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Cryo-Electron Tomography for Imaging and Quantitative Analysis of Beam-Sensitive Fuel Cell Materials

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Electron tomography offers access to volumetric information at nanoscale resolution, and has proven valuable for the study of energy-related materials as they often involve multiple phases assembling in intricate structures. However, being a dose-intensive technique, its application to electron-beam sensitive materials poses limitations. For instance, resolving the three-dimensional nanomorphology of proton exchange membrane fuel cell (PEMFC) catalyst layers (CL), an important component for their structure-performance optimization[1], has been historically challenged by beam-induced degradation of the ionomer phase. Here, we present an approach combining cryo-electron tomography, low dose imaging, and advanced computational methods for image restoration and segmentation to investigate the complete structure of these materials.

We studied samples fabricated with platinum supported on graphitized Vulcan (gVu) or high surface area Ketjenblack (KB) carbons with various ionomer contents, representative of materials used in PEMFCs. In order to preserve the catalyst layer structure, the KB sample was prepared with partial embedding and ultramicrotomy (Fig. 1a). To mitigate radiation damage to the ionomer network which is known to suffer from radiolysis within a few hundred e^-/nm^2 at room temperature[2], samples were cooled to liquid nitrogen temperature and imaged with electron dose rates below 35 $e^-/nm^2/s$, totaling less than 40 $e^-/Å^2$ for a complete tilt-series and resulting in little or no observable degradation during acquisition (Fig. 1b). Imaging was performed in BF-TEM mode and therefore, the SIRT algorithm was used for reconstruction in order to increase the contrast between ionomer and carbon, and to mitigate strong scattering artefacts from platinum (Fig. 1c). Due to the low electron dose, images contain significant levels of noise which corrupt the reconstructions (Fig. 2a). To facilitate interpretation and further processing, we used the cryo-CARE method (Fig. 2b), a deep-learning based denoising pipeline[3]. From qualitative and quantitative performance comparison we found it to perform better than other methods commonly available (Fig. 2d), and to improve the resolution as measured from Fourier shell correlation curves (Fig. 2e). Despite limited degradation and careful alignments, reconstruction artefacts from platinum and bright fringes as well as the low and irregular contrast between the ionomer and carbon phases challenge segmentation with conventional intensity-based methods. Here again, the generalization capabilities of deep learning methods were leveraged, and we used the Yapic toolbox[4] and a subset of manually annotated tomograms to train a classification model that was then applied to the entire reconstructions (Fig. 2c). The segmentation was quantitatively evaluated and found to perform well on all phases (Fig. 2f).

The results from the segmented reconstructions concerning all three phases and their interactions will be discussed for the different samples analyzed, including calculations of volume fractions, coverage, surface areas and thickness. Our approach offers a framework for studying an important part of the PEM fuel cells at the nanoscale, and provides structural information valuable for modeling.[5]

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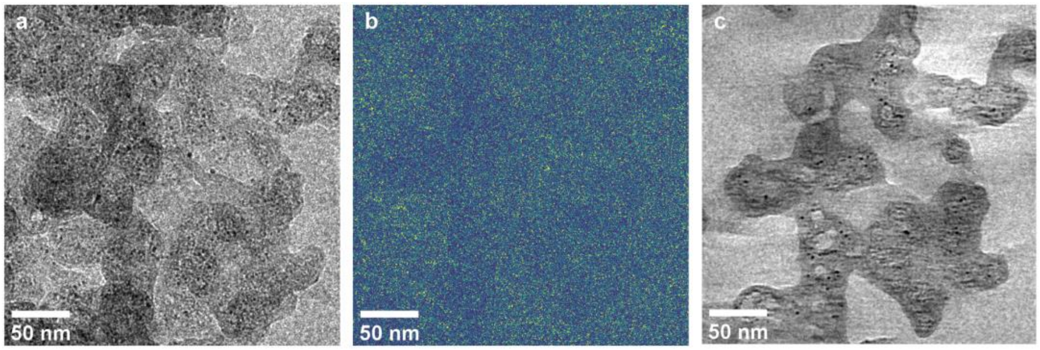

Figure 1. (a) BF-TEM image at 0° tilt of a microtomed cross-section of a catalyst layer fabricated with 20 wt% Pt/Ketjenblack and 800EW ionomer at 0.7 I/C wr. (b) Difference of intensity between two images of the area in (a) taken before and after tilt-series acquisition, showing that cryogenic temperatures and low dose mitigate radiation damage. (c) Central tomogram from the corresponding SIRT reconstruction demonstrating the preservation of the catalyst layer structure.

