Shape Stability of Octahedral PtNi Nanocatalysts for Electrochemical Oxygen Reduction Reaction Studied by in situ Transmission Electron Microscopy

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Supporting Information

ABSTRACT: Octahedral faceted nanoparticles are highly attractive fuel cell catalysts as a result of their activity for the oxygen reduction reaction (ORR). However, their surface compositional and morphological stability currently limits their long-term performance in real membrane electrode assemblies. Here, we perform in situ heating of compositionally segregated PtNi1.5 octahedral nanoparticles inside a transmission electron microscope, in order to study their compositional and morphological changes. The starting PtNi1.5 octahedra have Pt-rich edges and concave Ni-rich {111} facets. We reveal a morphological evolution sequence, which involves transformation from concave octahedra to particles with atomically flat {100} and {111} facets, ideally representing truncated octahedra or cuboctahedra. The flat {100} and {111} facets are thought to comprise a thin Pt layer with a Ni-rich subsurface, which may boost catalytic activity. However, the transformation to truncated octahedra/cuboctahedra also decreases the area of the highly active {111} facets. The morphological and surface compositional evolution, therefore, results in a compromise between catalytic activity and morphological stability. Our findings are important for the design of more stable faceted PtNi nanoparticles with high activities for the ORR.

KEYWORDS: in situ TEM, PtNi octahedra, PtNi cuboctahedra, surface segregation, oxygen reduction reaction

The future supply of renewable energy depends strongly on the development of novel high-performance catalysts for energy conversion and storage applications. In proton exchange membrane fuel cells recent developments of electrocatalysts used at the cathode site for the oxygen reduction reaction (ORR) have shown, for instance, that alloying Pt with a second metal can lead to an improvement in catalytic activity.1,2 The discovery of highly active {111} surfaces in the Pt3Ni system for the ORR3 was the starting signal to search for polymetallic octahedral materials in the field of electrocatalysis.4 Whereas the exceptionally high activities are continuously being improved,5 the durability of octahedral materials still remains an issue. With regard to the rational design of advanced catalyst materials, previous work has focused on the mechanisms of growth6−8 and degradation9 of PtNi octahedra. Degradation under electrochemical conditions was, for instance, described in terms of a loss of octahedral shape due to dissolution of Ni from the {111} facets or migration of Pt atoms at the surface.10 Several attempts have been made to suppress this degradation process. For example, Park et al.11 covered PtNi octahedral nanoparticles (NPs) chemically with an ultrathin Pt layer to prevent the dissolution of Ni. Other groups doped the PtNi octahedral surface by a third metal to successfully prevent degradation of the octahedral shape. For example Huang et al.5 used Mo, while Beermann et al.10 used Rh as a third element. They demonstrated that Rh doping of PtNi octahedra leads to a reduction in Pt surface migration and, thus, to the retention of octahedral shape.10 Furthermore, Cao et al.12 provided theoretical calculations of the beneficial behavior of a third metal. They reported that a third metal could reduce the equilibrium concentration of Ni surface atoms and, thus, limit the rate at which Ni atoms are dissolved from the particles. Moreover, Cao et al.12 predicted the stabilization of low-coordinated sites by introducing a third metal, e.g., Mo.

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Another concept for improving the stability of octahedral NPs is post-annealing of PtNi octahedra, as suggested and investigated by Ahmadi et al.13 By using in situ transmission electron microscopy (TEM), Pan et al.14 and Gan et al.15 applied thermal annealing to Pt-rich PtNi octahedra. Pan et al.14 observed a redistribution of Ni content close to the surface, toward more alloyed octahedra, while Gan et al.15 followed morphological changes, observing the formation of PtNi octahedra with a thin Pt shell on the {111} facets. In both cases, a highly active and stable catalyst was predicted for this kind of octahedra.

In the present work, in contrast to Pan et al.14 and Gan et al.15, we investigate the still poorly understood morphological changes and transformation mechanisms of Ni-rich PtNi octahedral NPs. As a result of their low Pt content, they offer large Pt mass-based activity benefits. This study involves morphological investigations performed using in situ TEM to gain insight into structure–stability relationships. On the basis of previous work13, we expose octahedral PtNi particles supported on carbon to thermal annealing under vacuum at different temperatures.

