# Nanostructure-conductivity relationship in environmentally friendly hydrocarbon PEMs as an alternative to the established PFSA ionomers

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Contrast-variation small-angle neutron scattering (SANS) on Nafion (PFSA) and sulfonated syndiotactic-polystyrene proton exchange membranes under in-beam controlled RH and T conditions with in-situ ionic conductivity measurement simultaneously with SANS measurements.

キーワード Keywords:contrast variation SANS; proton exchange membranes; in-beam controlled humidity

## １．目的 Objectives

The main objective of the experiment was to use contrast-variation small-angle neutron scattering (SANS) to investigate the complex morphology of proton exchange membranes based on PFSA Nafion and sulfonated syndiotactic polystyrene (s-sPS) under controlled conditions with regard to in-beam relative humidity (RH) and temperature (T). To monitor the state of the sample during the variation of contrast conditions using vapors with a selected $H_2O/D_2O$ ratio, the ionic conductivity was measured in situ throughout the SANS data acquisition.

## ２．方法 Methods

SANS measurements were performed using the SANS-J-II instrument from JRR-3 on Nafion117 (Chemours, Wilmington, DE, USA, 117 μm thick) and on in-house synthesized and manufactured deuterated s-sPS membranes (100 μm thick). For beam-controlled hydration, the dew point generator designed for neutron scattering and the sample cell with temperature control and ion conductivity measurement option from J-PARC were used. The dew point generator can supply hydration vapors with either $H_2O$, $D_2O$, or a mixture of both in a selected combination to enable controlled variation of the relative humidity on the sample between 10% and 85% while varying the sample temperature between 30°C and 80°C. Contrast variation SANS measurements were performed between 0.1 and 5 $nm^{-1}$, combining the main and wide-angle detectors at SANS-J-II.

## ３．結果及び考察 Results and Discussions

Figure 1 shows the scattering patterns of the two membrane types, which were recorded under different contrast conditions generated by hydration vapors of different H2O/D2O compositions, as indicated in the legends, at a relative humidity of 85% and a temperature of 30°C.

The scattering patterns of Nafion117 show the two main scattering features of PFSA membranes, namely the ionomer peak at approximately $Q_{ion}$ = 1.7 $nm^{-1}$ and the matrix broad shoulder at approximately $Q_{mat}$ = 0.3-0.6 $nm^{-1}$. The scattering of the two features is matched at different $H_2O/D_2O$ ratios. The data analysis in terms of partial scattering functions is still ongoing.

On the other hand, the s-sPS scattering patterns show a dominant $Q^{-2}$-like scattering at low Q, which results from the scattering of the randomly distributed polymer lamella stacks in the membrane, while a weak ionomer peak is observed at high Q under $H_2O$ contrast conditions. Under $D_2O$ contrast conditions, the total scattering is much lower and the ionomer peak disappears, which is due to the weak or vanishing contrast between the hydrated $D_2O$ and the components of the deuterated polymer

membrane. The degree of functionalization (sulfonation) of the s-sPS membrane is very low, as shown by the low ionic conductivity measured in parallel with the SANS data acquisition. This could explain the low ionomer peak of the s-sPS membrane compared to the Nafion117 membrane. However, as we have shown in our previous SANS studies, for accurate structural analysis of s-sPS-based hydrocarbon membranes, uniaxially deformed film samples should be used to reveal the scattering contributions of various components, lamellar stacks, hydrated amorphous domains, and ionic groups occurring in different detector sectors, thereby making the analysis more reliable. Data analysis is also ongoing.

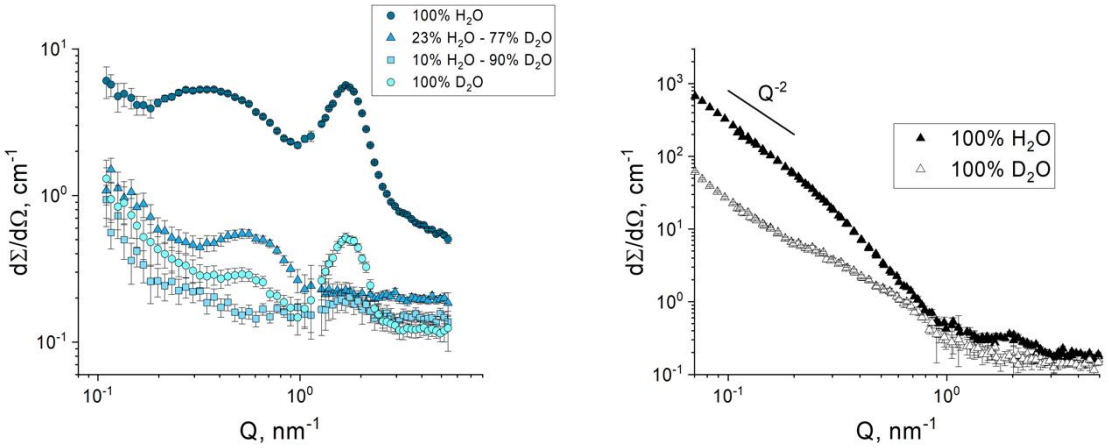


Figure 1 - Scattering patterns from the Nafion117 (left) and the s-sPS (right) membranes in different contrast conditions provided by using hydration vapors of selected $H_2O/D_2O$ ratios at RH = 85%.