Shape controlled octahedral Pt-Ni alloy nanoparticles are promising candidates as electrocatalysts for the oxygen reduction reaction (ORR) electrocatalysts for cathodes of low temperature Polymer Electrolyte Membrane fuel cells. Organic surfactants are used in order to control and tune particle composition, size, shape, and the distribution on the support material. Such methods request intense post-synthesis cleaning, or annealing procedures in order to remove the ligands, demanding for simpler cleaning and activation procedures. Here, we explore the effect of an acetic acid treatment of as-prepared Pt-Ni nanoparticles, applied prior to annealing. The resulting nanoparticles underwent an electrochemical surface characterization and were investigated in terms of their ORR activities and electrochemical long-term stability. After acid treatment the particles exhibit a Pt-rich surface, which changed slightly during annealing at 300 °C but drastically to a more homogeneous alloy after annealing at 500 °C due to Ni surface segregation. Besides changes in the (sub-)surface Pt and Ni composition, the octahedral shape did not survive the 500 °C treatment. An improved ORR activity was obtained after annealing at 300 °C. Our insights into effects and benefits of the described post-synthesis treatments aid our general understanding, but also may help improve the practical design of suitable treatment protocols of this class of ORR catalysts.

**Experimental**

*Synthesis of Pt-Ni/C oct.*—Pt-Ni/C octahedral nanoparticles were prepared by adding Pt(acac)2 (0.407 mmol, Pt 48% min., Alfa Aesar), Ni(acac)2 (0.934 mmol, 95.0%, Alfa Aesar), OAm (48 mL, 98.0%, Sigma Aldrich) and OAc (32 mL, 90%, Alfa Aesar) into a 100 mL three-neck-flask under reflux. After stirring for 5 minutes under nitrogen (N2) atmosphere at 60 °C the temperature was raised to 130 °C. At this temperature W(CO)6 (1.591 mmol, 97.0%, Alfa Aesar) was added rapidly, N2 purging was stopped and the reaction mixture was heated to 230 °C and then stirred for 50 minutes. After the reaction mixture was cooled down to room temperature toluene (20 mL, 99.8%, Roth) and ethanol (60 mL, 100%, VWR Chemicals) were added. The supernatant was removed by centrifugation (7800 rpm for 15 min) and dispersed in toluene (20 mL). The dispersion was added to a dispersion of Vulcan XC 72R (160 mg) in toluene (20 mL) and sonicated with an ultrasonic horn for 30 min. Ethanol (10 mL) was added and the catalyst was centrifuged (7800 rpm for 15 min), washed with ethanol (30 mL) three times, and freeze dried for 12 h.

**Acetic acid leaching and annealing of Pt-Ni/C oct.—**The synthesized powder was boiled in acetic acid (50 mL, ≥ 99.0%, Sigma Aldrich) at 60 °C for 30 minutes and subsequently washed with ethanol (30 mL) three times. After freeze drying for 12 h the powders were heated to 180 °C at a rate of 10 K min⁻¹ in a tube furnace in synthetic air atmosphere and left for 30 min. After purging with N2 for 30 min, the atmosphere was changed to hydrogen (4%/Ar) and the temperature was raised at a rate of 10 K min⁻¹ to 300 °C (H2/H2O) or to 500 °C (H2/H2O) and left for 1 h. Afterwards it was allowed to cool to room temperature in N2.

**Physico-chemical characterization.—**X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance (Siemens KFL Cu Kα X-ray tube and Lynx Eye detector) diffractometer in Bragg Brentano geometry using a Cu Kα1. The patterns were recorded between 20–80° with a step size of 0.05° and a 10 s measurement time at each step. Inductively coupled plasma analysis (ICP OES) (Varian) was used to determine the elemental composition of the synthesized particles. The selected wavelengths for the concentration determination were reported previously. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 20 S-TWIN with LaB6-cathode, 200 kV accelerating voltage and a resolution limit of 0.24 nm. Powder samples were dispersed on a 200 mesh Cu grid.

