Journal of Power Sources 208 (2012) 176–179

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Proton exchange membranes based on poly(2,5-benzimidazole) and sulfonated poly(ether ether ketone) for fuel cells

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ARTICLE INFO

Article history:
Received 10 October 2011
Received in revised form 6 February 2012
Accepted 10 February 2012
Available online 19 February 2012

Keywords:
ABPBI
SPEEK
Membrane
Conductivity
Fuel cells

ABSTRACT

The blend membranes based on poly(2,5benzimidazole) (ABPBI) and sulfonated poly(ether ether ketone) (SPEEK) with different sulfonation degrees (SD) have been synthesized and characterized. These blend membranes showed increased conductivities compared with the original ABPBI membrane. After being doped by H_3PO_4, a maximum conductivity of 1.09×10^{-1} S cm^{-1} of ABPBI with 16% SD SPEEK membranes was achieved at 100 °C, which is six times than the maximum 1.8×10^{-2} S cm^{-1} for the ABPBI membrane at 120 °C. In the case of ABPBI with 32%SD SPEEK membranes, maximum conductivity is 3.89×10^{-2} S cm^{-1} at 120 °C, double than the maximum 1.8×10^{-2} S cm^{-1} for the ABPBI membrane at 120 °C. Moreover, the ABPBI–SPEEK blend membranes exhibited higher thermal stability and acid/water uptake than the original ABPBI membrane. Compared with the original ABPBI membrane, ABPBI–SPEEK membranes may be promising electrolyte membranes for fuel cells at medium/high temperature.

1. Introduction

It is a new effort to develop high-temperature, low relative humidity polymer electrolyte-type membrane materials suitable for use in a polymer electrolyte-type membrane fuel cell (PEMFC). This effort will focus on alternative materials with performance up to 120 °C and low relative humidity [1]. Recently, poly(2,5-benzimidazole) (ABPBI) was put forward as an potential electrolyte for PEMFC at higher temperature operating. One reason is that poly(2,5-benzimidazole) (ABPBI) doped phosphoric acid (H_3PO_4) membranes exhibit high proton conductivity due to its high absorption capability of acid and durability at temperatures up to 180 °C [2–4], and high CO tolerance which allows the 3% of CO impurities in H_2 fuel with a small power loss in fuel cells [5]. On the other hand, the ABPBI polymer can be synthesized on low cost and with environmental friendless as compared to polybenzimidazole (PBI) [6,7]. H_3PO_4 is a very good proton conductor at high temperatures. As reported by Schechter and Savinell [8], its conductivity at 200 °C is as high as 0.8 S cm^{-1}. When mixed with polymers, the conductivity decreases with polymer percentage, as it could be expected. Water also helps to increase this conductivity as reported by Greenwood many years ago [9,10]. The conductivity and thermal stability of ABPBI membranes were improved by adding inorganic fillers [11–13]. Some papers reported ABPBI blend with other polymer membranes. Kim [15] synthesized ABPBI and PBI copolymers. The acid-doped AB-pPBI-X membranes showed an improved dimensional stability and mechanical property compared with the acid-doped ABPBI membrane, and acid-doped AB-pPBI-X membranes demonstrated a much improved mechanical stability relative to mPBI membranes. Poly(2,5-benzimidazole) (ABPBI) and poly(vinylphosphonic acid) (PVPA) blend membrane were synthesized by casting method [16]. Water uptake as well as the proton conductivity of the membranes were increased with increasing PVPA content.

Sulfonatied PEEK has been attractive as a polymer electrolyte for PEMFC due to its high proton conductivity, tough, and thermal stable properties [17,18]. An alternating copolymer (sPEEK-PBI) has been proposed using sulfonated poly(ether ether ketone) with inter- and intra-molecular ionic interactions [19]. This approach resulted in an improved mechanical strength. However, swelling or phase separation of blended membrane at an elevated temperature was observed in some cases resulting in dissociation of the membranes. Furthermore, there are no results on proton conduction reported yet.

In this work, we try to synthesize a copolymer using ABPBI with sulfonatied PEEK in order to improve proton conductivity and stability at medium or high temperature.