RESULTS AND DISCUSSION

The Ni-rich octahedral PtNi NPs that are studied here have a general composition of 40 at. % Pt and 60 at. % Ni, as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Figure 1A shows a representative high-angle annular dark field scanning TEM (HAADF STEM) image of the PtNi1.5 octahedral NPs, which have a vertex-to-vertex size along (100) of between 8 and 9 nm. In addition to octahedral NPs, spherical NPs with a diameter of between 2 and 3 nm are found. Figure 1B shows an HAADF STEM image of an octahedral NP oriented close to a (110) direction. The image shows a strip of bright contrast in the middle, concave facets, and rounded vertices. Figure 1C shows two orthogonal bright stripes on an HAADF STEM image of an octahedral NP oriented close to a (100) direction. The corresponding EDX composition map in Figure 1D demonstrates the presence of a Pt-rich skeleton, which is consistent with the bright HAADF STEM contrast visible in Figure 1C. Furthermore, the presence of partly Ni-rich facets (white arrows in Figure 1D), as well as partly empty facets (gray arrow in Figure 1D), is evident. In the neighboring spherical particle at the bottom left of the octahedron, the EDX map shows primarily the presence of Pt. This observation is consistent with previous work,13 which described the rapid growth of a Pt-rich hexapod from a spherical Pt nucleus along (100) directions and the delayed deposition of Ni on concave {111} sites.

The morphological stability of the PtNi1.5 octahedral NPs upon annealing was studied using in situ TEM. Heat treatment under vacuum was applied in two different setups, referred to as low magnification TEM (LMTEM) and high-resolution TEM (HRTEM).

Figure 2 shows an LMTEM image series of PtNi1.5 octahedral NPs examined under in situ thermal heating conditions from room temperature (RT = 23 °C) to 600 °C, using 100 °C stepwise heating (a continuation to 800 °C is included in the Supporting Information (SI) Figure S1). Two areas are marked with green and yellow circles, showing the same NPs at different temperatures. (Figure S2 in the SI shows an additional image series recorded during the same heating experiment.)

As described above, octahedral NPs with a vertex-to-vertex size of 8–9 nm along (100) and 2–3 nm spherical NPs are observed at RT. Thermal annealing at 200 °C was not found to lead to significant changes in the LMTEM images, but only to a slight decrease in the vertex-to-vertex size of the octahedra (Figure 2B). At 300 and 400 °C (Figure 2C and D), significant morphological changes are visible in both areas, with the vertices of the octahedra becoming rounded. At 500 and 600 °C (Figure 2E and F), the octahedral shape is lost and the particles become progressively more spherical in shape. Furthermore, former neighboring octahedra coalesce, including those enclosed by the yellow circle (see arrow in Figure 2D and E), whereas the small spherical NPs beside them remain unchanged. Heating to 700 and 800 °C does not induce further morphological changes (Figure S1 in the SI).

At higher temperatures, coalescence leads to sintering of the octahedral NPs (see arrow in Figure 2F and Figure S1 in the SI), whereas the smaller NPs are maintained. The observed coalescence and sintering of neighboring octahedral NPs was observed previously by Gan et al.15 for Pt-rich octahedra and was explained in terms of enhanced surface diffusion, which minimizes surface curvature.

In order to study the influence of electron beam irradiation during heating, additional images of NP agglomerates were recorded only at the beginning and after heating to 400 °C (Figure S3 in the SI). The same shape changes of the octahedral NPs were observed as on the stepwise beam irradiated octahedra, suggesting that electron beam induced effects can be neglected here.

In addition to the stepwise experiment, a continuous in situ heating experiment was performed (see the SI, page 4, for experimental details), supporting the findings from the stepwise heating experiment. The resulting image sequences (see supporting movie files at two different magnifications) indicate that all of the morphological changes occur gradually, starting at
Figure 2. (A–F) LMTEM image series of PtNi<sub>1.5</sub> octahedral NPs under in situ thermal heating conditions from 23 °C (RT) to 600 °C. Green and yellow circles mark identical NPs at different temperatures. The arrows indicate coalescence and sintering of two NPs.

At 50°C to 700 °C, the octahedra have slightly rounded vertices (Figure 3A), corresponding to an energetically more stable shape than sharp vertices. The vertex-to-vertex sizes of the octahedra along ⟨100⟩ are 8.6 nm (black circle), 8.7 nm (red circle), and 7.9 nm (blue circle). Heating to 150 °C does not result in significant morphological changes (Figure 3B). Further heating to 200 °C leads to the formation of octahedra with truncated vertices and less concave facets (Figure 3C).

