyPc is presented in Fig. 6. SEM images of the membrane surfaces and cross-sectional areas exhibited no pinholes or cracks (not shown).

Figure 6. Digital image of 3-trihydroxysilyl-1-propane-sulfonic acid/bis[(3-methyldimethoxy-silyl)propyl]-propylene oxide/bis(triethoxysilyl)octane (A/B/C) membrane containing 2% (w/w) poly-phthalocyanine (polyPc).

Ethyl-Phosphonic-Polysilsesquioxane Hybrid Membranes

The preparation of ethyl-phosphonic-polysilsesquioxane hybrid membranes using different precursors appeared during this study (29). We expanded that work by preparing membranes synthesized via sol-gel polymerization of the hydrolyzed product of diethoxyphosphorylethyltriethoxysilane (D) and several bridging aliphatic/aromatic organic and siloxane components as cross-linking agents (B, C, E, G, H, Fig. 1). The solutions were draw-cast on Teflon® or Mylar® substrates to produce membranes with thicknesses that ranged from 100 to 300 μm.

Membranes were prepared from several ratios of trihydroxysilylethanephosphonic acid (D) and bis[(3-methyldimethoxysilyl)propyl]-propylene oxide (B). These membranes, containing up to 60% D, are opaque, white, flexible, and dimensionally stable in boiling water. The maximum amount of D was limited to 60% because higher concentrations of the acidic component resulted in weaker membranes. Unlike the membrane systems with the pendant sulfonic acid, these membranes can be annealed up to 100°C without any change in color or flexibility.

Ground polyPc particles could be suspended in a 2:1 (w/w) ratio with D and 18 M H_2SO_4 without severe aggregation in the membrane. Unlike the sulfonic acid, the phosphonic acid is not acidic enough to dissolve the particles and required the introduction of a strong acid (H_2SO_4) to enable uniform distribution of the polyPc in the membrane. The resulting dark green membranes exhibited improved toughness (Table 1) and water-stability. ATR-FTIR analysis of the 60:40% (w/w) D/B, with and without polyPc, revealed the Si–O–Si peak at $\sim$1100 cm^{-1}, an indication that the inorganic backbone was formed during the condensation and drying. All these membrane have homogeneous compositions, smooth surfaces, and a wax-like texture.

Determination of Ion-Exchange Capacity (IEC), Water Uptake Ability, and Degree of Swelling by Water

The ion-exchange capacity (IEC) provides the density of the ionizable hydrophilic functional groups present in the membrane matrix, and is related to proton conductivity. Changing the ion content in the membrane can control both its water uptake and proton conductivity. It is desirable to increase the acid content of the membranes, but without compromising its dimensional stability. Table 2 summarizes these properties for both propylsulfonic acid and ethyl phosphonic acid polysilsesquioxane membranes. For A/B/C membranes, a higher IEC was obtained with larger percentages of A with concomitant reduction of

Table 2. Selected properties of membranes: ion-exchange capacity (IEC), water uptake ability, degree of swelling by water

Membrane composition (% w/w)	Experimental IEC, meq/g	% Water Uptake	% Swelling by Water
A/B/C			
60:40	4.50 ± 0.50	110	33
65:35	4.60 ± 0.70	120	35
70:30	4.65 ± 0.50	125	50
D/B/C			
50:50	3.20 ± 0.10	20	30
60:40	3.00 ± 0.10	25	36

the dimensional stability in water. Higher acid content for D/B/C membranes also translated to higher water uptake and less dimensional stability. At 60% D, the experimental IEC was 20% less than the calculated value (3.70 meq/g), and lower than the IEC with 50% acid, which may be due to partially hydrolyzed phosphonate groups. Confirmation of complete hydrolysis may be investigated using ^{31}P-NMR spectroscopy.

The potential effect of increased water uptake upon the incorporation of metal oxide particles in the membranes was not observed in this study. Although not expected, the addition of the polyPc also did not give any effect on these properties.

