Final Report

Novel Proton-Conducting Membranes for PEM Fuel Cells

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This project focused on research and development of novel polymer electrolyte membrane (PEM) for PEM fuel cells to be operated in a wide temperature range without the need for humidification. We started with investigations into the synthesis of novel materials containing protogenic groups/species (such as triazoles) and polymers grafted with protogeneic groups and derivatives; we then studied the processing and fabrication of polymer electrolyte membranes (PEM) based on these polymers and membrane-electrode assemblies (MEA); further, we evaluated the performances of fuel cells based on these materials. In the last year, we developed the new concept of reinforced high-temperature (HT) PEMs and new processes for fabrication of high-temperature electrodes and MEAs. In particular, the performances of the fuel cells based on the novel materials and processes are very impressive, representing the best ever achieved at 120°C without humidification. The research efforts have resulted in 16 publications (published or in preparation) and 18 patent applications and/or invention disclosures. The major scientific/technical accomplishments are briefly summarized as follows.


Part I-A. Hydrothermal stability and proton conductivity of Zr-H₃PO₄-gel containing hybrid inorganic-organic copolymer membranes.

Zr-containing hybrid inorganic-organic polymer membranes with compositions of 2MDSPPO-1 BTMSEB-2Zr, 2MDSPPO-2 BTMSEB-3Zr, and 2MDSPPO-1 BTESo-2Zr were tested. The membranes were immersed in H₃PO₄ for 20 – 48 hours, dried at 60°C for 2 days, and then boiled in large amount of water (0.5 g sample in 50 ml H₂O) at 100°C for 2 hours. The lost Zr, determined by ICP spectroscopy, is no more than 0.02 % of total Zr in the membranes. Solid state ³¹P NMR spectra of the boiled samples suggested that Zr-OPO₄H₂ clusters are very stable, only the free H₃PO₄ in the membranes was removed during the boiling process. These results confirmed that Zr-OPO₄H₂ clusters are stable in the hybrid inorganic-organic polymer network in fuel cell environments.

The boiled samples have high proton conductivity in high relative humidity (>10⁻³ S/cm above 50°C). H₂O⁺ ions transport proton between the adjacent Zr-OPO₄H₂ clusters.

Part I-B. Electrochemical stability and proton transport mechanism study of 1H-1,2,3-triazole, and 1H-1,2,4-triazole.

Heterocyclic compounds as shown in Scheme 1 were studied as proton conducting
groups to replace water. We found that 1H-1,2,3-triazole and 1H-1,2,4-triazole not only promote the proton transport effectively, but also have much higher electrochemical stability, compared with imidazole-based systems which have been extensively studied.

The ionic conductivity of pure 1H-1,2,3-triazole liquid is about $1.3 \times 10^{-4}$ S/cm at room temperature. As shown in Fig. 1 (a), with small amounts of acid dissolved in 1H-1,2,3-triazole, the conductivity increases dramatically. $^1$H-PFG-NMR studies of 1H-1,2,3-triazole/PSU polymer membranes showed that the self-diffusion coefficient of 1H-1,2,3-triazole as determined from $^1$H-PFG-NMR spectroscopy is about one fifth of the diffusion coefficient calculated from conductivity data of the membrane, suggesting that proton transfer between the triazole rings makes the major contribution to the observed ionic conduction. This is very important to designing 1H-1,2,3-triazole based PEMs with high proton conductivity.

In shown Figure 1 (b), the cyclic voltammetric studies indicated that 1H-1,2,3-triazole are electrochemically stable and suitable for fuel cell applications, compared with imidazole which is easily oxidized and absorbed onto the surface of Pt electrodes.

![Scheme 1. Molecule structure of heterocycles](image)

**FIGURE 1.** (a) The conductivity ratio of the acid-triazole mixture to the pure 1H-1,2,3-triazole ($\sigma_{\text{triazole}+\text{acid}}/\sigma_{\text{triazole}}$) against the concentration ratio of acid to the triazole ($C_{\text{acid}}/C_{\text{triazole}} \times 100$). (b) CV curves of 1H-1,2,3-triazole and Imidazole in N$_2$ and O$_2$.

**Part I-C.** Synthesis of polymers or copolymers with grafted triazole.
4-vinyl-1H-1,2,3-triazole has been successfully synthesized and polymerized to form...
polymers with triazole groups attached. Shown in Figure 2 are the conductivities of poly(4-vinyl-1H-1,2,3-triazole) in dry air. They are about $10^5$ times higher than those of poly(4-vinylimidazole) in the temperature range studied, suggesting that triazole groups can promote long-range proton motion in the polymer system far better than the imidazole groups. The proton conducting mechanism studies showed that, in the triazole-based polymers, the proton may be transported directly through the nitrogen bridges involving both of the N2 and N3 on the triazole ring, which is quite different from the imidazole system.

Several new vinyl-containing monomers with grafted triazole (1H-1,2,3- and 1H-1,2,4-) through a long soft chain have been synthesized successfully. Polymerization of these precursors is in progress. The long soft organic chain can ensure high local mobility of triazole rings for proton transport between adjacent triazole rings. Hopefully these polymers will have high proton conductivity.

