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Blend membranes based on Sulfonated poly(arylene ether sulfone) and poly(arylene ether)s containing benzimidazole groups

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Blend membranes based on Sulfonated poly(arylene ether sulfone) and poly(arylene ether)s containing benzimidazole groups

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INTRODUCTION

Development of new high-performance polymer membranes that retain their proton conductivity under low humidity conditions is one of the most critical requirements to commercialize PEMFC systems. Current sulfonated proton exchange membranes acquire proton conductivity by water that solvates ion and carries proton. Consequently, a loss of water under low RH conditions immediately results in a loss of proton conductivity. One approach to maintain proton conductivity under low RH conditions is to replace water with a less volatile proton solvent. Kreuer has pointed out the possibility to develop fully polymeric proton-conducting membranes based on nitrogen-containing heterocycles such as imidazole, benzimidazole, and pyrazole. We have attempted to blend those less volatile proton solvent with sulfonated copolymers such as polystyrene sulfonic acid, Nafion, poly(arylene ether sulfone, BPSH-xx). [Ref. DOE review meeting 2007 and 2008] However, we observed that imidazole was slowly sublimated out as temperature and humidity increases which could cause poisoning of electro-catalyst, corrosion and losing conductivity.

In this presentation, we report the synthesis of novel poly(arylene ether sulfone)s containing benzimidazole groups These benzimidazole containing polymer was blended with sulfonated poly(arylene ether sulfone). In the blend system, benzimidazole group attached to the polysulfone acts as a medium through the basic nitrogen for transfer of protons between the sulfonic acid groups. Proton conductivity of the blend membranes was investigated as a function of water content at 80°C and compared the performance with water based proton conduction system.

EXPERIMENTAL

Membrane preparation –

Sulfonated poly(arylene ether sulfone)s (BPSH-xx) was prepared from [4]. Commercially available polystyrene sulfonic acid (PSSA) was purchased from Aldrich. The poly(arylene ether sulfone) containing carboxylic acid group polymer (PAES-COOH) was synthesized using 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid, bis(4-fluorophenyl) sulfone, and anhydrous potassium carbonate. The poly(arylene ether sulfone) containing imidazole (PAES-COOH-Im) and/or benzimidazole group (PAES-COOH-BIm) were synthesized using PAES-COOH and 4(5)-(hydroxymethyl) imidazole and/or diaminobenzene, respectively.

Sulfonated polymer was blended with imidazole or imidazole containing polymers to prepare blend membranes.

RESULTS AND CONCLUSION

Fig. 1 shows the proton conductivities of PSSA and BPSH-100 blend with imidazole. The proton conductivity of PSSA-Imidazole membrane increased up to 80°C, while it decreased over 80°C at 50% RH due to the loss of imidazole through sublimation(Fig.1(a)). We confirm the loss of imidazole by sublimation by TGA under dry conditions (120 – 200oC). The sulfonated poly(arylene ether sulfone)(BPSH 100)-Imidazole membranes also showed similar behavior (Fig.1(b)). The proton conductivity of BPSH-Imidazole membrane was measured at 30°C as a function of RH and imidazole content. Proton conductivity increased with RH indicating that water still plays a key role in proton conduction in the presence of imidazole. Proton conductivity showed a minimum value when the ratio of sulfonic acid:imidazole is 1:1. This is likely attributed that strong hydrogen bonding between imidazole base and sulfonic acid group prevents fast proton exchange. Fig. 1 (c) shows the proton conductivity of BPSH-imidazole membrane as a function of lambda (i.e. number of water molecules per sulfonic acid group).

