

Supplementary Information for:
**Resolving the Three-dimensional Micro-structure of Polymer Electrolyte Fuel
Cell Electrodes using Nano-scale X-ray Computed Tomography**

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Sample preparation

To prepare Electrode 1 (E1), a catalyst suspension was prepared with 20 wt% Pt/Vulcan XC-72R (Electrochem, Woburn, MA), 5 wt% Nafion[®] DE-521 suspension (Ion Power, New Castle, DE), and de-ionized water. The Nafion loading was 35% wt. The mixture was agitated by a dip ultrasound mixer (Cole-Parmer, Vernon Hills, IL) for 10 minutes and stirred by magnetic stir bar overnight. It was then painted onto a 3 x 4 cm piece of 50 μm thick Kapton HN film (DuPont, Wilmington, DE). Kapton was chosen over a Nafion[®] membrane for these *ex-situ* studies because humidity-driven Nafion[®] expansion and contraction hindered high-resolution imaging in our preliminary work. Xie et al.[1] demonstrated that painting electrodes onto Kapton has no discernable impact on the electrode structure because of Kapton's good wettability to catalyst suspensions. Repeated painting continued, with 30 minutes in a 110°C oven between coats, until the gravimetrically determined platinum loading reached 0.9 mg/cm². The high loading was chosen to increase the electrode volume for more accurate MIP.

A second electrode (E2) was prepared having the same volumetric composition of Pt, carbon, and Nafion as E1. However, the catalyst ink suspension was prepared such that the finished electrode featured a large pore and agglomerate structure. This catalyst ink suspension was ion-exchanged with tetrabutylammonium hydroxide (TBAOH) following Wilson et al.'s [2]

method and featured glycerol as an additional solvent, and a shorter duration of ultrasonication (ca. 30 s).

A 3 x 3 cm section of the finished E1 electrode with Kapton backing was characterized by MIP to obtain pore size distributions; the MIP was performed by Porous Materials, Inc. (Ithaca, NY). TEM samples from the same piece of E1 were embedded in epoxy and examined in an ultra-microtome 100 nm thick.

A different small piece (ca. 5 mm equilateral triangle) from the same preparation of E1 with Kapton backing was cloven from the larger piece and placed in an UltraXRM-L200 (Xradia, Pleasanton, CA) for nanoXCT. The resolution of this instrument is 50 nm and the 3D reconstructions of this study have 32.5 nm cubic voxels. To stabilize the thin sample in a standing position during nanoXCT imaging, a triangular piece was bent with the electrode outward and the two free ends clipped together to create a loop. The radius of curvature was ca. 1 mm, which is two orders of magnitude greater than electrode thickness and thus insignificant.

Transmission Electron Microscopy

TEM samples from the same electrode were embedded in epoxy (EPON-Araldite[®], Huntsman Advanced Materials, Everburg, Belgium) for 4 days at 35°C to prevent sample bending, and then for an additional night at 55°C. An ultramicrotome slice was cut with a thickness of 100 nm and mounted in a Hitachi 7100 TEM. An accelerating voltage of 75 keV was used for imaging.

Image processing

The raw X-ray data was processed by proprietary software (Xradia, Inc.) to generate the unprocessed 3D reconstructions [3]. Subsequent analysis was performed using MATLAB (Mathworks, Natick, MA). First, MATLAB's image equalization function redistributed the raw

grayscale histogram intensities over the entire intensity range to aid in visualizing the data. Then, a thresholding operation split the data into binary values representing solid (agglomerate phase) and void (pore phase). In processing TEM data, we used a similar thresholding technique to split the image into binary solid- and pore-phase data. Using the thresholded data, we characterized the solid agglomerate and pore phase size distributions based on the fitting of inscribed spheres of different diameter within the volume of each phase.

MIP simulation

MIP measurements serve as valuable data for verifying nanoXCT reconstructions. However, due to the pore throat effect, the pore size distribution obtained from inscribed spheres cannot be directly compared with MIP data. To facilitate comparison with MIP, we developed a morphological computational simulation in MATLAB for generating virtual MIP data using an established approach [4]. For each iteration of decreasing pore size, an intrusion sphere diameter D was specified, which corresponds to a certain pressure in MIP. The difference in diameter between each iteration was limited to the 32.5 nm voxel side length. Starting from one face of the cubic 3D reconstruction space, inscribed sphere fitting determined where a sphere of diameter D could intrude into the sample volume – these sites were designated as “seed” sites. From these seeds, inscribed spheres of the same diameter were placed in every possible inward direction and checked for overlap with the solid phase. If there was no solid phase overlap, the program continued to intrude spheres into adjacent unoccupied volumes. When spheres could proceed in more than one direction, a new sphere seed site and path were initialized. A sphere intrusion branch became “dead” when no more spheres could be placed in any new direction without solid overlap, which could be due to a dead-end pore or a pore throat with a diameter less than the sphere radius. After all sphere paths became dead for a given radius, the volume

corresponding to that radius was computed and inserted to the pore size distribution. With this simulation, the XCT data was made to yield the pore volume representative of that measured by MIP. To statistically account for variations due to intrusion direction and starting faces, six simulations were performed starting from each face of the sample cube, from which the mean values and standard deviations were calculated.

