Structure-Property Relationship in Perfluorinated Sulfonic Acid Ionomers

Wi, S. (NHMFL), Lee, C.H., Kim, W.Y, Lim, Y.J., Ahn, J.H., Pyo, S.E., Hwang, J.P., OH, C.H., Park, I.K. (Dankook U., Energy Engineering)

Introduction

Perfluorinated sulfonic acid (PFSA) ionomers have been widely used as polymer electrolyte membrane (PEM) materials, particularly in PEM fuel cells, owing to their high proton conduction capability and excellent chemical durability under harsh electrochemical reaction atmospheres. The major objective of this study is to identify the chemical structure of PFSAs by solid-state ^{19}F NMR spectroscopy and to correlate hydrogen barrier properties with their structural features.

Experimental

Commercially available PFSA ionomers with different equivalent weight (EW), defined as the mass of one equivalent of $-SO_3H$ group, in dispersed solutions were used for membrane formation (water: normal propanol=55:45 wt.%). Each dispersion was converted into its free-standing membrane after thermal treatment at 190 ^{o}C for 12 minutes. ^{19}F solid-state magic-angle spinning (MAS) NMR spectroscopy was used for the structural characterization of each sample. Hydrogen permeability in Barrier (10^{10} cm^3_{stp} cm/sec cm^2 cmHg) was obtained using time-lag method [1].

Results and Discussion

Fig.1 (left) shows ^{19}F MAS NMR spectra of the PFSA ionomers. The ^{19}F spectrum of Nafion indicates the existence of branched $-CF_3$ and swivel ether (-O-) groups in the side chains. Meanwhile, 3M ionomers are composed of four-connected carbon (C4) structure in their side chains. ^{19}F MAS NMR spectrum also exhibits a small amount of C3 structure in addition to the majority of C2 structure in Aquivion (EW=720 g/eq). It was found that Ashai Kasei ionomer has C2 structure identical to Aquivion (EW=790). These architectural differences seem to be directly related with hydrogen barrier properties as shown in **Fig.1 (right)**. The bulkiness of the side chains is directly correlated to the packing density in the polymer matrix that the most branched Nafion polymer would make a loosely packed polymer matrix. Loosely packed Nafion ionomer chains have induced high hydrogen permeability, while the short side-chain ionomers with C2 to C4 architectures have much improved hydrogen barrier properties over the measurement range.

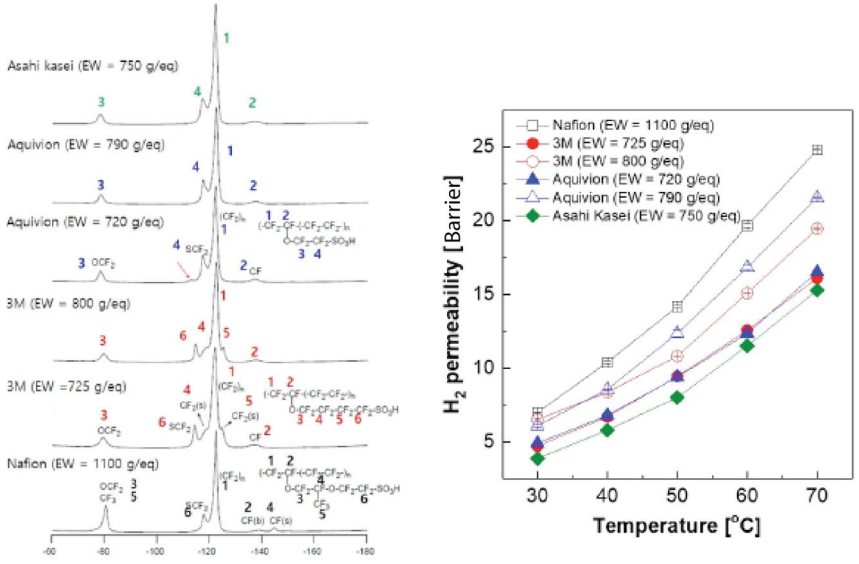

Fig.1 Structure-property relationship in PFSA ionomers: ^{19}F NMR spectra (left) and hydrogen permeability (right) in the membrane state.

Conclusions

The chemical architectures of commercially available PFSA ionomers were identified using solid-state ^{19}F MAS NMR spectroscopy. A strong correlation between the polymer structure and hydrogen permeability in the solid polymer matrix was found.

Acknowledgements

The NHMFL is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida. This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20153010031920), Hyundai Mobis, and Korean Electric Power Company (KEPCO) under the project # R16VA08. This research was also financially supported by MOTIE under the “Commercializing fuel cell electric vehicle component industry and R&D Support Program” (reference number P0000269) supervised by the Korea Institute for Advancement of Technology (KIAT).

References

[1] Rutherford, S.W., Adsorption, **3**, 283-312 (1997).
[2] Kusoglu, A., *et al.,* Chemical Reviews, **117**, 987-1104 (2017).