Microsc. Microanal. 21 (Suppl 3), 2015
doi:10.1017/S1431927615004791 Paper No. 0400

Quantitative Structural Analysis of Fuel Cell Catalysts and Carbon Supports by TEM and Cryo-STEM Tomography

Elliot Padgett[1], Nina Andrejevic[1], Zhongyi Liu[2], Koji Moriyama[3], Ratandeep Kukreja[4], Yi Jiang[5], Veit Elser[5], David A. Muller[1].

[1.] School of Applied and Engineering Physics, Cornell University, Ithaca, NY.
[2.] Chemical and Materials Systems Laboratory, General Motors, Warren, MI.
[3.] Honda R&D Co. Ltd. Automobile R&D Center, Haga-machi, Tochigi, Japan.
[4.] GM Global Powertrain Engineering, Pontiac, MI.
[5.] Department of Physics, Cornell University, Ithaca, NY.

The 3D microstructure of electrode materials plays a key role in electrochemical energy conversion and storage systems. In fuel cells, reactant transport to the catalyst through the carbon support and ionomer governs the limiting reactions but remains poorly understood. Two carbon materials commonly used as fuel cell catalyst supports are Vulcan, which has catalyst on the carbon surface, and Ketjen Black (HSC), which is porous and has catalyst in both the carbon interior and surface. Catalyst activity and degradation mechanisms depend on the distribution of catalyst particles on the support, which cannot be unambiguously determined by bulk measurements. We use TEM and STEM tomography to measure the size and spatial distribution statistics of platinum catalysts on carbon supports. Comparing measurements of total surface area by tomography with electrochemical measurements of the chemically active surface area, we find that catalyst particles embedded in the carbon interior are still chemically accessible. While TEM allowed rapid data acquisition, STEM allowed more reliable segmentation, reducing the systematic error in measured surface area from 37% uncertainty in TEM to 6% in STEM.

Quantitative measurements derived from tomography, especially surface areas and volumes, are sensitive to the segmentation of materials in reconstructed tomograms. Image contrast mechanisms limit the quality of segmentation that can be achieved. While bright field TEM provides high contrast for low-Z materials such as carbon, phase contrast creates speckle noise in high-resolution images of amorphous materials that broadens the distribution of intensities, (Fig 1a,b) blurring the reconstruction and compromising segmentation. Low angle annular dark field (LAADF) STEM provides an intensity scale that is monotonic with thickness, a low-noise background, and easier segmentation (Fig 1c,d).

We produced tomograms of different loadings of platinum particles on Vulcan and HSC carbon supports (Fig 2). Maintaining the sample at cryogenic temperatures using a LN_2-cooled tomography holder enables investigation of beam-sensitive materials such as ionomers [1] and supresses carbon contamination, which is problematic (especially for STEM) when carbon and low-Z elements are of interest. We identified platinum using threshold segmentation to determine the size and surface area distributions of hundreds of catalyst particles per sample (Fig 3). We identified the carbon surface using thresholding and morphological filtering to distinguish surface vs. interior platinum particles and measure the distance from catalyst to the carbon surface in HSC. TEM and STEM measure qualitatively similar surface area distributions (Fig 3), but the large threshold error in TEM limits its quantitative interpretation. In STEM it is clear that interior particles contribute roughly twice as much total surface area, but for particles larger than 2-3nm, most platinum surface is on the carbon exterior. We combine tomographic and electrochemical surface area measurements to better understand catalyst activity. We measure smaller surface areas from electrochemistry than tomography. Fig 3c indicates the fraction of platinum surface that is chemically inaccessible. Vulcan, with platinum only on the carbon exterior, and HSC, with two thirds of the platinum surface embedded in the carbon, show similar electrochemically active surface areas, implying that much of the embedded catalyst is chemically accessible. [2]

References:
[1] DA Cullen *et al*, Journal of The Electrochemical Society **161** (2014), pp. F1111-F1117.
[2] Funded by GM & Honda. EM Facility support from the NSF MRSEC program (DMR 1120296).

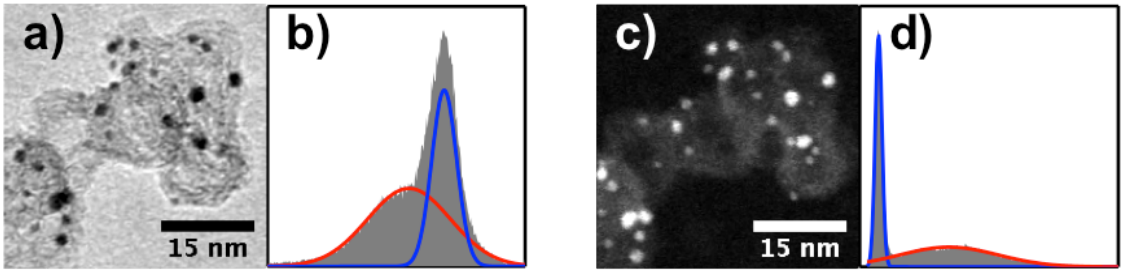

Figure 1. (a) TEM and (c) LAADF STEM images of platinum nanoparticles on HSC carbon taken with a 200kV FEI Tecnai F20. Corresponding histograms (b,d) from larger images show intensity distribution for carbon support film (blue Gaussian) and HSC carbon (red Gaussian).