This structural evolution can be explained in terms of the diffusion of Pt atoms from the vertices to the {111} facets. Such reconstruction of facets in bimetallic nanoparticles has been hypothesized in previous studies. An increase in temperature to 250 and 300 °C (Figure 3D and E) leads to truncation of the rounded vertices and, finally, to the formation of atomically flat {100} facets in addition to the {111} facets (see Figure 3K and L). The formation of {100} facets in addition to the {111} facets leads to a truncation of the octahedra. Ideally this process may lead to the formation of regular truncated octahedra or cuboctahedra. For simplicity, we will use the term cuboctahedra for {100}-truncated octahedral particles in this further course of this article, although the particles may not possess perfect cuboctahedral shape. This transformation corresponds as well to the decrease in vertex-to-vertex size along ⟨100⟩ observed using LMTEM. Further heating to 350 and 400 °C (Figure 3F and G) probably leads to further Pt atom surface diffusion and to the transformation of flat facets to more convex shapes by interdiffusion. Well-faceted cuboctahedra, gradually develop into round NPs. This process continues at increasing temperature up to 500 °C (Figure 3H). Although the formation of several spherical shaped NPs is observed, some flat {111} surfaces are visible, especially for the cuboctahedra enclosed by the blue circle in Figure 3. Heating up to 700 °C results in sintering of the NPs, in good agreement with the LMTEM results.

The observed formation of such cuboctahedral particles with almost atomically flat {100} facets represents an additional intermediate NP morphology. The formation of flat {100} facets in addition to {111} facets due to thermal annealing was not reported to occur in Pt-rich PtNi NPs by Gan et al. The transformation from concave octahedra to cuboctahedra could in fact be energetically favorable due to the presence of a {100} facet reconstruction, as pointed out in the theoretical work of Wang et al. Furthermore, previous theoretical and experimental works clarified how the reactivity toward the ORR varies over different single-crystal surfaces of Pt and PtNi catalysts. PtNi alloy {111} and {100} surfaces were then predicted to be catalytically more active for ORR than pure Pt surfaces. Furthermore, PtNi {111} surfaces have been reported to be superior to PtNi {100} surfaces.

Therefore, a transformation from a concave octahedron to a cuboctahedron, leading to a decrease of the exposed {111} facet area due to the formation of {100} facets, would on the one hand lower the surface ORR activity. On the other hand, the formation of a larger ratio of perfectly flat Pt-rich {111} surfaces with Ni-rich subsurfaces, like probably formed in our experiments, could improve the activity due to a change in reaction mechanism, as was suggested by DFT calculations of Duan and co-workers. The benefit of the observed transformation to cuboctahedral NPs is also explained in the theoretical work of Mahata et al., based on a detailed investigation of the surface energy and compressive strain. For cuboctahedra they found a shift in the d-band center position toward the Fermi level due to the presence of {111} and {100} facets. This stabilizes the intermediates due to a strong interaction between cuboctahedron and intermediates and, hence, might lead to an improved ORR activity.

However, the stability of such cuboctahedral NPs is expected to be more important than their influence on the activity itself. Previous work has shown that the leaching of Ni-enriched facets under electrochemical conditions leads to a loss in catalytic ORR activity. Cuboctahedra, in which Ni is protected in the centers of the {111} facets by a thin layer of Pt, should be...
more resistant to Ni leaching and could be stronger candidates for long-term catalysts. Such cuboctahedra could provide an optimal compromise between high activity and long-term morphological stability.

Based on our HRTEM results, Figure 4A–E illustrate a proposed morphological evolution sequence for the transformation of concave Ni-rich octahedra during in situ heating, alongside representative HRTEM images (F–M). The morphological evolution sequence starts with an initially concave octahedron that has Ni-rich facets (Figure 4A), as observed for the as-prepared NPs (Figure 1D). Upon thermal annealing, Pt diffuses from the edges toward the {111} facets and forms octahedra with partly filled {111} facets (Figure 4B), as observed in our in situ HRTEM results (Figures 3C and 4G). Further Pt diffusion leads to the formation of a truncated octahedron with flat {111} facets and additional flat {100} facets, as observed at 250 °C (Figure 3D). Continuation of this process leads to further truncation, an increase in {100} surface area, and, thereby, the formation of cuboctahedra, which most probably have a Pt shell (Figure 4C). Further heating at higher temperature leads to partly rounded-off facets (Figure 4D) and finally to the formation of spherical NPs (Figure 4E).

