Anhydrous proton-conducting electrolyte membranes based on hyperbranched polymer with phosphonic acid groups for high-temperature fuel cells

Takahito Itoh [a],*, Keita Hirai [a], Masashi Tamura [a], Takahiro Uno [a],
Masataka Kubo [a], Yuichi Aihara [b]

[a] Division of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurima Machiya-cho, Tsu, Mie 514-8507, Japan
[b] Samsung Yokohama Research Institute, 2-7 Sugasawa-cho, Tsurumi-ku, Yokohama 230-0027, Japan

Abstract

The two different molecular weight hyperbranched polymers (HBP(L)-PA-Ac and HBP(H)-PA-Ac) with both phosphonic acid group as a functional group and acryloyl group as a cross-linker at the chain ends were successfully synthesized as a new thermally stable proton-conducting electrolyte. The cross-linked electrolyte membranes (CL-HBP-PA) were prepared by their thermal polymerizations using benzoyl peroxide and their ionic conductivities under dry condition and thermal properties were investigated. The ionic conductivities of the low molecular weight CL-HBP(L)-PA membrane and the high molecular weight CL-HBP(H)-PA membrane were found to be 1.2×10^{-5} and 2.6×10^{-6} S cm^{-1}, respectively, at 150 °C under dry condition, and showed the Vogel–Tamman–Fulcher (VTF) type temperature dependence. Both membranes were thermally stable up to 300 °C, and they had suitable thermal stability as electrolyte membranes for the high-temperature fuel cells under dry condition. Fuel cell measurements using a single membrane electrode assembly cell with both cross-linked membranes were successfully performed.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Hyperbranched polymer; Phosphonic acid group; Proton conductivity; Cross-linked membrane; Fuel cell

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are the most promising candidates for electric vehicles and portable electrical power sources because they have high energy densities and high conversion efficiency, and they are environmentally benign systems [1–4]. These fuel cells have typically used perfluorinated, modified perfluorinated, partially fluorinated polymer electrolytes as the membranes to separate the electrodes and the oxygen and hydrogen (or methanol) gas streams [5,6]. The perfluorsulfonic acid polymer Nafion® is one of the most extensively studied proton exchange membrane for PEFC applications. However, it has a number of drawbacks that need to be overcome, which are the high cost, due to its complicated system construction, the durability, and the poor performance at temperature

above 80 °C due to the loss of the water. One of the arguments of the development of the new polymer electrolytes is the necessity to operate the fuel cell at high temperature conditions. The operation of the fuel cell at higher temperature than 100 °C is very interesting because anode catalysts poisoning by carbon monoxide are less important and the kinetics of the fuel oxidation will be improved and the efficiency of the cell should be significantly enhanced, and also the heat management will be simplified. Therefore, there has been a great demand of low cost and thermally stable electrolyte membranes for the high temperature PEFCs. Sulfonated aromatic polymers, organic–inorganic composite electrolyte membranes, and blend of different polymers with phosphoric acid have been explored [5–10]. In the first two types of electrolytes, the ionic conductivity depends upon the presence of water. Among the blends with phosphoric acid, poly(benzimidazole) has been successfully tested in the fuel cells which were operated at temperatures of up to 200 °C though long-term durability of these electrolytes have not been published yet [9,10]. Recently, as new poly-

HBP-PA-Ac
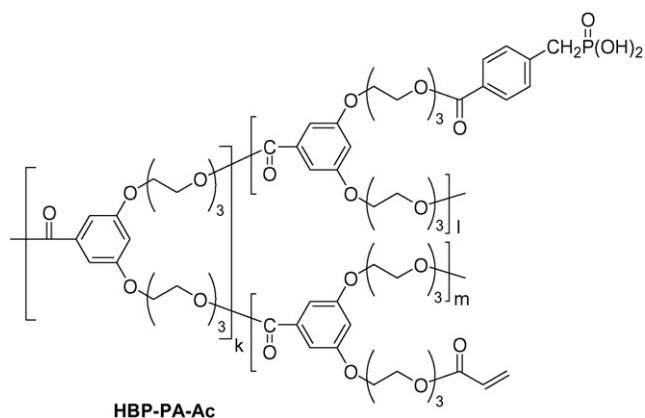
Scheme 1.

meric materials that are capable of fast proton conduction in the absence of any volatile compounds and that are durable at elevated temperatures, fully polymeric proton-conducting membranes based on nitrogen-containing heterocycles such as imidazole, benzimidazole, and pyrazole which have in many respects properties similar to those of water have been prepared and studied [11–16]. These approaches have been studied for applying them to the high temperature fuel cell systems because the proton conduction strongly depends on the presence of the water for the sulfonated polymer systems [17]. On the other hand, the ion-conducting phenomena have been widely investigated in dry polymer systems such as combinations of alkaline metal salts and polyethers [18–20]. Approaches to use dry polymer systems for proton conduction may be required at the temperature higher than 100 °C since the ionic conduction is generally cooperated with polymer chain motion. In addition, a single proton conductor is more desirable for avoiding evaporation and/or migration of low molecular proton media and acids. Recently, we prepared proton-conducting membranes based on the hyperbranched polymers with sulfonic acid groups [21] and the hyperbranched polymers with phosphonic acid groups [22], and investigated their ionic conductivities under dry conditions and thermal properties. For the case of the hyperbranched polymers with phosphonic acid groups (HBP-PA), though the presence of the phosphorous atom in the polymer has significantly improved the thermal stability of the polymer, phase separation phenomenon was observed in the preparation of interpenetrated membrane by the combination of HBP-PA with a hyperbranched polymer with acryloyl groups (HPB-Ac).

