Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 2986–2992

polymer

www.elsevier.com/locate/polymer

Anhydrous proton conducting polymer electrolytes based on poly(vinylphosphonic acid)-heterocycle composite material

Masanori Yamada, Itaru Honma*

Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan

Received 16 September 2004; received in revised form 20 January 2005; accepted 8 February 2005
Available online 10 March 2005

Abstract

The development of anhydrous proton conducting membrane is important for the operation of polymer electrolyte membrane fuel cell (PEMFC) at intermediate temperature (100–200 °C). In this study, we have investigated the acid–base hybrid materials by mixing of strong phosphonic acid polymer of poly(vinylphosphonic acid) (PVPA) with the high proton-exchange capacity and organic base of heterocycle, such as imidazole (Im), pyrazole (Py), or 1-methylimidazole (MeIm). As a result, PVPA-heterocycle composite material showed the high proton conductivity of approximately 10^{-3} S cm^{-1} at 150 °C under anhydrous condition. In particular, PVPA-89 mol% Im composite material showed the highest proton conductivity of 7×10^{-3} S cm^{-1} at 150 °C under anhydrous condition. Additionally, the fuel cell test of PVPA-89 mol% Im composite material using a dry H_2/O_2 showed the power density of approximately 10 mW cm^{-2} at 80 °C under anhydrous conditions. These acid–base anhydrous proton conducting materials without the existence of water molecules might be possibly used for a polymer electrolyte membrane at intermediate temperature operations under anhydrous or extremely low humidity conditions.

Keywords: Acid–base composite material; Anhydrous proton conductivity; Polymer electrolyte membrane fuel cells (PEMFC)

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are one of the attractive energy conversion systems to be used in many industrial applications including electric vehicles, mobile telephones, and on-site power generations [1–6]. Recently, the operation of PEMFC at higher temperature (100–200 °C) has been considered to provide many advantages, such as improved carbon monoxide (CO) tolerance of the platinum electrode, the higher energy efficiency, simplified heat managements, and co-generations [1–3,5–7]. However, the typical electrolyte material, such as Nafion® membrane, is not so stable at higher temperature (above 100 °C) and the proton conductivity decreases abruptly due to a loss of water from the membrane [8,9]. The proton transport in Nafion® membrane is due to the mobility of the water molecules in the membrane.

Investigations on anhydrous electrolyte systems with high proton conductivity at intermediate temperatures (100–200 °C) have been reported [1–3,5–7]. The proton transport under anhydrous (water-free) or low humidity conditions might be based on a non-vehicular mechanism, in which only protons are mobile from site to site without an assistance of diffusible vehicle molecules [10]. This type of the mechanism has been reported for polybenzimidazole(PBI)-phosphoric acid or PBI-sulfuric acid, [11–15] imidazole group immobilized polymer-acidic molecules, [16,17] sulfonated poly(ether-ether-ketone)-heterocycle, [18] ionic liquid, [19–22], and inorganic–organic copolymer [23]. However, these electrolytes membranes require the presence of liquid moieties, such as phosphoric or sulfuric acid solutions or ionic liquid, to enhance the proton conductivity. Furthermore, sulfonated-poly(ether–ether–ketone) based materials did not provide a high proton conductivity because of the low proton-exchange capacity. Polymer electrolytes with high proton-exchange capacity might be composite for the high proton conductivity under anhydrous condition, because a distance between protonic sites must be smaller.

In this study, we have prepared the acid–base composite materials by mixing of a strong phosphonic acid polymer

---

* Corresponding author. Tel.: +81 29 8615648; fax: +81 29 8615799.
E-mail address: i.homma@aist.go.jp (I. Honma).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.02.056

poly(vinylphosphonic acid) (PVPA) with the high proton-exchange capacity and an organic base heterocycle, such as imidazole (Im), pyrazole (Py), and 1-methylimidazole (MeIm). This PVPA-heterocycle composite material exhibited a large proton conductivity of 7×10^{-3} S cm^{-1} at 150 °C under anhydrous condition. Additionally, the thermal stability of composite material was found to increase with the mixing ratio of the heterocycle. Furthermore, the fuel cell test of PVPA-Im composite material using a dry H_2/O_2 showed the power density of approximately 10 mW cm^{-2} at 80 °C under anhydrous conditions.

2. Experimental section

2.1. Preparation of PVPA-heterocycle composite materials

Poly(vinylphosphonic acid) (PVPA) (M_w; 2×10^4) was obtained from Polysciences, Inc., PA. Imidazole (Im), pyrazole (Py), and 1-methylimidazole (MeIm) were purchased from Wako Pure Chemical Industries Ltd, Osaka, Japan and Tokyo Kasei Kogyo Co., Ltd, Tokyo, Japan. The molecular structures are shown in Fig. 1. Ultra-pure water (Milli-Q Gradient A10, Millipore Corp., MA) was used in all the experiments described. PVPA (100 mg/ml) and heterocycles were dissolved in water. The concentration of heterocycle in composite material was widely changed from 0 to 94 mol%. The PVPA-heterocycle solution (50–100 μl) was cast onto Teflon® plate and dried at room temperature or 70 °C for 1–3 days. The dried-membrane or -gel of PVPA-heterocycle composite was stripped from the Teflon® plate. The mixing ratio (mol%) of heterocycle was determined by

$$\text{mol\%} = 100 \times \frac{[\text{mole of heterocycle}]}{[\text{mole of phosphonic acid group in PVPA}] + [\text{mole of heterocycle}]}$$

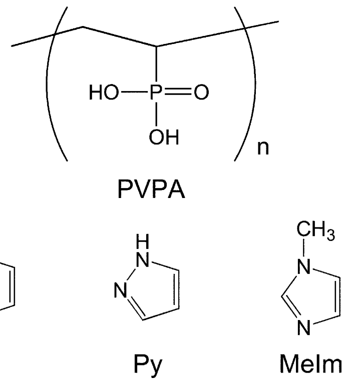

Fig. 1. Molecular structures of poly(vinylphosphonic acid) (PVPA), imidazole (Im), pyrazole (Py), and 1-methylimidazole (MeIm).

2.2. Characterization of PVPA-heterocycle composite materials

The thermal stability of these composite materials was analyzed by thermogravimetric-differential thermal analysis (TG-DTA) (TG-DTA 2000S, Mac Sciences Co., Ltd, Yokohama, Japan). TG-DTA measurement was demonstrated at the heating rate of 10 °C min^{-1} under dry-nitrogen flow. Infrared (IR) spectra were characterized using an IR spectrophotometer FTS-60 (Bio-Rad Laboratories, Inc., PA) with the attenuated total reflection (ATR) prism (Golden Gate Diamond ATR System, Specac Ltd, GA). The IR spectrum was measured with the resolution of 4 cm^{-1}.

2.3. Proton conductivity measurements of composite materials

Proton conductivity of PVPA-heterocycle composite materials was performed by the a.c. impedance method in a frequency range from 1 Hz to 1 MHz using an impedance analyzer SI-1260 (Solartron Co., Hampshire, UK) in a stainless steel vessel from room temperature to 160 °C [24–27]. The composite materials sandwiched between two platinum electrodes (diameter: 6 mm) with the Teflon® spacer. The direction of conductive measurement is perpendicular to the composite material. Conductivities of composite materials were determined from a typical impedance response (Cole–Cole plots). All the measurements in this experiment were carried out under dry-nitrogen flow. So, the measured impedance response indicates a anhydrous (water-free) proton conductivity of membranes [24–27].

2.4. Performance evaluation in fuel cell

The membrane electrode assembly (MEA) was prepared as follows: PVPA-Im solution was cast onto the hydrophilic PTFE filter (Millipore Corp., MA) and E-TEK Pt/C electrode with Pt loading 20 wt% (E-TEK Div. of De Nora N.A., Inc., NJ) was put on the membrane. These MEAs were dried at 70 °C for 1–3 days. The dried MEA was subjected into the electrochemical cell chamber. All the fuel cell measurements were executed under flowing of dry H_2/O_2 at 0.1 MPa, H_2 100 mL min^{-1} and O_2 100 mL min^{-1}. Current–voltage (I–V) characteristics of MEA were measured under anhydrous condition. The fuel cell operating temperature was less than 100 °C. The flow rates of the gases were controlled using mass-flow controllers.

3. Results and discussion

3.1. Preparation and characterization of PVPA-Im composite materials

The Poly(vinylphosphonic acid) (PVPA)-heterocycle solution was cast onto Teflon® plate and dried. The dried-membrane of PVPA-heterocycle was stripped from the Teflon® plate. Fig. 2 shows a photograph of a PVPA-89 mol% Im composite membrane. The free-standing membrane is transparent, flexible, and homogeneous. Fig. 3(a) and (b) shows the thermogravimetric (TG) and differential thermal analyses (DTA) of (1) pure PVPA material, (2) PVPA-44 mol% Im, (3) PVPA-76 mol% Im, (4) PVPA-89 mol% Im, (5) PVPA-93 mol% Im materials, and (6) pure Im materials, respectively, with a heating rate of 10 °C min^{-1} up to 300 °C under dry-nitrogen flow. Pure PVPA material without the mixing of Im showed the TG weight loss of approximately 5% at 150 °C (line (1) in Fig. 3(a)). This weight loss is due to the evaporation of water from the membrane. In contrast, the TG weight loss of the Im composite material diminished with the increase of the mixing ratio below 200 °C. Additionally, the endothermic peak due to the evaporation of water decreased with the mixing of Im molecules and the melting of Im was not observed below the mixing ratio of 89 mol% Im (line (1)–(4) in Fig. 3(b)). These results suggested that PVPA-Im composite material ($\leq$89 mol% Im) do not produce the diffusible ion by the melting of samples and is stable at the intermediate temperature ($<$160 °C). The TG weight loss above 200 °C may be an evaporation of Im molecules or condensation reaction of phosphonic group with the dehydration. Two endothermic peaks at 57.3 and 141.2 °C of PVPA-93 mol% Im composite material are the melting and boiling of Im phase, respectively.

