

Interfacial Surface Characterization of Hydrophobic-Hydrophilic Nano-Phase Separated PFSA Ionomers by Dynamic Nuclear Polarization

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Introduction

Perfluorinated sulfonic acid (PFSA) ionomers are used as polymer electrolyte membrane (PEM) materials in fuel cells, which are most currently used as the engine of hydrogen vehicles, owing to their high proton conduction capability and excellent chemical durability under harsh electrochemical reaction atmospheres.¹ The major objective of this study is to identify the morphological structure of PFSA ionomers. Solid-state NMR spectroscopy whose signal intensities are amplified by dynamic nuclear polarization (DNP) is a unique tool for investigating the morphological structure of the nano-phase separated ionomeric polymers on the molecular level. The interfacial surface of the hydrophobic-hydrophilic domains of PFSA ionomers was investigated by DNP magic-angle spinning (MAS) solid-state NMR spectroscopy for the first time. Fig. 1A shows a cartoon representation of the fully hydrated hydrophobic and hydrophilic domains of PFSA ionomers. Electrons of the biradical molecules that are infiltrated with water to the hydrophilic domains achieve electron polarizations in the magnetic field (14.1 T) under microwave irradiation (395 GHz). The electron polarization is then transferred to the protons of nearby water molecules, thereby dramatically increasing the NMR signal of protons that will be consecutively equilibrated among different protons by spin diffusion and then transferred by cross-polarization (CP) to the carbons in the main- and side-chains of PFSA polymers (no protons in the structure) that are within a few angstroms of the water molecules near the interface. Therefore, the ¹³C CPMAS spectrum obtained by this method naturally becomes a method of investigating the interface between the hydrophobic and hydrophilic domains of PFSA ionomers on the molecular level.

Experimental

Three different types of commercially available PFSA ionomers, Nafion (EW: 1100 g/eq), Aquivion (EW: 790 g/eq), and 3M (EW: 800 g/eq), that are dispersed in water/isopropyl alcohol were vacuum dried without heating for overnight. 30 μL of 10 mM AMUPOL biradical solution in 90% D₂O and 10 % H₂O was applied to 30 mg of each sample for hydration. The sample was packed into a 3.2 mm zirconia MAS rotor for DNP CPMAS experiment. We have utilized the NHMFL's 14.1 T DNP NMR spectrometer that is linked to a 395 GHz gyrotron.

Results and Discussion

Fig. 1B shows ¹H-¹³C CPMAS spectra of each sample obtained with (red line) and without (black line) microwave irradiation. The enhancement factors observed were 97, 45, and 39 for Nafion, Aquivion, and 3M samples, respectively. Contrary to the backbone main-chain ¹³C peaks observed in the conventional ¹³C MAS spectrum (data not shown), ¹³C peaks in each spectrum within 100~130 ppm range are very broad, indicating that carbons depicted from this method are mostly from the side-chains that are packed more disorderly than the main-chains in the polymer matrix. A sharper peak around 106 ppm in the Nafion spectrum (top) as a shoulder peak of the main peak spanning over 100 ~ 120 ppm is from the CF₃ groups from the side-chains.

Conclusions

A DNP-enhanced spectrum is strong enough to be able to investigate the phase boundaries of nano-phase separated hydrophobic and hydrophilic domains on the

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References

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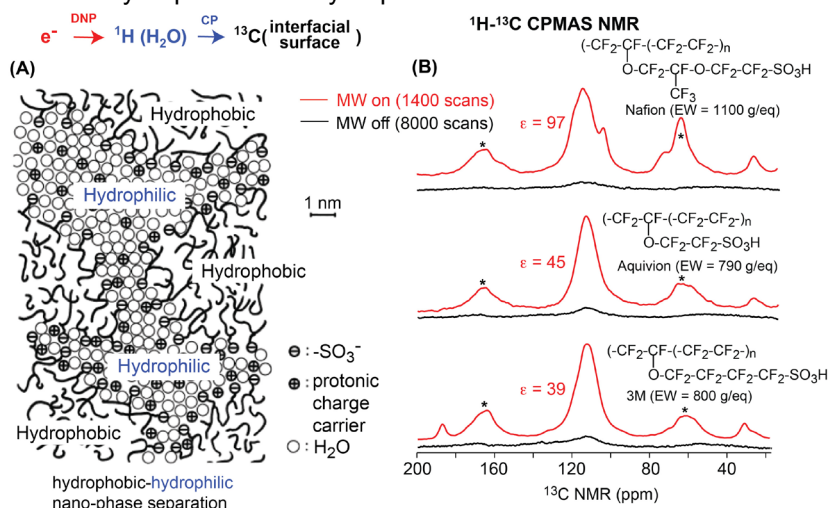


Fig.1 Cartoon representation (A) of hydrophobic and hydrophilic domains of PFSA ionomers and ¹H-¹³C CPMAS spectra of interfacial surface between the domains obtained with (red) and without (black) microwave irradiation. The asterisk symbols represent spinning sidebands.