



Sol–gel based sulfonic acid-functionalized silica proton conductive membrane

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ABSTRACT

Sulfonic acid-functionalized glass membranes have been synthesized via sol–gel reactions for low-power direct methanol fuel cells (DMFCs). Minimizing the fuel loss due to methanol crossover is the most important issue for creating long-life, low-power DMFC sources. The inorganic glass membrane is of interest due to its low methanol permeability compared to polymer membranes. Three different alkoxy silane reactants were investigated in the sol–gel reaction: 3-glycidoxypropyltrimethoxysilane (GPTMS), 3-mercaptopropyl trimethoxysilane (3MPS), and tetraethoxy orthosilicate (TEOS). The effect of oxidation time of the thiol group on the 3MPS, the mole fraction within the sol, and the water ratio in the reactant mixture were investigated. The ionic conductivity and methanol permeability has been characterized and optimized. The goal in this study was to find a balance between the ionic conductivity and methanol permeability, which determines the fuel conversion efficiency and device lifetime. The optimum glass membrane had a conductivity of 3.71 mS cm^{-1} , and methanol permeability of $2.17 \times 10^{-9} \text{ mol cm cm}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$, which was significantly better than Nafion or other previously reported membranes for this application.

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1. Introduction

Recent advancements in portable electronics have created a need for a new, higher density, lower cost, and longer life energy source. As demand for micro scale devices increase, such as for wireless sensors, so does the need for an energy source designed for low-power systems (μW to mW). Direct methanol fuel cells (DMFC) have received attention as a power source for low-power devices because DMFCs can be operated at atmospheric temperature and pressure and have the highest energy density of all convenient fuels. However, implementation of a low-power DMFC has several challenges, including lowering methanol permeability through a polymer-based electrolyte [1], orientation-independent operation, and development of a carbon dioxide vent from the fuel tank [2].

Improving the methanol conversion efficiency is the most significant challenge to achieve long-life. Several energy loss mechanisms exist [3]. Energy loss occurs due to a voltage drop, iR (where i is the current and R is the resistance membrane resistance) across the proton exchange membrane (PEM). In the case of low-current fuel cells, the membrane conductivity can be significantly lower than

high power cells since the current will be lower. Methanol permeability through the PEM is a critical issue because it results in fuel loss and lowers the effectiveness of oxygen reduction reaction at the cathode. Crossover through a Nafion membrane is a considerable problem for low-power, long-life fuel cells. Low-power cells can tolerate a modest loss in conductivity, resulting in lower iR drop compared to high-current fuel cells, in order to achieve lower methanol permeability for extended life and higher overall fuel conversion efficiency.

In previous studies, the polymer membrane surface was modified to block methanol transport [4]. Inorganic materials have been introduced into the membrane [5,6], and new inorganic membranes have been developed in order to reduce the methanol permeability through the proton exchange membrane [5,6]. In particular, Nogami, Uma, et al. have synthesized new inorganic electrolytes and characterized their behavior [7–11]. Methanol permeability has been reduced in these previous studies, however, the magnitude of the improvement is not adequate to achieve long-life DMFCs. The membranes have considerable water uptake and free volume resulting in methanol permeation. Consequently, there is interest in developing inorganic membranes specifically for low-power DMFC.

Silicate glasses are promising inorganic proton conducting materials due to their intrinsically low methanol permeability, but they have limited ionic conductivity ($10^{-6} \text{ S cm}^{-1}$) [7]. As a result, the glass structure needs to be adjusted to enhance their proton

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conductivity. Prakash et al., [7] fabricated phosphorous-doped silicate glasses (PSG) by plasma enhanced chemical vapor deposition (PECVD) and showed that PSG has potential as a PEM for low-power applications. The amount of phosphorous or other oxide in the glass can be tailored to enhance the structure, mechanical strength, and ionic conductivity. PECVD glass made from phosphine and silane yielded phosphor-silicate glass with ionic conductivity of $2.52 \times 10^{-4} \text{ S cm}^{-1}$. Though the conductivity was of interest for low-power DMFCs, PSG fabricated via PECVD suffers from low mechanical strength, and high equipment cost. It is also challenging to selectively tune the glass structure for proton conduction with PECVD.

An alternative fabrication method for glass membranes has been explored, involving a sol-gel process, which allows control of both the composition and structure of the glass. It is also less expensive and more rapid than vacuum processes. The sol gel process involves two reactions: hydrolysis and condensation using alkoxides as a precursor. In this process, hydrolysis and condensation takes place via 3 steps: i) nucleophilic substitution of the end group, ii) proton transfer from the attacking molecule to an alkoxide (within the transition state), and iii) removal of the end group as alcohol or water [8,9]. The characteristics and properties of the inorganic silica network are related to a number of sol-gel parameters. The parameters that affect the rate of hydrolysis and condensation reactions include: pH, mixing temperature, reaction time, precursor concentration, $\text{H}_2\text{O}/\text{Si}$ mole ratio (R), curing temperature, and reaction time.

Previous attempts to synthesize inorganic glass membranes via the sol-gel process used tetraethoxy orthosilicate (TEOS) [10–12]. Phosphorous was introduced into the silicon dioxide matrix to generate defects during the sol-gel reaction. However the ionic conductivity was limited, because high levels of the secondary oxide, necessary for improved ionic conductivity, caused cracks in the membrane. The glasses needed to be cured slowly for 3 days to 6 months [12–14] to prevent crack formation. Higher temperature also facilitated the full condensation of TEOS glass (e.g. $> 400^\circ\text{C}$) [11,12,15].