2. Experimental

2.1. Materials

3,4-Diaminobenzoic acid (DABA), 97%, and used without further purification. 99% methanesulfonic acid (MSA), polyphosphoric acid

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0378-7753/$ – see front matter.
doi:10.1016/j.jpowsour.2012.02.025

(PPA) 85%, white mineral oil, poly(ether ether ketone) (PEEK), sulfuric acid (98%) and phosphoric acid (85%) were purchased from Aldrich.

2.2. Synthesis of polymer

2.2.1. Synthesis of ABPBI polymer

Poly(2,5-benzimidazole) (ABPBI), was synthesized by condensation of 3,4-diaminobenzoic acid (DABA) in polyphosphoric acid (PPA) as reported in the literature [12].

2.2.2. Sulfonation of PEEK

SPEEK polymer with sulfonation degrees of 16% and 32% were obtained by sulfonation of poly(ether ether ketone). Following the procedure described in the publication [20]. The sulfonation degree was determined by the ion exchange capacity (IEC) as described by Li [21].

2.3. Preparation of ABPBI membranes, ABPBI/SPEEK membranes, and H_3PO_4 doping

The ABPBI membranes were prepared by evaporation of MSA solution as described as in the publication [14].

The preparation process of the ABPBI/SPEEK blend membrane was followed as details: the SPEEK polymer was added in MSA at room temperature until the polymer was dissolved completely. Then, the certain mass of ABPBI polymer was added in the solution and heated to 130 °C while mechanical stirring. The viscous solution was then cast onto flat bottom glass plates and the solution was removed by heating hot the plates in a ventilated oven at 200 °C until volatility ceased. Then, the membrane was peeled off. Subsequently the membranes were dried in a vacuum oven at 110 °C over night. The amount of SPEEK used in the membrane was 20% of ABPBI polymer. ABPBI–16% SPEEK and ABPBI mixed-32% SPEEK blend membranes were named as ABPBIS16 and ABPBIS32, respectively.

The dried ABPBI and ABPBI/SPEEK membrane were immersed in 85% H_3PO_4/H_2O (70:30 by volume) for 3 days at 70 °C.

2.4. Acid/H_2O absorption of membranes

The acid/water uptake measurement of membranes was done by drying them in a vacuum-dried oven at 110 °C for 3 h followed by weighing for results. The acid/water uptake was measured for the membranes placed into in 85%H_3PO_4/H_2O (70:30 by volume) for 3 days at 70 °C. After the acid adsorption, samples were quickly wiped to remove surface water by absorber paper and weighed again. The absorbed amount of H_3PO_4 and water (*W*%) was obtained with $W\% = (W_1 - W_0)/W_1 \times 100\%$. Where W_1 and W_0 are the masses of the membranes before impregnation and after drying, respectively.

2.5. Characterization

Thermal gravimetric analysis (TGA) was done using Thermal Analyzer STA 1500 (CCI-3, Rheometric Scientific) at air with 10 °C min^{-1}.

The membrane morphology was studied with a scanning electron microscope (SEM, Hitachi X650). The samples were Au-sputtered under vacuum before the SEM examination.

Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer Paragon 1000 Fourier transform spectrometer.

AC conductivity measurements as a function of temperature were made in air using a Hioki 3560 AC milliohm meter (HiTester) with fixed frequency (1 kHz)/voltages (20 mV). The area of electrode was 4 cm^2. The membrane was sandwiched between carbons electrode and packed in a sealed cell. The membrane in a test cell for conductivity was operated with a preceding hot-pressing step, with 20 kg cm^{-2} at 110 °C for 2 min. The proton conductivity of membrane was calculated using the relation $\sigma = d/RS$, where *d*, *R* and *S* are the thickness, resistance and face area of the membranes, respectively. The contact resistance between the cell components have been lumped with the membrane resistance. However, it was quite low compared with the membrane resistance.