![Figure 2](image)

(a) Ionic conductivities of poly(4-vinyl-1H-1,2,3-triazole) (—) and poly(4-vinylimidazole) (—), and (b) the mechanism of proton transport among 1H-1,2,3-triazole.

**Part I-D.** Hybrid inorganic-organic polymer membranes with grafted heterocycle with low Pkα values.

The heterocycles, including 1H-1,2,3-triazole (3Tri), 1H-1,2,4-triazole (4Tri), pyrimidine (Py), and 2-fluoropyrazine (FP), were grafted onto alkyltriolsilanes through organic chains. Two series of hybrid inorganic-organic polymer membranes with grafted heterocycles were synthesized and characterized:

**I-D-1.** $\text{H}_3\text{PO}_4$ doped hybrid polymers with grafted heterocycles, $x$ MDSPPO - $y$ TEOS - $z$ SiHc ($\text{Hc} = 4\text{Tri}, 3\text{Tri}, \text{or BI}$) - $n$ P,

Where $x$, $y$, and $z$ refer to the moles of Si in MDSPPO, TEOS, and SiHc ($\text{Hc} = 4\text{Tri}, 3\text{Tri}, \text{or BI}$), respectively, and $n$ is the moles of $\text{H}_3\text{PO}_4$. In this study, $x=2$, $y=0$ to 3, $z=1$ to 4, and $n=0$ – 5.

In these membranes, 1H-1,2,4-triazole and 1H-1,2,3-triazole can improve the proton conductivity of the membranes. This is the first time to realize the proton conductivity enhancement by addition of heterocycles to $\text{H}_3\text{PO}_4$ systems. As shown in Figure 3, The proton conductivity of the membranes with grafted
1H-1,2,4-triazole and 1H-1,2,3-triazole is higher than that of the membranes without grafted heterocycles, and much higher than that of the membranes with grafted benzimidazole (BI). The proton conductivity of 2M-2T-2Si4Tri-5P is \(4.3 \times 10^{-3}\) S/cm in anhydrous state at 140°C. These phenomena can be explained with the protonation process of heterocycles with the following equation:

\[
H_c + H_2PO_4 \rightleftharpoons H_cH^+ + H_2PO_4^-
\]

The equilibrium constant \(K\) can be calculated as

\[
\log K = \log K_{\text{acid}} - \log K_{HcH^+} = -PK_{\text{Acid}} + PK_{HcH^+}
\]

For \(H_2PO_4\)-benzimidazole system, \(\log K = -2.6 + 5.9 = 3.3\), which means that benzimidazole rings trapped protons, and transport from imidazole to \(H_2PO_4^-\) is difficult since it involves breaking hydrogen bonds. However, for triazole-\(H_2PO_4\), the equilibrium constant \(K\) is close to 1 for 1H-1,2,4-triazole (\(\log K = -2.6 + 2.6 = 0\)). The proton transport through the forming and breaking of hydrogen bonds between triazole rings and \(H_2PO_4\) molecules is much easier.

**FIGURE 3.** Proton conductivity of the membranes with compositions of 2 M-2 T-2 SiHc-5P (Hc = 3 Tri, 4Tri and BI) in anhydrous state compared with 2M-3T-5P.

**I-D-2.** \(-SO_3H\)-grafted hybrid polymers with grafted heterocycles

\[x \text{MDSPPO} - y \text{BTESO} - z \text{S} - m \text{SiHc} - n \text{Pr},\]

Where \(x, y, z,\) and \(n\) refer to the moles of Si in MDSPPO, BTESO, S, SiHc, and Pr, respectively. \(x=2, y=2, z=0\) to 3, \(m=1\) to 4, and \(n=0 - 2\). Hc=3Tri, 4Tri, Py, FP, and BI. S: trihydroxyisopropyl sulfonic acid.

Among these membranes with grafted \(-SO_3H\) groups and heterocycles, the membranes with grafted 1H-1,2,3-triazole and \(-SO_3H\) groups have the highest proton conductivity. This may be explained with the similar mechanism with that in heterocycle-\(H_2PO_4\) systems.

All the membranes with compositions of \(x \text{MDSPPO} - y \text{BTESO} - z \text{S} - m \text{SiHc} - n \text{Pr}\) have high proton conductivity in humidified environments. It is in the order of \(10^{-2}\) S/cm in RH \(-20\%\).
I-D-3. Other properties of the hybrid polymer membranes with grafted heterocycles.

All these membranes with MDSPPO are flexible with good mechanical strength. The thermal stability increased with increasing contents of heterocycles. The membranes with compositions of 2M-xT-ySi4Tri-5P (x=1,2, and 3; y = 4-x) are stable up to 250°C.

Part I-E. Interconnected heterocycles and the mixtures with acid-containing compounds and polymers.

1H-1,2,3-triazole and 1H-1,2,4-triazole were stabilized by interconnecting two triazole rings with an organic chain. Four organic chains were applied successfully: (1) \(-\text{C}_4\text{H}_8\); (2) \(-\text{C}_8\text{H}_{16}\); (3) \(-\text{CH}_2\text{-Ar-CH}_2\); and (4) \(-\text{C}_2\text{H}_4\text{O-}-\text{C}_2\text{H}_4\text{H}_2\text{H}_2\).

