^{2}D-NMR Studies of Dynamics and Microstructure in Different Proton Exchange Membrane

C. Y. Chen[1], P. J. Chu[2], L. N. Tsai[1]
[1]Industrial Technology Research Institute, R.O.C.
[2]National Central University, R.O.C.
MRL/ITRI, Chutung, Hsinchu, Taiwan 310, R.O.C.
910102@itri.org.tw

The main objective of this research is to study molecular dynamics, solvent sorption and diffusion properties of PVDF-g-SPS and Nafion117 membranes (Table1) by solid-state NMR technique. The two types of membrane were found to exhibit substantially different molecular dynamic properties due to the difference in microstructure and morphology.

A convenient gradient-NMR method was employed to understand the molecular diffusivity relation between the environment fuel concentration and polymer microstructure difference. Gradient-NMR testing is to move the probe slightly off the center location of the magnet. The gradient strength at each location is reached by field mapping. The gradient strength can be higher than commercial gradient unit can provide that. NMR measurements show difference water dynamic property (Figure2) and T1 relaxation time (Figure3) in two membranes. Typical water molecules freezing phenomenon were found in peak line width increasing when the temperature decrease but it has no change in PVDF-g-SPS System. This phenomenon is attributed to the PVDF-g-SPS PEM has a smaller cluster region than Nafion, so the water molecular is hard to freeze in sulfonic polystyrene nanosized aggregate structure. The T1 relaxation time results also provide further evidence. The water molecular was confined in a nanosizd domain in PVDF-g-SPS polymer electrolyte and has higher molecule dynamic property than Nasfion. The Water diffusivity in both Nafion and MRL films are similar, although the ion conductivity differs by nearly one order (Fig4). However, at high methanol concentration, Proton diffusion in Nafion increases substantially, while that in MRL film remains low, or becomes lower than that of pure water. This effect is responsible for the dramatic reduction of methanol crossover in the PVDF-g-SPS membrane.

Reference

1.Holmberg, S., J. Mater. Chem., 6, 1309-1317.
2.Hietala, S.,. J. Mater. Chem. 7, 721-727.
3.Ennari. J., Polymer, 38, 3733-3744.

Table1. Main Characteristics of the Membrane

	Nafion	PEM-A	PEM-B	PEM-C
DOG	--	60%	24%	26%
IEC (meq/g)	0.84	1.28	0.82	1.34
Con. (S/cm)	$5.3*10^{-2}$	$1.3*10^{-1}$	$4.8*10^{-2}$	$1.0*10^{-2}$
Per. (cm^2/sec)	$4.1*10^{-6}$	$8.3*10^{-7}$	$6.9*10^{-7}$	$1.1*10^{-6}$
C/P	$1.3*10^{4}$	$1.6*10^{5}$	$7.0*10^{4}$	$9.4*10^{3}$

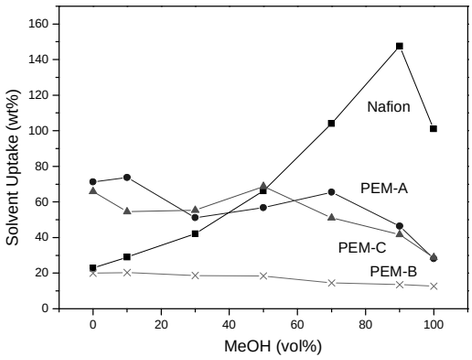

Fig1. Solvent uptake of PVDF-g-SPS membrane and Nafion117

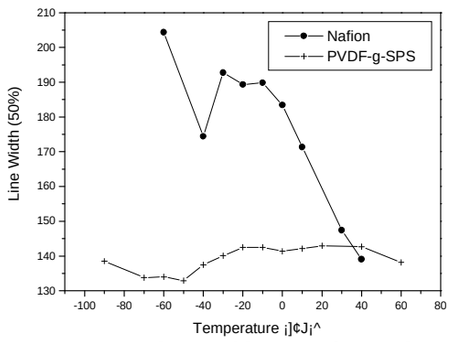

Fig2. Deuteron NMR line widths in Nafion and PVDF-g-SPS under different temperatures

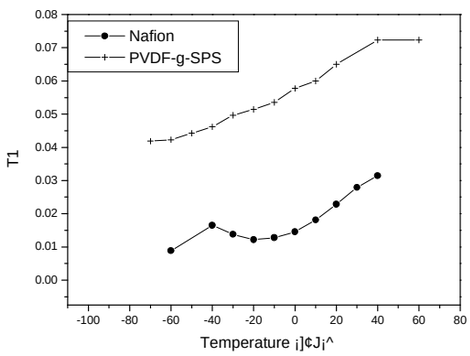

Fig3. Deuteron spin-lattice relaxation times in Nafion and PVDF-g-SPS under different temperatures

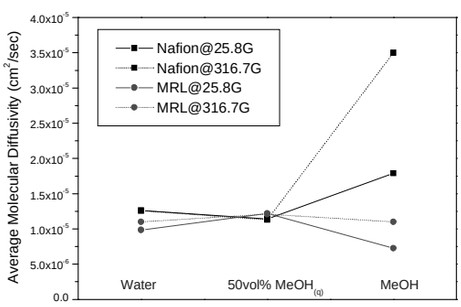

Fig4. Diffusivity of average molecules in Nafion and PVDF-g-SPS in different fuel concentrations