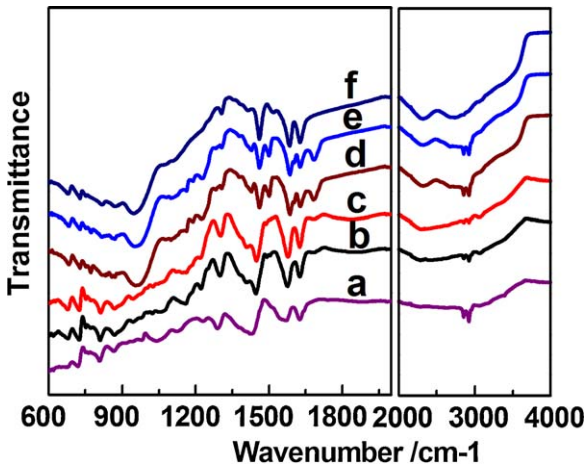

Fig. 1. FT-IR spectra of ABPBI, ABPBI–SPEEK membranes in absence/presence of H_3PO_4 ((a) ABPBI; (b) ABPBI-16S; (c) ABPBI-32S; (d) ABPBI-16SP; (e) ABPBI-32SPf-ABPBIP).

3. Result and discussion

3.1. FT-IR spectra

FT-IR spectra of ABPBI membranes and ABPBI–SPEEK blend membranes doped/undoped acid are shown in Fig. 1 with bands at about 1450 cm^{-2}, 1575 cm^{-2}, and 1626 cm^{-2} for undoped ABPBI and ABPBI–SPEEK membranes. For the doped ABPBI and ABPBI–SPEEK samples, bands can be assigned to the C=N and C=C stretching and at about 1460 cm^{-2}, 1585 cm^{-2} and 1629 cm^{-2} [6]. The band at 1685 cm^{-1} was appeared when ABPBI blend with SPEEK that was assigned to the carbonyl band [22]. The band at 1222 cm^{-1} was considered as the sulfonic acid group in SPEEK [23]. The bands in the range from 900 to 1053 cm^{-1} that result from the initial phosphoric acid treatment [24,25]. The addition of phosphoric acid also induces an increase in intensity of bands at 1504 cm^{-1} and 1685 cm^{-1}. However, the intensity of bands at 640–925 cm^{-1} was decreased.

3.2. SEM morphology

Fig. 2 shows the SEM morphology of the ABPBI and the ABPBI–SPEEK blend membranes. Fig. 2 shows the ABPBI membrane and the ABPBI–SPEEK blend membranes have compact distribution without holes. However, the ABPBI–SPEEK blend membranes display a fairly evident change in the ionomer morphology (see Fig. 2b and c) compared with the ABPBI membrane and have no phase separation as observed in the addition of the SPEEK blend membrane though they went through high-temperature up to 180 °C, suggesting that the blend membranes were homogeneous in nature and hence formed dense membranes.

3.3. Proton conductivity

By immersing the ABPBI membrane and ABPBI/SPEEK membranes into a H_3PO_4 (85%)/H_2O solution (70:30 by volume) at 70 °C for 3 days, it was observed that the acid uptake increased from