Verification of X-ray Images

Figure 1 presents 2D virtual slice images from the nanoXCT for the two electrodes prepared. Figure 1a shows E1 and Figure 1b shows E2. Figures 1c and 1d show magnified images of those in Figures 1a and 1b, respectively, for regions within the air and electrode. The thresholded electrode images are also shown. High frequency noise is evident in the air. However, this noise is not present in the pores of the electrode. This is primarily because the negative Zenike phase contrast generates a bright/dark halo next to objects with higher attenuation. Thus, the apparent intensity within the pores is lower. This halo is also clearly evident at the air|electrode interface in Figure 1a. This significantly increases the visibility of the pores and improves the signal to noise ratio (SNR) that is discussed next. This effect is the same as the bright halos observed in optical Zernike phase contrast imaging.

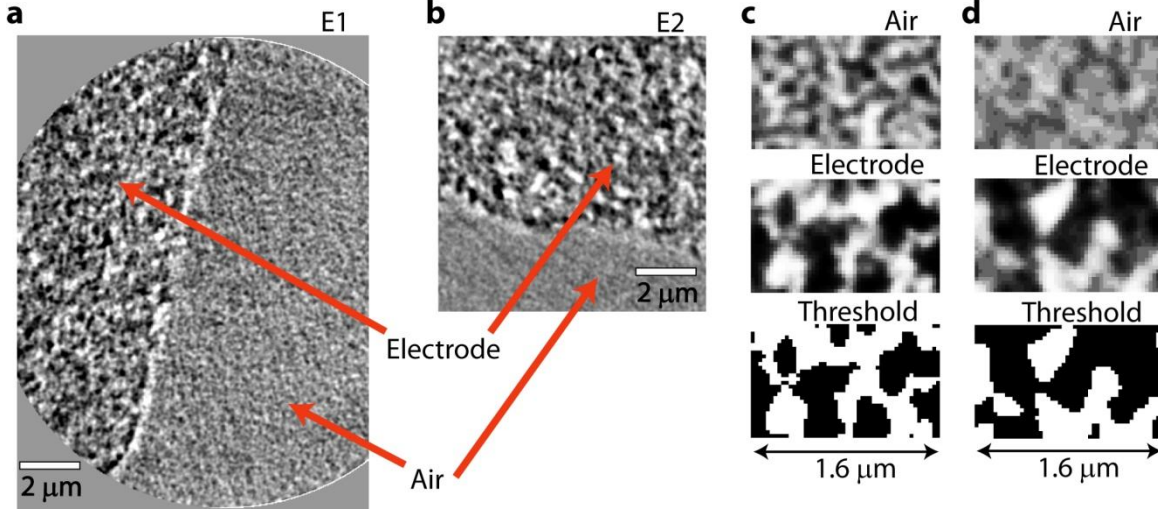


Figure 1 X-ray images. **a**, 2D X-ray slice of E1. The image includes the interface between the electrode and air. **b**, 2D X-ray slice of E2. **c**, A magnified image of the air and electrode regions of the electrode in **a** as well as the thresholded image of the electrode. **d**, A magnified image of the air and electrode regions of the electrode in **b** as well as the thresholded image of the electrode.

The SNR in the 2D nanoXCT slices is calculated by the ratio of signal variance in the electrode region to that in the air. The variance in the electrode is a modified variance, Var^* , that uses the mean from the air region. We calculate the SNR with the following expression:

$$SNR = \sqrt{\frac{Var^*(I_e)}{Var(I_a)}} = \sqrt{\frac{\sum_i^{N_e} \left[\left(\frac{1}{N_e - 1} \right) \left(I_i^e - \frac{1}{N_a} \sum_j^{N_a} I_j^a \right)^2 \right]}{\sum_i^{N_a} \left[\left(\frac{1}{N_a - 1} \right) \left(I_i^a - \frac{1}{N_a} \sum_j^{N_a} I_j^a \right)^2 \right]}} \quad (1)$$

where N is the number of pixels used calculated the variance and $N_e = N_a = N$. The SNR is estimated to be 2.05 ($N = 7237$ or $7.64 \mu m^2$) for E1. In contrast, for E2, the estimated SNR is 3.54 ($N = 9864$ or $10.42 \mu m^2$). The SNR is lower in E1 because there is greater interfacial area with smaller agglomerates, which entails more intermediate intensity values and reduces the variance relative to the second electrode.

