Immobilization of Imidazole in Polymer Electrolyte Membranes for Elevated Temperature Anhydrous Applications

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ABSTRACT: Polymer electrolyte composite membranes were cast from the mixture of Nafion® ionomer and 2-substituted imidazole. The existing flexible hydrocarbon chain on 2-position of imidazole facilitates proton transfer in the membrane at elevated temperature. The formed composite membrane showed an increased glass transition temperature and improved mechanical property compared with plain Nafion® membrane. At temperature above 100°C, the ionic conductivity of the composite membrane increases with the increase in temperature, reaching 5×10^{-3} S cm^{-1} at 160°C under anhydrous condition. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 382–387, 2012

Key words: polymer electrolyte membrane; imidazole; immobilization; ionic conductivity

INTRODUCTION

Polymer electrolyte membrane fuel cells operating at temperature above 100°C have attracted considerable interest as several advantages exist in such systems, including simplified heat management, increased carbon monoxide tolerance, enhanced electrochemical kinetics for electrode reactions, and even reduced cost by possibly using nonplatinum catalyst.[1,2] One of great technical challenges for fuel cells operated at elevated temperature is polymer electrolyte membrane that should maintain reasonable ionic conductivity with little dependence on relative humidity and should be mechanically stable at elevated temperature. The commonly used perfluoronated membranes for current fuel cell technology, e.g., Nafion® from Dupont, are not suitable for elevated temperature applications because of their strongly humidity-dependent ionic conductivity and relatively low

glass transition temperature. Thus, many approaches have been proposed to develop alternative membranes as described in recent reviews.[3,4]

One interesting approach for the development of elevated temperature membranes is to replace water with low-volatile proton solvent in the membrane. Heterocycles such as imidazole, triazole, or pyrazole have demonstrated to be promising candidates as they undergo a very similar behavior toward protons to that of water.[5] Both aromatic hydrocarbon polymer[6] and Nafion®[7–9] membranes impregnated with heterocycles have shown promising conductivity at temperature above 100°C and under anhydrous conditions. However, leaching of the heterocycles to the electrode can poison the catalyst, leading to low or even no performance of assembled fuel cell.[7] In addition, the swelling of membranes with heterocycles at elevated temperature might make the thermomechanical properties of membrane unsatisfactory. This has led researchers' attention to the immobilization of heterocycles inside the membrane. To facilitate proton transfer inside membranes via structure diffusion, heterocyclic moieties is required to have certain local mobility.[10] For examples, the immobilization of heterocycles via flexible spacers onto inorganic particles,[11] inorganic polymers,[12,13] organic oligomers, or polymers[10,14] has been investigated. Because of the relatively low ionic conductivity or the difficulty of membranes formation of bulk materials, the synthesized materials are generally required to be associated with proton
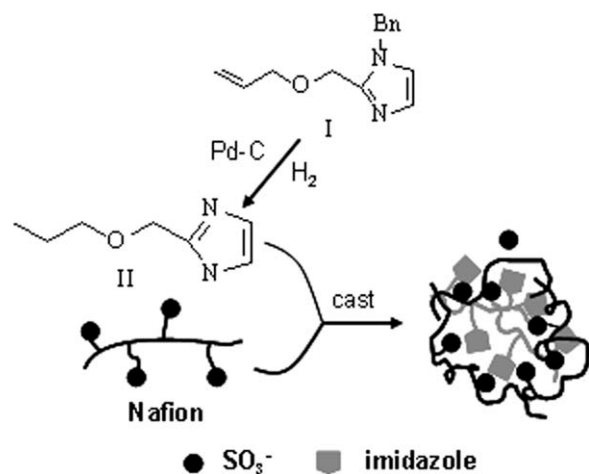
Figure 1 Scheme of Nafion®/immobilized imidazole composite membrane formation.

donors or polymer matrix for polymer electrolyte membrane applications.

