

Preparation of Inorganic–Organic Hybrid Proton Exchange Membrane with Chemically Bound Hydroxyethane Diphosphonic Acid

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ABSTRACT: Proton-conductive inorganic–organic hybrid intermediate-temperature membranes were prepared from 3-glycidoxypropyltrimethoxysilane (GPTMS) and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) by sol–gel process. To prevent the leaching out of phosphonic acid, triethylamine was used as catalyst to promote the reaction of HEDPA and GPTMS to immobilize phosphonic acid groups. Fourier transform infrared spectra revealed that phosphonic acid groups of HEDPA were chemically bounded to organosiloxane network as a result of the reaction of P–OH of HEDPA and epoxy ring of GPTMS. TG-DSC results indicated that the hybrid membranes were

thermally stable up to 250°C. The proton conductivity of the hybrid membranes increased with temperature from 30 to 130°C. The proton conductivity of hybrid membrane with the molar ratio of GPTMS/HEDPA = 2/1 can reach up to 1.0×10^{-3} S/cm under anhydrous condition at 130°C, which reveals that this membrane is a promising proton exchange membrane for intermediate-temperature proton exchange membrane fuel cell. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: inorganic–organic hybrid; sol–gel process; anhydrous proton conductivity; phosphonic acid

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are attracting increasing attention because of their high efficiency and low pollution levels as a kind of new energy. As one of the excellent electrolyte membranes, Nafion (a perfluorosulfonic acid membrane) is widely used in PEM fuel cells because of excellent stability, high proton conductivity, and good mechanical strength. However, the proton conductivity of Nafion depends on the content of water, because water is proton carrier. Therefore, the Nafion-like polymers show high conductivity only in high relative humidity (RH) condition. Once the operation temperature is higher than 100°C, the proton conductivity will decrease with the reducing water.¹ Furthermore, the sulfonic acid groups in Nafion will be oxidized when the temperature is high. In addition, when the temperature is lower than 100°C, several problems will occur, such as the CO poisoning

of catalysts, low energy conversion efficiency, and heat management problems. Therefore, rising operation temperature can increase power output, bring faster electrode kinetics and greater CO tolerance, and it can also diminish the need for active cell cooling. Many researchers begin to research on developing new proton exchange membranes that can be used at 100–120°C in recent years.^{2–5}

Till date, the inorganic–organic hybrid membrane based on organosiloxane is considered to be one of the best substituents of Nafion. In many studies,^{6–8} 3-glycidoxypropyltrimethoxysilane [(OCH₃)₃Si(CH₂)₃OCH₂CHOCH₂, GPTMS] are reported as starting material to prepare the inorganic–organic hybrid membranes. GPTMS contains three methoxy groups that can be hydrolyzed to form the Si–O–Si network structure, which offers good thermal stability to the membranes. The epoxy ring in GPTMS is used to form the organic phase of polyethylene oxide (pseudo-PEO networks), which can improve the flexibility and processing suitability of membranes.⁹ On the other hand, choosing excellent protogenic groups that show high proton conductivity in high temperature is also very important during the development of PEMFCs. It is reported that the phosphonic acid shows better performance than sulfonic acid under low RH conditions at intermediate temperature, because phosphonic acid shows greater ability of water absorption than sulfonic acid.^{10,11}

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Moreover, in high temperature, phosphonic acid groups can dissociate and bring many protons for transportation, which indicate that it is possible for membranes to transport proton in anhydrous condition. Therefore, it is possible for inorganic–organic hybrid membranes based on phosphonic acid to replace Nafion. However, the phosphonic acid is always doped to the polymer matrices, which makes the phosphonic acid leaching out of the membranes easily. To solve this problem, it is necessary to connect phosphonic acid groups to inorganic–organic matrix by chemical bond.¹² It is reported that 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) can be chemically bonded to the inorganic–organic hybrid network by the reaction of C–OH of HEDPA and GPTMS.¹³ However, the reaction of C–OH of HEDPA and GPTMS is hard to control, because the amount of P–OH is more than C–OH and the –OH groups connected to the phosphorus atom are more active. Therefore, P–OH of HEDPA can react with GPTMS to graft the HEDPA monomers to the –Si–O–Si– net structure, and this reaction is easy to control.

In this study, we synthesized inorganic–organic proton exchange membrane with chemically bound phosphonic acid using GPTMS and HEDPA as start materials via sol–gel process. To immobilize phosphonic acid within inorganic–organic network via C–O–P bond, we used triethylamine as catalyst to promote the reaction of P–OH and epoxy rings. The –Si–O–Si– net structures were formed by hydrolysis and condensation reaction of Si–OCH₃ of GPTMS. The phosphonic acid group of HEDPA contributes to the proton conduction because of its proton donor and acceptor properties. This method may effectively reduce the leaching out of the phosphonic acid. At the same time, we hope that this membrane can be conductive in anhydrous condition to avoid the hydrolysis of C–O–P bond. The structure and thermal stability of HEDPA/GPTMS membrane were analyzed, and the proton conductivity of hybrid membrane at various temperatures was also studied.

EXPERIMENTAL

Materials

GPTMS (liquid; Silicone New Material of Wuhan University, Wuhan/P.R.China), HEDPA (solid particles; Aladdin, Shanghai/P.R.China), and hydrochloric acid were used as received. The molecular structures of the starting compounds are shown in Figure 1. Triethylamine and ethanol were dried by molecular sieve and then distilled before use.

Preparation of the membranes

The membrane was prepared by sol–gel method. GPTMS and HEDPA were dissolved in ethanol with

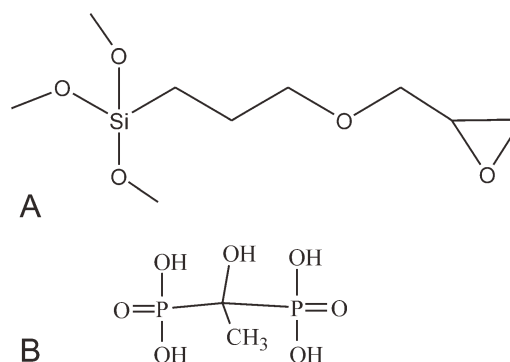


Figure 1 Molecule schemes of precursors as network formers: (A) GPTMS and (B) HEDPA.

stirring for 20 min till the solution was clear and colorless. Triethylamine was then added dropwise to the solution and stirred for 1 h at 110°C. An hour later, when the solution was cooled down to room temperature, concentrated hydrochloric acid that contains a certain amount of water was added dropwise to the solution and stirred for 1 h.¹⁴ The amount of water added is four times of the total Si in mole. The molar ratio of GPTMS/HEDPA/triethylamine is 2/1/0.2. Clear transparent solution was obtained through the above process, and we called it as sol. Then the sol was cast onto Teflon dishes, covered by glasses, and kept in a dry oven for 3 days at 60°C and for 24 h at 80 and 100°C. Finally, the membranes were further heated at 120°C for 6 h and at 150°C for 2 h.

Characterization of membranes

Infrared (IR) spectra were recorded with a Fourier transform IR spectrometer (FTIR; Nicolet, Nexus 470, Madison, WI). The thermal behavior of the hybrid membranes was analyzed by Thermogravimetry-Differential Scanning Calorimetry (TG-DSC) (TG-DSC, NETZSCH STA 499C) at a heating rate of 5°C/min from room temperature to 500°C under an air atmosphere.

Proton conductivity measurement

The proton conductivities were measured by AC impedance in anhydrous condition from 30 to 130°C on an electrochemical workstation (Autolab PG30/FRA; Eco Chemie, The Netherlands) from 10 Hz to 100 kHz.

The proton exchange membrane was put onto two parallel platinum wires and was sandwiched in a Teflon fixture. Then the whole equipment was put into a dry and clean sealed jar to keep membrane in dry air condition. Nyquist spectrum was obtained through alternating sinusoidal voltage applied by electrochemical workstation, which was analyzed to get the measured impedance value (*R*) of the

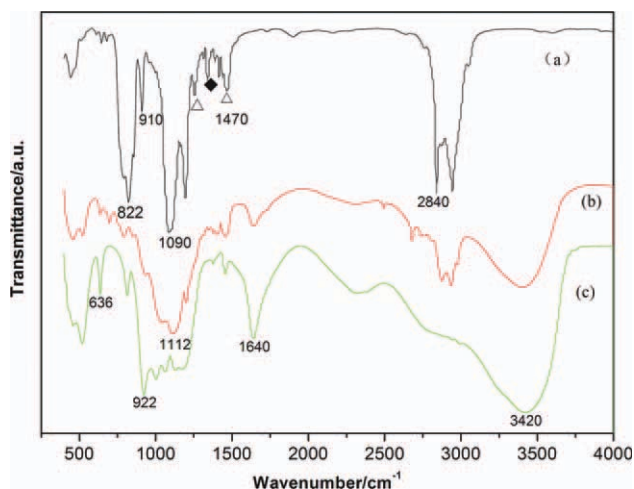


Figure 2 FTIR spectra of starting monomers and membrane: (a) GPTMS, (b) the hybrid membrane with the molar ratio of GPTMS/HEDPA = 2/1, and (c) HEDPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membrane. After that the proton conductivity (δ) was calculated according to the equation:

$$\delta = l/Rwd$$

where l , w , and d are the distance between the two electrodes, membrane width, and thickness, respectively.¹⁵

