J Polym Res (2013) 20:217
DOI 10.1007/s10965-013-0217-2

ORIGINAL PAPER

Proton-conducting blend membranes of Nafion/poly(vinylphosphonic acid) for proton exchange membrane fuel cells

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Received: 5 February 2013 / Accepted: 8 July 2013

Abstract Nafion/poly(vinylphosphonic acid) blends were synthesized and characterized in this work. Poly(vinylphosphonic acid), PVPA, was synthesized by the free-radical polymerization of vinylphosphonic acid. Then Nafion/PVPA blend membranes were prepared by means of film casting from Nafion/PVPA solutions with several molar ratios of PVPA repeat unit to –SO_3H. Homogeneous Nafion/PVPA films were produced. Nafion–PVPA interactions were studied by Fourier transform infrared (FT-IR) spectroscopy. Thermal properties were investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA results illustrated that all of these Nafion/PVPA electrolytes are thermally stable up to 400 °C. The membrane properties were further characterized by studying their morphologies using scanning electron microscopy (SEM). The proton conductivity of the Nafion/$P(VPA)_3$ blend membrane was 1.1×10^{-5} S/cm in an anhydrous state at 130 °C. The conductivities of the blends increased by at least three orders of magnitude upon hydration, exceeding 10^{-2} S/cm with RH=50 % at ambient temperature.

Keywords Nafion · Blend membranes · Poly(vinylphosphonic acid) · Proton conductivity · PEM fuel cell

Introduction

There has already been a great deal of research aiming at the development of membranes for polymer electrolyte membrane fuel cell (PEMFC) applications. Perfluorosulfonic acid membranes are commonly used as the polyelectrolyte, as they have high chemical stability and provide high proton conductivity in the fully hydrated state. Besides its high cost, a major weakness of Nafion is its low proton conductivity under low-humidity conditions, which leads to poor fuel cell performance at higher temperatures [1, 2]. Thus, there is a need for proton-conducting polymer electrolytes that can maintain high proton conductivity under low-humidity conditions. Working at higher temperatures (100–200 °C) brings some advantages, such as CO tolerance, easier heat and water management, faster electrode kinetics, and high energy efficiency [3, 4]. Therefore, the development of anhydrous proton-conducting membranes that are stable with respect to hydration and dehydration and can conduct protons to the nonaqueous phase has become necessary. A variety of alternative approaches have emerged in the search for water-free polymer electrolyte systems with sufficient proton conductivity at higher temperatures ($T>100$ °C). One approach is to use polymer acid complexes, and several promising systems based on PBI/H_3PO_4 have been reported [5–7]. Structural diffusion is dominant in acid-doped polymer electrolytes; in this case, the proton diffusion is mainly controlled by proton

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transport among acidic units [1]. It was reported that, under anhydrous conditions, incorporating phosphoric acid into Nafion yields a super acid, where the charged species that are generated are excess $H_4PO_4^+$ and immobilized $-SO_3^-$. Self-ionization of the phosphoric acid is reduced, yielding a lower concentration of $H_2PO_4^-$. Proton transport through structure diffusion is then reduced [8].

Another approach was to impregnate hydrophilic channels of perfluorosulfonic acid with aromatic heterocyclic proton solvents such as triazole, amino triazole, imidazole, butyl methyl imidazolium triflate, and benzimidazole, which enable proton diffusion at higher temperatures [9–14]. Although the use of these heterocyclic systems as composite components in an acidic polyelectrolyte has proven useful in the development of high-temperature-resistant films, leaching out of the solvent could be a problem for prolonged fuel cell applications. Alternatively, Nafion/polymer blends that are claimed to exhibit reduced methanol permeability and solvent exclusion have been reported. Such systems include Nafion/poly(1-vinyl-1,2,4-triazole) [15], Nafion/polybenzimidazole [16, 17], Nafion/PTFE [18, 19], sulfonated polypropylene oxide oligomers/Nafion [20], Nafion/poly(aryl ether ketone) [21], and PEO-PPO-PEO triblock copolymer/Nafion blend membranes [22].