To further ensure that the signal in the electrode region was not corrupted by the noise evident in the air, we performed a power spectrum analysis comparing the air and electrode

regions. The power spectrum was generated using the Fast Fourier Transform (FFT). Figure 2 presents the power spectra of the two electrodes as a function of the half wave length, which was chosen as a measure of feature length scale. Figure 2a and 2b were generated from 12.9 μm long vertical lines through the image in Figure 1a and Figure 2c and 2d were generated from 8.9 μm long horizontal lines through the image in Figure 1b. Figure 2a and 2c show signals that are separate from the noise in the air down to length scales slightly less than 80 nm. As expected, E1 has higher power spectrum peaks at the smaller length scales than E2 and it also has lower power spectrum peaks at the larger length scales.

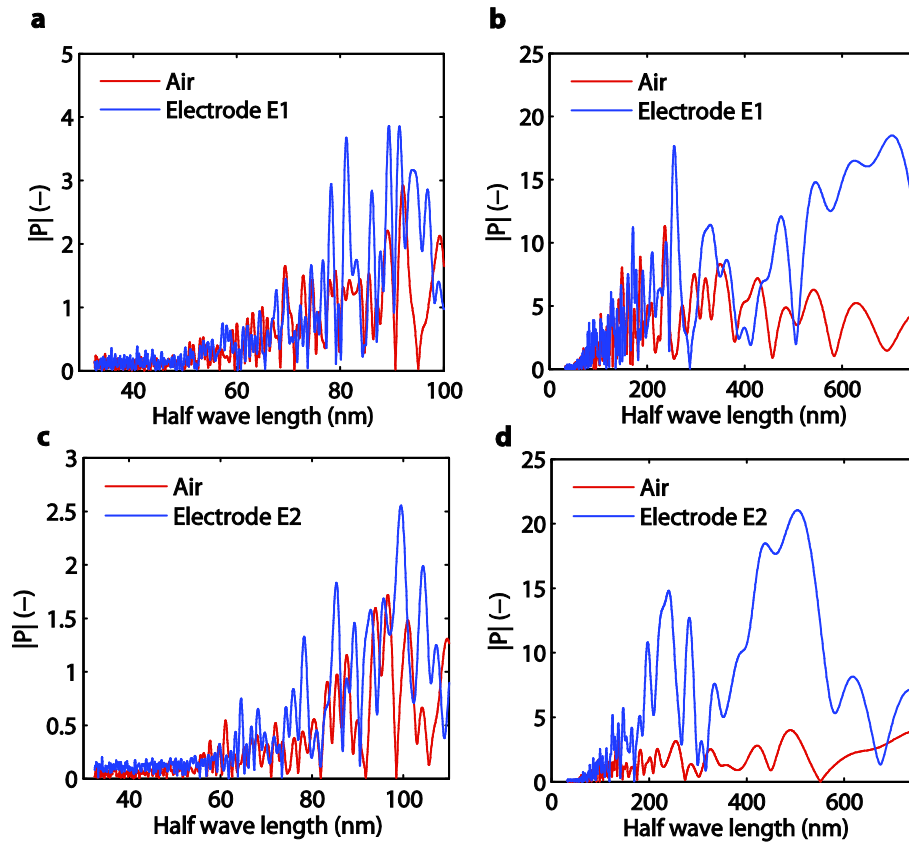


Figure 2 FFT power spectrum analysis of X-ray images. **a** and **b**, FFT power spectrum of X-ray image for E1. The power spectrum is plotted with respect to half wave length, which is a measure of feature length scale. **c** and **d**, FFT power spectrum of the X-ray image for E2. The power spectra are shown for small (**a**, **c**) and large (**b**, **d**) length scales.

Agglomerate diameter calculation

Using the solid agglomerate size distribution in Figure 5b of the main paper body, we have calculated the volume-average agglomerate diameter, D_{avg} , using the agglomerate phase volume fraction, PV , for the i^{th} diameter, D_i , and the volume for that sphere diameter to calculate a volume-average agglomerate volume, $V_{avg} = \sum_i PV_i \pi D_i^3 / 6$. The average diameter is then determined from the equation:

$$D_{avg} = \left[\frac{6}{\pi} V_{avg} \right]^{1/3} = \left[\sum_i PV_i D_i^3 \right]^{1/3} \quad (2)$$

References to Supplementary Methods Note

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