In this work, in order to suppress the phase separation and obtain the tough membrane suitable for fuel cell test, we synthesized the hyperbranched polymers (HBP-PA-Ac) (Scheme 1), which has both phosphonic acid as a proton source and acryloyl groups as a cross-linker in the same molecule, and investigated the ionic conductivity under dry conditions and thermal properties for the proton-conducting cross-linked electrolyte membrane (CL-HBP-PA) obtained by the polymerization of the HBP-PA-Ac and also we examined the fuel cell performance of the membranes in the oxygen and hydrogen fuel cells under non-humidified condition above 100 °C.

2. Experimental

2.1. Materials

The hyperbranched polymer with hydroxyl groups at the chain ends (HBP-OH) was prepared by the polymerization of methyl 3,5-bis[(8′-hydroxy-3′,5′-dioxaoctyl)oxy]benzoate, and separated into two parts, a low molecular weight hyperbranched polymer (HBP(L)-OH) and a high molecular weight hyperbranched polymer (HBP(H)-OH), according to the method reported previously [22,23], and their number-average molecular weights (M_n) were determined by gel permeation chromatography (GPC) (Tosoh HLC-803D with two columns of Tosoh TSKgel Multipore H_{XL}-M) with standard polystyrenes as a reference and tetrahydrofuran (THF) as an eluent. HBP(L)-OH: yield, 12.76 g (80%); $M_n = 4200$. HBP(H)-OH: yield, 2.86 g (18%); $M_n = 11,000$.

Benzoyl peroxide (BPO) was purified by the recrystallization from chloroform and methanol, and acrylic acid was distilled under reduced pressure in nitrogen. *N,N*-Dimethylaminopyridine (DMAP), dicyclohexylcarbodiimide (DCC), bromotrimethylsilane, and *N,N*-dimethylacetoamide (DMAc) were used as received.

2.2. Hyperbranched polymers with both diethyl phosphate and acryloyl groups at the chain ends (HBP-PE-Ac)

The low molecular weight hyperbranched polymer (HBP(L)-OH) (3.86 g, 8.38 mmol, $M_n = 4000$), acrylic acid (0.61 g, 8.38 mmol), DMAP (1.33 g, 10.09 mmol), and DCC (2.25 g, 10.09 mmol) were dissolved in 60 ml of dichloromethane at room temperature, and then stirred for 48 h under nitrogen. Deposited dicyclohexylurea was filtered off and the filtrate was placed under reduced pressure to remove volatile materials to give viscous oil. The viscous oil was purified by redissolution–reprecipitation methods using a mixture of dichloromethane and ethanol as a solvent and isopropyl ether as a precipitant (repeated three times), followed by a mixture of dichloromethane and ethanol as a solvent and hexane as a precipitant (repeated three times), and dried under reduced pressure to give a hyperbranched polymer (HBP(L)-Ac) with acryloyl groups partially at the chain ends. The resulting HBP(L)-Ac, 4-(diethoxyphosphorylmethyl)benzoic acid (2.28 g, 8.39 mmol), prepared from diethyl phosphite and 4-(bromomethyl)benzoic acid, DMAP (1.02 g, 8.38 mmol), and DCC (1.73 g, 8.38 mmol) were dissolved in 60 mL of dichloromethane at room temperature, and then stirred for 52 h under nitrogen. Deposited dicyclohexylurea was filtered off and the filtrate was placed under reduced pressure to remove volatile materials to give viscous oil. The viscous oil was purified by redissolution–reprecipitation methods using a mixture of dichloromethane and ethanol as a solvent and isopropyl ether as a precipitant (repeated three times), followed by a mixture of dichloromethane and ethanol as a solvent and hexane as a precipitant (repeated three times), and dried under reduced pressure to give a low molecular weight hyperbranched polymer (HBP(L)-PE-Ac) with both diethyl phosphate groups and acry-

loyl groups at the chain ends as a pale yellow viscous oil. The high molecular weight hyperbranched polymer (HBP(H)-PE-Ac) with both diethyl phosphate groups and acryloyl groups at the chain ends was also prepared as a pale yellow highly viscous oil from HBP(H)-OH (4.88 g, 12.17 mmol) by the same method as the procedure of synthesizing HBP(L)-PE-Ac.

