Structural Evolution and Lattice Strain Measurements of Electrochemically Cycled Pt_3Fe_2 Nanocatalysts Using Scanning Transmission Electron Microscopy

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Platinum based structurally ordered intermetallic coreshell nanocatalysts have been very recently found to exhibit enhanced catalytic activities and longevity in Polymer Electrolyte Membrane Fuel Cell (PEMFCs) applications with respect to their disordered counterparts.[1] A new class of ordered nanocatalysts based on the Pt_3Fe_2 structure, has shown a remarkable increase in its mass activity(229%) and specific activity(156%) when compared to pure platinum.[2] Also, studying their structural ordering and lattice contraction over progressing electrochemical cycles is highly critical in order to address their longevity in PEMFCs. We achieved this by characterizing both electrochemically cycled and non-cycled Pt_3Fe_2 nanocatalysts using aberration corrected scanning transmission electron microscopy(STEM) in an high angle annular dark field(HAADF) imaging mode. STEM-HAADF is found to be an effective imaging technique to characterize platinum based nanocatalysts for PEMFC applications.[3]

From our experiments and image simulations we infer that these nanoparticles exhibit an increased longevity because of their sustained structural ordering even after 10000 electrochemical cycles (Figure 1). However, their catalytic activity suffered a non-linear decrease over each progressing cycle.[2] Our observations indicate that the particles become spherical after 10000 cycles whereas those that are non-cycled remained mostly faceted. The loss of nanofacets is primarily due to redeposition of platinum possibly by Ostwald ripening. This is further confirmed by their HAADF-STEM images which reveal a platinum shell thickening (≈3ML) after 10000 cycles. In addition, we observed an increase in their average particle size after cycling resulting in a decrease in the surface area to volume ratio leading to a reduced mass activity.

The increase in the lattice strain lowers the d-band center of the nanoparticle leading to poorer adsorption of oxygenated species on the catalyst surface and hence improving their ORR activity.[4] We attribute such an enhancement in the catalytic activity of Pt_3Fe_2 nanocatalysts to their ordered intermetallic cores and an increased lattice strain(calculated to be 3.95%) from that of pure platinum. Lattice strain on electrochemically cycled and non-cycled nanoparticles is mapped (Figure 2) and the effect of strain on the catalytic activity will be discussed.

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References

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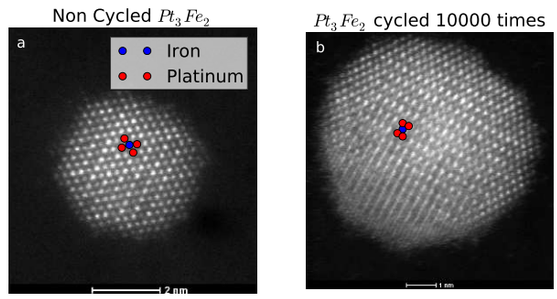

Figure 1 HAADF-STEM images of (a) non-cycled and (b) electrochemically cycled Pt_3Fe_2 catalyst nanoparticle clearly showing the sustained structural ordering visible through alternating bright and dark atomic columns. However, this effect is absent in the outer platinum shell in the case of a cycled particle(b) demonstrating a redeposition of platinum possibly by Ostwald ripening.

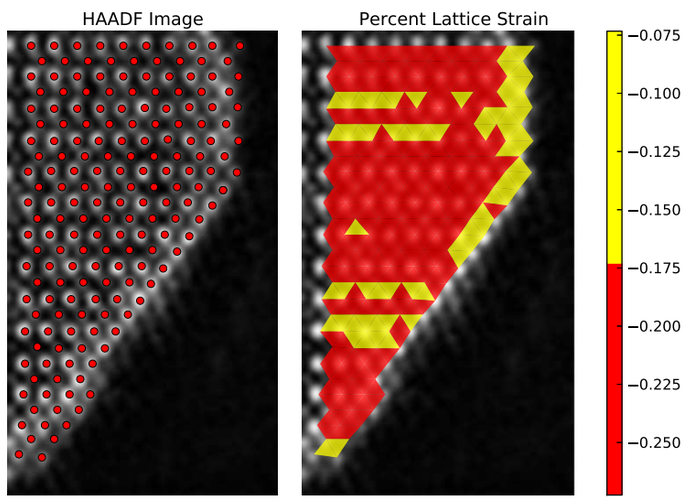

Figure 2 Atomic resolution lattice strain mapping of non-cycled Pt_3Fe_2 catalyst nanoparticle. It is evident that the ordered intermetallic core is at relatively high strain compared to that of the Pt rich shell. The colorbar indicates the calculated percentage lattice strain with respect to a pure platinum lattice.