Membranes based on phosphonic acid are quite promising due to their thermal stabilities and resistance to oxidation [23, 24]. The use of poly(vinyl phosphonic acid), PVPA (Fig. 1), as a blend component with Nafion would be interesting since PVPA bears phosphonic acid as a repeating unit and shows high proton conductivity [25, 26]. In addition, PVPA is a thermally as well as electrochemically stable polymer, so it can be used for high-temperature applications. In a recent study, a commercial Nafion membrane was modified by irradiating it in the presence of concentrated vinylphosphonic acid [27].

In the study described in the present paper, the homopolymer poly(vinylphosphonic acid), PVPA, was produced by the free-radical polymerization of vinylphosphonic acid. Blends were then prepared by film casting from commercial Nafion solutions and the PVPA at several stoichiometric ratios n (= [PVPA repeat unit]/[SO_3H]). The synthesis, molecular interactions, surface morphology, thermal properties, and proton conductivity of the blends are discussed later in this paper and compared with previously reported systems.

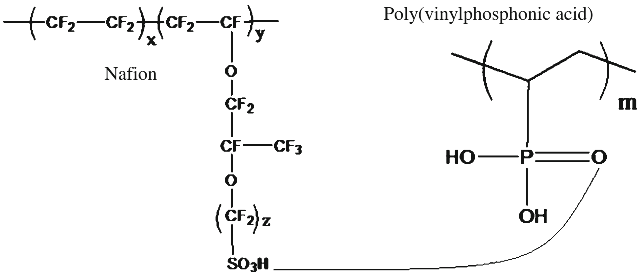


Fig. 1 Chemical structures of and interaction between poly(vinyl phosphonic acid) and Nafion

Materials and methods

Materials

Nafion solution (15 %, Ion Power, New Castle, DE, USA), Vinylphosphonic acid (> 95 %, Fluka, Buchs, Switzerland) and dimethyl formamide (DMF) (>99 %, Alfa Aesar, Ward Hill, MA, USA) were used as received. 2,2′-Azo(isobutyroic acid amidine)dihydrochloride (AIBADC) (97 %, Aldrich, St. Louis, MO, USA) was used as initiator.

Membrane preparation

Poly(vinylphosphonic acid) was produced by the free-radical polymerization of vinylphosphonic acid [28]. VPA and AIBADC were dissolved in distilled water. The reaction mixture was heated at 80 °C for 3 h. The product was further dissolved in water and dialyzed for purification. PVPA was dissolved in DMF and mixed with the commercial Nafion solution (15 %) at several molar ratios with respect to the sulfonic acid to PVPA repeat unit. The solutions were stirred until they were homogeneous and then cast on a polished Teflon plate. The solvent was slowly evaporated at 40 °C and then dried under vacuum at 80 °C for at least 24 h. The samples were denoted Nafion/P(VPA)$_n$ (Fig. 1), where the n is the mole ratio of VPA to $-SO_3H$. Thicknesses of the films ranged from 150 to 300 μm.

Characterization

The vibrational properties of the blend electrolytes were investigated with a Bruker (Ettlingen, Germany) Alpha Fourier transform infrared (FT-IR) spectrometer using the attenuated total reflection (ATR) technique.

The thermal stabilities of the materials were measured using a thermogravimetric analyzer (TGA) from Mettler Toledo (Columbus, OH, USA). The samples were heated from room temperature to 700 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were carried out on the Mettler Toledo instrument under an argon atmosphere. The samples were heated from −40 °C to 200 °C at a rate of 10 °C/min.

The surface morphologies of the blend membranes were investigated using a scanning electron microscope (SEM, XL30S-FEG, Philips, Eindhoven, Germany). All of the samples were sputtered with gold for 150 s before performing the SEM measurements.