Functionalized alkoxy silanes have been investigated as an additive to the sol-gel glass to improve the properties of the membranes. Tezuka [16] and Siwen [17] have added 3-glycidioxypropyltrimethoxysilane (GPTMS) to the phosphorous-doped TEOS mixture to enhance the mechanical strength. The glass membranes containing GPTMS were cured at lower temperature, below 200°C , for a shorter time period (less than 3 days). Park et al., fabricated GPTMS-based membranes by incorporating silicotungstic acid (STA) which served as a proton source [18,19]. The conductivity of the STA-GPTMS membrane was higher than previous membranes, however, the membrane was not chemically stable because the STA did not bond directly to the GPTMS. 3-mercaptopropyl trimethoxysilane (3MPS) was introduced as a second precursor for GPTMS-based membranes [20]. 3MPS was chemically bonded with GPTMS via the sol-gel reaction enhancing the chemical stability of the glass membrane. However, the effect of the sol-gel curing parameters on final properties of the functionalized glass membranes has not been investigated. Also, the methanol permeability coefficient of the functionalized glass membranes has not been reported.

In this study, sulfonic acid-functionalized glass membranes have been synthesized using functionalized alkoxy silanes via sol-gel chemistry. The ionic conductivity and methanol permeability of glass membranes have been studied as a function of the sol-gel components and processing conditions. The sol-gel parameters have been optimized to form conductive and ductile PEMs in low-power DMFCs. Compliant Pt/C-SiO₂ composite electrodes were prepared and used to form a membrane electrode assembly (MEA) on the glass membranes [21].

2. Experimental

The inorganic glass membranes were prepared using three alkoxy silanes: TEOS, 3MPS, and GPTMS. GPTMS and 3MPS were obtained from Gelest Corporation, and TEOS was obtained from Tokyo Kasei. Mixtures containing 90 mol.% of 3MPS, x mol.% of GPTMS, and $(10-x)$ mol.% of TEOS were prepared and dissolved in methanol and water. HCl was added drop-wise to the mixture and the solution was stirred for 4 h to allow hydrolysis and polycondensation to occur in forming the gel. To make free-standing membranes, the gel was infiltrated into a fiber glass matrix (Fisher Scientific), which was 600 μm thick and 2.5 μm average pore size. The composite membrane was pressed with two Teflon plates and air-dried at room temperature for 12 h. The glass membrane was then cured by heating to 60, 100, 150, and 225°C for three hours at each temperature. The highest three temperatures were done under vacuum. The samples were allowed to cool via convection for 12 h followed by conversion of the thiol to the sulfonic acid. The thiol groups in the glass membrane were oxidized with 10% hydrogen peroxide for 3 h at 60°C .

The voltammetry and impedance spectroscopy experiments were performed with a Perkins Elmer PARSTAT 2263 potentiostat. The membrane was placed between the two glass cells and a 1.0 M H₂SO₄ electrolyte solution was filled and impedance was measured at room temperature. The two platinum electrodes were placed on either side of the membrane at a fixed distance from either face of the membrane and connected to a potentiostat. The frequency of the impedance measurements ranged from 100 mHz to 1 MHz with an AC signal amplitude of 10 mV. At least one hour equilibrium time was allowed to take the data point and the final value was confirmed by undertaking multiple runs ensuring equilibrium. The conductivity measurements were reproducible with about 0.2% error, which was insignificant. The methanol permeability of the membrane was determined by sealing the membrane to the end of a methanol filled tube. The loss of methanol was determined gravimetrically. The permeability coefficient value was obtained within 1.8% error. The water uptake of the synthesized membrane was evaluated by comparing the weight of dry and wet membrane. The weight of dry membrane was measured after nitrogen dried for 24 h at 100°C . The weight of wet membrane was measured after soaked in water for 24 h at room temperature. The thermal stability of the synthesized membrane was measured through thermogravimetric analysis (TGA) using TA Instruments Q50 with a N₂ flowrate of 40 mL min^{-1} , and a heating ramp rate of 5°C min^{-1} from 25 to 500°C . Fourier transform infrared spectroscopy (FTIR) data were collected between 400 and 4000 cm^{-1} using a Perkin-Elmer 1600. Pt/C-SiO₂ composite glass electrodes were fabricated on the membranes to test the performance of the glass membranes synthesized here [21].

3. Results

The first issue faced in the creation of a proton conducting silica membrane was the formation of a stable glass matrix. SiO₂ glass membranes were prepared via the sol-gel reaction with a 1:3:7 mole ratio of TEOS:water:methanol. A three-fold excess of water with respect to silane was used to ensure complete hydrolysis and condensation of the TEOS. A seven-fold excess of methanol was used so that the mixture was miscible. One mole percent of hydrochloric acid per mole silane was added to catalyze the sol-gel reactions. P₂O₅ was added to the mixture in order to increase the ionic conductivity of the glass membrane by forming a phosphor-silicate glass matrix. The silicon-to-phosphorous atomic ratio was 19:1.

The conductivity of the phosphorous-doped glass increased with increasing phosphorous content, however, the mechanical sta-

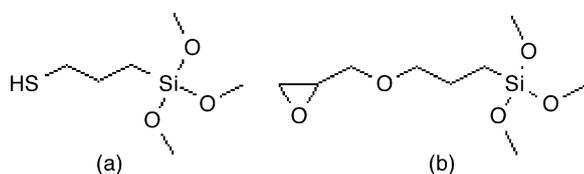


Fig. 1. Molecular structure of (a) 3MPS, and (b) GPTMS.

bility of the glass was reduced resulting in films with cracks, pores, and brittleness at the highest phosphorous loadings. Increasing the curing time helped to mitigate crack formation. The sol–gel reaction was allowed to proceed for 4 h at ambient temperature, followed by curing at 75, 150, and 250 °C for 3 h each. The glass membrane was fragile even when the phosphorous content (with respect to the silicon content) was as low as 5 wt.%. The resulting conductivity of the 5 wt.% phosphorous membrane was 10^{-5} S cm⁻¹, which is an order of magnitude lower than the PECVD fabricated phosphor-silicate glass membrane [7].

The incorporation of sulfonic acid groups attached to the glass matrix is a possible means to increase the conductivity and stability of the glass membrane while keeping a moderately fast curing process. Glass membranes with embedded sulfonic acid groups, controlled porosity, and mechanical toughness were synthesized by including two functionalized alkoxy silanes in the sol: 3MPS and GPTMS, as shown in Fig. 1. 3MPS has been previously investigated as a proton conducting moiety [5,20,22–24]. The thiol group within the 3MPS was converted to a sulfonic acid group before or after membrane fabrication by mild oxidation with hydrogen peroxide [5,25]. GPTMS has epoxide and trimethoxy silane functionalities so that it can provide cross-linking and flexibility to the silica structure.

