DEVELOPMENT OF POLYMER ELECTROLYTE MEMBRANES
FOR FUEL CELLS TO BE OPERATED AT HIGH TEMPERATURE
AND LOW HUMIDITY

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The Academic Faculty

by

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DEVELOPMENT OF POLYMER ELECTROLYTE MEMBRANES
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AND LOW HUMIDITY

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SUMMARY

Polymer electrolyte membrane fuel cells (PEMFCs) have been looked as potential alternative energy conversion devices to conventional energy conversion systems such as combustion engines. Proton conducting membranes (PEMs) are one critical component of PEMFCs. The development of novel electrolyte membranes with dense structure, good mechanical flexibility, and high proton conductivity, but with little or no dependence on humidity at temperatures above 100°C remains an important challenge to the realization of practical PEM fuel cells. In this thesis, to solve the technical difficulties existing in current high temperature PEM systems based on H₃PO₄ and imidazole, a new type of proton conducting species 1H-1,2,3-triazole has been explored, and proved to have high proton conductivity and also enough electrochemical stability for fuel cell applications. In further experiments, effective methods have been developed to synthesize triazole derivatives and polymers. The properties of the synthesized polymers have studied and reported in this thesis. Preliminary computational simulations have also been performed to study the proton conducting mechanism to provide intrinsic information of the proton conducting process in 1H-1,2,3-triazole. In the final part, research works on other proton conducting species including H₃PO₄ and other heterocycles have been reported.
CHAPTER 1
INTRODUCTION

1.1 Background of the Research and Problem Statement

Invented since the mid-19th century, fuel cells didn’t find their application until space exploration in the 1960’s. In past two decades, due to the concern of air pollution and possible fossil fuel depletion crisis, significant world-wide efforts have been devoted to developing fuel cells as potential alternative energy conversion devices to conventional energy conversion systems such as combustion engines. In fuel cells, the chemical energy is continuously converted into electrical power via redox reactions, typically by supplying fuels (pure hydrogen, hydrogen carbon fuels or chemical hydrides) on the anode side, and oxidant (oxygen or air) on the cathode side. Compared with combustion engines, fuel cells may have less environmental impact, and provide higher energy conversion efficiencies due to “the less limitation imposed by the second law of

![Figure 1.1. Simplified Ragone plot of the energy storage domains for fuel cells, batteries and super capacitors compared to internal combustion engines, turbines and conventional capacitors.](image-url)
thermodynamics on the operation of fuel cells” [1]. Also, different from batteries, fuel cells are open systems where the active masses undergoing the redox reactions are delivered from outside the cell. The simplified Ragone plot [2] (Fig. 1.1) discloses that fuel cell can be considered to be high-energy system and ideal for various stationary and mobile applications, in which the terms “specific energy” (in watt-hours per kilogram) or “energy density” (in watt-hours per liter) are used to compare the energy contents of a system, and the “specific power” (in watt per kilogram) or “power density” (in watt per liter) to express the rate capability. Currently, the practical applications of fuel cells are still hindered by some critical technical issues including the source, storage and delivery of fuel, the material failure and long term stability of fuel cell systems, the overall efficiency and unit costs of fuel cells.

A number of different types of fuel cells are currently under development. Figure 1.2 [2] describes the operation of typical fuel cells with their advantages and disadvantages.

---

**Figure 1.2 Summary of various fuel cell systems**

- **AFC**
  - Unreacted gases: H₂, CO, reaction gases
  - Reaction: H₂ → OH⁻ → O₂
  - Advantages: Mechanically rechargeable, Low cost KOR solution
  - Disadvantages: Limited active life, intolerant with CO₂ and CO

- **PEMFC**
  - Unreacted gases: H₂, CO₂, reaction gases
  - Reaction: H₂ → H⁺ → O₂
  - Advantages: Nonvolatile polymer electrolyte, CO₂ tolerant, low working temperature
  - Disadvantages: Expensive catalyst, CO poison, water management essential

- **DMFC**
  - Unreacted gases: CH₃OH, CO₂, reaction gases
  - Reaction: CH₃OH → H⁺ → O₂
  - Advantages: Direct fuel conversion, stable reaction intermediate, polymer electrolyte
  - Disadvantages: High catalyst loading, slow electrode kinetics, low efficiency

- **PAFC**
  - Unreacted gases: H₂, CO₂, reaction gases
  - Reaction: H₂ → H⁺ → O₂
  - Advantages: CO₀ replacing electrolyte, high fuel efficiency
  - Disadvantages: Low conductivity electrolyte, expensive catalyst, limited life

- **MCFC**
  - Unreacted gases: CO, H₂, CO₂, reaction gases
  - Reaction: CO₂ → O₂
  - Advantages: Fast electrode kinetics, high efficiency, CO₂/H₂ usable fuel
  - Disadvantages: Limited life, low sulfur tolerance

- **SOFC**
  - Unreacted gases: CO, H₂, CO₂, reaction gases
  - Reaction: CO₂ → O₂
  - Advantages: Fast electrode kinetics, high efficiency, tolerant of impurities
  - Disadvantages: High working temperature, material problems, less sensitive to sulfur
The PEMFC was first developed for the Gemini space vehicle \[^3\]. Typically working around 60-90°C using pure hydrogen as fuel, PEMFC has been developed for transport applications as well as for stationary and portable applications. The automotive industry’s first attempt at an automobile power by PEMFC was GM 1966 Electrovan, and now there are numerous prototype cars and buses being researched based on PEMFC around the world. Compared with other types of fuel cells, the high energy density, quick start-up capability, low operating temperature, and simplicity of construction are distinguish features of PEMFC.

The success of PEMFC technology is based on the development of Nafion (a DuPont registered trademark polymer), the perfluorosulfonic acid polymer membranes as the proton conducting electrolytes. In fuel cell condition with both oxidative and reductive environment, Nafion membranes provide excellent long-term stability due to the Teflon-like backbone and also good mechanical properties. Under fully hydrated condition, the dissociation and salvation of protons from the acid groups exhibit the membrane conductivity as high as 0.1 S cm\(^{-1}\). \[^4\] Also, the low permeability of oxygen and hydrogen with high CO\(_2\) tolerance of PEMFC makes it more applicable than other types of fuel cells.

Typically, two carbon layers loading with platinum catalysts are applied to both side of the center electrolyte layer, and porous carbon paper as gas diffusion layers are on the top of the catalytic layer to form membrane electrode assembly (MEA). Metal or graphite plates serve as both flow field and current collector on both sides of MEA. The costs from the catalyst have been decreased by lowering the platinum content significantly, currently around 0.1 mg/cm\(^2\) in anode side and 0.5 mg/cm\(^2\) in cathode side. However, Platinum-based catalysts are sensitive to H\(_2\)S and CO impurities. For example, at 80°C, 20ppm CO content in the fuel stream will results in a significant cell performance loss \[^5\]. As a consequence, they must be eliminated from the hydrogen fuel, which brings additional operating parts and costs to the system.
Water management is a critical issue for operating PEMFC. Figure 1.3 [6] illustrates different modes of water transport in PEMFC. The perfluorosulfonic acid polymer membranes need high water content to maintain high proton conductivity. When the proton transport from anode to cathode in the membrane, it carries water along while carrying the current. Operating at high current density, the anode side must be humidified to avoid dehydration due to the electro-osmotic drag. The cathode side needs to remove water in the air stream to prevent flooding of the active layer which may result in the slow oxygen diffusion to the catalytic layer and decrease of the cathode performance. Also, with high water vapor pressure in the feed-gas stream, the total pressure needs to be increased. Otherwise a low reactant-gas partial pressure will result in increased concentration over-potential.

Figure 1.3 Water transport modes in PEMFC.

The practical applications of PEMFC still face a lot of technical difficulties. Thermo management is one of the complications. Typically operating at 80°C with an efficiency of 40-50% produces large amount of heat [7], which has to be removed by cooling system to keep the working temperature stable. On the other hand, the heat
energy from a PEMFC stack at 80°C is not worth to recover. Other issues include the slow cathode kinetics, the source, purification, storage and delivery of hydrogen gas, the cost of Nafion membrane etc.

Recent research activities [4], [6] in PEMFC have focused on developing PEMFC operating above 100°C. There are several advantages for high temperature operation of fuel cells:

(I) for both electrodes, especially for cathode reactions, the electrochemical kinetics is improved. The Tafel equation (1) is used to describe the performance of PEMFC in the kinetically controlled regime, where \( E \), \( E_{rev} \), \( b \), \( i \), \( i_0 \), \( n \) and \( \alpha \) are the electrode potential, reversible potential, Tafel slope, current density, exchange current density, the number of electrons transferred in the rate-determining step, and the transfer coefficient respectively. Previous study of Nafion and other sulfonated polytrifluorostyrene based membrane shows the increase of \( i_0 \) with the increase of temperature. Also, Equations (2) and (3) illustrate the change of Tafel slope and OCV with the temperature changing.

\[
\begin{align*}
E &= E_{rev} + b \log i_0 - b \log i \\
b &= -2.3 \frac{RT}{amF} \Rightarrow \frac{\partial b}{\partial T} = -\frac{2.3R}{amF} \\
OCV &= 1.482 - 0.000845T + RT \ln \frac{P_{H_2}P_{O_2}^{0.5}}{P_{H_2O}}
\end{align*}
\]

(II) High temperature improves the CO tolerance of the catalyst. At low temperature, trace amount of CO can dramatically reduces the activity of Platinum based catalyst due to the strong absorption of CO on the Pt surface. Increasing the operating temperature of PEMFC is an effective way to alleviate CO poisoning effect due to the high negative entropy change associated with the adsorption of CO on Pt. The studies of Pt-Ru catalyst by Lakshmanan et al. [8] with polyetherether ketone membranes showed that the CO tolerance of the catalyst was improved from 50 to 1300ppm with the temperature
increasing from 70 to 120°C. For PEMFC based on the membrane of polybenzimidazole (PBI) doped with phosphoric acids, it was reported [9] that CO tolerance was dramatically enhanced from 25ppm at 80°C for current densities <0.3 A cm\(^{-2}\) to 1000ppm at 130°C, and up to 30,000ppm at 200°C. (The CO tolerance is defined as a voltage loss of <10 mV at certain current density.)

(III) For Nafion and other sulfonated polymer membranes based PEMFC, dehydration at the operating temperature above 100°C may dramatically lower the cell performance. By solving the key technique, to develop new polymer electrolyte membranes with high proton conductivity above 100°C at low humidity condition, the water management of PEMFC can be simplified, and the potential problems associated with cathode flooding will be eliminated. Also, the flow field design, which considers the liquid water accumulation in the cathode side for conventional PEMFC, will be simpler without the presence of two phase flow in the channel due to the simplified water management.

(IV) Other benefits from high temperature operation include the fast gas diffusion rate because of the elevated temperature and water vapor instead of liquid water, the decreased water solubility of oxygen and hydrogen in water, the simplified cool system and effective heat recover to improve the total energy efficiency due to the greater temperature difference between the fuel cell and ambient environment, the higher activity of catalysts and the possibility to develop new catalysts working at elevated temperature.

The development of PEMFC operating above 100°C encounters several major challenges including membrane conductivity, mechanically properties and stability, long-term catalytic layer stability problems including possible oxidation of carbon substrate and loss of platinum catalyst, material degradation of different components of fuel cell system at high temperature. However, because the most widely used electrolyte membrane Nafion dramatically lose its conductivity [10] (Figure 1.4) and mechanical
attributes at elevated temperature (Tg of dry Nafion membrane is between 130°C to 160°C), the development of new membranes having high proton conductivity at high temperature and low humidity condition, good mechanical properties, good thermal and chemical stability, will be the very first and the most important step for developing PEMFC operating above 100°C.

1.2 Research Objectives

The general goal of the research conducted for this thesis is to (i) develop new polymer electrolyte membranes for fuel cells operating above 100°C, Research targets include that (a) the conductivity of the membrane at 120°C needs to be above $10^{-3}$ S·cm$^{-1}$ for practical applications, and ideally as high as 0.1 S·cm$^{-1}$ at 20% relative humidity. (b) The membrane has acceptable mechanical properties including elongation and tensile strength of the membranes. (c) The membrane has good thermo and chemical stability, and durability.

Also, this research aims to develop high temperature PEMFC for automobile other than stationary applications. The state of the art of high temperature PEMFC is
based on phosphoric acid doped polybenzimidazole (PBI) membranes \cite{11}, which is considered to be more suitable for stationary applications due to the questionable long term stability issue. Therefore, for this research, besides investigation of new polymer matrix containing phosphoric acid, developing new electrolytes totally different from H$_3$PO$_4$/PBI system will be a more important objective.

1.3 Outline of Research Work

To achieve the research goal, we are focusing on developing new proton conductors to replace water. Some heterocyclic compounds, such as imidazole\cite{12} have been reported having high proton conducting ability. However, no successful imidazole based PEMFC have been reported. Therefore, we will start the research by looking for new heterocyclic compounds as the proton conductors instead of imidazole. The ionic conductivity, the proton conducting process, and the electrochemical stability of the new candidates will be investigated experimentally to prove the potential for new proton conductors based polymer membranes for PEMFC operating above 100°C. By finding new proton conductors, extensive studies will be done to develop effective synthetic methodology for synthesizing the related derivatives and polymers for new proton conducting groups. The conductivity of these newly developed polymer membranes will be investigated in details. Also, theoretical studies of the proton conducting mechanism in proton conductors in proton conducting system will help to understand the major factors related to proton conducting process. The research work of computational modeling about proton conducting system will be conducted through quantum mechanical calculations.

Besides developing new proton conductors, the research about PEMs based on previously reported systems such as phosphoric acid will also be conducted to investigate various possibilities for developing new PEMs for fuel cell operating above 100°C.
1.4 Organization of the Dissertation

In Chapter 2, first some of the critical issues for designing new PEMs for high temperature PEMFC are discussed, together with the review of advantages and disadvantages of possible candidate systems. Also the background knowledge about membrane electrode assembly of PEMFC is introduced in this chapter.

In Chapter 3, the previous theoretical works about hydrogen bonds and proton conducting process are reviewed, which are important to deeply understand different factors related to the proton conductivity of PEMs.

In Chapter 4, the experimental work about the small organic molecule, $1H$-$1,2,3$-triazole, including the conductivity studies, pulsed-field gradient NMR studies, electrochemical stability and fuel cell tests.

In Chapter 5, the synthesis and studies of triazole derivatives and triazole attached polymers are reported. The effects of polymer backbones and acid groups on proton conductivity of resulted polymer membranes are investigated and discussed.

In Chapter 6, results of preliminary theoretical studies of proton conducting mechanism in $1H$-$1,2,3$-triazole based systems are reported, including the studies of triazole/triazolium cation complex and triozole/triazolium cation/sulfonic(phosphonic) acid anion complex.

In Chapter 7, research results about PEMs based on phosphoric acid and heterocyles including imidazole and 1,2,4-triazole are reported.

Final Chapter 8 is the conclusions and recommendations.
1.5 References

1  http://web.mit.edu/afs/athena.mit.edu/org/m/mecheng/fcp/about%20f%20cells.html. (04/2007)


CHAPTER 2

BACKGROUND

2.1 High Temperature Polymer Electrolyte Membranes

To develop new polymer electrolyte membranes for fuel cell operating above 100°C, proton conductivity, mechanical properties, thermo and chemical stability are the major factors that need to be concerned at the same time to achieve a balance for practical fuel cell applications. A number of membrane systems have been studied, and related work has been reviewed from different aspects in recent years.\cite{1-4} Here, different systems are reviewed by comparing the properties, advantages and disadvantages of the major components of PEMs including proton conducting carriers, mobile protons, polymer matrix and microstructure.

2.1.1 Proton Conducting Species

Proton conducting species are mainly responsible for transporting protons in short and long ranges. From the atomic level, only oxygen and nitrogen are suitable for carrying proton in the PEMFCs, due to chemical stability and suitable binding constant of oxygen and nitrogen to protons. Possible proton conducting species with oxygen include water, oxygen anion, hydroxyl anion, alcohol, ether, ester, carboxylic acid, inorganic oxoacid, oxygen-containing heterocycles. For nitrogen, those include ammonia, amino groups, nitrogen-containing heterocycles. By considering the reduction/oxidation and high temperature environments, only several species are applicable in HT-PEMFCs and discussed here.

1) H$_2$O: The high equivalent conductivity of excess protons in aqueous solutions has been recognized for a long time. However, neither pure nor doped ice has been reported to have good proton conductivities. Nafion and other sulfonated polymer,\cite{5,6,7} when fully hydrated, provide high proton conductivity under 100°C. Some solid hydrates,
such as the layered compounds $\text{H}_3\text{OUO}_2\text{XO}_4 \cdot 3\text{H}_2\text{O}$ ($\text{X}=\text{P, As}$), were confirmed by Shilton and Howe \cite{8} in 1976 to have high proton conductivity above a phase transition, as show in Figure 2.1. \cite{9} For other acidic phosphates and phosphonates of zirconium, and the heteropolyacid hydrates, their proton conductivity is highly related to the presence of water.

![Figure 2.1 Proton conductivity of some representative water containing compounds.](image)

Water molecules are chemically and thermally very stable in PEMFC conditions. Also, it can be easily supplied from the gas stream or produced from cathode processes. However, by increasing temperature higher than 100°C, the high vapor pressure makes water molecules not stable in the electrolyte membranes. To retain high water contents at high temperature is the major challenges for hydrated acidic polymers used for HT-PEMFCs. There are theoretical \cite{6,7} and experimental\cite{10-13} indications that by increasing the acidity, concentration and mobility of acid groups in the membrane, high proton conductivity may be possible at low hydration levels. Perfluorosulfonic polymers shows high water retaining ability due to the superacidity of $-\text{CF}_2\text{SO}_3\text{H}$ groups, and the conductivity data under high temperature low humidity condition have been reported (Figure 1.4 and Figure 2.2)\cite{12}.
Figure 2.2 AC conductivity vs. temperature for different 3M PFSA monomers, measured by a point conductivity probe. The humidification was held at a constant 80°C dew point.

Miyatake et al.\textsuperscript{[13]} reported their studies of sulfonated polyimide with fluorenyl groups. The copolymer with highly sulfonated polyimide and hydrophobic fluorenyl moieties shows specific water uptake and the highest high-temperature conductivity for sulfonated polymers (Figure 2.3), indicating possible ways to improve water uptake ability and high proton conductivity of acidic polymer membranes at high temperatures.

Figure 2.3 (Left) Water uptake of SPIH-X at 85°C and 93% RH; (Right) Humidity dependence of the proton conductivity of SPIH-X at 80°C, 100°C and 120°C.
(2) H₃PO₄: Phosphoric acid (H₃PO₄) is a highly viscous liquid, and was first used in phosphoric Acid Fuel Cells (PAFCs), which were developed in 1960s and also the first type of fuel cells to be commercialized. The operating temperature of PAFCs is in the range of 150°C-220°C.

Phosphoric acid shows a very high degree of self-dissociation of ~7.4%, due to the reasonably high $K_a$ and $K_b$ in terms of equilibrium constants. Therefore, in H₃PO₄ based electrolytes, H₃PO₄ acts as both the proton donating species and the proton conducting species. The estimated proton mobility of phosphoric acid at the melting point (T=42°C) is $2 \times 10^{-5}$ cm²/s with the total conductivity $7.7 \times 10^{-2}$ S/cm, and $^1$H PFG NMR experiments also proved this extremely high proton mobility. [6]

Litt and Savinell[1] first proposed and developed the basic polymer polybenzimidazole (PBI), doped with H₃PO₄ as the high temperature PEM. The PBI fiber provides enough mechanical strength, stability and acid absorption ability at the same time to the composite membranes. Several methods have been used to dope phosphoric acid to the polymer: (1) the cast polymer membranes were immersed into the phosphoric acid solution. (2) PBI polymer and acid were directly cast from a solution of PBI and H₃PO₄ in trifluoroacetic acid solution. (3) PBI was prepared in polyphosphoric acid (PPA) and directly cast to form membranes. H₃PO₄ was formed by controlled hydrolysis of PPA. Even though the doping level is similar, the properties of membranes prepared by different methods are quite different. By comparing with the data from other methods (Figure 2.4), Benicewicz’s group[14] reported that the conductivity of their PBI-H₃PO₄ membranes formed by method (3) as they called the “sol-gel” process is the highest, due to the much higher molar ratio of H₃PO₄ to PBI unit without sacrificing the mechanical strength of the resulted membranes at high temperature.
Phosphoric acid doped PBI membranes possess good performance at elevated temperature, even at 200°C. Also, under continuous operation, PBI-H₃PO₄ based PEMFCs have reported lifetimes of 3500 and 500h at 120°C and 150°C, respectively. Table 2.1[15] summarized the reported performance of acid doped PBI membranes.

Table 2.1 Single PEMFC data based on phosphoric acid doped PBI membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Testing Conditions</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃PO₄/PBI</td>
<td>190, 170, 150, and 100°C, H₂/O₂, atmospheric pressure</td>
<td>0.6V, 630, 430, 300, and 160mAcm⁻²</td>
</tr>
<tr>
<td>H₃PO₄/PBI</td>
<td>150°C, H₂/O₂, atmospheric pressure</td>
<td>0.54V, 250mAcm⁻²</td>
</tr>
<tr>
<td></td>
<td>150°C, H₂/air, atmospheric pressure</td>
<td>0.41V, 250mAcm⁻²</td>
</tr>
<tr>
<td>H₃PO₄/PBI</td>
<td>160°C, H₂/air, atmospheric pressure</td>
<td>0.6V, 400mAcm⁻²</td>
</tr>
<tr>
<td>H₃PO₄/PBI</td>
<td>170°C, H₂/O₂, 1 bar</td>
<td>0.6V, 350mAcm⁻²</td>
</tr>
<tr>
<td></td>
<td>130°C, H₂/O₂, 1 bar</td>
<td>0.6V, 180mAcm⁻²</td>
</tr>
<tr>
<td>H₃PO₄/PBI</td>
<td>200°C, H₂/O₂, atmospheric pressure</td>
<td>0.6V, 700mAcm⁻²</td>
</tr>
<tr>
<td></td>
<td>200°C, 3% CO/CH₂/O₂, atmospheric pressure</td>
<td>0.6V, 570mAcm⁻²</td>
</tr>
<tr>
<td>H₃PO₄/PBI</td>
<td>190°C, H₂/O₂, 1 bar</td>
<td>0.6V, 430mAcm⁻²</td>
</tr>
</tbody>
</table>

Few recent papers[16] reported the performance degradation of PBI-H₃PO₄ based HT-PEMFCs. It was found that similar as in PAFCs, the degradation mainly comes from the aggregation of platinum catalysts, which possibly due to the dissolution and redeposition of platinum particles in phosphoric acid at high temperature and migration of
platinum crystallites on the carbon support. Also, the leaching of H₃PO₄ from the electrodes may also gradually lower the cell performance. For PEMFCs, liquid water maybe produced in cathode side, when the operating temperature is lower than 100°C at atmospheric pressure. Therefore, for automobile applications, which require multiple thermal cycles with frequent shutdown and restart, the PBI-H₃PO₄ based HT-PEMFCs are still problematic.

(3) Heterocycles: Among various nitrogen-containing species, some heterocycles are most likely to be the proton carriers applied for HT-PEMFC, because the high electron density on nitrogen is partially reduced by the conjugated aromatic system and the oxidative stability of nitrogen is improved. Kreuer et al. [2] first proposed heterocyclic compounds imidazole and pyrazole as the proton conducting groups. The proton conducting ability of imidazole was determined by measuring the conductivity of sulfonated PEEK doped with imidazole and pyrazole at elevated temperature (Figure 2.5), and also by studying the proton mobility through \(^1\text{H}\) PFG NMR experiments.

![Figure 2.5 AC Conductivities of (a) imidazole and (b) pyrazole intercalated into sulfonated PEEK membranes. The conductivity of the hydrated membrane is shown for comparison.](image-url)
Imidazole also acts as a proton donating groups through the dissociation of the proton from the -NH group in imidazole. The conductivity of liquid imidazole was reported as high as $10^{-3}$ S/cm at the melting point of 90°C. Later work focused on the study of (i) imidazole doped acidic polymer such as Nafion and (ii) imidazole derivatives and polymers (Figure 2.6)[6]. The imidazole grafted polymer shows noticeable proton conductivity at high temperature without external humidification, which provides a potential way to design so-called “intrinsic proton-conductive” polymers for high temperature applications. By covalently tethering the proton carriers to the polymer backbones, the leaching or evaporation of free proton conducting molecules, such as H$_3$PO$_4$ and imidazole from the electrode and electrolyte layers, can be avoided to get stabilized conductivity and performance of the membrane at high temperatures.

