ESRF	**Experiment title:** **Resolution of the nanomorphology of polymer electrolytes for energy storage application by GISAXS**	**Experiment number**: 02-02-851
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Report:

Objective & expected results:
We have recently developed a new aromatic ionomer with controlled architecture, e.g., multi-block copoly(arylene ether sulfone) bearing perfluorosulfonic acid functions, as alternative materials to Nafion for proton-exchange membrane fuel cells (PEMFCs). As a PEM, the aromatic ionomer showed higher proton conductivity and performance than those of currently commercial PEM, Nafion® N212. The superior properties of the former are propably due to the nanostructured morphology originated from the multiblock structure in combination with the superacidity of perfluorosulfonic acid functions. The SANS profile of thick ionomer films (above 10 μm) in hydrated state showed two well-defined scattering maxima indicating a multi-phase separation at two different length scales. The GISAXS experiment aimed at investigating the impact of film thickness and substrate nature on the morphology of aromatic ionomer thin films (below 10 μm) towards application in catalyst layers with the objective of developing a wholy aromatic ionomer-based PEMFC. In addition, an in-situ study on how the membrane is formed during cast process was planned.

Results and the conclusions of the study:
We used the D2AM beamline in GISAXS configuration to perform the experiment. The incoming energy was set to 9 keV, with incident angle 0.2 and 0.4 degrees onto the surface of the sample to obtain the GISAXS 2D patterns with different penetration depths. The XPAD3 detector was positionned at 164 cm from the centre of the sample. Short measurements (typically 30 s) were done at different areas on the sample in order to prevent from radiation damage. The samples were prepared in advance for thicknesses above 1 micron or spin-coated using the PSCM lab spin-coater and the film thickness was measured with the ellipsometer. We could obtain homogeneous films in the range 5 - 400 nm, coated on Silicon wafers.

Impact of thickness on morphology:
The GISAXS profiles of thin ionomer films with different thickness (Fig. 1a) cast from dimethylsulfoxide (DMSO) on hydrophilic substrate proved a strong influence of the ionomer films thickness on morphology. The correlation peak measured at approximately 0.02 $Å^{-1}$ is due to the block superstructure, e.g. alternating

hydrophobic/hydrophilic zones of typically few hundreds nms in size. The optimized hydrophilic/hydrophobic phase separation was obtained in membranes with 50-90 nm in thickness. From peak position using Bragg equation, the correlation distance *d* between the hydrophilic and hydrophobic block was found to be ~33, 46, and 51 nm for membranes with thickness from 20 to 90 nm, 200 nm, and 400 nm, respectively.

Impact of susbtrate hydrophilicity:
In terms of the substrate nature, two types of substrate were used, i.e., SiO_2-deposited silicon substrate (namely hydrophilic substrate) and trimethylsilane-deposited silicon substrate (namely hydrophobic substrate). The GISAXS patterns of 400 nm thick ionomer films (Fig. 1b) reveal a huge impact of the substrate nature on the morphology of ionomer film. The membrane cast on the hydrophilic substrate possesses much more phase hydrophilic/hydrophobic separation than that of membrane cast from hydrophobic substrate. In fact, a well-defined scattering maxima was observed in GISAXS pattern of membrane cast on hydrophilic substrate while a monotone dacay of scattering wave vector was seen for membrane cast from hydrophobic substrate.