The conditions for conversion of the 3MPS thiol to a sulfonic acid were first investigated. Two micrometer thick glass membranes containing 3MPS were prepared by the sol–gel reaction using a starting mixture with a mole ratio of 1:3:5 (3MPS:water:methanol). One drop of HCl was added to 6 mL of solution to catalyze the sol–gel reaction. The mixture was stirred for one hour at ambient temperature. The film was deposited on a metalized wafer and cured at 180 °C for 12 h. The thiol moiety in glass film was oxidized to sulfonic acid by soaking the film in 10% hydrogen peroxide at 60 °C for 2 h. The conversion from thiol to sulfonic acid was confirmed by FTIR analysis. Fig. 2 shows the FTIR spectrum of the cured and oxidized film. The thiol peak at 2570 cm⁻¹ is seen before oxidation. The thiol peak was smaller after an hour of oxidation, and full conversion occurred within 2 h of oxidation in peroxide. However,

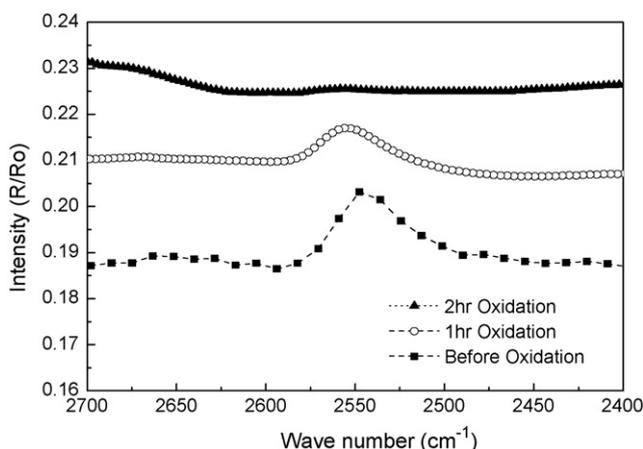


Fig. 2. Fourier Transform Infrared Spectra of the thiol peaks assigned at 2570 cm⁻¹ before the oxidation step, after an hour and two hours of oxidation.

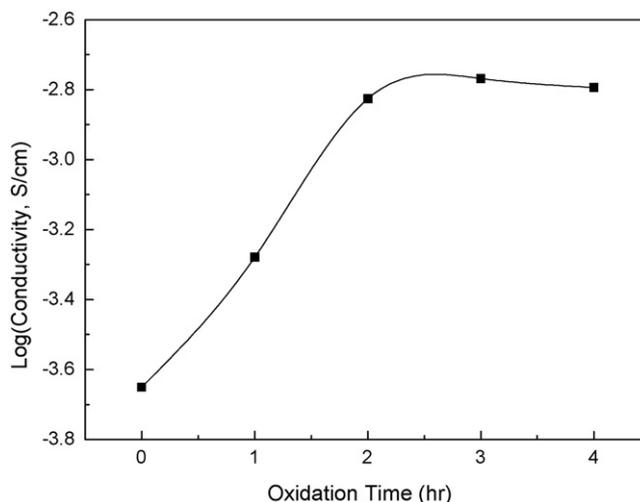


Fig. 3. Ionic conductivity as a function of oxidation time at 60 °C by 10% hydrogen peroxide.

when the thiol groups were converted to sulfonic acid by adding the hydrogen peroxide during the sol–gel reaction (before membrane fabrication), the sol was not fully condensed to form the glass structure because the negatively charged sulfonic acid groups present during the reaction prevented silanes from undergoing condensation. The pretreated membrane lost their mechanical structure and easily dissolved in methanol.

The oxidation conditions for conversion of the thiol to sulfonic acid may be different for thicker films, such as a 600 μm thick glass membrane. A thick membrane (632 μm) was oxidized with 10% hydrogen peroxide at 60 °C for varying times and examined by FTIR. The conductivity and permeability of the synthesized glass membranes were measured as a function of oxidation time. Fig. 3 shows that the ionic conductivity increased with the oxidation time up to three hours. The initial ionic conductivity of the glass membrane was 2.24×10^{-4} S cm⁻¹, and it increased to 5.26×10^{-4} S cm⁻¹ after 1 h of oxidation, and further increased to 1.7×10^{-3} S cm⁻¹ after 3 h of oxidation. The slope of ionic conductivity is related to the conversion rate of thiol groups to the sulfonic acid groups.

An increase in conductivity is a benefit, if the methanol permeability does not increase at as fast a rate. Fig. 4 shows the methanol permeability for the same samples as reported in Fig. 3. The permeability decreased with oxidation time until it reached a steady-state

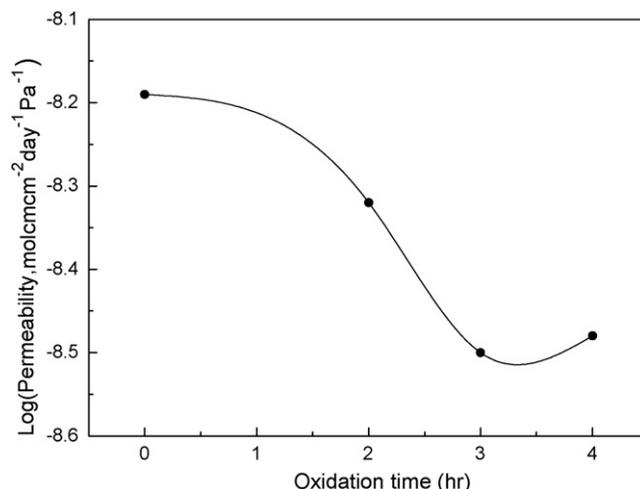


Fig. 4. Methanol permeability as a function of oxidation time at 60 °C by 10% hydrogen peroxide.

