doi:10.1017/S1431927622002598

Microsc. Microanal. 28 (Suppl 1), 2022

Imaging Sensitive Catalyst Active Site Structure by 30 keV Electron Ptychography

Michael J. Zachman[1*], Hasnain Hafiz[2], Dong Young Chung[3], Vojislav Stamenkovic[3,4], Edward F. Holby[5] and David A. Cullen[1]

[1.] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA.
[2.] Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, USA.
[3.] Materials Science Division, Argonne National Laboratory, Argonne, IL, USA.
[4.] The Samueli School of Engineering, University of California, Irvine, Irvine, CA, USA.
[5.] Sigma Division, Los Alamos National Laboratory, Los Alamos, NM, USA.
* Corresponding author: zachmanmj@ornl.gov

Many promising next-generation catalysts for processes such as CO_2 reduction [1] and green hydrogen generation and conversion [2,3] utilize single metal atoms embedded in a host carbon network as active sites. The lattice structure around the metal atom at these sites has a direct impact on properties such as the activity and durability of the site, so understanding this structure and its variations from site to site is crucial for developing advanced materials. Conventional scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) have proven essential for demonstrating the atomically dispersed nature of the metal atoms and local presence of coordinated elements such as nitrogen [4,5], but have more limited ability to directly reveal the lattice structure around these sites. In addition, these sites are often beam-sensitive and damage rapidly under typical 60 keV low-voltage conditions, making determination of site structure with certainty challenging. To provide a better understanding of the structures present in these catalysts, a technique is therefore needed that can provide information about both the metal atom and surrounding lattice structure, as well as variations in this structure across a material, while minimizing damage.

Here, we provide atomic-scale structural information about these sites and the surrounding lattice while minimizing knock-on damage by performing electron ptychography with a 30 keV probe. We use a platinum group metal (PGM)-free catalyst as a model system that contains iron sites embedded in a graphitic network. These catalysts have the potential for enabling low-cost, commercially viable hydrogen fuel cells and electrolyzers, and understanding their active site structure is critical for controlling degradation [6]. To establish the range of safe beam energies for imaging PGM-free catalyst active site structures, we developed a combined *ab initio* molecular dynamics–density functional tight-binding (AIMD-DFTB) method to calculate knock-on displacement threshold energies (KODTE) of proposed structures at finite temperatures (Fig. 1a). Using typical instrument and acquisition parameters, these calculations were then converted to cumulative probabilities for knock-on damage to occur during an acquisition (Fig. 1b). Based on these results, a 30 keV probe minimizes knock-on damage for even the most sensitive sites.

Experimentally, we find good agreement with these calculations. Figure 2a-b shows annular dark-field (ADF) imaging of a metal site embedded in a PGM-free catalyst with a 60 keV probe. While these images reveal metal atom positions and some information about the surrounding lattice, acquisitions result in knock-on damage at the site, rapidly resulting in removal of the metal atom. As shown in Fig. 2c-d, ptychography at 30 keV minimizes residual probe aberrations [7-10] sufficiently to produce atomic-scale images of the metal sites and surrounding lattice, while also minimizing structural modifications during acquisition. The increased understanding that 30 keV electron ptychography techniques will therefore provide about the atomic structure of these sites will accelerate design of a host of low-cost and high-performance catalyst materials [11].