HBP(L)-PE-Ac: yield, 3.37 g (69%). M_n = 4200. Acryloyl group content: 35% (determined by ^{1}H NMR measurement). IR (NaCl): ν_{CH} 2938 cm^{-1}, $\nu_{C=O}$ 1720 cm^{-1}, $\nu_{C=C}$ 1596 cm^{-1}, $\nu_{P=O}$ 1240 cm^{-1}, ν_{C-O} 1175 cm^{-1}, ν_{P-O} 1026 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.89 (d, J = 7.92 Hz), 7.40 (d, J = 7.92 Hz), 7.02 (br), 6.76 (br), 6.31 (d, J = 17.2 Hz), 6.21 (dd, J = 9.2, 17.2 Hz), 5.90 (d, J = 9.2 Hz), 4.35 (br), 4.19 (br), 4.07 (br), 3.93 (m), 3.72–3.60 (br), 3.14 (d, J_{H-P} = 20.8 Hz), 1.14 (t, J = 6.93 Hz); ^{13}C NMR (CDCl$_3$): δ 166.0 (C=O), 165.9 (C=O), 165.4 (C=O), 159.4 (Ar), 137.1 (Ar, J_{C-P} = 9.6 Hz), 131.6 (Ar), 131.4 (Ar), 129.8 (Ar), 129.2 (Ar), 128.5 (Ar), 128.2 (Ar), 107.9 (Ar), 106.4 (Ar), 70.5 (CH$_2$), 70.4 (CH$_2$), 69.3 (CH$_2$), 69.0 (CH$_2$), 68.8 (CH$_2$), 67.4 (CH$_2$), 63.9 (CH$_2$), 63.8 (CH$_2$), 63.4 (CH$_2$), 62.0 (CH$_2$, J_{C-P} = 6.1 Hz), 33.6 (CH$_2$, J_{C-P} = 137.8 Hz), 16.1 (CH$_3$, J_{C-P} = 6.1 Hz). Found: C%, 55.77%; H%, 6.66%.

HBP(H)-PE-Ac: yield, 4.23 g (61%). M_n = 11,000. Acryloyl group content: 40%.

2.3. Hyperbranched polymers with both phosphonic acid and acryloyl groups at the chain ends (HBP-PA-Ac)

HBP(L)-PE-Ac (2.62 g, 4.48 mmol, M_n = 4200) was dissolved in 70 mL of dichloromethane, and into the solution was added slowly bromotrimethylsilane (2.0 mL, 15.0 mmol) by using a syringe and then the mixture was stirred under nitrogen for 19 h. The reaction mixture was placed under reduced pressure to remove solvent to give a viscous residue, to which was added 70 mL of methanol and then stirred for 18 h. The resulting solution was placed under reduced pressure to remove the solvent and give a residue as a pale yellow highly viscous oil, which was dissolved in a small amount of *N,N*-dimethylformamide (DMF). The resulting solution was poured into a large amount of isopropyl ether to deposit the product, which was purified in three cycles of a dissolution–reprecipitation method. DMF and isopropyl ether were used as a solvent and a precipitant, respectively, and finally washed with isopropyl alcohol and dried under reduced pressure to give a low molecular weight hyperbranched polymer (HBP(L)-PA-Ac) with both phosphonic acid and acryloyl groups at the chain ends as pale yellow viscous oil. The high molecular weight hyperbranched polymer (HBP(H)-PA-Ac) with both phosphonic acid and acryloyl groups at the chain ends was also prepared as pale yellow solids from HBP(H)-PE-Ac (4.42 g, 7.69 mmol) by the same method as the procedure of synthesizing HBP(L)-PA-Ac.

HBP(L)-PA-Ac: yield, 2.05 g. IR (NaCl): ν_{OH} 3416 cm^{-1}, ν_{CH} 2938 cm^{-1}, $\nu_{C=O}$ 1718 cm^{-1}, $\nu_{C=C}$ 1598 cm^{-1}, $\nu_{P=O}$ 1277 cm^{-1}, ν_{C-O} 1176 cm^{-1}, ν_{P-O} 1011 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.85 (d, J = 7.59 Hz), 7.36 (d, J = 7.59 Hz), 7.01 (br), 6.74 (br), 6.34 (d, J = 17.3 Hz), 6.21 (dd, J = 9.6, 17.3 Hz), 7.36 (d, J = 9.6 Hz), 4.33 (br), 4.18 (br), 4.05 (br), 3.72–3.57 (br), 3.04 (d, J_{H-P} = 22.1 Hz); ^{13}C NMR (DMSO-d_6): δ 165.7 (C=O), 165.6 (C=O), 165.3 (C=O), 159.6 (Ar), 140.4 (Ar, J_{C-P} = 9.5 Hz), 131.7 (Ar), 131.4 (Ar), 129.8 (Ar), 128.9 (Ar), 128.2 (Ar), 127.5 (Ar), 107.7 (Ar), 106.0 (Ar), 70.1 (CH$_2$), 69.8 (CH$_2$), 68.9 (CH$_2$), 68.2 (CH$_2$), 67.5 (CH$_2$), 67.3 (CH$_2$), 64.3 (CH$_2$), 64.2 (CH$_2$), 63.7 (CH$_2$), 63.5 (CH$_2$), 35.6 (CH$_2$, J_{C-P} = 138.9 Hz). Found: C%, 53.25%; H%, 6.31.