The proposed Pt and Ni distribution in the morphological evolution sequence (Figure 4) is in accordance with HAADF STEM images (see SI, Figure S4). A change in Z-contrast was observed upon heating, which can be correlated to a stronger intermixing of Pt at the facets. Furthermore, EDX maps of heat-treated NPs (see SI, Figure S5) clearly show a Pt surface enrichment at 300 °C, which is in accordance with the proposed mechanism.

CONCLUSION

In conclusion, we have performed in situ heating of octahedral PtNi1.5 NPs with Pt-rich edges and concave Ni-rich facets in the TEM. Our observations, which were performed between RT and 800 °C, reveal a morphological evolution sequence in the
transformation of concave octahedra during thermal annealing under inert conditions (vacuum). The following states are observed: concave octahedra; octahedra with partly flat {111} surfaces; cuboctahedra; cuboctahedra with a partial loss of {111} facets; spherical NPs (Figure 4). Starting from concave octahedra, heating results in the diffusion of Pt atoms, leading first to the formation of almost atomically flat cuboctahedral facets and, upon further heating, to the formation of spherical NPs. Our results reveal that the flat {111} surfaces of the cuboctahedra are stable over a wide temperature range. The development of an understanding and control over this process provides synthetic possibilities for tuning the stability—activity relationships of octahedral NPs in fuel cell electrocatalysis. The ability to achieve a balance between Pt shell thickness, Ni subsurface enrichment, and an optimized ratio between {111} and {100} facets promises to lead to long-term stable and active catalysts.

EXPERIMENTAL SECTION

Synthesis. According to Cui et al.,22 0.2 mmol of Pt(acac)2 and 1.4 mmol of Ni(acac)2 were dissolved in 50 mL of dimethylformamide by ultrasonication for 5 min. The homogeneous solution was transferred into a glass-lined stainless steel autoclave. The sealed autoclave was heated from RT to 130 °C within 30 min. The temperature was held 42 h before it was cooled to RT. Afterward the particles were supported on carbon (Vulcan XC72R) by 5 min of ultrasonication and around 23 h of static conditions at RT. Finally, the PtNi/C was washed with ethanol/water several times and treated with a freeze-drying method.

Physical and Chemical Characterization. ICP-OES. ICP-OES was used for elemental and compositional analysis using a Varian 715-ES spectrometer with a CCD detector. Standards with a known concentration were coanalyzed with the samples.

Low-Magnification TEM. LMTEM was performed at a FEI Tecnai G20 S-TWIN transmission electron microscope with a LaB6 cathode operated at an accelerating voltage of 200 kV (ZELMI Centrum, Technical University of Berlin).

High-Resolution TEM. HRTEM was performed using a FEI Titan 80-300 TEM with a Cs corrector for the objective lens (CEOS GmbH). The microscope was operated at 300 kV.

Scanning Transmission Electron Microscopy. STEM was performed using a FEI Titan 80-200 (“ChemiSTEM”) electron microscope with a Cs-probe corrector (CEOS GmbH) and an HAADF detector.24 The microscope was operated at 200 kV. In order to achieve the “Z-contrast” conditions, a probe semiangle of 25 mrad and an inner collection semiangle of the detector of 88 mrad were used. Compositional maps were obtained with energy-dispersive X-ray spectroscopy (EDX) using four large-solid-angle symmetrical Si drift detectors. For EDX elemental mapping, Pt L and Ni K peaks were used. The error of the EDX composition measurement is ±2 at. %.

in situ TEM. For in situ TEM experiments a heating holder (DENSsolutions B.V.) was applied. The catalyst was dispersed onto a MEMS chip equipped with four-point measurement for precise temperature control and a distinct heating zone on a SiNx film and SiNx-coated windows for LMTEM and carbon-coated windows for HRTEM and STEM. In LMTEM the temperature was changed instantly in steps of 100 °C and the specimen was annealed for about 20 min at constant temperature (stepwise heating experiment; for details to continuous heating experiment see SI, page 4). In HRTEM and STEM the temperature was changed in steps of 50 °C and the specimen was annealed for about 5–10 min at constant temperature.

ASSOCIATED CONTENT

† Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b09202.

Video showing image sequences of a continuous in situ LMTEM heating experiment (AVI)
Video showing image sequences of a continuous in situ LMTEM heating experiment (AVI)
Additional images of in situ LMTEM measurements, details of a continuous in situ LMTEM heating experiment, as well as additional STEM images (PDF)

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