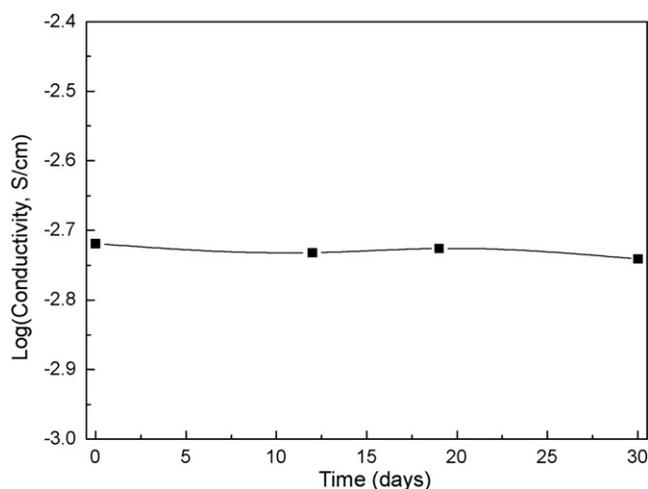


Fig. 5. Stability in ionic conductivity of a three hour oxidized membrane soaked in 10 M methanol over 30 days.

value after 3 h oxidation time. The initial permeability coefficient was $6.52 \times 10^{-9} \text{ mol cm cm}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$ and after 3 h oxidation it decreased to $3.19 \times 10^{-9} \text{ mol cm cm}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$. The chemical stability in methanol was tested by soaking the synthesized membranes in a 10 M methanol solution followed by measuring the change in conductivity. Fig. 5 shows that the conductivity of the 3 h oxidized glass membrane was stable for more than 30 days, after which the test was terminated.

The physical properties, particularly the fracture toughness and robustness, have been found to be a strong function of the sol mixture. 3MPS-GPTMS membranes have been synthesized with varying amounts of 3MPS ranging from 10% to 90%. It was found that the mole ratio of 3MPS had to be kept above 90% to maintain mechanically stable, crack-free membranes. When samples were prepared with less than 90% 3MPS, the glass membranes fractured during curing.

TEOS was added to the 3MPS-GPTMS glass membrane in order to densify the matrix and promote a high degree of cross-linking. It was found that in the absence of TEOS, the glass membrane cracked easily when only GPTMS and 3MPS were used. GPTMS and 3MPS are larger molecules than TEOS which would result in fewer cross-links per unit volume. In addition, it would be harder to achieve complete reaction because of the distance between functional groups [26]. The addition of TEOS increased the cross-link density resulting in membranes without cracks. In addition, TEOS reduced the degree of phase separation [22].

In the optimized membranes, the mole ratio of TEOS and GPMTS was varied but the sum remained 10 mol.%. The conductivity and permeability of the synthesized membranes were measured and are shown in Figs. 6 and 7. The conductivity of the membranes before oxidation increased with GPTMS mole ratio, as shown in Fig. 6. GPTMS by itself provides limited proton conduction through the ethylene oxide moiety. Cations can migrate between the oxygen sites of ethylene oxide [19,27,28]. Thus, the conductivity of GPTMS-TEOS membrane was greater than $10^{-7} \text{ S cm}^{-1}$. After three hours oxidation in hydrogen peroxide, the conductivity of each sample increased to more than $10^{-3} \text{ S cm}^{-1}$. The highest conductivity, 1.9 mS cm^{-1} , was obtained with 4% GPTMS.

The methanol permeability was evaluated for each of the membranes in Fig. 6, as shown in Fig. 7. The permeability improved with addition of GPTMS and was lowest at 3 mol.%. For a sample with no GPMTS, the permeability of the membrane was measured to be $8.25 \times 10^{-9} \text{ mol cm cm}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$. The permeability decreased to $3.19 \times 10^{-9} \text{ mol cm cm}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$ for a sample with 3 mol.% GPTMS and then increased again because excess epoxy groups

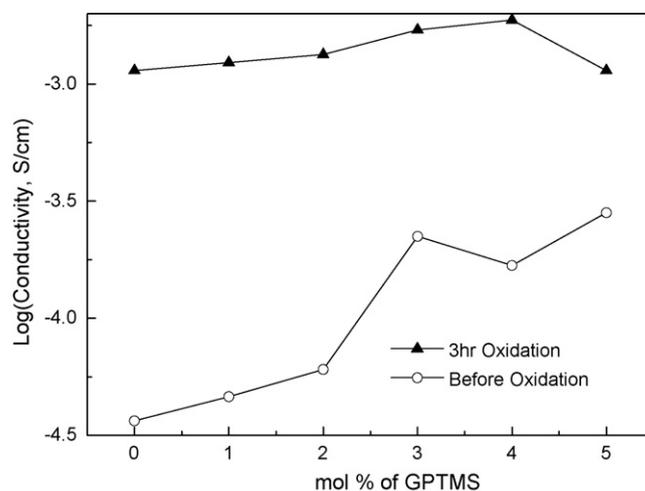


Fig. 6. Ionic conductivity as a function of a molar ratio of GPTMS before oxidation and after three hours of oxidation.

might tighten the glass structure resulting in cracks. Even though the conductivity of the 4 mol.% GPTMS membrane was higher than the 3 mol.% membrane, the selectivity (conductivity/permeability) of the 3 mol.% membrane was highest due to the lower methanol permeability. The optimization membrane was fabricated from a 90–7–3 mol.% of 3MPS-TEOS-GPTMS mixture.

Fig. 8 shows that as the GPTMS content increased, the intensity of the FTIR peak at 1100 cm^{-1} , which corresponds to silicon dioxide vibrations, increased while the silanol peak at $3200\text{--}3600 \text{ cm}^{-1}$ decreased. The peaks were normalized to the peak height of the thiol group in 3MPS, which remained constant in the samples. This result supports the previous observations that the methanol permeability was lowest at 3 mol.%, since a more complete silicon dioxide matrix will likely block methanol transport compared to the samples with a greater number of hydrophilic silanol groups.