Herein, we report the development of polymer electrolyte membranes containing 2-substituted imidazole, as schematically shown in Figure 1. The composite membranes were formed by evaporation of solvent from the mixture of Nafion and the synthesized organic molecules. The thermomechanical property was enhanced by the complex formation of sulfonic acids group with imidazole. The introduction of simple hydrocarbon linkers facilitates the local mobility of imidazole compared with the reported immobilization of imidazole on a polymer backbone or on inorganic nanoparticles,[11–14] especially at elevated temperature.

EXPERIMENTAL

Synthesis of 2-allyloxymethyl-1-benzylimidazole I

The precursor was synthesized according to literature[12] by hydroxyformylation of 1-benzylimidazole (Alpha) and further nucleophilic substitution with allyl bromide (Aldrich) in anhydrous tetrahydrofuran using sodium hydride as catalyst. The raw product was further purified using column chromatography (Silicagel 60, Aldrich) using ethyl acetate/acetone (1 : 1, v/v) as elution.

Synthesis of 2-propanoxymethylimidazole II

The compound I (2.5 g, 11 mmol) was dissolved in methanol (30 mL) and mixed with Pd/C (1 g, 10% Pd). The mixture was flushed with hydrogen and was stirred under hydrogen atmosphere for 3 days at 50°C. The catalyst was then filtered off. After removal of solvent, the product of yellowish oil (1.08 g, 71.3%) was obtained. ^{1}H NMR (CDCl$_3$, 300 MHz): 0.85–0.92 ppm (t, 3H, CH$_3$), 1.53–1.65 ppm (m, 2H, MeCH$_2$), 3.37–3.47 ppm (t, 2H, OCH$_2$), 4.62 ppm (s, 2H, ImCH$_2$O), 7.04 ppm (s, 2H, Im), 8.43 (broad, 1H, NH).

Formation of composite membrane

Commercial Nafion® dispersion (5 wt %, DuPont) was evaporated at 100°C and re-dissolved in N-methyl-2-pyrrolidinone (NMP) with the same concentration of resin under stirring. Compound II (0.2 g) was dissolved in 10 mL NMP and the solution was added to 10 mL Nafion® solution. The mixture was stirred 2 h, followed by ultra-sonication for 10 min. The membrane was recast by pouring the suspension into a Teflon dish, followed by heat-treatment at 160°C. The so-formed membrane was cleaned by treatment at 80°C for 30 min in 5 wt % H$_2$O$_2$, deionized water, 0.5M H$_2$SO$_4$, and deionized water for more than 40 h. The membrane was finally dried at 100°C for 2 h under vacuum before test.

Characterization of membranes

Solid-state NMR (Varian InfinityPlus 400) technique was applied to investigate the immobilization of imidazole moieties inside the membrane. The resonance frequencies for ^{1}H and ^{13}C NMR were 400.133 and 100.615 MHz, respectively. Samples for NMR measurement were prepared by grinding polymer films under liquid nitrogen. Fourier transform infrared spectra (FTIR, Bio-Rad FTS 300) were recorded with a resolution of 4 cm^{-1} to investigate the interaction between the imidazole moieties and polymer matrix. Elemental analysis of the membrane was carried out on VarioEL III (Germany).

Thermomechanical analysis (TMA, NETZSCH) was carried out with purging nitrogen to determine glass transition temperature (T_g) of membranes (12 mm × 3 mm). Experiments were run from 30 to 200°C with a temperature ramp rate of 20 °C min^{-1}. Tensile strength of the formed dry membranes was tested on an Electromechanical Universal Testing Machine (WDW-1C) based on Chinese Standard QB-13022-91 at room temperature. The membranes were cut into stripes of 6 mm × 40 mm. The samples were measured at a strain rate of 50 mm/min. The pulling stress was slowly increased and the strain with different stresses was recorded. Three repetitions of the measurements were made for each sample. Thermal stability was determined using thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) on Perkin–Elmer Instrument at a rate of 10 deg min^{-1} under nitrogen. The sample was immersed into deionized water for 1 h at room temperature and was further treated under vacuum at 60°C for 10 h before TGA and DSC measurements.