Figure 2.6 Proton conductivity of various imidazole-based systems.
However, previously there were no successful fuel cell tests reported based on acidic polymers with imidazole doping or imidazole grafted polymers, possibly due to the poisoning effect of imidazole to the platinum catalysts \[17\]. A very recent paper \[18\] reported acceptable cell performance, by using Nafion doped with H$_3$PO$_4$ and imidazole together, and by applying new Pt-Co-Mo catalyst.

Although the boiling point of imidazole is as high as 256°C, the slow evaporation or leaching of small imidazole molecules still may lower the conductivity of the imidazole doped membrane. For polymers with imidazole tethered, the difficulty is in either very low conductivity or insufficient mechanic strength. As reported \[19\], both the copolymer of 4-vinylimidazole with vinylphosphonic acid and the copolymer with 2-acrylamido-2-methylpropanesulfonic acid provide very low proton conductivity (10$^{-8}$-10$^{-10}$ S/cm at 120°C) without external humidification. Besides the low conductivity, the thermooxidative degradation of imidazole and other heterocyclic compounds may also be a difficulty for applying these materials for long-term HT-PEMFC applications.

(4) Other proton conducting species: By exposing some inorganic oxides to water atmosphere at high temperature, the oxygen vacancies in the oxides are replaced by hydroxyl groups from the dissociation of water vapor, and the left protons form covalent bonds with the lattice oxygen. The water uptake and the concentration of incorporated protons highly depend on the concentration of oxygen vacancies in oxides and the rate of water incorporation reactions. The diffusion of these incorporated protons in the lattice of oxides results in the conductivities of these oxides. Among them, the highest proton conductivity was observed in oxides with perovskite-type structures (ABO$_3$) with cubic or slightly reduced symmetry, as shown in Figure 2.7\[6\]. Another typical inorganic proton conducting materials are acidic salts of oxo-acids such as CsHSO$_4$ \[9\]. At T≈140°C, there exists a first-order phase transition of CsHSO$_4$, and above this point the solid shows the proton conductivity as high as ~10$^{-2}$ S/cm, which results from the hydrogen transportation between sulfate groups. However, to apply these inorganic proton conducting materials
to HT-temperature PEMFCs, there are still some severe disadvantages: (1) the low conductivities in the temperature \(<200^\circ C\), which maybe even worse when doped into polymer matrix, due to the large interfacial resistance. (2) The instability of these oxides to the liquid water. (3) Mechanic properties of these solid oxides and their composites with polymers.

![Figure 2.7 Proton conductivities of various oxides. (Bold lines are the conductivities of Perovskite-type structure oxides. For comparison, the conductivity of the oxide ion conductor yttria-stabilized zirconia YSZ is shown.)](image)

Recently, a few groups \cite{20,21} reported some kinds of ionic liquid, such as imidazolium bis-(trifluoromethanesulfonyl)imide (HImTFSI) and 2,3-dimethyl-1-octylimidazolium triflate possess proton conducting ability and may be applied for PEMFCs at elevated temperature. However, only part of the high total conductivity is related to proton conduction in these systems. The stability, leaching and electro-osmotic drag of ionic components in the membrane are disadvantages for these systems. Till now, there are no acceptable cell performance data reported for ionic liquid based membranes.
2.1.2 Proton Donating Groups

In an electrolyte membrane, the electronic and ionic conductivities are generally tensor quantities relating the current density $i_0$ to the applied electric field $E$ in accordance with Ohm’s law. The scalar expression for the mobile-ion current density along the direction of $E$ has the form

$$i_0 = \sigma_i E = c_i q v_s, \quad (1)$$

where $v$ is the mean velocity of the mobile ions of charge $q$ and $c_i$ is their concentration. As the charge-carrier mobility $u \equiv v/E$,

$$\sigma_i = c_i q u_i \quad (2)$$

So the proton conductivity of PEM is proportional to the concentration of both protonated cations and deprotonated anions, and also their mobility in the membrane. Except pure $\text{H}_3\text{PO}_4$, Proton conducting species such as water and imidazole have very low self-dissociation level which results in the low concentration of charge carriers and low conductivity of pure materials. By adding strong Bronsted acids as proton donating groups or strong bases as proton accepting sites to promote proton transfer reactions with proton conducting groups, the conductivity of resulted system can be improved dramatically. Due to instability of basic charge carriers to oxygen or carbon dioxides, strong acid doping is more suitable in PEMFC environment.

By considering the fuel cell working condition, only several acidic groups are applicable for PEMFCs and described in Table 2.2. Phosphonic acids are studies in recent

<table>
<thead>
<tr>
<th>Acid groups</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Examples and ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CF₂SO₂H</td>
<td>Strongest acidity and good stability</td>
<td>Desulfonation, reduction</td>
<td>Nafion, 3MPFSA</td>
</tr>
<tr>
<td>-PhSO₂H, -CH₂SO₂H</td>
<td>Strong acidity, synthetic simplicity</td>
<td>Desulfonation, redox stability</td>
<td>BAM3G, sPEEK,</td>
</tr>
<tr>
<td>-PhPO₂H₃, -CH₂PO₃H₂</td>
<td>Redox and thermo-stability, two</td>
<td>Synthetic complexity, dehydration</td>
<td></td>
</tr>
<tr>
<td>-CF₂PO₃H₂</td>
<td>dissociable protons per unit</td>
<td>condensation</td>
<td></td>
</tr>
<tr>
<td>-SO₂NH₂SO₂⁻</td>
<td>Low polarity, synthetic versatility</td>
<td>Synthetic complexity, Redox and hydrolysis Stability, large size.</td>
<td></td>
</tr>
</tbody>
</table>
years to replace sulfonic acid for better redox and thermostablity. Also one phosphonic unit may provide two mobile protons, although the dissociation constant of the second proton is low. On the other hand, when the acids are tethered to the polymer backbones to avoid leaching and migration in the electric field, the introduction of phosphonic acids to the polymer backbones, compared with the direct sulfonation for sulfonic acids, is more complicated. Also, dehydration condensation between phosphonic groups is one potential problem for these membranes. Few papers\cite{22} discussed the possibility to use sulfonimide as the acids in PEMs, however its redox and hydrolysis stability are still questionable in fuel cell condition.

Controlling the content of proton donating groups and their distributions in the membranes is critical to improve the proton conductivity and also maintain good mechanical properties of the membranes. Base on the studies of imidazole related systems\cite{6}, the effect of salts formation between acids and basic proton conducting groups low the effectiveness of acids promoting proton conduction, especially in the fully polymerized membranes. The details mechanism related to proton conduction will be discussed in the next chapter. Also, introducing large amount of strong acids into polymers increase the polarity of the polymer and result in the brittleness or decrease of mechanic strength of the membranes. Water swollen in high humidity and T$\textless$100$^\circ$C is also a major technical difficulty for the polymer with high content of acid groups.

2.1.3 Polymer matrix

The major part of polymer electrolyte membranes is the polymer matrix, which is responsible for providing the mechanic properties of the membrane and a stable working environment for the proton donating and conducting groups. By considering the redox and the hydrothermal condition in PEMFCs, a number of typical polymer systems such as polyester, epoxy are not suitable. Also, the choice of polymer backbones is limited by the
synthetic chemistry, mechanical and chemical properties of the polymers. Figure 2.8 [10,11,12] describes the chemical structures of the polymers applied or studied in PEMFCs.

Fluoronated Polymer

Nafion™ ionomer

Dow ionomer

3M ionomer

BAM3G

ETFE-g-PSSA

Aromatic Polymer

poly-p-phenylene

poly-p-phenylene oxide

poly-p-phenylene oxide

polyetheretherketone

poly-p-phenylene sulfide

poly(4-phenoxycarbonyl-1,4-phenylene)

poly(arylene ether)

Figure 2.8 Various Polymer Structures of interest for developing PEMs.
Figure 2.8 Various Polymer Structures of interest for developing PEMs. (Continued)

Carbon-fluorine backbone in Perfluorinated and partially fluorinated polymers gives these materials excellent long-term stability. Also, the tensile strength of Nafion membranes is about 40 MPa, and the elongation is larger than 200% at 23°C, 50% relative humidity. The permeability of both oxygen and hydrogen through the membrane is as low as $10^{-11}-10^{-10}$ mol·cm$^{-1}$·s$^{-1}$·atm$^{-1}$. However, possibly due to the relatively low Tg of Nafion membranes (between 130°C and 160°C for the dry membrane) and aggregations/phase separation in polyelectrolytes, these membranes lose the mechanical stability and low the performance dramatically at high temperature and low humidity.
condition, especially when very thin films (<50µm) is applied. Reinforced by different fibers including PTFE, polysulfone and glass, the composite PFSA shows improved mechanical properties at elevated temperature. By doping inorganic compounds such as SiO₂ and TiO₂ nanoparticles within a range, both the water absorbing ability and mechanical properties can be improved.

Developing alternative acidic polymer systems for PEMs focuses on synthesizing aromatic polymers such as poly(ether ether ketone)s, poly(sulfone)s, poly(imide)s, and incorporating acid groups by different strategies. The aromatic polymers are attractive for PEMs because of their well-known oxidative and hydrolytic stability under harsh condition, their superb thermal (Tg>150°C, Tm>300°C) and mechanical properties (Tensile strength >50Mpa), and also because many different chemical structures including partially fluorinated materials are possible. Introduction of sulfonic acid groups to the polymer backbone has been accomplished by a polymer postmodification or by direct polymerization of sulfonated monomers, as shown in Figure 2.9 [10] for sulfonation of polysulfone (PSU) and copolymers, and the content and distribution of acid groups in polymers can be controlled delicately.

The synthetic fiber, Polybenzimidazole (PBI) possesses high Tg (450°C) and Tm (760°C). The tensile strength of PBI is 160Mpa and elongation at break is about 3%. The PBI-H₃PO₄ membranes show high proton conductivities at high temperature and low humidity condition. However, the chemical stability of PBI to acidic solution and oxygen is fairly poor, which makes it still problematic for long term applications in HT-PEMFC, although ~5000h continuous HT PEMFC performance has been achieved.

Several inorganic polymer and hybrid systems have been studied [11]. Polysiloxane and related hybrid materials have good thermal and chemical stability due to the high Si-O-Si bond strength of ~445kJ/mol. They can be synthesized by polymerization different siloxane monomers or through sol-gel process at room temperature. Also, zirconium oxide can be introduced into the hybrid materials by
Figure 2.9 Introduction of sulfonic acid groups to PSU and copolymers.
sol-gel process using organic precursors of zirconia, and then absorb H$_3$PO$_4$ to the materials [23]. The reported chemical and thermal stability of polyphosphazene [24], various chemistry for attaching side chains for ion exchange sites and polymer cross-linking onto the –P=N- polymer backbones, make polyphosphazene potentially attractive materials for PEMs. Allcock et al have developed the sulfonation methods of polyphosphazene and studied the related surface chemistry. For polyphosphazene, the poor mechanic strength resulted from the low Tg of polyphosphazene and the hydrolysis stability at elevated temperature are major technical challenges for applying those polymers for HT-PEMFCs.

2.1.4 Microstructure

Proton conduction is a result of long-range proton motion. Obviously, the existence of long-range static or dynamic proton conducting pathway is one of the necessity to achieve high proton conductivity. Therefore, the microstructure of PEMs is one of the most importance factors for the proton conduction in the membranes. Previous studies [25,26,27] on Nafion and sPEEK provide an insight view for the relation between microstructures and proton conductivity. Revealed by various techniques including small

![Figure 2.10 Nano-size phase separation in the microstructures of Nafion and sPEEKK.](image)
and wide angle X-ray scattering, neutron scattering, dielectric spectroscopy, NMR etc, in the Nafion membrane, there exists nano-separation of hydrophobic/hydrophilic domains in the presence of water. Among different models to describe the size and structure of domains, the studies of Kreuer \cite{25} and Ise \cite{28} reported the estimates of channel diameters, channel separation, degree of branching and the number of dead-end channels in both Nafion and sPEEKK. As shown in figure 2.10 \cite{25}, sPEEKK has narrower water-filled channels than those in Nafion and they are less separated and more branched with more dead-end pockets. These results are consistent with the facts: Compared with PTFE, the PEEKK backbone is less acidic and less flexible, and the sulfonic acid groups in sPEEKK are less acidic, and it needs the polymer with higher humidity or higher ion exchange capacity to achieve the same high proton conductivity as that of Nafion.

Controlling the microstructure of the PEMs by introducing copolymer blocks has been investigated to improve the proton conductivity and mechanical properties of the membrane. For example, by introducing bulky unsulfonated diamines into polyimides shown in Figure 2.8, the regular parallel packing of the polymer backbones can be changed into a more open structure with greater inter-chain spacings and more free volume available.\cite{13} This results in higher water uptakes and therefore higher conductivity. Mecerreyes \cite{29} et al reported an interesting way to adjust the microstructure of PBI membranes: the porous (pore size <100nm) PBI films were prepared by leaching out a low-molecular-weight compounds using a selective solvent of the porogen from polymer/porogen mixtures. Compared with the bulk polymers, the acid uptake of the membranes and therefore the ionic conductivity of the films increased with the porosity. Umeda and Uchida \cite{30} reported that by applying a external electric field of 2kV·cm\(^{-1}\), a polymer recast from a solution containing poly(acrylic acid), poly(vinyl butyral) and fluoroalkyl graft polymer exhibited 10 times higher proton conductivity than that prepared without electric field. SEM and AFM studies identified large hydrophilic domain in the polymer were formed under external-field treatment.
Controlling microstructure of the PEMs to improve the properties of PEMs is still an open field with a lot of potentials. Especially for H₃PO₄ and heterocycles based HT-PEMs, few works have been done to investigate the distribution and construction of hydrophilic domains containing proton conductors and proton donators and hydrophobic/less hydrophilic domains as polymer backbones, with their effects on the proton conductivity and mechanical properties of PEMs.

2.2 Membrane Electrode Assembly

At the heart of a functional PEM fuel cell is the membrane electrode assembly (MEA). The MEA in a single PEM fuel cell is pictured in Figure 15 (a). Typically, the MEA is between two flow field plates that are normally mirrored to make a bipolar plate when cells are stacked in series for higher voltages. The MEA consists of a polymer electrolyte membrane, catalyst layers and gas diffusion layers (GDL), and the electrode herein is considered as the components that span from the surface of the membrane to gas channel and current collectors.

As illustrated in Figure 2.11 (b), three typical transport processes happen in a PEMFC electrode: (1) The transport of protons from the PEM to the catalyst; (2) the transport of the electrons from the current collector/catalyst to the catalyst./current

![Figure 2.11](a) Schematic of A single PEMFC. (b) Triple phase boundary in electrodes
Collector through gas diffusion layer; (3) the transport of the reactant and product gases to and from the catalyst layer and the gas channels. The existences of triple phase (protons, electrons and gases) boundary in catalyst layer is critical to the efficiency of the catalyst and therefore the overall cell performance. Part of the optimization of an MEA design surrounds the topic of correctly balancing the transport processes through adjusting the distributions of the amount of volume in the catalyst layer between the transport media for each of the three phases to reduce transport losses.

2.2.1 **Gas Diffusion Layer**

The porous gas diffusion layer in PEMFC is responsible for (a) the effective diffusion of reactant and product gases to and from the catalyst layers, and (b) transport of electrons to and from the catalyst layer. The typical GDL is constructed from porous carbon paper or carbon cloth, and the thickness is in the range of 100-300µm. Also, in high humidity condition, the GDL assists in the water management by controlling the amount of water to reach and be held at the membrane for hydration. To prevent the congestion of pores of GDL by liquid water, Teflon coating is used in GDL for waterproof.

2.2.2 **Catalyst Layer**

The catalyst layer, referred as the active layer, directly contacts with the PEM and the GDL. The catalyst layer consists of the proton conducting materials (normally similar as the materials in PEM), the catalyst (typically platinum or platinum alloys) distributed (PTFE) on carbon black particles, and possibly the PTFE polymer as the bounding materials in some types of Nafion based PEMFCs. In Nafion based PEMFCs, the size of Pt/C agglomerates is around several hundred nanometers. With the development of catalyst preparation and MEA fabrication, the platinum loading has been lowered to 0.4 mg/cm² or even 0.014mg/cm² as reported, and the cost of the catalyst is no longer the major barrier to the commercialization of PEMFCs based on Nafion. However, for the
reported PEMFCs based on PBI-H₃PO₄ membranes, high platinum loading (0.5-1.0 mg/cm²) is required possibly due to the adsorption of the acid on platinum surface.

The catalyst layer needs to be porous for reactant and product gas diffusion. Therefore, there exists an optimum amount of proton conducting materials impregnated into the catalyst layer. Low loading will result in insufficient proton conduction to the catalyst surface and therefore increase the interfacial resistance. On the other hand, very high loading of the polymer may low the porosity of the catalyst layer and limit the mass transportation. Also, the stability of proton conducting materials in the catalyst layer is obviously another important factor for stable performance of the PEMFC.

2.2.3 MEA Fabrication

For Nafion based PEMFCs, there are mainly two modes for fabricating MEA with (1) the catalyst layer supported on the GDL and (2) the catalyst layer supported on the PEM.[31]

Figure 2.12 (a) illustrates the first fabricating mode. Typically, the catalyst particles are first bound to a hydrophobic PTFE, and then cast to the diffusion layer. In order to provide ionic conduction, the GDL supported catalyst layer is then impregnated with ionomers Nafion by brushing or spraying. The MEA is formed by sandwiching the PEM with two prepared catalyst layers with GDL and pressed to together at elevated temperatures and pressures. To apply catalyst on the GDL, other methods including vacuum deposition and electro-deposition have been investigated. Also, by optimizing the platinum content in the Pt/C catalyst particles, the impregnation of Nafion and other alternative membrane materials, and the hot-press procedure, the performance of the MEA has been improved and the platinum loading lowered.

The present convention in fabrication catalyst layers for PEMFCs is described in Figure 2.12 (b). Wilson [32] introduced this so-called “thin-film” technique in his 1993 patent. In this method, the catalyst particles mixed with Nafion in solvents to form
catalyst ink. Then the catalyst layer is applied to the each side of the PEM either by spraying the ink directly to the surface of the PEM or by transfer printing method in which the catalyst layer is cast to a PTFE blank first and then decaled on to the membrane from the PTFE blank by hot-press. The “thin-film” catalyst layers have been found to operate at almost twice the power density of PTFE-bound catalyst layers. Moreover, thin-film MEA manufacturing techniques are more established and applicable to stack fabrications.

For HT-PEMFC, current research interest is mainly on developing new PEMs. Systematic studies of MEA fabrication based on HT-PEMs will be after achieving a reliable and effective PEM. There are some researches [33,34] reported based on PBI-H$_3$PO$_4$ membranes by applying similar methods as for MEA fabrications based on Nafion.

Figure 2.12 Flow chart for the fabrication mode of the MEA with the catalyst layer (a) supported on the GDL, and (b) supported on the PEM.
2.3 References


32. Wilson, M. S., U.S. Pat. No. 5,234,777, **1993**.


CHAPTER 3
THEORY OF HYDROGEN BONDING AND PROTON CONDUCTION

3.1 Hydrogen Bonding and Hydrogen Transfer Reactions

As the only cation without electron shell, the proton has high charge density and inevitably interacts with the electron density of its environment. In nonmetallic compounds, the proton normally has strong interactions with the valence electron density of only one or two nearest neighbors. In the situation of one proton interacting with two neighbors, the proton may be involved in two bonds in the form of X---H----Y: a short, strong covalent bond with the proton donor (X= O, N, S, C, F..), and a longer, weak bond with a proton acceptor (Y=O, N, F, ..). This is so-called an asymmetrical hydrogen bond. In the case of a symmetrical hydrogen bond, two bonds are equivalent, such as in H₅O₂⁺.

The existence of hydrogen bond has been determined experimentally and theoretically [1-4]. The properties of a hydrogen bond that can be measured experimentally include: (1) the intermolecular distance of X and Y (hydrogen bond distance) in a complex with an X---H----Y hydrogen bond; (2) the binding enthalpy of the hydrogen-bonded complex; (3) the frequency shift of the X-H stretching vibration in the infrared (IR) spectrum of a complex as a consequence of hydrogen bonding; (4) the coupling constant ²Jxy between nuclei X and Y across the hydrogen bond. Hydrogen bond has been generally thought of as originating from electrostatic dipole-dipole interactions. However, the large J coupling between nuclei X and Y clearly identifies that the covalent nature of hydrogen bond is not negligible. [4] In more complicated “Blue-shifting” hydrogen bonds [5], the London dispersion energy turns to be the dominant stabilization energy contribution.

The hydrogen bond is a quite weak directional interaction, with the bond energy in the order of some kT (~0.1-0.6 eV) which is about one order of magnitude lower than
the energy of other types of chemical bonds. Therefore, the hydrogen bonding is very flexible and adaptable to its environment and sensitive to thermal fluctuations. With the existence of stronger bonds of both proton donor and acceptor, the hydrogen bond distance will be more confined.

Hydrogen bonding is important in both biological process and material properties. For proton conduction, it determines the conducting species, and may also get involved into the conducting process by providing a path for proton transfer from a proton donor to a proton acceptor. In few proton conductors, the proton transfer along hydrogen bonds appears to be the rate-limiting step. The proton transfer phenomenon is recently referred as a fundamental property of the hydrogen bond.

A typical hydrogen transfer process, as $X\text{—H—}Y \rightarrow X\text{—}H\text{—}Y$, is usually associated with an activation barrier along the reaction coordinate. As described by Kreuer [6], Figure 3.1 schematically illustrates the proton transfer between two adjacent oxygens, where the proton is covalently bond to one of the oxygen atoms and the proton-transfer coordinate is denoted $q$.

![Figure 3.1 Schematic of coordinates determining proton-transfer reactions: $q$, the proton position with respect to the center of the hydrogen bond; $Q$, the separation coordinate between donor and acceptor; $S$, the multi-dimensional solvent coordinate.](image_url)
If simply consider the surrounding solvent molecules as a static, isotropic environment, the potential $E(Q, q)$ along the hydrogen bond is presented as a double-well curve, as described in figure 3.2(a) which is symmetrical due to the symmetrical hydrogen bond. The energy barrier of the proton transfer reaction is decreased with the decreasing separation of proton donor and acceptor. Previous semi-empirical calculations [7] show that for the hydrogen bond of R-O-H---O-R, $E_Q(q)$ is $\sim 1\text{eV}$ when $Q=300\text{pm}$, and for $Q$ below $\sim 250\text{nm}$, it is eventually lower than the zero point energy ($\sim 0.19\text{eV}$) of the OH oscillator.

In a rigid array of proton donors and acceptors, the proton vibration provides the necessary activation enthalpy, and the attempt frequency is comparable with the donor/acceptor stretching frequency ($\sim 10^{14} \text{ s}^{-1}$ for OH). In Figure 3.2(b), the fluctuation of coordinate $Q$ lowers the energy barriers and it may open proton transfer pathways with faster transfer rate. In some limited cases, the position of the proton is fixed and no excitation of the proton transfer coordinate $q$ involved. This is so-called “adiabatic” proton transfer (Figure 3.2 (c)), which is completed only by the moving of proton donor and acceptor, and the attempt frequency is normally one to two orders of magnitudes lower.

Figure 3.2 Different proton transfer modes in the potential $E(q, Q)$. Dashed lines indicate the transition states. [6]
By considering the solvent coordinates $S$ for the proton transfer potential, especially when hydrogen bonds are mutually involved in solvent interactions, there are two major implications: (1) self-localization: the solvent accommodates to the particular position of the proton in the hydrogen bond, stabilizes the position energetically and polarizes the hydrogen bond. (2) The solvent fluctuations may lead to the solvent-induced proton-transfer process. In polar solvent, for the symmetrical hydrogen bonds, the two possible sites become inequivalent. Also, with the temperature decreasing and the proton transfer rate decreasing, the self-localization becomes static in the low-temperature phase other than transient in the high-temperature phase. For the system with strong proton/proton interactions, the temperature for this phase transition is normally higher than the decomposition or melting point of the compound.

### 3.2 Proton Conduction Mechanism.

Kreuer described animatedly two typical proton conduction mechanism in his previous paper as shown in Figure 3.3. The Grotthuss Mechanism, also known as “hopping” or “structure diffusion” mechanism, was proposed by von Grotthuss as early as 1806 (Figure 3.3, top). The process consists of two steps: (1) the proton translation motion along the hydrogen bond through a proton transfer reaction; (2) the subsequent reorientation (rotation) of the proton donors and acceptors thus formed for a continuous

![Proton Conduction Mechanism](image)

Figure 3.3 Proton conduction mechanism. Top: Grotthuss Mechanism. Bottom: Vehicle mechanism
proton-transport trajectory. The Grotthuss Mechanism is believed to be responsible for the proton conduction in ice, inorganic solids and proteins. The Vehicle Mechanism (Figure 3.3, bottom) means the proton bonds to a “vehicle” such as H₂O or NH₃ and migrate. The relevant rate for the observed conductivity depends on the molecular diffusion rate of the protonated vehicle. In aqueous solution or proton conducting materials using small molecules as conducting groups, the Vehicle Mechanism may play an important role.

For Grotthuss Mechanism, there still exist some arguments in details. As in water or imidazole, long range hydrogen bonding chain may be formed due to the proton donating and accepting ability in one single molecule. When an extra proton from acids enters into the chain, proton transfer reactions may happen synchronously as in a “domino set”, through the part or the whole of hydrogen bonding chain length (Figure 3.4). However, this mechanism still needs theoretical and experimental evidence. Also, in the system having only proton accepting sites, extra protons introduced only can be conducted step-by-step through independent events of proton transfer reactions.[9]

![Figure 3.4 A possible synchronous proton transfer mechanism](image)

Detailed studies of proton conducting process in inorganic and organic proton conductors have been studied extensively.[10-13] For HT PEMs, especially when consider a fully polymerized membrane in which the proton conducting groups and proton
donating groups are fixed to the polymer backbones, the dynamic diffusion of charge species is limited. As a result, the Gra thuss Mechanism other than the Vehicle Mechanism may play the major role for proton conduction in those systems.

### 3.3 Theoretical Studies of Proton Conduction Mechanism

To study proton conduction process in PEMs, different experimental techniques has been applied. However, due to the complexity of the proton conduction process and the absence of output signals resulted from a single proton transfer step, theoretical modeling has proved to be a more powerful method to understand the detailed conduction mechanism and different factors related to the conductivity of materials.

Quantum mechanical (QM) calculations or quantum chemistry is to calculate the stationary states of the molecules and the transition between these states base on quantum mechanics. By solving the time-independent Schrödinger equation (3.1),

$$H(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) \quad (3.1)$$

The molecular wave function, $\Psi(\mathbf{r}, \mathbf{R})$ is yield, in which $\mathbf{r}$ represents the $3n$ coordinates of all $n$ electrons, and $\mathbf{R}$ as the coordinates of all $A$ nuclei, and the total molecular energy, $E(\mathbf{R})$, is parametrically dependent only on the nuclear positions. Here, the Hamiltonian, $H(\mathbf{r}, \mathbf{R})$ is an operator and its explicit form in atomic units is

$$H = -\frac{\hbar^2}{2} \sum_i \frac{\nabla^2_{\mathbf{r}_i}}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla^2_{\mathbf{r}_e}}{m_e} - \frac{1}{4\pi\varepsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{8\pi\varepsilon_0} \sum_{i\neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{8\pi\varepsilon_0} \sum_{i\neq j} \frac{e^2 Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (3.2)$$

Where the mass of the $i$th nucleus at $\mathbf{R}_i$ is $M_i$; the $j$th electron with mass $m_j$ is located at $\mathbf{r}_j$. The first two terms are the kinetic energy operators for the nuclei and electrons, respectively. The last three terms are the Coulomb interaction between electrons and nuclei, between electrons and other electrons, and between nuclei and other nuclei, respectively. It is impossible to solve this equation exactly. Therefore, an approximation
must be applied to find acceptable eigenstates from the equation: (1) With Hartree-Fock approximation \cite{14,15}, the function of 3n variables for the exact equations is reduced to be n molecular orbitals of three variables. Every molecular orbital describes the probability distribution of one single electron moving in the average field of all other electrons. By minimizing E(R) variationally, the optimum molecular orbitals are determined. Based on Hartree-Fock approximation, a given, fixed and finite set of functions referenced as the atomic orbital basis set can be applied to expand the unknown molecular orbitals for further approximation.\cite{16} The use of large basis sets may bring high accuracy but is very time-consuming at the same time. (2) Different from Hartree-Fock approximation \cite{17}, density functional theory (DFT) seeks to determine the exact ground state energy and electron density directly, without solving a many-electron wave function. DFT relies on two fundamental theorems: (a) The external potential v(r), the ground-state energy \(E_{\text{vfo}}[n(r)]\) and all properties of the ground state is determined by the ground-state electron density \(n(r)\). (b) Given the functionals of kinetic energy \(T_s[n(r)]\) and exchange correlation energy \(E_{\text{xc}}[n(r)]\), the energy is minimized, thereby providing a variational principle to determine the density. DFT simplified the calculations dramatically and has been a powerful method for modeling large molecules.

QM calculations have been used in studies of proton conduction in PEMs to identify the local structure, the hydrophobicity or hydrophilicity of the fragments, proton dissociation of acid groups, aggregations of groups through hydrogen bonds. Due to the limited size of calculated system (<100 atoms typically), the set-up of environment around the calculated system always has large influence on the final results. Paddison et al. \cite{18} have done a series of first-principles-based electronic structure calculations for
perfluorosulfonic acid polymers. They began their work by concerning the interaction of water with the terminal portion of the side chains of Nafion, probed the acidity of CF$_3$SO$_3$H with a single water molecule and determined a transition state consisting of the ion pair CF$_3$SO$_3$$^-$ and H$_3$O$^+$ with an activation energy of 4.7 kcal/mol after inclusion of electrostatic free energy. Subsequently, they conducted a series of explicit water electronic structure calculations with both triflic and para-toluene sulfonic acids. By systematically adding water molecules, they found that no dissociation of the proton was observed with both acids until three water molecules were added, and when a sixth water molecule is added, a complete separation of the excess proton from the anion takes places, as shown in Figure 3.5 [18]. This suggests that with sufficient water, the proton is shielded from direct electrostatic interaction with the sulfonate anion by an intermediate layer of water molecules. Also, they performed QM calculations on the fragment of the

![Figure 3.5 Separation of the hydrated proton from the conjugate anion: (a) triflic acid and (b) para-toluene sulfonic acid. Shown are fully optimized (B3LYP=6-31G**) conformations for clusters with six water molecules.](image)
Dow PEM consisting of two side chains, and the results (Figure 3.6) show that the di-sulfonic acid polymer fragments, compared with the single triflic acid water cluster, do not require a water content of at least $3\text{H}_2\text{O}/\text{SO}_3\text{H}$ for some proton dissociation to occur, due to the interaction between two sulfonic acid groups.

![Figure 3.6](image)

Figure 3.6 Fully optimized (B3LYP/6-31G**) conformations for a two-side chain fragment of the Dow PEM (a) without water and (b) with four water molecules.

Another principal tool in the theoretical study of proton conducting materials is molecular dynamics (MD) simulation, where atoms and molecules are allowed to interact for a period of time under classical laws of physics.[19] For molecular systems with a large number of atoms, it is impossible to find the properties of such complex systems analytically. MD simulation circumvents this problem by using numerical methods. The implemented predetermined potentials in MD referenced as force field, are either empirical or derived from independent electronic structure calculations to describe or approximate the inter-atomic interactions. Through calculation of the time dependent behavior of a molecular system within certain force field, MD simulations provide detailed information about proton conducting process, proton diffusion rate in the material, as well as the fluctuations and conformational changes of the polymer material. Deng et al.[20] have investigated the proton diffusion in imidazole and trifluoroimidazole.
impregnated Nafion membranes using classical MD simulations. The periodic simulation cell for calculation contains four Nafion chains, 40 imidazolium (or trifluoroimidazolium) and 80 neutral imidazole (or trifluoroimidazole). The vehicular diffusion of the protonated molecules was calculated from the slope of the mean square displacement (MSD) with time:

\[
D_{\text{MSD}} = \lim_{t \to \infty} \frac{\left\langle \left( \vec{r}(t) - \vec{r}(0) \right)^2 \right\rangle}{6t} \quad (3.3)
\]

where \( r \) is the position vector and \( t \) is the time, and the brackets indicate an average over all the protonated carriers in the system and over the equilibrium trajectory. The proton transfer rate \( k(r) \) through the hydrogen bond and the diffusion rate \( D_H \) through hopping were also calculated as:

\[
k(r) = \kappa(T, r) \frac{k_B T}{2 \pi \hbar} \exp\left(-\frac{E_b(r) - \hbar \omega_1(r)/2}{k_B T}\right) \quad (3.4)
\]

\[
D_H = \frac{1}{6Nt} \int_0^\infty \sum_i \sum_j k_{ij} r_{ij}^2 P_{ij} dt \quad (3.5)
\]

where \( r \) is the distance between the proton donor and acceptor N atoms, \( E_b(r) \) is the energy barrier to transfer the proton between these N atoms, \( \omega_1(r) \) is the frequency of the zero point energy correction, \( k_{ij} \) is the hopping rate from the \( i \)th protonated carrier to the \( j \)th neutral one, and \( P_{ij} \) is the probability of an ion being able to jump from site \( i \) to site \( j \).

Ab initio Molecular Dynamics (AIMD) simulation provides a way to combine classic MD simulation with QM calculations, which basically computes the forces acting on the nuclei from electron structure calculations that are performed at each MD time step in the generated trajectory of the molecules. Therefore, one important aspect of AIMD is to choose a particular approximation for solution of the Schrödinger equation to approximate the inter-atomic interactions. Due to the covalent nature of hydrogen bonds and quantum chemical process for a proton transfer reaction, AIMD is considered as a more accurate method to describe dynamic proton conducting process in a hydrogen
bonding network. However, the correlation lengths and relaxation times that are accessible are much smaller than via classic MD simulations. Münch et al. have reported the Car-Parrinello-type *ab initio* molecular dynamics (CPMD) simulations \(^{21}\) for the diffusion mechanism of an excess proton in imidazole molecule chains, as shown in Figure 3.7 \(^{22}\). The results show that the proton diffusion through a Grotthuss mechanism involves proton transfer and reorientation of the imidazole ring, which is a local rather than long-range cooperative process. Compared with the fast proton transfer step (~0.3 ps at \(T=390\text{K}\)), the reorientation step is found to be the rate-determining step, for which the time scale is estimated to be approximately 30 ps at \(T=390\text{K}\).

![Figure 3.7 Possible proton transfer process in imidazole.](image)

\(^{21}\) Münch, et al., \(\text{J} \) \(\text{Am. Chem. Soc.}\) \(\text{J}\) (2023).  
\(^{22}\) Münch, et al., \(\text{J} \) \(\text{Am. Chem. Soc.}\) \(\text{J}\) (2023).
3.3 References


CHAPTER 4

1H(2H)-1,2,3-TRIAZOLE AS PROTON CONDUCTORS

4.1 Introduction

Proton-conducting membranes are a critical component to fuel cells, reforming of biomass and hydrocarbon fuels, hydrogen separation/purification, contaminant removal, gas sensing, and other processes relevant to energy storage and conversion. The development of novel electrolyte membranes with dense structure, good mechanical flexibility, and high proton conductivity, but with little or no dependence on humidity at temperatures above 100°C remains an important challenge to the realization of practical PEM fuel cells. Compared with the extensively studied perfluorosulfonic polymer membranes [1, 2, 3] in which the proton conductivity depends critically on humidity, PEMs based on H₃PO₄ [4], imidazole [5] and other functional groups [6, 7] may allow fuel cell operation above 100°C without the need of humidification, which could minimize or eliminate some of the key difficulties facing PEM fuel cells, including CO poisoning and the management of water, heat, and pressure. To date, however, the application of these membranes in fuel cells is still problematic because of their low proton conductivity or inadequate stability under practical fuel cell operating conditions.

Heterocycles such as imidazole were studied by Kreuer et al. [5] as proton solvent in PEMs for fuel cells. The conductivity of liquid imidazole was reported [8] as high as 10⁻³ S/cm at the melting point of T_m= 90 °C. It was proposed [9] that imidazole conducts proton through intermolecular proton transfer (Figure 4.1). The introduction of imidazole has generated much excitement in recent years with the hope that the investigations of imidazole-based polymer electrolytes may lead to PEMs with high proton conductivity, good mechanical properties, and long-term stabilities. [10-14] Unfortunately, the electrochemical stability of the imidazole group appears to be inadequate for fuel cell
applications\textsuperscript{[15]}. To date, functional fuel cells based on imidazole-containing PEMs are yet to be demonstrated.

1\textit{H}-1,2,3-triazole (Figure 4.1) has a similar molecular structure as that of imidazole and thus may conduct proton via a similar mechanism as in imidazole. Unlike imidazole ($T_m=90^\circ\text{C}$), 1\textit{H}-1,2,3-triazole ($T_m=23^\circ\text{C}$) is a liquid at room temperature. Also, 1\textit{H}-1,2,3-triazole has a tautomer 2\textit{H}-1,2,3-triazole (Figure 4.1), and the tautomerism may happen through intra- or inter-molecular proton transfer\textsuperscript{[16]}. Although 2\textit{H}-1,2,3-triazole is more stable in the gas phase, 1\textit{H}-1,2,3-triazole becomes more stable in solution\textsuperscript{[17]} because of its larger dipole moment. Also, 1\textit{H}-1,2,3-triazole ($\text{PKa}_1=1.17$, $\text{PKa}_2=9.26$)\textsuperscript{[18]} is much more acidic than imidazole ($\text{PKa}_1=7.18$, $\text{PKa}_2=14.52$)\textsuperscript{[19, 20]}, which may significantly influence proton conduction of 1\textit{H}-1,2,3-triazole-based solid electrolytes. In this chapter, the proton conducting ability and electrochemical stability of 1\textit{H}-1,2,3-triazole has been studied to identify it as a new type of proton conductors practical for HT-PEMFC applications. For comparison, electrochemical stability including previous reported poisoning effect of imidazole to platinum of imidazole has been studied both experimentally and theoretically.

Figure 4.1 Structures of imidazole and 1\textit{H}-1,2,3-triazole
4.2 Experimental Section

Chemicals: $1H$-1,2,3-triazole, imidazole, sulforic acid, phenylsulfonic acid, phenylphosphonic acid, benzenesulfonamide, polysulfone polymer (average $M_n$ ca. 26,000), chlorosulfonic acid, Tetrabutylammonium hexafluorophosphate (TBAPF6), dichloroethane were purchased from Aldrich. Other solvents and chemicals used were purchase from VWR. 18MΩ deionized water used for pH titration analysis was obtained from a Millipore Milli-Q system.

Preparation and Characterization of Sulfonated Polysulfone: Sulfonated polysulfone (sPSU) was prepared as described in Figure 4.2: 15g PSU (~0.017 mol repeat unit) was dissolved into 200ml dichloroethane. With nitrogen gas purging and rigorous stirring, 2.66ml (~0.04mol) chlorosulfonic acid in 46ml dichloroethane was added into the polymer solution dropwise in 2 hours. For another experiment, 1.33ml (~0.02mol) chlorosulfonic acid was used to prepare sPSU with lower sulfonation degree. After adding acids, the mixture was kept stirred overnight. The product was precipitated from the solution and separated by filtration, followed by washing with ethanol and water for several times. The prepared sPSU polymer was dried at 120°C under vacuum for two weeks before transferred into a glovebox filled with dry argon. Thermogravimetric analysis (TGA) was performed on a Rheometric Scientific STA 1500 to confirm the removal of water from the polymer. The ion-exchange capacity (IEC) of the sPSU was determined using $^1H$ NMR in d$_6$-DMSO and pH back titration. For the titration, the

![Figure 4.2 Preparation of sulfonated polysulfone polymer](image)

Figure 4.2 Preparation of sulfonated polysulfone polymer
weighted polymer sample was soaked into 20ml 0.100 mol/l standard NaOH solution and sealed overnight. The HCl solution with known concentration was used for the back titration. The ion exchange capacity of the sulfonated polymer was determined from the average of three trials.

**Preparation of sPSU/triazole membranes**: To incorporate triazole into the sPSU to form sPSU-triazole membranes, dried sPSU (IEC of 1.40 mequiv/g) polymers were immersed in pure liquid 1H-1,2,3-triazole and sealed in a glass vial. Upon heating to 90°C and kept for 24 hours, triazole was imbedded into the polymer. The ratio of [1H-1,2,3-triazole] to [-SO₃H] was calculated from the weight of the polymer before and after immersion in 1H-1,2,3-triazole. Three samples with different ratio were prepared.

**Conductivity Measurements**: A Solartron 1255 frequency response analyser and a Solartron 1286 potentiostate/galvanostat interfaced with a computer were used for conductivity measurements. Shown in Figure 4.3 (a), for liquid sample, the ionic conductivity was measured in a typical conductivity cell with two platinum electrodes. Sample preparation and conductivity measurements were performed inside the glove box

![Figure 4.3](image_url)

Figure 4.3 Experimental set-up for conductivity measurements of (a) liquid and (b) membrane samples.
dried with P₂O₅. To measure the conductivity of various acids-triazole solutions, the liquid or solid acids were added in batches into triazole solution, and the solutions was weighted and tested, until the precipitation has been formed in the solution. 0.1 M KCl aqueous solution was used as the standard solution and it has the conductivity of 0.01264 S/cm at 24°C. For polymer membranes, a conductivity cell (Figure 4.3 (b)) with two stainless pellets as electrodes were used. Cells were assembled and sealed inside the glove box dried with P₂O₅ but the conductivity measurements were performed outside of the glove box with a constant flow of dry air through the conductivity cell.

1H-PFG-NMR Experiments: A measure of the translational motion of a molecule is called self-diffusion. From reference [21], “Pulsed-field gradient (PFG) NMR can be used to measure translational diffusion by applying externally controlled magnetic field gradients. These gradients spatially encode the position of each nuclear spin. This spatial distribution can be decoded after waiting a short time by applying a second gradient. The spins that have moved during the waiting time between the encoding and decoding steps will acquire a net phase change. The summation of the accumulated phases over the entire sample will lead to partial cancellation of the observable magnetization and hence an attenuation of the NMR signal. This signal attenuation is dependent on the strength of the applied gradients, the time between the gradients (diffusion time) and the diffusion coefficient of the molecules under study.” The decrease in signal intensity as a function of gradient strength can be described by the Stejskal Tanner equation 4.1

\[ I(q) = I_0 e^{-Dq^2 \Delta'} \]  

where \( D \) is the diffusion coefficient, \( \Delta' = \Delta - \delta/3 \) where \( \delta \) is the diffusion time and \( \delta \) is a correction factor for finite gradients. \( q = \gamma g \delta \), \( \gamma \) is the gyromagnetic ratio, where \( g \) is the amplitude of the applied gradient and \( \delta \) is the duration of the applied gradient. A plot of \( I(q) \) versus \( q^2 \Delta' \) yields an exponential decay curve which is fitted to obtain the diffusion coefficient.”
To measure the samples from 50 to 150°C, stimulated Echo sequence ran on a MARAN 23 (Resonance Instruments benchtop spectrometer) operating at 23 MHz. $\Delta$ was 100 ms, and varied in steps ranging between 0.5 and 3 ms to produce a data set with varying echo intensities. Echo intensities were fitted through the Stejskal Tanner equation to obtain the diffusion coefficient.

**Cyclic Voltammetry Experiments:** A typical three-electrode cell was first filled with 0.1 mol·dm$^{-3}$ CH$_3$CN solution of TBAPF$_6$ as the electrolyte. To study the electrochemical stability, 1H-1,2,3-triazole or imidazole dissolved in CH$_3$CN was added to make the final concentration equal to 5×10$^{-3}$ mol·dm$^{-3}$. The solution was purged with N$_2$ or O$_2$ for 30 min with ~30 ml/min flow rate before measurements and with very low flow rate during the test. Cyclic voltammetric measurements were performed with potential sweep rate of 50 mV/s using a platinum work electrode, a platinum auxiliary electrode and an Ag/Ag$^+$ reference electrode (0.1 mol·dm$^{-3}$ AgNO$_3$-CH$_3$CN containing 0.1 mol·dm$^{-3}$ TBAPF$_6$). The data were recorded using a solartron 1286 potentiostate/galvanostate interfaced with a computer. After measurements of imidazole, the surface of the Pt electrode was polished carefully using TExMET® 1000 polishing cloths from Buehler and cleaned with deionized water.

**Fuel Cell Tests of sPSU/Triazole Membranes:** To directly verify that 1H-1,2,3-triazole are electrochemically stable under fuel cell operating conditions, the fuel cell performance of sPSU doped with 1H-1,2,3-triazole was studied. The polymer was hotpressed to form ~300 µm thin membranes. 1H-1,2,3-Triazole in ethanol were first added to two 5 cm$^2$ Pt electrodes (HT 250E-W high temperature ELAT® GDE microporous layer with 5 g/m$^2$ Pt loading from E-Tech) and dried at 60°C. By sandwiching the sPSU-tirazole polymer membrane between two electrodes and hotpressed at 80°C, 0.5t pressure for several minutes, the resulted MEA was put into a
typical 5cm² single cell for fuel cell tests, as shown in Figure 4.4. After assembling the cell, the nitrogen flow rates of gas inlet and outlet of cathode and anode sides of the cell were measured with a glass bubbler flow meter to avoid gas leaking of the cell. For tests, Dry H₂ and O₂ (as fuel and oxidant, respectively at 50ml/min) were supplied to the cell (5cm²) without any humidification. The temperature was controlled by a thermocouple temperature sensor plugged in one side of the cell. The data were recorded using a solartron 1286 potentiostate/galvanostate interfaced with a computer.

Computational details (Collaboration with Dr. Jenhang Wang): To study the poisoning mechanism of imidazole to Pt electrodes, as described in Reference [22], “the surface adsorptions of imidazole and 1H-1,2,3-triazole are studied by Vienna ab initio simulation package (VASP), implementing density functional theory (DFT). The exchange-correlation function treated with the generalized gradient approximation (GGA) with the Perdew-Wang 1991 (PW91) formulation, and the projector-augmented wave method (PAW), an all-electron method combining the accuracy of augmented plane waves with the cost-effective pseudopotentials implemented in VASP, are applied for the calculation.
A 32-Pt super cell with dimension of $2a \times 2a \times 2a$ along (100) x (010) and (001) directions, $5 \times 5 \times 5$ Monkhorst-Pack $k$-points, and a 400-eV cutoff energy are employed for the bulk calculation. The computed lattice constant, 3.99 Å, is in good agreement with the experimental value of 3.92 Å$^{20}$ and the computational value of 4.01 Å.

The super cell to model the Pt(111) surface is a three-layer slab with 20-Å vacuum space. Each layer, a $(\sqrt{6} \times \sqrt{2})$ surface with eight Pt atoms, has a surface area of $9.778 \times 5.645 \text{ Å}^2$. The employed surface area and vacuum space, similar to previous work, are considered to be large enough to avoid any the interactions from neighboring absorbed species. The Monkhorst-Pack $k$-points is set as $3 \times 5 \times 1$ along (112) x (110) x (111) directions, respectively, and the cutoff energy is kept at 400 eV. The top two layers are relaxed and bottom one layer is fixed at computed lattice constant during the optimization. The computed -42.8 kcal/mol adsorption energy of CO/Pt(111) system at atop site agrees well with the value (-44.7 kcal/mol) in calorimetric experiment with low CO coverage, which indicates the validation of the calculation at current level.

The electrochemical properties are computed by Gaussian03 packages. The standard redox potential of interested species can be predicted by applying the polarized continuum model (PCM) on a reliable gas-phase adiabatic ionization potential (IP), which can be computed by a hybrid Hartree-Fock/density functional theory (HF/DFT) method (B3LPY), including Becke’s three-parameter nonlocal-exchange function with the correlation functional of Lee-Yang-Parr, and the standard all-electron split-valence basis set 6-311++G(2df,2p). This method to predict the redox potentials was proven to be trustworthy by examining 270 structurally unrelated organic molecules in the previous work and was applied for current study.”
4.3 Experimental Results and Discussions

The ionic conductivity of liquid $1H$-1,2,3-triazole was measured for the first time in the temperature range of 25°C to 80°C, shown in Figure 4.5. The charged species are certainly from the self-dissociation of triazole molecules. By further increasing temperature, there existed noticeable evaporation of $1H$-1,2,3-Triazole. At room temperature, close to the melting point (23°C) of $1H$-1,2,3-triazole, the conductivity of triazole is $1.3 \times 10^{-4}$ S/cm. Imidazole as shown in at the melting point of 90°C, has the conductivity around $\sim 10^{-3}$ s/cm estimated from Figure 4.6. In liquid form at same temperature, the conductivity of imidazole should be slightly higher than that of triazole. Based on the equation $\sigma \cdot T = \sigma_0 \cdot \exp(-E_a/RT)$, if neglect the concentration change of charged species at elevated temperature, the estimated apparent activation energy of proton conduction in triazole is around 24 kJ/mol, which is similar as that for imidazole, and also close to the

![Chemical reaction and graph](image)

Figure 4.5 Temperature dependence of ionic conductivity of $1H$-1,2,3-triazole.
Figure 4.6 Temperature dependence of ionic conductivity of imidazole (Ο-) and 1H-1,2,3-triazole (→).