THERMAL STABILITY OF MEMBRANES

Propyl-Sulfonic Polysilsesquioxane Hybrid Membranes

The thermal behavior of the membranes under N_2 atmosphere was investigated by TGA. The TGA traces of the propyl-sulfonic-polysilsesquioxane (60:40% A/B) and Nafion® membranes are shown in Fig. 7(a) and (b), respectively. Taking the onset of weight loss, the thermogram in Fig. 7(a) shows that membrane A/B is stable up to 157°C, and weight loss (~6%) below this temperature is likely due to water associated with the sulfonic acid.

Incorporation of another crosslinker, bis(triethoxysilyl)-1,8-octane (C) slightly increased the onset of degradation up to 71% weight loss at 180°C compared to 82% weight loss at 158°C for A/B membranes without C. However, addition of metal oxide nanoparticles, particularly fumed silica nanoparticles, did not significantly change the thermal stability of the A/B/C membrane. Addition of the polymeric phthalocyanine

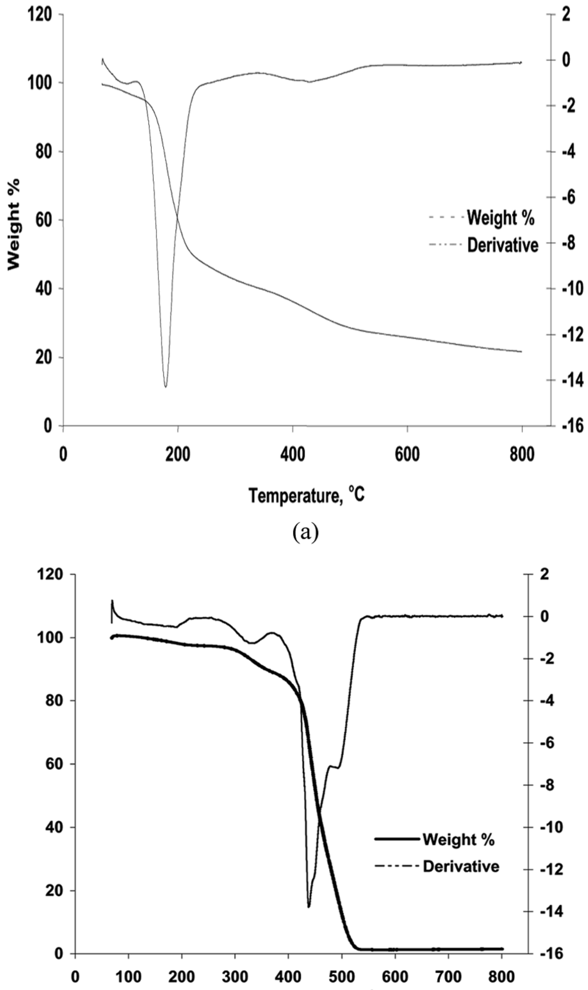

Figure 7. Thermograms of (a) 60:40% 3-trihydroxysilyl-1-propane-sulfonic acid/ bis[(3-methyldimethoxy-silyl)propyl]-propylene oxide (A/B), and (b) Nafion® 117 membranes.

particles also did not contribute any improvement to the membrane's thermal stability. Nafion®'s thermogram showed that the perfluorosulfonic acid membrane starts to degrade around 300°C. Compared to Nafion® 117 membranes, these propylsulfonic polysilsesquioxane membranes exhibited lower thermal stability. Although they have exhibited acceptable stability in the range of the present experimental temperatures ($\leq$80°C), their long-term stabilities in fuel cell conditions need to be further improved.

A/B/C membranes formed by base catalysis and then acidified by 1.0 M HCl and A/B/C membranes catalyzed with an acid show the same thermogram profiles, with major degradation occurring roughly at the same temperature ($\sim$160°C). In contrast, thermograms of the membrane prepared via base-catalyzed polymerization, but without subsequent acidification, showed that the major degradation occurs at a somewhat higher temperature (200°C). This result suggests that the sulfonate group, once acidified, contributes to the lower thermal stability, due to its highly oxidative properties (30).

