

## Novel inorganic/organic hybrid membranes for proton exchange membranes

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### Abstract

Two types of inorganic/organic hybrids comprising Brønsted acid-base ionic groups have been prepared and studied for proton exchange membranes (PEM) applications. The hybrid membranes have a highly cross-linked silicon-oxygen backbone and trifluoromethanesulfonimide (HTFSI) doped organic amine groups. The Si-O backbone provides the membranes thermal/chemical/mechanical properties and the HTFSI-doped amine end groups provide the proton conducting properties. The membranes exhibited proton conductivities of  $10^{-3}$  S/cm at elevated temperature ( $\geq 130$  °C) and anhydrous conditions. Under fully hydrated conditions, the membranes showed high proton conductivity ( $10^{-2}$  S/cm) and low methanol/water crossover rate.

### I. Introduction

Direct methanol fuel cells (DMFC) are considered as promising alternative energy sources for small-scale portable power generation. The proton exchange membrane (PEM), a central part of a fuel cell system, serve both as proton conductor as well as a methanol barrier between the cathode and anode electrodes, and have been the most critical issue for DMFC systems. The traditional PEMs, such as Nafion® membranes and other perfluorinated sulfonic acid (PFSA) polymer membranes, exhibit excellent proton conductivity and durability at fully hydrated conditions. However, these membranes suffer severe methanol crossover, which leads to low cathode performance and fuel waste in a DMFC system.

Proton conduction in PEMs follows either the vehicular mechanism or Grotthuss mechanism. In the vehicular mechanism, protons transfer through the PEM together with small molecules such as H<sub>2</sub>O in the form of H<sup>+</sup>-*n*H<sub>2</sub>O clusters, whereas in the Grotthuss mechanism, protons hop via hydrogen bonds from one active site to the neighboring one without any accompaniments.<sup>1,2</sup> Considering the complete miscibility between water and methanol, PEMs that conduct protons mainly through the vehicular mechanism, such as PFSA polymer membranes, may not be intrinsically suitable for DMFC applications, because of unavoidable methanol crossover accompanying the H<sup>+</sup>-*n*H<sub>2</sub>O current under fuel cell operating conditions. PEMs that can efficiently conduct protons through the Grotthuss mechanism have the obvious advantage for reducing the methanol crossover in DMFC systems.

Brønsted acid-base ionic liquids derived from small molecule organic amine and equimolar trifluoromethanesulfonimide (HTFSI) have been reported to be highly proton conducting (in the range of  $10^{-2}$  S/cm) in the molten phase and anhydrous conditions<sup>3</sup>. The proton-conduction in these molten ionic salts was proposed to follow the combination of both the Grotthuss mechanism and the vehicular mechanism<sup>4</sup>. Polymerization of these ionic liquids

into solid-state membranes may be a promising approach for novel PEMs with low methanol crossover.

In this study, 3-dimensionally cross-linked inorganic/organic hybrid membranes based on polyethylenimine (PEI) and polysilsesquioxane were prepared through sol-gel processing. The highly cross-linked silicon-oxygen structure of the membranes is beneficial to reduce methanol crossover. HTFSI was added during sol-gel processes to dope the amine groups and form Brønsted acid-base pairs as proton conducting functional groups. Since the organic amines are covalently bonded to the membrane network, the possibility of vehicular conduction under anhydrous conditions is virtually eliminated, and therefore, the proton conduction in the membranes should follow the Grotthuss mechanism almost exclusively. The membranes exhibited proton conductivity of  $10^{-3}$  S/cm at elevated temperature ( $\geq 130$  °C) and anhydrous conditions and approached  $10^{-2}$  S/cm under fully hydrated conditions. Since the proton conduction in the membranes involves the Grotthuss mechanism and the membranes have highly cross-linked networks, the methanol crossover of the membranes was detected to be ~ 1 orders of magnitude lower than that of Nafion®-117 membrane under wet conditions and 50°C.

## II. Experimental

### 2.1 Materials

Poly (2-ethyl-2-oxazoline) (M.W.= 500K, Aldrich), lithium trifluoromethanesulfonimide (Li-TFSI, 3M company), H<sub>2</sub>SO<sub>4</sub> (96%, from Mallinckrodt), N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (IPTES) (Gelest Inc.) and 3-glycidoxypropyltrimethoxysilane (GLYMO) (98%, Aldrich) were used as received.

Trifluoromethanesulfonimide (HTFSI) was vacuum (~ 0.1 mmHg) distilled from a 1:6 molar ratio of Li-TFSI in conc. H<sub>2</sub>SO<sub>4</sub> in a procedure similar to the reported one utilizing Na-TFSI.<sup>5</sup> Melting point: 55.5-56.5 °C. NMR (DMSO-d<sub>6</sub>): <sup>1</sup>H:  $\delta$  13.81 (s). <sup>13</sup>C:  $\delta$  112.57 (s), 117.30 (s), 122.04 (s), 126.78 (s).

Linear PEI was prepared according to the literature by hydrolyzing poly (2-ethyl-2-oxazoline) (M.W.= 500k) in aqueous HCl solution.<sup>6</sup> NMR (methanol-d<sub>4</sub>): <sup>1</sup>H:  $\delta$  2.73 (s, 4H), 4.84 (s, 1H). <sup>13</sup>C:  $\delta$  48.45 (s).

### 2.2 Membrane preparation

*PEI membranes:* The membranes were prepared by first dissolving 0.17 g of PEI in 2.0 mL of ethanol with the subsequent addition of 0.17 g of GLYMO followed by stirring for 0.5 hour at room temperature. 2.22 g of HTFSI solution (50wt% in ethanol) was then added dropwise and stirred for another 0.5 hour at room temperature. The resultant solution was cast onto a level PTFE surface, air dried at room temperature for 1 day, and then heated to 80 °C overnight to give freestanding, flexible membranes. The thickness of the membranes ( $180 \pm 20$   $\mu$ m) was simply controlled through varying the solution amount during casting.

*Polysilsesquioxane membranes:* IPTES (2.0 g) and GLYMO (0.4 g) were first mixed in methanol (3.0 mL) and stirred overnight at room temperature. 4.2 g of an HTFSI/ethanol solution (50wt%) were then added and stirred for ~2 hours at room temperature. The resultant solution was cast onto a porous glass paper substrate (HOVOSORB®, Hollingsworth & Vose Company, thickness = 89  $\mu\text{m}$ ), followed by air drying for 1 day and aging at 80 °C overnight to form a continuous membrane. The thickness of the membranes ( $180 \pm 20 \mu\text{m}$ ) was controlled by adjusting the solution amount during casting.

### 2.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the membranes were carried out using a Perkin Elmer Pyris 1 TGA under O<sub>2</sub> atmosphere, heating from 90 °C to 800 °C at a rate of 10 °C/min.

### 2.4 Proton conductivity

The proton conductivities of membranes were measured using 2-probe ac impedance method. Nano-sized Pt black catalyst (fuel cell grade) was coated on both sides of the membranes to minimize the electrode-membrane interface impedance and to work as two electrodes. A PC controlled frequency response analyzer (VoltaLab® PGZ301, Radiometer Analytical S.A.) was used to record the membranes' complex impedance over the frequency range of 100 KHz to 0.1 Hz. All measurements were carried out under ambient pressure and well-controlled temperature and humidity by using a 5-cm<sup>2</sup> single cell and a fuel cell testing station (Fuel Cell Technologies Inc.). The membranes' resistances (ohms) were determined from Nyquist plots where the curve intersects the real axis or the point that is the closest to the real axis.

### 2.5 Methanol / water crossover measurement

The rate of methanol crossover through the membranes was measured using a 5-cm<sup>2</sup> single cell and a fuel cell testing station (Fuel Cell Technologies Inc.). 2.0 M of aqueous methanol aqueous was fed to the anode side at a flow rate of 0.3 cc/min by a peristaltic pump. Dry N<sub>2</sub> was fed to the cathode side at a flow rate of 250 cc/min or 500 cc/min. The cell temperature was controlled at 50 °C. A gas chromatograph (GOW-MAC Instrument Co., Model: SERIES 350) with an 80/100 Porapak P column and thermal conductivity detector was used to monitor water/methanol concentration in the outlet gas of the cathode side. The methanol crossover rate was calculated in the units of  $\mu\text{mol} / (\text{s} \cdot \text{cm}^2)$ .