Proton conductivity studies of the samples were performed using a Novocontrol (Hundsangen, Germany) Alpha-N highresolution dielectric analyzer. The films were sandwiched between platinum blocking electrodes and the conductivity was measured in the frequency range from 1 Hz to 3 MHz as a function of temperature, which was varied from 20 °C to 160 °C in 10 °C intervals.

Results and discussion

FT-IR spectroscopy

The molecular structures of the Nafion/PVPA blend membranes were characterized by FT-IR spectroscopy. Figure 2 shows the FT-IR spectra of the Nafion/PVPA membranes. The FT-IR spectrum of pristine PVPA shows strong bands at 1,040–910 cm^{-1} (that relate to asymmetric stretching vibrations of the (P–O)H) and at 1,150 cm^{-1} (that corresponds to P=O stretching). The phosphonic acid group gives an additional band in the region of 1,700–1,630 cm^{-1} [29]. –OH stretching of the same group produces a broad band at 3,300–2,850 cm^{-1}. According to the literature, the characteristic Nafion peaks are observed at 1,365 cm^{-1} (SO_3H), 1,052 cm^{-1} (SO_3^-), and 1,140 cm^{-1} (C–F) [12]. After blending, a broad peak appeared between 2,000 and 3,500 cm^{-1}, corresponding to the hydrogen-bonding network. At higher PVPA contents, there is a large increase in the intensity of the peak at 908 cm^{-1} due to P–(O–H) stretching, which may result from the protonation of P=O units in PVPA.

Thermal analysis

Operation of a PEMFC at high temperatures brings several advantages: increased kinetic rates of the cell reaction, fewer problems related to catalyst poisoning, etc. Therefore, the thermal stability of the proton-conducting polymer membrane is very important during applications of it. The thermal stability of the perfluorosulfonic acid polymer with an equivalent molecular weight of 1,100 has been studied by several groups [30]. They reported that weight changes that occurred up to 280 °C were due only to water, while loss of sulfonic acid groups started to occur above 300 °C. Figure 3 shows thermogravimetry curves of the Nafion/PVPA blend membranes. Weight loss from PVPA starts at 130 °C; this is due to the condensation of phosphonic acid moieties [23]. The insertion of PVPA into Nafion increased the thermal stability of the membranes. Clearly, all of the Nafion/P(VPA)$_n$ blend membranes decompose above 400 °C. The weight change up to this temperature increases in parallel with the PVPA content. This weight change can be attributed to the condensation of phosphonic acid units, especially for Nafion/P(VPA)$_6$.