Surface morphology of formed membranes was examined using atomic force microscopy (AFM,
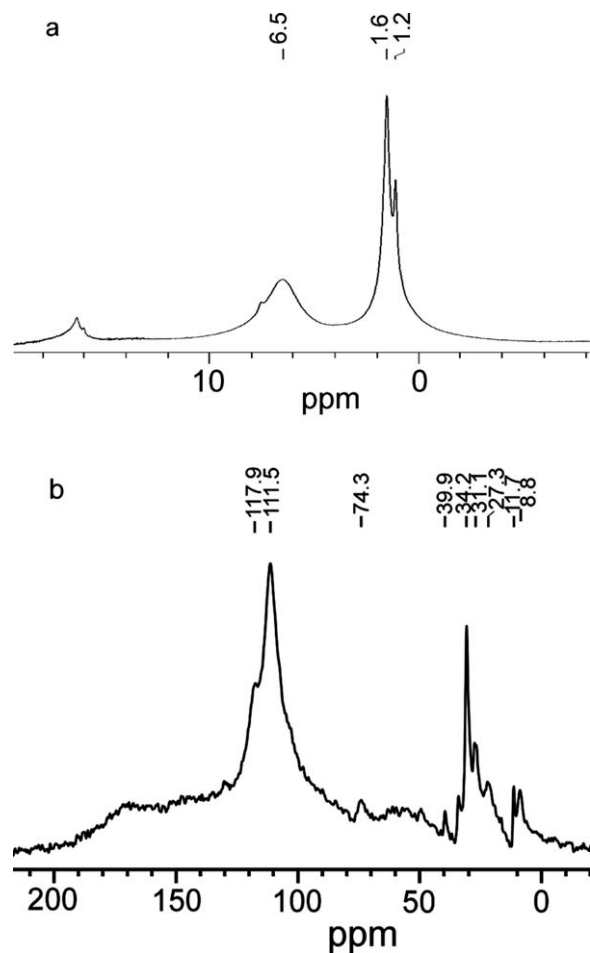
Figure 2 ¹H NMR (a) and ¹³C NMR spectra of Nafion®/immobilized imidazole composite membrane.

Nanoscope IV). Electrostatic force microscopy (EFM, Nanoscope IV) measurements were carried out simultaneously by monitoring the detector signal amplitude at 6V and using conductive layer coated single crystal silicon tips with a nominal radius of 10 nm. Each sample line was scanned at two heights above the surface. In the first scan, the tips response was dominated by the short-range Van der Waals force under the tapping mode and recorded the surface morphology of the membrane. The second scan was taken under Interleave Mode at the height of 20 nm to detect the electric field force of the membrane.

Ionic conductivity measurements of membranes were carried out using an impedance analyzer (AutolabFG30/FRA, Eco Chemie, Netherlands) without external humidification using a homemade testing cell at different temperatures.[15] Two gold coated copper electrodes were placed on the same face of membranes that were sandwiched between two PTFE sheets. The distance between the two electrodes was 3 cm. Membranes were dried under vacuum at 80°C for 2 h before measurements. Electrochemical impedance spectra (EIS) were recorded in the frequency range of 10 Hz and 100 KHz and the

signal amplitude of 10 mV. The ionic conductivity of membrane was calculated from the resistance of membrane obtained from EIS.

