Microstructural investigation of octahedral PtNiRh fuel cell catalyst nanoparticles produced by a new synthesis route

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Advanced octahedral PtNi catalysts with high oxygen reduction reaction (ORR) activities [1-4] and PtNi alloys with high ethanol oxidation reaction (EOR) activities [5] have been reported in recent years. It is well established that PtNi nanooctahedra have extremely high catalytic activities, exceeding those of Pt benchmark catalysts by up to 30 times [6], as a result of the presence of (111) facets. One of the key challenges in the development of such shaped catalysts is to improve long-term stability, i.e., to prevent the loss of the octahedral shapes of the nanoparticles during long-term electrochemical cycling. Previous work has shown that the ORR on octahedral PtNi catalysts leads to the preferential leaching of Ni from the particle surfaces and to the loss of highly active (111)-oriented surfaces, leading to a strong degradation in catalytic activity [4]. These and other theoretical and experimental studies have provided evidence for the strong dependence of catalytic performance on structure and composition and underlined the importance of careful atomic scale microstructural and compositional analysis as a basis for the rational design of active and stable catalysts.

Here, we present a detailed microstructural study of well-defined stable octahedral-shaped PtNiRh alloy nanoparticle catalysts and correlate the elemental distribution in the particles with their shape stability after electrochemical potential cycling. The particles are investigated using high-angle annular dark field (HAADF) imaging in probe-corrected FEI Titan scanning transmission electron microscopes (STEMs) combined with atomic-scale compositional analysis using energy-dispersive X-ray spectroscopy in an FEI TITAN ChemiSTEM equipped with a Super-X detector.

Figure 1 shows HAADF images of representative octahedral particles (a) before and (b) after electrochemical potential cycling. Even after long-term electrochemical potential cycling (30000 cycles), the octahedral shape is still retained. By using a newly modified synthesis route that involves the use of oleylamine, oleic acid and $W(CO)_6$, stable Rh-doped PtNi alloy particles that keep their octahedral shape and high catalytic activity even after long-term cycling are obtained [1,3].

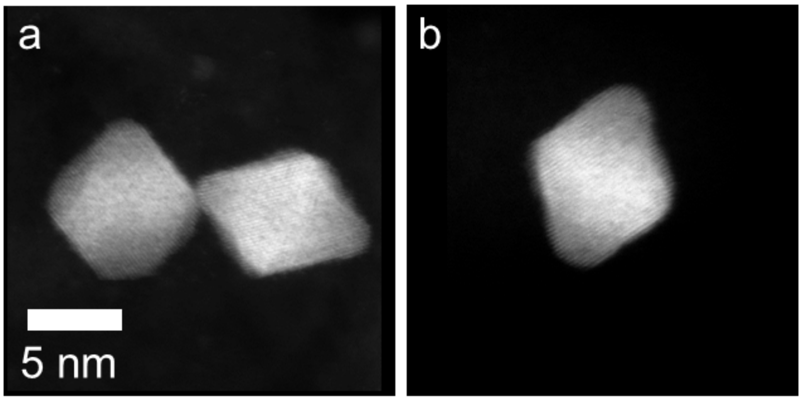

Figure 1: High resolution HAADF STEM images of PtNiRh octahedral nanoparticles after (a) 4 k and (b) 30 k cycles, respectively.

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