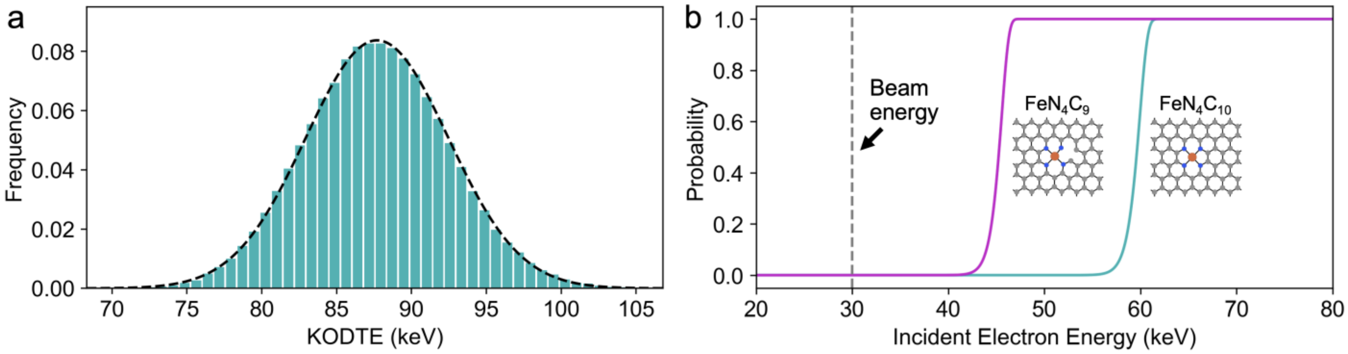

Figure 1. Knock-on displacement threshold energy (KODTE) calculations from the combined AIMD-DFTB method. (a) At a finite temperature, thermal lattice vibrations result in a spread of damage probabilities, rather than a well-defined KODTE. Here, KODTEs for various initial atom positions and velocities are shown for an FeN_4C_{10} structure at 300 K. (b) Using typical acquisition parameters, these distributions are converted to a cumulative probability of knock-on damage occurring during a given dataset acquisition. Here, an FeN_4C_{10} structure has approximately a 50% chance of damaging when using a 60 keV probe, while a site with a neighboring defect, FeN_4C_9, damages at significantly lower energies. To avoid knock-on damage for a variety of structures, we use a 30 keV probe for our experiments.

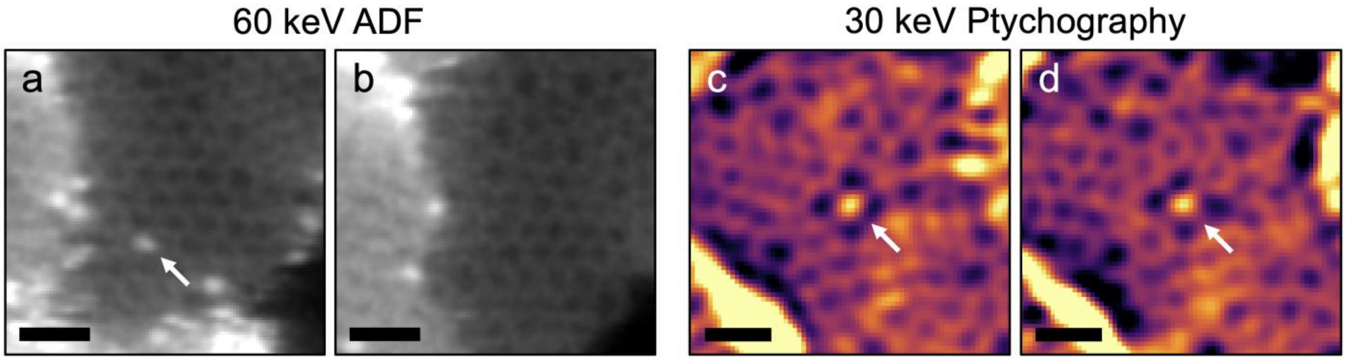

Figure 2. Comparison of 60 keV annular dark-field (ADF) imaging and 30 keV ptychography results. (a) ADF clearly reveals information about the metal atoms and some information about the surrounding structure. (b) Repeated acquisition shows that the 60 keV probe readily alters the structure, however, in this case resulting in removal of the metal atom from the site. (c-d) Ptychography performed at 30 keV enables high signal-to-noise ratio atomic-scale imaging of the metal site and surrounding lattice by minimizing residual probe aberrations. In this case, repeated acquisitions to not significantly alter the structure surrounding the metal atom. Note that slow etching of graphitic basal plane edges does occur at the vacuum level of the STEM instrument, which can alter strain in the lattice and eventually modify the structure around the metal site. Scale bars, 5 Å.

References:

[1] T Zheng et al., Joule **3** (2019), p. 265.
[2] Y Xue et al., Nat. Commun. **9** (2018), p. 1460.
[3] H Zhang et al., Energy Environ. Sci. **12** (2019), p. 2548.
[4] HT Chung et al., Science **357** (2017), p. 479.
[5] Z Gao et al., Top. Catal. (2022).
[6] U Martinez et al., Adv. Mater. **31** (2019), p. 1806545.
[7] JM Rodenburg and RHT Bates, Philos. Trans. R. Soc. London. Ser. A **339** (1992), p. 521.
[8] H Yang et al., Nat. Commun. **7** (2016), p. 12532.
[9] CM O'Leary et al., Ultramicroscopy **221** (2021), p. 113189.
[10] T Pennycook et al., Microsc. Microanal. **25**(S2) (2019), p. 2684.
[11] Research sponsored by the Hydrogen and Fuel Cell Technologies Office, Office of Energy Efficiency and Renewable Energy, US Department of Energy (DOE). Electron microscopy was conducted at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility.