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S. Granados-Focil^a; J. R. Conway^a; Y. Meng^a; L. J. Smith^a

^a Gustaf Carlson School of Chemistry and Biochemistry, Clark University, Worcester, MA

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Triazole Functionalized Sol-Gel Membranes, Effect of Crosslink Density and Heterocycle Content on Water Free Proton Conduction and Membrane Mechanical Properties

S. GRANADOS-FOCIL,* J.R. CONWAY, Y. MENG and L.J. SMITH

Gustaf Carlson School of Chemistry and Biochemistry, Clark University, Worcester, MA

Freestanding, ion conducting, membranes were synthesized by incorporating triazole-containing tetracyclosiloxanes into a polyethylene glycol-tetraethyl orthosilicate (PEG-TEOS) based sol-gel matrix. These membranes show comparable or higher proton conductivities than their linear, liquid, polysiloxane analogs and fall within an order of magnitude of the target ion mobilities for use in proton exchange membrane fuel cells (PEMFC's). The absence of any unbound PEG or cyclic siloxane was confirmed by proton nuclear magnetic resonance ($^1\text{H-NMR}$), while the chemical structure and composition of the membranes was corroborated by Fourier transform infrared (FTIR) spectroscopy. Thermogravimetric analysis (TGA) indicated that the membranes are stable up to 180°C and differential scanning calorimetry (DSC) analysis showed complete suppression of PEG crystallization after incorporation of the triazole-functionalized cyclosiloxanes. An increase in the molecular weight of the PEG chains used to create the sol-gel matrix produced membranes with increased flexibility and higher proton conductivities at temperatures below 100 °C. Pulse field gradient echo (PFG) NMR studies showed an increase in the apparent diffusion coefficient of the sol-gel threaded cyclosiloxane motifs compared to the linear polysiloxanes, indicating a significant reduction on the coupling between mechanical strength and ion transport capability.

Keywords: Sol-gel membranes, anhydrous proton conduction, PEMFC, fuel cells, triazole functionalized polymers

1 Introduction

The need for environmentally friendly power sources for stationary, portable and transportation applications has motivated the development of a number of promising alternatives (1–4). Among these, proton exchange membrane fuel cells (PEMFC's) are particularly attractive due to their relative high power density and pollutant-free operation (2, 3, 5). A key challenge facing the use of PEMFC's is the need for durable proton exchange membranes whose proton transport ability does not decrease drastically above the boiling point of water (5–8). High temperature operation improves the overall efficiency of the system and could potentially reduce the cell cost by decreasing the required catalyst loading and simplifying the heat management of the device (9).

Several studies derived from the seminal work of Kreuer and coworkers (10, 11), have explored the use of hydrogen-bonded chains of imidazole and benzimidazole as an alter-

native to water mediated proton transport (12–18). Subsequent reports have studied the effect of polymer backbone mobility and heterocycle nature on the proton transport ability (19–21). These results showed that the heterocycle mediated proton transport efficiency depended mainly on the glass transition temperature of the polymer matrix and the mass fraction of charge carriers. Although some previously reported materials constitute encouraging steps towards water free proton conduction, preparation of mechanically robust, highly conductive, membranes remains a challenge. An attractive alternative consists on minimizing the membrane's coupling between proton conduction and mechanical strength by trapping cyclic oligomeric proton conducting motifs within a lightly crosslinked polymer matrix.

Here, we report the synthesis of a series of polyethylene glycol-tetraethyl orthosilicate (PEG-TEOS) sol-gel matrices containing varying amounts of triazole functionalized cyclosiloxane as the conducting motifs and different PEG lengths between crosslinks. The resulting crosslinked membranes showed proton conductivities higher or comparable to those observed for the liquid, linear, polysiloxane analogs. An increase in the molecular weight of the PEG chains used to create the sol-gel matrix produced membranes with enhanced flexibility and higher proton

*Address correspondence to: S. Granados-Focil, Gustaf Carlson School of Chemistry and Biochemistry, Clark University, 950 Main Street, Worcester, MA, 01610. E-mail: sgranados-focil@clarku.edu

conductivities at temperatures below 100°C. Increases in the relative amount of cyclic siloxane to PEG resulted in higher proton conductivities and reached a maximum value at a cyclosiloxane to PEG ratio of 24 to 1. This is a significant improvement from previous reports attempting to produce proton conducting membranes by condensation of heterocycle containing triethoxysilanes and TEOS (22, 23). FTIR spectroscopy confirmed the incorporation of the tetracyclosiloxane units into the sol-gel matrix. TGA analysis revealed that the membranes are stable up to 180°C and DSC measurements showed that incorporation of the triazole cyclosiloxane motifs completely suppressed crystallization of the PEG chains. PFG-NMR studies showed an increase in the apparent diffusion coefficient of the sol-gel trapped cyclosiloxane motifs compared to the linear polysiloxanes, suggesting a significant reduction on the coupling between mechanical strength and ion transport capability.

2 Experimental

2.1 Materials

Azidomethyl pivalate was prepared as reported in the literature (24). All other reagents were purchased from Sigma-Aldrich and used as received.

2.2 Characterization

¹H-NMR (200 MHz) and ¹³C-NMR (50 MHz) spectra were obtained on a Varian Mercury NMR Spectrometer. FTIR spectra were recorded in the ATR mode using a Perkin-Elmer Spectrum 100, spectrometer. Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA Q500 thermogravimetric analyzer with a heating rate of 10°C/min from room temperature to 600°C under nitrogen purge. DSC analysis was performed on a Perkin Elmer DSC 7 analyzer under N₂ atmosphere at a heating rate of 10°C/min. Gel permeation chromatography (GPC) measurements were done using a PE LC 200 pump coupled to a Varian 356-LC refractive index detector and 2 PolarGel-M columns from Polymer Laboratories. All GPC measurements were performed at 50°C using 0.01M LiBr in DMF as the eluent. Electrochemical impedance data was obtained using a Solartron 1287 potentiostat/1260 frequency response analyzer in the 0.1 Hz–1 MHz range. The measurements were performed under vacuum to ensure an anhydrous environment. PFG NMR solid state experiments were run on a Varian Inova 400 MHz wide bore NMR spectrometer with an 8 mm probe from Doty Scientific. The apparent diffusion constant of the penetrant (D_{app}) was measured with the stimulated echo pulse sequence shown in Figure 1, by observing the signal of the peak of interest. The duration, δ , of the gradient pulse is 2 ms, and the recycle time is 5 times of T_1 . The time Δ over

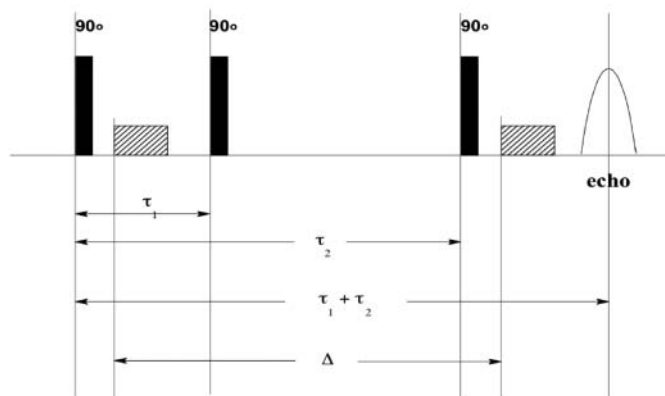


Fig. 1. Pulse-field-gradient (PFG) stimulated echo sequence. The time over which diffusion occurs is denoted as Δ . Shaded boxes are gradient pulses.

which diffusion occurs in this experiment was varied from 20 ms to 1 s. At each value of Δ , the apparent diffusion constant is determined from the initial decay of the echo amplitude as a function of the square of the gradient field strength. Accounting for the finite length of the gradient pulse, the attenuation of the echo is given by Equation 1 below, where γ is the gyromagnetic ratio, g is the gradient strength.

$$E_g = \exp(-\gamma^2 g^2 D_{app} \delta^2 (\Delta - \delta/3)) \quad (1)$$

2.3 Synthesis

The overall synthetic scheme for the linear and cyclic triazole containing siloxanes is illustrated in Scheme 1 below.