One of the important parameters in the reactivity of the sol–gel is the amount of water. The effect of water ratio on the glass membrane structure has been investigated by varying the mole ratio of water-to-silicon (R) from 1 to 5 and carrying out the sol–gel reaction, holding other variables constant (4 h sol–gel reaction, 90–7–3 mol.% 3MPS-TEOS-GPTMS, curing temperature at 60, 100, 150, and 225°C for three hours at each temperature, 3 h oxidation in hydrogen peroxide at 60°C). As seen in Fig. 9, the weight loss

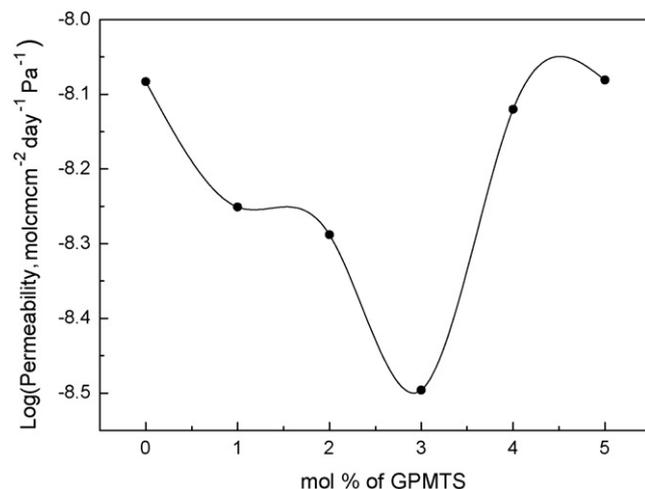


Fig. 7. Methanol permeability as a function of the molar ratio of GPMTS.

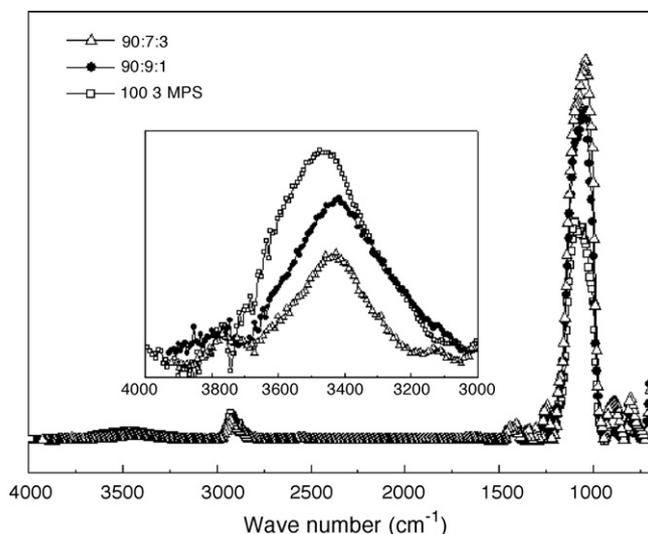


Fig. 8. Fourier Transform Infrared Spectra of different composition of 3MPS to TEOS to GPTMS (90:7:3, 90:9:1 of 3MPS:TEOS:GPTMS, 100% 3MPS).

in the TGA was fairly linear for a water ratio of $R=1$. The thermal instability in the final film was likely due to insufficient water in the sol-gel for the gelation reaction. When R was increased from 2 to 5, the weight loss at 100°C was due to evaporation of excess water and methanol. Higher values of R resulted in more excess water and methanol (17.95% loss for $R=2$, 24.89% loss for $R=3$, 41.28% loss for $R=4$, and 48.36% loss for $R=5$). The glass membrane itself was stable up to 340°C . At $R=5$, the free-standing membrane cracked due to excessive water evaporation.

The effect of the water ratio on conductivity and permeability of the glass membranes are shown in Figs. 10 and 11. Fig. 10 shows that the methanol permeability increased with an increase in R . The minimum permeability coefficient of $2.17 \times 10^{-9} \text{ mol cm cm}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$ was achieved with an R value of 2. Fig. 11 shows that ionic conductivity decreased from 3.71 to 1.46 mS cm^{-1} as the R value increased from 2 to 4. The highest selectivity in this experiment was achieved at $R=2$.

The difference in conductivity between the sol-gel glass and Nafion is of interest. The conductivities of two optimized glass membranes were measured as a function of temperature from 25 to 90°C . Fig. 12 shows that the conductivity of the glass

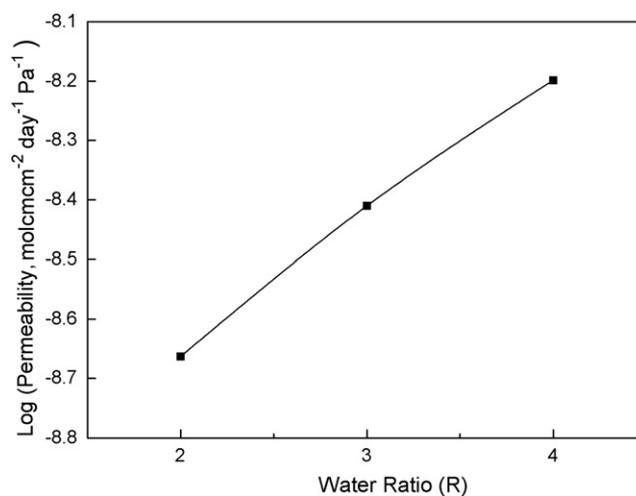


Fig. 10. Methanol permeability as a function of water ratio to silicon (R).

