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Overcoming Artifacts in Imaging Nanometer-thick Ionomer Layers in Anion Exchange Membrane Fuel Cells

Michael Colletta[1], Yao Yang[2], Berit H. Goodge[1,3], Héctor D. Abruña[2] and Lena F. Kourkoutis[1,3]

[1.] School of Applied and Engineering Physics, Cornell University, Ithaca, NY, USA.
[2.] Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY, USA.
[3.] Kavli Institute at Cornell, Cornell University, Ithaca, NY, USA.

A major focus of anion exchange membrane fuel cell (AEMFC) research revolves around the study of the performance and degradation of the catalyst layer structure [1]. This complex structure typically consists of catalyst nanoparticles, such as platinum, loaded onto a carbon support along with a dispersion of polymeric ionomer. The interactions between the catalyst-loaded carbon particles and the ionomer have a direct impact on both the ionic and electronic conductivity in the catalyst layer [2,3]. A robust approach to characterize the distribution of ionomer in the catalyst layer is therefore important to advance our understanding of fuel cell performance. Here, we show that low-dose cryo-TEM imaging enables direct imaging of the ionomer and its distribution in the catalyst layer of AEMFCs.

Low-dose cryo-TEM is a well-established technique used in the field of structural biology [4,5]. The same methods used to reduce beam damage in biological specimens can be applied to study energy materials such as organic polymers and liquid electrolytes [6,7]. It has been shown that ionomer materials for proton exchange membrane fuel cells, such as Nafion and perfluorosulfonic acid (PFSA), are highly radiation sensitive, requiring doses $<10^4$ e/Å^2 when performing elemental mapping techniques such as STEM-EDX and STEM-EELS even under cryogenic conditions [8,9]. Nevertheless, imaging of ionomers is often performed at room temperature where artifacts can hamper interpretation as we will show below [9,10]. The samples imaged in this work consist of a dispersion of platinum-loaded carbon black and the alkaline ionomer quaternary ammonia poly (N-methyl-piperidine-co-p-terphenyl) (QAPPT).

The results of initial attempts to image the ionomer using low-angle annular dark-field (LAADF) STEM imaging on a TFS/FEI Titan Themis at an acceleration voltage of 120 kV are shown in Fig. 1. The sample was prepared using a catalyst-ionomer composite ink in an ethanol solution with a mass ratio of 4:1. The ink was drop-cast onto a lacey carbon grid, which was subsequently dried at room temperature and baked at 80°C overnight in a vacuum chamber. Despite the baking procedure, carbon contamination during imaging at room temperature can result in the build-up of a carbon layer on the surface of the sample, preventing accurate measurements of the ionomer distribution (Fig. 1). The carbon support, which is distinguished by its graphitic structure (Fig. 1.a), rapidly accumulates carbon contaminants after exposure to the electron beam (Fig. 1.b-c). Cooling the same sample to near liquid nitrogen temperature drastically reduced carbon contamination, while possible ice contamination is also seen to have a minimal effect on the catalyst support surface (Fig. 1.d). The ionomer layer was not observed here, likely due to the high electron dose used to achieve sub-nanometer resolution cryo-STEM imaging.

Having demonstrated the necessity of cryogenic imaging, we transitioned to studying the ionomer distribution on a TFS Talos Arctica, operated at 200kV, which is optimized for low-dose cryo-EFTEM imaging. Fig. 2 shows the characterization of the critical electron dose for this ionomer, performed on a

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catalyst-ionomer composite ink with a mass ratio of 1:1. This sample was imaged over a range of electron doses from ~18 e/Å^2 to ~1800 e/Å^2. A standard method of critical dose estimation is to fit a signal such as the diffraction-spot intensity, specimen thickness or spectroscopic signature to an exponential curve and defining the critical dose as the reduction in the signal by a factor of 1/e [11]. This definition of critical dose results in a dose limit of ~990 e/Å^2; however, applying this dose would lead to a misrepresentation of the ionomer thickness. After only ~290 e/Å^2, the thickness of the ionomer is already reduced by approximately 10% and the ionomer also exhibits increased contrast variations, indicating morphological changes and degradation of the ionomer material. To preserve the ionomer structure, a limiting dose of ~150 e/Å^2 is chosen for future characterization, corresponding to a less than 5% decrease in ionomer layer thickness.

The complex 3D structure of the catalyst layer requires electron tomography for full characterization of the ionomer distribution. Typically, a copper Quantifoil grid with 2 µm holes or a lacey carbon grid is used for imaging; however, for the larger doses required for tomography, smaller holes provide greater structural support and limits sample movement under the electron beam. Fig. 2.d shows the carbon film used to support the catalyst-ionomer composite samples discussed above. With the appropriate conditions for ionomer imaging established, further characterization of the ionomer distribution in various ionomer loading conditions was performed. In this work, catalyst-ionomer mass ratios of 1:1, 1:4, and 1:10 were analysed. A decrease in ionomer thickness is shown in the comparison of the 1:1 and 1:4 mass ratios. While the ionomer thickness remained relatively consistent between the 1:10 and 1:4 samples, the 1:4 is found to have increased uniformity in ionomer coverage on the surface of the carbon support structure [12].

