



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



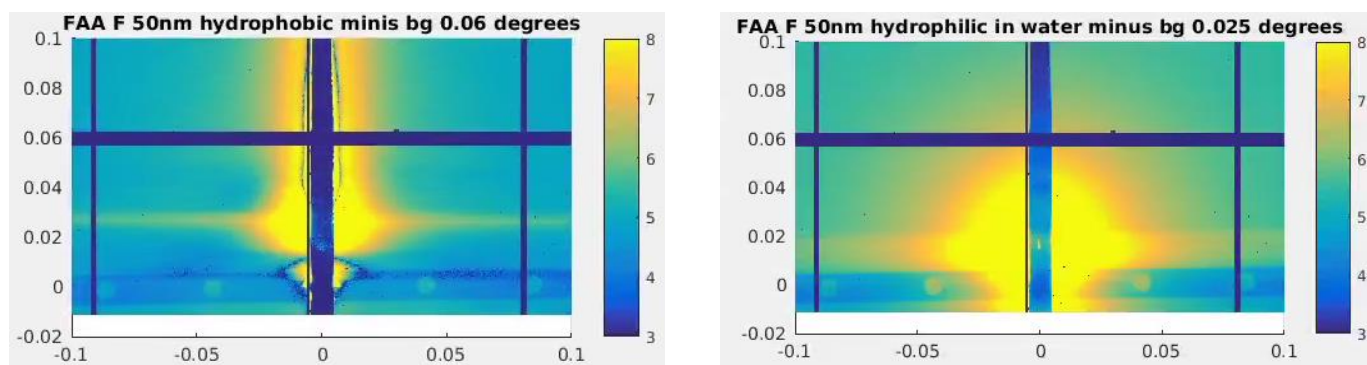
	<b>Experiment title:</b> <b>GISAXS investigation of near-surface morphology of anion-conducting domains in anion-exchange ionomer membrane materials</b>	<b>Experiment number:</b> MA-3827
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 08 Dec 2017 to: 12 Dec 2017	<b>Date of report:</b> 20 Jan 2021
<b>Shifts:</b> 12	<b>Local contact(s):</b> Veijo Honkimäki	<i>Received at ESRF:</i>
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## Report:

The main goal was to examine surface-induced orientation and phase-separated morphology in thin films of FAA and PPO in vapor and under water using GISAXS, similar to previous successful observations in Nafion ESRF experiments [1,2]. The FAA and PPO films belong to the anion-exchange membrane (AEM) materials that are being extensively studied as promising alternatives to more traditional proton exchange membranes (PEMs) such as Nafion [3], yet many questions, including microstructure and microphase separation in AEMs are open [4-6]. FAA and PPO films 10-70 nm thick were prepared on Si wafers (natively hydrophilic and OTS-treated to render them hydrophilic). F-form was possible to prepare only for FAA, along with HCO<sub>3</sub> and Br forms for both PPO and FAA. Prior to measurements at ESRF, the thickness of all samples had been evaluated by ellipsometry and was verified by X-ray reflectivity (XRR, from spacing of Kiessig fringes) before GISAXS examination during experiments at ID31 (ESRF), which showed a good agreement. Evaluation of differences in swelling at 30 and 88-90% humidity using XRR was also attempted, yet its sensitivity and accuracy was inferior to ellipsometry [6].

To observe the orientation it was crucial to be able to observe the ionomeric peak of these materials (even as a shoulder). The data published by Marino and Kreuer [4] showed that the ionomer peak in FAA is around 0.05-0.1 Å<sup>-1</sup> (for comparison Nafion has a peak at ~ 0.15 Å<sup>-1</sup>, more narrow and more sharply phase-separated). However, Marino and Kreuer's data indicate that the peak which depends on ion form (OH and F are best) and gets more pronounced as hydration increases, yet even then it is quite weak and not easily observed. Apparently, for this reason, it was unfortunately impossible to observe any ionomer peaks in inherently much noisier GISAXS spectra at 0.05-0.1 Å<sup>-1</sup> for all samples prepared. The figure shows representative 2D GISAXS spectra of FAA-F (Q scales in Å<sup>-1</sup>), corrected by subtracting the spectrum of

respective empty cell (mainly, widows). The left spectrum is for vapor environment (RH~88%) and the right one is under water, at near critical incident angles, at which scattering intensity is maximized. The appearance of Yoneda peak (a horizontal streak at  $Q \sim 0.024 \text{ \AA}^{-1}$  in vapor and  $\sim 0.01\text{-}0.015 \text{ \AA}^{-1}$  in water, well in agreement with calculated theoretical values) confirms the spectra are proper GISAXS. Yet, even in this highly sensitive  $Q_y$  range, the ionomer peak expected at  $Q \sim 0.05\text{-}0.1 \text{ \AA}^{-1}$  was undetectable. Apparently, the microphase-separation and interphase contrast in AEMs used was not sharp enough to observe a well-pronounced ionomeric peak and infer surface-induced alignment of conductive nanochannels. To verify the difficulty to observe the ionomeric peak was related to the nature of the samples rather than technical issues, Nafion spectrum was measured as well and did show a pronounced ionomer peak that agreed with previous reports [1,2].



The results were included and discussed in a recently published paper that focuses on the structure and water uptake thermodynamics of AEMs in thin films, as compared to the same materials in a bulk [6]. Its abstract is appended below.

## References

1. Bass, M., Berman, A., Singh, A., Konovalov, O., Freger, V. *Macromolecules*, 44, 2893-2899, **2010**.
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3. Varcoe J. R., Atanassov P., Dekel D. R., Herring A. M., Hickner M. A., Kohl P. A., Kucernak A. R., Mustain W. E., Nijmeijer K., Scott K., Xu T., and Zhuang L.; *Energy Environ. Sci.*, 7, 3135-3191, **2014**.
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6. Shrivastava U.N., Zhegur-Khais A., Bass M., Willdorf-Cohen S., Freger V., Dekel D.R., Karan K. *J. Phys. Chem. C* 124, 23469–23478, **2020**

## **Water Content and Ionic Conductivity of Thin Films of Different Anionic Forms of Anion Conducting Ionomers**

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*J. Phys. Chem. C*, 124, 23469–23478, **2020**; DOI: 10.1021/acs.jpcc.0c04278

### **ABSTRACT**

Typically, in polymer electrolyte-based electrochemical devices such as electrolyzers and fuel cells, ionomers in the catalyst layers are present as ultrathin films coating the electrochemically active component. Acidic ionomer thin films have been extensively characterized over the past decade, yet there are few reports on the alkaline ionomer thin films. Here, we present a study on anion-exchange ionomers; specifically, we investigate the water content and conductivity of fluoride, bromide, and carbonate forms of 50 nm thick FAA3 and PPO ionomer thin films at 30 °C and 0–90% RH. A thermodynamic analysis was performed to compute the Gibbs free energy of anionic interaction with water to discuss the impact of anion type on the anionic mobility. Structural analysis using GISAXS was performed on the anion-exchange ionomer thin films. Furthermore, conductivity and water content relationships between FAA3 thin films and membranes and between FAA3 and PPO thin films were compared and discussed in terms of structure and ion clustering.