The activation energy for water in Nafion (~21kJ/mol) and H₃PO₄ in PBI membranes (~24kJ/mol).

Different inorganic and organic acids were dissolved into triazole and Figure 4.7 describes the relation between the ratio of $\sigma_{\text{acid,solution}} / \sigma_{\text{triazole}}$ and the molar ratio of acid to triazole. First, by adding small amount of strong acids to triazole, the conductivity of the solution was dramatically increased, compared with the conductivity of triazole liquid, due to the increase of charged species from the proton transfer reactions between triazoles and acid groups. When the molar ratio of acid to triazole was around 5% to 6%, the conductivity reached to the maximum. By adding more acid, the conductivity could not be further improved due to the significant increase of viscosity of the solution, which lowered the mobility of charged species in the solution. The measurements were stopped when there were insoluble salts formed in the solution. Secondly, stronger acids such as phenylsulfonic acid and sulfuric acid may dissociate proton more effectively, therefore
improved the proton conductivity of the solution more effective than the weaker acids including phenylphosphonic acid and benzenesulfonamide.

![Figure 4.7](image)

Figure 4.7 Conductivity increase of various acids/1H-1,2,3-triazole solutions with increased acid concentration at room temperature.

The highest conductivity for these solutions was around 0.014S/cm. From the data, we didn’t observe the size effect of acid molecules on the proton conductivity. It is possible that the protonated triazoles were mainly responsible for the measured conductivity.

Previous studies [5] reported by doping imidazole to Nafion or sPEEK sulfonated polymers, the resulted polymer membranes showed high proton conductivities at elevated temperature. For our experiments, we chose polysulfone(PSU), one type of engineering polymers. Polysulfone is rigid and transparent thermoplastic materials with good thermal stability and mechanic strength, and its glass transition temperature is around 185°C. The
sulfonation process of PSU has been studied in details. Sulfonation through chlorosulfonic acid in dichloroethane is a mild method, in which the sulfonation degree can be controlled by adjusting the usage of the chlorosulfonic acid.

The $^1$H NMR data of polysulfone and the synthesized sPSU were shown in Figure 4.8. After sulfonation, two resonance peaks of protons on the aromatic rings around 6.8-7.4ppm and 7.5-8.0ppm on PSU were split. Based on Noshay and Robeson’ studies $^{23}$, the sulfonation degree $f$ can be calculated from the equation 4.2:

$$f = \frac{12 - 4R}{2 + R} \quad (4.2)$$

where $R$ is the ratio between the integrated area $S_1$ (6.8-7.4ppm) and $S_2$ (7.5-8.0ppm). From $f$, we can calculate the ion exchange capacity (IEC) of the sPSU sample from the equation 4.3:
Table 4.1 IECs of sPSU samples determined by $^1$H NMR and pH titration.

<table>
<thead>
<tr>
<th></th>
<th>sPSU_1</th>
<th>sPSU_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEC by $^1$H NMR</td>
<td>1.56mmol/g</td>
<td>1.41mmol/g</td>
</tr>
<tr>
<td>IEC by pH titration</td>
<td>1.42mmol/g</td>
<td>1.39mmol/g</td>
</tr>
</tbody>
</table>

Also pH back titration was used to determine the IEC of the sPSU and shown in Table 4.1. Because of much smaller sampling scale of $^1$H NMR, pH titration provided more reliable data with less error, especially for sPSU with low sulfonation degree. The product with high IEC was more brittle and powder-like with darker colour. sPSU_1 with IEC= 1.40mmol/g was chosen for further experiments.

![Figure 4.9 Ionic conductivities of 1H-1,2,3-triazole intercalated into sulfonated polysulfone polymer membranes with three different ratio of [1H-1,2,3-triazole] to [-SO$_3$H].](image-url)
By heating sPSU with liquid triazole, homogenous, elastic polymer solids were formed. The conductivities of different samples with different molar ratio of triazole to sulfonic acid groups were reported in Figure 4.9. First, at same temperature, by increasing the molar ratio of triazole to sulfonic acids from 4.9 to 8.3, the conductivity of the polymer was improved. However, from the studies of acid-triazole solutions, it is believed that further increasing the ratio of [triazole]/[acid] may result in the conductivity decrease. Secondly, by increasing the temperature from room temperature to 120°C, the conductivity of the polymer was increased. During the experiment, we found that by keeping the polymer at 120°C for few hours, the measured conductivity gradually decreased, which was resulted from the losing of triazole by slow evaporation. In Figure 4.10, previously reported data for imidazole/sPEEK was shown to compare with triazole/sPSU. Triazole and imidazole in sulfonated polymer have similar activation energy for proton conduction, but significantly higher than that for liquid triazole or water in sulfonated polymer, which is possibly due to the limited mobility of molecules in polymer matrix and larger volume of heterocycles. Above all, the high proton conductivity of triazole/sPSU polymer in relatively low temperature range makes it promising for designing new fully polymerized HT-PEMs.

Figure 4.10 Temperature dependence of ionic conductivity of (a) 1H-1,2,3-triazole/sPSU and (b) imidazole/sPEEK.
\(^1\)H PFG-NMR experiments have been performed on Liquid 1\(H\)-1,2,3-triazole and the triazole/sPSU with \(n=8.3\). By plotting \(\ln(I/I_0)\) against \((\gamma g\delta)^2(\Delta-\delta/3)\), the diffusion coefficient of the tested sample was derived from the slope of the fit line. The data of liquid triazole and triazole/sPUS were shown in Figure 4.11 and Figure 4.12 respectively. For all experiments, various protons were not differentiated. For polymer samples, the influence of protons on polymer backbones was neglected due to the low diffusion rate of the polymer compared to small heterocycles. The temperature dependence of diffusion coefficients of imidazole, 1\(H\)-1,2,3-triazole, imidazole/sPEEK, triazole/sPSU were illustrated in Figure 4.13.

![Graphs showing diffusion coefficients](image)

Figure 4.11 Diffusion Coefficients of 1\(H\)-1,2,3-Triazole by \(^1\)H PFG-NMR
Figure 4.12 Diffusion Coefficients of Triazole/sPSU ([Triazole]/[-SO_3H]=8.3) by $^1$H PFG-NMR
Figure 4.13 Conductivity and self-diffusion coefficient ($D_\sigma$ and $D_H$) for imidazole and 1H-1,2,3-triazole intercalated into sulfonated polymers. The self-diffusion coefficient of protons in liquid imidazole and triazole are shown for comparison.

If assume the ionic conductivity is totally from the translation motion of protonated species, we can calculate the coefficient $D_\sigma$ from the Nernst-Einstein equation:

$$\sigma = \frac{c_i D_{ii} z^2 F^2}{RT} \quad (4.4)$$

For triazole/sPSU with $[\text{triazole}]/[-\text{SO}_3\text{H}] \approx 8.3$, the measured density is 1.03g/cm$^3$ and $F$ equals 96485 s·A/mol, and it is assumed that the sulfonic acid groups in the membrane are completely dissociated and $C_{\text{H}^+} = C_{\text{SO}_3\text{H}}$ in the calculation of $D_\sigma$. The self-diffusion coefficient $D_H$ of imidazole or triazole in the polymers measured from $^1$H PFG-NMR is assumed to be close to the diffusion coefficient of protonated species but should be higher theoretically. As shown in Figure 4.13, for triazole/sPSU, $D_\sigma/ D_H$ is about 4.0,
which means most of the proton conduction in the materials is not from the self-diffusion of the protonated triazoles. The proton conduction through structure diffusion (or Grothus mechanism) plays a major role in the system. For imidazole/sPEEK (n=6.7), $D_\sigma/D_H$ is around 2.6. Previous studies reported that $D_\sigma/D_H$ decreased with the molar ratio of imidazole to acids decreasing from 6.7 to 2.3, which shows that for structure diffusion of protons, the intermolecular distance between proton conducting groups is an important factor.

Besides proton conducting ability, the electrochemical stability is another important issue for applying triazoles for PEM fuel cell applications. The Cyclic voltammetry experiments have been done for both imidazole and 1H-1,2,3-triazole in organic electrolyte solution at room temperature, and the I-V curves were shown in Figure 4.14.

Figure 4.14 Typical cyclic voltammograms of imidazole (curve 2) and triazole (curve 3) with baseline (curve 1), $C=5\times10^{-3}$ mol dm$^{-3}$ in 0.1 mol dm$^{-3}$ TBAPF6-CH3CN solution.
As shown in Figure 4.14, for $1H$-1,2,3-Triazole, in the voltage range of 0.0-1.8V vs $Ag^+/Ag$ in CH$_3$CN (NHE= $Ag^+/Ag$ - 0.54V), there was no oxidation peaks appeared. Also, the multiple-cycle scans up to 50-100 cycles in N$_2$ or O$_2$ condition presented almost the same I-V curves for the triazole solution.

By adding imidazole to the triazole solution or using imidazole solution separately, during the first cycle, we observed a broad irreversible oxidation peak around 1.0V (~1.5V vs NHE). For a typical H$_2$-fueled PEM fuel cell, the OCV is around 1.0V-1.2V. The cyclic voltammetry experiments proved that imidazole was not stable enough under this condition. As illustrated in Figure 4.15, during the experiment, we found that after first cycle, the current density of the oxidation peak decreased in the flowing cycles, and the peak finally disappeared after several cycles. Refreshing the imidazole solution

![Cyclic voltammograms of $5 \times 10^{-3}$ mol·dm$^{-3}$ imidazole in 0.1 mol·dm$^{-3}$ TBAPF6-CH3CN solution. (curve 1: baseline, 2: the 1$^{st}$ cycle, 3: the 2$^{nd}$ cycle, 4: the 5$^{th}$ cycle)](image-url)
could not repeat the oxidation peak. Only when we took the Pt working electrode out of the solution and polished the surface, the oxidation peak appeared again. Obviously, there were some absorbed species on the Pt surface resulting in the malfunction of electrodes. Also, it was found that by simply soaking the electrode in acidic solutions or organic solvents, the surface couldn’t be cleaned, and it was suspect there was a pretty strong absorption or bonding of imidazole related species on Pt surface. However, either surface Raman or IR spectrum could not give reasonable intensity to indicate the existence of absorbed species. Alternatively, computational modelling was applied to explain the poisoning mechanism of imidazole to platinum electrodes, and the results were discussed in the final part of this chapter.

Fuel cell tests of triazole/sPSU polymer membranes provided a direct way to identify the electrochemical stability of 1H-1,2,3-triazole in fuel cell condition. To lower the interfacial resistance between the membrane and electrodes, liquid 1H-1,2,3-triazole was doped into the gas diffusion electrodes (GDE) with Nafion and PTFE implanted. The membrane electrode assembly (MEA) was prepared by hot-pressing, and some performance data were reported in Figure 4.16.

![Figure 4.16 V-I and power density curves obtained from fuel cell tests of triazole/sPSU polymer membranes](image162x110.png)
The highest OCV and Current density we achieved from the experiments were 0.8V and 30mA/cm². With temperature increasing, the OCV was dropped. During the experiments, we found there were a lot of small bubbles formed in the membranes. The OCV drop may result from the gas permission through the membranes. The low mechanical strength of the membrane at high temperature also caused shape deforming and gas leaking. However, keeping at relatively low temperature, we obtained stable cell performance in dry air condition, which partially proved the electrochemical stability of 1H-1,2,3-triazole under fuel cell condition. Still, only when there exist triazole-based PEMs with both high proton conductivity and enough thermal/mechanical stability, it is possible to fully identify the electrochemical stability of 1H-1,2,3-triazole for HT PEM fuel cell applications.

Through computational modelling, we studied the adsorption of heterocycles including imidazole, 1H(2H)-1,2,3-triazole, 1H(4H)-1,2,4-triazole, 2-methanesulfonyl-1H-imidazole on the platinum surface, as shown in Figure 4.17. The calculated N-Pt bond distance and the adsorption energies were listed in Table 4.2.

Table 4.2 Pt-N bond distances, r(Pt-N) in Å, and adsorption energies, \( E_{\text{ads}} \) in kcal/mole, obtained from the structures shown in 4.16.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(Pt-N)</td>
<td>2.080</td>
<td>2.384</td>
<td>2.146</td>
<td>2.075</td>
<td>2.354</td>
<td>2.100</td>
<td>2.115</td>
<td>2.077</td>
</tr>
<tr>
<td>( E_{\text{ads}} )</td>
<td>-19.0</td>
<td>-7.5</td>
<td>-17.7</td>
<td>-19.7</td>
<td>-12.3</td>
<td>-21.6</td>
<td>-20.5</td>
<td>-24.8</td>
</tr>
</tbody>
</table>

As mentioned before, for the typical poison specie CO on Pt electrodes, at high temperature (>100°C), the reversible adsorption/desorption equilibrium shifted and the poisoning effect was alleviated a lot. Compared with CO (\( E_{\text{ads}} = -42.8 \) kcal/mol), imidazole, 1H(2H)-1,2,3-triazole an 1H(4H)-1,2,4-triazole have much less adsorption energies(~20kcal/mol). If the poisoning mechanism of imidazole is mainly through the adsorption of imidazole on Platinum surface, we should have observed from the experiments either (a)1,2,3-triazole have the same poisoning effects which will result in the failure of fuel cell tests at low temperature, or (b) at high temperature, acceptable fuel
Figure 4.17 Scheme of heterocyclic molecules absorbed on the surface of platinum.
cell performance can be achieved based on imidazole-doped polymer membranes. The pervious studies of imidazole-based membranes for HT PEMFCs and our fuel cell studies on 1,2,3-triazole indicate that imidazole may poison the platinum electrodes through another mechanism.

As described in Figure 4.18, we suggested a three-step adsorption-oxidation-deprotonation mechanism for the poisoning process of imidazole. Due to relatively low oxidation potential of imidazole (0.95V, in Table 4.3), after absorbed on the platinum surface, the imidazole molecule on the cathode for a PEMFC or on the working electrode during the cyclic voltammetry experiments is further oxidized to be a charge cation. With the assistant from either the solvent molecule or another imidazole as a base, an exothermal deprotonation reaction can be easily performed with low energy barrier (~2.3kcal/mol in the case of using an imidazole as the base) to finally form a stable imidazole-Pt complex. The adsorption energy of this complex calculated is -43.0 kcal/mol, which is close to that of CO on Pt. Based on this mechanism, it is the high electrochemical stability of triazole which avoids the possible poisoning effect to platinum, and all other experimental results for imidazole and triazole are well explained. Further experimental evidences are required to fully prove this mechanism.

Figure 4.18 Illustration of a possible three-step poisoning mechanism of imidazole on platinum surface.
Also, we calculated the oxidation potential of imidazole, 1H(2H)-1,2,3-triazole, 1H(4H)-1,2,4-triazole and 2-methanesulfonyl-1H-imidazole in CH₃CN solution, and the results were reported in Table 4.3, compared with the experimental results.

<table>
<thead>
<tr>
<th></th>
<th>IP&lt;sub&gt;calc.&lt;/sub&gt; (eV)</th>
<th>IP&lt;sub&gt;expt.&lt;/sub&gt;</th>
<th>E&lt;sub&gt;0 calc.&lt;/sub&gt; (V)</th>
<th>E&lt;sub&gt;0 ext&lt;/sub&gt; (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>8.68</td>
<td>8.81</td>
<td>0.95</td>
<td>1.0</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>4H-1,2,4-triazole</td>
<td>9.84</td>
<td></td>
<td>2.10</td>
<td></td>
</tr>
</tbody>
</table>

All the computed IPs agrees well with experimental values and imidazole has the lowest IP than the other azoles. With an electron-withdraw -SO₂- group, 2-methanesulfonyl-1H-imidazole shows a higher IP than that of imidazole. Similarly, triazole rings are less favorable to be oxidized with higher IPs compared with imidazole, since one of the carbon atoms of imidazole is replaced by a nitrogen atom with higher electro-negativity. The electrochemical stability of 1H(4H)-1,2,4-triazole and 2-methanesulfonyl-1H-imidazole makes them possible for HT PEMFC applications and the related studies were reported in Chapter 7.

**4.4 Conclusions**

In this chapter, we have examined the proton conducting ability and electrochemistry stability of 1H(2H)-1,2,3-triazole. The conductivity measurements and cyclic voltammetry experiments have shown that 1H(2H)-1,2,3-triazole has considerable proton conducting ability and adequate electrochemical stability for PEM fuel cell application. The low temperature proton conduction and fuel cell performance, also the proton conduction through structure diffusion determined by ¹H PFG-NMR in triazole/sPSU membranes make it promising to design fully polymerized membranes for HT PEMFC applications. Also, through theoretical studies in this chapter the possible poison mechanism of imidazole to platinum electrodes was discussed.
4.5 References


CHAPTER 5

1H(2H)-1,2,3-TRIAZOLE DERIVATIVES AND POLYMERS

5.1 Introduction

Similar as H\textsubscript{2}O, H\textsubscript{3}PO\textsubscript{4} and imidazole, 1H(2H)-1,2,3-triazole has been identified as an effective proton conductor. However, except water, to dope small molecules to the polymer matrix, the resulted membranes always face leaking problems of small molecules, either by evaporation or by dissolving into liquid water outside of the membrane. Also, the osmotic drag effect may change the distribution of the small molecules in the membrane gradually and therefore increase the resistance of the membrane. As a fact, there are no studies reported about multiple on-off cycle tests for PEMFCs based on PBI-H\textsubscript{3}PO\textsubscript{4} till now. With these considerations, to achieve the target of our project, to develop HT-PEMs for mobile applications, designing and synthesizing fully polymerized PEMs based on triazole with high proton conductivity is necessary and very important.

Because only 1H(2H)-1,2,3-triazole is commercial available, synthesis of 1H(2H)-1,2,3-triazole derivatives turns to be the very first step. As shown in Figure 5.1, 1,2,3-triazole ring can be constructed from (a) Huisgen cycloaddition \cite{1}, (b) Banert reactions \cite{2,3}, and (c) click reactions \cite{4}. For method (a) an (c), the R’ group on N1 should be cleaved to achieve 1H-1,2,3-triazole. Since the following PEM studies require simple and effective synthesis, only (b) and (c) were under consideration for our research due to the low yields, slow reaction rate and potential danger for route (a).

As discussed in Chapter 2, the choice for suitable polymer backbones for HT PEMs is limited because of the stability concern in fuel cell condition. Polyethylene and polysiloxane polymers were the polymer system we have looked into, and the research work mainly focused on studies of the monomer and polymer synthesis and the proton conductivity of materials. Since the ionic conductivity of the membrane is related to the
(a) Huisgen Cycloaddition

\[ R_1\equiv R_2 + R_3^+N\equivN \xrightarrow{\Delta} \frac{R_2N\equivR_1}{N\equivR_3} + \frac{R_1N\equivR_2}{N\equivR_3} \]

(b) Banert Reaction

X = halide or sulfonate  sigmatropic shift

\[ R\equiv R_2 X \xrightarrow{\text{NaN}_3} R\equiv R_2 N_3 \xrightarrow{40-70^\circ C} \text{MeOH/H}_2\text{O} \text{ or Dioxane/H}_2\text{O} \]

Nuc: \( \text{Nuc}: \) \( \text{OH}^-, \text{RO}^-, \text{N}_3^-, \text{RS}^- \)

 allenyl azide  cyclization  triazafulvene

(C) Click Reaction

\[ R_1^+N\equivN + R_2\equiv \xrightarrow{\text{Cu}^+} \text{H}_2\text{O/BlOH, RT} \]

(Major)

Figure 5.1 Synthesis of 1,2,3-triazole derivatives.

concentration of the charge species and also the mobility of proton conducting groups, the chemical and physical structure of the polymer backbones and side-chains, the concentration of protogenic acidic species in the copolymer, may have great influence on the proton conduction.
Thermal stability, conductivity in humid condition and other properties of the synthesized polymers were also discussed in this chapter. As a fact, all these properties including proton conductivity, mechanical, thermal and chemical stability, when combined into one membrane system, they always interact with each other and make the studies complicated. The main target of the research in this chapter is to clarify these interactions and explore various routes to solve the technical difficulties.

5.2 Experimental Section

Chemicals and Instruments: Organosilanes were purchased from Gelest, Inc., solvents were from VWR, Inc., and other chemicals were purchased from Alrich, Inc. Merck silica gel (70-230 mesh) and thin layer chromatography (TLC) plates for flash chromatography were purchase from Sorbent Technologies, Inc. The chemical structures of the synthesized compounds were typically confirmed by $^1$H NMR. For the compounds never reported, they were also confirmed by MS, and high-resolution mass spectrometry (HRMS). NMR: δ in ppm vs SiMe4 (0 ppm, $^1$H, 300 MHz). MS: selected peaks; m/z. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Rheometric Scientific STA 1500 and a TA instrument 2050. Gel permeation chromatography (GPC) was performed on a Shimadzu GPC equipped with a LC-10ADvp pump and a UV detector to determine the number and weight average molecular weight of synthesized polymer. A Solartron 1255 frequency response analyser and a Solartron 1286 potentiostate/galvanostat interfaced with a computer were used for conductivity measurements. Fourier transform infrared (FTIR) spectroscopy measurements were performed on thin pellets composed of 5% sample and 95% KBr using a Bruker Equinox 55 spectrometer. CHN elementary analysis was performed on PerkinElmer 2400 Carbon, Hydrogen, Nitrogen Analyzer in University of Georgia.

Synthesis of 1,2,3-Triazole Derivatives: Shown in Figure 5.2, several 1,2,3-triazole derivatives were synthesized through Banert reactions described in Reference [2] and [3].
**Prop-2-ynyl-4-methylbenzenesulfonate (5.1):** Propargyl alcohol (33g, 0.59mol) and p-toluenesulfonyl chloride (76g, 0.4mol) were dissolved in 150ml ether. With stirring at 0°C, 30g NaOH in 60ml water was added into the solution slowly. After stirred for one hour, the mixture was washed with water and separated. After dried with anhydrous MgSO₄, the solution was evaporated under reduced pressure, and 72.5g liquid product (0.34mol, 85% yield) was provided. ¹H NMR (CDCl₃, 300 MHz) δ 2.44 (s, 3H), 2.48 (t, J=2.45, 1H), 4.67 (dd, J= 2.50, 2H), 7.34 (d, J= 8.01, 2H), 7.79 (d, J= 8.26, 2H).

**5-((2-Methoxyethoxy)methyl)-1H-1,2,3-triazole (5.3):** Compound 5.1 (7.5g, 35.7mmol) and NaN₃ (3g, 46.1mmol) was dissolved in 50ml dioxane and 5ml water. At 40°C, stirred for 2 hours, TLC showed the absence of the reactant 5.1. 20ml dioxane was added and the precipitation was removed by filtration. By adding 4g NaOH in 36ml water, the mixed solution was stirred at 70°C overnight. The resulted solution was neutralized by HCl solution. After evaporation under reduced pressure, the residue was distillation in vacuo to provide 1.0g liquid product (10.0mmol, 28% yield). ¹H NMR (CDCl₃, 300 MHz) δ 3.43 (s, 3H), 3.63 (m, 2H), 3.72 (m, 2H), 4.74 (s, 2H), 7.75 (s, 1H).

**5-Hydroxymethyl-1H-1,2,3-triazole (5.4):** Compound 5.1 (10.5g, 50.0mmol) and NaN₃ (4g, 61.5mmol) was dissolved in 10ml allyl alcohol and 3ml water. At room temperature, stirred for 3 days, TLC showed the absence of the reactant 5.1. 50ml allyl alcohol was added and the precipitation was removed by filtration. By adding 6g NaOH, the mixed solution was stirred at 70°C overnight. The resulted solution was neutralized with by HCl solution and extracted with ethyl acetate. After dried with anhydrous MgSO₄, the solution was evaporated under reduced pressure. The residue was further distilled in vacuo to provide 2.9g liquid product (20.8mmol, 42% yield). ¹H NMR (CD₃OD, 300 MHz) δ 4.73 (s, 2H), 7.76 (s, 1H).