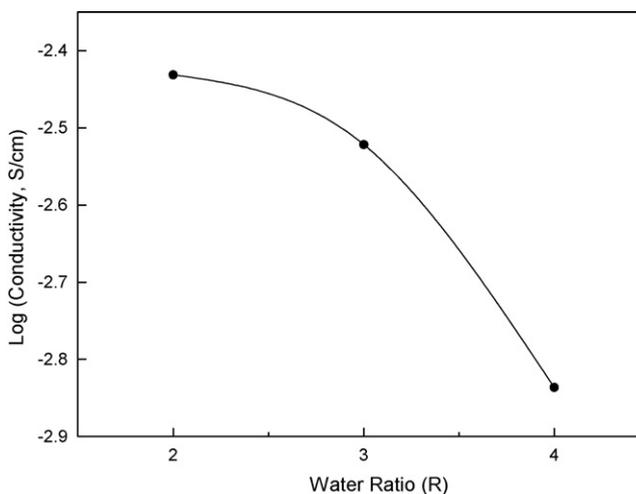


Fig. 11. Ionic conductivity as a function of water ratio to silicon (R).

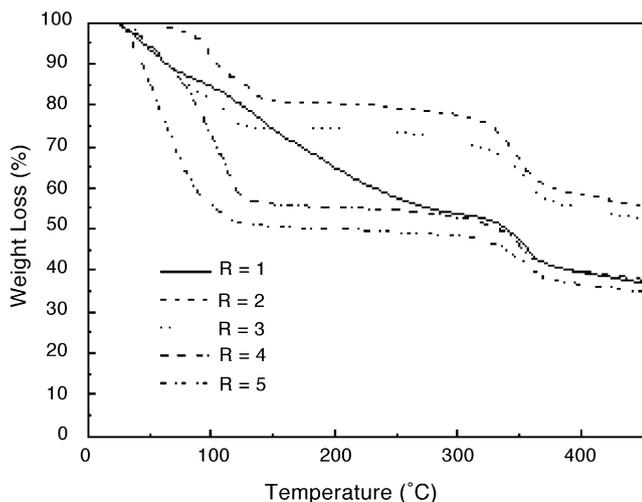


Fig. 9. Thermogravimetric analysis of glass membranes synthesized by varying the molar ratios of water to silicon (R) from 1 to 5.

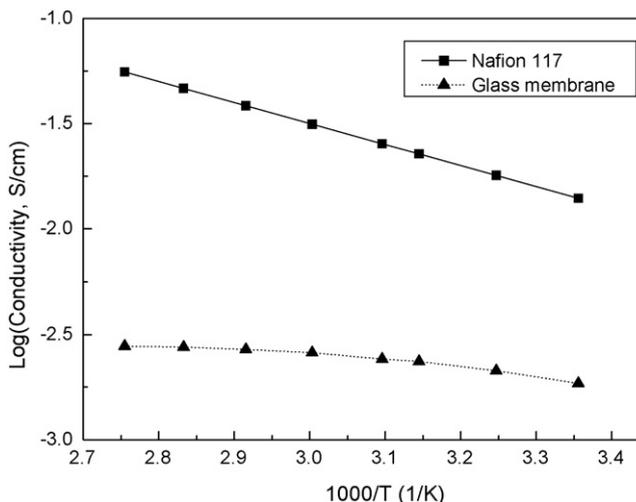


Fig. 12. Ionic conductivity dependence on the temperature.

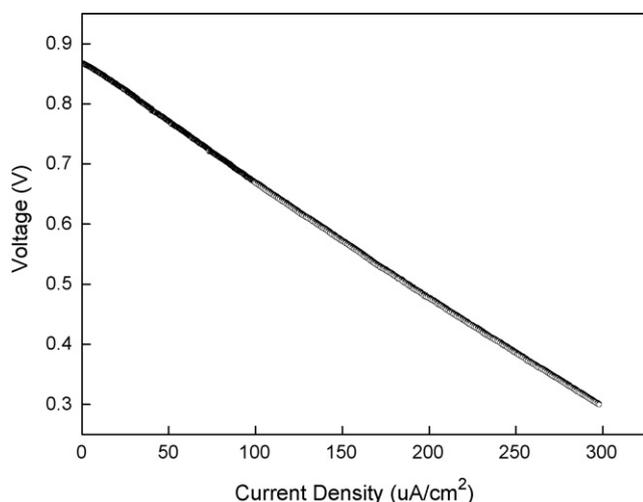


Fig. 13. A linear polarization curve for a fully passive DMFC with a synthesized glass membrane and glass electrodes; 23 °C 2 M methanol, 10 mV s⁻¹.

membranes was less dependent on temperature than Nafion. The activation energy was calculated from an Arrhenius relationship, Eq. (1).

$$\sigma = k \exp\left(-\frac{Ea}{RT}\right) \quad (1)$$

where σ is the conductivity, Ea is the activation energy, T is the temperature, R is the gas constant, and k is a pre-exponential term. The activation energy of the optimized glass membrane was 2.38 kJ mol⁻¹. This value was clearly smaller than the activation energy of Nafion, which was 9.34 kJ mol⁻¹. The water uptake of glass membranes was 4–6%, which was also much less than Nafion which has about 30% water [29].

An MEA was fabricated from a 90–7–3 mol.% (3MPS-TEOS-GPTMS) glass membrane oxidized for 3 h in hydrogen peroxide. The compliant glass anode and cathode were prepared by incorporating the Pt/C nanoparticles in the silicon dioxide matrix, and the glass catalyst were painted on both sides of the glass membrane.

The silicon dioxide matrix for the catalyst layer was made from the sol-gel reaction of 3-(trihydroxysilyl)-1-propanesulfonic acid (3TPS) and GPTMS. The sulfonic acid group in the 3TPS provided proton conductivity in the catalyst layer. The mole ratio of 3TPS and GPTMS was 1:1. Four mL of methanol and 3 drops of HCl were added to 5 mL of the mixture. After reacting the sol-gel for three hours, an equal mass of sol-gel and Pt/C were combined and mixed together for 1 h. The mixture was painted on the membrane and cured at 50 °C for 12 h. The final Pt loading was 1 mg cm⁻². Additional studies on the metal catalyst and its optimization are underway and will be the subject of a future report.

The electroless deposition of platinum was used to increase the total platinum loading on the MEA. The total amount of platinum deposited electrolessly was about 0.1 mg cm⁻². The electroless platinum also improved the sheet conductivity of the MEA, as described previously [21]. Fig. 13 shows the polarization curve for a passive (no recirculation) DMFC operated at room temperature with 2 M methanol as the fuel at the anode and an air cathode. The open circuit voltage was 868 mV and the current density at 600 mV was 132 µA cm⁻².

