Correlating Surface Strain with Activity in Commercial Platinum Catalysts

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The introduction of another species, usually a transition metal or lanthanide, into platinum to form a bimetallic particle of composition causes expansion or contraction of Pt-Pt bond distances, altering the electronic structure of the nanoparticle surface and thus its performance of as a catalyst. Based on this principle, alloyed platinum nanoparticles are employed as highly efficient electrocatalysts for the oxygen reduction reaction (ORR) that underpins the operation of hydrogen fuel cells [1]. The catalytic activity of such particles is highly dependent on their composition and structure, with the relationship between performance and activity across alloys of different elements typically presented as a volcano plot. Strain is typically measured non-locally, for example using X-ray diffraction (XRD) to measure the average Pt-Pt over thousands of individual particles. However, the small size of particles ($1 - 2$ nm) and non-uniformity of true commercial catalyst distribution means the XRD-measured strain may not be precise enough to establish a solid structure-performance dependence.

In this work we use high-resolution scanning transmission electron microscopy (STEM) to gain new insights into the localization of strain in a range of commercial platinum alloyed nanoparticles Pt_3M/C (where M = Co, Fe, Ni, Cr, Cu, Sn). The nanoparticles range between $0.5 - 5$ nm in radius and are dispersed on a carbon black support (Fig. 1A). A probe-corrected STEM (sub-Ångstrom resolution) in high-angle annular dark field (HAADF) mode enables visualization of the atomic columns of each nanoparticle, with no apparent variation in contrast between columns confirming the presence of a solid solution (Fig. 1B). To ensure that the pristine nanoparticles are representative of the working catalysts, imaging of acid-treated and post-cycling particles was performed, revealing minimal structural and compositional change.

To investigate possible localized strain that may be beyond the sensitivity of XRD, we perform strain mapping on high-resolution STEM micrographs. This was achieved through a set of preprocessing steps (stack alignment, Wiener filter and Fourier filtering), followed by identification of atomic column positions using atomap [2] and subsequent measurement of the nearest neighbor columns for each position (Fig. 1C). In order to establish a metric for the proximity of a specific atomic column to the surface of the nanoparticle (in the x-y plane), we label each column with a layer index (Fig. 1D). Comparing these metrics across approximately 10-20 particles of each of the six alloys, in addition to the pure Pt/C nanoparticle, reveals a small positive strain at the surface of the nanoparticles that rapidly drops off with increasing layer depth. The relation is shown for a representative Pt_3Co/C nanoparticle in Figure 2A.

Using this distribution, the volcano plot for these specific Pt_3M/C alloys can be refined by establishing a layer depth threshold. Considering all atomic columns, the strain in the alloys measured via STEM is in close agreement with our XRD data, where the polycrystalline Pt activity is excluded from even the most general trends. However, considering only atomic columns from the outermost layers, to which oxygen is chemisorbed during reduction, a qualitatively better fit is obtained with the theoretical values

predicted in literature, as well as the experiment polycrystalline value (Fig. 2B).

We expect that this methodology, where the relative position of atoms within a nanostructure can be indexed and correlated with physical or chemical measurements, will be useful for future studies concerning surface kinetics and may serve as an auxiliary technique to the typical bulk analysis of nanostructures.

References:

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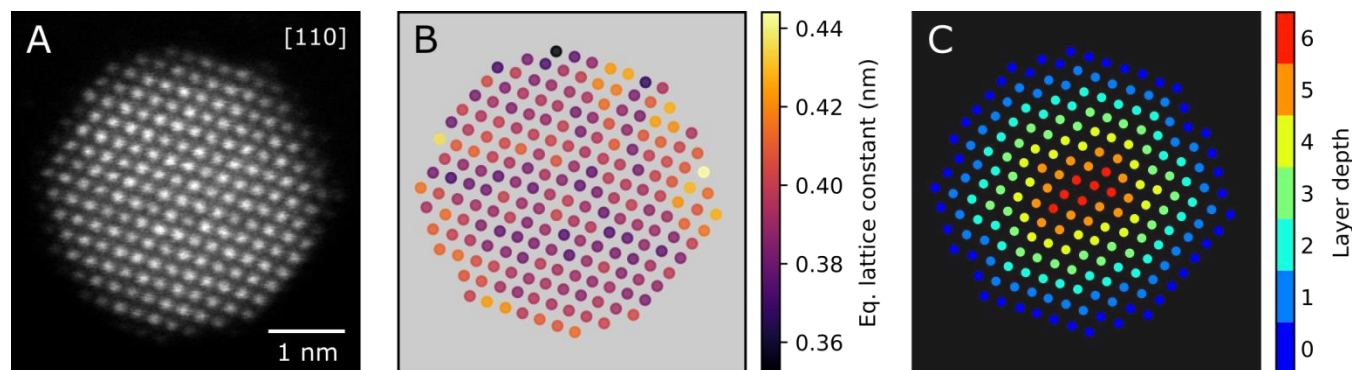
Figure 1. Strain mapping and layer labelling for a representative Pt_3Co/C nanoparticle. A) Experimental HAADF-STEM micrograph, B) map of equivalent lattice constant computed from Pt-Pt distances, C) layer depth labels
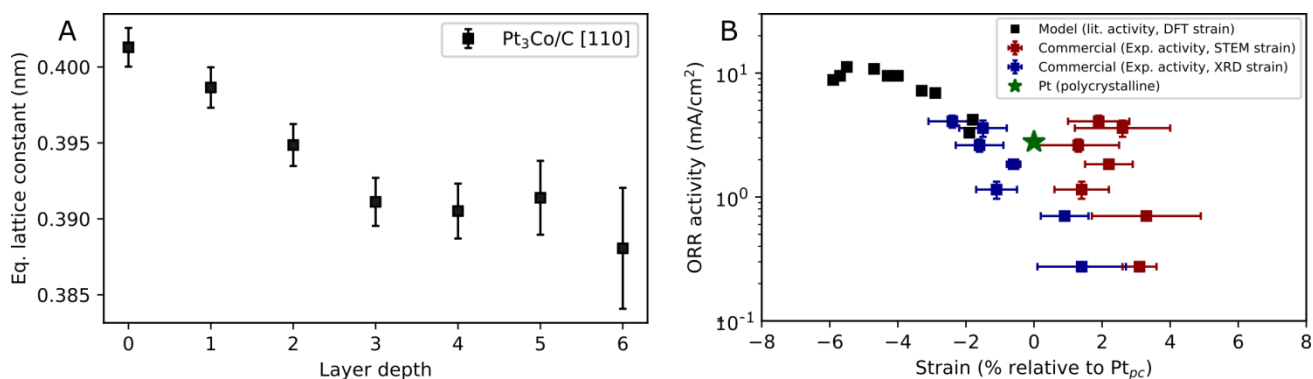

Figure 2. Correlation of strain and position relative to the nanoparticle surface. A) Equivalent lattice constant vs. layer depth for the nanoparticle in figure 1. B) Refined volcano plot incorporating data from model catalysts in literature (strain computed via DFT) [3] and commercial catalysts (strain measured by XRD and STEM). Only atomic columns at the surface (layer depth ≤ 1) are considered for the STEM data.