

Understanding Pt-Co Catalyst Degradation Mechanism: from *Ex-situ* to *In-situ*

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The design of the next generation of electrocatalysts for the oxygen reduction reaction (ORR) is a key step for commercializing proton-exchange membrane fuel cells (PEMFCs). Of particular interest is to understand the degradation mechanism of the electrocatalysts, which generally undergo coarsening and lowers their active surface area. Despite long-standing interest in this mechanism, there has been no definite conclusion of what the coarsening mechanism is - whether it is Ostwald ripening or coalescence, perhaps due to a lack of suitable techniques that can track catalysts under operating conditions. Here we study the coarsening of Pt-Co electrocatalysts with the scanning transmission electron microscope (STEM), using *ex-situ* techniques such as aberration corrected electron energy-loss spectroscopy (EELS) and 3-D electron tomography, and an *in-situ* technique employing a electrochemical liquid cell holder.

By engineering a stable intermetallic phase, we have developed an ordered Pt₃Co nanostructure, which exhibits better catalytic efficiency and durability than a disordered alloy. Aberration-corrected EELS imaging has revealed that such Pt₃Co nanocomposite is composed of an ordered core, with about 3 monolayers of Pt on the surface (Fig.1a), which contribute to the improved catalytic activity and higher stability [1]. Using a labeled TEM grid as an electrode, we have directly tracked over 300 Pt₃Co nanoparticles at the nanoscale, with one-to-one correspondence before and after electrochemical cycling [2]. To understand how these particles are transformed during cycling, electron tomography is used to visualize the particle structure changes in 3-D, enabling the reconstruction of the same locations of Pt₃Co. From these *ex-situ* studies, we have discovered that nanoparticle migration and coalescence have played important roles leading to the loss of surface area and eventually the degradation of catalytic activity (Fig. 1b-c).

To further explore the Pt₃Co coarsening mechanism, we have developed an *in-situ* imaging technique using an electrochemical liquid flow holder custom built by Protochips. Here we demonstrate the cyclic voltammetry (CV) of Pt nanoparticles inside electron microscope in 0.1M H₂SO₄ during imaging (Fig. 2a), which qualitatively matches *ex-situ* behavior. This provides the groundwork for performing quantitative electrochemistry under *in-situ* conditions. We then image the Pt₃Co coarsening (Fig. 2b), where a constant voltage of +1.0V (vs. Pt) is applied. After 38s, carbon support corrosion begins at the 'neck' of two carbon assemblies, where the current density is highest. As a result, nanoparticles start to migrate on the surface, followed by sintering events (86s-260s). Additionally during voltage cycling we observe the coarsening process, shown in the false-colored image in Fig. 2c, where multiple Pt₃Co move toward each other (66 cycles) and merge (132 cycles). During these studies, we ensure that the electron beam does not affect the nanoparticles without cycling on the time scale of the electrochemical experiments. While further studies are necessary, we have observed coarsening events are caused by particle coalescence. These results from *in-situ* experiments are consistent with our discovery from *ex-situ* 3-D electron tomography, suggesting that stabilization of catalyst support, minimization of nanoparticle movement or reduced loading are potentially valuable for slowing down the degradation of PEMFCs system. [3]

References

- [1] D. Wang, *et al.*, *Nature Materials*, 12 (1), 81-87, 2013
 [2] Y. Yu, *et al.*, *Nano Letters*, 12 (9), 4417-4423, 2012
 [3] Work Supported by the Energy Materials Center at Cornell, a DOE EFRC (BES Award # DESC0001086).

