Imaging Catalyst Structure and Durability at the Atomic Scale

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A key feature of catalyst aging is the increasing inhomogeneity in the size and structural distributions of catalyst nanoparticles. The thousand-fold increase in electron energy loss spectroscopy (EELS) mapping speeds over conventional microscopes allows us to collect data from millions of spectra. Experiments that were previously unthinkable, requiring days of microscope time can now be performed in under an hour, allowing us to obtain atomic-resolution chemical structure in individual nanoparticles (Fig. 1), yet record a statistically significant sample from an inhomogeneous population [1,2]. This allowed us to map hundreds of Pt-Co nanoparticles to show atomic-scale elemental distributions across different stages of catalyst aging in a proton-exchange-membrane fuel cell and relate Pt-shell thickness to treatment, particle size, surface orientation, and ordering. Nanoparticle systems—especially during electrocatalysis—are heterogeneous and have multiple competing processes running in parallel. Thus, identifying and quantifying dominant mechanisms requires statistics on scores to hundreds of particles in order to reliably connect the microstructure to the bulk properties. Particle coarsening is the dominant degradation chemistry that limits the catalyst's efficiency. While Ostwald ripening and coalescence are traditionally viewed as independent and often competing coarsening mechanisms, we find Ostwald ripening of the Pt shell occurs more rapidly on coalesced particles, suggesting that controlling coalescence could also slow the Ostwald ripening rate, and hence slow the degradation of catalytic activity [1].

Electron tomography allows us to reconstruct the tortuous 3D nature of dealloyed catalysts [3]. To directly visualize the underlying processes responsible for the loss of electrocatalytic activity in the cathode as a first step we also applied electron tomography to track, in three-dimensions, the trajectories and morphologies of each Pt-Co nanocatalyst on a specially labeled fuel cell carbon support (Fig 2b,c) [4]. For real time studies of electrochemical aging, we are developing in-situ liquid flow-cells for the electron microscope with micropatterned electrodes to image catalyst aging at the nanoscale during electrochemical cycling.[5]

References:

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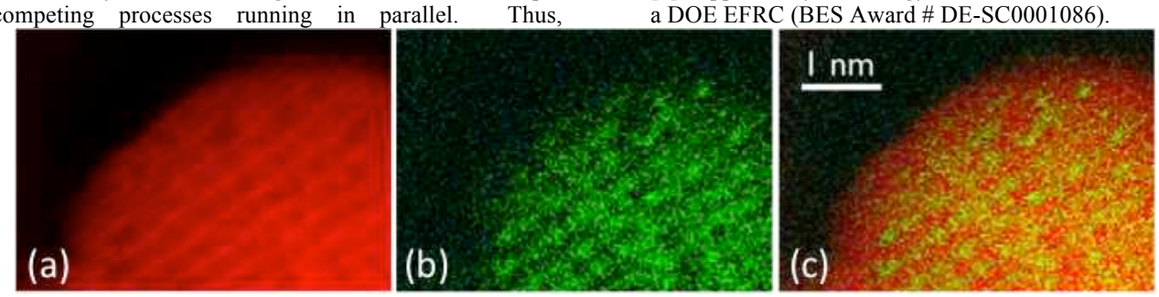

FIG. 1. Atomic Resolution EELS of an ordered Pt_3Co Nanoparticle (a) Simultaneous HAADF STEM tracks the Pt concentration (100% Co would be a 16% correction) (b) Co $L_{2,3}$ EELS map (c) Overlay reveals a 3ML Pt-rich shell [2]

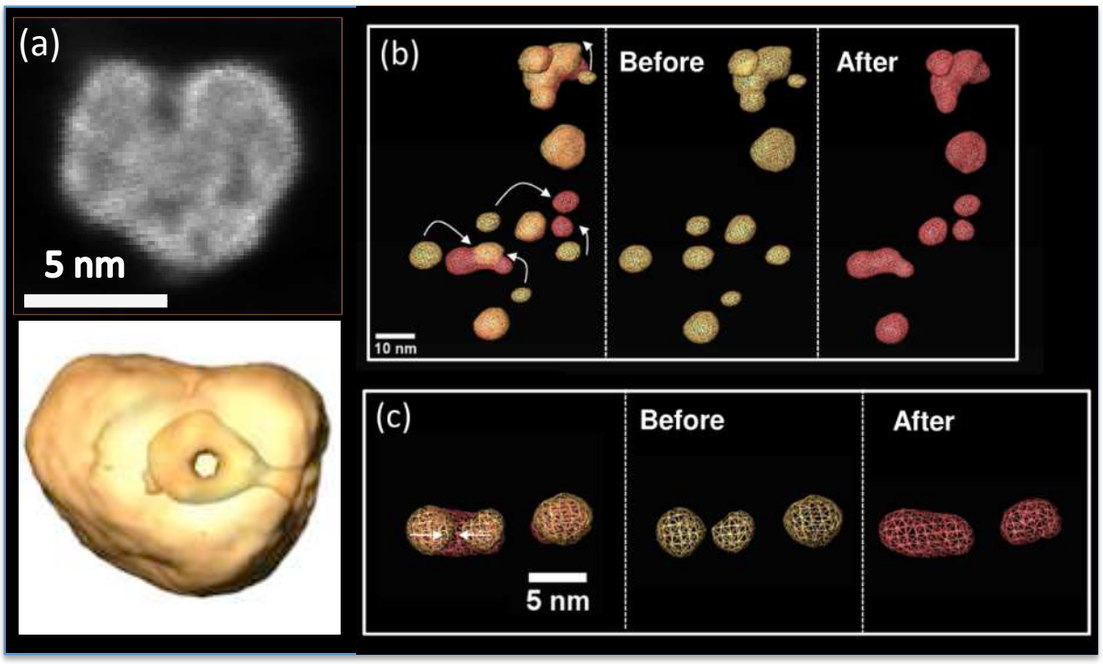

FIG. 2. Electron Tomography reconstruction of catalyst nanoparticles. (a) 3D Reconstruction of a Spongy PtCo3 particle after dealloying, where a cross-section (top) shows the Pt-rich skin around leached regions and (bottom) the connection of internal voids to the surface, arguing for a surface-driven dealloying process [3]. (b)-(c) 3-D electron tomography reconstruction of Pt_3Co nanoparticles before (*gold*) and after (*red*) 30,000 electrochemical cycles. Nanoparticle migration and coalescence are labeled with white arrows [4].