

Tracking Degradation in Individual Catalyst Nanoparticles Under Fuel Cell-Relevant Cycling Conditions by Identical-Location STEM

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Reducing carbon emissions calls for a rapid shift from fossil fuels to renewable energy. Hydrogen-powered fuel cell electric vehicles (FCEVs) are a promising technology to reduce carbon emissions, especially for heavy-duty vehicles, which account for more than 20% of transportation emissions [1]. Heavy-duty applications require greater longevity of the key oxygen reduction reaction (ORR) electrocatalyst in proton exchange membrane fuel cell (PEMFC), which has prioritized research and development efforts towards catalysts with high durability [2].

In this work, we employ identical-location scanning/transmission electron microscopy (IL-S/TEM) to understand degradation mechanisms of ORR electrocatalyst for heavy-duty applications. In IL-S/TEM, the catalyst of interest is deposited on a gold TEM grid and undergoes *ex-situ* potential cycling in an aqueous environment to simulate the accelerated stress test (AST) performed in fuel cell membrane electrode assemblies (MEAs) [3]. The same regions of catalyst material are examined before and after cycling, providing direct observations of potential degradation processes such as nanoparticle migration, coalescence, and detachment from the carbon support [4]. Typically, there is a lack of direct correlation between degradation in aqueous solutions and MEA tests performed under similar ASTs, however. Specifically, Ostwald ripening has not been identified as a major contributor to degradation in most prior IL-S/TEM studies [3-5], in stark contrast to what has been observed in MEA tests [6]. To address this, we first aimed to recreate the MEA degradation process in the aqueous environment used for IL-STEM experiments, then used the modified cycling protocol to track the degradation phenomena of individual catalyst particles at the atomic scale.

Typical degradation processes were observed for a traditional Pt/C catalyst (with 2-3 nm Pt particle size) in IL-STEM using the same AST cycling protocol used in MEA tests, which is 30,000 cycles between 0.6 V and 0.95V. However, as shown in Figure 1a-d for a state-of-the-art commercial PtCo/C catalyst with 4-5 nm particle size, almost no change in the PtCo particles was observed using this standard AST protocol. This led to systematic variation of several experimental parameters to resolve the discrepancies between MEA tests and cycling in an aqueous environment. As shown in Figure 1e-h, we found that extending the potential window (to 0.4-1.0V) and incorporating Pt ions in the electrolyte were key factors for driving Ostwald ripening, as evidenced by a relative decrease in the proportion of small versus large particles, combined with trends toward more spherical particle shapes.

With MEA degradation processes reliably recreated in IL-STEM experiments, the evolution of individual PtCo particles can be tracked by aberration-corrected STEM imaging and energy-dispersive X-ray spectroscopy (EDS) to elucidate degradation mechanisms at the atomic scale. Figure 2 shows preliminary results for a single PtCo particle after 30,000 cycles between 0.6V and 1.0V. Since only the upper potential limit was extended compared to the standard potential window, Pt dissolution dominated over redeposition, and a slight reduction of the particle size was observed. The rough edges and steps on the left side of the particle became smoothed and the entire particle became more spherical. EDS maps revealed a thin Pt shell developed after cycling due to Co leaching and Pt redeposition. In this talk, results from additional experiments will be presented, with a focus on differences in degradation rates and mechanisms for particles which reside within versus on the exterior of the porous carbons support. Results from this work will shed light on degradation mechanisms of PtCo catalyst in fuel cell relevant environment and improve the catalyst design for heavy-duty applications [7].