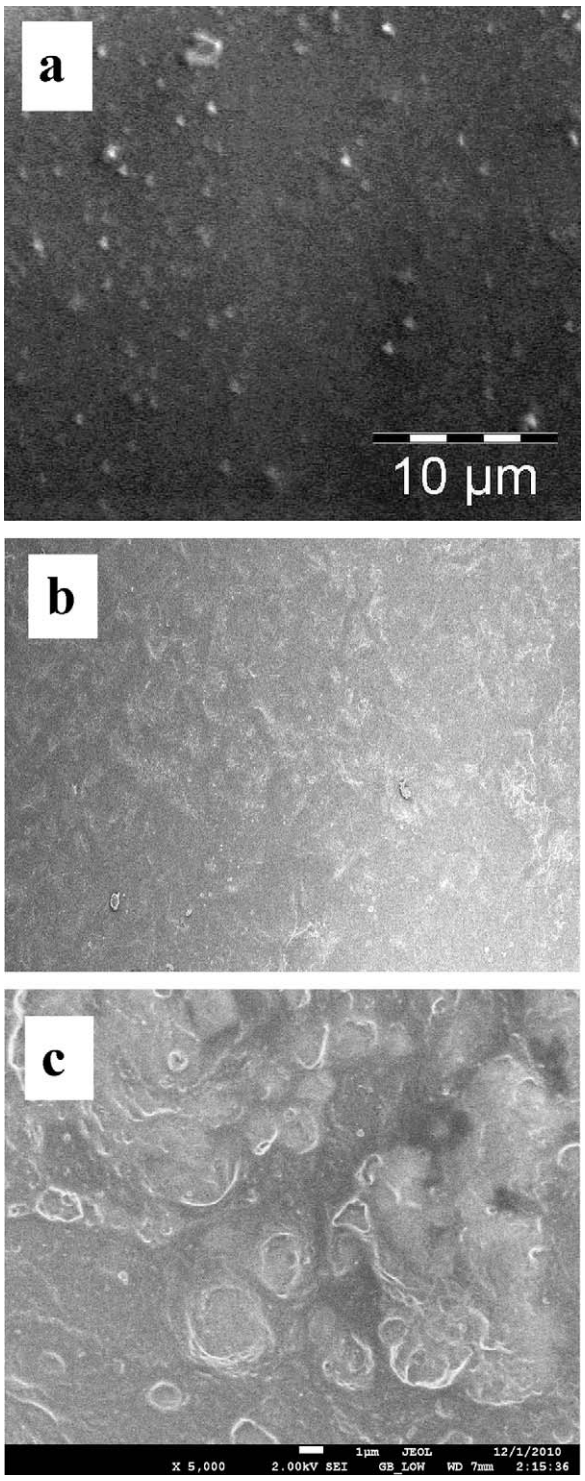

Fig. 2. SEM images of ABPBI and ABPBI–SPEEK membranes. ((a) ABPBI; (b) ABPBI16S (magnification: 5000×); and (c) ABPBI32S).

the value of 63% for ABPBI membranes up to 86% for the ABPBIS16 membrane and 82% of the ABPBIS32 membrane. Fig. 3 shows that the conductivity of the ABPBI membrane and ABPBI/SPEEK membranes as a function of temperature after acid uptake. Conductivities on ABPBI/SPEEK membranes were increased with the increasing of temperature and reached to a maximum and then decreased with increased temperature. A maximum conductivity of 1.09×10^{-1} S cm^{-1} of ABPBIS16 membranes was achieved at 100 °C, which is six times than the maximum 1.8×10^{-2} S cm^{-1} for the

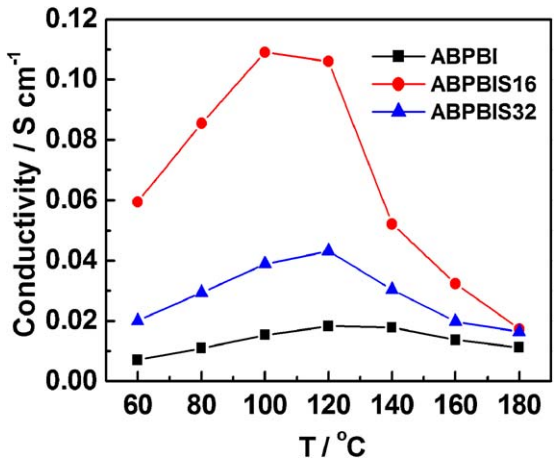

Fig. 3. Proton conductivities of ABPBI, ABPBI–SPEEK membranes doped with H_3PO_4 as a function of temperature.

ABPBI membrane at 120 °C. In the case of ABPBIS32, maximum conductivity is 3.89×10^{-2} S cm^{-1} at 120 °C, double than the maximum 1.8×10^{-2} S cm^{-1} for the ABPBI membrane at 120 °C. However, in the case of ABPBIS16, after 120 °C, conductivity drops quickly and reaches same value with ABPBIS32 at 180 °C. It is possible because absorbed water was evaporated when temperature is increasing.

To further eliminate the effect of absorbed humidity of the membrane, the cell was heated at 180 °C until it stabilized and the measurements of conductivity were recorded while cooling and are shown in Fig. 4. A maximum conductivity was about 1.6×10^{-2} S cm^{-1} for both ABPBIS16 and ABPBIS32 membranes at 180 °C in dry condition, higher than 1.1×10^{-2} S cm^{-1} obtained in the case of the ABPBI membrane.