4. Discussion

Sulfonic acid-functionalized glass membranes have been synthesized via a sol-gel reaction using 3MPS, GPTMS and TEOS for low-power DMFCs. The inorganic glass membrane is of interest

due to its lower methanol permeability than polymer membranes. Minimizing the fuel loss through crossover is the most important issue in long-life DMFCs. The goal of this study was to find the balance between the conductivity and permeability which determines the efficiency and performance. The conversion of thiol to sulfonic acid, contribution of the different sol components to the membrane properties, and water ratio in the sol have been investigated.

The overall methanol permeability coefficient of the samples, shown in Figs. 4, 7 and 10, were on the order of 10⁻⁹ mol cm cm⁻² day⁻¹ Pa⁻¹, which is at least three orders of magnitude lower (improvement) compared to Nafion, 2.1 × 10⁻⁶ mol cm cm⁻² day⁻¹ Pa⁻¹ [30]. However, the ionic conductivities shown in Figs. 3, 6 and 11 were on the order of 10⁻³ S cm⁻¹, which is two orders of magnitude lower than Nafion, 0.08 S cm⁻¹ [1,30].

The conductivity and permeability differences between glass and polymer membranes are related to the proton transport mechanism in each material. Bulk transport and surface transport mechanisms have been discussed in the literature [12]. In both cases, the proton is transported through the electrolyte by binding to functionalized stationary anions such as sulfonic acid groups. The transport mechanism is dictated by the chemical properties of the membrane and the chemical environment surrounding the anionic sites within the membrane. In case of bulk transport, protons are solvated (H⁺(H₂O)_λ) and move with a relatively large solvent shell with λ ranging from 2 to 4. On the other hand, surface transport has less water transport with λ between 0 and 1. The electro-osmotic drag (EOD) coefficient, λ , is one factor in water transport through the membrane, in addition to water diffusion as a result of the concentration gradient [31]. Since polymer membranes, such as Nafion have a relatively large free volume compared to glass membranes, greater amounts of water can be transported with the proton. Bulk transport is generally the dominant transport mechanism for the polymeric anion exchange membranes. One ramification of high EOD in Nafion is the sensitivity of its conductivity to relative humidity and residual. Water is needed for conductivity in a polymer membrane, however, excess water can be detrimental to cell performance. Liquid films can form on the electrodes disrupting the delivery of gaseous reactants, especially oxygen to the air-breathing cathode. Methanol permeability is also an issue because materials which facilitate water permeation, generally, have high methanol permeability, such as by mixed clusters H⁺ (H₂O)_λ (CH₃OH)_y [12]. Diffusion of methanol through the high free volume within the polymer is also an issue. The linear relationship between conductivity and permeability for several polymer membranes has been reported in the literature [32]. Therefore, it is desirable to have a material with a lower proton solvation in order to decrease the methanol permeation for a low-power fuel cell. It is critical to make the surface transport dominant over bulk transport in the synthesized electrolytes, since surface transport requires less water. The free volume should be minimized to allow a minimum of adsorbed water leading to surface transport. The density of the functional groups and distance between neighboring sites are important parameters.

The particular behavior of conductivity and permeability for the glass membranes with respect to polymeric ones was shown in Figs. 3 and 4. While the conductivity increased with thiol oxidation time (i.e. higher conversion of the thiol to sulfonic acid), the permeability decreased. This is contrary to the linear relationship between conductivity and permeability for polymeric membranes where an increase in conductivity leads to an increase in permeability. It is likely that the conversion of the thiol to sulfonic acid in the rigid glass matrix lowers the free volume while increasing the density of acid sites. Lowering the free volume reduces methanol permeability.

Table 1
The effect of oxidation time on selectivity.

Oxidation time (h)	Selectivity
0	4.54
2	5.50
3	5.73

A similar behavior was observed by varying the mole fraction of GPTMS. Figs. 6 and 7 show that the permeability decreased with additional GPTMS (zero to 3 mol.% GPTMS), while the ionic conductivity increased with increasing GPTMS. The additional GPTMS provided a greater fraction of silica matrix, Fig. 8, and likely less free volume. Less free volume results in lower methanol permeability and closer packing of the sulfonic acid groups providing a pathway for protons. The higher permeability and lower conductivity with excess water during reaction, Figs. 10 and 11, can also be the result of added free volume due to trapped water during reaction.

The different transport mechanism in the glass membrane resulted in a lower effective activation energy for proton transport, as shown in Fig. 12. The lower activation energy for conductivity in the glass membrane is consistent with a surface transport mechanism [12]. The activation energy of glass membranes (2.4 kJ mol⁻¹ average) was four times lower than that of Nafion (9.3 kJ mol⁻¹).

The importance of balancing conductivity and permeability to achieve high energy conversion efficiency was presented here. The trade-off between conductivity and permeability can be captured by defining selectivity (*S*) as the log of the ratio of proton conductivity to methanol permeability, Eq. (2).

$$S = \log \frac{\text{Conductivity}}{\text{Permeability}} \quad (2)$$

The advantage of using a glass membrane even with its limited conductivity can be verified by comparing the selectivity value of glasses to Nafion. Tables 1–3 show the selectivity of samples examined in the different experiments here. The highest selectivity, 6.23, was achieved with an oxidation time of 3 h, a membrane composition of 90–7–3 mol.% 3MPS-TEOS-GPTMS, and an *R* ratio of 2. For comparison, a Nafion membrane has a conductivity of 0.08 S cm⁻¹ and permeability of 2.6 × 10⁻⁶ mol cm cm⁻² day⁻¹ Pa⁻¹, resulting in a selectivity of 4.48. Thus, the glass membranes had a 56 times improvement (linear scale) in selectivity compared to Nafion.

