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Microstructural investigation of shaped fuel cell catalyst nanoparticles

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The sustainable storage and conversion of energy in fuel cells, Li air batteries and electrolyzers depends strongly on the use of high performance nanoparticle catalysts. The development of stable, highly active catalysts for the oxygen reduction reaction (ORR) at the cathodes of polymer electrolyte membrane fuel cells is a significant challenge. A promising approach to increase catalytic activity is the use of octahedral bimetallic nanoparticles. As a result of the presence of highly catalytically active (111)-oriented surfaces in Pt3Ni [1, 2], they are considered to be “dream electrocatalysts” for the ORR [3, 4]. Recent studies have uncovered an element specific anisotropic growth in octahedral PtNi nanoparticles, taking the form of Pt-rich frames and Ni-rich facets [5, 6]. ORR on such PtNi catalysts leads to preferential leaching of Ni from the particle surface, as well as to the loss of highly active (111)-oriented surfaces and a strong degradation in catalyst activity [5]. These and other theoretical and experimental studies have provided evidence for the strong dependence of catalyst performance on structure and composition and underlined the importance of careful microstructural and compositional analysis on the atomic scale.

Here, we present a detailed microstructural study of well-defined octahedral shaped binary PtNi, PtCo and ternary PtNiCo alloy nanoparticle catalysts, which are grown using different techniques and subjected to different chemical and thermal annealing steps. The particles are investigated using high-angle annular dark field (HAADF) imaging in probe-corrected FEI Titan scanning transmission electron microscopes (STEMs) and atomic-scale compositional analysis using electron energy electron-loss spectroscopy (EELS) and energy-dispersive X-ray (EDX) spectroscopy in an FEI ChemiSTEM equipped with a Super-X detector. The experiments are supplemented by in situ heating experiments performed under environmental conditions at up to 1 bar pressure using a MEMS-based static gas closed cell specimen holder (DENS solutions, Delft, NL).

Figure 1 shows HAADF images and EDX spectrum images records from the octahedral particles during a series of thermal annealing and acidic leaching experiments. Before leaching, structural anisotropy is observed, with Ni-rich (111)-oriented facets and a Pt-rich hexapod frame. After leaching, Ni has been preferentially removed, to leave a concave octahedral Pt-rich frame, which leads to strong degradation in catalytic performance. In order to understand the anisotropic growth behavior related to the deposition of the transition metal, various growth experiments were performed, involving the addition of Co as a third element or the replacement of Ni by Co. Specific structural features were found in the ternary catalyst; while the noble metal Pt is distributed in the catalyst in the same way as in the binary catalyst (i.e., in the form of a hexapod frame), the transition metals are nearly homogenously distributed in the facets of the octahedron, with Ni building an encasement around the octahedron.

Figure 1. HAADF STEM images and EDX spectrum images of PtNi octahedral nanoparticles studied (A) before and (B) after acidic leaching, demonstrating an anisotropic compositional distribution and preferential leaching.