RESULTS AND DISCUSSION

The motivation of this work is to develop composite membranes in which the imidazole moieties were immobilized for elevated temperature applications under anhydrous conditions. To this, hydrophobic hydrocarbon chains were chemically bonded to 2-C position of imidazole and the composite membrane was formed by recasting the hybrid solution, as schematically shown in Figure 1. Solid-state NMR technique was used for investigation of immobilization. Before NMR measurement, the membrane was soaked in deionized water for 40 h and dried under vacuum for 2 h at 80°C. The weight of the dry membrane ($\sim$ 0.633 g) did not change before and after soaked in water, indicating no leaching of the impregnated imidazole moieties from the membrane. ¹H NMR and ¹³C NMR spectra of the formed composite membrane were shown in Figure 2. As Nafion® is a perfluoronated polymer and no hydrogen bonds to carbon, the resonance peaks in ¹H NMR spectrum [Fig. 2(a)] below the chemical shift of 10 ppm were attributed to the impregnated hydrocarbon molecules. The appearance of resonance peaks in high field region (1.2 and 1.6 ppm) indicates the successful immobilization of imidazole moieties inside the membrane. The broad resonance peak around chemical shift of 6.5 ppm was assigned to hydrogen atoms on imidazole ring and OCH_2 groups and the small resonance peak at low field (16.2 ppm) was assigned to the proton existed in the membrane. ¹³C NMR spectrum [Fig. 2(b)] of the membranes further proved the immobilization as the resonance peaks in the region of 27–40 ppm resulted from the saturated CH_2 groups and the resonance peaks at 8.8 and 11 ppm resulted from the end methyl groups. Since the membrane was soaked in deionized water for 40 h and dried before NMR measurements, it can be concluded that the imidazole moieties are immobilized inside the membrane.

To quantitatively determine the amount of synthesized imidazole motifs inside the membrane, elemental analysis were carried out. The contents of C, H, and N inside the membrane were 26.89%, 0.996%, and 4.242%, respectively. From the total weight of the membrane (0.633 g) and the molecular weight of the synthesized compound (140 g/mol) and the EW value of Nafion (1100), the weight of immobilized imidazole motif in the membrane is about 0.1343 g and the number of imidazole moiety associated with per sulfonic acid group is about 2.1. This result indicates that about 32% imidazole motifs were leached out during the post-treatment of membranes since
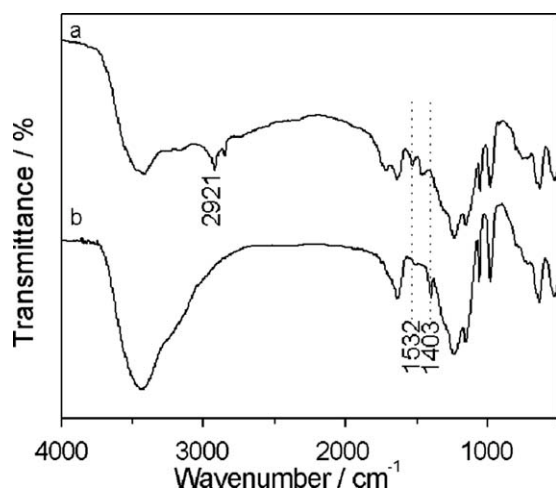
Figure 3 FTIR spectra of Nafion®/immobilized imidazole composite membrane (a) and the plain Nafion® membrane (b). The dot lines are guide to eyes.

the initial amount of the synthesized imidazole motifs added in the membrane is about 0.2 g. However, the synthesized imidazole motifs after post-treatment of membrane were immobilized inside the membrane as discussed in previous section.

Figure 3 shows FTIR spectra of Nafion® membrane and the formed composite membrane. Compared with Nafion® membrane, the appearance of absorption peaks at 2921 and 1532 cm^{-1} assigned to C—H stretching vibration and C=N stretching vibration bands indicates that the imidazole moieties were immobilized in the membrane. The absorption peak at 1403 cm^{-1} corresponded to the asymmetric stretching of S=O was disappeared in the formed composite membrane, indicating the strong interaction (acid-base) between the sulfonic acid groups and the existed imidazole moieties.

One of the great technical barriers for plain Nafion® membranes operated at elevated temperature is the relatively low T_g. TMA measurements were carried out to investigate the T_g and thermomechanical properties of formed membranes. Figure 4 shows TMA curves of the formed composite membrane and recast Nafion® membrane. The T_g for composite membrane calculated from TMA curve is about 162°C that is about 40°C higher than that of plain Nafion® membrane (124°C). It can also be seen that the formed composite membrane is mechanically stable up to 200°C whereas the plain Nafion® membrane is mechanically stable up to 167°C. Since imidazole is a base, the complex formation between sulfonic acid groups on Nafion® and imidazole through electrostatic interaction leads to an increased T_g and improved thermomechanical property of the composite membrane.