3.2. Molecular structure of PVPA-Im composite materials

Next, we demonstrated the infrared (IR) measurement of PVPA-Im composite material. Spectra of composite materials were measured by the attenuated total reflection (ATR) method. IR spectra of (a) pure PVPA material, (b) PVPA-13 mol% Im, (c) PVPA-44 mol% Im, (d) PVPA-76 mol% Im, (e) PVPA-89 mol% Im, and (f) pure Im materials, respectively, are shown in Fig. 4. The absorption

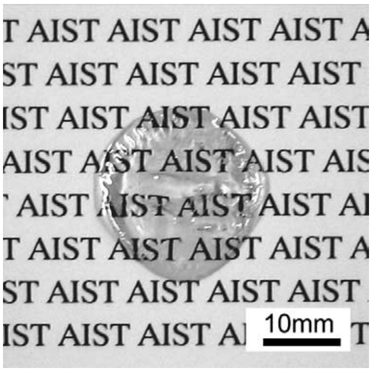

Fig. 2. Photograph of PVPA-89 mol% Im composite material. The free-standing membrane is transparent, flexible, and homogeneous.

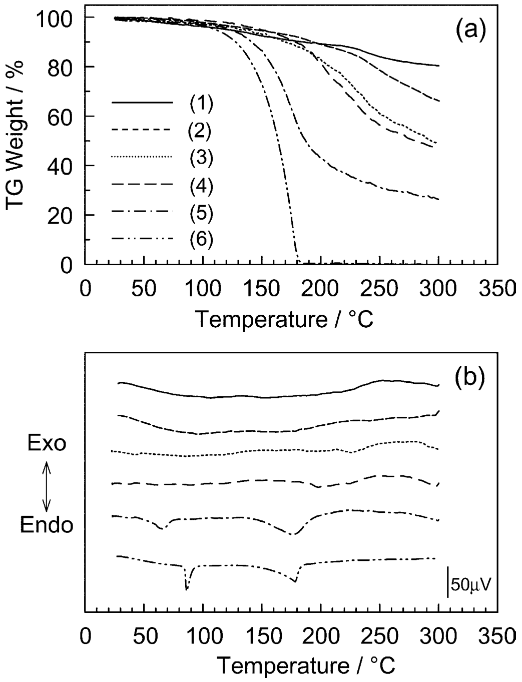

Fig. 3. TG (a) and DTA (b) curves of PVPA-Im composite materials with the heating rate of 10 °C min^{-1} under dry-nitrogen flow. (1) Pure PVPA material, (2) PVPA-44 mol% Im, (3) PVPA-76 mol% Im, (4) PVPA-89 mol% Im, (5) PVPA-93 mol% Im, and (6) pure Im materials.

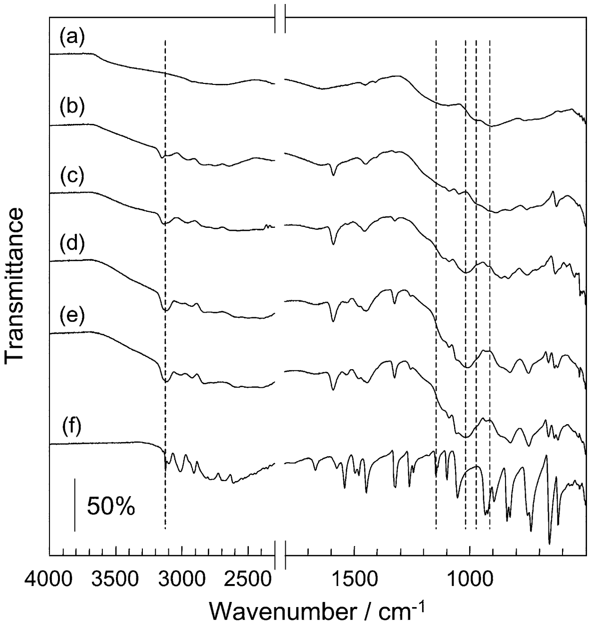

Fig. 4. Infrared (IR) spectra of PVPA-Im composite materials with different mixing ratio of Im. Spectra of composite materials were measured by the attenuated total reflection (ATR) method. (a) Pure PVPA material, (b) PVPA-13 mol% Im, (c) PVPA-44 mol% Im, (d) PVPA-76 mol% Im, (e) PVPA-89 mol% Im, (f) pure Im materials.

band at 1140 cm^{-1}, which can be attributed to the phosphonyl group (P=O) of PVPA, [28–33] disappeared when Im were mixed in the PVPA material. Additionally, the absorption bands at 904 and 983 cm^{-1}, a symmetric and an asymmetric vibration of P–O of PVPA, [28–33] also decreased and disappeared. In contrast, the $-PO_3^{2-}$ band [28–33] at 1010 cm^{-1} increased with the mixing of Im molecules. These results indicated that P–OH group of PVPA deprotonates by the mixing of Im and forms the $P–O^-$ group. This structure of $P–O^-$ group with deprotonation has been reported for the salt formation of PVPA [28–30]. On the other hand, the absorption band at ca. 3100 cm^{-1} with the mixing of Im, the stretching band of N–H group, [26–34] are relatively increased with the increase of Im in comparison with the spectrum of pure Im material. Such phenomena have been reported in polybenzimidazole(PBI)-phosphoric acid complex, [13,35] PBI-sulfuric acid complex, [13,35] poly(4-vinylimidazole)-phosphoric acid complex, [32] and mono-dodecylphosphate (MDP)-benzimidazole (BnIm) composite material [24] for the protonation to non-protonated –N=group of heterocycle. These results suggest that P–OH group of PVPA deprotonates by the mixing of Im and form the $P–O^-$ group. This free proton interacts with non-protonated –N= group of Im molecules. Therefore, the complex of PVPA and Im produces the acid-base salt, including imidazolium organic salts, in the acid-base composite material.

3.3. Proton conductivity of PVPA-Im composite material under anhydrous condition.

Proton conductivities of PVPA-Im composite material were determined by the a.c. impedance method over the frequency range 1 Hz–1 MHz under dry-nitrogen flow. So, the measured impedance indicates a anhydrous (water-free) proton conductivity of the membranes [24–27]. A typical impedance response (Cole–Cole plots) of PVPA-Im materials showed a feature similar to that of highly ionic conducting membrane, such as Nafion®, organic/inorganic hybrid membrane doped with heteropolyacids [36–38], MDP-BnIm composite material, [24] 2-undecylimidazole (UI)-MDP composite material [25], and uracil-MDP composite salt [26] (data not shown). The resistances of composite material were obtained from the extrapolation to the real axis. In contrast, these composite samples did not indicate the electronic conductivity at the DC condition. Additionally, the diffusible ions other than proton have not existed in the composite materials. Therefore, the impedance responses are due to the pure anhydrous proton transfer in composite salts.

The proton conductivity was obtained by repeating measurements on the same sample four times, from room temperature to 160 °C under anhydrous condition. The conductivity slightly decreased with the repeating and reached a steady state at more than three times. The steady-state conductivities of PVPA-Im composite materials with different Im mixing amount of (△) pure PVPA material, (▲) 44 mol% Im, (□) 61 mol% Im, (■) 76 mol% Im, (○) 83 mol% Im, (●) 89 mol% Im, (◇) 91 mol% Im, (◆) 93 mol% Im, and (×) 94 mol% Im composite materials at various temperatures were shown in Fig. 5. The conductivity of PVPA-Im composite material increased with the temperature and reached a maximum conductivity at 150 °C. Fig. 6 shows the steady-state proton conductivity at 150 °C of the composite material as a function of Im mixing ratios. The conductivity increased with the mixing ratio of Im and reached a maximum conductivity of 7×10^{-3} S cm^{-1} at the mixing ratio of 89 mol% Im under anhydrous condition. Afterward, the conductivity decreased with the increase of mixing ratio (>89 mol%). Fig. 7 shows the Arrhenius plots of proton conductivity for (△) PVPA-83 mol% Im, (○) −89 mol% Im, and (×) −91 mol% Im composite materials. The conductivities are plotted almost on the straight line in all temperatures. The data suggest that proton conducting mechanism is same for the composite materials with almost identical activation energy (E_a). Arrhenius formula was described as follows:

$$\sigma = A \exp\left(\frac{-E_a}{k_B T}\right) \tag{1}$$

where σ=proton conductivity under anhydrous condition, A=frequency factor, E_a=activation energy, k_B=Boltzmann constant, and T=absolute temperature. Eq. (1) was transformed to Eq. (2):

$$\ln \sigma = \ln A + \left(\frac{-E_a}{k_B T}\right) \tag{2}$$

Therefore, activation energy can be estimated from the slope using an Eq. (2). The activation energy was estimated to be 0.22–0.34 eV. These values are one order higher than that of fully swelled Nafion membrane, [39] and almost the same as other materials, such as solid electrolytes [40–42],

