

Growth and degradation of advanced 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 an extensive microstructural study of the growth and degradation behavior of various octahedral Pt-alloy nanoparticles using in situ 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 with Ni-rich {111} facets leading to complex structural degradation during ORR electrocatalysis. The Ni-rich {111} facets are preferentially etched, resulting in the formation of first concave octahedra and then Pt-rich skeletons that have less active facets (Figure 1)[1]. Furthermore, we reveal element-specific anisotropic growth as the reason for the compositional anisotropy and the limited stability. During the 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)[2]. While the growth of Pt-rich hexapod is a ligand-controlled kinetic process, the step-induced deposition of the Ni-rich phase at the concave surface resembles a thermodynamically controlled process accomplished in much longer time. In order to tune the atomic-scale microstructure of the octahedra for long-term stability, we illustrate the effect of varying the growth conditions on morphology and compositional segregation by producing trimetallic PtNiCo nanooctahedra and comparing "one-step" and newly-developed "two-step" synthesis routes [3]. 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. Figure 3 shows a sequence of structural changes taking place on an octahedral nanoparticle during in situ heating up to 800°C using a MEMS chip heating holder (DENSsolutions, Delft, NL). It can be observed that Pt-rich corner atoms diffuse and subsequently fill the concave Ni-rich {111} facets, forming perfectly octahedral nanoparticles with flat Pt-rich {111} surfaces (Figure 3) [4].

References:

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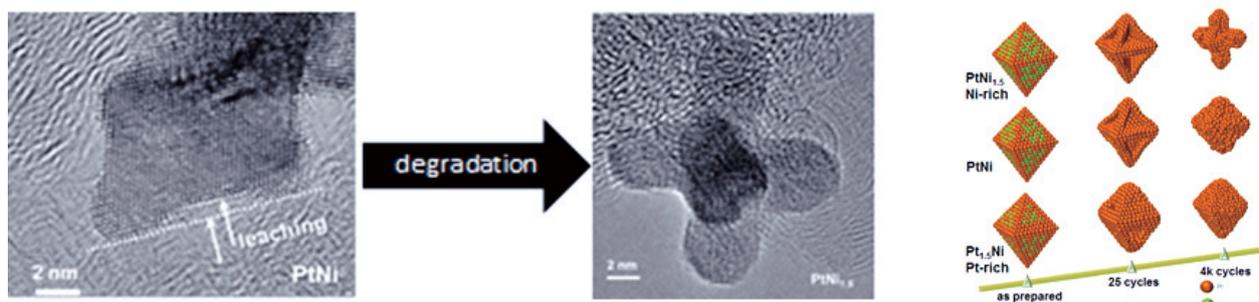


Figure 1: Degradation of octahedral nanoparticles during ORR electrocatalysis. The Ni-rich facets are preferentially etched, resulting in concave octahedra and finally Pt-rich skeletons.

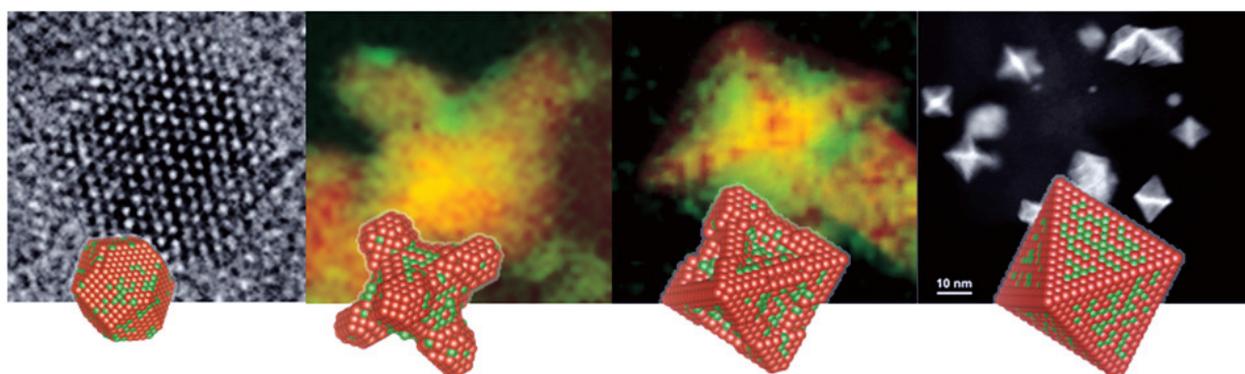


Figure 2: TEM, HAADF STEM and EELS mapping (Pt: red, Ni: green) of the compositionally anisotropic growth of octahedral PtNi nanoparticles after 4, 8, 16 and 42 hours of solvothermal synthesis.

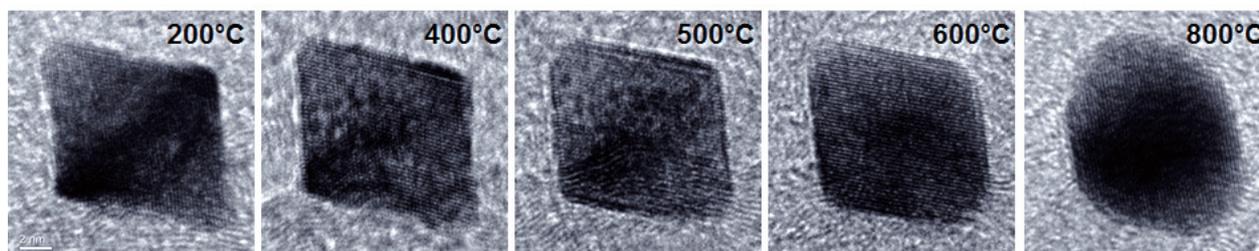


Figure 3: TEM image series of a PtNi octahedral nanoparticle during in situ annealing from 200 to 800°C.