

## Spectroscopic Imaging of a Statistically Significant Ensemble of Pt-Co Nanoparticles by Aberration Corrected STEM

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The proton exchange membrane fuel cell is a promising alternative to the use of fossil fuels to power automobiles as it uses hydrogen fuel and oxygen to form water as the only byproduct. However, the drop in the oxygen reduction reaction (ORR) activity with continued operation currently precludes fuel cells from meeting the DOE targeted lifetime [1]. Currently Pt-based nanoparticles are the most effective catalysts for the ORR; combination with other transition metals, such as Co, provides a further enhancement in the catalytic activity [2]. Here we show that particle coalescence during voltage cycling is an important coarsening mechanism leading to this well-documented loss of catalytic activity. To do so, we collected over one million electron energy loss spectra (EELS) with an aberration-corrected scanning transmission electron microscopy (STEM) to construct 2-D spectroscopic images of the Pt and Co distributions in hundreds of nanoparticles. This unprecedented quantity of data allowed us to perform a chemical exploration of an ensemble of nanomaterials with atomic resolution and draw statistically significant conclusions from the heterogeneous ensemble.

We investigated the Pt-Co nanoparticles using a Nion 100KeV 5th-order aberration-corrected STEM ( $\alpha_{\max} = 33$  mrad) with high spatial resolution ( $\sim 1\text{\AA}$ ), high beam current and high collection efficiency for EELS. With nearly 300 pA of usable beam current, a 64 x 64 pixel spectrum image that readily shows the Pt  $N_3$  and Co  $L_{2,3}$  edges can be recorded in under 10 minutes and larger maps (e.g. 150 pixel by 150 pixel) in approximately 40 minutes.

We first map the particles as received from the commercial supplier. As shown in Fig. 1a, there is an approximately three atomic layer thick ( $0.77\pm 0.02\text{nm}$ ) Pt-rich shell surrounding a Pt-Co core. Following voltage cycling in the fuel cell (Fig. 1b, Fig. 2b), we find a significant divergence from the relatively homogenous population of the as-received sample (Fig. 2a). In particular, many particles exhibit multiple Pt-Co cores enclosed in a Pt-rich shell, indicating that particle coalescence is an important sintering mechanism. There is also a strong dependence of the Pt-rich shell thickness on the particle size as shown in Fig. 2c. When as-received particles undergo a high temperature anneal, the Pt-rich shell is absorbed into the particle (Fig. 1c). However, we find the preferential segregation of an atomically thin Pt-rich skin on the [111] crystallographic facet (Fig. 3a), the first such chemical identification. Finally, when these particles are subjected to an acid treatment to mimic the environment of the cathode, the Pt-rich shell of the as-received sample is restored (Fig. 1d) with no facet dependence (Fig. 3b). [3]

1. M. Watanabe. *J Electrochem Soc* 141, 2659 (1994).

2. V. R. Stamenkovic et al. *Nature Materials*, 6, 41 (2007).

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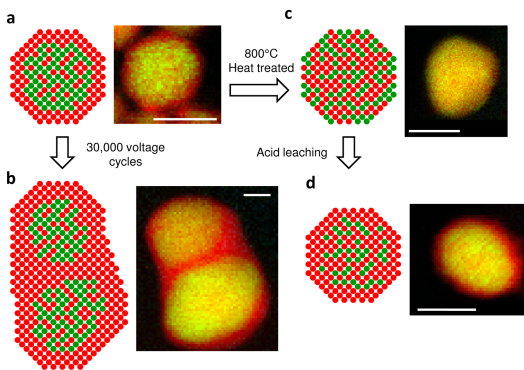


FIG. 1. Four typical EELS spectroscopic images of Pt-Co particles from (a) as-received, (b) 30,000 cycled, (c) heated treated and (d) heat treated and acid leached samples respectively. The relative Pt concentration is shown in red and the Co concentration in green. The scale bar for each image is 5 nm.