For electrochemical characterization a three electrode setup was used. The preparation of the ink and the electrode and the electrochemical setup were described before. The electrochemical activation was performed in 0.1 HClO4 via potential cycling (0.05–1.0 VHE with...
100 mV s⁻¹ (for 20 cycles) under N₂ protected atmosphere. The Hupd based electrochemical active surface area (ECSA) was evaluated using the last cycle before the activity measurements. The charge values (Q₀) were calculated by integrating the respective cyclic voltammogram (CV) between 0.05 and 0.4 V and were normalized with respect to the theoretical value of Q₀ₜheoretical = 210 μC cm⁻². For CO oxidation, the electrolyte was saturated with N₂ for 15 min. Afterwards, the working electrode was lowered into the electrolyte at 0.05 V RHE with 400 rpm rotation speed. Then, the gas was switched to CO for 10 minutes followed by a gas change to N₂ again. Three CVs were recorded (0.05–1.0 V RHE with 50 mV s⁻¹, 0 rpm). To determine the CO-based electrochemical active surface area, the voltammogram after the CO strip was subtracted from the CO-stripping voltammogram. The positive area of the resulting peak was integrated to obtain the CO-adsorption strength of CO to the particle surface. A shift to higher values of around 41 ± 0.7 VRHE, whereas the development of the main peak position was different within the materials with prolonging cycle number. Generally, the position of the main CO stripping is influenced by the adsorption strength of CO to the particle surface. A shift to higher potentials was caused by stronger adsorption energies of CO and can be interpreted as a Pt enrichment of the nanoparticle surface. HAc exhibited a more anodic peak potential after activation, compared to the initial and the after 4k stability state (Figure 2D). HAc₅₀₀ showed a more anodic peak potential after activation, which remained constant after 4k potential cycles. Importantly, an additional shoulder at around 0.8 V RHE appeared after 4k cycles, suggesting the emergence of a new surface site or facet with somewhat stronger CO binding. For HAc₅₀₀, the position of the main CO oxidation peak shifted to higher potential after 4k cycles, indicating again the formation of a Pt-enriched particle surface, probably due to Ni-leaching from the more homogeneous alloy surface.

From the electrochemical surface voltammograms of hydrogen and CO, the electrochemical active surface areas (ECSAs) were determined. Figure 3A shows the numbers for the ECSA obtained by integrating the charges associated with hydrogen under potential deposition (Hupd) and CO oxidation normalized to the respective charge values based on Hupd, showed a drastic increase in ECSA value after 4k cycles (see also Figure 3B). In contrast, CO stripping revealed larger ECSA values, which was expected for Pt alloy based systems, but they also showed a quite different trajectory after 4k cycles stability (Figure 3A, hatched bars). HAc and HAc₅₀₀ values decreased or stayed constant, within the error compared to the activated state. HAc₅₀₀, however, which showed constant ECSA values based on Hupd showed a drastic increase in ECSA value after 4k cycles (see also Figure 3B). This observation suggest the formation of an octahedral shape for the HAc sample with an average edge length of 8.2 ± 1.2 nm (Figure 1C and Figure S2), which is in the same order of magnitude as before HAc treatment (8.4 ± 1.1 nm) (Figure 2S). For HAc₃₀₀ (Figure 1D and Figure S2), octahedral edges are mostly rounded off, which is in contrast to our previous study without the preceding HAc treatment; there, the octahedral shape was retained and stable after the 300°C treatment. After annealing at 500°C, the octahedral particle shape was almost completely lost, and particles in close proximity coalesced (Figure 1E and Figure S2). It is important to note that the acetic acid treatment itself did not change the original octahedral shape (Figure S2), but did induce corrosive defects in the particle surface, which promoted a loss in shape during subsequent heat-treatment.