RESULTS AND DISCUSSION

FTIR analysis of the membranes

Figure 2 shows the FTIR spectra of GPTMS, HEDPA, and the hybrid membrane with the molar ratio of GPTMS/HEDPA = 2/1. As shown in Figure 2 (Peak a), the absorption at 822 cm^{-1} is due to the stretching vibrations of the methoxy group of Si–OCH₃ in GPTMS. The absorption at around 1090 cm^{-1} is attributed to Si–O–C vibrations. The peaks at around 1470 and 1250 cm^{-1} marked with open triangles are from oxirane methylene bending vibrations and breathing vibrations of the epoxy ring, respectively, and the antisymmetric epoxy ring deformation absorption peak is at 910 cm^{-1} . Several absorptions marked with filled diamonds are assigned to the vibrations of –CH₂ and –CH of GPTMS. Figure 2 (Peak c) shows the spectra of HEDPA monomers. Several absorptions in the $2250\text{--}2800\text{ cm}^{-1}$ range are due to the P–OH bond.¹⁶ The absorptions at 922 and 1002 cm^{-1} are assigned to the stretching vibrations of P–OH. The P–OH bending vibration peak is at 1641 cm^{-1} .

When GPTMS was reacted with HEDPA, as shown in Figure 2 (Peak b), the narrow peak of

Si–OCH₃ at around 1090 cm^{-1} nearly disappeared. The Si–O–Si symmetric stretching vibrations peak appear at 792 cm^{-1} and its bending mode appears at 460 cm^{-1} .¹⁷ The absorption peak at 1112 cm^{-1} is attributed to the Si–O–Si stretching vibrations of the dense silica net. All the results indicate that the hydrolysis and condensation of silicon alkoxides occurred. Moreover, it is obvious that the absorptions of epoxy ring all disappeared, all kinds of absorptions of P–OH turn more narrow and weaker as shown in Figure 2 (Peak b), and a new absorption at 2679 cm^{-1} is the frequency doubling absorption of C–O–P bond. This observation supports the fact that phosphonic acid groups are chemically bonded to the Si–O–Si net via the reaction of epoxy rings and P–OH, which can effectively prevent HEDPA leaching out from the membrane. At the same time, several new absorptions appear at $2760\text{--}2740\text{ cm}^{-1}$, which are resulted by –CH₂ stretching vibrations of –O–CH₂–O–. Hence, it can be concluded that the organic phase of PEO (pseudo-PEO chains) is formed by the ring-opening polymerization reaction of epoxy rings that may be catalyzed by triethylamine. The possible structure of the hybrid membrane is shown in Figure 3.

Therefore, we can conclude that HEDPA has been successfully chemically bonded to Si–O–Si net using C–O–P bond. The organic phase of PEO (pseudo-PEO chains) has also been observed to improve the flexibility of the membranes. Two pictures of the appearance of the membrane are shown in Figure 4. The obtained self-standing membrane was transparent and the surface of the membrane was smooth. The membrane has excellent flexibility though the mechanical strength is hoped to be more improved.

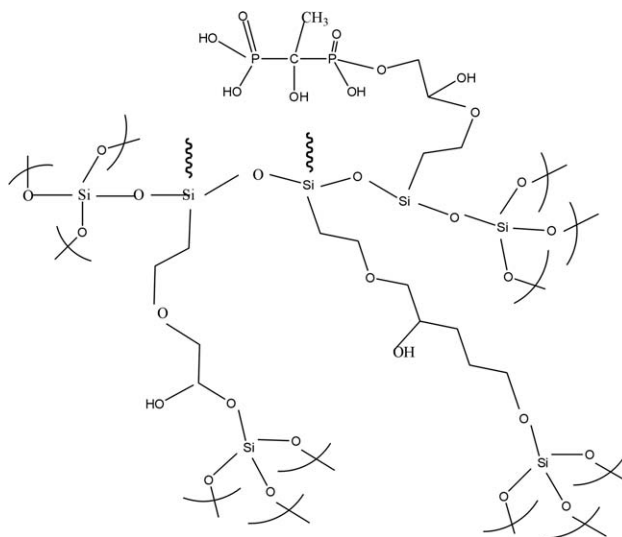


Figure 3 Possible structure of hybrid membrane.