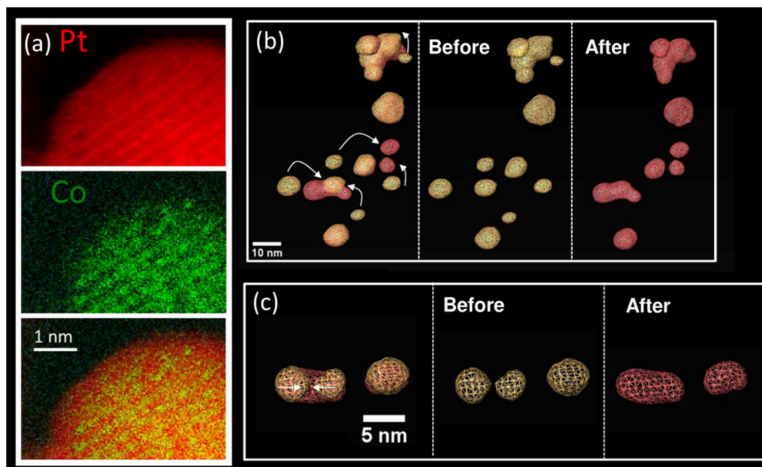


Fig. 1. *Ex-situ* study. (a) Atomic resolution EELS mapping of an ordered Pt₃Co intermetallic nanoparticle, with the simultaneously recorded ADF image representing Pt due to Z-contrast (red), Co L_{2,3} (green) and overlay of Pt and Co. About 3 monolayers of Pt are found on the surface. (b)-(c) 3-D electron tomography reconstruction of Pt₃Co nanoparticles before (golden) and after (red) 30,000 electrochemical cycles during the operating conditions of PEMFCs. Nanoparticle migration and coalescence are observed and are accountable for the loss of activity.

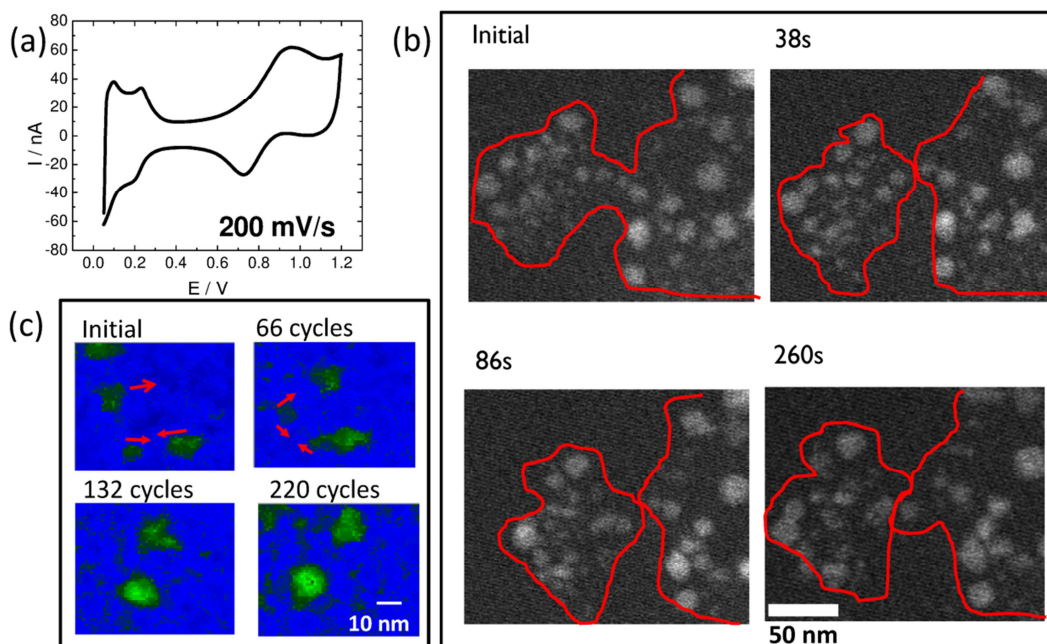


Fig. 2. *In-situ* study. (a) Cyclic voltammetry (CV) of Pt nanoparticles on a carbon working electrode in 0.1M H₂SO₄ at a scan rate of 200 mV/s. The CV curve is performed inside electron microscope during imaging. (b) Time-resolved HAADF images of Pt₃Co at a constant voltage of +1.0 V (vs. Pt), with a red curve highlighting the boundary of the carbon support. We observe nanoparticle migration and coalescence assisted by carbon support corrosion during the electrochemical aging. (c) Coalescence behavior of Pt₃Co, as a function of cycles. False-color is used to enhance contrast.