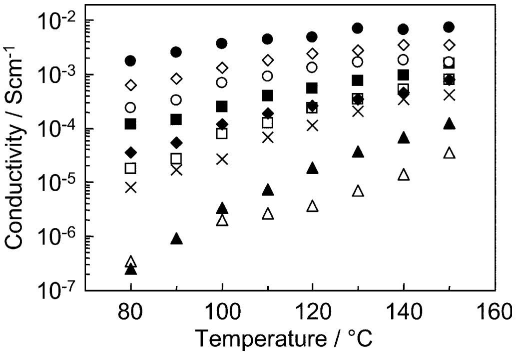

Fig. 5. Proton conductivities of PVPA-Im composite materials with different Im mixing ratio under anhydrous condition. Proton conductivity was performed by the a.c. impedance method between 1 Hz and 1 MHz using an impedance analyzer. Conductivities indicated the steady-state conductivity with the repeating of three times. Mixing ratios of Im are △, 0 mol% Im (pure PVPA material); ▲, 44 mol% Im; □, 61 mol% Im; ■, 76 mol% Im; ○, 83 mol% Im; ●, 89 mol% Im; ◇, 91 mol% Im; ◆, 93 mol% Im; and ×, 94 mol% Im.

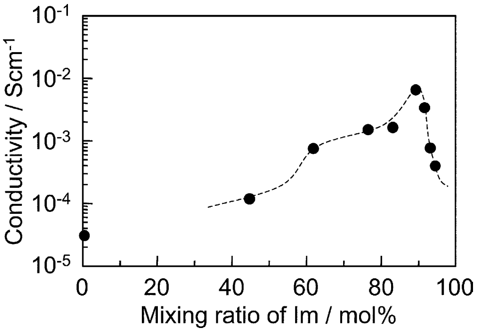

Fig. 6. Change of the steady-state proton conductivities at 150 °C as a function of Im mixing ratio from 0 to 94 mol%. Proton conductive measurements were demonstrated under anhydrous condition.

fullerene derivatives (fullerenol), [43,44] UI-MDP composite materials, [25] and uracil-MDP composite salt [26], reported as anhydrous proton conductors. This result supports that the proton transporting mechanism in PVPA-Im composite material is not a vehicular mechanism.

3.4. Performance evaluation in fuel cell

Fuel cell test of PVPA-89 mol% Im composite membrane electrode assembly (MEA) performed under anhydrous condition (dry H_2/O_2). Fig. 8 shows I–V characteristics of the MEA at 80 °C under anhydrous condition. The open circuit voltage of approximately 0.75 V is a conventional potential for hydrogen/oxygen cell and it indicates a small gas permeability through the membrane. Maximum power density of approximately 10 mW cm^{-2} was obtained at the current density of 35 mA cm^{-2} and the cell voltage of 0.3 V. The anhydrous conductivity of the membrane material can be estimated from the I–V characteristics of PVPA-89 mol% Im composite materials, where the slop between 0.25 and 0.45 V represents an ohmic drop in the electrolyte for this case. Therefore, the calculated substantial anhydrous conductivity (DC conductivity through the membrane) is 5×10^{-4}–1×10^{-3} S cm^{-1} at 80 °C. These values are almost same as the anhydrous conductivity data from the impedance spectroscopy (AC conductivity) at 80 °C (Fig. 5). Therefore, the conductivities of Fig. 5 indicate the substantial anhydrous proton conductivities without the diffusion of any other foreign charged molecules.

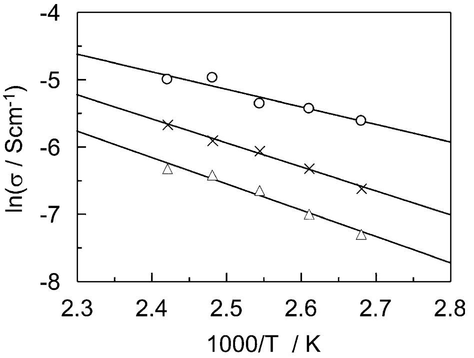

Fig. 7. Arrhenius plots of PVPA-83 mol% Im, PVPA-89 mol% Im, and PVPA-91 mol% Im composite materials. Solid lines are results of the least-squares fitting. Activation energies of the proton transfer under anhydrous condition were estimated from the slope of Eq. (2). Mixing ratios of Im are △, 83 mol% Im; ○, 89 mol% Im; ×, 91 mol% Im.