3.4. Thermal analysis

Thermal properties of the ABPBI membrane and the ABPBI–SPEEK membrane were studied by thermogravimetric analysis (TGA). The TGA and DTA (Fig. 5) of ABPBI membranes and ABPBI–SPEEK membranes doped with H_3PO_4 were performed from 50 °C to 1000 °C. The ABPBI–SPEEK membranes showed improved thermal stability compared with ABPBI membrane. As displayed in Fig. 5, most water on ABPBI membrane is lost below 100 °C and there is exothermic peak at around 190 °C that may be caused by condensation reaction of phosphoric group

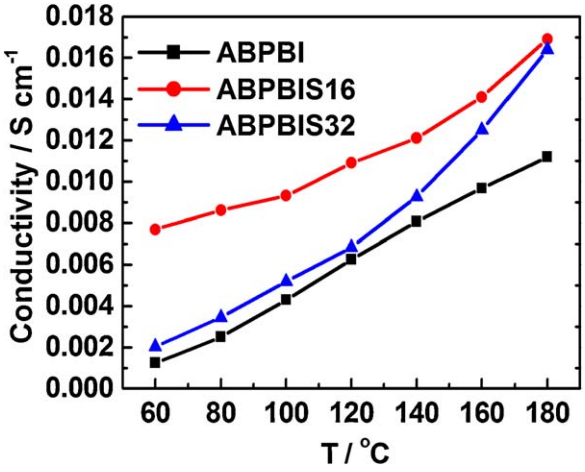

Fig. 4. Proton conductivities of ABPBI, ABPBI–SPEEK membranes doped with H_3PO_4 in dry condition.

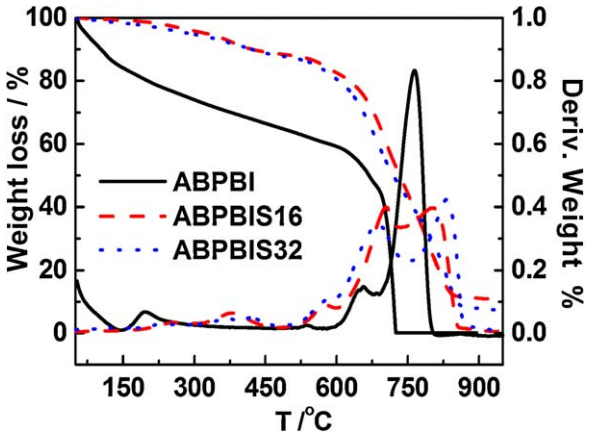

Fig. 5. TGA and DTA of the ABPBI membrane and ABPBI/SPEEK membranes doped with H_3PO_4.

with the dehydration. The initial weigh loss of the ABPBIS16 and ABPBIS32 membranes were 380 °C and 420 °C, respectively. Which is mainly associated with loss of the sulfonic groups. And the exothermic peaks at 575 °C on both ABPBI–SPEEK membranes corresponded to the degradation of backbone of PEEK. Those results showed higher decomposition temperature of SPEEK than other reports. [26,27]. And the onset degradation temperature of ABPBI matrix on ABPBIS16 and ABPBIS32 were 705 °C and 685 °C membranes, respectively, which are higher than that 655 °C of ABPBI membrane. On the other hand, the maximum exothermic peak on the ABPBIS16 and ABPBIS32 membranes were 800 °C and 835 °C, respectively, and higher than 765 °C on ABPBI membrane, which was resulted from the interaction between sulfonic groups and benzimidazole groups [28]. Our results demonstrated ABPBI–SPEEK composite membranes have more higher thermal stability than ABPBI membrane.

4. Conclusions

The novel ABPBI–SPEEK blend membranes have been synthesized. The properties of ABPBI–SPEEK membranes were investigated. The results suggested that ABPBI–SPEEK membranes exhibited improved proton conductivities at high temperature and thermal stability, high acid uptake when compared with the original ABPBI membrane which suggests that ABPBI–SPEEK membrane may be a promising polymer electrolyte for fuel cells at high temperature.

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