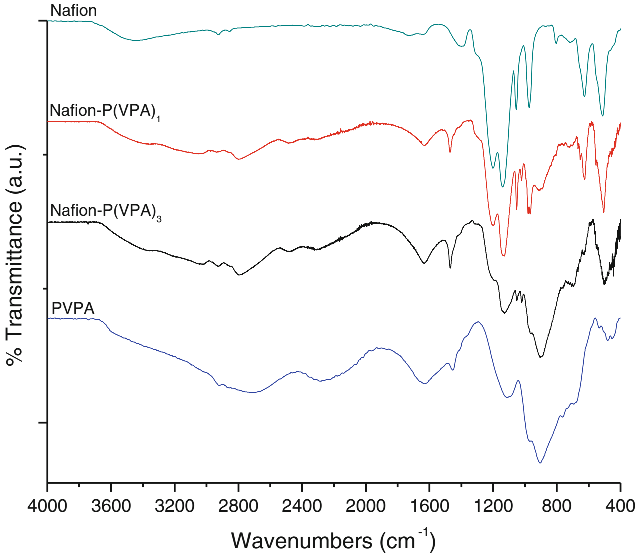


Fig. 2 FT-IR spectra of Nafion/PVPA blend membranes and pristine PVPA

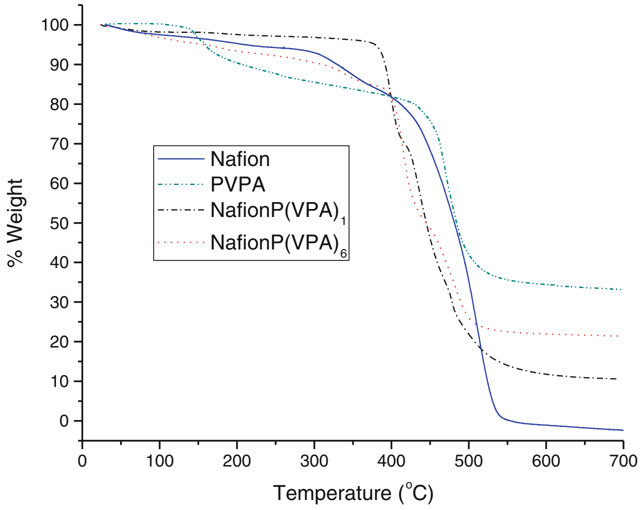


Fig. 3 TG thermograms of Nafion/PVPA blend membranes at a heating rate of 10 °C/min

The thermal properties of the blend membranes were further investigated by performing differential scanning calorimetry,

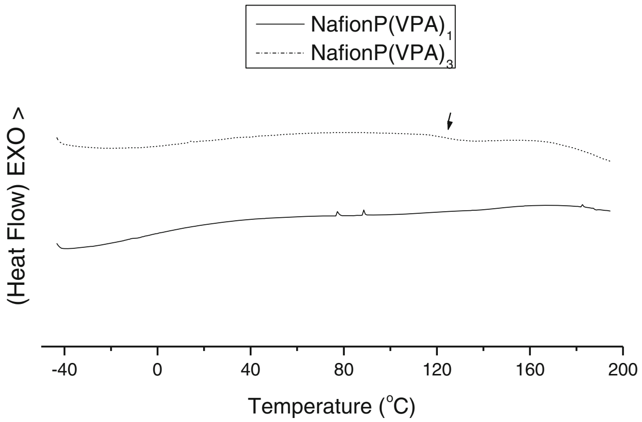


Fig. 4 DSC traces of Nafion/P(VPA)$_1$ and Nafion/P(VPA)$_3$, as recorded in an inert atmosphere at a heating rate of 10 °C/min

Fig. 5 SEM micrographs of the surfaces of **a** Nafion/P(VPA)$_1$ and **b** Nafion/P(VPA)$_3$