**5-(Allyloxy)methyl-1H-1,2,3-triazole (5.5):** Compound 5.1 (10.5g, 50.0mmol) and NaN₃ (4g, 61.5mmol) was dissolved in 15ml 2-methoxyethanol and 3ml water. At room
temperature, stirred for overnight, TLC showed the absence of the reactant 5.1. The precipitation was removed by filtration. By adding 6g NaOH, the mixed solution was

stirred at 70 °C overnight. The resulted solution was neutralized with HCl solution and extracted with ethyl acetate. After dried with anhydrous MgSO₄, the solution was evaporated under reduced pressure. The residue was further distilled in vacuo to provide 3.3g liquid product(21.0mmol, 42% yield). ¹H NMR (CDCl₃, 300 MHz) δ 4.06 (d, J=5.73, 2H), 4.68 (s, 2H), 5.18-5.31 (dd, J=13.8, 2H), 5.90 (m, 2H), 7.73 (s, 1H).

Click reaction was developed by Sharpless group recently. This reaction is a 1,3-dipolar cycloaddition between an organo azide and a terminal alkyne. Normally, azide and alkyne groups are very stable, not sensitive to pH, temperature, solvent and other functional groups. But catalyzed by Cu(I) cations, at room temperature they can form 1,2,3-tirazole ring highly specifically, and with high yields. Certain kinds of ligands can stabilize Cu(I) cations in the solution and accelerate the reaction. Currently, click reactions have been widely used for developing new drug and new materials due to the mild reaction condition, high yield and region-selectivity. As described in Figure 5.3, the 1,2,3-triazole derivatives were synthesized through click reactions. The 4-methoxybenzyl
Figure 5.3 Synthesis of 1,2,3-triazole derivatives through Click Reactions.
group was chosen as the N-substitution group, which can be removed by refluxing in trifluoroacetic acid. [5]

1-(Chloromethyl)-4-methoxybenzene (5.6): 4-methoxybenzyl alcohol (70g, 0.51mol) was mixed with CH$_2$Cl$_2$ 50ml. With stirring, 70ml SOCl$_2$ (0.96mol) in 100ml CH$_2$Cl$_2$ was added dropwise into the solution in one hour, and the HCl gas produced was absorbed by KOH solution. The solution was stirred at room temperature for another 3 hours, and 100ml water was added dropwise into the solution. After the reaction was finished, the organic layer was separated and washed with water several times and dried with anhydrous MgSO$_4$. The solvent was removed by evaporation under reduced pressure, and
71.3g liquid product (0.46mol, 90% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) 3.81 (s, 3H), 4.57 (s, 2H), 6.92(d, $J$=8.76, 2H), 7.25 (d, $J$=8.75, 2H).

1-(Azidomethyl)-4-methoxybenzene (5.7): Compound 5.6 (46.5g, 0.30mol) and NaN$_3$ (25g, 0.38mol) were mixed with ethanol-water (100ml:50ml) solution, and stirred at room temperature overnight. After evaporation under reduced pressure to remove ethanol, 100ml CH$_2$Cl$_2$ and 50ml water were added into the residue. The organic layer was separated and dried with anhydrous MgSO$_4$. CH$_2$Cl$_2$ was removed by evaporation and 46g liquid product (0.28mol, 95% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) 3.82 (s, 3H), 4.27 (s, 2H), 6.89(d, $J$=8.67, 2H), 7.31 (d, $J$=8.62, 2H).

1-(4-Methoxybenzyl)-4-hydroxymethyl-1,2,3-triazole (5.8): Compound 5.7 (22g, 0.13mol) and propargyl alcohol (12g, 0.21g) were mixed with 100ml t-BuOH and 100ml water. 2g Cu powder was added as the catalyst. After stirred at room temperature for five days, the solvent was removed by evaporation. 150ml CH$_2$Cl$_2$ was added into the residue and the mixture was stirred for few minutes. The precipitation was removed by filtration, and ethyl acetate was removed by evaporation. 50ml ether was added into the residue, and the product was quickly precipitated. With filtration and washing with ether for several time, 26g light gray solid product (0.12mol, 92% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) 3.79 (s, 3H), 4.73(s, 2H), 5.43(s, 2H), 6.89(d, $J$=8.71, 2H), 7.22 (d, $J$=8.69, 2H), 7.42 (s, 1H). MS (70 eV) 219.1(M+, 13), 160.1 (8), 121.1 (100). EI-HRMS $m/e$ calculated for (M+) C$_{11}$H$_{13}$N$_3$O$_2$ 219.1008, found 219.1016.

1-(4-Methoxybenzyl)-4-chloromethyl-1,2,3-triazole (5.9): Alcohol 5.8 (10g, 45.7mmol) was mixed with CH$_2$Cl$_2$ 20ml. With stirring, 10ml SOCl$_2$ (137mmol) in 30ml CH$_2$Cl$_2$ was added dropwise into the solution, and the HCl gas produced was absorbed by KOH solution. The solution was stirred at room temperature overnight, and 30ml water was added dropwise into the solution. After the reaction was finished, the organic layer was separated and washed with water several times and dried with anhydrous MgSO$_4$. The solvent was removed by evaporation under reduced pressure, and 10.8g solid product
(45.5mmol, 100% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) 3.79 (s, 3H), 4.65 (s, 2H), 5.43 (s, 2H), 6.88 (d, $J$=8.35, 2H), 7.22 (d, $J$=8.35, 2H), 7.45 (s, 1H). MS (70 eV) 237.1 (M+, 22), 174.1 (16), 121.1 (100), 78.1 (6). EI-HRMS $m/e$ calculated for (M+) C$_{11}$H$_{12}$ClN$_3$O$_2$ 237.0669, found 237.0643.

**1-(4-Methoxybenzyl)-4-bromomethyl-1,2,3-triazole (5.10):** PBr$_3$ (25g, 92.4mmol) was dissolved in 150 ml CH$_2$Cl$_2$, and alcohol 5.8 (10g, 45.7mmol) in 100ml CH$_2$Cl$_2$, was added dropwise. The HBr produced was absorbed by KOH solution. The solution was stirred at room temperature overnight, and 50ml water was added dropwise into the solution. After the reaction was finished, the organic layer was separated and washed with Na$_2$CO$_3$ saturated solution several times and dried with anhydrous MgSO$_4$. The CH$_2$Cl$_2$ was removed by evaporation under reduced pressure, and the residue was washed with ether several times and dried to provide solid product 11g (39mmol, 85% yield). $^1$H NMR (CDCl$_3$, 300 MHz) 3.81 (s, 3H), 4.57 (s, 2H), 5.47 (s, 2H), 6.90 (d, $J$=8.67, 2H), 7.25 (d, $J$=8.52, 2H), 7.53 (s, 1H). MS (70 eV) 281.1 (M+, 10), 205.2 (22), 174.1 (33), 121.1 (100), 78.1 (8). EI-HRMS $m/e$ calculated for (M+) C$_{11}$H$_{12}$BrN$_3$O$_2$ 281.0164, found 281.0149.

**1-(4-Methoxybenzyl)-1,2,3-tirazol-4-yl)methyl 4-methylbenzenesulfonate (5.11):** Alcohol 5.8 (4.4g, 20mmol) and p-toluenesulfonyl chloride (4.0g, 20.9mmol) were dissolved in anhydrous THF 80ml. NaH (60%) 1g was slowly added into the solution with stirring. After two hour, 0.3 to 0.5 g NaH was added into the solution to complete the reaction. The solvent was then removed by evaporation under reduced pressure at $T$$\leq$30°C. 100ml ethyl acetate and 2M HCl 20ml were added into the residue. The organic layer was separated and dried with anhydrous MgSO$_4$. After removing the solvent by evaporation, the product was purified by flash column chromatography (1:1 ethyl acetate-hexane) to provide 6.13g solid product (16.4mmol, 82% yield). $^1$H NMR (CDCl$_3$, 300 MHz) 2.41 (s, 3H), 3.78 (s, 3H), 5.12 (s, 2H), 5.39 (s, 2H), 6.87 (d, $J$=8.68, 2H), 7.18 (d, $J$=8.58, 2H), 7.28 (d, $J$=8.11, 2H), 7.46 (s, 1H), 7.73 (d, $J$=8.32, 2H). MS (70 eV)
EI-HRMS m/e calculated for (M+) C_{18}H_{19}N_{3}O_{4}S 373.1096, found 373.1091.

1-(4-Methoxybenzyl)-1,2,3-triazol-4-carbaldehyde (5.12): Alcohol 5.8 (21.9 g, 100 mmol) and MnO\textsubscript{2} (26.1 g, 300 mmol) were mixed in 250 ml CH\textsubscript{2}Cl\textsubscript{2} and stirred at room temperature for one week. After filtration and evaporation, 17.3 g liquid product (80 mmol, 80% yield) was provided. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) 3.81 (s, 3H), 5.51 (s, 2H), 6.91 (d, \textit{J}=8.42, 2H), 7.25 (d, \textit{J}=8.19, 2H), 7.95 (s, 1H), 10.10 (s, 1H). MS (70 eV) 217.1 (M+, 19), 188.1 (35), 160.1 (10), 121.1 (100), 91.0 (8), 78.0 (12). EI-HRMS m/e calculated for (M+) C_{11}H_{11}N_{3}O_{2} 217.0851, found 217.0821.

1-(4-Methoxybenzyl)-4-vinyl-1,2,3-triazole (5.13): Methyltriphenylphosphonium bromide (9.11 g, 25.6 mmol) was dissolved in 50 ml anhydrous THF. At T=\textendash78\degree C in the argon, BuLi (2.0 M in cyclohexane, 14.8 ml, 29.6 mmol) was added dropwise into the solution, and the mixture was stirred for one hour. At room temperature, the solution was stirred for another 30 minutes, and aldehyde 5.12 (4.28 g, 19.7 mmol) in anhydrous THF 25 ml was slowly added into the solution with stirring. The mixture was stirred overnight and the solvent was then removed by evaporation under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate-hexane, gradient 1:30 to 1:1) to provide 2.49 white solid product (11.6 mmol, 59% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) 3.80 (s, 3H), 5.30 (dd, \textit{J}=11.17, 1H), 5.44 (s, 2H), 5.83 (dd, \textit{J}=11.17, 1H), 6.67 (m, 1H), 6.89 (d, \textit{J}=8.75, 2H), 7.23 (d, \textit{J}=8.39, 2H), 7.38 (s, 1H). MS (70 eV) 215.1 (M+, 20), 86.2 (9), 121.1 (100). EI-HRMS m/e calculated for (M+) C_{11}H_{13}N_{3}O 215.1059, found 215.1081.

1-(4-Methoxybenzyl)-1,2,3-triazol-4-carbonitrile (5.14): Aldehyde 5.12 (2.17 g, 10 mmol) and NH\textsubscript{2}OH\cdotHCl (0.83 g, 12 mmol) were dissolved in N-methyl pyrrolidone 15 ml, and the solution was heated overnight at T=110\degree C. The resulted solution was poured into water and extracted with ethyl acetate. After dried by anhydrous MgSO\textsubscript{4}, the solvent was removed by evaporation under reduced pressure. The residue was purified by
flash column chromatography (1:1 ethyl acetate-hexane) to provide 1.28g product (6.0mmol, 60% yield). 3.82 (s, 3H), 5.52(s, 2H), 6.93(d, J=8.43, 2H), 7.26 (d, J=8.38, 2H), 7.94 (s, 1H). MS (70 eV) 214.1(M+, 50), 185.1 (25), 121.1 (100), 78.1 (11). EI-HRMS m/e calculated for (M+) C11H10N4O 214.0855, found 214.0871.

1-(1-(4-Methoxybenzyl)-1,2,3-triazol-4-yl)but-3-en-1-ol (5.15): Aldehyde 5.12 (1.70g, 7.8mmol) and Mg (0.59g, 24.2 mmol) were mixed with 5ml anhydrous THF. At 0 °C in the argon, allyl bromide (1.90g, 15.7mmol) in 5ml anhydrous THF was slowly added into the solution and the mixture was stirred for 30min. 1M HCl 10ml added and the product in the solution was extracted with ethyl acetate. After dried with anhydrous MgSO4, the solvent was removed by evaporation to provide 1.76g product (6.8mmol, 87% yield). 1H NMR (CDCl3, 300 MHz) 2.53-2.68 (m, 3H), 3.80 (s, 3H), 4.93 (m, 1H), 5.14 (t, 2H), 5.43 (s, 2H), 5.81 (m, 1H), 6.89 (d, J=8.75, 2H), 7.23 (d, J=8.79, 2H), 7.36 (s, 1H).

1-(1-(4-Methoxybenzyl)-1,2,3-triazol-4-yl)but-3-en-1-one (5.16): (a) Alcohol 5.15 (0.52g, 2mmol) in 1.5ml CH2Cl2 was added into Pyridinium Chlorochromate (PCC) (0.54g, 2.5mmol) in 1ml CH2Cl2, and the mixture solution was stirred for 30min. 10ml Ether was added and the precipitation was removed by filtration. By removing the ether, 130mg product (0.50mmol, 25% yield) was provided. (b) Compound 5.14 (0.214g, 1mmol ), allyl bromide ( 0.182g, 1.5mmol) and Zn (0.26g, 4mmol) were mixed in 5ml THF. At 0°C, AlCl3 (0.053g, 0.4mmol) was added into the mixture, and the solution was stirred at room temperature for two hours. 10ml 2MHCl was added and the mixture was stirred for 5min. The solution was extracted with ethyl acetate. After dried with anhydrous MgSO4, the solvent was removed by evaporation, and the residue was purified by flash column chromatography. 40mg product (0.16mmol, 16% yield) was provided. 1H NMR (CDCl3, 300 MHz) 3.79 (s, 3H), 3.86 (dt, J=6.90, 2H), 5.21 (m, 2H), 5.48 (s, 2H), 6.06 (m, 1H), 6.89 (d, J=8.74, 2H), 7.23 (d, J=8.76, 2H), 7.94 (s, 1H).

1-(4-Methoxybenzyl)-4-(but-3-enyl)-1,2,3-triazole (5.17): Compound 5.10 (14.1g, 50mmol) was dissolved in 150ml anhydrous THF, with CuI (0.1g) added into the solution.
After the solution was bubbled with Argon for 30 min, allyl magnesium bromide (2.0M in THF, 30ml, 60mmol) was added dropwise into the solution at 0°C. The solution was stirred at room temperature for another three hours, and THF was removed by evaporation. Water was added into the residue and the mixture solution was extracted by ethyl acetate. The organic layer was separated and dried with anhydrous MgSO₄. After removing ethyl acetate by evaporation, ether was used to dissolve the product and remove the reactant impurities. After removing ether, 7.0g product (28.8mmol, 58% yield) was provided. ¹H NMR (CDCl₃, 300 MHz) 2.38 (q, 2H), 2.76 (t, 2H), 3.78 (s, 3H), 4.97 (m, 2H), 5.40 (s, 2H), 5.79 (m, 1H), 6.87 (d, J=8.75, 2H), 7.19 (t, 3H). MS (70 eV) 243.1 (M+, 9), 139 (13), 121.1 (100), 78 (9). EI-HRMS m/e calculated for (M+) C₁₄H₁₇N₄O 243.1372, found 243.1381.

1-(4-Methoxybenzyl)-4-allyl-1,2,3-triazole (5.18): Compound 5.10 (8.46g, 30mmol) was dissolved in 60ml anhydrous THF, with CuI (60mg) added into the solution. After the solution was bubbled with Argon for 30 min, allyl magnesium bromide (2.0M in THF, 45ml, 90mmol) was added dropwise into the solution at 0°C. The solution was stirred at room temperature for another three hours, and THF was removed by evaporation. Water was added into the residue and the mixture solution was extracted by ethyl acetate. The organic layer was separated and dried with anhydrous MgSO₄. After removing ethyl acetate by evaporation, ether was used to dissolve the product and remove the reactant impurities. After removing ether, 4.8g product (21.0mmol, 70% yield) was provided. ¹H NMR (CDCl₃, 300 MHz) 3.47 (d, J=6.66, 2H), 3.80 (s, 3H), 5.09 (m, 2H), 5.30 (s, 2H), 5.92 (m, 1H), 6.87 (d, J=8.66, 2H), 7.19 (t, 3H). MS (70 eV) 229.1 (M+, 15), 121.1 (100), 78 (8). EI-HRMS m/e calculated for (M+) C₁₄H₁₇N₄O 229.1215, found 229.1215.

(5.19): Alkene 5.17 (7.6g, 31.3mmol), diethoxymethylsilane (10g, 74.4mmol) and H₂PtCl₆ (42mg/ml in isopropanol, 0.4ml) were mixed with anhydrous toluene 10ml in a Schrenk tube. The tube was then filled with Argon and sealed. The solution was stirred at 80°C for 3 days and ¹H NMR proved the absence of alkene. After evaporation under
reduced vacuum to remove the unreacted silane and alkene, 11.2g liquid product (29.7mmol, 95% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.11 (m, 3H), 0.59-0.92 (m, 2H), 1.20 (m, 6H), 1.39 (m, 2H), 1.64 (m, 2H), 2.67(m, 2H), 3.71-3.81 (m, 7H), 5.41 (s, 2H), 6.87 (d, $J= 8.70$, 2H), 7.17 (m, 3H). MS (70 eV) 377.2(M+, 4), 348.2(4), 251.1(4), 203.1 (4), 133.1 (6), 121.1(100), 77(4). El-HRMS m/e calculated for (M+) C$_{19}$H$_{31}$N$_3$O$_3$Si 377.2135, found 377.2131. 

(5.20): Alkene 5.17 (9.2g, 37.9mmol), triethoxysilane (15g, 91.3mmol) and H$_2$PtCl$_6$ (42mg/ml in isopropanol, 0.4ml) were mixed with anhydrous toluene 10ml in a Schrenk tube. The tube was then filled with Argon and sealed. The solution was stirred at 85°C for 4 days and $^1$H NMR proved the absence of alkene. After evaporation under reduced vacuum to remove the unreacted silane, 15.0g liquid product (36.8mmol, 97% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.62 (m, 2H), 1.20 (m, 9H), 1.47 (m, 2H), 1.64 (m, 2H), 2.64(m, 2H), 3.72-3.82 (m, 9H), 5.41 (s, 2H), 6.87 (d, $J= 8.82$, 2H), 7.17 (m, 3H). MS (70 eV) 407.1(M+, 3), 261.1(6), 269.1(8), 203 (7), 163.1 (11), 121(100), 77(5). El-HRMS m/e calculated for (M+) C$_{20}$H$_{33}$N$_3$O$_4$Si 407.2240, found 407.2276.

(5.21): Alkene 5.18 (7.7g, 33.6mmol), diethoxymethylsilane (6.72g, 50.0mmol) and H$_2$PtCl$_6$ (42mg/ml in isopropanol, 0.4ml) were mixed with anhydrous toluene 20ml in a Schrenk tube. The tube was then filled with Argon and sealed. The solution was stirred at 80°C for 2 days and $^1$H NMR proved the absence of alkene. After evaporation under reduced vacuum to remove the unreacted silane and alkene, 11.9g liquid product (32.7mmol, 97% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.09 (m, 3H), 0.59-0.96 (m, 2H), 1.19 (m, 6H), 1.67-1.92 (m, 2H), 2.30-2.98 (m, 2H), 3.71-3.81 (m, 7H), 5.40 (s, 2H), 6.87 (d, $J= 8.62$, 2H), 7.18-7.26 (m, 3H).

**Preparation and studies of 1,2,3-triazole based PEMs:** To study 1,2,3-triazole based PEMs, polyethylene (Figure 5.4) and polysiloxane polymers (Figure 5.5) with 1,2,3-triazole in the side chain were synthesized. Also, hybrid membranes using polysiloxane...
polymer and organosilane crosslinkers were prepared through sol-gel process.

**Poly(1-(4-Methoxybenzyl)-4-vinyl-1,2,3-triazole)** (5.22): Monomer 5.13 (2.34g, 10.8mmol) was dissolved in DMF 20ml. Azobisisobutyronitrile (AIBN) 15mg was added and the solution was deoxygenated and filled with argon. After stirred at 65°C overnight, the solution was concentrated and poured into 50ml ethyl acetate, and the polymer was precipitated from the solution. The mixture was sonicated and filtered, and the resulted polymer was washed with ethyl acetate several times and dried in the oven. 1.7g polymer (73% yield) was achieved. 

$^1$H NMR (d$^6$-DMSO, 300 MHz) $\delta$ 1.00-2.60 (br, -CH-CH$_2$-), 3.60-3.80 (br, CH$_3$OPh-), 5.20-5.60 (br, -CH$_2$-Ph), 6.80-7.00 (br, H-Ph), 7.00-7.40 (br, H-Ph), 7.50-7.70 (br, H-C=N).

**4-Vinyl-1$H$-1,2,3-triazole** (5.24): Monomer 5.13 (0.91g, 4.2mmol) was dissolved in 60ml TFA and refluxed for two days. TFA was removed by evaporation and the residue was dissolved in methanol. The precipitated byproduct was removed by filtration. Methanol was removed by evaporation. The residue was dissolved in CH$_2$Cl$_2$ and washed with saturated NaHCO$_3$ solution. After dried by anhydrous MgSO$_4$, the solution was concentrated and distilled under vacuum to provide 0.195g liquid product (2.0mmol, 47.6%). The product was dissolved in CH$_2$Cl$_2$ and stored in freezer to avoid self-polymerization. 

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 5.48 (d, $J=11.28$, 2H), 5.92 (d, $J=17.84$, 2H), 6.69 (m, 1H), 7.91 (s, 1H). $^{13}$C NMR (118.61, 124.12, 127.88, 143.91). MS (70 eV) 95.1(M+, 100), 40.9(60). EI-HRMS m/e calculated for (M+) C$_4$H$_5$N$_3$ 95.0483, found 95.0453.

**Poly(4-vinyl-1$H$-1,2,3-triazole)** (5.23): (1) Polymer 5.23 (1.7g) was dissolved in 100ml trifluoroacetic acid (TFA). After refluxed in TFA for one day, $^1$H NMR showed the complete removal of 4-methoxybenzyl groups. TFA was removed by evaporation and the resulted mixture was washed by ethyl acetate several times to remove the green byproduct. The white solid product were washed with water several times and dried in
the vacuum at 120°C for one day. 0.74g product (99% yield) was achieved. (2) Monomer 5.22 (0.36g, 3.8mmol) was dissolved in DMF 0.9ml. Azobisisobutyronitrile (AIBN) (1 wt% and 10 wt%, for two samples respectively) was added and the solution was deoxygenated and filled with argon. After stirred at 65°C overnight, the polymer gel was formed. Some DMF were added to dissolve the gel, and the resulted solution was poured into 30ml ethyl acetate. The polymer was precipitated from the solution, and the mixture was sonicated and filtered. The product was again sonicated in ethyl acetate and filtered several times and then dried in the oven. The yields were around 40 to 70%. $^1$H NMR (d$^6$-DMSO, 300 MHz) $\delta$ 1.00-2.60 (br, -CH-CH$_2$-), 7.00-7.80 (br, H-C=N).

**Poly(1-(4-Methoxybenzyl)-4-vinyl-1,2,3-triazole-co-vinyl phosphonic acid ) (5.25):**

Monomer 5.13 (0.43g, 2mmol) and vinyl phosphonic acid (0.5/2/3/4/8 mmol respectively for five samples) were dissolved in DMF 0.5ml. Azobisisobutyronitrile (AIBN) 4mg was added and the solution was deoxygenated and filled with argon. After stirred at 65°C overnight, the solution was concentrated and poured into 50ml ethyl acetate, and the polymer was precipitated from the solution. The mixture was sonicated and filtered, and the resulted polymer was washed with ethyl acetate several times and dried in the oven. 1.7g polymer (73% yield) was achieved. $^1$H NMR (d$^6$-DMSO, 300 MHz) $\delta$ 1.00-2.60 (br, -CH-CH$_2$-), 3.40-3.80 (br, CH$_3$OPh-), 5.00-5.60 (br, -CH$_2$-Ph), 6.20-6.80 (br, H-Ph), 6.80-7.20 (br, H-Ph, 2H), 7.20-7.50 (br, H-C=N, 1H).

