Effect of Post Treatment of Sulfonated Poly(Arylene Ether Sulfone) Copolymers on Proton Conductivity

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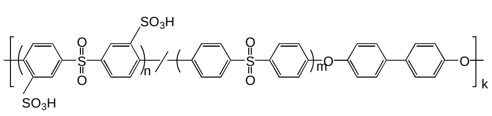
Introduction

Proton exchange membrane (PEM) is one of the most critical components of fuel cell operation. Generally, maximizing proton conductivity of PEMs is desirable to fuel cell operation. However, the conductivity must be balanced with water absorption of PEMs since too great water absorption may result in mechanical degradation, dimensional instability and high methanol permeability. Recently, sulfonated poly(arylene ether sulfone) copolymers (BPSH, Figure 1) by direct copolymerization of sulfonated monomer have been synthesized for fuel cell membrane applications as potential replacements for Nafion®. The BPSH copolymers have a high proton conductivity, low methanol permeability, and good thermal property.[1,2] Moreover, the membranes by direct copolymerization allows for precise control of degree of disulfonation through monomer feed ratio. However, for precise control of the proton conductivity, physical change of the membranes should be considered as well. In this paper, the influence of post treatment of the BPSH copolymers on proton conductivity is analyzed.



BPSH-XX

Figure 1. Chemical structure of BPSH; XX indicates degree of disulfonation.

Experimental

Biphenyl-based wholly aromatic poly(arylene ether sulfone)s containing pendant sulfonate group were prepared by direct aromatic nucleophilic substitution. Detailed synthesis procedures and characterization of these copolymers were reported previously.[1,2] The copolymers in their salt form were then converted to corresponding acid form either by two different post treatments: 1) by immersion in 1.5 M sulfuric acid solution at 30°C for 24 hours, followed by immersion in deionized water at 30°C for 24 hours (*Method 1*), or 2) by boiling in 0.5 M sulfuric acid solution for 2 hours, followed by immersion in boiled deionized water for 2 hours (*Method 2*). All specimens were stored at 30°C in deionized water at least 5 days before any test. ^1H NMR results did not showed any post sulfonation or sulfuric acid residue after the post treatments.

Table 1. Influence of post treatment on proton conductivity at 30°C in liquid water

Post Treatment	Proton conductivity (S/cm)				
	BPSH -30	BPSH -40	BPSH -50	BPSH -60	Nafion 117
Method 1	0.047	0.077	0.128	0.160	0.114
Method 2	0.064	0.098	0.150	0.312[a]	0.115

[a] hydrogel formation; mechanically unstable.

Results and Discussion

Table 1 demonstrated the influence of post treatment on proton conductivity at 30°C. The result showed that the treatment in boiling conditions (*Method 2*) resulted in considerable increase in proton conductivity for all BPSH membranes whereas Nafion® showed little difference in the conductivity between the two post treatments. Figure 3 shows the dependence of the proton conductivity of BPSH-30 copolymer on relative humidity at 80°C in water vapor. Interestingly, the proton conductivity and water absorption of the two copolymers was similar when relative humidity was less than 80%, whereas the conductivity and water absorption increased significantly when relative humidity was over 80%. Based on the previous results[2], this nonlinear increase of water absorption by *Method 2* is probably due to the formation of continuous ionic domains.

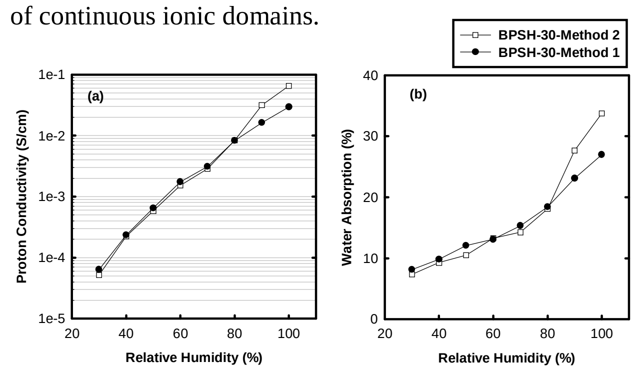


Figure 3. Dependence of the (a) proton conductivity and (b) water absorption of BPSH-30 on relative humidity at 80°C.

Figure 4 shows the influence of temperature on proton conductivity. The membranes treated by *Method 2* showed higher proton conductivity and less temperature dependence over the temperature range 70-140°C. It is also found that even at over 100°C in water vapor, the effect of post treatment did not disappear, in spite of a noticeable increase in proton conductivity was observed in the membrane treated by *Method 1* at 90°C.

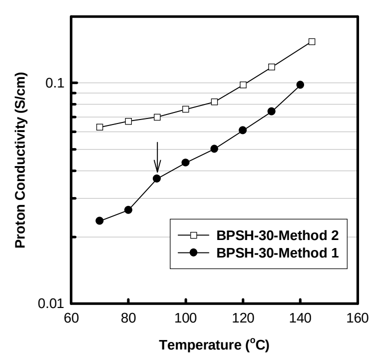


Figure 4. Influence of temperature on proton conductivity.

Conclusion

This paper focused on the effect of post treatment on the membrane property. It was found that treatment of BPSH copolymers in boiling water conditions produced higher proton conductivity and water absorption. Further research on morphology, methanol permeability and stability is in progress.

References

1. Wang, F.; Hickner, M,; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinski, T.; and McGrath, J.E. *Macromol. Symp*., 175, 387-395, 2001.
2. Wang, F.; Hickner, M.; Kim Y.S.; Zawodzinski, T.; McGrath, J.E. *J. Memb. Sci*., 2002, in print.