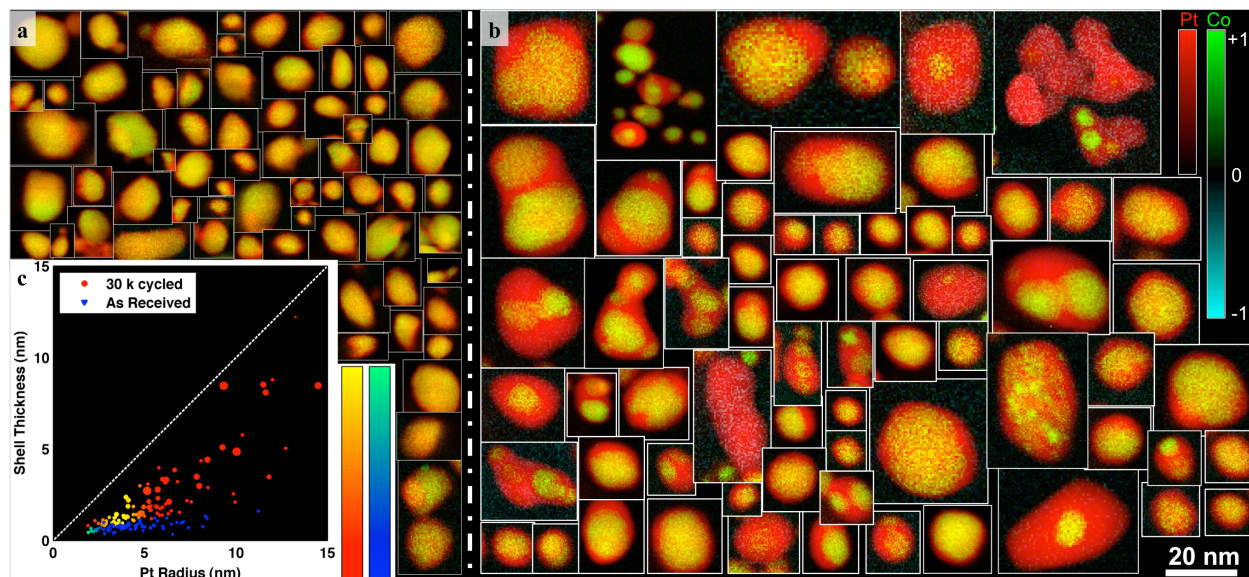


FIG. 2. Collage of the EELS Spectroscopic Images collected from the (a) as-received and (b) the voltage cycled sample. The relative Pt concentration is plotted in red and the Co concentration ranging from green to turquoise. Only a selection of particles is shown due to space constraints. c) Comparison of the mean Pt-rich shell thickness with the mean Pt radius for the particles in (a) and (b). The color of the marker indicates the area-normalized probability of the particle occurrence with yellow and green most likely for (a) and (b) respectively. A larger marker signifies a greater number of distinct Co cores.

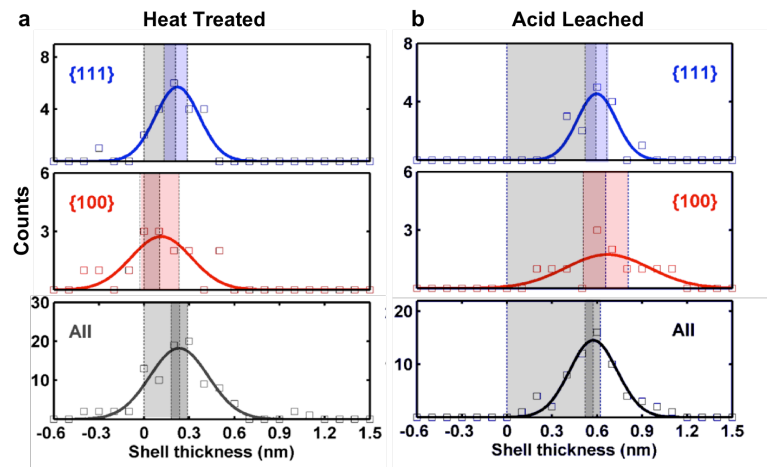


FIG. 3. The facet dependence of the Pt-rich shell thickness of (a) the heat-treated sample and (b) the acid-leached sample. The left and right boundaries of colored shaded area marks the two standard error of the mean (95.4% confidence interval) and the boundary of the gray shaded area marks the average shell thickness.