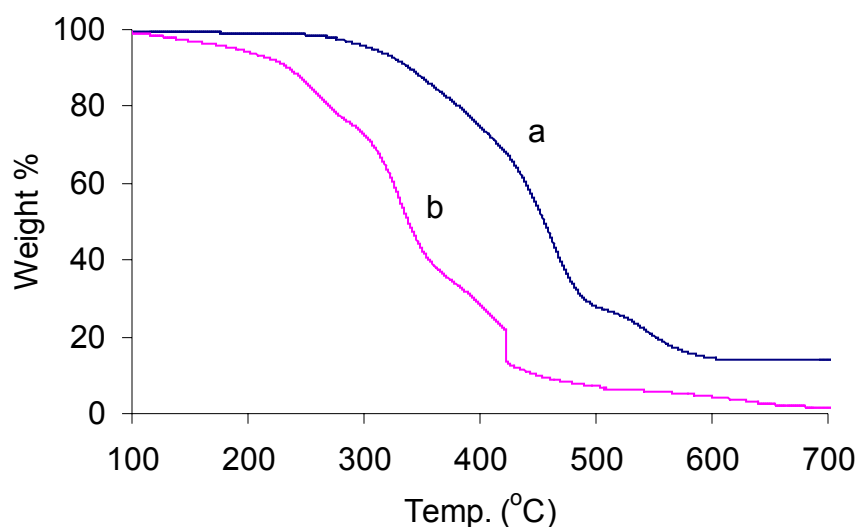
## III. Results and discussion

### 3.1 Membrane preparation

The membranes were prepared from GLYMO, HTFSI and PEI (or IPTES) through sol-gel processes as described in the experimental section. GLYMO serves as a cross-linker here

to enhance the physical properties of the membranes. In this case, the epoxy end of GLYMO reacts with the amine nitrogen to form covalent bonds, while the trimethoxysilane end of GLYMO hydrolyzes and condenses with silane groups on itself to form a cross-linking point in PEI polymer matrix, or together with the silane groups of IPTES to form the 3-dimensional Si-O network of the polysilsesquioxane membrane. The amine groups of PEI or IPTES were doped with HTFSI during the sol-gel process to form proton-conducting active sites. The resulting membranes have reasonable mechanical and heat resistance, as evidenced by no dimensional change and damage during the Pt catalyst coating processes (~ 85 °C and 300 psig).

TGA shows that the membranes were stable under O<sub>2</sub> atmosphere without distinct weight loss (< 5%) until ~ 180 °C for PEI membranes and ~ 300 °C for polysilsesquioxane membranes (Figure 1). The better thermal stability observed for the latter one could be due to its high Si-O inorganic content in the membrane.

