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Growth and degradation of octahedral Pt-alloy nanoparticle catalysts for fuel cells

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Octahedral Pt-Ni nanoparticles are highly attractive as fuel cell catalysts due to their extraordinarily high activity for the oxygen reduction reaction (ORR). A deep understanding of their atomic-scale structure, degradation and formation is a prerequisite for their use as rationally designed nanoparticle catalysts with high activity and long-term stability.

Here, we present results from a comprehensive microstructural study of the growth and degradation behavior of various octahedral Pt-alloy nanoparticles using transmission electron microscopy (TEM) and Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX). We show that octahedral nanoparticles often show compositional anisotropy in the form of Ni-rich {111} facets, which lead to complex structural degradation during ORR electrocatalysis. The Ni-rich {111} facets are etched preferentially, resulting in the formation of first concave octahedra and then Pt-rich skeletons that have less active facets [1]. Furthermore, we reveal element-specific anisotropic growth as the reason for the compositional anisotropy and limited stability. During solvothermal synthesis, a Pt-rich nucleus evolves into precursor nanohexapods, followed by the slower step-induced deposition of Ni on the concave hexapod surface to form octahedral facets (Figure) [2]. Whereas the growth of Pt-rich hexapods is a ligand-controlled kinetic process, the step-induced deposition of the Ni-rich phase on the concave surface resembles a thermodynamically-controlled process and is accomplished over a much longer time. Furthermore, we demonstrate how Pt atom surface diffusion may produce a protective Pt surface layer on top of the Ni-rich facets, resulting in advanced and more stable octahedral catalysts. During *in situ* heating up to 800 °C using a microelectromechanical systems (MEMS) chip heating holder (DENSsolutions, Delft, NL), we observed that Pt-rich corner atoms diffuse and fill the concave Ni-rich {111} facets, thereby forming octahedral nanoparticles with flat Pt-rich {111} surfaces [3].

References:

[1] Gan L, Cui CH, Heggen M, Dionigi F, Rudi S, Strasser P, Science 2014; 346: 1502.

[2] Cui CH, Gan L, Heggen M, Rudi S, Strasser P, Nature Materials 2013; 12: 765.

[3] Gan L, Heggen M, Cui CH, Strasser P, ACS Catalysis 2016; 6: 692.

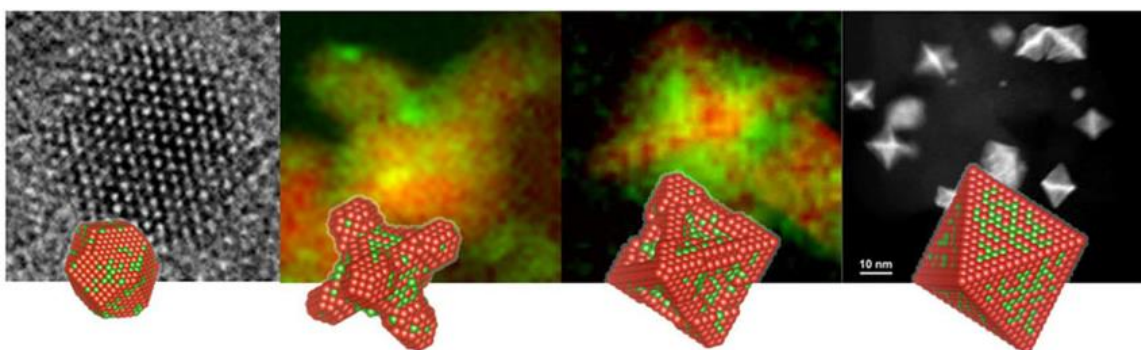


Figure 1. Microstructural study comprising high-resolution TEM, HAADF-STEM and EELS mapping, uncovering an element-specific compositionally-anisotropic growth mechanism of octahedral PtNi nanoparticles. The electron microscopy images and the corresponding models show the elemental distributions of Pt (red) and Ni (green) in particles that are at different states of growth after 4, 8, 16, and 42 hours of solvothermal synthesis.