The immobilized triazole compounds have higher melting points and higher boiling points. For example, two 1H-1,2,4-triazole connected on the ends of \(-\text{C}_4\text{H}_8\) chain has a melting point of 149°C and boiling point 560°C. They are ideal for application as electrolytes for fuel cells operated above 120°C. Meanwhile, they are water-insoluble.

The immobilized triazole compounds have high proton conductivity. By doping small amount of acids, the proton conductivity increased sharply. They were doped into Nafion membranes. The proton conductivity increased with increasing triazole contents, reaching \(10^{-4}\) S/cm in anhydrous state above 120°C. It is expected to find some suitable \(-\text{SO}_3\text{H}-\) containing polymers to dope such immobilized triazole compounds to realize high proton conductivity.

Part I-F. Synthesis and properties of \(-\text{CF}_2\text{-PO}_3\text{H}_2\) groups containing Membranes (attached on alkoxysilane).

The fluorinated group of \(-\text{CF}_2\text{-PO}_3\text{H}_2\) was attached onto alkoxysilane successfully through an organic chain. The hybrid inorganic-organic polymer membranes with grafted \(-\text{CF}_2\text{-PO}_3\text{H}_2\) groups have higher proton conductivity than those without \(-\text{CF}_2\) groups in both anhydrous state and in humidified environments. Meanwhile, the membranes with grafted \(-\text{CF}_2\text{-PO}_3\text{H}_2\) groups derived from the following precursor are hydrothermal stable in water and acid aqueous solution.

\[
\begin{array}{c}
\text{OC}_2\text{H}_8 \\
\text{OC}_2\text{H}_8 \\
\text{Si} \\
\text{OC}_2\text{H}_8 \\
\text{O} \\
\text{F} \\
\text{F} \\
\text{OC}_2\text{H}_8 \\
\end{array}
\]

DMFP

Part II-A. Development of new types of polymeric materials based on 1H-1,2,3-triazole and 1H-1,2,4-triazole and their derivatives.

II-A-1 Proton conductivity of poly(4-vinyl-1H-1,2,3-triazole) with different molecular weight.

Poly(4-vinyl-1H-1,2,3-triazole) with $M_w \approx 4.5 \times 10^4$, $M_w / M_n = 2.06$ was successfully synthesized (see Scheme 1). Shown in Figure 1 are the conductivities of samples with higher and lower molecular mass and those of poly(4-vinylimidazole). It is clear that the molecular mass has considerable effects on the conductivity of the poly(4-vinyl-1H-1,2,3-triazole), especially at higher temperatures. This result also suggests that the conductivity of the polymer can be further improved by modifying the backbone and side-chain to improve the local mobility of 1H-1,2,3-triazole group.

II-A-2 Hybrid inorganic–organic polymers with grafted 1H-1,2,3-triazole

1H-1,2,3-triazole was grafted on hybrid inorganic–organic polymer backbones through an organic chain (see Scheme 2). Linear polymer derived from Precursor I is viscous liquid, and its conductivity
reaches $1.6 \times 10^{-3}$ S/cm at 120°C in anhydrous state. To improve the mechanic properties and proton conductivity, tetraethoxysilane was introduced into Polymer I as a cross-linker, and small amount of $\text{--SO}_3\text{H}$ (grafted onto the backbone through an organic chain) was used as an extra proton source. The results were summarized in Table 1. From the table, we can see that the local mobility of triazole groups and the ratio of triazole in the membrane are the key factors responsible for the proton conductivity of the membranes. Polymer II derived from Precursors I and II have both high proton conductivity and good mechanical properties owing to the fact that Precursor II can work as a cross-linker, and does not decrease the content of triazole in the polymers. We are keeping working on this system to further improve the proton conductivity.

Table 1. Properties of new polymers with grafted 1,2,3-triazole

<table>
<thead>
<tr>
<th></th>
<th>Triazole content (w/w %)</th>
<th>Conductivity at 120°C, dry argon</th>
<th>Mechanic strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(4-vinyl triazole)</td>
<td>~70%</td>
<td>$[10^{-3}, 10^{-2}]$</td>
<td>brittle</td>
</tr>
<tr>
<td>Pure polymer I</td>
<td>~40%</td>
<td>$[10^{-2}, 10^{-3}]$</td>
<td>Very soft</td>
</tr>
<tr>
<td>Polymer I with crosslinking reagent and acid doping</td>
<td>25%-35%</td>
<td>$[10^{-4}, 10^{-5}]$</td>
<td>Good</td>
</tr>
<tr>
<td>Polymer I with Nafion</td>
<td>~27%</td>
<td>$[10^{-3}, 10^{-4}]$</td>
<td>Good</td>
</tr>
<tr>
<td>Polymer II (Precursor I/II 3/2)</td>
<td>~40 %</td>
<td>$2.8 \times 10^{-4}$</td>
<td>Good</td>
</tr>
</tbody>
</table>

II-A-3 Hybrid inorganic-organic polymers with grafted 1H-1,2,4-triazole

1H-1,2,4-triazole - grafted hybrid inorganic-organic polymers were synthesized (see Scheme 3). Similar to that with grafted 1,2,3-triazole, the linear polymer with 1,2,4-triazole is a viscous solid, and the proton conductivity is very high, reaching $2 \times 10^{-3}$ S/cm at 120°C. To get membranes with good mechanical strength, cross-linkers were added to the linear polymer. The compositions of the samples were listed in Table
2, and the proton conductivities of these samples in anhydrous state were presented in Figure 2. The samples with cross-linkers have lower proton conductivity because of the lower local mobility of triazole rings. Small amount of grafted $-\text{SO}_3\text{H}$ groups enhanced the proton conductivity. Further effort has to be made to improve the proton conductivity.