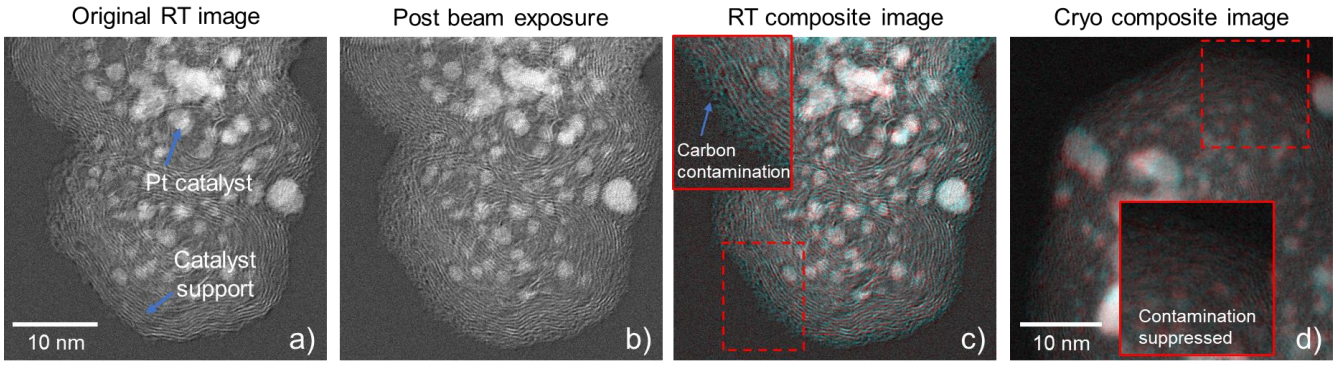

Figure 1. a) HAADF-STEM image of a catalyst-ionomer composite acquired at 120 kV and ambient temperature. b) The same region is imaged again after 180s of beam exposure. c) An RGB composite image of a) and b). The cyan color highlights the carbon contamination that has built up during beam exposure. d) A similar composite image obtained near liquid nitrogen temperature highlighting changes in cryo-STEM image contrast after 10 minutes of beam exposure. The surface remains mostly unchanged as carbon build-up is suppressed at these low temperatures.

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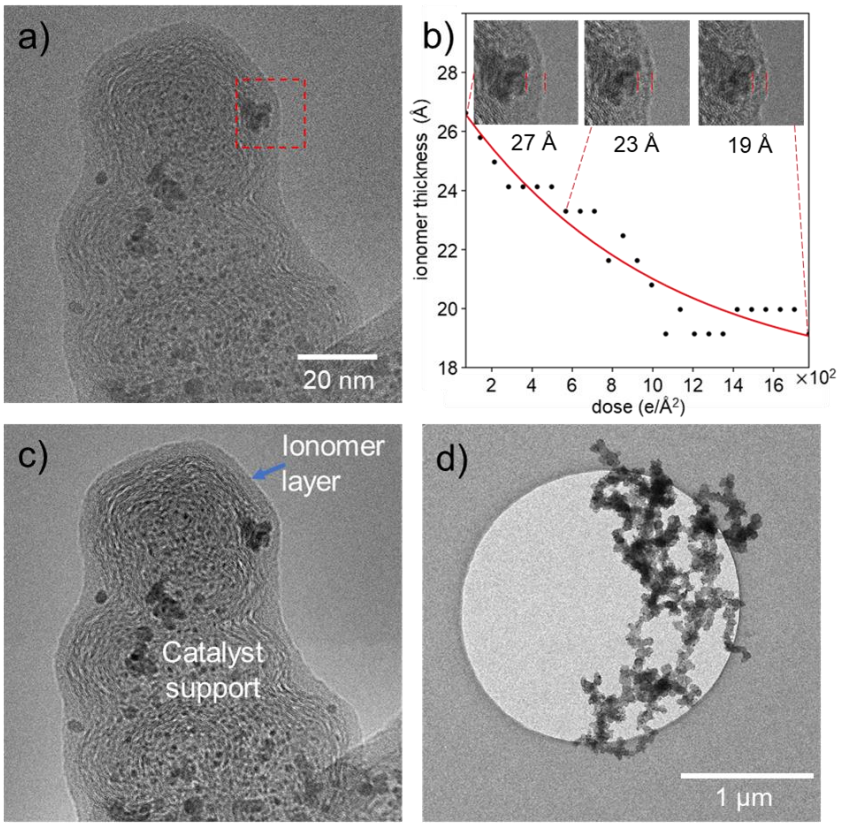

Figure 2. a) Cryo-TEM image of a catalyst-ionomer composite acquired with a total dose of ~18 e/Å^2. b) Quantification of the ionomer thickness from a series of cryo-TEM images shows that the ionomer degrades rapidly with increasing dose. c) The ionomer layer is clearly resolved in a sum of 6 image frames with a cumulative dose of ~108 e/Å^2. d) Catalyst-ionomer composite sample suspended over a 2 µm hole of a Quantifoil carbon TEM grid.

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