TGA and DSC were applied to determine the stability of the formed composite membrane, as shown
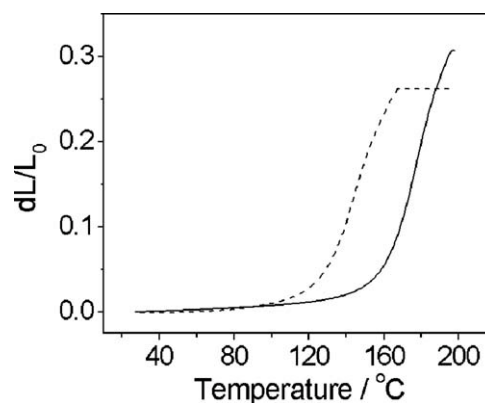

Figure 4 TMA curves of Nafion®/immobilized imidazole composite membrane (solid line) and plain Nafion® membrane (dash line).

in Figure 5. For comparison, the TGA and DSC curves for plain Nafion membrane were plotted in the same figure. The weight loss for both membranes before 200°C was attributed to the free and bound water inside the membrane. The plain Nafion® membrane was observed to be thermally stable up to 290°C at which the decomposition of sulfonic acid groups starts, whereas the composite membrane was thermally stable up to 330°C due to the complex formation of sulfonic acid groups and imidazole moieties through electrostatic interactions. From the DSC curve of composite membrane, the endothermal-peak at 170°C was attributed to the glass transition temperature of the membrane, which agrees well with the TMA measurement in the previous section. For the plain Nafion membrane, the T_g is about 40°C lower than that of composite membrane. This indicates that the composite membrane formed in this study can be operated at much higher temperature range for fuel cell applications.

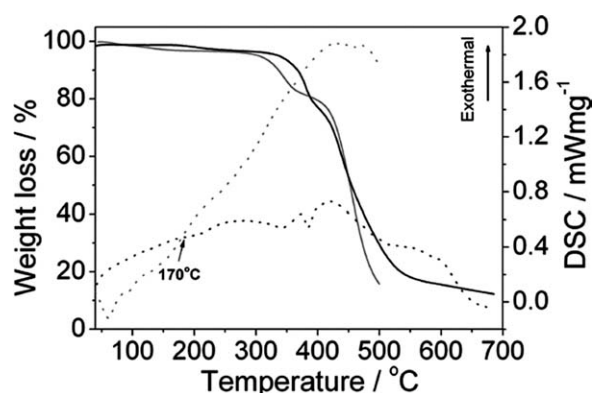One of the very important parameters for a qualified polymer electrolyte membrane is the mechanical

Figure 5 TGA curves (solid lines) and DSC curves (dot lines) of Nafion®/immobilized imidazole composite membrane (black lines) and plain Nafion® membrane (gray lines).
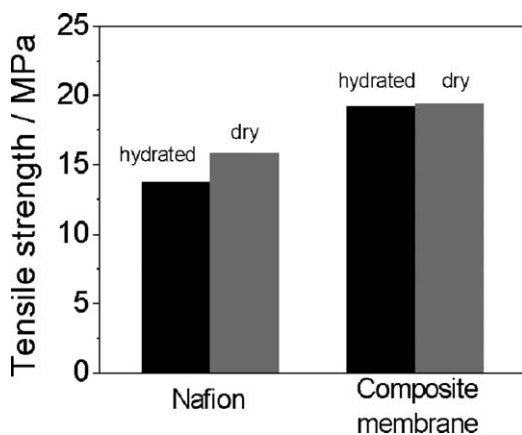
Figure 6 Tensile strengths of Nafion®/immobilized imidazole composite membrane and plain Nafion membrane with 5% elongation at dry (gray) and hydrated (black) conditions.