Finally, the energy conversion efficiency of a DMFC with a glass membrane can be compared to a Nafion membrane, using the energy loss analysis presented previously [3]. The useful power delivered from a fuel cell, *E_U*, is given in Eq. (3).

$$E_U = iV_{op} \quad (3)$$

Table 2
The effect of mol.% GPTMS on selectivity.

mol.% of GPTMS	Selectivity
0	5.14
1	5.34
2	5.41
3	5.73
4	5.39

Table 3
The effect of water ratio on selectivity.

Water ratio	Selectivity
2	6.23
3	5.89
4	5.36

where *i* is the fuel cell current and *V_{op}* is the operating voltage. IR voltage drop from ionic transport through the proton exchange membrane causes a loss in power, *E_R*, Eq. (4).

$$E_R = \frac{i^2 \rho \delta_1}{A_1} \quad (4)$$

where ρ is the ionic resistivity of the membrane, δ_1 is the membrane thickness, and A_1 is the area. Then, the energy loss (%) due to IR drop can be calculated by Eq. (5).

$$\text{IR loss} = \frac{E_R}{E_R + E_U} \times 100 \quad (5)$$

For Nafion 117, it has a conductivity of 0.08 S cm⁻¹ and 178 μm thickness. The IR loss is 0.01% for a surface area of 1 cm², operating at 0.5 V and 200 μA, while the IR loss for a more typical current, 100 mA, is 4.3%. For low-power cells, the current will be at the low end of this range and thus, the conductivity may be substantially reduced as well.

The maximum loss in power, *E_X*, due to crossover is given by Eq. (6).

$$E_X = \left(\frac{P \Delta p A_2}{\delta_2} \right) n F V_{ocv} \quad (6)$$

where *P* is the permeation coefficient of the membrane, Δp is the pressure drop across the membrane, A_2 is the exposed membrane area available for fuel transport through the membrane, δ_2 is the electrolyte thickness, *n* is the number of equivalents per mole, and *F* is Faraday's constant. Then, the fuel loss from crossover (neglecting *iR* loss) can be calculated by Eq. (7).

$$\text{Fuel loss} = \frac{E_X}{E_X + E_U} \times 100 \quad (7)$$

The fuel loss of Nafion 117 using Nafion permeability of 2.62 × 10⁻⁶ mol cm cm⁻² day⁻¹ Pa⁻¹ [30] is 99.9%. Despite Nafion's high conductivity, Nafion is not a good electrolyte for low-power sources unless extremely low surface area electrodes were used. Extremely low surface area is a problem because that would require exceptionally high-current density and fuel transport problems.

The energy loss due to crossover decreases when a higher selectivity glass membrane is used in a low-power DMFC. A specific quantity of the membrane, the aspect ratio of the membrane (α = membrane thickness/membrane area), can be defined from Eqs. (4) and (5). This design variable effects both fuel and IR loss. As shown in Fig. 14, there is a linear relationship between the aspect

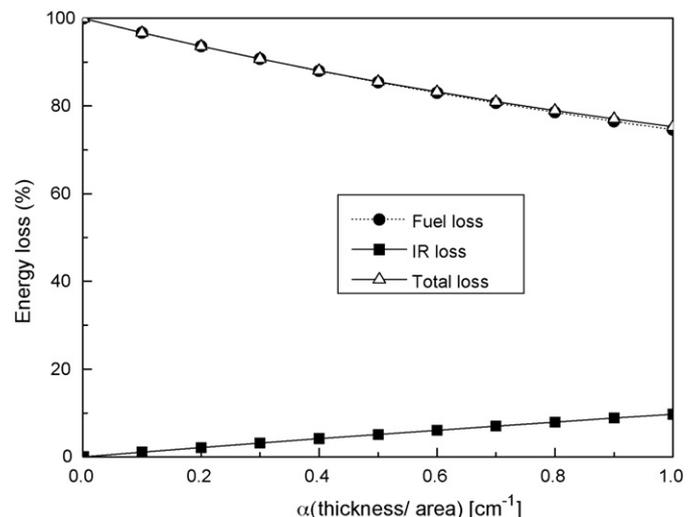


Fig. 14. Energy losses as a function of alpha of optimized glass membrane with a selectivity of 6.23 when fuel cell operates at 200 μA and 0.5 V.

ratio and IR loss, and an inverse relationship with fuel loss through crossover. Fig. 14 shows the two relationships in the case of the optimized glass membrane with a selectivity of 6.23 for a fuel cell operating at 200 μA and 0.5 V. The total loss (%) was calculated by Eq. (8).

$$\text{Total loss} = \frac{E_X + E_R}{E_X + E_R + E_U} \times 100 \quad (8)$$

The total loss varies between 75.2% and 99.8% as a function of α . The lowest energy loss, 75.2%, can be achieved by adjusting the thickness and area of the glass membrane.

5. Conclusion

High selectivity glass membranes have been synthesized via sol–gel reaction using 3MPS, GPTMS and TEOS as the precursors. The conversion of the thiol in 3MPS to sulfonic acid, contribution of the different sol components to the membrane properties, and water ratio in the sol have been investigated. The highest selectivity, 6.23, was achieved with 3 h oxidation time, 90:7:3 of 3MPS:GPTMS:TEOS and R ratio of 2. The ionic conductivity was 3.71 mS cm^{-1} and the permeability was $2.17 \times 10^{-9} \text{ mol cm cm}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$. The glass and polymer membrane behaviors have been studied and the conductivity and methanol permeability were characterized. The results indicate that the two properties were affected by the free volume in the glass. Less free volume results in lower methanol permeability and closer packing of the sulfonic acid groups providing a pathway for protons. The lower activation energy for proton transport in the glass membrane, compared to Nafion, supports the surface transport mechanism in the glass. The fuel cell performance of the optimized glass membrane was tested with the Pt/C-SiO₂ electrodes for both anode and cathode. The OCV was 868 mV and the current density at 600 mV was 132 $\mu\text{A cm}^{-2}$. The total energy loss of the DMFC decreased from 99.9% to 75.2% by replacing the Nafion to the synthesized glass membrane.

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