![Chemical structures and Scheme 3 Polymers with grafted 1H-1,2,4-triazole and cross-linkers.](image)

**Table 2 Compositions of Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>C-Si-4Tri</th>
<th>O-S-4Tri</th>
<th>TEOS</th>
<th>O-Si-SO$_3$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample I</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sample II</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Sample III</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Sample IV</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Sample V</td>
<td>2</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Part II-B. Stability and microstructure studies on Zr-based membranes

Zr-based membranes were found to have high chemical stability (Fenton test, 3 days), and their proton conductivity keep stable even in high relative humidity (at 100°C, RH 100%, 12 hours). TEM tests proved that Zr was planted into the hybrid inorganic-organic polymer networks and no aggregation or crystallization of Zr-O was observed (see Figure 3). In addition, new process was developed to fabricate high quality membranes with a thickness of less than 100 microns.
**Figure 3** (A) TEM bright field image of Zr-membrane and (B) EDAX spectrum on the area of image (A).

**Part II-C. Compounds and polymers with –SO2- grafted imidazole**

Synthesis of Fluorinated-imidazole containing compounds and polymers was tried, but failed. However, we found that –SO2- group is effective to reduce the electron density of imidazole rings and improve its electrochemical stability (see Figure 4). The synthesis of –SO2- group containing compounds and polymers is very easy (see Scheme 4). The mixtures of 2-ethylsulfonyl imidazole and benzenesulfonic acid have high proton conductivity from 100°C to 180°C (see Figure 5). They are promising electrolyte materials for fuel cells and other electrochemical devices.

![Scheme 4](image)

**Scheme 4** –SO2- group attached compound and polymer.

**FIGURE 4** Typical cyclic voltammograms (CV) of 2-ethylsulfonyl-Imidazole (A) and imidazole (B) with baselines, C= 5×10^{-3} mol·dm^{-3} in 0.1 mol·dm^{-3} TEAP-CH3CN solution.
Part II-D. Synthesis of alkoxyisilyl-ended precursors with long organic chains

To replace PPO chain with pure Carbon chain to improve the thermal stability of the membranes in high temperature range, new precursor (see Scheme 5) was synthesized. We are preparing hybrid inorganic-organic polymers with it.

\[
\begin{align*}
H_2C- & (CH_2)_{12} \quad \text{(2)} \\
\text{H}_3C-SiH & \quad \text{H}_2PtCl_6 \\
\text{OC}_2H_5 & \quad \text{OC}_2H_5 \\
\text{OC}_2H_5 & \quad \text{OC}_2H_5 \\
\text{OC}_2H_5 & \quad \text{OC}_2H_5 \\
\end{align*}
\]

Scheme 5 New precursor for hybrid polymers.

Part II-E. MEA preparation and fuel cell tests

The process to prepare gas diffusion electrodes and MEA based on hybrid inorganic-organic polymers has been developed. Initial fuel cell tests on the obtained MEA showed that the process is simple, effective and reliable. For example, the fuel cell with membrane 2M-2Be-3 Zr (immersed in 8 M H_3PO_4 for 6 hours) output a large current at 105°C in low relative humidity (see Figure 6).
Figure 6. V-I curve of fuel cell at 105°C with H₂/O₂ bubbled with water vapor at RT. Electrolyte membrane 2M-2Be-3 Zr (immersed in 8 M H₃PO₄ for 6 hours).
III. Accomplishments in the 3rd year (1/6/2006 – 1/5/2007)

Part III-A. Development of polymers and copolymers with heterocycles and phosphonic acids grafted.

III-A-1 Synthesis and studies of polyethylene based copolymers

In last annual report, we reported the synthesis and proton conductivity of poly(4-vinyl-1H-1,2,3-triazole). To further improve the proton conductivity, we synthesized the poly(4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid) with different molar ratio of triazole to phosphonic acids (Table 1). The thermal properties of these copolymers were measured by TGA and shown in Figure 1. The conductivities of copolymers in dry air condition were described in Figure 2.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Triazole : acid for monomers</th>
<th>Triazole : acid in copolymer</th>
<th>Mw (PS-DMF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4 : 1</td>
<td>1 : 0.69</td>
<td>3.9 x 10^5</td>
</tr>
<tr>
<td>B</td>
<td>1 : 1</td>
<td>1 : 1.34</td>
<td>3.1 x 10^5</td>
</tr>
<tr>
<td>C</td>
<td>2 : 3</td>
<td>1 : 1.94</td>
<td>2.8 x 10^5</td>
</tr>
<tr>
<td>D</td>
<td>1 : 4</td>
<td>1 : 2.52</td>
<td>3.8 x 10^5</td>
</tr>
</tbody>
</table>

Table 1 poly(4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid)

Figure 1 TGA of poly(4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid)
Figure 2: Temperature dependence of conductivities of poly(4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid)

The copolymers showed thermal stability up to 200°C. At 120°C, dry condition, the conductivities of the copolymers are still in the range of $10^{-5}$ to $10^{-6}$ s/cm. The local mobility of proton conducting groups including triazole and phosphonic acid is limited by the polymer backbones, which may result in the low conductivity of these copolymers.