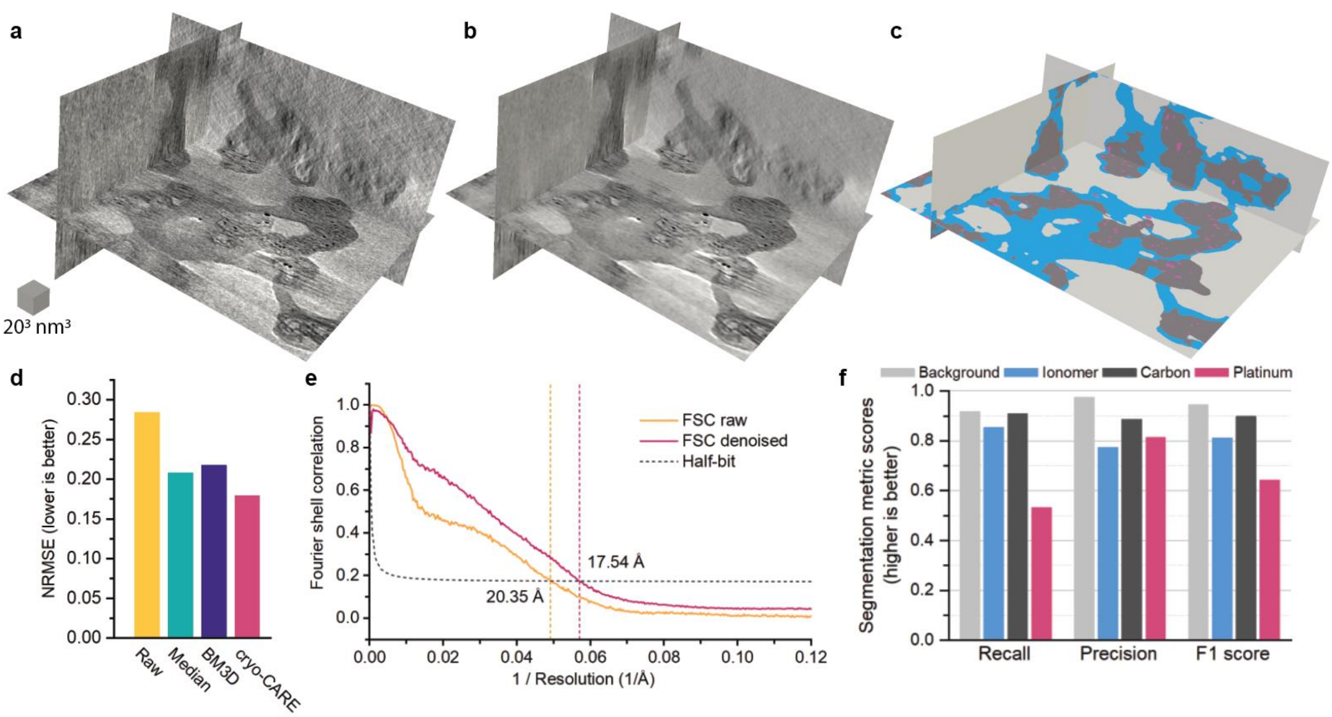

Figure 2. Multi-orthoslice view of (a) the raw SIRT reconstruction presented in Figure 1 and results after (b) denoising with the cryo-CARE method and (c) multi-phase segmentation of carbon (dark gray), ionomer (blue), Pt nanocatalysts (pink) and background (light gray). The denoising performance was evaluated from (d) normalized root mean square error (NRMSE) comparison and (e) Fourier shell correlation (FSC) curves. (f) Evaluation of the segmentation performance.

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