

## ANALYSIS OF IONIC CLUSTER STRUCTURE IN POLYMER ELECTROLYTE MEMBRANES

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It is widely known that the effective proton conduction of Nafion<sup>®</sup> membranes are derived from the microscopic phase separation between the ionic domains and the fluorocarbon matrix.[1] Small-angle X-ray scattering (SAXS) has been utilized to investigate their ionic cluster structures.[2-3] A large number of SAXS investigations for Nafion<sup>®</sup> membranes have been reported, however the relationship between the ionic cluster size and water uptake for novel polymer electrolytes is not still clear. Moreover, there are few reports about morphology of hydrated hydrocarbon polymer electrolyte membranes. In this study, SAXS of Nafion<sup>®</sup>112 membranes was studied in order to clarify the change of the ionic cluster size versus water uptake. SAXS measurement was also performed on sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (S-PPBP) membranes (2.8 meq/g) as hydrocarbon polymer electrolytes.

### Experimental

Nafion<sup>®</sup>112 and S-PPBP membranes were placed in a sealed bag with controlled relative humidities using a saturated aqueous solution of salt. Sample membranes were put into an aluminum sample holder with Kapton<sup>®</sup> window. The water uptake of the sample was quantitatively determined prior to SAXS measurements. SAXS measurements were performed on a Rigaku RINT2500TN (Cu K $\alpha$ , 45 kV, 200 mA). The experiments were carried out in a transmission mode, covering a  $q$  range from 0.01 to 2.1 nm<sup>-1</sup>, where  $q$  is the scattering vector defined as  $q = (4\pi/\lambda) \sin\theta$ .

### Results and discussion

Figure 1 shows SAXS profiles of Nafion<sup>®</sup>112 membranes with different water uptake. As the water uptake increased, the peak attributed to the ionic cluster structure shifted to lower scattering angle and the intensity of the peak increased. From this result, it was suggested that the Bragg spacing derived from the ionic cluster structure expanded, and the electron density of the cluster increased.

Figure 2 shows the peak position of the ionic cluster reflection for Nafion<sup>®</sup>112 membranes as a function of water uptake. The Bragg spacing value linearly increased against water uptake. The slope of the line changed over 10wt.% water uptake. To clarify the factor of this change, differential scanning calorimetry measurements were carried out. These results showed the existence of free water molecules above 8 wt.% water uptake. It was suggested that the shifts of Bragg spacing were attributed to the increase of bound water below 8 wt.% and free water above 8 wt.% of water uptake.

From the SAXS measurements of S-PPBP membranes, no peaks of the ionic cluster structure reflection were observed irrespective of the water uptakes. It was implied that the absorbed water molecules were homogeneously distributed over the S-PPBP membrane. This result suggests that hydrocarbon based polymer electrolytes do not have a tendency to easily form Nafion-like ionic cluster structures due to the less

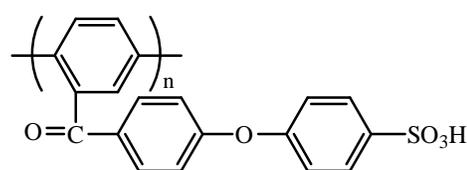
flexibility and hydrophobicity compared with Nafion<sup>®</sup> membranes. It also noted that the proton conductive mechanism of the S-PPBP is different from that of Nafion<sup>®</sup>. Indeed, the proton conductivity of S-PPBP strongly depends on relative humidity rather than that of Nafion<sup>®</sup>.

### Acknowledgement

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### Reference

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Scheme 1 Structure of S-PPBP.

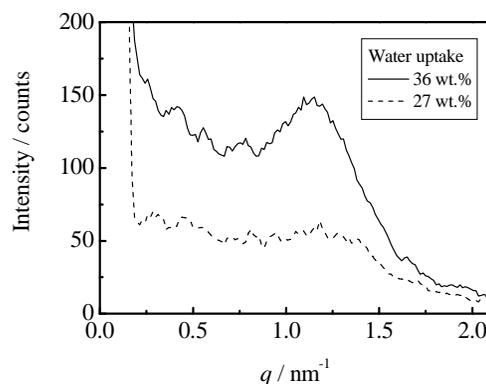


Figure 1 Small-angle X-ray scattering profiles of Nafion<sup>®</sup>112 membranes with different water uptakes.

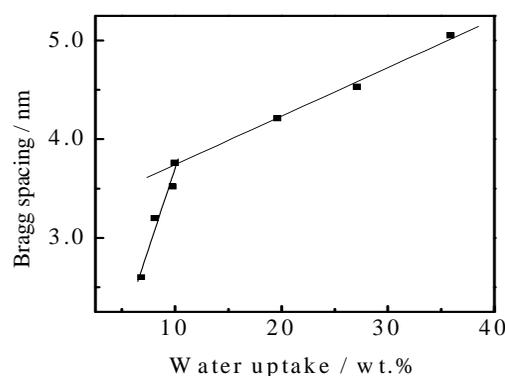


Figure 2 Bragg spacing of Nafion<sup>®</sup>112 membranes as a function of water uptake.