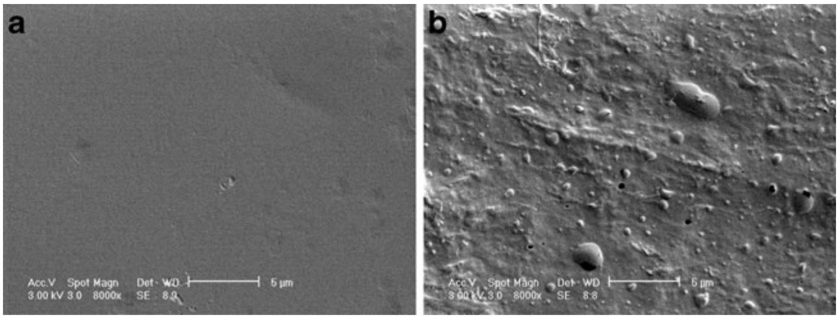
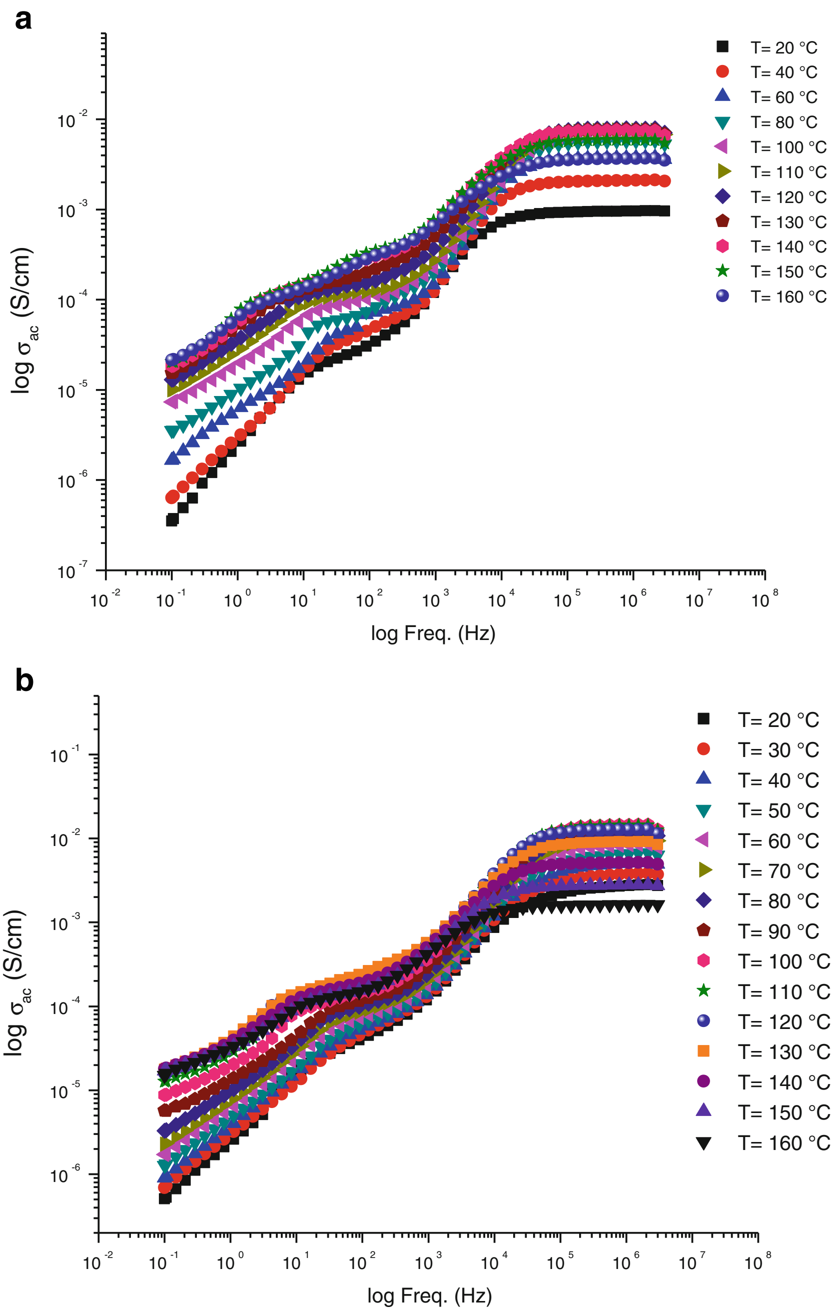


Fig. 6 AC conductivity (logarithmic scale) vs. frequency for **a** Nafion/P(VPA)$_1$ and **b** Nafion/P(VPA)$_1$ blend membranes at several temperatures



DSC (Fig. 4). Although the PVPA homopolymer exhibits a glass transition at around −23 °C [31], the Nafion/P(VPA)$_1$ membranes did not show a glass transition up to 200 °C. However, the Nafion/P(VPA)$_3$ sample had a T_g of approximately 122 °C. The absence of a T_g for Nafion/P(VPA)$_1$ and the presence of a high T_g for Nafion/P(VPA)$_3$ can be attributed to interpolymer interactions, which may restrict the segmental mobility of the PVPA in the hydrophilic channels of Nafion.

SEM micrographs

The surface morphologies of the Nafion/PVPA blend membranes were investigated by scanning electron microscopy (Fig. 5). Due to strong interactions between the sulfonic acid groups of Nafion and the phosphonic acid units of PVPA, no phase separation occurred during solvent evaporation, so homogeneous films formed. This result is also consistent with the DSC curves of the blend membranes, where no separate T_g transition of the impregnated PVPA was observed. On the other hand, the surface roughness increased with the PVPA content because of microphase separation at higher PVPA contents.