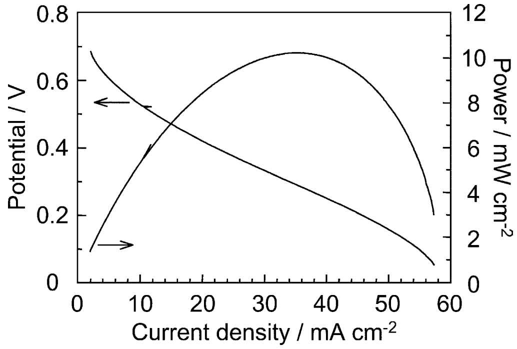

Fig. 8. I–V characteristics of PVPA-89 mol% Im composite materials with E-TEK Pt/C electrode (Pt loading 20 wt%) at 80 °C cell temperature under anhydrous conditions. The fuel cell measurement was made by flowing of dry H_2/O_2 at 0.1 MPa, H_2 100 mL min^{-1} and O_2 100 mL min^{-1}.

3.5. Proton conductivity of various heterocycle composite materials

Finally, we demonstrated the difference of proton conductivity based on type of basic heterocycle. So, we examined the relation of the acid dissociation constant (pK_a values) of heterocyclic molecules and anhydrous proton

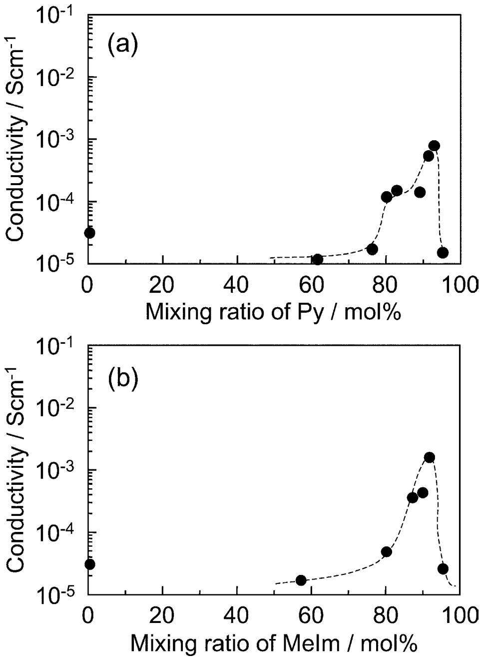

Fig. 9. Proton conductivities of (a) PVPA-Py and (b) PVPA-MeIm composite materials at 150 °C as a function of heterocycle mixing ratios. Conductivities indicated the steady-state proton conductivity under anhydrous condition with the repeating measurement of three times.

conductivity under intermediate temperature. Fig. 9(a) and (b) shows the steady-state proton conductivity at 150 °C under anhydrous condition of PVPA-pyrazole (Py) and PVPA-methylimidazole (MeIm) composite materials, respectively, with different pK_a values. The conductivity of these composite materials also increased with the mixing amount of heterocycle molecules. Additionally, at the mixing ratio of >93 mol%, the proton conductivity abruptly decreased. Maximum conductivities under anhydrous condition were 8×10^{-4} and 1×10^{-3} S cm^{-1} at PVPA-93 mol% Py and PVPA-91 mol% MeIm composite materials, respectively. These mixing ratios of heterocycle are almost as same as PVPA-Im composite material or sulfuric acid-imidazole material [18]. These results suggested that the composite materials with 90 mol% heterocycle are useful for the proton conducting membrane under anhydrous or extremely low humidity conditions. In contrast, the anhydrous proton conductivities of pure pyrazole and 1-methylimidazole molecules could not be measured by the melting and evaporation at intermediate temperature.

Nafion® membrane has been used in the PEMFC technologies under high humidity condition. This membrane is an acid polymer with sulfonic acid groups and the proton-exchange capacity is approximately 1000. In contrast, PVPA is a strong acid polymer with phosphonic acid groups and the exchange capacity is approximately 50 which is 20 times larger than Nafion® in the proton density. As a results, the PVPA material has shorter distance of proton transfer than that of Nafion® and becomes a proton conducting electrolyte membrane under anhydrous condition. Therefore, the proton conducting mechanism has proposed as follows: the transport of the proton can occur from protonated guest molecules to a non-protonated neighbor host molecule. [45–47] Namely, their protonated and non-protonated nitrogen in heterocycle may act as donors and acceptors in proton transfer reactions. In our experiment, a phosphate group of PVPA and nitrogen atoms of heterocycle ring can behave as a both proton donor and acceptor in acid–base complex membrane. In fact, IR spectra indicated the formation of acid-base salt, such as imidazolium organic salts. The proton in PVPA-heterocycle composite materials can be rapidly transferred to neighbor molecule with small activation energy of 0.22–0.34 eV. On the other hand, PVPA-heterocycle composite material showed the maximum proton conductivity at the mixing ratio of 90 mol% heterocycle. These phenomena are due to the construction of proton conductive pathway in composite material. Afterward, the proton conductivity abruptly decreased since the number of proton donor molecules, such as protonated heterocycle, decreased at the mixing ratio of >90 mol%.