To investigate the effect of the combined acetic acid/annealing treatment on the surface properties of the catalysts and their catalytic ORR performance, the three materials were investigated in a three-electrode rotating disc electrode setup. Figures 2A–2C show the cyclic voltammetry in oxygen-free conditions normalized to the amount of Pt on the electrode. This analysis reveals the surface electrochemical faradaic and capacitive behavior of the catalyst surface in absence of catalytic reactants. Hydrogen under potential deposition (Hupd) regions are well-developed for HAc (Figure 2A) and HAc₃₀₀ (Figure 2B) in the initial as well as in the activated state; they indicate the presence of Pt atoms and domains at the particle surface. Characteristic redox waves at around 0.2, 0.3 and 0.4 V RHE sharpen with progressing electrochemical cycling up to 4k cycles, suggesting the faceting of the Pt-rich surface. For HAc₅₀₀, the Hupd region is only weakly developed in the initial state and after activation, indicating a rather Ni-rich surface (Figure 2C) due to a more homogeneous alloy surface (Pt and Ni distribution) after annealing at high temperature. For HAc₅₀₀, the position of the main CO oxidation peak shifted to higher potential after 4k cycles, indicating again the formation of a Pt-enriched particle surface, probably due to Ni-leaching from the more homogeneous alloy surface.
Figure 1. Introduction of samples; A Scheme of post-synthesis samples treatment; B X-Ray diffraction patterns of the Pt-Ni/C samples after post-synthesis treatment in comparison to the untreated sample, red columns indicate the reflection position of pure fcc Pt (#00-004-0802), green columns indicate the reflection position of pure fcc Ni (#00-004-0850); C-D TEM images of the Pt-Ni/C samples after post-synthesis treatments, HAc (C), HAc_300 (D), HAc_500 (E).

Figure 2. Electrochemical surface characterization of Pt-Ni/C after post-synthesis treatment. A-C Cyclic voltammograms recorded in N2 sat. HClO4 with 100 mV s$^{-1}$ between 0.05 and 1.0 V$_{RHE}$ of the initial samples, after activation and after 4k cycles stability test; CO oxidation profiles recorded in N2 sat. HClO4 with 50 mV s$^{-1}$ between 0.05 and 1.0 V$_{RHE}$ after purging with CO. Red lines indicate the sample HAc (A, D), blue line the samples HAc_300 (B, E) and green lines the sample HAc_500 (C, F).
of an additional surface side, which do not adsorb hydrogen but CO and OH species.

It has been reported, that the charge ratio of Hupd to CO, \(Q_{\text{CO}}/2Q_{\text{Hupd}}\), may have some qualitative predictive power as to the surface/sub-surface Pt-to-Ni composition.\(^{21}\) \(Q_{\text{CO}}/2Q_{\text{Hupd}}\) values close to 1.0 were reported to suggest a pure Pt or Pt-rich surface, a thick Pt shell or a uniform distribution of Pt and Ni. Values closer to 1.5 suggest a Pt-skin type surface, where a Pt rich top layer is supported by a Ni-richer second atomic layer.

HAc exhibited a charge ratio value of 1.29 and likely represents a situation with a thin Pt surface shell-like structure, probably caused by the acetic acid treatment (Figure 3A, numbers between the bars). After activation and 4k cycles the charge ratio values decreased progressively, consistent with a thickening of the Pt shell or the formation of a more homogeneous surface alloy. The formation of a thicker Pt shell is rather likely, due to the peak developments discussed in the cyclic voltammograms obtained in N\(_2\) protected atmosphere.

HAc_300 behaves quite differently, after activation the \(Q_{\text{CO}}/2Q_{\text{Hupd}}\) value decreased from 1.26 to 1.18, but increased again after 4k cycles to 1.49. This is consistent with the notion of an initial thickening of the Pt shell, as it also have been observed for HAc. The subsequent increases, on the other hand, suggesting a more “Pt-skin” type particle surface composition, is likely caused by Ni atomic segregation into the sub-monolayer regions during annealing at 300 °C in H\(_2\).\(^{13,18,22,23}\) This advanced structure is also suggested by the additional peak occurrence in the CO stripping voltammograms and has been observed in a similar set of samples before.\(^{18}\)

HAc_500, finally, showed a large initial charge ratio value of 1.70 indicating a defect Ni-rich surface, in line with the weak Hupd features shown in Figure 2C. With subsequent electrochemical potential cycling, these charge ratio values decreased again due to strong Ni leaching, now creating a thick Pt-enriched surface, which also is supported by the cyclic voltammograms in N\(_2\) atmospheres discussed above and the increase in the CO stripping peak potential.