However, promising preliminary results on the preparation of membranes containing the same propylsulfonic acid group with tin(II) 2-ethylhexanoate as catalyst showed thermal stabilities increased to up to 300°C without any obvious physical manifestation of membrane oxidation. It is speculated that even with the addition of C and annealing, complete condensation may have not been achieved. To ensure full condensation, tin(II) 2-ethylhexanoate was added prior to annealing. Raman spectroscopic studies are currently being performed to confirm complete condensation in membranes prepared with the catalyst.

Ethyl-Phosphonic Polysilsesquioxane Membranes

Ethyl phosphonic polysilsesquioxane membranes exhibit better thermal stabilities compared to the propyl sulfonic membranes. Figure 8 shows that the 60:40% D/B with 1.5% (w/w) C membrane is stable until 339°C, and exhibits only a 1% weight loss at 135°C, which is likely due to water. The loss of water was observed at a higher temperature due to strong hydrogen bonding to the phosphonic acid group (39). The addition of polyPc slightly increased the membrane's thermal stability up to 350°C, with only a 2% weight loss at 120°C.

PROTON CONDUCTIVITY TESTING

Propyl Sulfonic Polysilsesquioxane Hybrid Membranes

Conductivity values, as a function of temperature and relative humidity, for the A/B/C membranes are listed in Table 3. At 50°C and low (25% R.H.) relative humidity, the 50:50% (w/w) A/B/C membranes exhibited proton conductivities of $\sim 10^{-4}$ S/cm. The proton conductivities

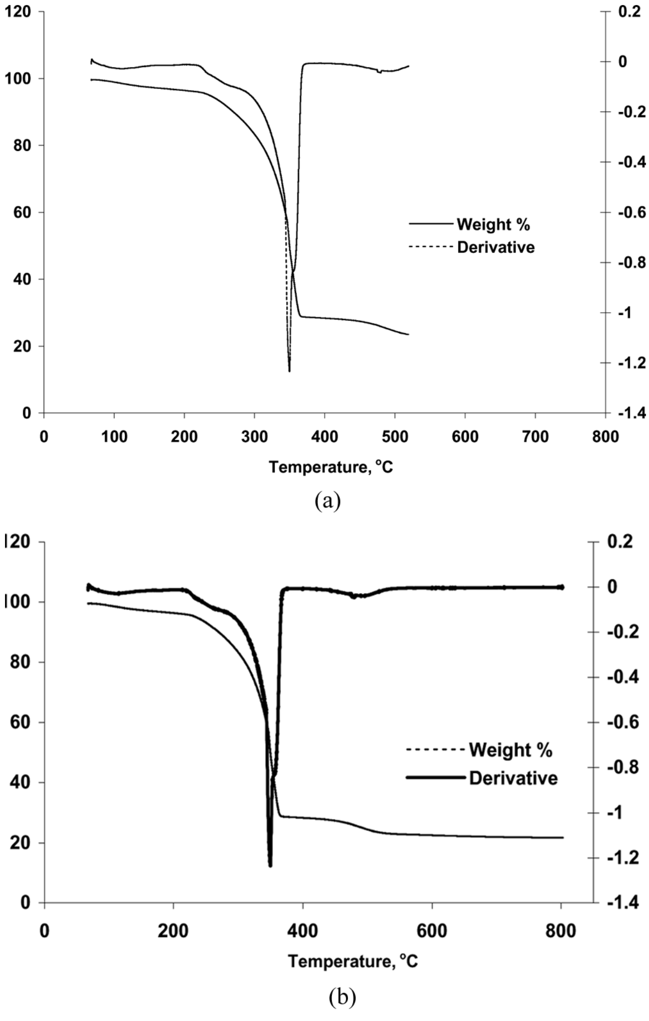

Figure 8. Thermograms of 60:40% trihydroxysilylethanephosphonic acid/bis[(3-methyldimethoxysilyl)propyl]-propylene oxide/bis(triethoxysilyl)octane (D/B/C) membrane, (a) with and (b) without polyPC.

increased with increasing relative humidity, reaching ~3×10^{-2} S/cm under fully humidified conditions. At 80°C, there was a small decrease in proton conductivity in fully humidified conditions that can be attributed to the degradation of the membrane at this temperature, and/or to excessive swelling. A similar trend was observed in the proton conductivities for the membranes with 60% and 65% sulfonic acid, but with