Anhydrous proton conductivity of PVPA-heterocycle composite materials showed differences of approximately one order of magnitude, depending on the molecular structure of basic heterocycles. These different conductivities of composite materials are due to the pK_a value of heterocyclic molecules. The pK_a values of heterocycle molecules [48] and the maximum proton conductivity at 150 °C under anhydrous condition are listed in Table 1. The basicity of heterocycle molecules of Im is larger than that of Py (see the pK_{a1} value in Table 1). Clearly, the conductivity of PVPA-Im composite material is larger than PVPA-Py composite material. These results suggest that pyrazole molecule with the low basicity do not act as a proton donor and acceptor in composite material since the free proton from the PVPA molecule could not strongly interacts with non-protonated –N=group of pyrazole ring. In contrast, the pK_{a1} value of MeIm molecules is as same as that of Im molecules. However, the conductivity of PVPV-MeIm composite material is lower than that of PVPA-Im. This phenomenon is due to the molecular structure of imidazole. The Im molecules have been reported the construction of molecular cluster, consisting of approximately 20 molecules, [48] through the intermolecular hydrogen bonding. As a result, PVPA-Im composite material might possess fast proton transfer of inter-heterocycle molecules in the composite material. However, MeIm molecules do not construct the molecular cluster with the intermolecular interaction in membrane and cannot provide fast proton transfer kinetics in inter-heterocycle molecules. Based on the basicity and clustering mechanism, PVPA-Im composite material are supposed to possess the highest proton conductivity of 7×10^{-3} S cm^{-1} at 150 °C under anhydrous condition in many different types of PVPA-heterocycle composite materials. These results suggest that the basicity and molecular structure of heterocycle in acid-base composite material are important factors to obtain the anhydrous proton conductivity at the intermediate temperature condition.

4. Conclusion

We have investigated the proton conducting properties of acid-base complex material by mixing of poly(vinylphosphonic acid) (PVPA) with high proton exchange capacity and heterocycle molecules, such as imidazole (Im), pyrazole (Py), and 1-methylimidazole (MeIm). The PVPA-heterocycle

Table 1
Maximum proton conductivities of PVPA-heterocycle composite material and acid dissociation constants (pK_a values) of various heterocycle molecules

PVPA-heterocycle	Maximum conductivity[a] (S cm^{-1})	pK_a value of heterocycle[b]	
		pK_{a1}	pK_{a2}
PVPA-Im	7×10^{-3}	7.2	14.5
PVPA-Py	8×10^{-4}	2.5	14
PVPA-Melm	1×10^{-3}	7.4	

[a] Maximum proton conductivity at 150 °C under anhydrous condition.
[b] Ref. [48].

composite electrolyte showed a large proton conductivity of $7\times10^{-3}\,\mathrm{S\,cm^{-1}}$ at 150 °C under anhydrous condition. Additionally, the thermal stability of the composite material has been increased by the mixing of heterocycle molecule. The temperature dependence of the proton conductivity indicated the Arrhenius type behavior with an activation energy of 0.22–0.34 eV, which suggest the mechanism without the presence of vehicle molecules such as water. Furthermore, the fuel cell test of PVPA-Im composite material using a dry H_2/O_2 showed the power density of approximately $10\,\mathrm{mW\,cm^{-2}}$ at 80 °C under anhydrous conditions. The acid–base composite material may have potential not only for the polymer electrolyte membrane fuel cells (PEMFC) operated at intermediate temperature under anhydrous (water-free) or extremely low humidity conditions but also for electrochemical devices including electrochromic displays, chemical sensors, and others.

Acknowledgements

This work was supported by R&D program of PEMFC by New Energy and Industrial Technology Development Organization (NEDO), JAPAN.

References

[1] Kerres JA. J Membr Sci 2001;185:3.
[2] Rikukawa M, Sanui K. Prog Polym Sci 2000;25:1463.
[3] Kreuer KD. J Membr Sci 2001;185:29.
[4] Carrette L, Friedrich KA, Stimming U. Chemphyschem 2000;1:162.
[5] Kreuer KD. Chemphyschem 2002;3:771.
[6] Schuster MFH, Meyer WH, Schuster M, Kreuer KD. Chem Mater 2004;16:329.
[7] Li Q, He R, Jensen JO, Bjerrum NJ. Chem Mater 2003;15:4896.
[8] Sone Y, Ekdunge P, Simonsson D. J Electrochem Soc 1996;143:1254.
[9] Sumner JJ, Creager SE, Ma JJ, Desmarteau DD. J Electrochem Soc 1998;145:107.
[10] Kreuer KD. Chem Mater 1996;8:610.
[11] Bouchet R, Miller S, Duclot M, Souquet JL. Solid State Ionics 2001;145:69.
[12] Kawahara M, Morta J, Rikukawa M, Sanui K, Ogata N. Electrochim Acta 2000;45:1395.
[13] Bouchet R, Siebert E. Solid State Ionics 1999;118:287.
[14] Schechter A, Savinell RF. Solid State Ionics 2002;147:181.
[15] He R, Li Q, Xiao G, Bjerrum NJ. J Membr Sci 2003;226:169.
[16] Schuster M, Meyer WH, Wegner G, Herz HG, Ise M, Schuster M, et al. Solid State Ionics 2001;145:85.
[17] Pu H, Meyer WH, Wegner G. Macromol Chem Phys 2001;202:1478.
[18] Kreuer KD, Fuchs A, Ise M, Spaeth M, Maier J. Electrochim Acta 1998;43:1281.
[19] Sun J, MacFarlane DR, Forsyth M. Electrochim Acta 2001;46:1673.
[20] Sun J, Jordan LR, Forsyth M, MacFarlane DR. Electrochim Acta 2001;46:1703.
[21] Noda A, Susan MABH, Kudo K, Mitsushima S, Hayamizu K, Watanabe M. J Phys Chem B 2003;107:4024.
[22] Susan MABH, Noda A, Mitsushima S, Watanabe M. Chem Commun 2003;938.
[23] Li S, Liu M. Electrochim Acta 2003;48:4271.
[24] Yamada M, Honma I. Electrochim Acta 2003;48:2411.
[25] Yamada M, Honma I. J Phys Chem B 2004;108:5522.
[26] Yamada M, Honma I. Chem Phys Chem 2004;5:724.
[27] Yamada M, Honma I. Angew Chem Int Ed 2004;43:3688.
[28] Ellis J, Wilson AD. Polym Int 1991;24:221.
[29] Greish YE, Brown PW. Biomaterials 2001;22:807.
[30] Greish YE, Brown PW. J Am Ceram Soc 2002;85:1738.
[31] Corbridge DEC. Topics in phosphorus chemistry. New York: Wiley; 1969.
[32] Bozkurt A, Meyer WH. Solid State Ionics 2001;138:259.
[33] Bozkurt A, Meyer WH, Gutmann J, Wegner G. Solid State Ionics 2003;164:169.
[34] Silverstein RM, Webster FX. Spectrometric identification of organic compounds. New York: Wiley; 1998.
[35] Glipa X, Bonnet B, Mula B, Jones DJ, Rozière J. J Mater Chem 1999; 9:3045.
[36] Honma I, Nakajima H, Nishikawa O, Sugimoto T, Nomura S. Solid State Ionics 2003;162–163:237.
[37] Honma I, Nakajima H, Nishikawa O, Sugimoto T, Nomura S. J Electrochem Soc 2003;150:A616.
[38] Honma I, Nakajima H, Nishikawa O, Sugimoto T, Nomura S. J Electrochem Soc 2002;149:A1389.
[39] Zawodzinski TA, Derouin C, Radzinski S, Sherman RJ, Smith VT, Springer TE, et al. J Electrochem Soc 1993;140:1041.
[40] Baranov AI, Sinitsyn VV, Vinnichenko VY, Jones DJ, Bonnet B. Solid State Ionics 1997;97:153.
[41] Li YM, Hibino M, Miyayama M, Kudo T. Solid State Ionics 2000; 134:271.
[42] Iwahara H. Solid State Ionics 1996;86-88:9.
[43] Hinokuma K, Ata M. Chem Phys Lett 2001;341:442.
[44] Li YM, Hinokuma K. Solid State Ionics 2002;150:309.
[45] Hickman BS, Mascal M, Titman JJ, Wood IG. J Am Chem Soc 1999; 121:11486.
[46] Goward GR, Schuster MFH, Sebastiani D, Schnell I, Spiess HW. J Phys Chem B 2002;106:9322.
[47] Münch W, Kreuer KD, Silvestri W, Maier J, Seifert G. Solid State Ionics 2001;145:437.
[48] Acheson RM. An introduction to the chemistry of heterocyclic compounds. 3rd ed. Canada: Wiley; 1976.