HBP(H)-PA-Ac: yield, 3.11 g.

2.4. Preparation of the cross-linked electrolyte membranes

A given amount of the HBP(L)-PA-Ac or the HBP(H)-PA-Ac was dissolved in DMAc to obtain the 50 wt.% HBP-PA-Ac solution, and then to the solution were added a BPO (3 wt.% of HBP polymer) as a radical initiator and a fumed silica (SiO$_2$, 10 wt.% of HBP polymer) as a thickener. The resulting viscous suspension was poured on a parting agent-coated poly(ethyleneterephthalate) (PET) sheet, spread with doctor blade to get a constant thickness membrane, and DMAc was evaporated slowly at 100 °C for 24 h to prepare a casting membrane. Finally, the membrane was dried and cross-linked by heating at 120 °C for 48 h. The dried membranes were peeled from the parting agent-coated PET sheet to obtain the film of 95 μm thickness, and then stored inside the glove box.

2.5. Measurements

The ionic conductivities were determined by using ac impedance method on a Autolab PGSTAT30 (Eco Chemie) controlled by a personal computer. The polymer electrolyte samples (13 mm in diameter and approximately 95 μm thick) were put into two identical platinum blocking disk electrodes with a Teflon$^®$ spacer for ensuring the membrane thickness. The electrodes were held in a semi-open PTFE cell with stainless steel electrodes. The impedance measurements were carried out from 1 Hz to 1 MHz in the temperature range of 80–150 °C. All cell preparation and the measurements were performed under argon atmosphere (dew point < −85 °C).

The thermal stability of the cross-linked electrolyte membrane was investigated using thermogravimetric analysis with a TG/DTA 6200 instrument (Seiko Instruments Inc.). The samples were weighted, loaded in a Pt pan, and heated from 50 to 500 °C at a heating rate of 10 °C min^{-1} under air (200 mL min^{-1}). Aluminium oxide powder was used as a reference material. The differential scanning calorimetry (DSC) measurement was performed using a DSC 6200 differential scanning calorimeter (Seiko Instruments Inc.). The samples were sealed in Au-coated stainless steel pans under argon atmosphere, and scanned from −100 to 150 °C with a scanning rate of 10 °C min^{-1}.

Equivalent weight (Ew) of phosphonic acid function for the cross-linked electrolyte membranes was determined from phosphorous content by using inductively coupled plasma (ICP) method. The measurement was performed using a Inductively Coupled Plasma SPS-1700HVR (SII NanoTechnology Inc.).

The fuel cell measurement was carried out with a single membrane electrode assembly (MEA) cell. Gas diffusion electrodes with 20 wt.% Pt loading (Pt/Vulcan XC-72, Electrochem Inc., Massachusetts) were used to prepare to the MEA. The

active area for the anode and cathode was 9 cm². A membrane was sandwiched between the two electrodes, and the resulting MEA was pressed at 10 kg cm⁻² at room temperature. Polarization (I–V) performances were determined by a potential scan using a Solartron 1260 electrochemical station with a scanning rate of 20 mV s⁻¹ under a flow of dry H₂ (100 mL min⁻¹)/O₂ (100 mL min⁻¹).

3. Results and discussion

3.1. Preparation of the hyperbranched polymers with both phosphonic acid and acryloyl groups at the chain ends (HBP-PA-Ac) and the cross-linked electrolyte membranes (CL-HBP-PA)

The hyperbranched polymers with both phosphonic acid and acryloyl groups at the chain ends (HBP-PA-Ac) were successfully synthesized according to a synthetic route as shown in Scheme 2.

The hyperbranched polymer with hydroxyl groups at the chain ends (HBP-OH) was synthesized from methyl 3,5-bis[(8′-hydroxy-3′,6′-dioxaoctyl)oxy]benzoate monomer by the same method as the procedure reported previously [22,23], and they were separated into two parts, low molecular weight polymer fraction (HBP(L)-OH, M_n = 4200) and high molecular one (HBP(H)-OH, M_n = 11,000), by the redissolution–reprecipitation method using THF as a solvent and methanol as a precipitant. The low molecular weight HPB(L)-OH and the high molecular weight HBP(H)-OH were reacted with acrylic acid in the presence of DCC and DMAP at room temperature to give the HBP(L)-Ac and the HBP(H)-Ac, respectively, as yellow highly viscous oils. The obtained HBP(L)-Ac and HBP(H)-Ac were reacted with 4-(diethoxyphosphorylmethyl)benzoic acid in the presence of DCC and DMAP at room temperature to give the HBP(L)-PE-Ac in a 69% yield and the HBP(H)-PE-Ac in a 61% yield, respectively, as yellow highly viscous oils. The reactions of the HBP(L)-PE-Ac and the HBP(H)-PE-Ac with bromotrimethylsilane, followed by solvolysis in methanol, afforded the hyperbranched polymers (HBP(L)-PA-Ac and HBP(H)-PA-Ac) with both phosphonic acid groups and acryloyl groups at the chain ends as pale yellow solids, which were purified by dissolution–reprecipitation method using DMF as a solvent and isopropyl ether a precipitant, respectively, and finally washed with isopropyl alcohol. Acryloyl group contents of the HBP(L)-PA-Ac and the HBP(H)-PA-Ac were determined by ¹H NMR measurement to be 35 and 27%, respectively. Both polymers (HBP(L)-PA-Ac and HBP(H)-PA-Ac) are soluble in DMF, N,N-dimethylacetoamide (DMAc), and dimethylsulfoxide, but insoluble in benzene, chloroform, THF, isopropyl ether, methanol, ethanol, acetonitrile, and water.