2.3.1. Synthesis of 3-allyloxy-prop-1-yne (1)

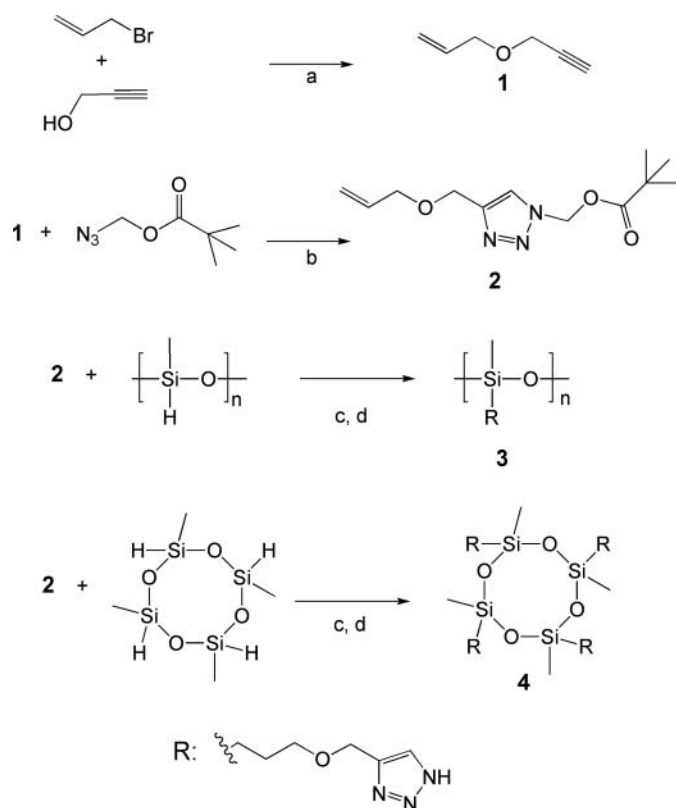
Compound 1 was obtained according to a previously reported procedure (25) and used without further purification.

2.3.2. Synthesis of 4-(allyloxy-methyl)-[1,2,3]triazol-1-ylmethyl pivalate(2)

Compound 2 was obtained and purified according to a previously reported procedure (25).

2.3.3. Synthesis of Tz5Si (3) and cTz5Si (4)

The hydrosilylation and POM cleavage reactions were carried out according to previously reported procedures (21) to yield approximately 75% of Triazole-5-Siloxane, Tz5Si, **3** and cyclotetrazole-5-siloxane, cTz5Si **4**. Solvent was removed under reduced pressure to yield an opaque viscous oil for both compounds, **3** and **4** (yield ~ 80%). Both compounds showed the same signals in their NMR spectra. ¹H-NMR (DMSO-d₆) δ 0.042 (3H, s), 0.48 (2H, m), 1.70 (2H, quin), 3.69 (4H, bs), 7.84 (1H, s), 14.3 (1H, s), ¹³C-NMR (DMSO-d₆) δ -0.81, 12.45, 24.30, 69.58, 71.54, 131.58, 146.28.



Sch. 1. Synthesis of Tz5Si and cTz5Si. **a)** NaH/DMF, RT, 2 h; **b)** CuSO₄, Sodium ascorbate, tBuOH/H₂O (2:1); **c)** Toluene, Pt (0), 80°C, 24 h; **d)** NaOH/MeOH (0.1M), 8 h R.T.

2.3.4. Sol-gel Membrane Synthesis

Varying amounts of PEG, TEOS and cTz5Si were dissolved in a 60:40 v:v mixture of THF:1M aq. HCl and stirred at 50°C overnight, followed by 2 h of heating at 80°C. The resulting viscous solution was spread over glass slides and annealed at 80°C for 3 h, then heated under vacuum at 50°C for 3 h and finally at 140°C for 8 h to complete the condensation. The resulting freestanding films were peeled off the glass slides and soaked repeatedly (typically 2–3 times) in THF for 12 h to remove any unbound cTz5Si and unreacted PEG. Removal of unbound starting material was confirmed by ¹H-NMR. Incorporation of the triazole motifs into the PEG-TEOS matrix was corroborated by FTIR.

3 Results and Discussion

3.1 Sol-gel Membrane Synthesis

Optimization of the sol-gel composition was carried out by first preparing a series of membranes with increasing amount of PEG relative to TEOS, the best results were obtained using a ratio of 1 mole of PEG per mole of TEOS.

Table 1. Sol-gel membrane compositions determined from FTIR analysis

Sample	PEG (MW)	Theoretical PEG:cTz5Si ratio ^a	Experimental PEG:cTz5Si ratio ^a	Incorporation efficiency (%)
1	1000	1:4	1:3.5	87
2	1000	2:8	1:3.7	92
3	1000	1:8	1:6.5	81
4	1000	1:12	1:10	83
5	1400	1:12	1:9	75
6	3400	1:12	1:7.8	65
7	3400	1:16	1:13	69
8	3400	1:24	1:17	71

^aAll compositions are normalized to the number of added TEOS moles.