During the experiments, we also synthesized two other copolymers (I) and (II). As shown in Figure 3, without any acidic protons on the heterocycles, these copolymers also show similar proton conductivities as that of copolymers grafted with 1H-1,2,3-triazole. These results show the complexity and also potential to design a fully polymerized PEM based on heterocycles and phosphonic acids.
Figure 3 Temperature dependence of conductivities of copolymers with heterocycles and phosphonic acids grafted.

**III-A-2 Synthesis and studies of polysiloxane based copolymers**

Through studies of polyethylene based copolymers, we further synthesized the polysiloxane based copolymers with triazole and phosphonic acids grafted. These copolymers are soft gel at high temperature and the conductivities of the copolymers were illustrated in Figure 4. Compared with polyethylene based copolymers, they provide high proton conductivities but low mechanical properties. The introduction of phosphonic acids could not improve the conductivities of resulted PEMs effectively at dry air condition.
III-A-3 Synthesis and studies of block copolymers

To increase the mechanical strength of polysiloxane polymers, we also synthesized the block copolymers (III) as

The conductivities of two samples were shown in Figure 5. The membranes have improved the mechanical strengths but lower proton conductivities compared with polysiloxane polymer with 1H-1,2,3-triazole grafted.
Part III-B. Development of hybrid membranes with H$_3$PO$_4$ doping

III-B-1 Fuel cell and stability tests of Zr/Si-PPO-Si based membranes.

In early this year, we reported some fuel cells tests on Zr/Si-PPO-Si hybrid membranes. The performance data of one single cell based on sample of 2M-2Oc-2.5 Zr immersed in 8M H$_3$PO$_4$ were shown in Figure 5.

Figure 4 Temperature dependence of conductivities of PEEK-1H-1,2,3-triazole attached polysiloxane block copolymers.

Figure 5 Fuel cell performance of Zr-based membrane with a composition of 2M-2Oc-2.5 Zr immersed in 8M H$_3$PO$_4$.

As reported in monthly reports (01,02), the OCV and cell performance at the beginning of the cell
tests dropped dramatically when the temperature and testing time increased. After kept at 120°C for several hours, the membranes turned to be very brittle and there existed small cracks on the membrane. During the membrane preparation process, we found that these membranes degraded after kept at 120°C for one to two days, especially when there existed considerable amount of water inside the membranes. Also, the very high content of H₃PO₄ made the Zr doped membranes brittle and mechanically weak, but low content of H₃PO₄ resulted in the low conductivity of the membranes.

III-B-2 Synthesis and studies of Si-PEO-Si, Si-PTMO-Si based hybrid membranes.

Based on the observations of Zr/Si-PPO-Si based hybrid membranes, we doubt it is the stability of Si-PPO-Si in highly acidic and humid condition that cause the failure of the resulted hybrid membranes. To improve the stability of the hybrid membranes, we synthesized Si-PEG-Si and Si-PTMO-Si, as shown in Figure 6.

a)  
\[
\begin{align*}
\text{HO-(CH₂CH₂O)ₙ-H} & \xrightarrow{\text{(1) NaH, THF}} \text{CH₂=CH-CH₂O-(CH₂CH₂O)ₙ-CH₂-CH=CH₂} \\
& \xrightarrow{\text{(2) allyl bromide}} \text{CH₃C₂H₄O₂SiH} \\
& \text{H₂PtCl₄} \\
& \text{CH₃(C₂H₄O)₂CH₂CH₂CH₂O-(CH₂CH₂O)ₙ-CH₂CH₂CH₂Si(C₂H₅O)₂CH₃} \\
& \text{(Si-PEG-Si)}
\end{align*}
\]

b)  
\[
\begin{align*}
\text{HO-(CH₃CH₂CH₂CH₂O)ₙ-H} & \xrightarrow{\text{(1) NaH, THF}} \text{CH₂=CH-CH₂O-(CH₂CH₂CH₂O)ₙ-CH₂-CH=CH₂} \\
& \xrightarrow{\text{(2) allyl bromide}} \text{CH₃C₂H₄O₂SiH} \\
& \text{H₂PtCl₄} \\
& \text{CH₃(C₂H₄O)₂CH₂CH₂CH₂O-(CH₂CH₂CH₂O)ₙ-CH₂CH₂CH₂Si(C₂H₅O)₂CH₃} \\
& \text{(Si-PTMO-Si)}
\end{align*}
\]

Figure 6 Synthesis of Si-PEG-Si and Si-PTMO-Si

From the similar sol-gel procedure, we prepared Zr/Si-PEG-Si and Zr/Si-PTMO-Si hybrid membranes. Compared with Zr/Si-PPO-Si hybrid membranes, these two types of new hybrid membranes were stiffer. However, similar thermal stability problems existed in these newly developed membranes with H₃PO₄ doping. Also, it was observed that all these siloxane precursors, when mixed with concentrated phosphoric acid solution and heated at 120°C, decomposed in several hours.