Table 3. Proton conductivity values for (% w/w) A/B/C membranes

		Proton conductivity × 10^{-2} S/cm		
Temperature, °C	% RH	50:50	60:40	65:35
50	25	0.02	–	–
	40	0.05	0.18	0.45
	60	1.74	1.28	2.89
	100	2.97	4.44	3.69
60	40	0.054	0.05	0.37
	80	1.74	1.91	1.13
	100	3.05	4.31	3.98
70	40	0.07	0.01	0.41
	80	2.03	2.19	2.97
	100	2.94	4.38	2.97
80	40	0.87	0.01	0.56
	80	3.09	2.55	3.33
	100	2.71	3.06	4.03

somewhat slightly higher proton conductivity values. Above 80°C, proton conductivity values were no longer reproducible even after more than 12 hours of humidification. This result is consistent with our observation of discoloration at temperatures >80°C stemming from the highly oxidative nature of the covalently linked sulfonic acid. Excessive water swelling at high humidification could also be problematic.

The increase in proton conductivity with increasing sulfonic acid concentration indicates that the proton-carrier density is directly associated with these covalently linked groups. The addition of the crosslinker, C, may serve to promote the formation of a nano-morphology resulting in an improved nanophase separation. It has been shown (6) that, among several bridged alkylsiloxane hybrids containing different numbers of carbon atoms (C2, C6, C8, C10, and C14), the optimum carbon length chain for proton conductivity is 8. As ionic conductivity is based on continuous channels inside the membrane, the C8 chain length is considered to form an optimized channel network structure in the hybrid macromolecules (6). Proton conductivities of A/B membranes, prepared with tetraethoxysilane (TEOS), were lower than those with C (1.59×10^{-3} S/cm vs. 2.78×10^{-3} S/cm at 50% R.H. and 80°C, respectively). Hence, the presence of the flexible alkyl chain in C improves both the flexibility of the membrane and the proton conductivity.

For A/B/C membranes with 1.5% (w/w) fumed SiO_2 nanoparticles, there was a 30% increase in proton conductivity at 80°C and fully humidified conditions. Nano-sized particles of metal oxides have been reported

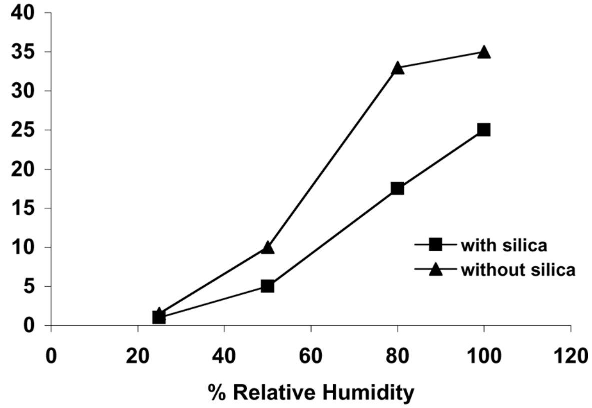

Figure 9. Proton conductivity of a 60:40% (w/w) A/B membrane containing 1.5% (w/w) C and 2% (w/w) fumed silica as a function of relative humidity and temperature.

to enhance the water retention and the resulting proton conductivity under high temperatures and zero to low humidity conditions (27,38). For membranes with 60% (w/w) A and 2% (w/w) fumed SiO_2 nanoparticles, there was a very small increase in proton conductivity at 80°C and fully humidified conditions, as shown in Fig. 10. However, the expected effect of the addition of the nanosized metal oxide particles for improved proton conductivity at low (25%) relative humidity conditions and high