Incorporation of the triazole cyclosiloxanes into the sol-gel mixture resulted in an improvement of the mechanical strength and toughness of the membranes compared to the matrices prepared from only PEG and TEOS.

The FTIR analysis showed that the cTz5Si incorporation efficiency varied between 90% and 60% depending primarily on the molecular weight of the PEG chains. The membranes' composition was determined by measuring the relative absorption intensities of the Si-O (1020 cm⁻¹) and CH₂-O- (1100 cm⁻¹) stretching bands in the FTIR spectra (26). These relative intensities were interpolated into a calibration curve constructed by measuring the relative absorbances from standard cTz5Si/PEG blends of known composition. The results from this analysis are summarized in Table 1 below.

The composition analysis showed that the cTz5Si incorporation efficiency decreases as the molecular weight of the PEG chains increases. This is attributed to a decrease in the concentration of PEG chain ends participating in the crosslinking reactions as the polyether chain length increases. Incomplete crosslinking results in open ends within the sol-gel network unable to efficiently trap the cTz5Si.

After the membrane curing and solvent rinsing processes, the recovered unreacted species were analyzed by FTIR and NMR spectroscopy. The spectra of the recovered species were consistent with the spectra for the starting materials. GPC analysis on these samples revealed no change in the molecular weight of the recovered triazole containing cyclosiloxane, cTz5Si, after the crosslinking and curing processes.

3.2 Thermal Analysis

Thermogravimetric analysis of the samples revealed no weight loss up to 180°C and long-term stability (weight loss <0.002% wt/h) at 140°C. Differential scanning calorimetry of all cTz5Si containing samples showed no melting transition for the PEG chains and one glass transition in the range of -25°C to -20°C. In contrast, a control

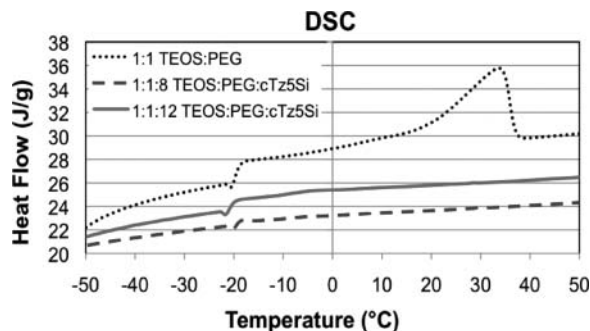


Fig. 2. DSC of the sol-gel membranes with and without incorporated cTz5Si.

sol-gel sample with no added cTz5Si showed a glass transition at -20°C and a melting transition centered at 36°C (Fig. 2). The absence of crystalline PEG domains within the cyclosiloxane containing sol-gel membrane, suggests that incorporation of cTz5Si into the matrix interferes with PEG crystallization. However, the relatively constant glass transition temperature observed for the membranes, regardless of the incorporated amount of cTz5Si, suggests a more complex interaction than simple plasticization of PEG by the cyclosiloxane.

3.3 Effect of Membrane Composition on Proton Conductivity

The proton conductivity, (Fig. 3), increased as the amount of added cTz5Si increased, reaching a maximum at 10 moles of cyclosiloxane per 1 chain of PEG and 1 mole of TEOS. Further increases in the amount of cTz5Si produced less conductive membranes, due to the observed decrease in condensation efficiency as suggested by the larger amounts

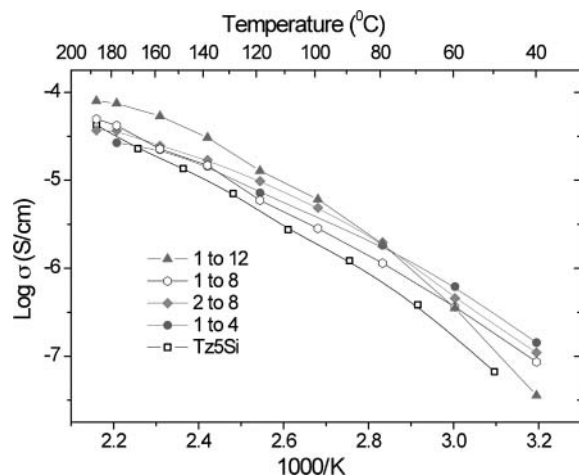


Fig. 3. Proton conductivity of the sol-gel membranes as a function of composition, linear polysiloxane, Tz5Si, included for comparison. Compositions correspond to the theoretical values (Table 1).