III-B-3 Synthesis and studies of Si-C₃-1,2,4-triazole polysiloxane polymers.
As described in figure 7, a new siloxane precursor Si-C3-1,2,4-triazole was synthesized in one-pot reaction simply. By heating with concentrated phosphoric acid solution at 120°C for two days, Si-C3-1,2,4-triazole has no any noticeable decomposition or degradation. Therefore it is a good candidate to replace Si-PPO-Si in hybrid membranes previously studied to absorb phosphoric acids. Initial tests showed that the suitable composites and sol-gel processes need to be studied to get as good mechanical strength as Zr/Si-PPO-Si hybrid membranes have. Another possible method is to find suitable supporting materials to make composite membranes containing siloxane precursors and phosphoric acid.

**Part III-C. Computational studies of heterocycles based PEMs.**

**III-C-1 Studies of oxidation potential of heterocycles and imidazole poisoning effect to Pt catalyst.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$IP_{\text{calc}}$ (eV)</th>
<th>$IP_{\text{expt}}$</th>
<th>$E^0_{\text{calc}}$ (V)</th>
<th>$E^0_{\text{expt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>8.68</td>
<td>8.78</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>2-methanesulfonyl-1H-imidazole</td>
<td>9.16</td>
<td></td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>1H-1,2,3-triazole</td>
<td>9.72</td>
<td>10.00</td>
<td>1.90</td>
<td>1.8</td>
</tr>
<tr>
<td>2H-1,2,3-triazole</td>
<td>9.99</td>
<td></td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td>1H-1,2,4-triazole</td>
<td>9.93</td>
<td>10.06</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>2H-1,2,4-triazole</td>
<td>9.84</td>
<td></td>
<td>2.10</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Adiabatic ionization potentials, $IP$, and standard redox potentials, $E^0$ vs. Ag/Ag, in acetonitrile of the heterocycles.

The quantum mechanic calculations were performed to study the oxidation potential of heterocycles and imidazole poisoning effect to Pt catalyst. As shown in table 2, triazoles and sulfonimidazole showed much higher electrochemical stability than imidazole. Also, a new type of imidazole poisoning mechanism to Pt catalyst was proposed as illustrated in Figure 8, which clearly explained the poison process of imidazole to the Pt surface by forming a strong N-Pt covalent bond.
III-C-2 Studies of proton conduction by MD simulations.

MD simulations have been applied to study the proton conduction of acids in water or 1H-1,2,3-triazole, as described in Figure 9. The MD simulations gave acceptable results for acid in water system. However, the results showed that for 1H-1,2,3-triazole system, the existed force fields for the simulation were not effective, especially for more complicated polymer system with triazole groups attached.

Figure 8 Oxidation and $\text{H}^+$ transport processes of imidazole on Pt(111) surface.

Figure 9 Configuration of 200 H$_2$O + 1H$_3$O$^+$ + 1CF$_2$CF$_2$SO$_3^-$.
IV. Accomplishments in the 4th year (1/6/2007 – 1/5/2008)

Part IV-A. Reinforced HT PEM

Fig. 1 Appearance images of 1,2,4-triazole grafted polysiloxane cross-linked with Si-C8 and TEOS precursor membrane (top), expanded porous PTFE film (bottom left), and reinforced HT membrane (bottom right).

To prepare the porous PTFE supported hybrid membranes, we first (1) hydrolyzed the siloxane Si-C3-1,2,4-triazole and Si-C8-Si in methanol, then (2) prepared the sol solution of Si-C3-1,2,4-triazole and Si-C8-Si with H₃PO₄, and (3) soaked the PTFE film in the sol solution, dried at room temperature overnight and then at 120°C in an oven for several hours. The resulted reinforced high temperature membrane (RHTM) was transparent, as shown in Figure 1. Compared with 1,2,4-triazole grafted polysiloxane cross-linked with Si-C8 and TEOS precursor membrane (top), RHTM was mechanically stable without any cracking fracture, which suggested that expanded PTFE reinforcement was an effective to improve membrane mechanical stability for HT operation.

Therefore, the following membrane was named by RHTM, which consisted of 1,2,4-triazole grafted polysiloxane cross-linked with Si-C8 and TEOS precursor, doped with phosphoric acid and reinforced by ePTFE.
Table 1 Effect of various cross-linker regents on the performance, morphology, properties of our RHTM membranes*

<table>
<thead>
<tr>
<th>Cross-linker regent</th>
<th>RHTM membrane performance/morphology properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RHTM membranes before HT&amp;LH operation</td>
</tr>
<tr>
<td></td>
<td>perf.</td>
</tr>
<tr>
<td>Si-C₈</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>TEOS</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-C₈+TEOS (1:1)</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-C₂</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Note,
1) all the membranes prepared at room temperature and heat-treated at 130 °C for 10 hrs,
2) and based on the expanded PTFE membrane (50 micron thick) from USA Company,
3) The membrane morphology referred by yellow frame of the images in followed Fig. 2.