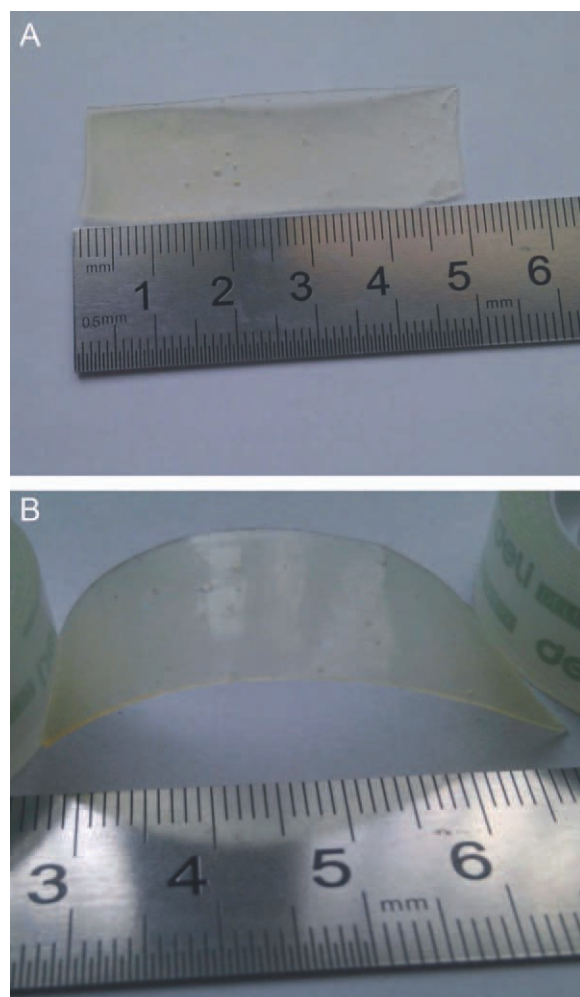


Figure 4 Photographs of hybrid membrane: (A) horizontal membrane and (B) flexural membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal stability of the membranes

Figure 5 shows the TG-DSC curves of the HEDPA monomer [Fig. 5(A)] and HEDPA/GPTMS hybrid membrane [the molar ratio of HEDPA/GPTMS = 1/2; Fig. 5(B)] measured in dry air from room temperature to 500°C. For HEDPA monomers, as shown in Figure 5(A), the small weight loss of about 2.05% is observed from room temperature to 117°C and an endothermic peak appears at 117°C, which is due to the desorption of absorbed free water. The weight loss of about 8.41% from 117 to 180°C is due to the strongly absorbed water. In the range of 180–250°C, the total weight loss is about 17.71% and an endothermic peak is seen at 196°C, followed by a sharp exothermic peak at 237°C. The endothermic peak at 196°C with weight loss is probably ascribed to the water loss from the intramolecular and intermolecular condensation of P(O)(OH)₂ groups.^{12,18} However, there is no obvious weight loss when the exothermic

peak appears at 237°C, which is attributed to the gasification of HEDPA.

For the TG-DSC curves of hybrid membrane, as shown in Figure 5(B), the weight loss of about 8.39% from room temperature up to 250°C with a very weak endothermic peak at the range of 50–100°C is due to the evaporation of physics absorbed water and the water produced by the dehydration of P—OH. The weight loss of about 44% in the range of 250–300°C with an exothermic peak at around 297°C results from the decomposition of the organic part of the hybrid membrane. Moreover, no exothermic peak at around 237°C is observed, which suggests that HEDPA has not been gasified. Therefore, it is confirmed that HEDPA has been chemically bound to the Si—O—Si net.

It can be concluded that the prepared membrane is thermally stable up to 250°C, which is attributed to the presence of Si—O—Si backbones. The chemically bound HEDPA also contributes to the thermal stability. Therefore, the obtained hybrid membranes have excellent thermal stability for being used in PEMFCs operating at intermediate temperature.