**Poly(4-vinyl-1H-1,2,3-triazole-co-vinyl phosphonic acid ) (5.26):** (1-5) Polymer 5.25 (1-5) were dissolved in 30ml trifluoroacetic acid (TFA). After refluxed in TFA for one day, $^1$H NMR showed the complete removal of 4-methoxybenzyl groups. TFA was removed by evaporation and the resulted mixture was sonicated in ethyl acetate and filtered for several times to remove the byproduct and TFA. The white solid polymers were dried in the vacuum at 120°C for one day before further tests. (6) Monomer 5.22
Figure 5.4 Synthesis of Poly(4-vinyl-1H-1,2,3-triazole) and the copolymers with phosphonic acids.
(0.34g, 3.6mmol) and vinyl phosphonic acid (0.39g, 0.36mmol) were dissolved in DMF 0.5ml. Azobisisobutyronitrile (AIBN) 3mg was added and the solution was deoxygenated and filled with argon. After stirred at 80°C overnight, the polymer gel was formed. Some DMF were added to dissolve the gel, and the resulted solution was poured into 30ml ethyl acetate. The polymer was precipitated from the solution, and the mixture was sonicated and filtered. The product was again sonicated in ethyl acetate and filtered several times and then dried under vacuum at 120°C. 0.68g product (94% yield) was provided. \(^1\)H NMR (d^6-DMSO, 300 MHz) \(\delta\) 1.00-2.60 (br, -CH-CH_2-), 6.60-7.80 (br, H-C=N).

**Poly(1-vinyl-1,2,4-triazole-co-vinyl phosphonic acid)** (5.27): 1-Vinyl-1,2,4-triazole (0.26g, 2.8mmol and 0.30g, 3.1mmol ) and vinyl phosphonic acid (0.43g, 4mmol and 0.051g, 0.5mmol ) were dissolved in DMF 0.5ml. Azobisisobutyronitrile (AIBN) 5mg was added and the solution was deoxygenated and filled with argon. After stirred at 80°C for two hour, the polymer gel was formed. Some DMF were added to dissolve the gel, and the resulted solution was poured into 30ml ethyl acetate. The polymer was precipitated from the solution, and the mixture was sonicated and filtered. The polymer was again sonicated in ethyl acetate and filtered several times and then dried under vacuum at 120°C. The yields were 90% (0.71g) and 97% (0.34g) respectively. \(^1\)H NMR (d^6-DMSO, 300 MHz) \(\delta\) 1.00-2.60 (br, -CH-CH_2-), 7.80-8.40 (br, H-C=N).

**Polysiloxane (5.28), (5.29) and (5.32):** Monomer 5.19/5.20/ 5.19-5.20 (~30mmol) was dissolved in TFA 80ml and refluxed for four days. \(^1\)H NMR showed the complete removal of 4-methoxybenzyl groups. TFA was then removed by evaporation, and the resulted mixture was sonicated in methanol, followed by filtration to remove the green byproduct. The polymer solution was concentrated and filtered again for several times. After filtration, the solvent was removed by evaporation and the gel product was dried under vacuum at 80°C for one day before tests. \(^1\)H NMR (d^6-DMSO, 300 MHz) \(\delta\) -0.5-0.5 (br, CH_3-Si), 0.2-2.60 (m, br, Si-(CH_2)_n-), 7.20-7.60 (br, H-C=N).
Figure 5.5 Preparation of polysiloxane polymer and hybrid membranes with triazole/phosphonic acid grafted.
Figure 5.5 Preparation of polysiloxane polymer and hybrid membranes with triazole/phosphonic acid grafted. (Continued)

**Hybrid membrane (5.30), (5.31), (5.33), (5.34) and (5.35):** Polysiloxane 5.28/5.29/5.32 was dissolved in THF. For crosslinking, methyltriacetoxysilane, SiO₂ and tetraethoxysilane were added selectively into the solution in different ratio. The solution was stirred at overnight at room temperature. 3-trihydroxysilylpropyl sulfonic acid or 2-trihydroxysilylethyl phosphonic acid was added into the solution (the mole ratio of acid/triazole, 5%~20%). The mixture solution was stirred for one day at room temperature and poured into a teflon mold. The resulted membrane was first dried at 60°C and then at 120°C for several days before tests.

**Diethyl 3-(diethoxymethylsilyl)propylphosphonate (5.36):** Triethyl phosphite (75ml, 0.44mol) and (3-chloropropyl)dimethoxymethylsilane (75ml, 0.42mol) were heated at 170°C under argon for 48 hours. Another 20ml triethyl phosphite was added, and the
solution was kept at 170°C for another four days. The distillation under vacuum provided 65g liquid at 1.5mmHg, 120°C. By mixing 65g liquid with 65g ethanol, the solution was refluxed for one day. After removing the ethanol by evaporation, 74g liquid product (0.24mol, 57% yield) was provided. ¹H NMR (CDCl₃, 300 MHz) δ 0.04(s, 3H), 0.70 (t, 2H), 1.10 (br, m, 12H), 1.76(br m, 4H), 3.65 (q, 4H), 4.10(br m, 4H).

**Polysiloxane (5.37):** Monomer 5.36 (10g, 32mmol) was dissolved in concentrated 100ml and refluxed overnight. ¹H NMR showed the complete hydrolysis of ethyl phosphonate. The HCl solution was then removed by evaporation. HCl left in the product was removed by dissolving the polymer again in the water and distillation, till the polymer solution has no detectable Cl⁻ (detected by AgNO₃ solution). The final product was dissolved in 50ml Ethanol. ¹H NMR (CD₃OD, 300 MHz) δ -0.12 (br, CH₃-Si), 0.53 (br m, SiCH₂), 1.56 (br m, -CH₂CH₂-P).

**Polysiloxane copolymer (5.40):** (1) Polysiloxane 5.37 (7.8ml 0.64M Ethanol solution, 5mmol) and monomer 5.21(2.04g, 5mmol) were mixed. At room temperature, the solution was stirred overnight. After evaporation, 30ml TFA was added and the resulted solution was refluxed for four days. ¹H NMR showed the complete removal of 4-methoxybenzyl groups. TFA was then evaporated, and the resulted mixture was sonicated in methanol, followed by filtration to remove the green byproduct. The polymer solution was concentrated and filtered again for several times. After evaporation, the final product was dried at 120°C for several days before tests. (2) Monomer 5.36 (3.12g, 10mmol) and monomer 5.21 (4.07g, 10mmol) and triethylethoxysilane(0.12g, 1mmol) were mixed and 0.05M KOH solution(0.3ml) was added into the solution. By heating the mixture at 160°C for 16 hours, ethyl acetate was added and the solution was washed with water. The organic layer was separated and dried with anhydrous MgSO₄. After evaporation, 5.55g product (5.39) was achieved. ¹H NMR (CDCl₃, 300 MHz) δ -0.1-0.1 (br, CH₃-Si), 0.4-1.0(br, -CH₂-Si), 0.8-1.0 (br, -CH₂-(C-C=N)), 1.2-1.4 (br, CH₃-C-O-), 1.4-2.0 (br, -CH₂-
C=N), 3.6-3.8 (br, -CH2-O-P), 3.9-4.2 (br, -CH2CH2-P), 5.3-5.5 (br, CH3O-), 6.6-6.8(br, Ph-H), 7.1-7.4(br, Ph-H and -CH=N). The copolymer 5.39 (5.55g) was first dissolved in 20ml TFA and refluxed for four days. 1H NMR showed the complete removal of 4-methoxybenzyl groups. TFA was then evaporated, and the residue was washed with toluene to remove the byproduct. After evaporating the toluene, 6ml concentrate HCl was added, and the resulted solution was refluxed overnight. 1H NMR showed the complete hydrolysis of ethyl phosphonate. The HCl solution was then removed by evaporation. HCl left in the product was removed by dissolving the polymer again in the water and distillation, till the polymer solution has no detectable Cl- (detected by AgNO3 solution). The final product was dried at 110ºC for several days before tests and 2.7g solid product was achieved. 1H NMR (d6-DMSO, 300 MHz) δ -0.1-0.2 (br, CH3-Si), 0.4-1.0(br, -CH2-Si and -CH2-(C-C=N)), 1.4-2.0 (br, -CH2-C=N), 3.9-4.2 (br, -CH2CH2-P), 7.4-7.6( br , -CH=N).

4-Allyl-1H-1,2,3-triazole (5.41): Compound 5.18(7.5g, 32.8mmol) was dissolved in 200ml TFA and the solution was refluxed for four days. 1H NMR showed the complete removal of 4-methoxybenzyl groups. The solution was concentrated and methanol was then added. The resulted mixture was sonicated in methanol, followed by filtration to remove the green byproduct. After evaporation, CH2Cl2 was added into the residue, and small amount of anhydrous Na2CO3 powder was added into the solution to remove the TFA left. After filtration and evaporation, the residue was distilled under vacuum to provide 2.0g liquid product (18.5mmol, 56% yield). 1H NMR (CDCl3, 300 MHz) 3.48 (d, J=6.68, 2H), 5.09 (m, 2H), 5.95 (m, 1H), 7.51(s, 1H). MS (70 eV) 109.1(M+, 85), 80(75), 40.9(55). EI-HRMS m/e calculated for (M+) C5H7N3 109.0640, found 109.0595. For siloxane 5.42, the reaction of 5.41 and methyltriethoxy silane (1.5-2.2 equiv.) catalyzed by H2PtCl6 showed very slow react rated. 1H NMR showed that after refluxing the solution at 90ºC in the Schrenk tube for two weeks, there was only 10-20% siloxane produced.

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Conductivity measurements of prepared PEMs: (1) For polymer 5.23, 5.26 and 5.27, they were grinded into powders, and hot-pressed at 120°C for 20-30min to get transparent pallets. The conductivity of the sample was measured for room temperature to 150°C using the cell as described in Figure 4.2 (b). (2) Small inorganic and organic acids were doped into polymer 5.23 by co-condensation from methanol. The resulted powder was dried at 120°C, grinded and hot-pressed to form pallets for conductivity tests. (3) For polysiloxane polymers 5.28 and 5.29, because they are highly viscous gel at elevated temperatures, the conducting cell as shown in Figure 4.2 (a) was used to measure their conductivities. (4) For all hybrid membranes and polysiloxane copolymer, they were directly pressed to form membranes at room temperature and also tested using the cell shown in Figure 4.2 (b). (5) The conductivity of the membrane under 20% humidity condition was also tested by purging 80°C water vapor saturated air into the testing cell or the fuel cell as described in Figure 4.3.

TGA, GPC and CHN analysis: (1) TGA has been performed for polymer samples 5.23 and 5.26. The temperature for TGA was first increased from room temperature to 80°C and kept at 80°C for two hours to remove possible solvent left in the polymer. Then the temperature was back to room temperature and again increased to 500°C with the rate of 10°C/min. The tests were in the dir air condition. (2) THF and DMF were used as the mobile phase respectively and polystyrene as the standard for the GPC tests of polymer samples 5.23 and 5.26. The concentrations of samples were around 10mg/ml. (3) Polymer samples for CHN analysis were dried under vacuum at 120°C for two days and sealed in vials before tests.

5.3 Experimental Results and Discussion

For the synthesis of 1,2,3-triazole derivatives, two different methods were studied: Banert Reactions and Click Reactions. Banert Reactions could provide $1H$-1,2,3-triazole ring directly. However, there exist several disadvantages: (1) Through Banert
reactions, the structures of the resulted triazole derivatives were limited. As a fact, to further introduce the double bond to the ring, it is necessary to substitute the hydrogen on N1 with more stable groups. (2) The yields of Banert reaction are relatively low, typically <50%. (3) The reactants, such as propargyl bromide or prop-2-ynyl-4-methylbenzenesulfonate are highly electrophilic and volatile compounds, which can cause serious skin allergy. The mild reaction condition and high yields make Click Reactions suitable for the synthesis of 1,2,3-triazole derivatives. A suitable substitution groups on N1 is the key to provide 1H-1,2,3-triazole rings. The experimental results showed 4-methoxybenzyl group reported in Ref. [5] is one of the best choices due to its stability to normal acid/base and oxidation/reduction condition and the complete removal of this group by refluxing in TFA. As described in Figure 5.3, different 1,2,3-triazole derivatives were successfully prepared in high yields. For most of the compounds, the whole synthesis route does not need purification by flash column, and the reactions can be done at room temperature. For the key step to form 1,2,3-triazole ring by Click Chemistry, we used copper powder instead of Cu⁺, which simplified the synthesis and purification processes.

Through the synthesis of vinyl, allyl, and butenyl triazole, different siloxanes of triazole were prepared by hydrosilation reactions catalyzed by H₂PtCl₆. The experiments showed that H₂PtCl₆ is better than other catalysts such as Karstedt’s catalyst for these hydrosilation reactions. The reactions typically take several days to complete, and the resulted product was a mixture of different siloxanes with silyl groups attached to one of the carbon in the original double bond. It was found that small part of the monomers was condensed to form oligomers during the hydrosilation reactions, purification process and in storage.

Poly(4-vinyl-1H-1,2,3-triazole) was synthesized from two different methods as described in Figure 5.4: (a) For sample 5.23-1, the monomer 5.13 was first polymerized in DMF, and the average Mₙ of resulted polymer 5.25 was 2.2×10⁴ and polydispersity
was around 2.0. By heating polymer 5.25 in TFA, the 4-methoxybenzyl groups were completely removed. (b) For sample 5.23-2, the monomer 5.13 was first refluxed to provide monomer 5.24 and then polymerization in DMF. From route (b), the yield was lower due to the washing and distillation process to purify monomer 5.24 before polymerization. Also, in the experiments, we found that monomer 5.24 is not stable when stored in the air condition, and can be self-polymerized to form high molecular weight polymers. Also, the polymerization of monomer 5.23 with 1% initiator provided much high molecular weight product that cannot dissolve well in normal organic solvents. To achieve similar molecular weight as from route (a), 10% initiator was applied for the polymerization of monomer 5.24.

![Figure 5.6 IR spectra of Poly(4-vinyl-1H-1,2,3-triazole) from two different synthetic methods and polymer mixed with TFA.](image)

However, for route (a), there exists possibility to introduce small amount of TFA into the basic triazole polymer product, which may have effects on the conductivity of the resulted polymers. To identify this, we dissolved the polymer 5.23 from route (b) in TFA
and concentrated the solution under reduce pressure. Without any washing process, the concentrated polymer-TFA mixture was dried at 120°C under vacuum for 2 days. TFA left in the polymers was calculated to be 35 wt%. IR spectra of polymer 5.23-1, 5.23-2 and 5.23-TFA mixture were shown in Figure 5.6. Undissociated TFA has an identical peak around 1740 cm⁻¹ belonging to –C=O, and the protonated triazole rings have a ring C-N stretching peak around 1610 cm⁻¹.⁶,⁷ IR spectrum of sample 5.23-1 showed that the polymer prepared from the method (a) contains small amount of TFA, and it was found that the TFA content depended on the washing process.

![Graph showing temperature dependence of ionic conductivity of poly(4-vinyl-1H-1,2,3-triazole) from method a (■) and method b (▲), compared with the conductivity of poly(4-vinylimidazole)(○)]

Figure 5.7 Temperature dependence of ionic conductivity of poly(4-vinyl-1H-1,2,3-triazole) from method a (■) and method b (▲), compared with the conductivity of poly(4-vinylimidazole)(○).⁸
Figure 5.8 Temperature dependence of ionic conductivity of poly(4-vinyl-1H-1,2,3-triazole) and polymers with different acids doping.

The conductivities of polymer 5.23-1 and 5.23-2 were shown in Figure 5.7, together with the conductivity data of poly(4-vinylimidazole) previously reported [8]. Compared with poly (4-vinylimidazole), poly(4-vinyltriazole) provides higher ionic conductivity at the same temperature. The higher conductivity of sample 5.23-1, compared with that of sample of 5.23-2, is possibly resulted from the small amount of TFA in the polymer to increase the concentration of charge species. When we doped small acids into the polymer, the conductivities of these samples were also improved and shown in Figure 5.8. Introducing small acids to the basic triazole polymer improved the proton conductivity of resulted polymer composites by increasing the concentration of charged species through acid-base proton transfer reactions.

Similar as 1H-1,2,3-triazole (PKa=9.26) groups, phosphonic acid groups (PKa=2.10 for methylphosphonic acid) have both proton donating ability and proton conducting ability, and they are more acidic than 1H-1,2,3-triazole but weaker than sulfonic acid groups (PKa=-1.54 for methylsulfonic acid), if simply compare the PKa in
Due to the weak basicity of 1H-1,2,3-triazole (for protonated triazole, PKa=1.17), it is expected that in the triazole-phosphonic acid mixture, the major components will be a neutral hydrogen bonded network, with minor part of triazole cation and phosphate anion salts, and it is also expected in such system, both phosphonic acid and triazole groups can make contributions to the proton conduction. The acid-base proton transfer reactions were discussed through QM calculations in chapter 6.

In this chapter, poly(4-vinyl-1H-1,2,3-triazole-co-vinyl phosphonic acid) were synthesized, as described in Figure 5.4. Samples of 5.26-1,2,3,4,5 were synthesized with different molar ratio of triazole/phosphonic acid, by first copolymerization and followed removal of 4-methoxythylbenzene groups. The average Mn for all samples was around 3-4×10^5 and polydispersity was around 1.3-1.4. Sample 5.26-6 was prepared by copolymerizing 4-vinyl-1H-1,2,3-triazole with vinylphosphonic acid in DMF. The ratio of phosphonic acid/triazole in all samples was listed in Table 5.1.

Table 5.1 Ratio of monomers before reaction and in the copolymer. a: from CHN analysis; b: same as the reactant ratio due to the high yield(94%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>mole ratio(in reactants) of triazole/phosphonic acid</th>
<th>Molar ratio (in copolymers) of triazole/phosphonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.26-1</td>
<td>4:1</td>
<td>1:0.69a</td>
</tr>
<tr>
<td>5.26-2</td>
<td>1:1</td>
<td>1:1.34a</td>
</tr>
<tr>
<td>5.26-3</td>
<td>1:1.5</td>
<td>1:1.94a</td>
</tr>
<tr>
<td>5.26-4</td>
<td>1:2</td>
<td>1:1.77a</td>
</tr>
<tr>
<td>5.26-5</td>
<td>1:4</td>
<td>1:2.52a</td>
</tr>
<tr>
<td>5.26-6</td>
<td>1:1</td>
<td>1:1b</td>
</tr>
</tbody>
</table>

The IR spectra of all copolymer samples were shown in Figure 5.9. With the increase of phosphonic acid contents, the intensity of the peak around 1610 cm\(^{-1}\) from the protonated (or hydrogen bonded) triazole ring increased. Also, a broad band of phosphonic acids (-P=O and P-O-H stretching) around 800 cm\(^{-1}\) to 900 cm\(^{-1}\) was also observed. From the observation of the peak intensity around 1740 cm\(^{-1}\) and 1610 cm\(^{-1}\), the amount of TFA left in the polymers were much lower than that in homopolymers 5.23-1(Figure 5.7). For copolymer 5.26-6, the purification process of triazole monomer
before copolymerization avoid the relic of TFA in the copolymer. The conductivities of the copolymers were shown in Figure 5.10 (a). The conductivities of all copolymers are higher than that of poly(4-vinyl-1H-1,2,3-triazole) and comparable with the conductivity of poly(vinylphosphonic acid) which is a low molecular weight soft gel under high temperature. Among the copolymers, copolymer 5.26-3 with the molar ratio of triazole/phosphonic acid ≈1:2 has the highest conductivity, which also has better mechanical strength than that of poly(vinylphosphonic acid).

The conductivity of poly(4-vinylimidazole-co-vinylphosphonic acid) from previous studies was shown in Figure 5.10(b). Similar as in Figure 5.7, the conductivity of triazole-phosphonic acid copolymer is also about $10^2$ - $10^3$ times higher than that of imidazole-phosphonic acid copolymer at temperature >100°. (In the low temperature, the conductivity of the copolymer is sensitive to the humidity condition.) Imidazole is a much more basic heterocyclic compound than triazole, therefore the concentration of charged species in imidazole-phosphonic acid copolymer is much higher. However, the
Figure 5.10 Temperature dependence of ionic conductivity of (a) poly(4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid) and (b) poly(4-vinylimidazole-co-vinylphosphonic acid)
low concentration of proton conducting species and rigid hydrogen network limit the proton conduction in imidazole-phosphonic acid copolymers.

During the studies of 1H-1,2,3-triazole-phosphonic acid copolymers, we found that the copolymer with N-4-methoxybenzyl groups (copolymers 5.25) also have considerable ionic conductivities. Therefore, poly(1-vinyl-1,2,4-triazole-co-vinyl phosphonic acid) with 50 mol% 1,2,4-triazole was synthesized as described in Figure 5.4, and the conductivity of this copolymer was shown in Figure 5.11, compared with copolymers 5.26-6 and 5.25-2. It is surprising that poly(4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid) has the lowest proton conductivity among three copolymers. Without the extra proton on the nitrogen, the heterocycles in the copolymer only act as the proton conducting groups, and most likely the proton conducting mechanism has also been changed. The possible reason for higher proton conductivities in copolymer 5.27

![Graph showing temperature dependence of ionic conductivity](image)

**Figure 5.11** Temperature dependence of ionic conductivity of poly(4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid) (5.26-6, 50 mol% triazole), poly(1-vinyl-1,2,4-triazole-co-vinyl phosphonic acid) (5.27, 50mol% triazole) and poly(1-(4-methoxybenzyl)-4-vinyl-1,2,3-triazole-co-vinylphosphonic acid) (5.25-2, 57% triazole).
and copolymer 5.25-2 is that the organic groups on the nitrogen may break the hydrogen network between triazole and acids, and bring more local mobility to the proton conducting species. The data in Figure 5.11 showed the complexity to design heterocycle-acid copolymer for PEM applications.

The TGA data of homopolymer and copolymers were illustrated in Figure 5.12. The homopolymer was thermally stable up to 220°C. For copolymers, above 150°C, there were slow weight loss due to the water evaporation from the copolymer, and there existed considerable weight loss above 250°C. For the practical HT-PEM applications, some degree of humidity condition may help to prevent the phosphonic groups from dehydration.

![Figure 5.12 TGA of (4-vinyl-1H-1,2,3-triazole-co-vinylphosphonic acid) copolymers and homopolymer.](image)

To further improve the proton conductivity of the polymer based on 1H-1,2,3-triazole. Polysiloxane polymer 5.28 and 5.29, the hybrid membranes through sol-gel
process, and polysiloxane copolymers containing triazole and phosphonic acids were prepared, as illustrated in Figure 5.5. The experiments showed that the hydrosilation reactions of 4-allyl-1H-1,2,3-triazole (from 5.41 to 5.42) had very low reaction rate, therefore the polysiloxane polymers were synthesized through first hydrosilane and followed removal of N-4-methylbenzyl groups. To synthesize polysiloxane copolymer 5.40, concentrated HCl need to be used to hydrolyze the ester bond. HCl was removed from the copolymer by multiple-time distillation of water from the copolymer-water mixture. The IR spectrum of polysiloxane polymers 5.28, 5.29 and copolymer 5.40 were shown in Figure 5.13. The peak around 1610 cm\(^{-1}\) showed the existence of TFA in the polysiloxane polymer 5.28 and 5.29 due to inefficient washing procedure. From the peak intensity around 1740 cm\(^{-1}\) of copolymer 5.40, there were low content of TFA left in the copolymer due to the distillation process.

![Figure 5.13 IR spectra of Polysiloxane polymer with triazole grafted.](image-url)
Figure 5.14 Temperature dependence of ionic conductivity of polysiloxane polymers grafted with 1H-1,2,3-triazole and copolymers of triazole and phosphonic acid.

The conductivities of polymer 5.28, 5.29, copolymer 5.39 and 5.40 were reported in Figure 5.14. The high proton conductivity of polysiloxane polymers 5.28 and 5.29 were resulted from the fluid character of these polymers at high temperature and TFA left in the polymer. The copolymers of triazole and phosphonic acid showed lower conductivities than the polysiloxane polymer, possibly due to higher Tg of copolymers resulted from the hydrogen bonding between triazole and phosphonic acid. Similar as in Figure 5.11, the copolymer with 4-methoxybenzyl groups on the triazole rings provided higher proton conductivity than that of 1H-1,2,3-triazole copolymer.

To improve the mechanical properties of the polysiloxane polymers, different sol-gel processes have been tested to prepare the hybrid membranes (5.30-5.35) based on polysiloxane polymer 5.28 and 5.29. However, for the membranes providing acceptable mechanical strength in the testing temperature range (room temperature to 150°C), the
conductivities were low, typically in the range of $10^{-4}$ to $10^{-5}$ s/cm at 120°C, dry air condition. Compared with the polysiloxane polymer, the content of triazole groups and the local mobility of triazole ring in the hybrid membranes are lower. Therefore, to achieve a fully polymerization HT-PEM with high proton conductivity and also good mechanical properties, various possible factors to improve proton conductivities need to further studied.