As shown in Fig. 1 and 2, and Table 1, the RHTM membrane morphology varied with components properties, such as cross-linker, PTFE film, acid doping quantity and doping way, etc. To improve membrane morphology and performance at high temperature and low/non-humidity, our RHTM membranes based on 1,2,4 triazole-grafting polysilicane, cross-linker regent (e.g. tetraethyl orthosilicate, bis(triethoxysilyl)octane and bis(methylidioethoxysilyl)ethane (donated as TEOS, Si-C8 and Si-C2)), and expanded PTFE film, were investigated. The phosphate acid (about 20wt.%) will be added during membrane fabrication. The membranes employed various cross-linker exhibited distinguished morphology and performance. The membrane appearance could be white, semi-transparent, or fully transparent. The fuel cell performance employing our RHTM membranes was improved if proper cross-linker regent used. Table 1 showed Effect of various cross-linker regents on the performance/morphology properties of our RHTM membranes. The TEOS+Si-C8 cross-linker was the best one among above ones when employed in our RHTM membranes system on the basis of membrane morphology and performance. As shown in Fig. 3 and 4, the RHTM with Si-C₈ and TEOS mixed cross-linker was much stable than pure ones.
Fig. 2 Appearance of 1,2,4-triazole-grafting polysilicane RHTM membranes employing Si-C₈ and TEOS cross-linker. The membranes in blue frame (25 micron) and the yellow frame (50 micron thick) were fully transparent and semi-transparent, respectively.

Fig. 3 The cell OCV employing RHTM membrane with Si-C₈ cross-linker (Left) or TEOS (Right) as a function of cell temperature. The electrode employed in our RHTM fuel cell system is modified Nafion-electrode.
Fig. 4 The cell OCV employing RHTM membrane with Si-C₈ and TEOS as a function of cell temperature. The electrode employed in our RHTM fuel cell system is modified Nafion-electrode.

Fig. 5 Polarization curves of single cell employing our single-layer (left) and tri-layer (right) RHTM membrane operated at 120 °C and ambient dry H₂/O₂ during different cycles. The electrode employed in our RHTM fuel cell system is modified Nafion-electrode.

Shown in Fig. 5, our tri-layer membrane exhibited much stable fuel cell performance at 120 °C, and dry ambient atmosphere H₂/O₂ conditions. The skin layer with grafted protogenic species could be effective to prevent the leaching of PA acid from the central layer.

Since modified Nafion-based electrode can not meet HT PEM fuel cell requirements, it is essential to develop home-made HT electrode to minimize interface resistance between membrane and electrode, as shown in Part IV-B.
Part IV-B. HT Electrodes and MEAs

Brief description of our electrode preparation process

Electrode component parameters ---

Pt loading in electrode designed as 1-1.5 mg/cm²

The binder loading in electrode designed variously, typically as about 0.125 mg/cm²

For easy description,

A --- triazole-grafting polysiloxane, Si-C8/TEOS, in alcohol, 10 wt.%
B --- PVdF solution in NMP, 5 wt%
C --- Pt on XC-72 carbon, 60 wt%
D --- PA acid doping, 10-20 mg/cm²

Process: dry at room temperature overnight, then dry at 60 – 80°C to avoid cracking, finally at 130°C for half hour.

Fig. 6 Home-made HT electrode #1, #2, Nafion-based electrode, and gas diffusion layer (GDL), respectively. Each electrode with 1 cm² effective area.

Fig. 7 High temperature PEM fuel cell performance comparison between home-made electrode (#1) and modified Nafion-based electrode. The electrolyte membrane was RHTM membrane. The fuel cell operated at 120 °C with dry ambient pressure H₂/O₂.
Table 1. Series 1 of component parameters of home-made HT electrode with PVdF

<table>
<thead>
<tr>
<th>No.</th>
<th>Compo.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D / PA doping @ preparation</th>
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Table 2. Series 2 of component parameters of home-made HT electrode without PVdF

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<th>B</th>
<th>C</th>
<th>D / PA doping @ preparation</th>
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</table>
Fig. 8 Polarization curves comparison of single cell employing home-made series 1 (left) and series 2 (right) electrodes, operated at ambient dry H2/O2, 120 °C.

Fig. 9 Polarization curves comparison of single cell employing home-made series 1 (left) and series 2 (right) electrodes, and operated at ambient dry H2/O2, 120 °C. The electrodes here include acid doping during electrode preparation.

Fig. 10 Polarization curves comparison of single cell employing home-made series 1 (left) and series 2 (right) electrodes with or without acid doping during electrode preparation procedure, operated at ambient dry H2/O2, 120 °C.
As shown in Fig. 8, #1 electrode and #8 exhibited the best performance in series 1 and series 2, respectively. In Fig. 9, the electrodes #11, #12, #13, #14 in series 1 and #15, #17, #18, #19 in series 2, behaved better performance than that in Fig. 8 due to the phosphoric acid doping during the electrode preparation, instead of doping PA acid after electrode formed. For comparison, Fig. 10 shows the electrode performance as a function of acid doping way (PA acid doped during or after electrode formation).

![Graph](image)

Fig. 11 HT PEM fuel cell performance employing HT electrode (#19), operated at ambient dry H2/O2, 120 °C.

Fig. 11 shows the best fuel cell performance employing our RHTM membrane and home-made electrode. The peak power density reached 0.22 W/cm2, and short circuit current density arrived at 1.45 A/cm2, as shown in Fig. 12. This is due to our membrane and electrode modification.

