

MS3.002

Microstructural study of octahedral Pt-alloy nanoparticle fuel cell catalysts

M. Heggen¹, P. Strasser², R. Dunin-Borkowski¹

¹Forschungszentrum Jülich GmbH, Jülich, Germany

²TU Berlin, Department of Chemistry, Berlin, Germany

Pt-alloy nanoparticles (NPs) with octahedral shapes are attractive as fuel cell catalysts 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 NP catalysts with high activity and long-term stability (1). Here, we present results from a comprehensive microstructural study of the growth and degradation of various octahedral Pt-alloy NPs performed using *ex situ*, *in situ* and identical location high-resolution transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (STEM), combined with electron energy-loss spectroscopy and energy-dispersive X-ray spectroscopy (EDX). We show that the NPs often show compositional anisotropy and form Ni-rich {111} facets, leading 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 (2). We also reveal element-specific anisotropic growth as the reason for their 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 (Fig. 1) (3). *In situ* thermal annealing of phase-segregated octahedral Pt-Ni alloy NPs was performed to study their morphological stability and surface compositional evolution. Pristine octahedral Pt-Ni NPs show Pt-rich corners/edges and concave Ni-rich {111} facets. Time-resolved image series reveal that, on being annealed up to 800 C, the Pt-rich surface atoms at the corners/edges diffuse onto and subsequently cover the concave Ni-rich {111} surfaces, leading to the formation of perfectly flat Pt-rich {111} surfaces with Ni-rich subsurface layers. These results suggest a feasible approach for the synthesis of shaped Pt-alloy NPs with Pt-rich {111} surfaces and Ni-rich subsurface layers that are catalytically active and stable for the ORR, with important implications for the rational synthesis of durable highly-active shaped Pt-alloy fuel cell electrocatalysts (4). Surface doping of octahedral Pt-Ni NPs with a third element such as Mo or Rh is found to be an effective method for stabilization of the octahedral shapes of the NPs thereby improving their long-term stability during electrochemical cycling (5,6). We present results from a systematic comparison of Rh-doped and undoped Pt-Ni NPs by STEM EDX before and after 4k and 8k electrochemical cycles. Whereas undoped NPs are observed to lose their octahedral shapes and to become nearly spherical after 8k cycles as a result of Pt surface diffusion, Rh-doped Pt-Ni NPs have more stables after 4k, 8k and even 30k cycles.

References:

(1) Heggen M, Gocyla M, Dunin-Borkowski RE, Advances in Physics X 2017; 2: 281.

(2) Gan L, Cui CH, Heggen M, Dionigi F, Rudi S, Strasser P, Science 2014; 346: 1502.

(3) Cui CH, Gan L, Heggen M, Rudi S, Strasser P, Nature Materials 2013; 12: 765.

(4) Gan L, Heggen M, Cui CH, Strasser P, ACS Catalysis 2016; 6: 692.

(5) Huang X et.al. Science 2015 ; 348: 1230.

(6) Beermann V, Gocyla M, Willinger E, Rudi S, Heggen M, Dunin-Borkowski RE, Willinger MG, Strasser P, Nano Letters 2016; 16: 1719.

Fig. 1