Also, for all the polymers and copolymer we synthesized, the conductivities at 120°C under low humidity condition (typically 20%) were measured as mentioned. However, by purging the humidified air through the testing cell, the conductivities of these membranes could not be improved significantly. The polymers with high phosphonic acid or sulfonic acid contents showed longer water-losing time, but the high conductivities due to the water brought from the preparation process still dropped down after a long heating time. Detailed studies of water effect require a test in-situ in the fuel cell and it needs the membrane with good mechanical strength at high temperature. Currently, these polyethylene and polysiloxane based polymers were not suitable candidates for these studies.

5.4 Conclusions
In this chapter, the synthesis of 1,2,3-triazole derivatives and polymers was reported. The conductivity and other properties of the prepared polymers were described and discussed. The $1H$-1,2,3-triazole, when grafted onto the polymer backbones, showed comparable proton conducting ability as the phosphonic acids. Also, as an organic heterocyclic compound, it brings low polarity to the material and also various possibilities to modify the material to improve the conductivity. Combining with its electrochemical stability identified in Chapter 4 and thermo-stability, it is believed that 1,2,3-triazole based polymers are one of promising candidates for the HT PEM materials. Improving both the conductivity and mechanical properties of the materials are needed for further studies.
5.5 References


CHAPTER 6
THEORETICAL STUDIES OF PROTON CONDUCTION IN 1H(2H)-1,2,3-TRIAZOLE

6.1 Introduction

The proton conduction is related to both the proton transfer reaction in the hydrogen bonding complex and the translation motion or rotation of proton conducting groups and charge species in the materials. Computational calculations, as a powerful tool nowadays, can be used either to understand different steps in the proton conducting process or to model the whole proton conduction in the materials. Most importantly, a rational model based on the large amount of experimental data can provide a simplified and effective way for predicting the properties of material in advance.

It have been discussed in Chapter 3 and Chapter 4 that 1H(2H)-1,2,3-triazole can effectively promote proton conduction in a polymer electrolyte membrane (PEM). In a way similar to H₂O, H₃PO₄, or imidazole used in PEMs, 1H(2H)-1,2,3-triazole may conduct proton through either the vehicle mechanism or Grotthuss mechanism. The latter is especially important to the design of PEMs with triazole groups attached to the backbones. Because of the demonstrated ability of 1H(2H)-1,2,3-triazole to promote proton transport, triazole-containing PEMs hold great promise for a new generation of PEM fuel cells that could be operated at high temperatures (above 100°C) with low relative humidity.

The Grotthuss-type proton motion along an imidazole molecular chain is sketched in Figure 6.1 [1, 2]. Clearly, once a proton is transferred from one imidazole ring to an adjacent one, reorientation (or flipping) of the imidazole moiety becomes necessary for subsequent inter-molecular proton transfer to take place in the same direction. It is this reorientation step that was reported [3] as the rate-limiting step for long-range proton conduction along the molecular chain; it might as well be the major impediment to high
proton conductivity in imidazole-based materials. In contrast, triazole-based systems might open the possibility for different mechanisms, as suggested by the existence of several proton-carrying isomers: Neutral triazole has two tautomers, 1H-1,2,3-triazole (A) and 2H-1,2,3-triazole (B), and so does protonated triazole, 1,3-diH (a) and 1,2-diH-1,2,3-triazolium (b) cations.

![Proton conduction in imidazole through Grotthuss mechanism](image)

Figure 6.1 Schematic of proton conduction in imidazole and the structures of 1H(2H)-1,2,3-triazole and 1,2(1,3)-diH-1,2,3-triazolium cations.

As discussed in Chapter 3, QM calculations for modeling the structure or energy-related properties in small scale (typically <100 atoms) based on quantum mechanics and classical MD simulations to model the properties of material in large scale through classical mechanics are two typical calculation methods. The calculation methods between them, such as ab initial MD are still in the early stage of development. To explain and predict proton conduction in the materials, it is necessary to go through all steps in the proton conducting process by applying all three calculation methods.

However, before we started our research on 1H-1,2,3-triazole, both experimental and theoretical studies of 1H(2H)-1,2,3-triazole have been limited [4,5,6] primarily to the exploration of the tautomerism between the neutral isomers A and B. Little is known
about the tautomerism of the 1,2-diH and 1,3-diH-1,2,3-triazolium cations \(a\) and \(b\) or the interactions among these four species.\(^7\) Therefore the computational model reported in this chapter was first focused on determining how one triazolium cations interact with another neutral triazole molecules and how the short-range proton transfer reaction proceeds in complexes involving more than one triazole unit. During the next step, the sulfonic acid, phosphonic acid and triazole anions were introduced into the triazolium-triazole complex to study the counter ion effects on the complex structure and energy. In the final part, the thermodynamic calculation of the proton transfer reactions between acids and triazoles have also been done to discuss the acid doping on proton conduction in basic polymers.

6.2 Computational Details

All calculations were performed with the GAUSSIAN 03 package\(^8\). A hybrid Hartree-Fock/density functional theory (HF/DFT) method, B3LPY, which includes Becke’s three-parameter nonlocal-exchange function with the correlation functional of Lee-Yang-Parr, was used for the geometrical optimization of the local minima and transition states with no constrained degrees of freedom.

**Calculations on triazole/triazolium dimers:** The initial geometries were from the triazole crystal structures determined by X-ray diffraction\(^9\). All geometries were fully optimized and final energies were calculated in gas phase at the HF/6-31G(d) and B3LYP/6-311+G(d) levels of theory. Harmonic vibrational frequency calculations were then performed at the B3LYP/6-311G+(d) level to confirm the optimized structures as minima and evaluate zero-point vibrational energy (ZPE) corrections.

**Calculations on three-molecule complexes:** By considering the counter ion and environment effect, the three-molecule complexes of \(\text{C}_2\text{N}_3\text{H}_2^-\) (triazole anion)-
triazole/triazolium dimers, CH$_3$PO$_3$H–triazole/triazolium dimers and C$_5$H$_6$SO$_3$–triazole/triazolium dimers were also computed by introducing the third molecules of C$_2$N$_3$H$_7^–$, CH$_3$PO$_3$H$^–$ and C$_6$H$_5$SO$_3$–, respectively into the triazole/triazolium dimmers. The geometrical structures of these dimer and trimer systems were fully optimized and the most stable energy of the optimized structures was computed in gas phase. The basis set used in this work is the standard all-electron split-valance basis set 6-311G+(d,p) including polarization d-function on non-hydrogen atoms, was employed. Final energies were calculated at the B3LYP/6-311+G(d,p) levels, without zero-point-energy (ZPE) corrections due to the computational complexity.

In the trimer system, the most energetically favored structures are in the forms with three neutral molecules in the gas phase. To consider the stability in the forms of ionic complexes, the geometrical structures were optimized restrictedly by fixing the H-N bonds of triazolium. The energetic differences between molecular and ionic complexes were calculated also.

**Calculation on equilibrium constants of proton transfer reactions:** The standard Gibbs free energies of interested species were predicted by applying the polarized continuum model (PCM) on reliable internal energies of gas-phase reactions, which can be computed by a hybrid Hartree-Fock/density functional theory (HF/DFT) method (B3LYP), including Becke’s three-parameter nonlocal-exchange function with the correlation functional of Lee-Yang-Parr, and the standard all-electron split-valance basis set 6-311+G(d,p). The computed Gibbs free energies of reactions will be applied for the pKa values in the equation of pKa = ΔG /RTln10.
6.3 Results and Discussions

First, we reproduced the results of previous calculations on the various tautomers \( A, B, a, \) and \( b \). For neutral triazole in the gas phase, \( B \) is more stable than \( A \) by 18.6 kJ/mol. Since \( A \) (\( \mu = 4.64 \) D) has a significantly larger dipole moment than \( B \) (\( \mu = 0.21 \) D), however, \( A \) becomes increasingly more stable with the medium polarity. As a protonated cation, tautomer \( a \) is more stable than \( b \) by 49.1 kJ/mol. The \( A \leftrightarrow B \) or \( a \leftrightarrow b \) tautomerisms may greatly assist in the inter- and intra-molecular proton transfer in the system. As has been reported earlier, these tautomeric processes may involve either solvent molecules or the formation of dimers, trimers, or other complexes to lower the energy barriers and assist proton conduction.

To study inter-molecular proton transfer, initial structures of neutral/protonated triazole complexes were built by combining one of the two neutral tautomers \( A \) or \( B \) with one of the two cations \( a \) or \( b \) through a single \( N-H-N \) hydrogen bond and varying the dihedral angle between the two molecular planes. To select stable geometries, we performed geometry optimizations at the HF/6-31G(d) level, which led to thirteen possible configurations of the complexes; further geometry optimizations and frequency calculations at the B3LYP/6-311+G(d) level produced the complex structures shown in Figure 6.2, with the corresponding energy values summarized in Table 6.1. We also considered coplanar complexes with two hydrogen bonds between the neutral and protonated triazole molecules as the initial structures; after geometry optimization, however, all these structures reduced to those presented in Figure 6.2.

We find that, stable complexes are formed via hydrogen-bond formation between an \( -NH \) group on the protonated triazole as proton donor and a nitrogen atom on the
Group A-a

A-a-p1

A-a-p2

Group A-b

A-b-p1

A-b-p2

A-b-p3

Group B-a

B-a-p1

B-a-v1
Figure 6.2 Possible structures of triazole/triazolium dimmer complexes.
neutral triazole as proton acceptor. The distance between two nitrogen atoms in the hydrogen bond is in the range 2.69 - 2.75 Å. The thirteen structures can be distributed into four groups: A-a, A-b, B-a, B-b. In groups B-a and B-b, some complexes have two optical isomers, in which the two planes of the triazole molecules are perpendicular to each other; tautomer B has more flexibility to form stable complexes with protonated cations because of its symmetry.

Table 6.1 Energy calculated at the B3LYP/6-311+G(d) level and possible complex after proton transfer.

<table>
<thead>
<tr>
<th>SP Energy (a.u.)</th>
<th>G&lt;sub&gt;298&lt;/sub&gt; (a.u.)</th>
<th>G&lt;sub&gt;relative&lt;/sub&gt; (kJ/mol)</th>
<th>ΔG&lt;sub&gt;298&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (kJ/mol)</th>
<th>Possible complex after proton transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-242.28591</td>
<td>-242.25326</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>-242.29388</td>
<td>-242.26034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>-242.63643</td>
<td>-242.58926</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>-242.61640</td>
<td>-242.57054</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-a-p1</td>
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<td>-484.86602</td>
<td>17.9</td>
<td>-61.7 A-b-p2</td>
</tr>
<tr>
<td>A-a-p2</td>
<td>-484.96818</td>
<td>-484.87284</td>
<td>0.0</td>
<td>-79.6 A-a-p2</td>
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<tr>
<td>A-b-p1</td>
<td>-484.94638</td>
<td>-484.85037</td>
<td>59.0</td>
<td>-69.8 B-b-p1/p3/v3/v4</td>
</tr>
<tr>
<td>A-b-p2</td>
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<td>-484.85815</td>
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<tr>
<td>A-b-p3</td>
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<td>-36.0 A-a-p3</td>
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<td>-36.0 A-a-p3</td>
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<td>-484.84841</td>
<td>64.1</td>
<td>-46.0 B-b-v1/v2</td>
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<td>B-b-v2</td>
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<td>-484.84841</td>
<td>64.1</td>
<td>-46.0 B-b-v1/v2</td>
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<tr>
<td>B-b-v3</td>
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<td>-484.84865</td>
<td>63.5</td>
<td>-46.7 A-b-p1</td>
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<td>B-b-v4</td>
<td>-484.94343</td>
<td>-484.84865</td>
<td>63.5</td>
<td>-46.7 A-b-p1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Standard Gibbs free energy change for the coupling reactions between A/B and a/b through hydrogen bonding.

Earlier studies on ionic hydrogen bonds in other systems reported bond strengths in the range 20 - 150 kJ/mol.<sup>[10]</sup> Evaluations of the standard Gibbs free energy change for the reaction (A/B) + (a/b) → (A/B)-(a/b) are given in Table 6.1. In addition, the reaction barriers of these inter-molecular proton transfer processes, C<sub>2</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> + C<sub>2</sub>N<sub>3</sub>H<sub>3</sub> → C<sub>2</sub>N<sub>3</sub>H<sub>3</sub> + C<sub>2</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup>, are computed to be 4 - 8 kJ/mol based on the energies predicted at the B3LYP/6-311+G(d) level with ZPE corrections. The results indicate that the protonated triazole cations in triazole-based materials have great tendency to form
various complexes with neutral triazole molecules through ionic hydrogen bonds. As illustrated in the comparative energy diagram of Figure 6.3, the most stable structure is \( A-a-P2 \) while the least stable one are \( B-b-v1/v2 \); the energy difference between them is about 64.1 kJ/mol. The comparative energy diagram allows us to discern three classes of systems: all the \( B-b \) structures have higher energy; nearly all \( A-b \) and \( B-a \) structures belong to a medium energy class while \( A-a-P2 \) is the only member of the low energy class. As shown in Table 6.1, if proton transfers from the cation to the neutral triazole through the ionic hydrogen bond in the complex, the resulted complex still belongs to the same class. The transformation of complexes in different classes needs the breaking of hydrogen bonds and further rotation. Because the complexes in the same class have very small energy differences (0 - 20 kJ/mol) and the proton transfer reaction barriers are quite small, we conclude that the inter-molecular proton transfer reactions are feasible for all complexes.

Figure 6.3 Comparative energy diagram of triazole/triazolium dimer complexes.
Based on our calculations, A-a-P2 has the lowest energy in gas phase and is the most likely complex responsible for inter-molecular proton transfer under the condition in which the tautomer $A$ is the major species of neutral triazoles, such as in a polar medium. After a proton transfers from cation $a$ to neutral $A$ through the hydrogen bond, the resulting complex is nearly identical, with $A$ and $a$ having switched positions. This process is similar to that in an imidazole-containing system.

In a less polar environment, tautomer $B$ was reported to be more stable than tautomer $A$ and was the major form in two isomers. We note that it is possible for the less stable $B$-b group complexes in the high-energy class to transform to complex $B$-a-p1/v1/v2 through energetically favorable inter-molecular proton transfer reactions and rotations. Thus, complexes such as $B$-a-p1/v1/v2 could turn out to be the most likely complexes under less polar conditions. However, other complexes (such as $A$-b-p3 and the $B$-b group complexes) will be involved in the proton inter-molecular transfer process as well.

Based the optimized geometries of triazolium/triazole dimmers, three different anions including $C_2N_3H_2^-$ (triazole anion), $CH_3PO_3H^-$ and $C_5H_6SO_3^-$, were introduced to the dimmers to form three-molecule complex. In the initial geometries of complex with triazole anion, N1(N3) on the triazole anion was chosen to form linear hydrogen bond with triazolium cations. The observed relaxed geometries of three-molecule complexes were in the forms with three neutral molecules in the gas phase, labeled as “relax” in the figure of Appendix A. In order to consider the stability in the forms of ionic complexes, the geometrical structures were optimized restrictedly by fixing the H-N bonds of triazolium and labeled as “mod” in the figure of Appendix A. The calculated energy data were shown in Table 6.2.
Table 6.2 Energy of three-molecule complex calculated at the B3LYP/6-311+G(d,p) level.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E_{relax} (a.u.)</th>
<th>E_{mod} (a.u.)</th>
<th>ΔE (kJ/mol)</th>
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<tr>
<td>C2N3H2 (A-a-p1)</td>
<td>-726.9011043</td>
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<tr>
<td>C2N3H2 (A-a-p2)</td>
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<td>C2N3H2 (A-b-p1)</td>
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<td>C2N3H2 (A-b-p2)</td>
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<td>C2N3H2 (A-b-p3)</td>
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<td>C2N3H2 (B-a-p1)</td>
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<td>C2N3H2 (B-a-v1,v2)</td>
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<table>
<thead>
<tr>
<th>Complex</th>
<th>E_{relax} (a.u.)</th>
<th>E_{mod} (a.u.)</th>
<th>ΔE (kJ/mol)</th>
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<th>E_{mod} (a.u.)</th>
<th>ΔE (kJ/mol)</th>
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<th>ZPE (kJ/mol)</th>
<th>E+ZPE (kJ/mol)</th>
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From Table 6.2, Figure 6.4 and Figure 6.5 were achieved. As shown in Figure 6.4, the three energy classes in dimmers are changed to be two classes in three-molecule complexes. The largest energy difference in same type of three-molecule complexes is around 40kJ/mol, which is less than that for dimers (65 kJ/mol). It is also observed that 1,2-di\(H\)-1,2,3-triazolium cation \(b\) with larger dipole moment exists in most of the three-molecule complexes that belongs to the low energy level class. As mentioned, cation \(b\) is calculated to be far less stable (\(\Delta E = 49.1\)kJ/mol) than 1,3-di\(H\)-1,2,3-triazolium cations \(a\) in single form, and is stabilized more effectively than \(a\) by the introduced anions in the complex. Therefore it is possible that by introducing acids, the dimers in group \(B-b\) and \(A-b\) described play more important role in proton conduction in stead of group \(B-a\) and \(A-a\) as mentioned before.

![Figure 6.4](image.png)

Figure 6.4 Energy diagram of acid-triazole/triazolium complexes.
By comparing the energy difference between $E_{\text{relax}}$ and $E_{\text{mod}}$ in Figure 6.5, the influence of acidity of the acid groups on the protonation of triazole-triazole dimer were illustrated. Calculated in gas phase condition, the phenylsulfonic acid showed high possibility to protonate the triazole to form triazolium/triazole dimers due to its strong acidity. For methylphosphonic acids, there exists big difference between complexes with different dimer geometries, which shows that beside the acidity, there exists structure effects on the stability of acid anion-triazole/triazolium complexes. For both phenylsulfonic acids and methylphosphonic acids, the complexes with $A-b-p_2$, $A-b-p_3$ and $B-b-v_1,v_2$ dimers have lower $\Delta E$ than that of other complexes. By observing the geometries of these six complexes, for example the structure of $C_5H_6SO_3^-$ (B-b-v1,v2) as shown in Figure 6.6, the hydrogen bonding ring within the structure (mod) with short bond length, is the key to provide both the stability to the structure and high degree of dissociation of proton from acid to the triazole.

Figure 6.5 $\Delta E$ diagram of acid-triazole/triazolium complexes
To form the ring structure, protonation of triazole to form triazolium \( b \) is a requirement. It is three N atoms in the triazole make all things happen: (1) formation of hydrogen bonding ring structure in the complex with acids; (2) dissociation of proton from acids to triazole rings; (3) the ability to accept other hydrogen bonds out of the complex with available nitrogen atoms.

Due to limitation of computational complexity, it is hard to do calculations with systems containing more triazole molecules. However, if the ring structure provides in the calculations represents the real structures in the materials, they may have both positive and negative effects on proton conduction in the materials: (1) The proton dissociation from acids to triazoles is assisted; (2) The isomerization of \( 1H-1,2,3\)-triazole and \( 2H-1,2,3\)-triazole may be happened in the ring;(3) The long range proton diffusion is limited by limiting proton transfer in the complex. Obviously, all effects are related to the local mobility of triazole and acid groups in the materials. Further studies need to been done to figure out these effects.

The calculation at B3LYP/6-311+G(d) level provided the equilibrium constants of acid-base reactions(Table 6.3a,b). Because these data have not been corrected based on experimental data, and it is also hard to identify the solvent condition in a polymer
system, the data here only relatively describe the effect of the solvent condition and acidity/basicity of the acid/base on the equilibrium of the acid-base reaction. To some degree, they support that in a 1:1 molar ratio of phosphonic acid/base mixed polymer system, unlike imidazole, only small part of 1,2,3-triazole form salts with the acids.

Table 6.3 (a) Calculated free energy of acids and bases in gas, water and heptane.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gas (K, atm)</th>
<th>Water (K, atm)</th>
<th>Heptane (K, atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole (im)</td>
<td>-226.128454</td>
<td>-226.136068</td>
<td>-226.151823</td>
</tr>
<tr>
<td>Imidazolium (im⁺)</td>
<td>-226.497208</td>
<td>-226.548642</td>
<td>-226.609301</td>
</tr>
<tr>
<td>Imidazole anion (im⁻)</td>
<td>-225.56158</td>
<td>-225.609957</td>
<td>-225.666757</td>
</tr>
<tr>
<td>1H-1,2,3-triazole (Tri_A)</td>
<td>-242.13727</td>
<td>-242.145939</td>
<td>-242.163415</td>
</tr>
<tr>
<td>1,3-dih-1,2,3-triazolium (Tri_a⁺)</td>
<td>-242.482101</td>
<td>-242.536208</td>
<td>-242.600968</td>
</tr>
<tr>
<td>2H-1,2,3-triazole (Tri_B)</td>
<td>-242.149691</td>
<td>-242.19691</td>
<td>-242.16271</td>
</tr>
<tr>
<td>1,2-dih-1,2,3-triazolium (Tri_b⁺)</td>
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<td>-242.518926</td>
<td>-242.58853</td>
</tr>
<tr>
<td>1,2,3-triazole anion (Tri⁻)</td>
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<td>-275.567904</td>
<td>-275.629606</td>
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<tr>
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<td>-312.364573</td>
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<td>HSO₄⁻</td>
<td>-311.446071</td>
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<td>-311.557294</td>
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Table 6.3 (b) Calculated ΔG and pKa of acid-base reactions in gas, water and heptane.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>△G(298K,1atm) in gas, kcal/mol</th>
<th>△G(298K,1atm) in hep., kcal/mol</th>
<th>△G(298K,1atm) in H2O,kcal/mol</th>
<th>pKa in gas</th>
<th>pKa in hept</th>
<th>pKa in H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2im→im^+ and im^-</td>
<td>124.32</td>
<td>71.25</td>
<td>17.31</td>
<td>91.14</td>
<td>52.23</td>
<td>12.69</td>
</tr>
<tr>
<td>2Tri_A→Tri_a^+ + Tri^-</td>
<td>129.69</td>
<td>75.16</td>
<td>19.30</td>
<td>95.08</td>
<td>55.10</td>
<td>14.15</td>
</tr>
<tr>
<td>2Tri_B→Tri_b^+ + Tri^-</td>
<td>148.93</td>
<td>90.71</td>
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<td>109.18</td>
<td>66.50</td>
<td>19.22</td>
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<td>7.80</td>
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<td>136.72</td>
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<td>105.36</td>
<td>59.44</td>
<td>8.78</td>
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<td>54.1</td>
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<td>36.50</td>
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<tr>
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<td>123.25</td>
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<td>-24.27</td>
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<tr>
<td>CH₃SO₃H + Tri_A</td>
<td>107.55</td>
<td>54.1</td>
<td>-1.17</td>
<td>88.79</td>
<td>36.50</td>
<td>-11.76</td>
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<td>CH₃SO₃H + Tri_B</td>
<td>123.25</td>
<td>67.3</td>
<td>6.19</td>
<td>104.50</td>
<td>4.70</td>
<td>-4.40</td>
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<tr>
<td>H₃PO₄ + im</td>
<td>74.65</td>
<td>32.25</td>
<td>-11.09</td>
<td>54.73</td>
<td>23.64</td>
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<tr>
<td>H₃PO₄ + Tri_A</td>
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<td>1.41</td>
<td>65.73</td>
<td>33.90</td>
<td>1.04</td>
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<tr>
<td>H₃PO₄ + Tri_B</td>
<td>105.36</td>
<td>59.44</td>
<td>8.78</td>
<td>77.24</td>
<td>43.58</td>
<td>6.43</td>
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<td>H₂SO₄ + im</td>
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<td>54.09</td>
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<td>H₂SO₄ + Tri_A</td>
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<td>-4.4</td>
<td>76.61</td>
<td>36.43</td>
<td>-3.23</td>
</tr>
</tbody>
</table>

6.4 Conclusions

In this chapter, the QM calculations on triazolium/triazole dimers and acid-triazolium/triazole three-molecule complexes have been reported. The calculations of equilibrium constants of acid-base reactions are also described. The data show that the three nitrogen atoms on 1,2,3-triazole may greatly change the proton conduction pathway in the triazole based materials. Also compare with imidazole, triazole has shown quite different acid/base properties, which may be important for proton conduction in acid-base mixed polymers.
6.5 References


CHAPTER 7

OTHER HETEROCYLES AND H₃PO₄

7.1 Introduction

To accept or donate protons, nitrogen-containing heterocycles are the most suitable choice. Besides 1H(2H)-1,2,3-triazole, other heterocycles are possible to be used as proton conducting materials for HT PEM applications. Previously, fluorinated imidazole [¹] was suggested as a proton conductor with similar proton conducting ability and alleviated poisoning effect to Pt. By considering the electrochemical and thermal stability of various heterocycles, also the synthetic complexity and potential environment effects, 1,2,4-triazole and imidazole derivatives have been studied in our research. Proton conductivity, electrochemical and thermal stability of these compounds have been discussed in this chapter.