In summary, the peak power density of our RHTM high temperature PEM fuel cell employing home-made electrode reached 0.22 W/cm2, at dry and ambient pressure H2/O2 operation, relative to 0.10 W/cm2 of modified Nafion-based electrode. The membrane resistance could be reduced by decreasing membrane thickness, but the interface resistance of the electrode still needs to be reduced through modification of proper component ratio. Now some major achievements were that the home-made HT electrode may be on the right way and the membrane areal specific resistance was reduced to 0.2 ohm cm2. Our HT PEM fuel cell performance was comparable to [Q.F. Li, H.A. Hjuler, and N.J. Bjerrum, Journal of Applied Electrochemistry, 2001, 31, 773.], or a little better than [J. A., Asensio, and P. Gomez-Remero, Fuel Cells, 2005, 5, 336.] that of commercial PBI/H3PO4 system based on the same gases operation pressure, although the free H3PO4 acid doing level of our RHTM membrane was only 10% of PBI/H3PO4 system reported above. Therefore, it was very promising for practical operation of our RHTM PEM fuel cell operated at high temperature.
Part IV-C. Correlation of Microstructure/morphology and performance of home-made HT electrode

![SEM images](image1.jpg)

Fig. 12 SEM images with high magnification of home-made HT electrode (#19). The left top, right top and bottom represent surface planform of catalyst layer, cross-sectional image of catalyst layer with low magnification, and the one with high magnification, respectively.

![SEM images](image2.jpg)

Fig. 13 SEM images with high magnification of home-made HT electrode (#2). The left, right images represent cross-sectional image of catalyst layer with low magnification, the one with high magnification, respectively.

As shown in Fig. 12 and 13, the introducing of acid catalyzing regent is an effective method for controllable catalyst layer microstructure through in-situ polymerization of binder. The former suggested a cellular-shape CL microstructure, whereas the latter a layer-shape CL microstructure. The microstructure of the CL can be correlated with the performance, as shown in Fig. 12.
**Part IV-D. Temperature effect on PEM fuel cell performance**

Figure 14. Comparison of performance of Nafion-based commercial MEA and high temperature membrane operated at 80 °C and different humidity condition.

Figure 15. Comparison of membrane resistance of Nafion-based commercial MEA and high temperature membrane operated at different temperature with dry gas.
Figure 16. Performance curve of single cell employing our RHTM membrane (left) and commercial Nafion membrane (right) operated at temperature ranging from 80, 95, 105 and 120 °C, dry ambient atmosphere H₂/O₂.

Shown in Fig. 14, 15 and 16, the RHTM membrane exhibited much better, stable fuel cell performance at HT and dry conditions, in comparison to that of commercial Nafion-based MEA. This is due to proton conduction mechanism difference. Our RHTM membrane proton conduction mechanism was based on PA acid associated with triazole, otherwise, Nafion-based PEM one was water-bounded mechanism. Also, our RHTM membrane demonstrated good performance, mechanical, thermal stability. In summary, our RHTM membrane behaved good fuel cell performance at high temperature and dry conditions, and very promising for high temperature PEM fuel cell operation.
V. Publications and invention disclosures/patent applications

Part V-A. Invention disclosures/Patent applications


11. Siwen Li, Zhen Zhou, Yuelan Zhang, Meilin Liu, Wen Li, Sulfoyl-grafted heterocycles Based Materials for Proton-Conducting Electrolytes, *filed on Dec 09, 2005, GT ID 3688.*

12. Zhen Zhou, Siwen Li, Meilin Liu, Wen Li, Linear hybrid inorganic-organic polymers with grafted heterocycles for intermediate-temperature fuel cells

13. Siwen Li, Zhen Zhou, Yuelan Zhang, Meilin Liu, Wen Li, and Masayuki Sugawara, Hybrid inorganic-organic polymers based gas diffusion electrodes, MEAs and fuel cells, and methods thereof


15. S. Li, Z. Zhou, Y. Zhang, M. Liu, W. Li “Membrane-electrode-assemblies based on hybrid inorganic-organic polymers”


**Part V-B. Publications**

1. Zhen Zhou, Siwen Li, Yuelan Zhang, Meilin Liu, Wen Li, An active group promoting proton transport in polymer electrolyte membranes: 1H-1,2,3-triazole, *Journal of the American Chemical Society* 127, 10824 (2005).


4. Siwen Li, Zhen Zhou, Yuelan Zhang, Meilin Liu, Wen Li, Kohei Hase, and Toshiya Saito, 1H-1,2,4-Triazole: an Ideal Proton-Conducting Solvent for Proton Electrolytes, *Chemistry of Materials* 17, 5884, (2005).
5. Siwen Li, Zhen Zhou, Yuelan Zhang, Meilin Liu, Wen Li, 1H-1, 2, 4-Triazole: an Ideal Proton-Conducting Solvent for Proton Electrolytes, *Chem. Mater.* 17, 5884 (2005).


7. Siwen Li, Zhen Zhou, Meilin Liu, Wen Li, Junzo Ukai, Kohei Hase, and Masatsugu Nakanishi, Novel proton conductive hybrid inorganic-organic membranes grafted phosphoryl groups, to be submitted.