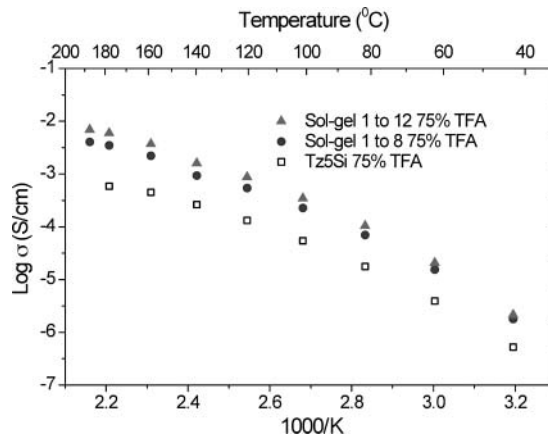


Fig. 4. Proton conductivity of TFA doped sol-gel membranes and the linear polysiloxane, Tz5Si, included for comparison. Compositions correspond to the theoretical values (Table 1).

of unbound PEG found by $^1\text{H-NMR}$. Increases in the amount of PEG beyond two chains per TEOS molecule produced tacky membranes without further increases in proton conductivity.

Doping of the sol-gel membranes with up to 75% mol of trifluoroacetic acid produced further increases in the proton conductivity of roughly 2 orders of magnitude, these increases are ascribed to the larger charge carrier density resulting from the protonation of the heterocyclic nitrogens in the triazole rings (Fig. 4). The thermal properties of the doped membranes remained virtually unchanged when compared to their undoped counterparts, both glass transition and onset of degradation temperatures were the same before and after the doping process.

3.4 Effect of PEG Molecular Weight on Proton Conduction

An increase in the molecular weight of the PEG chains, while attempting to keep molar composition constant (entries 4–6 in Table 1), produced increasingly flexible membranes. Their conductivity temperature dependence was similar to the one observed when increasing the length of the linker between the polymer backbone and the heterocycle that was observed for the linear analogs (19). The membranes with longer PEG chains between crosslinks showed higher conductivity at temperatures below 100°C , while the membranes with shorter PEG chains between crosslinks showed a higher conductivity at temperatures above 120°C (Fig. 5). This was attributed to the lower charge carrier crosslink density and higher flexibility of the membranes with longer PEG chains.

3.5 Effect of PEG to cTz5Si Ratio on Membrane Properties

Since the use of longer PEG chains produced more flexible membranes with better transport ability at temperatures

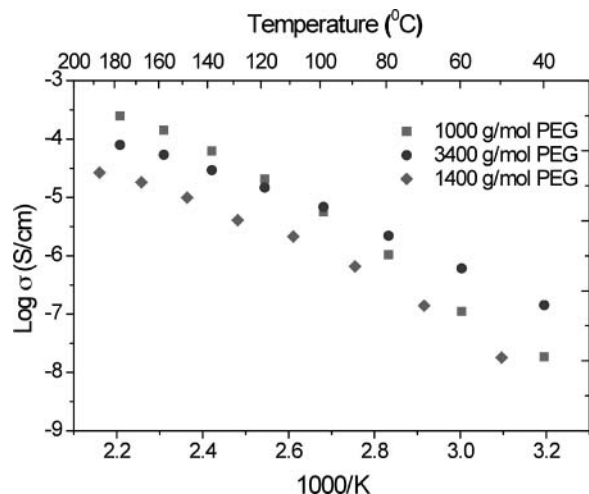


Fig. 5. Proton conductivity of the sol-gel membranes with different crosslink densities as a function of temperature. Compositions correspond to the theoretical values (Table 1).

below 100°C, the number of cTz5Si molecules per PEG chain was systematically increased beyond the 1:12 ratio in order to find the optimal composition for the sol-gel matrices with longer PEG chains. Increases in the amount of incorporated cyclosiloxane, while keeping the PEG molecular weight constant, produced a five-fold increase in the resulting proton conductivity up to a PEG to cTz5Si ratio of 1:17 (Fig. 6). All these membranes showed higher proton conductivity than the linear polysiloxane analog, suggesting that the presence of the polar PEG matrix promotes proton transport. A more detailed study focused on quantifying the free ion concentration, as a function polymer matrix dielectric constant, is currently under way to better explain these observations.