On the other hand, PBI-H₃PO₄ is still a promising PEM system currently for any stationary applications, and possibly for mobile applications also, if there exist any ways to solve the technical difficulties including acid leaking. During the research, we have also looked into developing new membranes containing H₃PO₄. There are several requirements for this new type of membranes: (1) enough H₃PO₄ absorption ability; (2) enough thermal, chemical and electrochemical stability, especially at elevated temperature and high acidity condition; (3) enough mechanical strength in the temperature range studied. As a fact, there are only few suitable basic polymer fiber systems. Even for PBI, the long term hydrolysis stability under humidity condition and electrochemical stability are still part of the concern.

The previous studies on SiO₂-H₃PO₄ suggested the potential to use inorganic/organic silicon based hybrid membranes with H₃PO₄ doped for new HT PEMs. The bond energies are 549 kJ/mol, 536kJ/mol and 477kJ/mol for Si-O in Me₃Si-O-SiMe₃, Me₃Si-OH and Me₃Si-OEt respectively, and it is 369kJ/mol for Si-C in H₃Si-CH₃. [²] The
enthalpy for the hydrolysis of Si-O-Si in Me₃Si-O-SiMe₃ is estimated around 26kJ/mol. The strong acid catalyzes both the condensation and hydrolysis reactions. Therefore in hybrid membranes with H₃PO₄ doping, when working above 100°C under low humidity, the hydrolysis stability should not be a concern, but may turn to be a problem at low temperature with the existence of liquid water.

Previously our groups reported [3] silicone based inorganic/organic hybrid membranes doped with H₃PO₄ for HT PEM applications. The poly(propylene oxide) polymer chain (7.3) in the membrane is responsible for both the absorption of H₃PO₄ and the elasticity/elongation of the membranes. The membranes showed acceptable proton conductivities (10⁻²-10⁻⁴ cm/S at 120°C, dry condition), however the fuel cell test showed low performance, and the membrane was not thermally strong and stable. The research in this chapter has addressed the possible reason and solution for these problems in hybrid membrane studies.

7.2 Experimental Section

Chemicals and Instruments: Organosilanes were purchased from Gelest, Inc., solvents were from VWR, Inc., and other chemicals were purchased from Aldrich, Inc. Merck silica gel (70-230 mesh) and thin layer chromatography (TLC) plates for flash chromatography were purchase from Sorbent Technologies, Inc. The chemical structures of the synthesized compounds were typically confirmed by ¹H NMR. NMR: δ in ppm vs SiMe₄ (0 ppm, ¹H, 300 MHz). MS: selected peaks; m/z. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Rheometric Scientific STA 1500 and a TA instrument 2050. A Solartron 1255 frequency response analyser and a Solartron 1286 potentiostate/galvanostat interfaced with a computer were used for conductivity measurements.

Preparation of 1H-1,2,4-Triazoles/4-dodecylbenzenesulfonic acid mixture and sPSU/triazole membranes: The mixtures of 1H-1,2,4-triazole and 4-dodecylbenzenesulfonic acid (C₁₂PhSO₃H) were made by co-dissolving them in ethanol
and then evaporating the solvents in a vacuum at 80 °C. To incorporate triazole into the sPSU to form sPSU-triazole membranes, dried sPSU (IEC of 1.40 mequiv/g) polymers were immersed in pure liquid 1H-1,2,3-triazole and sealed in a glass vial. Upon heating to 120°C and kept for 24 hours, triazole was imbedded into the polymer. The ratio of [1H-1,2,4-triazole] to [-SO3H] was calculated from the weight of the polymer before and after immersion in 1H-1,2,3-triazole. Three samples with different ratio were prepared.

**Preparation of 2-ethylsulfonyl-1H-imidazole (7.2) and its mixtures with benzenesulfonic acid:** 2-ethylsulfonyl-Imidazole was prepared with the method described in Ref. [4], and the product was confirmed by 1H NMR and mass spectroscopy. 2-ethylsulfonyl-Imidazole and benzenesulfonic acid were dissolved in methanol and stirred for 10 minutes. After the solvent was removed, the same was dried at 80 °C under vacuum. [5]

**Cyclic Voltammetry Experiments:** A typical three-electrode cell was first filled with 0.1mol⋅dm⁻³ CH₃CN solution of TBAPF6 as the electrolyte. To study the electrochemical stability, 1H-1,2,4-triazole or 2-ethylsulfonyl-1H-imidazole dissolved in CH₃CN was added to make the final concentration equal to 5×10⁻³ mol⋅dm⁻³. The solution was purged with N₂ or O₂ for 30min with ~30ml/min flow rate before measurements and with very low flow rate during the test. Cyclic voltammetric measurements were performed with potential sweep rate of 50 mV/s using a platinum work electrode, a platinum auxiliary electrode and an Ag/Ag⁺ reference electrode (0.1 mol⋅dm⁻³ AgNO₃-CH₃CN containing 0.1mol⋅dm⁻³ TBAPF6). The data were recorded using a solartron 1286 potentiostate/galvanostate interfaced with a computer.

**Preparation of polysiloxane polymer with 1,2,4-triazole grafted(7.9):** 1H-1,2,4-triazole (6.9g, 0.1mol) and dimethoxymethyl-3-chloropropyl silane (18.2g, 0.1mol) and KOH(6.8g, 0.12mol) were mixed in MeOH 100ml and the solution were refluxed for three days. After evaporated the solvent, the residue was dissolved in CH₂Cl₂ and the
solution was washed with water. The organic layer separated was dried with anhydrous MgSO$_4$ and evaporated to provide 17.1g oil (~100% yield). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ -0.2-0.1 (br m, CH$_3$-Si), 0.2-0.6 (br, -CH$_2$-Si), 1.6-2.0 (br, -CH$_2$-C-Si), 4.0-4.2 (br, -CH$_2$-N), 7.8-8.4 (br, -CH=N). $^{13}$C NMR $\delta$ -0.27, 14.26, 23.87, 52.14, 143.43, 152.1.

**Preparation of siloxane Si-PEG-Si (7.6):** (a) NaH (60% in mineral oil, 9.6g, 0.24mol) was mixed with 100 THF. With stirring, PEG600 (60g, 0.1mol) in THF 150ml was added dropwise into NaH solution at 0°C. Allyl bromide (31.5g, 0.26mol) in 30ml THF was slowly added and stirred at room temperature overnight. 10ml water was slowly added into the solution and the solution was filtered and evaporated to remove the solvent. The residue was dissolved in CH$_2$Cl$_2$ and the filtration was done with a short silica gel column. After solvent evaporated, 47.1g diallyl PEG600 (7.5) (0.069mol, 69% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 3.59 (d, ~48H), 3.96 (dt, $J$=5.66, 4H), 5.16 (qq, 4H), 5.86 (m, 2H). (b) Diallyl PEG600 (17g, 0.025mol) was mixed with methyldiethoxysilane (13g, 0.1mol), and several drops of H$_2$PtCl$_6$-isopropanol solution (42mg/ml) was added. At 100°C stirred for two days, the reaction was completed. After evaporation under reduced pressure, 23.6 liquid product (0.25mol, 10% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.0-0.10 (m, 6H), 0.47 (br m, 4H), 0.70 (br m, 4H), 1.12 (m, 12H), 1.53 (br m, 4H), 3.4-3.9 (br m, ~56H).

**Preparation of siloxane Si-PTMO-Si (7.8):** (a) NaH (60% in mineral oil, 9.6g, 0.24mol) was mixed with 100 THF. With stirring, PTMO650 (65g, 0.1mol) in THF 150ml was added dropwise into NaH solution at 0°C. Allyl bromide (34g, 0.26mol) in 30ml THF was slowly added and stirred at room temperature overnight. 10ml water was slowly added into the solution and the solution was filtered and evaporated to remove the solvent. The residue was dissolved in CH$_2$Cl$_2$ and the filtration was done with a short silica gel column. After solvent evaporated, 47.1g diallyl PTMO600 (7.7) (0.046mol, 46% yield) was provided. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 1.60 (m, ~30H), 3.38 (m, ~30H),
3.96 (dt, J=5.66, 4H), 5.16 (qq, 4H), 5.86 (m, 2H). (b) Diallyl PEG600 (13.8g, 0.02mol) was mixed with methyldiethoxysilane (11.8g, 0.09mol), and several drops of H₂PtCl₆-isopropanol solution (42mg/ml) was added. At 100°C stirred for two days, the reaction was completed. After evaporation under reduced pressure, 19.7 liquid product (0.25mol, 100% yield) was provided. ¹H NMR (CDCl₃, 300 MHz) δ 0.0-0.10(m, 6H), 0.47(br m, 4H), 0.70 (br m, 4H), 1.12 (m, 12H), 1.60(m, ~34H), 3.38 (m, ~30H), 3.95(br m, 8H).

**Typical sol-gel process to prepare hybrid membrane:** (a) Siloxane monomers (7.3, 7.6, 7.8), as the major components of hybrid membranes and crosslinkers (7.4 or TEOS) were mixed in ethanol, and small amount of 1N HCl was added into the solution. After stirred overnight at room temperature, the solution was added with additives (Zr(OBu)₄/acetyl acetone) and stirred for several hours. The resulted sol was poured into plastic dishes. The gelation process and slow evaporation of solvent were performed at room temperature then 60°C for one week. The membranes were further dried at 100°C or 150°C for one to two days. The resulted membranes were soaked into 6M-10M H₃PO₄ for several days to absorb H₃PO₄. The resulted membranes were dried at 60°C for one to two weeks before tests. (b) Siloxane monomers (7.9), as the major components of hybrid membranes and crosslinkers (7.4 or TEOS) were mixed in methanol, and small amount of 1N HCl was added into the solution. After stirred overnight at room temperature, the solution was added with 86% H₃PO₄ solution and stirred for several hours. The resulted sol was poured into plastic dishes. The gelation process and slow evaporation of solvent were performed at room temperature then 60°C for one week. The membranes were further dried at 120°C for one to two days before tests.

**Conductivity measurements and Fuel cell Tests:** Same methods as reported in Chapter 4, experimental section were applied.
Figure 7.1 Chemical structures of heterocycles, siloxane monomer and polymers used.
7.3 Experimental Results and Discussions

1H-1,2,4-Triazole has a similar molecular structure as that of imidazole and therefore may conduct protons via a similar mechanism as imidazole. Compared with imidazole \((T_{mp} = 89^\circ C, T_{bp} = 257^\circ C)\), 1H-1,2,4-triazole has a higher melting point \((120^\circ C)\) and a similar boiling point \((256^\circ C)\) owing to its strong hydrogen bonds. The \(pK_a\) values of 1H-1,2,4-triazole \((pK_{a1} = 2.39, pK_{a2} = 9.97)\) are much lower than those of imidazole \((pK_{a1} = 7.18, pK_{a2} = 14.52)\).

Figure 7.2 Proton conductivity of 1H-1,2,4-triazole mixed with C\textsubscript{12}PhSO\textsubscript{3}H in anhydrous state. The inserted figure presents the conductivity dependence of the mixtures on acid concentrations.

To increase the concentration of proton charge carriers and to suppress the motion of the acid group, the large molecule acid C\textsubscript{12}PhSO\textsubscript{3}H was added to 1H-1,2,4-triazole. As shown in Figure 7.2, the proton conductivities of the mixtures increased with acid concentration, reaching a maximum at \(~9\) mol %. Similar phenomena were reported in
imidazole-acid systems, reflecting the change of the proton charge carrier concentration and the geometric constrains introduced by the addition of acids. The conductivity is 0.02 S/cm at 120°C for the sample with 9 mol % acid.

To study proton conductivity of 1H-1,2,4-triazole in a solid polymeric membrane, 1H-1,2,4-triazole was intercalated into a sulfonated polysulfone (sPSU) membrane. As shown in Figure 7.3, the conductivity increased with the concentration of 1H-1,2,4-triazole. For a membrane with \( n = 8 \) (\( n \) is defined as the ratio of \([1H-1,2,4-triazole]\) to [-SO\(_3\)H]), the conductivity reached \( 1.5 \times 10^{-3} \) S/cm at 100°C and \( 5.0 \times 10^{-3} \) S/cm at 140°C. Since the sPSU polymer itself has very low ion conductivity under anhydrous (or low humidity) conditions, it is believed that the 1H-1,2,4-triazole is responsible for the observed ionic conductivity of sPSU-1H-1,2,4-triazole membranes.

Figure 7.3 Ionic conductivities of 1H-1,2,4-triazole (4Tri) and that intercalated into sulfonated polysulfone polymers (\( n = \text{triazole-ring}/\text{-SO}_3\text{H} \) in mole).
Figure 7.4 Typical cyclic voltammograms (CV) of $1H$-1,2,4-triazole with baselines, $C = 5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ in 0.1 mol·dm$^{-3}$ TEAP-CH$_3$CN solution.

Shown in Figure 7.4 are some cyclic voltammograms for $1H$-1,2,4-triazole and imidazole in CH$_3$CN solution purged with N$_2$. No obvious redox peaks observable for $1H$-1,2,4-triazole in a wider potential range, 0 to +1.8V (vs Ag/Ag$^+$), and no obvious change took place in the subsequent 50 cycles. Similar results were observed when the CH$_3$CN solutions were purged with O$_2$. These results imply that $1H$-1,2,4-triazole has adequate electrochemical stability under fuel cell conditions.

Also, the imidazole derivative 2-ethylsulfonayl-$1H$-imidazole (7.2) was synthesis simply from commercial available 2-mercapto-$1H$-imidazole. 2-ethylsulfonyl-imidazole has a conductivity of $3.0 \times 10^{-4}$ S/cm at its melting point ($\sim156^\circ\text{C}$, as measured by TGA in Ar), which is about 33% of the conductivity $1.0 \times 10^{-3}$ S/cm of imidazole at melting point $\sim92^\circ\text{C}$. The lower conductivity of 2-ethylsulfonyl-imidazole may be attributed to
the decrease of self-diffusion of 2-ethylsulfonyl-imidazole molecules because of its larger size compared with imidazole molecules. To increase the concentration of proton charge carriers, benzenesulfonic acid was added to 2-ethylsulfonyl-imidazole. As shown in Figure 7.5, the proton conductivities of the mixtures increased with acid concentration, reaching a maximum at ~17 mole % (1 mole acid with 5 mole 2-ethylsulfonyl-imidazole).

![Figure 7.5 Proton conductivity of the mixtures of 2-ethylsulfonyl-1H-imidazole. Inserted is the proton conductivity versus composition at 140°C.](image)

Both computation (in Chapter 4) and cyclic voltammogram experiment proved that –SO₂⁻ group is an effective group to improve the electrochemical stability and compatibility to Pt catalyst of imidazole owing to its strong electron-withdrawing effects. As shown in Figure 7.6, no obvious redox peaks observable for 2-ethylsulfonyl-Imidazole in a wider potential range, 0 to +1.8V (vs. Ag/Ag⁺), and no obvious change took place in the following 50 cycles. Similar results were observed when the CH₃CN solutions were purged with O₂. These results imply that 2-ethylsulfonyl imidazole has adequate electrochemical stability under fuel cell conditions.
Compared with 1\textit{H}-1,2,3-triazole, 1\textit{H}-1,2,4-triazole and 2-ethylsulfonyl imidazole have much higher melting points. Below melting point, they have very low proton conductivities but increase a lot after melting. For small molecule doping, they have higher thermal stability than that of 1\textit{H}-1,2,3-triazole. However, to consider grafting of these groups to polymer backbones, PEMs with these two groups may have low proton conductivity, similar as the imidazole grafted polymers.

If evaluate from the proton conductivity of the membranes, H$_3$PO$_4$ doped membranes are still the best. In this chapter, we reported our research about the inorganic/organic hybrid membranes with H$_3$PO$_4$ doped for HT PEM applications. The initial work was done by Siwen Li in our group. As described in the experimental section, the first hybrid system he was looked into is based on siloxane Si-PPO-Si (7.3). Another siloxane Si-C$_8$-Si (7.4) was used as the crosslinker. Also, when Zr was added into the performed sol, the resulted membranes have higher mechanical strength than the membrane without Zr doped. All these hybrid membranes can absorb H$_3$PO$_4$ from the
high concentration of H$_3$PO$_4$ aqueous solutions. The conductivities of these membranes highly depend on the H$_3$PO$_4$ content, ranging from 10$^{-2}$ to 10$^{-4}$ s/cm at 120°C in the air. However, during the fuel cell tests, it was found: (1) the membranes with high content H$_3$PO$_4$ have poor mechanical properties and not applicable for HT PEM tests; (2) some of the membranes with acceptable mechanical properties and conductivities could provide considerable cell performance at short time when temperature was at 120°C. However, the cell performance quickly degraded, and the cracks were found on the membranes.

It was suspected that the PPO units in the membrane was not stable enough under high acidity, high temperature condition. Si-PTMO-Si and Si-PEO-Si were then synthesized. However, the hybrid membranes based on these siloxanes have similar instability at high temperature. It was observed that (1) all three siloxane monomers, when mixed with 86% H$_3$PO$_4$ and heated to 120°C, decomposed in two hours to black solution (3) The hybrid membranes, when dropped H$_3$PO$_4$ on the surface and dried at 120°C, was eroded by the acids. (3) The hybrid membranes based on three monomers, after taken out from H$_3$PO$_4$ solution and quickly dried at 120°C, these membranes were deformed and cracked quickly. All these phenomena showed that the thermal stability of these membranes depends on the water and acid contents in the membranes, and the hydrolysis stability of C-O-C bonds under high acidity condition could be a major reason.

As illustrated in Figure 7.1, the new type of polysiloxane (7.9) was prepared to substitute Si-PPO-Si in the membrane. The polysiloxane polymer was synthesized in a one-pot reaction, catalyzed by NaOH. From $^1$H NMR and $^{13}$C NMR, the methoxyl groups were completely removed. Calculated from the yields, there existed only small amount of hydroxyl groups. Therefore, there possibly exists large amount of D3 and D4 cyclic siloxanes under this reaction condition as previously studied [2]. By heating the polymer mixed with concentrated H$_3$PO$_4$ at 120°C for 2 two days, there were no any noticeable decomposition happened.
The hybrid membranes were synthesized through the sol-gel process with \( \text{H}_3\text{PO}_4 \) solution added before membrane formation. Two membranes have synthesizes with the molar ratio of Si-C3-Triazole: Si-C8-Si: \( \text{H}_3\text{PO}_4 \) = 1:0.56:1 and 1:0.56:3 respectively. The membranes, when dried at 120\(^\circ\)C turned to be soft, but still kept good shape overnight. The conductivities of two membranes were reported in Figure 7.7. At 120\(^\circ\)C, dry air condition, the conductivity of these membranes is around \( 10^{-3} \text{S/cm} \).

![Figure 7.7 Temperature dependence of conductivities of hybrid membranes with the molar ratio of Si-C3-Triazole: Si-C8-Si: \( \text{H}_3\text{PO}_4 \) = 1:0.56:1 and 1:0.56:3.](image)

After dried at 120\(^\circ\) and cooled down to room temperature, these membranes turned to stiff and very brittle. It is possibly due to the short chain length of polysiloxane polymer 7.3 under sol-gel condition, especially if there existed large amount of D3 or D4 cyclic siloxane. Adjusting the properties of the polysiloxane polymer 7.3 and adding other additive are possible pathways to solve the problem of mechanical properties.

### 7.4 Conclusions

In this chapter, the heterocycles other than 1,2,3-triazole were studied as proton conductors. 1H-1,2,4-triazole and 2-ethylsulfonayl-1H-imidazole were reported to be
proton conductors as effective as imidazole but more electrochemically stable than imidazole. In another part, the inorganic/organic hybrid membranes containing H$_3$PO$_4$ were studied as HT PEMs. By developing a new type of polysiloxane polymer with 1,2,4-triazole attached, the hybrid membranes based on the new polymer has high proton conductivity and better thermal stability than previously studied hybrid membranes base on Si-PPO-Si siloxane.

7.5 References


CHAPTER 8
FUTURE WORK AND OUTLOOK

To design polymer electrolyte membranes for high temperature fuel cells is a very challenging topic. In this thesis work, a new type of proton conductors 1H-1,2,3-triazole has been studied. The synthesis of triazole derivatives and polymers has also been explored. The polymers and copolymers containing triazoles showed considerable proton conductivities under dry condition but still not high enough for practical applications.

To further develop PEMs based on triazole with high proton conductivity and good mechanical properties, improving the mechanic strength of polymer backbones and adjusting local mobility of side chains for the triazole-acids copolymers will be important and effective methods to reach the target.

The computational modeling in this work provides some interesting results for understanding proton conduction in triazole based system. However, for QM calculations, the difficulty lies in the environment setting-up, and for MD simulation to model proton conduction, it is the effectiveness of the force field. In the future work, an effective and reliable way needs to be explored to build connections between MD and QM, either through *ab initio* MD or other methods.

Above all, PEMs based on heterocycles hold the largest potential for developing high temperature PEMs to be operated at high temperature and low humidity.
APPENDIX A

GEOMETRY OF THREE-MOLECULE COMPLEXES
$C_2N_3H_2^-(A-a-p1)$

$C_2N_3H_2^-(A-a-p2)$
$C_2N_3H_2^+(A-b-p1)$

$C_2N_3H_2^+(A-b-p2)$
mod

C₂N₃H₂⁻(A-b-p3)

relax

mod

C₂N₃H₂⁻(B-a-p1)
C$_2$N$_3$H$_2^\cdot$ (B-a-v1,v2)

C$_2$N$_3$H$_2^\cdot$ (B-b-p1)
mod

\[ \text{C}_2\text{N}_3\text{H}_2^{\text{B-b-v1,v2}} \]

relax

C\text{mod} \hspace{1cm} \text{relax}

\[ \text{C}_2\text{N}_3\text{H}_2^{\text{B-b-v3,v4}} \]
\textbf{mod} \hspace{2cm} \textbf{relax}

\textbf{mod} \hspace{2cm} \textbf{relax}

\textbf{CH}_3\textbf{PO}_3\textbf{H} \cdot \textbf{(A-a-p1)}

\textbf{CH}_3\textbf{PO}_3\textbf{H} \cdot \textbf{(A-a-p2)}
\[
\text{mod} \quad \text{relax}
\]

\[
\text{CH}_3\text{PO}_3\text{H}(A-b-p1)
\]

\[
\text{mod} \quad \text{relax}
\]

\[
\text{CH}_3\text{PO}_3\text{H}(A-b-p2)
\]
$\text{mod}$ $\text{relax}$

$\text{CH}_3\text{PO}_3\text{H} \cdot (A-b-p3)$

$\text{mod}$ $\text{relax}$

$\text{CH}_3\text{PO}_3\text{H} \cdot (B-a-p1)$
mod  \hspace{1cm} \text{relax}

\begin{align*}
\text{CH}_3\text{PO}_3\text{H} \cdot (\text{B-a-v1, v2}) \\
\text{mod} \hspace{1cm} \text{relax} \\
\text{CH}_3\text{PO}_3\text{H} \cdot (\text{B-b-p1})
\end{align*}
\[ \text{mod} \quad \text{relax} \]

\[ \text{CH}_3\text{PO}_3\text{H}\cdot(B-b-v1,v2) \]

\[ \text{mod} \quad \text{relax} \]

\[ \text{CH}_3\text{PO}_3\text{H}\cdot(B-b-v3,v4) \]
mod

relax

PhSO₃⁻(A-b-p1)

mod

relax

PhSO₃⁻(A-b-p2)
mod               relax

PhSO$_3^{-}$(A-b-p3)

mod               relax

PhSO$_3^{-}$(B-a-p1)
\[ \text{mod} \quad \text{relax} \]

\[ \text{PhSO}_3^-(B-a-v1,v2) \]

\[ \text{mod} \quad \text{relax} \]

\[ \text{PhSO}_3^-(B-b-p1) \]
mod

relax

PhSO$_3$-(B-b-v1,v2)

mod

relax

PhSO$_3$-(B-b-v3,v4)
VITA

Zhen Zhou was born in Changsha, Hunan Province of China. He received his B.S. in Chemistry from Jilin University in Changchun, China in 1998. In 2001, he has received his M.S. in Polymer Science, under the guidance of Dr. Jiacong Shen and Dr. Bai Yang in Jilin University, before coming to Georgia Tech to pursue a doctorate in chemistry department. In five more years studies in Georgia Tech, he has been working on organic fluorescent dyes in Dr. Fahrni’s group and then on polymer materials for fuel cell applications under the guidance of Dr. Meilin Liu and Dr. C. P. Wong.