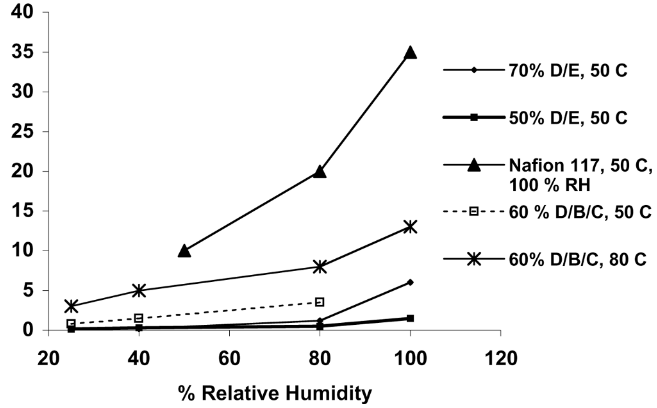

Figure 10. Proton conductivity of several membranes with trihydroxysilylethanephosphonic acid, D and Nafion® 117 membrane as a function of relative humidity and temperature.

temperature was not observed in this study. In the same way, addition of a small amount of polyPc (2% w/w) in the membrane system did not produce any changes in the membrane's proton conductivity, suggesting its incorporation neither enhances nor destroys the membrane structure necessary for proton transport, enhancements to mechanical properties notwithstanding (40).

For A/G membranes containing 60% acid, proton conductivity was observed to increase slightly with increasing temperature, and the highest proton conductivity was obtained at 70% R.H. and 80°C as 1.75×10^{-3} S/cm. At higher temperatures and fully humidified conditions, the value of conductivity decreased. A/E membranes with 60% A were also prepared as clear, colorless membranes exhibiting a maximum proton conductivity of 1.80×10^{-3} S/cm at 100% R.H. and 80°C. These results are summarized in Table 4.

For the proton conductivity measurements obtained, the values increased with increasing temperature, usually until 70°C, above which the membranes were no longer stable. As proton conductivity is in general thermally stimulated, it is reasonable to expect a rise in conductivity with temperature. It appears that at temperatures >80°C, thermal degradation/dehydration of the membranes starts to predominate (41).

Compared to Nafion® 117 membranes (~0.04 S/cm at 50°C, 100% R.H., Fig. 11), the propyl sulfonic polysilsesquioxane membranes exhibited lower proton conductivity. In Nafion® membranes, the sulfonic acid end groups form nano-size aqueous micelles in the presence of water as well as channels within the polymer's hydrophobic backbone (36,42–44), providing efficient $H^+–nH_2O$ migration paths. In propyl sulfonic polysilsesquioxane membranes, the three-dimensionally cross-linked Si–O backbone could limit the formation of these channels and impede the migration of $H^+–nH_2O$ clusters. In this case, the formation of the highly 3D network using crosslinkers, B along with C, may have restrained the proton transport, thereby resulting in lower proton conductivity.

In general, the proton conductivities of membranes, A/B/C membranes decrease at higher temperatures, even with a higher amount of

Table 4. Proton conductivity values for other propylsulfonic acid membranes with 60% A

Membrane composition	Operating conditions	Proton conductivity $\times 10^{-2}$ S/cm
60:40% A/G	70% R.H., 80°C	1.75
60:40% A/E	100% R.H., 80°C	1.80

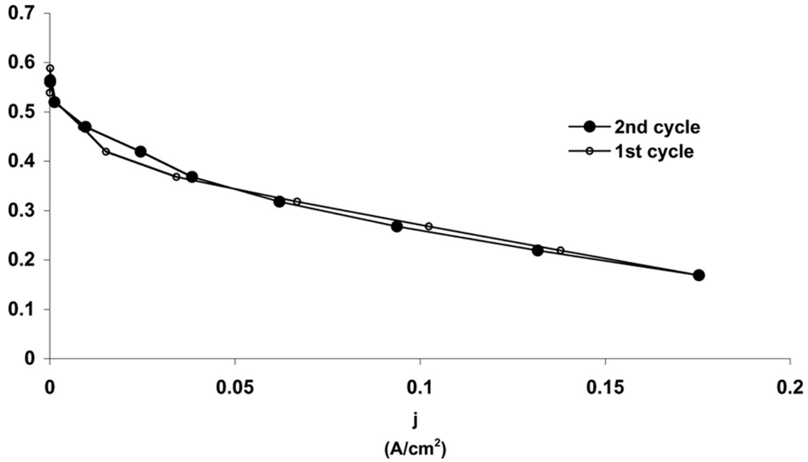

Figure 11. Polarization curves of a single cell with a propyl sulfonic polysilsesquioxane hybrid membrane (60:40% (w/w) A/B/C membrane). Experimental condition: run with 8% (w/w) aqueous methanol and 50 mL/min O_2 flow rate at 50°C. 1st cycle: 0.8 V to 0.2 V; 2nd cycle: 0.2 V to 0.8 V.

