

Cryogenic STEM for probing soft materials and interfaces in energy devices

Danielle Markovich, Yue Yu, Michael Colletta and Lena Kourkoutis

School of Applied and Engineering Physics, Cornell University, United States

Soft materials play an important role in energy devices including polymer membranes and ionomers in fuel cells, and polymer or liquid electrolytes in batteries. These materials pose major challenges for high-resolution characterization by TEM or STEM. They are highly radiation sensitive and imaging contrast is typically low. Traditionally, contrast enhancement for TEM studies of polymer membranes is achieved by heavy-element stains or ion-exchange. While these methods have allowed characterization of ionic domains in membranes, artifacts may be introduced due to incomplete or non-specific staining or swelling behavior resulting from ion-exchange [1]. Microscopic techniques that overcome these limitations are critical to advancing the development of energy devices involving soft materials.

Here, we will discuss advances in cryo-STEM for reliable characterizations of beam-sensitive materials such as ion-conducting polymer membranes and ionomers in fuel cells, and interfaces in batteries. Cryogenic cooling of the sample inside the microscope reduces ionization damage and enables the use of techniques beyond simple 2D imaging for probing the internal organization of energy materials. For example, methods such as cryo-electron tomography have given insight into the 3D structure of the hydrophilic-hydrophobic microphase separation in hydrated Nafion, used as proton conductor for proton exchange membrane fuel cells, revealing an interconnected channel-type network and domain spacings on the order of 5 nm [1].

Combining cryogenic temperatures with methods such as electron spectroscopy and 4D-STEM presents new opportunities in the characterization of energy devices. EELS, in conjunction with cryo-STEM imaging, can be used to study the elemental distribution of ionomers in the catalyst layer of fuel cell membrane-electrode-assemblies. Mapping the ionomer at micron length scales has previously been achieved using EDX at room temperature [2, 3]. In order to achieve nm-scale mapping of the radiation sensitive ionomer, however, cryogenic cooling as well as highly sensitive detectors are necessary allowing collection of sufficiently high SNR spectra even at low dose. In addition, 4D-STEM can provide insight into the organization of crystalline domains within fuel cell polymer membranes [4] and their effects on the membrane's mechanical properties, conductivity and durability. Figure 1 gives one example of cryogenic scanning nanobeam diffraction applied to map of the organization of crystalline domains in alkaline anion exchange membranes. We will show how the combination of cryogenic cooling, low dose imaging conditions and a sensitive detector push the resolution to ~2 nm despite the material's extreme radiation sensitivity. New cryo-STEM methods are poised to drive significant advances in understanding of energy materials and device, and improvements in hardware, new imaging methods and data analysis approaches will accelerate the process.

This work was supported as part of the Center for Alkaline-based Energy Solutions (CABES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0019445.

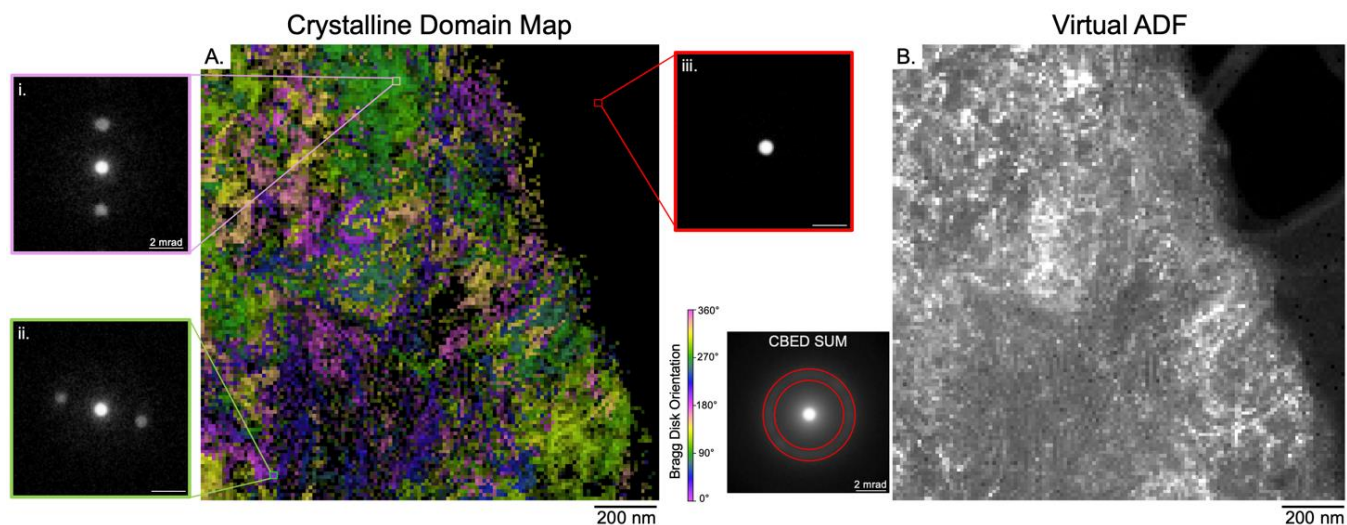


Figure 1. Figure 1. Cryogenic 4D-STEM for structural characterization of polymer fuel cell membranes. (A) Cryogenic scanning nanobeam electron diffraction performed at 300 kV with a ~ 2 nm size probe using an EMPAD and at low dose conditions enables mapping of crystalline domains in polymer membranes. (B) In the virtual annular dark field image using the detector angles marked with red circles in the summed CBED pattern highlight highly crystalline areas of the film.

References

- [1] F.I. Allen *et al.*, ACS Macro Letters **4** (2014), p. 1.
- [2] L. Osmieri *et al.*, Applied Catalysis B: Environmental **257** (2019), p. 117929.
- [3] X. Liang *et al.*, Chemistry of Materials **31** (2019), p. 7812.
- [4] O. Panova *et al.* Nature Materials **18** (2019), p. 860.