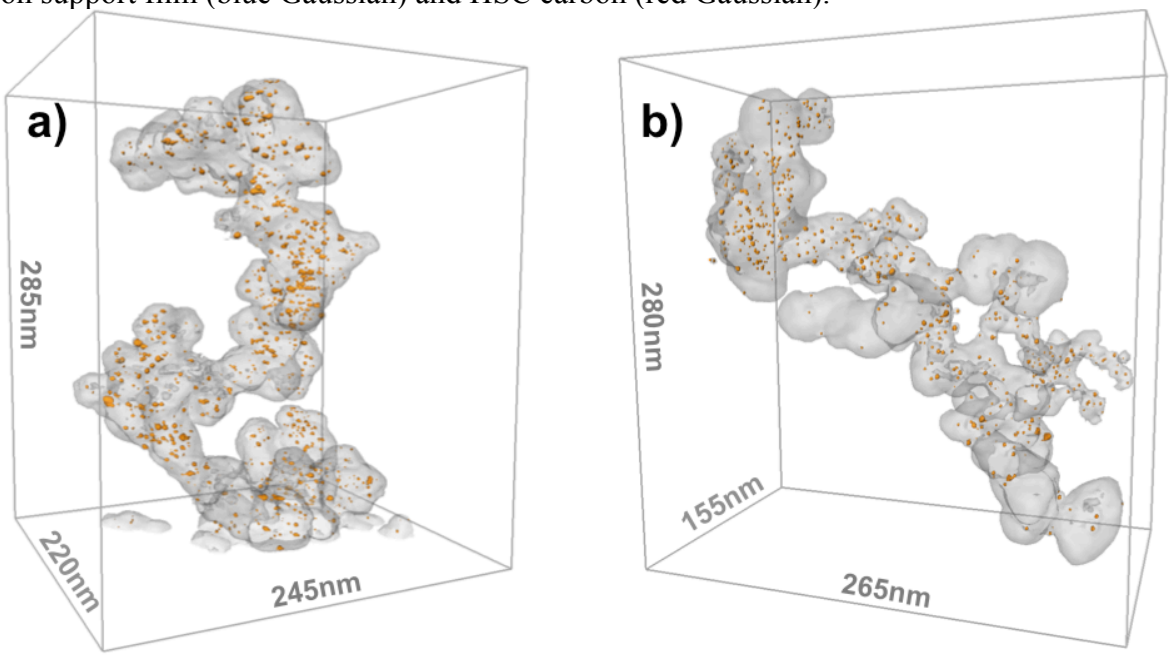

Figure 2. Isosurface renderings of (a) TEM (FEI T12, 120kV) and (b) cryo-STEM (FEI F20, 200 kV) tomograms of platinum particles (orange) on HSC carbon support (grey).

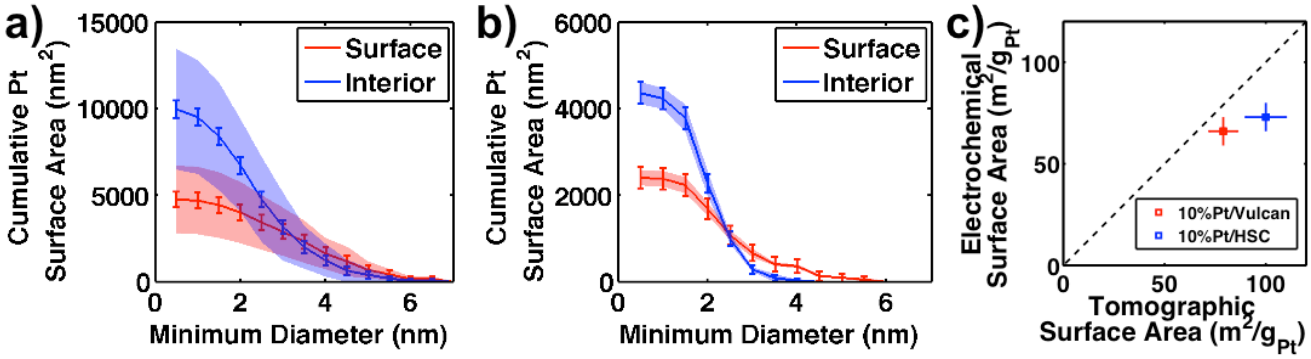

Figure 3. Cumulative surface area of all platinum particles above a minimum diameter in (a) TEM and (b) STEM reconstructions, with particles on HSC surface and interior separated. Error bars represent statistical uncertainty; shaded areas represent uncertainty due to platinum segmentation. (c) Specific surface areas from TEM tomography and hydrogen adsorption/desorption for Pt on HSC and Vulcan.