strength which may strongly affect the durability of the membrane. The mechanical strength of the formed composite membrane was investigated. Figure 5 shows the tensile strength of formed composite membranes with 5% elongation at both fully hydrated and dry states. As comparison, the tensile strength of recast Nafion® membrane was recorded in the same figure. It is evident, that the tensile strength for composite membranes is much higher than that of recast Nafion membrane at both dry and fully hydrated states. The difference in tensile strength at dry and hydrated conditions for composite membrane is just 0.2 MPa that is much smaller than the fatigue strength of 1.5 MPa for polymer electrolyte membranes as pointed out by Tang et al.,[16] suggesting that the formed composite membrane is mechanically stable during the fuel cell operation. Since the introduced imidazole moieties in the membrane can act as cross-linkers through the electrostatic interaction, the tensile strength can be enhanced and the swelling of the membrane can be limited. Thus, higher tensile strength of the formed composite membrane and the smaller difference in tensile strength at dry and hydrated conditions were observed compared with the plain Nafion membrane.

The morphology of the formed composite membrane was investigated using tapping mode atomic force microscopy (TM-AFM). Figure 6(a) shows TM-AFM image of the formed composite membrane. Clear phase separation was observed on the surface of the formed composite membrane. Electrostatic force image [Fig. 6(b)] revealed that ionic clusters were formed on the surface of the formed composite membrane. The formed ionic clusters with average diameter of 200 nm facilitate the transporting process of proton and the according proton conductivity can be enhanced.

Figure 7 shows the ionic conductivity of the formed composite membrane without humidification as a function of temperature. Although the membrane was dried before the conductivity test, it can adsorb water molecules from the humid air. The slight decrease in ionic conductivity with increasing temperature up to 110°C was attributed to the evaporation of adsorbed water from the membrane. The ionic conductivity increases with further increase in temperature, indicating that the impregnated imidazole moieties involve in proton transfer at elevated temperature. However, the ionic conductivity observed here is about 5×10^{-3} S cm^{-1} at 160°C under anhydrous condition, which is about one order of magnitude lower than that of recast Nafion®/unmodified imidazole membrane supported by porous glass paper.[7] However, the supporting porous glass paper reported in the literature may
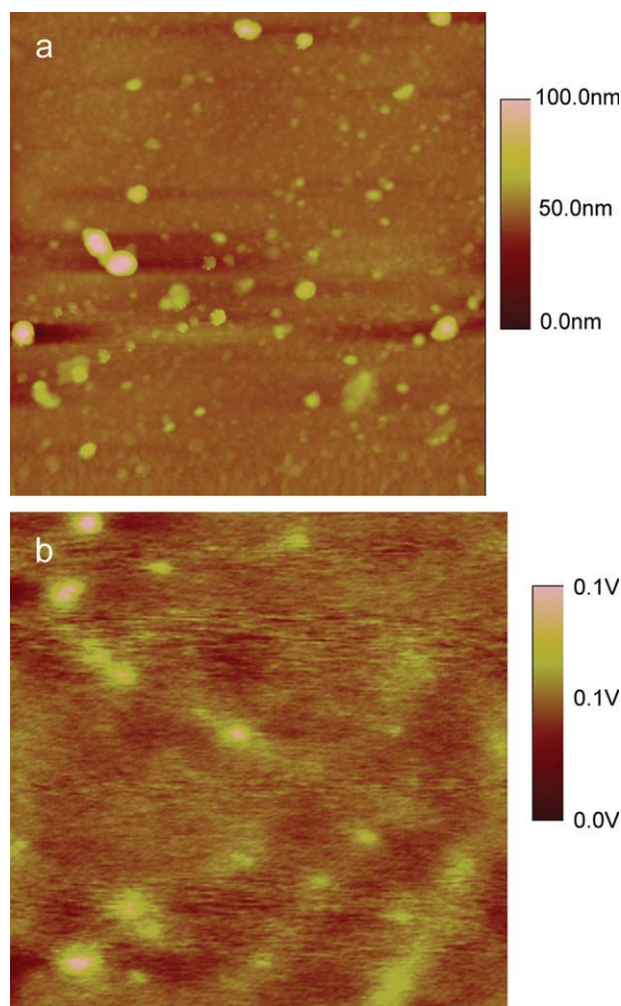