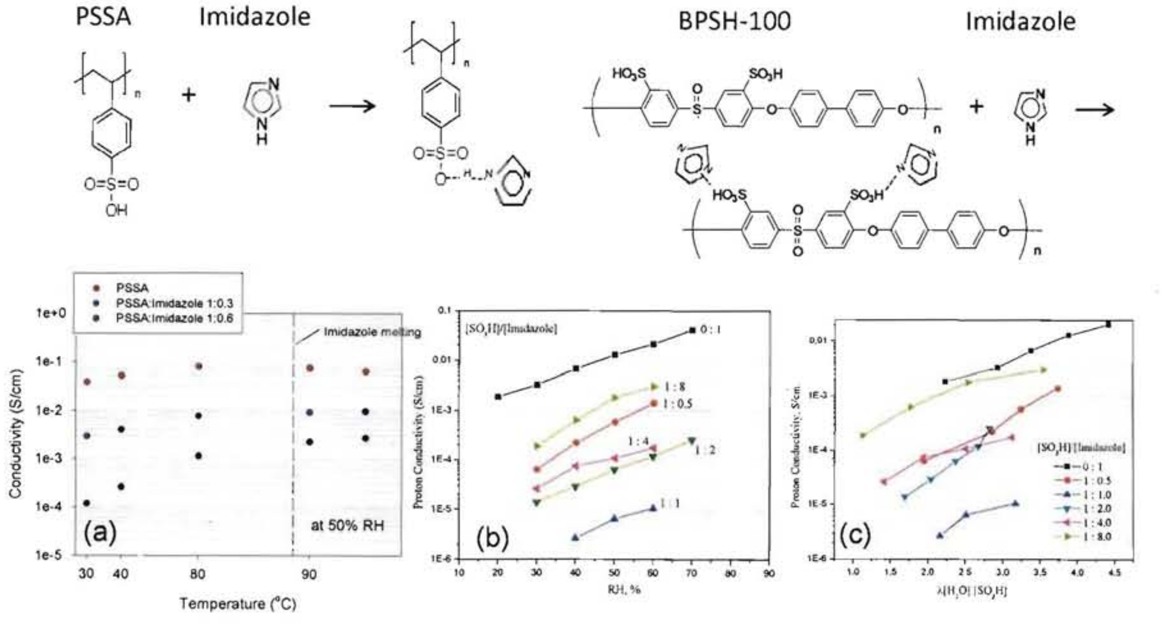

Figure 1. Proton conductivities of imidazole blend membranes

Slow leaching of free imidazole can be prevented as imidazole group was tethered in polymer chain. A novel poly(arylene ether sulfone)s containing benzimidazole groups was synthesized. Figure 2 shows the synthetic scheme of the imidazole tethered polymers. FT-IR results Shows that PAES-COOH polymers has strong absorption bands at 1730 cm^{-1} that originated from stretching vibrations of C=O. The C=O peak of PAES-COOH-Im polymer shifted and broad at 1700cm^{-1} due to esterification reaction. The C-N and N-H group of imidazole was shown at 1369 cm^{-1} and 1557 cm^{-1}, respectively. The strong absorption at 1730cm^{-1} due to the C=O asymmetric stretching in PAES-COOH almost disappeared in PAES-COOH-BIm, indicating the conversion of all of the carboxylic acid groups into benzimidazole groups. The C=N stretching at 1634 cm^{-1} was shown in PAES-COOH-BIm. These spectral confirm the formation of benzimidazole side groups on poly(arylene ether sulfone)s.

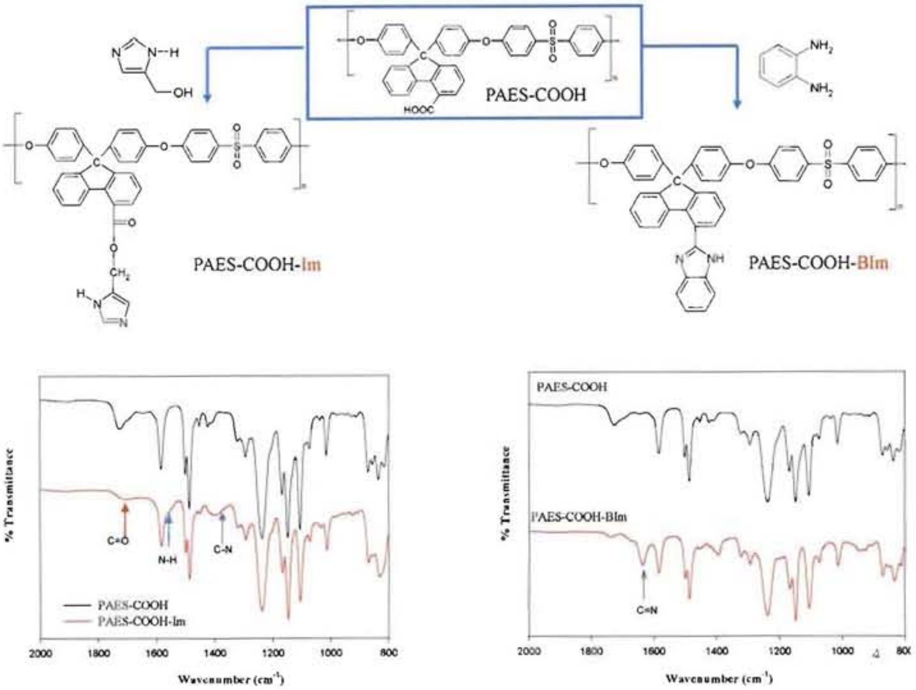

Figure 2. FT-IR of polymer membrane containing imidazole or benzimidazole groups

The polymer containing imidazole or benzimidazole groups were blend with sulfonated poly(arylene ether sulfones)(BPSH 35, IEC = 1.54 meq/g). The composition of blend membranes was listed in Table 1.