Equivalent weights (Ew) of the HBP(L)-PA-Ac and the HBP(H)-PA-Ac were determined from phosphorous content by using inductively coupled plasma (ICP) method to be 1140 for the HBP(L)-PA-Ac and 1350 for the HBP(H)-PA-Ac, respectively.

The cross-linked electrolyte membrane (CL-HBP-PA) could be formed by solvent casting technique on parting agent-coated PET sheet at room temperature, and by the cross-linking reaction using BPO as a radical initiator. On this solvent casting, 10 wt.% fumed silica as a thickener was added to the HBP-PA-Ac solution in DMAc to obtain a large size homogeneous film with a given thickness. Without addition of fumed silica, we failed to prepare large size membranes suitable for fuel cell test. Moreover, although the formation of the cross-linked membranes by solvent casting on the glass plate without fumed silica was possible, we filed to peel them without break.

3.2. Ionic conductivities

The temperature dependence of the ionic conductivities for the CL-HBP(L)-PA and the CL-HBP(H)-PA membranes at the temperature range of 80–150 °C was shown in Fig. 1. Ionic conductivities of both electrolyte membranes were found to be 1.2×10^{-5} S cm⁻¹ for the CL-HBP(L)-PA membrane and 2.6×10^{-6} S cm⁻¹ for the CL-HBP(H)-PA membrane, respectively, at 150 °C under dry condition. Both the CL-HBP(L)-PA and the CL-HBP(H)-PA membranes showed lower ionic conductivities by about one order than the corresponding hyperbranched polymers without acryloyl groups (10^{-4} to 10^{-5} S cm⁻¹ at 135 °C) reported previously [22]. This is due to a lower content of the phosphonic acid groups, that is, the loss in the carrier number caused by the replacement of phosphonic acid groups with the acryloyl groups into the same molecule. Ionic conductivity data of the both electrolyte membranes were interpreted well using the Vogel–Tamman–Fulcher (VTF) equation (1) [24–26]:

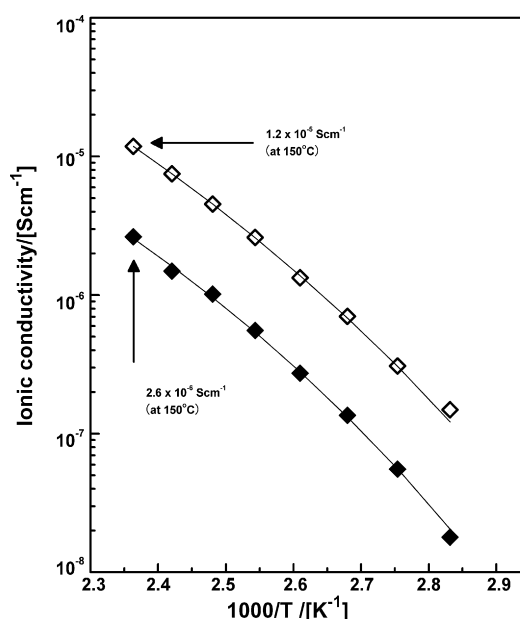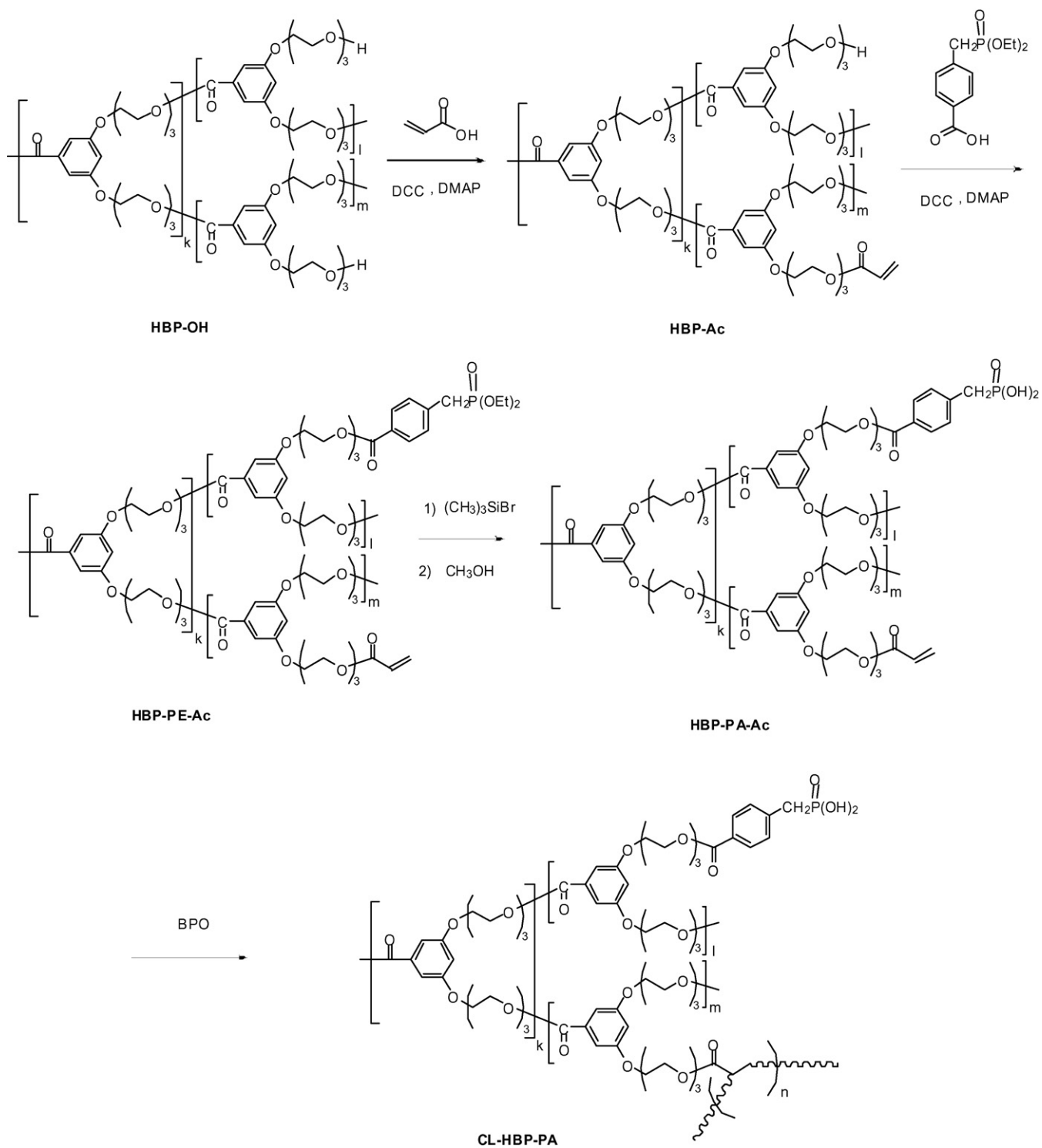$$\sigma(T) = AT^{-1/2} \exp\left(-\frac{B}{T - T_0}\right) \tag{1}$$

Fig. 1. Arrhenius plots of the ionic conductivity for the CL-HBP(L)-PA (◊) and the CL-HBP(H)-PA (♦) membranes.

Scheme 2.

where σ and T are the ionic conductivity and the absolute temperature, respectively. A, B and T_0 are the fitting parameters and correspond to carrier ion number, activation energy, and the temperature where the free volume vanishes, respectively. VTF parameters were summarized in Table 1. The observation of the VTF type behavior indicates that the proton conduction in the electrolyte membranes is cooperated by polymer chain

motion. And also, the CL-HBP(L)-PA membrane showed the higher ionic conductivity than the CL-HBP(H)-PA membrane, which is due to the larger A value, corresponding to number of carrier protons, for the CL-HBP(L)-PA membrane in comparison with the CL-HBP(H)-PA membrane and the smaller free volume for the CL-HBP(H)-PA membrane than the CL-HBP(L)-PA membrane as shown in the higher glass transition

Table 1
VTF parameters obtained by fitting the ionic conductivity data to Eq. (1)

Electrolyte membranes	A (S cm^{-1} K$^{-1/2}$)	B (K)	T_0 (K)	R^2
CL-HBP(L)-PA	2.68	1953	213	0.999
CL-HPB(H)-PA	0.34	1683	231	0.999

temperature of the CL-HBP(H)-PA membrane as described in later.

3.3. Thermal properties

DSC measurement was carried out at the temperature range of -100 to $150\,^\circ$C for the CL-HBP(L)-PA and the CL-HBP(H)-PA membranes under argon. DSC traces of the CL-HBP(L)-PA and the CL-HBP(H)-PA were shown in Fig. 2, indicating that they are completely amorphous. The T_gs were found to be $26.8\,^\circ$C for the CL-HBP(L)-PA membrane and $38.8\,^\circ$C for the CL-HBP(H)-PA membrane, respectively. Lower ionic conductivity observed for the CL-HBP(H)-PA membrane in comparison with the CL-HBP(L)-PA membrane might be ascribed to the higher T_g of the CL-HBP(H)-PA membrane, that is, the reduction of free volume in the CL-HBP(H)-PA membrane as observed in polymer electrolytes composed of poly(ethylene oxide) (PEO) and PEO-related polymers with lithium salts [18–20].