Figure 7 TM-AFM image (a) and EFM image (b) Nafion®/immobilized imidazole composite membrane. The size for both image is 5 μm ×5 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
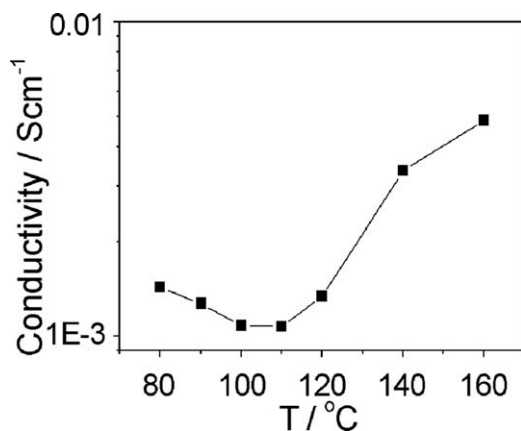
Figure 8 Proton conductivity of Nafion®/immobilized imidazole composite membrane as a function of temperature without external humidification.

lead to unsatisfactory mechanical properties of formed membrane, which was not reported. Compared with unmodified imidazole, the 2-substitution of imidazole with hydrophobic hydrocarbon chain leads to the decrease in local segmental motion. Accordingly, the ionic conductivity decreases as the proton transfer in such a system is dominated by structure diffusion as described in similar systems by Schuster et al.[10]

In addition, the temperature-dependent conductivity data above 110°C of the formed composite membrane (Fig. 8) obeys Arrhenius' law, i.e., the data are linearly regressed in a logarithm scale of conductivity versus the inverse of temperature in Kelvin. The activation energy can be calculated from the slope of regressed lines. Although the number of imidazole associated with per sulfonic acid group in this study ($\sim$ 2.1) is slightly higher than that of free imidazole impregnated Nafion® membranes ($\sim$ 1.8) reported in literature,[7] the ionic conductivity of the composite membrane developed here is smaller. The activation energy of the formed composite membrane was cal-
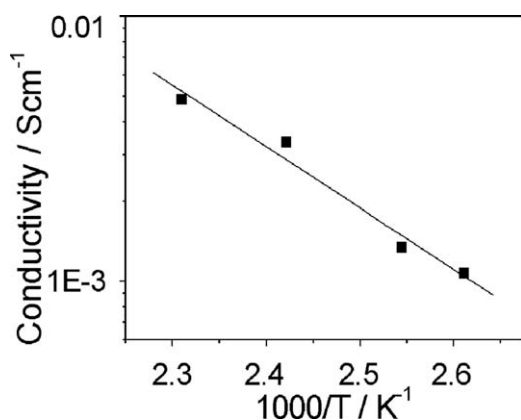

Figure 9 Proton conductivity of Nafion®/immobilized imidazole composite membrane at elevated temperature and the regressed fitting according to Arrhenius' law.

culated as 40 kJ mol^{-1} that is higher than that of bulk imidazole (24 kJ mol^{-1}),[6] indicating that the immobilization of imidazole makes the proton transfer less activated.

CONCLUSIONS

Polymer electrolyte membrane comprised of Nafion® and imidazole moieties immobilized in the membrane through 2-substitution using hydrophobic hydrocarbon chains was developed for elevated temperature and anhydrous applications. The introduced imidazole moieties act not only a proton transportation media, but also as cross-linkers in the membrane. Compared with plain Nafion® membrane, the formed composite membranes exhibited higher Tg and better thermomechanical property because of the complex formation of sulfonic acid groups with imidazole. The ionic conductivity of the formed composite membrane increases with the increase in temperature at the temperature above 100°C, obeying Arrhenius' law, and reaches 5 × 10^{-3} S cm^{-1} at 160°C under anhydrous condition.

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