acid, such that this may be attributed to the start of the degradation of the membrane under these highly oxidizing conditions.

Ethyl Phosphonic Polysilsesquioxane Hybrid Membranes

Conductivity values for 60:40% (w/w) ethyl phosphonic polysilsesquioxane membranes with 1.5% (w/w) C (D/B/C) at 50 and 80°C at different relative humidity conditions are shown in Fig. 10. In general, there was a marked increase in conductivity when temperature was increased. Phosphonic acid concentrations less than 60% by weight gave proton conductivity values that were not reproducible and, above this concentration, membranes without C were soluble in water even at room temperature. With the addition of 1.5% (w/w) C, however, the % D could be increased while maintaining the membrane stability in water. Likewise, there was a dramatic increase in the conductivity under 100% R.H. conditions. This increase can be attributed to the fast transport of the H_3O^+ or a vehicle mechanism, enhancement of proton hopping via the Grotthuss mechanism (44–46,3). Compared to D/B/C membranes, membranes derived from precursor E have lower proton conductivity (60% less) at the same % D. The membrane with the more flexible B chains may have larger domains in which water can form pathways for proton transport (16,48). Regardless of the crosslinker, the proton conductivity values for these D membranes are very small ($<10^{-4}$ S/cm) under low R.H. with values approaching 10^{-2} S/cm only at 100% R.H. indicating that these hybrid membranes require water for proton transport.

Single Cell Performance Testing of Propyl Sulfonic Polysilsesquioxane Membranes

The polarization performance of single cells fabricated with propyl sulfonic polysilsesquioxane membranes was investigated under direct methanol fuel cell operating conditions at 50°C. Aqueous methanol solutions (8% w/w) and oxygen or air were fed to the anode and cathode, respectively. The methanol solution flowed at a rate of 0.33 mL/min through a tube heated at 50°C while the oxygen was fed at either 50 or 100 mL/min. Figure 7 shows the polarization curves for the 60:40% A/B/C membrane at 50 mL/min O_2 flow rate. When the cell was operated with oxygen at the cathode, the A/B/C membrane showed an open circuit voltage (OCV) of 0.60 V, i.e., comparable to that of Nafion® membranes (49) and did not change when the O_2 flow rate was increased to 100 mL/min. min. Future work includes the measurement of methanol crossover.

CONCLUSIONS

In this study, two systems of novel proton-conducting membranes were prepared and investigated for PEMFC applications. The membranes with the empirical formula of $R–Si–(O)_{1.5}$ consisted of a cross-linked Si–O backbone and a pendant organic side chain comprising propyl sulfonic or ethyl phosphonic acid groups. This inorganic-organic hybrid structure takes advantage of the thermal/mechanical/chemical stability brought by the inorganic component, and the flexibility and proton-conducting properties of the organic component.

The propyl sulfonic polysilsesquioxane precursor membranes, combined with several silyl-bearing crosslinkers, produced membranes through sol-gel processing that exhibited proton conductivities as high as 10^{-2} S/cm at various relative humidity and temperature conditions. The proton conductivity of these membranes increased with increased acid content and relative humidity conditions, indicating its strong dependence on the presence of water. Under direct methanol fuel cell conditions, OCV of 0.60 V was obtained at 50°C.

The ethyl phosphonic acid polysilsesquioxane membranes exhibited better thermal stability but somewhat lower proton conductivity at the same conditions as their sulfonic acid counterparts. The proton conducting properties are also highly dependent on water, as shown by the significant increase in proton conductivity as relative humidity increases.

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