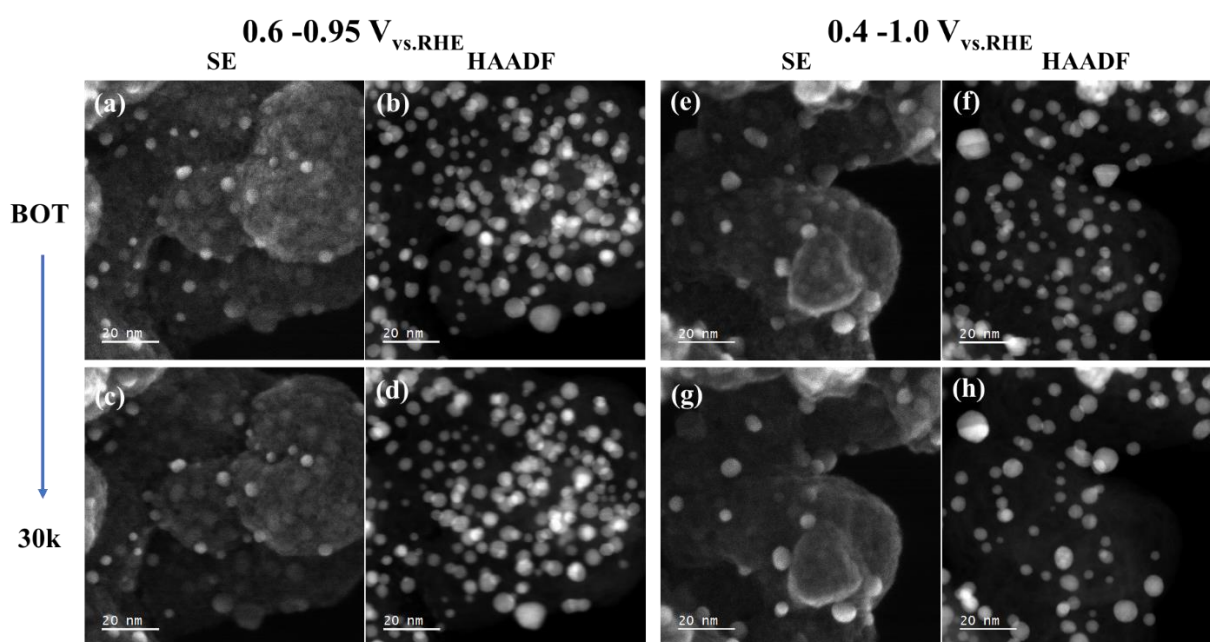


Figure 1. IL-STEM images of PtCo supported on carbon cycled using different potential windows for 30k cycles with Ar-purged H_2SO_4 at 80°C . (a)-(d): cycled between 0.6V and 0.95V; (e)-(h): cycled between 0.4V and 1.0V; (a), (c), (e), (g) are secondary electron (SE) images; (b), (d), (f), (h) are simultaneously-recorded HAADF images. BOT: beginning of test.

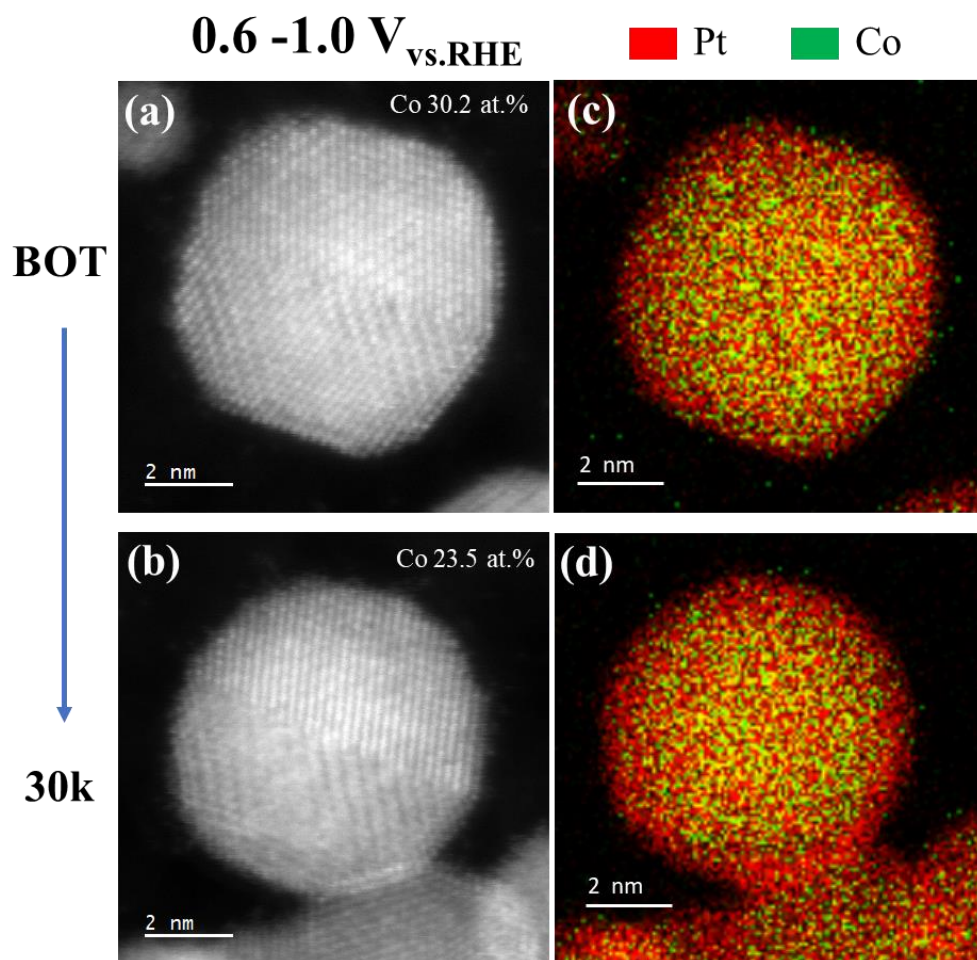


Figure 2. An individual PtCo particle cycled between 0.6V and 1.0V for 30k cycles in Ar-purged H₂SO₄ at 80°C. (a) and (b) are HAADF images at BOT and after 30k cycles, respectively. (c) and (d) are EDS maps of Pt (red) and Co (green) at BOT and after 30k cycles, respectively. The overall Co at.% of the particle decreased from 30.2% to 23.5% after cycling.

References:

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- [7] This material is based on work performed by the Million Mile Fuel Cell Truck (M2FCT) Consortium, technology managers Greg Kleen and Dimitrios Papageorgopoulos, which is supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Technologies Office. Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the

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