

***Operando* Electron Microscopy of Electrochemically Driven Structural Changes in Nanoparticle Catalysts with Controlled Size**

Serin Lee¹, Frances M. Ross^{1*}

¹ Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, U.S.A.

* Corresponding author: fmross@mit.edu

The need to reduce fossil fuel dependency has driven materials development for rechargeable batteries, fuel cells, electrochemical capacitors, hydrogen storage and production, and the electrocatalytic CO₂ reduction reaction [1]. Catalyst selection plays a central role in each electrochemical energy conversion process to speed up the reaction rate and therefore improve efficiency [2]. Catalysts composed of nanoparticles (NPs) with their high surface to volume ratio are the first choice for many reactions, some of the best-known being noble metal-based nanoparticles. Pt-based catalysts are widely used in fuel cells, including for the hydrogen oxidation and oxygen reduction (ORR) reactions for proton exchange membrane fuel cells (PEMFCs) [3]. Pt-based catalysts are also utilized in direct methanol and ethanol fuel cells for the alcohol oxidation reaction and ORR at the cathode [4],[5].

Catalyst performance and lifetime depend on both high surface reactivity and stability to deactivation under the operating conditions. Catalyst deactivation is a complex process that can proceed through several pathways and depends on temperature, gas pressure, liquid composition, support material, applied potential and nanoparticle shape, composition and size distribution [2]. Pt-based catalysts, for example, deactivate through a combination of processes including dissolution and diffusion. These lead to a loss of smaller particles to reduce the total system surface energy (electrochemical Ostwald ripening [6]) that results in fading of the performance. Understanding the mechanism and kinetics of deactivation processes can help efforts to develop catalysts with superior performance and lifetime.

We describe changes in the morphology of nanoparticle catalysts under operating conditions imaged using liquid cell transmission electron microscopy with heating and biasing capability. To obtain quantitative measures of structural change we use ensembles of relatively large particles with well-defined size distributions. Electrochemical structural changes and growth kinetics at controlled temperature provide operando probing of nanoparticle stability. In particular, we focus on 60-80°C, the operating temperature of PEMFC using Pt nanoparticle catalysts, and 0.1M perchloric acid electrolyte. During repeated pulsing or cyclic voltammetry, we measure the evolution of particles with unimodal and bimodal size distributions to tune the strength of the Ostwald ripening during cycling. Measurement of particle positions, sizes and thickness (via image intensity) on videos enable volume to be tracked for each particle and coalescence events to be analyzed.

Figure 1 shows structural changes in Pt nanoparticles that have unimodal and bimodal size distributions after cycling over a voltage window of -1.0V to 1.0V. For the unimodal case, some of the particles near the working electrode show traits of coalescence. Dendritic morphology near the working electrode suggests diffusion limited growth from dissolved Pt ions during the experiment. The bimodal nanoparticles showed dendritic growth near the counter electrode as well as hints of Ostwald ripening, and structures such as the bridge formed between two nanoparticles near the working electrode. The behavior at the working and counter electrodes appeared to depend on cycling voltage, as shown in

Figure 2. Cycling at lower voltage window, -0.4V to 0.4V , showed more dendritic growth near the working electrode, whereas particles near the counter electrode did not show distinct structural changes. More verification on the potential effect of dissolved ion from the Pt electrode on the growth of Pt nanoparticles is needed, but these results suggest that the cycling voltage may be used to emphasize different modes of morphology change. We will also introduce temperature control to observe electrochemical structure changes under more realistic conditions, interpreting the results using our understanding of the temperature effect on the concentration of electron beam-induced radiolysis species and the ions reacting with those species in the electrolyte.

This study will contribute to understanding the deactivation mechanism of nanoparticle catalysts under operating conditions by quantifying the electrochemically induced structural evolution as a function of parameters including temperature and size distribution. We are excited to apply the findings from liquid cell microscopy to provide insights to design catalyst materials with improved performance [7].