Table 1. Composition of blend membranes

Blend ratio	Wt.% PAES-COOH-Im in blend membrane	[-SO_3H]/[Imidazole]	[Imidazole]/[-SO_3H]
0.5 : 1	33	2.07	0.48
1 : 1	50	1.04	0.96
	Wt.% PAES-COOH-BIm in blend membrane		
0.5 : 1	33	2.1	0.48
1 : 1	50	1.06	0.94

The λ (number of water molecular per sulfonic acid group) was shown in Figure 3. The λ of blend membranes showed lower than that of BPSH 35 due to lower IEC.

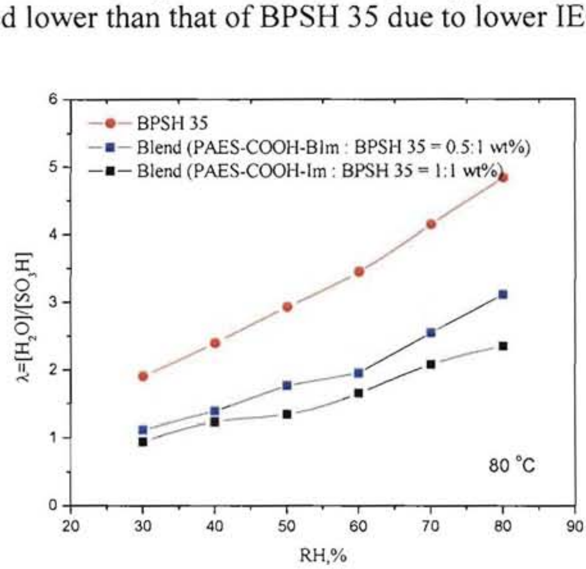

Figure 3. λ (number of water molecular per sulfonic acid group) with RH% at 80°C

The proton conductivities of these membranes were shown in Figure 4. The blend membranes showed lower proton conductivity compared to BPSH 35 membrane.

The blend membrane with low water molecules per sulfonic acid group (λ) showed the high proton conductivity compared to pure sulfonated polymer (Figure 4 (b)). For examples, the proton conductivities of BPSH 35, PAES-COOH-BIm, and PAES-COOH-Im at λ = 2 are 0.61×10^{-3}, 5.1×10^{-3}, and 9.1×10^{-3} S/cm, respectively.

It means that the imidazole and/or benzimidazole group attached to the polysulfone acts as a medium through the basic nitrogen for transfer of protons between the sulfonic acid groups.

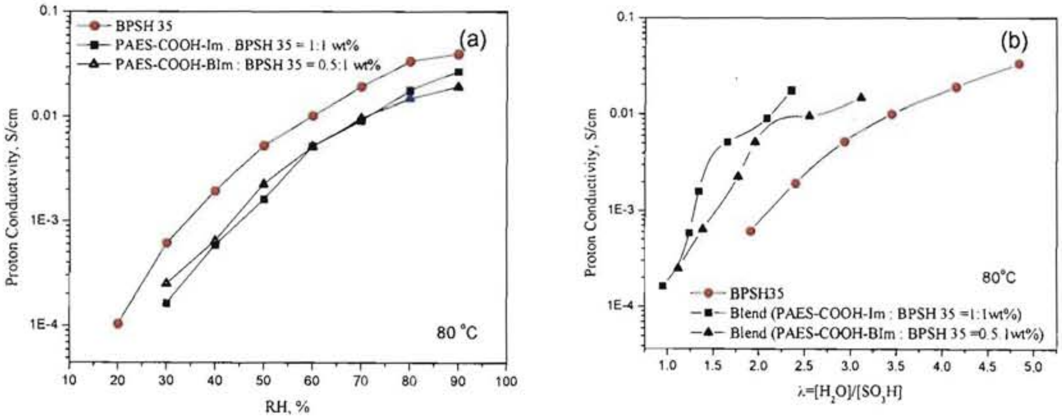

Figure 4. Proton conductivities of blend membranes

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