TG measurement was carried out under air to investigate the thermal stability for the CL-HBP(L)-PA and the CL-HBP(H)-PA membranes. The TG traces for both electrolyte membranes were shown in Fig. 3, where the polymers showed a two-stage decomposition and began to decompose at the temperature of about $300\,^\circ$C. They have much better thermal stability than the hyperbranched polymer with sulfonic acid groups reported previously [21], and such high thermal stability is due to the phosphorous atoms present in the polymers. The weight loss in the temperature range of 300–$400\,^\circ$C amounted to 40%, which corresponded approximately to the weight percent of the ethylene oxide chain unit in the polymers, indicating that the decomposition might take place an ether chain in the polymers. Anyway, it is sure that they have suitable thermal stability as electrolyte membranes for the high-temperature fuel cell under dry conditions.
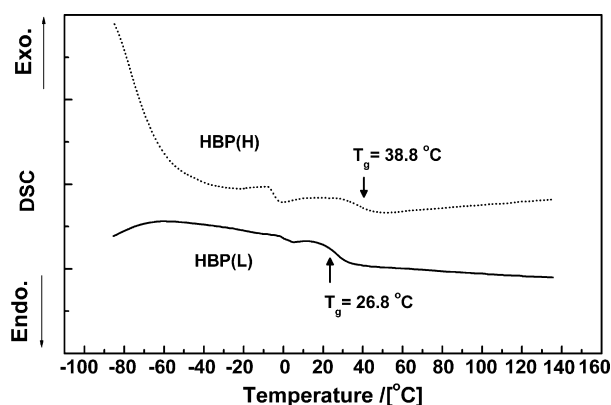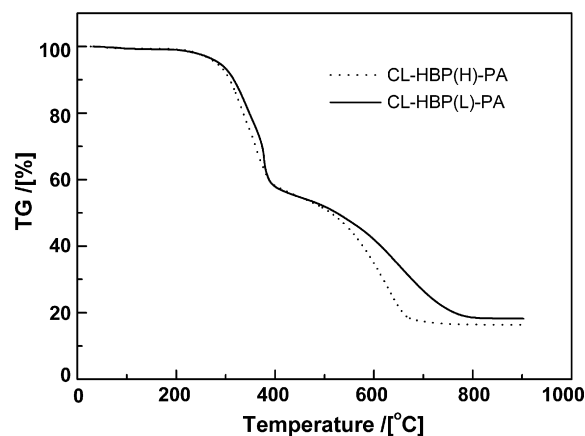

Fig. 3. Thermogravimetry traces of the CL-HBP(L)-PA (—) and the CL-HBP(H)-PA (– – –) membranes under air.

3.4. Fuel cell measurement

The polarization (*I–V*) characteristics of the CL-HBP(L)-PA and the CL-HBP(H)-PA membranes were measured using a test fuel cell. The voltage profiles observed at cell temperature of $150\,^\circ$C under non-humidified conditions were shown in Fig. 4. Dry hydrogen and dry oxygen gases were used as the fuel and the oxidant, respectively. The fuel cell using the CL-HBP(L)-PA membrane showed larger current density than that of the cell using the CL-HBP(H)-PA membrane. This result agrees with the fact that the conductivity of the CL-HBP(L)-PA membrane was higher than that of the CL-HBP(H)-PA membrane. The open-circuit voltages (OCV) were obtained to be 0.76 V for the CL-HBP(L)-PA membrane and 0.53 V for the CL-HBP(H)-PA membrane, respectively. Both OCV values are much lower than the theoretical value of 1.23 V. The reason for the low OCV might be related to gas cross-over or internal micro-short circuit due to poor mechanical strength of the membranes. However, the poor electrochemical active surface
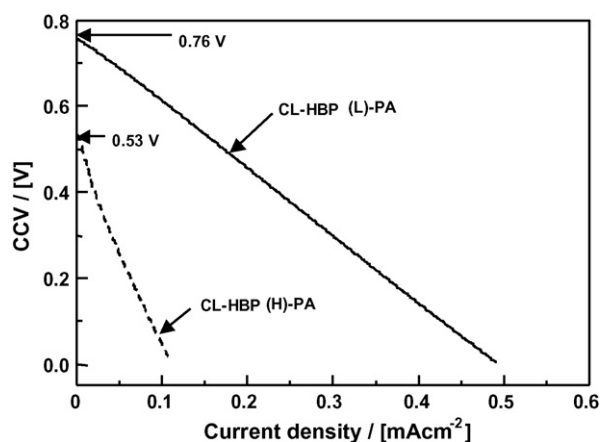

Fig. 2. DSC traces of the CL-HBP(L)-PA (—) and the CL-HBP(H)-PA (– – –) membranes under argon.