Figure 4 illustrates the experimentally observed surface and subsurface conditions of the discussed materials based on our combined analyses of cyclic voltammograms, CO stripping voltammograms and \(Q_{\text{CO}}/2Q_{\text{Hupd}}\) values.

Comparing the values among the samples in the initial stages, HAc probably exhibited a pronounced Pt shell, while HAc_500 was Ni-rich in its surface. Thus, a temperature treatment significantly changes the surface composition, even of relatively Pt-rich surfaces, by creating more homogeneous surface alloys. This effect starts to emerge at temperature above 300 °C, because the HAc_300 sample exhibits a mostly Pt enriched surface. Annealing at 300 °C under the chosen conditions seems to have a comparable effect on the particle surface like the activated HAc as both exhibit the same \(Q_{\text{CO}}/2Q_{\text{Hupd}}\) value. The initial conditions of the surfaces have a high influence on the surface changes during electrochemical cycling. HAc sample only showed a thickening of the Pt shell with increasing number of electrochemical cycles, which was also happening to HAc_500 even though the initial state was much more Ni-rich. A thickening of the Pt shell was also happening to HAc_300 after activation, but after 4k cycles the particle surface was changing in a different way according to the additional shoulder in the CO stripping profile (Figure 2E) and the \(Q_{\text{CO}}/2Q_{\text{Hupd}}\) values (Figure 3A). The presence of a Pt-skin like structure, supported by the \(Q_{\text{CO}}/2Q_{\text{Hupd}}\) value of 1.49, also offers a reasonable explanation for the emergence of the additional CO profile shoulder, which was indeed reported for Pt-skin like surface in single crystals.\(^{21}\)

To correlate the detailed surface compositional changes with the resulting experimental oxygen reduction reaction (ORR) activities, linear sweep voltammetry in oxygen saturated electrolyte was used, and the Pt-mass based current densities were determined (Figure 3C). HAc_300 showed the highest ORR activity after activation and after

![Figure 4](image-url)
4k cycles stability test, with no activity drop after 4k cycles (drop is within the error). After activation HAc showed a slightly lower activity than HAc_300 and a small drop in activity after 4k stability, HAc_500, which overall showed the smallest ORR activity was stable after 4k cycles, which was likely due to the loss in octahedral shape. In general, all measured ORR activities are in the same order of magnitude. In comparison to ORR activities usually reported for octahedral Pt-Ni nanoparticles, our observed ones are rather low, possibly due to the formation of a more defect particle surface induced by leaching and annealing. Nevertheless, HAc_300 exhibits the highest ORR activity and a good electrochemical stability. Thus, annealing at 300°C after an acetic acid treatment seems to lead to an improved surface and subsurface condition, resulting in slightly higher ORR activities.

Other than in our previous study, annealing had a smaller impact on the resulting ORR activity and stability values when performed on acid leached samples. Without a preceding acid treatment particles are much more sensitive in terms of heat treatments, but in principle the same trends were overserved.

Conclusions

To conclude, in this contribution we have investigated how an initial acid treatment preceding a thermal annealing affects the surface electrochemistry and catalytic ORR activity of shaped Pt-Ni nanoparticles. We conclude that the initial post-synthesis acid treatment generates a Pt-enriched surface on octahedral Pt-Ni nanoparticles. With subsequent annealing at 300°C, first a more Pt enriched surface was generated before, at high temperatures of 500°C, we observed a strong migration of Ni to the particle surface, generating a Ni-richer surface. The Pt enriched surface after annealing at 300°C leads to improved ORR activity and quite good stability. Thus, it appears that the combination of acid leaching followed by annealing leads to surface compositional conditions of the shaped Pt-Ni nanoparticles beneficial for efficient and stable electrocatalytic oxygen reduction performance.

Acknowledgments

We thank the Zentraleinrichtung für Elektronenmikroskopie (ZELMI) of the Technical University Berlin for its support with TEM measurements. Financial support was given by Deutsche Forschungsgemeinschaft (DFG) grants HE7192/1-2 (“Nanokalige Pt-Legierungselektrtkatalysatoren mit definierter Morphologie”) and by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) under grant 03SF0527A (“LoPlaKats”).

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