Multiple ADF-STEM Towards the Optimization of Electron Tomography Reconstructions of Pt/C fuel cell catalyst nanostructures

Alessandra da Silva, Thomas David, Zineb Saghi and Laure Guetaz

CEA-Grenoble, United States

Hydrogen fuel cells have are the subject of intense research within the field of sustainable alternative energies due to their lack of harmful exhaust emissions and high energy efficiency compared to conventional fuels. However, further development is required to reduce their costs, where Pt loading is a key factor. Optimization of the cathode catalysts demands accurate description and understanding of the relation between the catalyst support and the Pt nanoparticles in order to improve engineering of the reaction sites.

High-Angle Annular Dark-Field Scanning Transmission Electron microscopy (HAADF-STEM) tomography is a powerful 3D technique at the nanoscale. The HAADF-STEM signal has elemental contrast which monotonically increases with $Z^2$; however, when applied to the 3D analysis of Pt/C fuel cells, this technique faces some challenges due to the relative low atomic number of carbon when compared to platinum. Reconstruction artifacts from the Pt nanoparticles, such as the missing wedge and diffraction contrast interfere with the carbon reconstruction due to its low ADF intensity, introducing uncertainty and leading to misinterpretation in the visualization of the carbon regions.

We present strategies to mitigate these artifacts applied to Pt/C catalyst, for a graphitized 30 wt% Pt-loaded C catalyst (TEC10EA30E-HT, from Tanaka Kikinzoku Kogyo K.K., Japan). Firstly, at the experimental level, two electron tomography tilt series from the Pt/C catalyst were simultaneously acquired with different detectors: an ADF-STEM series, where the lower collection angle allowed for better visualization of the carbon regions and a HAADF-STEM series where mostly the Pt nanoparticles were well defined and could be clearly identified.

Secondly, the reconstructions were performed using combined information from these two detectors. Automated procedures were developed to improve the reconstruction quality of the carbon support. The Pt nanoparticles were removed from each ADF-STEM projection using a mask calculated by applying a threshold to the corresponding HAADF-STEM projection. The absent information in the ADF-STEM projection leftover by removing the Pt nanoparticles was replaced by interpolating the pixels in the surrounding area using an inpainting algorithm based on the fast marching method. Both series were reconstructed individually and then combined. This method is found to significantly improved the visualization of the carbon in the resulting combined reconstruction, whilst maintaining the quality of the Pt reconstruction obtained from traditional methods, as shown in figure 1.

Figure 2 shows the rendered 3D volume as well as a slice through the reconstruction where the Pt nanoparticles are commonly found on the junctions of the hollow carbon substrate. Using the experimental and reconstruction strategies presented in this work, the morphology of the hollow carbon support and the platinum nanoparticles are simultaneously resolved.

The experiments were performed using a double aberration correction FEI Titan TEM, operated with a FEG at 200 kV. The tomography series were taken over a typical tilt range of around $\pm 70^\circ$ at $2^\circ$
step with a pixel size of 0.14 nm. All processes involved in this work were performed using open access tools. The image processing of the tilt series and analysis were performed using Python scripts and the alignments of the series were performed using the Pt nanoparticles as fiducial markers\(^8\). The HAADF-STEM reconstructions were performed using weighted back projection (WBP) and the reconstruction of the ADF-STEM series were performed using the SIRT technique\(^9\). Rendering was performed using Tomviz\(^{10}\).

**Figure 1.** Figure 1 Comparison of the resulting slices obtained with different reconstruction techniques. Slices from A) HAADF-STEM reconstruction using WBP B) ADF-STEM reconstruction using SIRT (100 iterations) c) inpainted ADF-STEM using SIRT (100 iterations) d) combination of HAADF-STEM and ADF-STEM

**Figure 2.** Figure 2 Reconstruction resulting from the combination of ADF- and HAADF-STEM datasets from the Pt/C catalyst. a) A slice through the reconstruction showing hollow carbon particles (depicted with white arrows) and also the platinum nanoparticles (which appear bright in the image), b) 3D rendering of the combined reconstruction showing the Pt nanoparticles in red and the carbon support in grey.

References