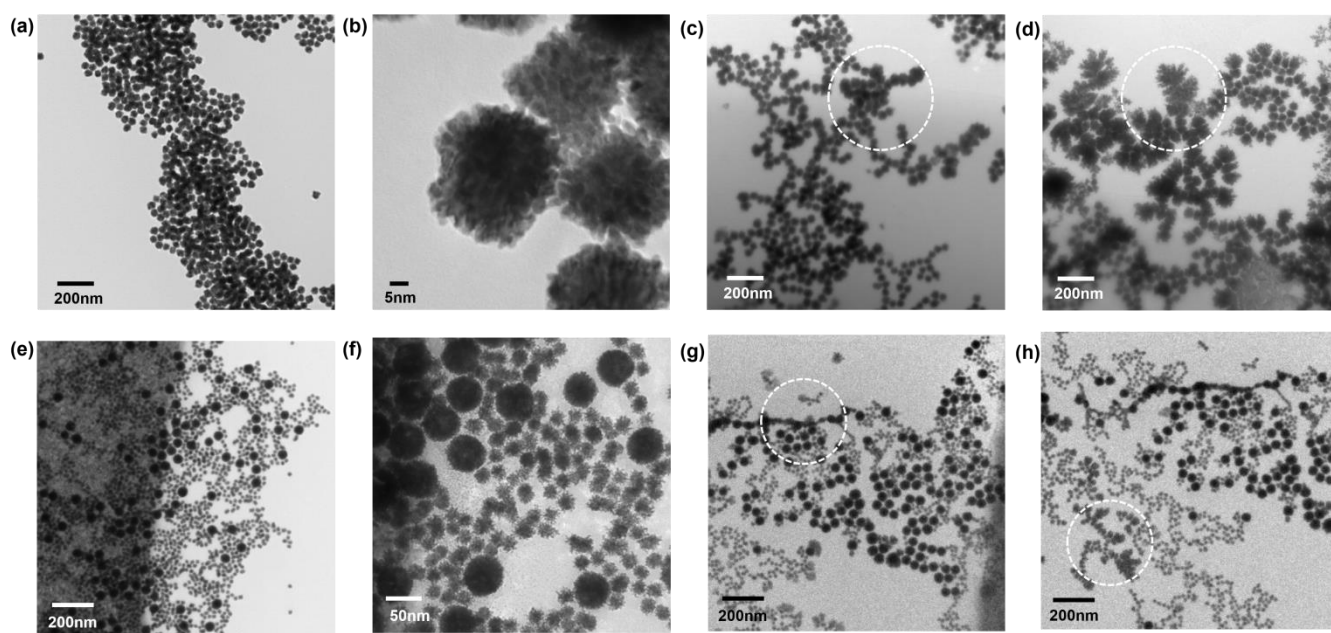


Figure 1. Electrochemical cycling of unimodal (a-d) and bimodal (e-h) Pt nanoparticles over a voltage window of -1.0V to 1.0V , before (a, b, e, and f) and after (c, d, g, and h) cycling. Note the irregular initial surface of the particles. (c) shows coalescence and dendrite growth near the working electrode, starting from the network of unimodal nanoparticles, and (d) shows dendrite formation of unimodal particles on the electrode surface. (g) shows coalescence and dendrite growth near the working electrode, starting from the network of bimodal nanoparticles, and (h) shows dendrite formation of bimodal particles on the electrode surface.

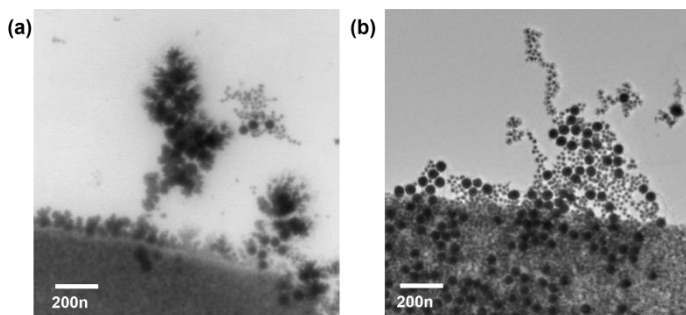


Figure 2. Electrochemical cycling of bimodal Pt nanoparticles over a voltage window of -0.4V to 0.4V. (a) shows particles near the working electrode, and (b) shows particles near the counter electrode.

References:

- [1] J. R. Varela et al., *J. Mater. Res.* **2021**, *36*, 4071.
- [2] S. Hwang et al., *Adv. Energy Mater.* **2020**, *10*, 1.
- [3] A. H. Ramírez et al., *J. Mater. Res.* **2021**, *36*, 4192.
- [4] B. R. Camacho et al., *J. Mater. Res.* **2021**, *36*, 4227.
- [5] J. R. Rodríguez et al., *J. Mater. Res.* **2021**, *36*, 4216.
- [6] T. J. P. Hersbach et al., *ACS Catal.* **2021**, *11*, 9904.

[7] The authors acknowledge support from Mathworks and Bosch. The opinions and views expressed in this publication are from the authors and not necessarily from MathWorks. This research made use of facilities and instrumentation supported by NSF through the Massachusetts Institute of Technology Materials Research Science and Engineering Center DMR-1419807, as well as facilities at MIT.nano.