Proton conductivity

The frequency-dependent proton conductivities of the samples were measured by an AC impedance method over the range 1 Hz to 3 MHz at various temperatures under a dry nitrogen flow. AC conductivities ($\sigma_{ac}(\omega)$) were calculated using the following equation:

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_o, \qquad (1)$$

where $\sigma'(\omega)$ is the real part of the conductivity, $\omega=2\pi f$ is the angular frequency, ε_o is the vacuum permittivity ($\varepsilon_o=8.852\times10^{-14}$ F/cm), and $\varepsilon''$is the imaginary part of the complex dielectric permittivity (ε^*). The samples were dried under a vacuum at 80 °C for at least 24 h prior to the measurements.

Curves of the alternating current (AC) conductivity σ_{ac} versus the frequency are shown in Figs. 6a and b for 50 %-relative-humidified Nafion/P(VPA)$_1$ and Nafion/P(VPA)$_3$, respectively. At lower frequencies, conductivity increases up to a certain level due to electrode polarization. A leveling off over 2–3 decades was then observed at intermediate frequencies. The direct current (DC) conductivities σ_{dc} of the samples were derived from those plateau regions using linear curve fitting.

The temperature dependence of the proton conductivity is illustrated for anhydrous Nafion/P(VPA)$_n$ systems in Fig. 7. The conductivity of the Nafion/P(VPA)$_n$ system depends on the composition, temperature, and relative humidity (RH). The proton conductivities of the samples mainly increase with increasing temperature. The proton conductivity of the Nafion/P(VPA)$_3$ sample is higher than that of Nafion/P(VPA)$_1$. The anhydrous blend membranes have proton conductivities of around 10^{-5} S/cm. On the other hand, the

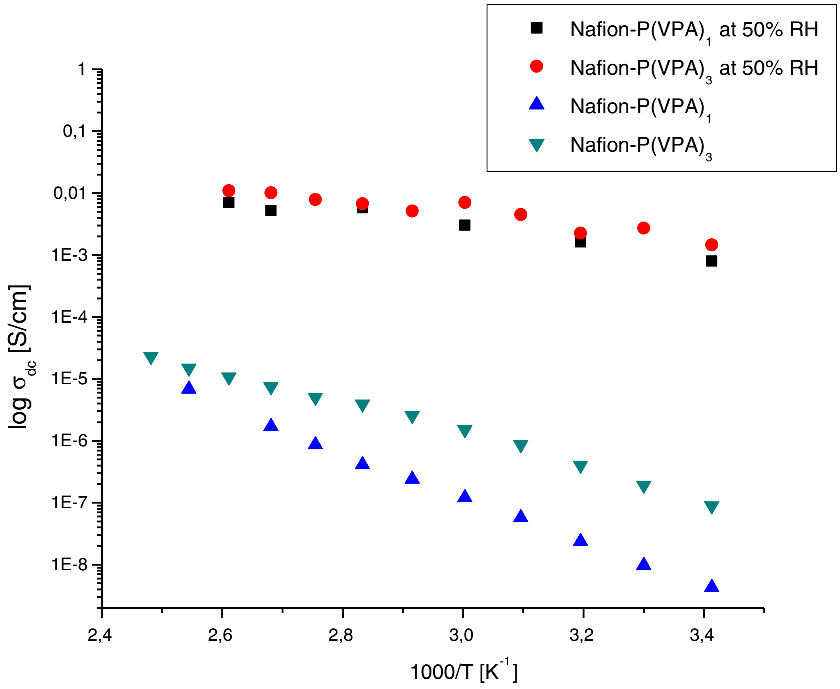


Fig. 7 Proton conductivity (logarithmic scale) versus reciprocal temperature for anhydrous Nafion/PVPA blend electrolytes

proton conductivities of the samples rise with humidification, with the highest conductivity achieved for a 1:3 composition: 1.1×10^{-2} S/cm at 110 °C. Above 110 °C, the conductivity gradually decreases due to a loss of absorbed humidity.