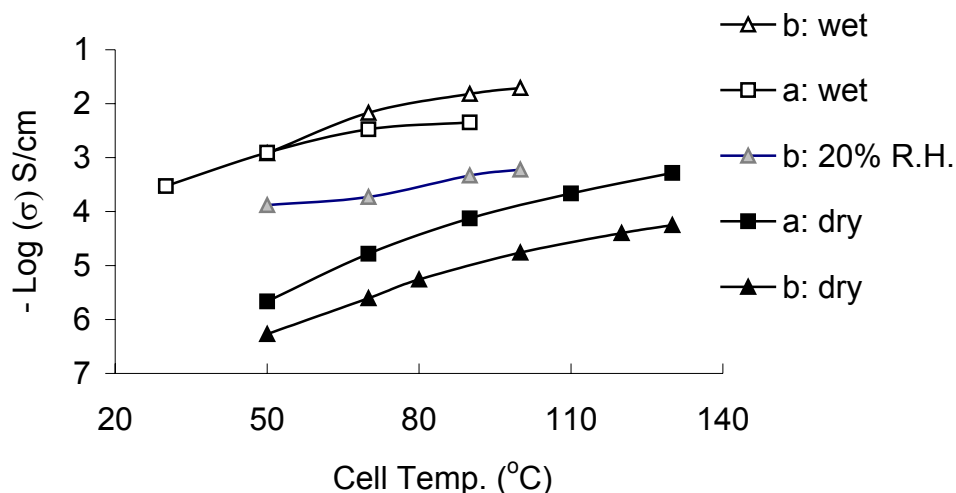


**Figure 1.** TGA of polysilsesquioxane membrane (a) and PEI membrane (b)

### 3.2 Proton conductivity

Figure 2 shows the proton conductivities as a function of cell temperature for a polysilsesquioxane membrane (curve a) and a PEI membrane (curve b). Under dry N<sub>2</sub> atmosphere, the polysilsesquioxane membrane exhibited good proton conductivity, which increased with an increase in temperatures, reaching ~ 10<sup>-3</sup> S/cm at 130 °C. Since there was essentially no water in the system under such conditions and the amine/HTFSI ion pairs are covalently bound to the membrane matrix, proton conduction in these membrane should be realized through the Grotthuss mechanism only. In Grotthuss mechanism, the hopping of protons between / among the amino nitrogen sites and TFSI<sup>-</sup> anion sites is realized through deprotonation / protonation processes, which are directly affected by vibration, rotation and reorientation of amine/HTFSI groups. Therefore, the local mobility of functional groups plays a critical role on the diffusion of protons in membranes. The amine/HTFSI groups in the polysilsesquioxane membranes have high local mobility because they are located at the end of

pendant organic chains. Thus, compared to the PEI membranes, in which amine/HTFSI groups are a part of polymer backbone, these membranes exhibited ~ 1 order of magnitude higher proton conductivity at 130 °C and anhydrous condition.



**Figure 2.** A plot of proton conductivity versus cell temperature for polysilsesquioxane membrane (a) and PEI membrane (b)

The presence of water in the membranes exhibited a significant effect on the proton conductivities of both types of membranes. Under humidified conditions, the overall proton conduction in the membranes could be due to both the vehicular and Grotthuss mechanisms, since the introduction of water into the membranes can directly affect the proton diffusion in both cases. In the Grotthuss mechanism, water molecules increase the rate of proton transfer between proton donors and acceptors, as reported by the literature<sup>7</sup> wherein the transfer of protons from N-H<sup>+</sup> to H<sub>2</sub>O to N-H is faster than directly from N-H<sup>+</sup> to N-H. In the vehicular mechanism, the introduction of water in the membranes could provide an additional vehicular effect by forming H<sup>+</sup>-nH<sub>2</sub>O clusters. Under fully hydrated conditions, the proton conductivity of the membranes increased by > 2 orders of magnitude relative to water-free conditions.

### 3.3 Methanol / water crossover

Both kinds of membranes proved to be excellent methanol/water barriers for DMFC applications. The PEI membrane exhibited an ~ 1 order of magnitude lower methanol crossover rate and approximately 5X lower water crossover rate compared to a Nafion®-117 membrane at 50 °C. The mechanism of methanol/water crossover in the membranes is unclear. It could be related to both the nature of membrane material and its nano-structure. The nano-size porous structure of Nafion® membranes under fully hydrated conditions<sup>8</sup> and the alcohol-affinity of PFSA polymers could explain its higher methanol/water crossover rate and ratio. The polysilsesquioxane membranes have highly 3-dimensionally cross-linked Si-O network, resulting in its dense structure. Therefore, the membranes exhibited even lower methanol/water crossover rates and ratios than the PEI membranes.

**Table 1.** Methanol / water crossover rate at 50 °C

Sample	Membrane area (cm <sup>2</sup> )	N <sub>2</sub> flow rate (cc/min)	H <sub>2</sub> O crossover $\mu\text{mol}/(\text{s} \cdot \text{cm}^2)$	MeOH crossover $\mu\text{mol}/(\text{s} \cdot \text{cm}^2)$	MeOH / H <sub>2</sub> O (mol/mol)
Nafion-117	5.29	500	3.1	0.29	1 / 11
	5.29	250	2.2	0.23	1 / 9.7
PEI membrane	5.5	500	0.53	0.030	1 / 18
	5.5	250	0.52	0.026	1 / 20
Polysilsesquioxane membrane	5.5	500	0.23	0.0078	1 / 30
	5.5	250	0.20	0.0081	1 / 25

#### IV. Conclusion

In this study, two types of proton exchange membranes, PEI membranes and polysilsesquioxane membranes, containing immobilized HTFSI doped amine groups have been successfully prepared. The membranes exhibit good thermal and chemical stability at elevated temperature and O<sub>2</sub> atmosphere. The polysilsesquioxane membranes gave proton conductivities of 10<sup>-3</sup> S/cm at high temperature and water free conditions, which follow the Grotthuss mechanism. An increase in operating temperature and local mobility of amine/HTFSI groups in membranes led to higher proton conductivity. The presence of water in the membranes significantly improved the membranes' proton conductivity by enhancing the proton-hopping rates and introducing possible proton conduction through the vehicular mechanism. Both types of membranes exhibited benignly low methanol/water crossover, which is particularly attractive for DMFC applications.

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