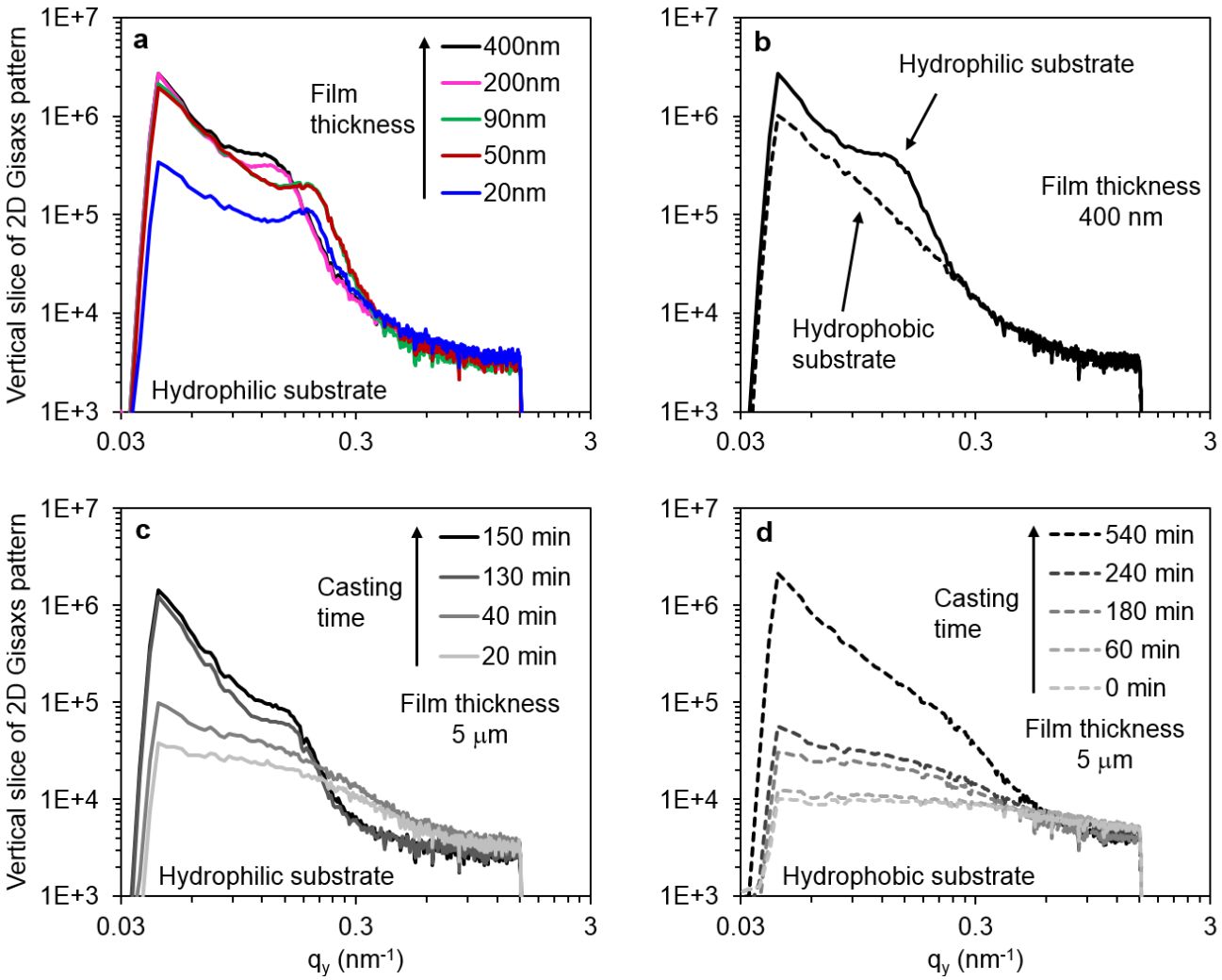

Figure 1. (*a) GISAXS profiles of thin ionomer membranes cast on hydrophilic substrate with different thickness. (b) GISAXS profiles of 400nm ionomer membranes cast on hydrophilic and hydrophobic substrates. In-situ GISAXS profiles of 5μm ionomer membranes during cast process at 60 °C on (c) hydrophilic and (d) hydrophobic substrates.*

The in-situ measurement (Figure 1c–d) was conducted on thicker film of 5 μm in thickness due to the short evaporation time of DMSO solvent from thin membranes. We clearly see the evolution of membrane morphology during solvent evaporation.

Publication(s): in preparation