Fig. 4. The current vs. voltage characteristics of test fuel cells at $150\,^\circ$C using the CL-HBP(L)-PA (—) and CL-HBP(H)-PA (– – –) membranes as an electrolytes under non-humidified conditions. Dry hydrogen gas and dry oxygen gas were used as fuel and oxidation gas, respectively.

area is also presumed due to inexistence of the electrolyte in the electrodes. This might influence the lower OCV too. In general, cell performance is affected by a variety of factors such as the MEA technique used, ionic conductivity of the membranes, the degree of the cross-linking in the membranes, and the electrochemical reaction at the three-phase boundary. Although it is necessary to improve and optimize these factors in order to attain the better cell performance, successful fuel cell test using the CL-HBP(L)-PA and the CL-HBP(H)-PA membranes based on the concept of the proton conduction coupled with the polymer chain motion under non-humidified conditions was demonstrated.

4. Conclusion

We investigated the anhydrous proton-conducting membranes for use in the polymer electrolyte fuel cells at high temperature. We synthesized the two different molecular weight hyperbranched polymers (HBP(L)-PA-Ac and HBP(H)-PA-Ac) with both phosphonic acid group as a functional group and acryloyl group as a cross-linker at the chain ends as a new thermally stable proton-conducting electrolyte, and obtained the cross-linked electrolyte membranes (CL-HBP-PA) by their thermal polymerizations using benzoyl peroxide. The ionic conductivities of the low molecular weight HBP(L)-PA-Ac membrane and the high molecular weight HBP(H)-PA-Ac membrane were found to be 1.2×10^{-5} and $2.6 \times 10^{-6} \, \text{S cm}^{-1}$, respectively, at $150\,^{\circ}\text{C}$ under dry condition, and showed the VTF type temperature dependence. Both membranes were thermally stable up to $300\,^{\circ}\text{C}$, and they had suitable thermal stability as an electrolyte in the polymer electrolyte fuel cell operating under dry condition. Fuel cell measurements using a single membrane electrode assembly cell with both cross-linked membranes were successfully performed. The possibility of approaches to use dry polymer system for the proton conduction was demonstrated.

References

[1] K.D. Kreuer, Chem. Mater. 8 (1996) 610.
[2] S. Srinivasan, R. Mosdale, P. Stevens, C. Yang, Annu. Rev. Energ. Environ. 24 (1999) 281.
[3] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345.
[4] C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, A.B. Bocarsly, J. Power Sources 103 (2001) 1.
[5] O. Savadogo, J. N. Mater. Electrochem. Syst. 1 (1998) 47.
[6] O. Savadogo, J. Power Sources 127 (2004) 135.
[7] L.E. Karlsson, P. Jannasch, J. Membr. Sci. 230 (2004) 61.
[8] P. Jannasch, Curr. Opin. Colloid Interf. Sci. 8 (2003) 211.
[9] J.S. Wainright, J. Wang, D. Weng, R.F. Savinell, M. Litt, J. Electrochem. Soc. 142 (1995) L121.
[10] J. Wang, R.F. Savinell, J.S. Wainright, M. Litt, H. Yu, Electrochem. Acta 41 (1996) 193.
[11] M. Schuster, W.H. Meyer, G. Wagner, H.G. Herz, M. Ise, M. Schuster, K.D. Kreuer, J. Maier, Solid State Ionics 145 (2001) 85.
[12] M.F.H. Schuster, W.H. Meyer, M. Schuster, K.D. Kreuer, Chem. Mater. 16 (2004) 329.
[13] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29.
[14] H.G. Herz, K.D. Kreuer, J. Maier, G. Scharfenberger, M.F.H. Schuster, W.H. Meyer, Electrochem. Acta 48 (2003) 2165.
[15] J.C. Persson, P. Jannasch, Chem. Mater. 15 (2003) 3044.
[16] J.C. Persson, P. Jannasch, Macromolecules 38 (2005) 3283.
[17] K.D. Kreuer, M. Schuster, S.J. Paddison, E. Spohr, Chem. Rev. 104 (2004) 4637.
[18] F.M. Gray, Solid Polymer Electrolytes: Fundamentals and Technological Applications, VCH Publishers, New York, 1991.
[19] B. Scrosati (Ed.), Applications of Electroactive Polymers, Chapman and Hall, London, 1993, p. 251.
[20] F.M. Gray, Polymer Electrolytes, The Royal Society of Chemistry, London, 1997.
[21] T. Itoh, Y. Hamaguchi, T. Uno, M. Kubo, Y. Aihara, A. Sonai, Solid State Ionics 177 (2006) 185.
[22] T. Itoh, Y. Hamaguchi, K. Hirai, T. Uno, M. Kubo, Y. Aihara, A. Sonai, in: T. Fuller, C. Bock, S. Cleghorn, H. Gasteiger, T. Jarvi, M. Mathias, M. Murthy, T. Nguyen, V. Ramani, E. Stuve, T. Zawodzinski (Eds.), ECS Trans., vol. 3, No. 1, 2006, p. 113.
[23] T. Itoh, M. Ikeda, N. Hirata, Y. Moriya, M. Kubo, O. Yamamoto, J. Power Sources 81–82 (1999) 824.
[24] H. Vogel, Phys. Z. 22 (1921) 645.
[25] G. Tamman, W. Hesse, Z. Anorg. Allg. Chem. 156 (1926) 245.
[26] G.S. Fulcher, J. Am. Ceram. Soc. 8 (1925) 339.