Study of Water Dynamics in Superacidic Hydrocarbon Proton Exchange Membranes Using Solid-State and Pulsed-Field Gradient NMR Spectroscopy

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Introduction

Polymer membranes that are able to conduct protons at low humidity simplify on-board automotive humidification schemes and enable fuel cells to operate at higher temperatures (>100 °C), which would increase the activity of the platinum catalyst and reduce poisoning of the catalyst by carbon monoxide. An approach to obtain these properties is to synthesize ion-containing block copolymers that would form distinct hydrophobic and hydrophilic nanophase separations in the polymer matrix by introducing highly sulfonated hydrophilic and hydrophobic blocs.[1] The PI's research group has developed a series of sulfonated aromatic polymers that show enhanced proton conductivity at low relative humidity conditions (see Figure 1).[2] Our previous results suggest that by increasing the acidity of the terminal sulfonate group with fluorine substitution (sPS-S_1 of Figure 1), higher proton conductivity was obtained for the superacidic polymer electrolyte membranes (PEMs). Although higher proton conductivity was obtained for sPS-S_1, its enhancement due to increased acidity is an overstatement. More detailed studies of transport properties of water and the correlation of acidity and water properties are needed. The knowledge of water transport property in the polymer matrix will enhance the understanding of the morphology of PEMs, the state and behavior of water, and various other in-situ phenomena within operating proton-exchange membrane fuel cells (PEMFCs).

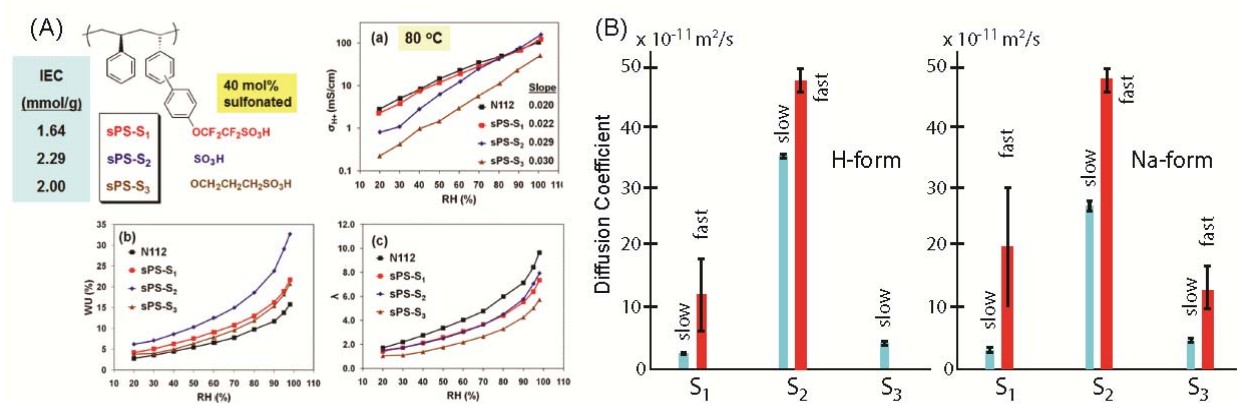

Fig.1 (A) Examples of sulfonated aromatic polymers developed by the PI's group and their fuel cell membrane properties: (a) proton conductivity, (b) water uptake, (c) hydration number (number of water molecules per sulfonate) as a function of relative humidity. (B) Bimodal slow and fast water diffusion coefficients of H- and Na-form polymer systems measured by PFG NMR.

Experimental

Pulsed field gradient (PFG) NMR spectroscopy was utilized to determine the transport of water in the polymer matrices.

Results and Discussion

Water diffusion in the polymer matrices determined by PFG NMR show bimodal diffusion behavior with slow and fast diffusion components that exhibit close correlations to the length of the side chains that the sulfonate groups tethered. The polymer matrix with the shortest sulfonate sidechains exhibits the biggest water uptake and diffusion coefficients.

Conclusions

The water uptake and diffusion in the block copolymer system is altered by varying the side-chain length and incorporating fluorines in the side chain. The polymer system with ePS-S_1 group exhibits the least water uptake and smallest water diffusion coefficients.

Acknowledgements

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References

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[2] Chang, Y., *et al.,* Macromolecules, **44**, 8458–8469 (2011).