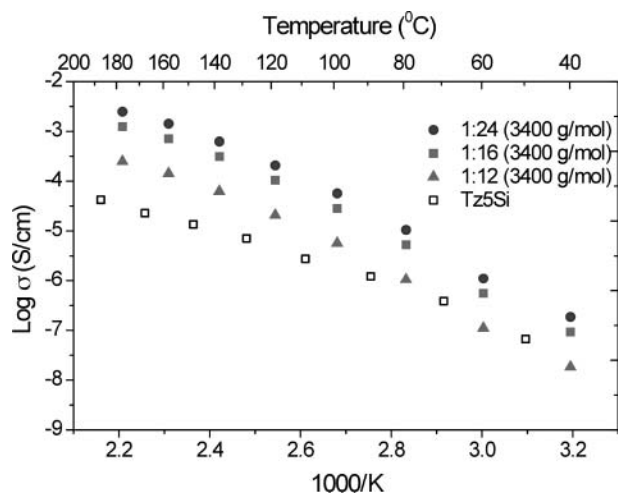


Fig. 6. Proton conductivity of the sol-gel membranes with different crosslink densities as a function of temperature.

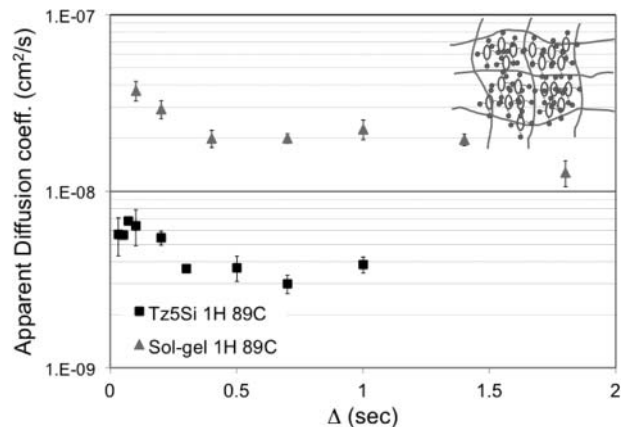


Fig. 7. Proton apparent diffusion coefficients from PFGE-NMR experiments at 89°C as a function of diffusion time (time lapse between gradients) for the sol-gel membranes and the linear polysiloxane, Tz5Si.

3.6 PFGE-NMR Studies

In order to confirm whether the ion transport has been decoupled from the polymer matrix mobility, we conducted a series of solid-state NMR experiments to measure individual apparent diffusion coefficients, for several groups within the sol-gel membranes (27). Apparent diffusion coefficients obtained from PFGE-NMR for the cyclosiloxanes (CH₃ attached to the Si, $\delta = 0.5$ ppm) are several orders of magnitude higher than those found for the PEG chains in the sol-gel matrix (CH₂ attached to the O in PEG, $\delta = 3.5$ ppm). This is consistent with a structure where the triazole containing tetracyclosiloxanes are not covalently attached to the crosslinked matrix but are trapped within it. Proton diffusion for the methyl group attached to the silicon atoms was measured for the freestanding, sol-gel incorporated, cyclic tetramers and the linear polysiloxane analogs. The diffusion coefficient for the sol-gel trapped cycles was 5–10 times faster than the one observed for the liquid, linear, polysiloxanes (Fig. 7). The differences in apparent diffusion coefficients are consistent with the differences in proton conductivity measured by impedance spectroscopy and suggest that the absence of covalent bonding between the PEG-TEOS matrix and the proton transporting triazole motifs significantly decouples polymer matrix mobility from proton transport ability.

There are several questions still unanswered about the detailed solid-state structure of these membranes and further insight is expected from ongoing dynamic mechanical analysis and dielectric spectroscopy studies.

4 Conclusions

Incorporation of triazole containing cyclic siloxanes into a PEG-TEOS sol-gel matrix produced water-free, proton

conductive and mechanically stable membranes. In spite of their lower charge carrier density, the crosslinked membranes showed proton conductivities higher or comparable to those observed for the liquid, polysiloxane analog and improved mechanical strength compared to the linear polysiloxanes. The proposed target structure where the triazole bearing cyclotetrasiloxanes are not covalently bonded to the polymer matrix, thus reducing the coupling between ion transport and mechanical strength, is supported by PFGE-NMR measurements. These results suggest that non-covalent incorporation of small proton conducting molecules into an inert sol-gel matrix may provide a new pathway for mechanically robust, water free, proton conductive membranes. Extensions on this approach to other ion transporting systems such as lithium transporting membranes for rechargeable batteries and iodide transporting membranes for dye sensitized solar cells are currently being explored.

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