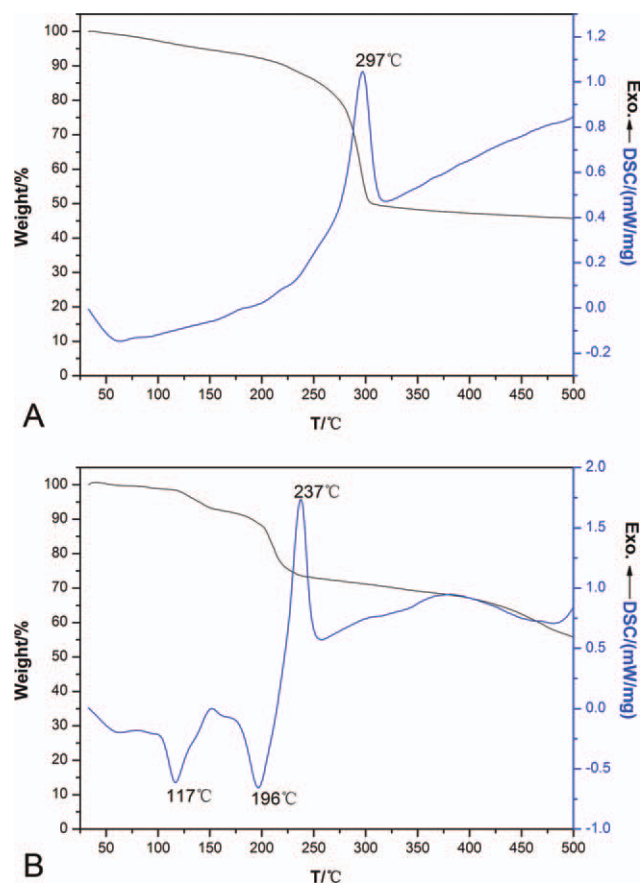


Figure 5 TG-DSC curves of (A) hybrid membrane and (B) HEDPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Proton conductivity

The proton-conductive properties of the prepared hybrid membrane were measured by AC impedance. Curve a in Figure 6 shows the impedance spectroscopy of the hybrid membrane under dry air at room temperature. All the curves (a–f) including a half-circle are similar to the standard theoretical Nyquist spectrum, which indicates that the membrane owns ordered proton transport paths. The transport path is possibly formed by absorbed water and phosphoric acid groups.¹⁹ The membrane resistances were obtained from the intercept on the real axis. As shown in Figure 6, in general, the resistance of the membrane decreases with the increasing temperature, because the proton transport paths turn more perfect and more protons was produced with the increasing temperature.

The proton conductivity of the membrane was calculated from the impedance data using the equation:

$$\delta = l/Rwd$$

The curve of proton conductivity of the membrane with the increasing temperature was obtained, as shown in Figure 7. In general, the proton conductivity increases with the increasing temperature from 30 to 130°C under dry air condition. The increasing temperature makes the organic chains more and more flexible, which is favorable for the grafted $-\text{PO}_3\text{H}_2$ to congregate and increase the proton mobility. On the other hand, the growth rate of the conductivity from 30 to 90°C is the lower than that in

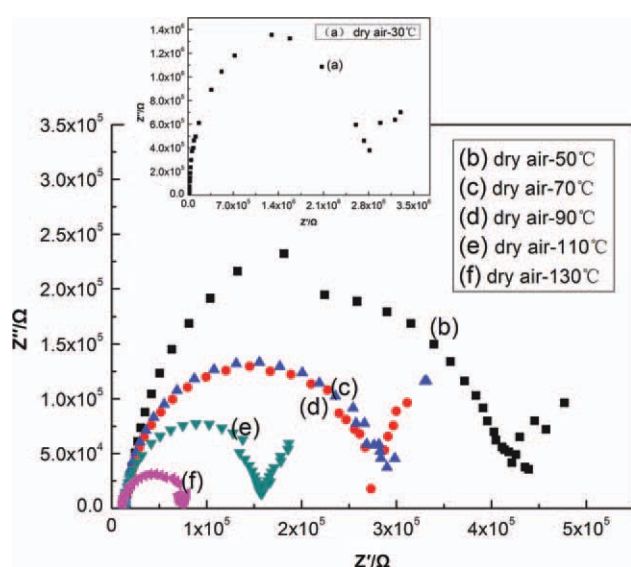


Figure 6 Nyquist plots of the hybrid membrane (GPTMS/PA = 2/1) at different temperatures under dry air: (a) 30, (b) 50, (c) 70, (d) 90, (e) 110, and (f) 130°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