The proton conductivities of perfluorosulfonic acid membranes are highly humidity dependent because these structures have sulfonic acid groups and hydration is crucial to maintaining their conductivity. The conductivity increases linearly with water content, and maximum conductivity is reached at 100 % relative humidity [32]. The conductivity drops above 100 °C humidity due to dehydration of the membrane. Several attempts have been made to improve the conductivities of hydrated perfluorosulfonic acid systems at higher temperatures [33]. In an earlier work, Nafion membranes were modified with vinyl phosphonic polymers using the ionizing radiation technique [27]. Proton conductivities were around 10^{-3} S/cm at the equilibrium water content.

In this blend system, proton conductivity may occur via the phosphonic/sulfonic acid units, which aggregate to form dynamical hydrogen-bonded chains, supporting long-range proton transport. The proton conductivities of the blend membranes were 3×10^{-3} S/cm at room temperature and exceeded 10^{-2} S/cm at 110 °C (RH=50 %). These results show that the Nafion/PVPA system, with its high thermal stability and acceptable proton conductivity, may be a candidate for high-temperature PEMFC applications.

Conclusions

In this work, novel high-temperature-stable, proton-conducting polymer-blend membranes based on the Nafion/P(VPA)$_n$ system were investigated. The membranes were prepared successfully by solution casting, which allowed controlled impregnation of the Nafion with PVPA. The materials showed high chemical and thermal stabilities: the Nafion/P(VPA)$_n$ systems decomposed well above 400 °C. DSC and SEM results demonstrated that the Nafion/P(VPA)$_n$ membranes were homogeneous, irrespective of composition. From the FT-IR studies, it was found that protons dissociated from the acidic groups and protonated phosphonic acid units of the polymer, leading to hydrogen-bonding network formation. In the anhydrous state, the Nafion/P(VPA)$_1$ system had the highest proton conductivity of 1.1×10^{-5} S/cm at 130 °C. After humidification, the conductivities of the samples increased by about four orders of magnitude (0.012 S/cm) at the same temperature. These results demonstrate that the insertion of PVPA into hydrophilic channels of Nafion results in the production of thermally and mechanically stable membranes that are candidates for application as polymer electrolyte membranes in fuel cells.

References

1. Schuster ME, Meyer WH (2003) Anhydrous proton-conducting polymers. Annu Rev Mater Res 33:233–261
2. Kreuer KD (2001) On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. J Membr Sci 185(1):29–39
3. Jensen JO et al (2007) High temperature PEMFC and the possible utilization of the excess heat for fuel processing. Int J Hydrog Energy 32(10–11):1567–1571
4. Vengatesan S et al (2008) High temperature operation of PEMFC: a novel approach using MEA with silica in catalyst layer. Int J Hydrog Energy 33(1):171–178
5. Pu HT, Meyer WH, Wegner G (2002) Proton transport in polybenzimidazole blended with H_3PO_4 or H_2SO_4. J Polym Sci Part B Polym Phys 40(7):663–669
6. He RH et al (2003) Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors. J Membr Sci 226(1–2):169–184
7. Samms SR et al (1996) Thermal stability of proton conducting acid doped polybenzimidazole in simulated fuel cell environments. J Electrochem Soc 143(4):1225–1232
8. Savinell R et al (1994) A polymer electrolyte for operation at temperatures up to 200°C. J Electrochem Soc 141(4):L46–L48
9. Yang C et al (2001) Approaches and technical challenges to high temperature operation of proton exchange membrane fuel cells. J Power Sources 103(1):1–9
10. Kreuer KD et al (1998) Imidazole and pyrazole-based proton conducting polymers and liquids. Electrochim Acta 43(10–11):1281–1288
11. Li SW et al (2005) 1H-1,2,4-triazole: an effective solvent for proton-conducting electrolytes. Chem Mater 17(24):5884–5886
12. Kim JD et al (2007) Anhydrous proton-conducting properties of Nafion-1,2,4-triazole and Nafion-benzimidazole membranes for polymer electrolyte fuel cells. J Electrochem Soc 154(4):A290–A294
13. Rauhut G (2003) Modulation of reaction barriers by generating reactive intermediates: double proton transfer reactions. Phys Chem Chem Phys 5(5):791–800
14. Sen U et al (2008) Anhydrous proton conducting membranes for PEM fuel cells based on Nafion/azole composites. Int J Hydrog Energy 33(11):2808–2815
15. Sen U, Bozkurt A, Ata A (2010) Nafion/poly(1-vinyl-1,2,4-triazole) blends as proton conducting membranes for polymer electrolyte membrane fuel cells. J Power Sources 195(23):7720–7726
16. Wycisk R et al (2006) Direct methanol fuel cell membranes from Nafion-polybenzimidazole blends. J Power Sources 163(1):9–17
17. Ainla A, Brandell D (2007) Nafion-polybenzimidazole (PBI) composite membranes for DMFC applications. Solid State Ionics 178(7–10):581–585
18. Yu TL et al (2004) Nafion/PTFE composite membranes for fuel cell applications. J Polym Res Taiwan 11(3):217–224
19. Lin HL et al (2009) Silicate and zirconium phosphate modified Nafion/PTFE composite membranes for high temperature PEMFC. J Polym Res 16(5):519–527
20. Lin YF et al (2007) Sulfonated poly(propylene oxide) oligomers/Nafion® acid–base blend membranes for DMFC. J Power Sources 172(2):570–577
21. Kim IT, Choi J, Kim SC (2007) Blend membranes of Nafion/sulfonated poly(aryl ether ketone) for direct methanol fuel cell. J Membr Sci 300(1–2):28–35
22. Hu J et al (2008) PEO-PPO-PEO triblock copolymer/Nafion blend as membrane material for intermediate temperature DMFCs. J Appl Electrochem 38(4):543–550