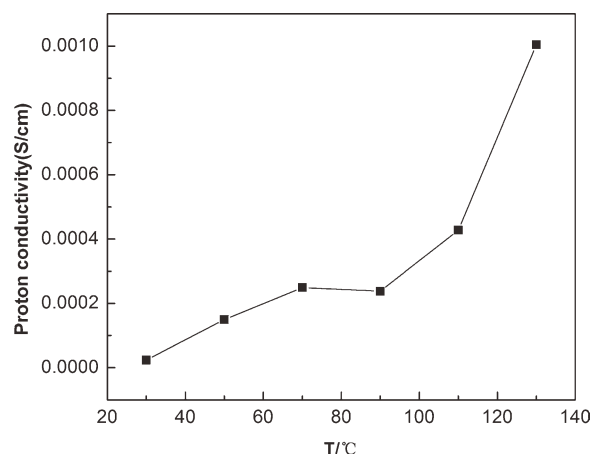


Figure 7 Proton conductivity of hybrid membrane depending on temperature.

the range of 90–130°C, because there are two different proton-conductive mechanisms at two different temperature ranges. In the range of 30–90°C, the absorbed water existing in the hybrid membrane and the strong interaction between water and phosphonic groups by hydrogen bonds play the most important role in the proton conductivity. In addition, the proton conductivities of 70 and 90°C are 2.49×10^{-4} and 2.38×10^{-4} S/cm, respectively. A little difference of the proton conductivity indicates that the proton transportation is influenced by the reducing water with the increasing temperature. Moreover, from 90 to 130°C, the self-dissociation of phosphonic groups produced many protons and greatly enhanced the proton conductivity, especially at 130°C. The proton conductivity is up to 1.0×10^{-3} S/cm at 130°C under anhydrous condition, which is higher than the other similar phosphonic acid-based membranes.

To discuss more details about the proton-conductive properties of the membrane, the activation energy for the proton conductivity was calculated using the Arrhenius equation:

$$\delta = A/T \exp(-E/kT)$$

where E is the activation energy for ionic migration, k is the Boltzman's constant, T is the absolute temperature, and A is the pre-exponential factor being a constant in certain temperature range. The activation energy (E) of the proton conductivity (σ) was derived from the slope of Arrhenius-type plot. The curve in the form of $\ln(\sigma T)$ versus $1000/T$ is shown in Figure 8. The activation energy value is 0.40 eV in the temperature range of 30–90°C, whereas the activation energy value of 90–130°C is 0.49 eV, which suggests that the proton conductivity changes more quickly from 90 to 130°C than that from 30 to 90°C. This conclusion confirms the differences of the

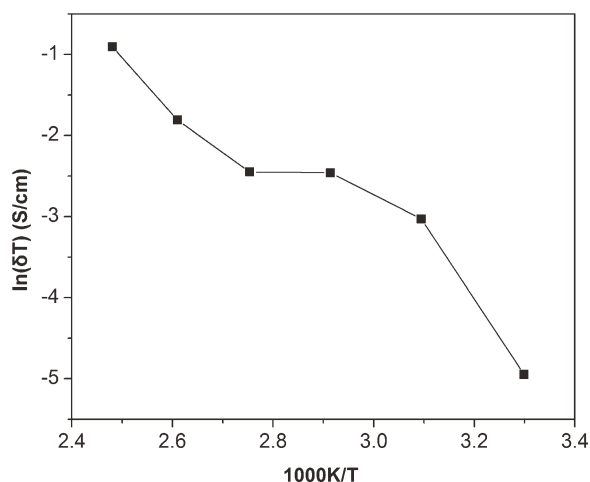


Figure 8 Arrhenius-type plot of proton conductivity of hybrid membrane.

proton-conductive mechanisms between the two different temperature ranges. The detailed proton-conductive mechanisms will be investigated in the following study.

CONCLUSIONS

Novel inorganic–organic hybrid membranes with chemically bound phosphoric acid have been successfully prepared from GPTMS and HEDPA by sol–gel process. With the addition of triethylamine during the reaction process, HEDPA monomers are much easier to be grafted to organosilicon inorganic–organic hybrid net. The FTIR results show that HEDPA has been successfully grafted to the inorganic–organic hybrid net. The hybrid membrane is thermally stable up to 250°C in an air atmosphere, which is attributed to the presence of tolerant inorganic SiO₂ net and chemically grafted HEDPA in the hybrid matrix. The proton conductivity of 1.0×10^{-3}

S/cm has been obtained at 130°C under anhydrous condition. When compared with other phosphonic acid-based membranes, the hybrid membranes perform better properties especially in anhydrous condition. This hybrid membrane is potential to be used for intermediate-temperature PEMFCs.

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