23. Jiang DD et al (1999) TGA/FTIR studies on the thermal degradation of some polymeric sulfonic and phosphonic acids and their sodium salts. Polym Degrad Stab 63(3):423–434
24. Schuster M et al (2005) About the choice of the protogenic group in PEM separator materials for intermediate temperature, low humidity operation: a critical comparison of sulfonic acid, phosphonic acid and imidazole functionalized model compounds. Fuel Cells 5(3):355–365
25. Acar O et al (2009) Proton conducting membranes based on poly(2,5-benzimidazole) (ABPBI)-poly(vinylphosphonic acid) blends for fuel cells. Int J Hydrog Energy 34(6):2724–2730
26. Aslan A, Bozkurt A (2009) Development and characterization of polymer electrolyte membranes based on ionical cross-linked poly(1-vinyl-1,2,4 triazole) and poly(vinylphosphonic acid). J Power Sources 191(2):442–447
27. Florjańczyk Z, Wielgus-Barry E, Poltarzewski Z (2001) Radiation-modified Nafion membranes for methanol fuel cells. Solid State Ionics 145(1–4):119–126
28. Bingol B et al (2006) Synthesis, microstructure, and acidity of poly(vinylphosphonic acid). Macromol Rapid Commun 27(20): 1719–1724
29. Bozkurt A, Meyer WH (2001) Proton conducting blends of poly(4-vinylimidazole) with phosphoric acid. Solid State Ionics 138(3–4):259–265
30. Chu D et al (1990) Infrared reflectance absorption-spectroscopy (IRRAS)—study of the thermal stability of perfluorinated sulfonic-acid ionomers on PT. J Appl Electrochem 20(1):157–162
31. Celik SU et al (2008) Anhydrous proton-conducting properties of triazole-phosphonic acid copolymers: a combined study with MAS NMIR. Phys Chem Chem Phys 10(39):6058–6066
32. Gardner CL, Anantaraman AV (1998) Studies on ion-exchange membranes. II. Measurement of the anisotropic conductance of Nafion. J Electroanal Chem 449(1–2):209–214
33. Rikukawa M, Sanui K (2000) Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers. Prog Polym Sci 25(10):1463–1502