TEM ex situ and in situ heating study on shape stability of octahedral PtNi nanocatalysts

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In case of polymer electrolyte fuel cells (PEFCs) Platinum is still the most used catalyst for the oxygen reduction reaction (ORR) at the cathode - where PtNi alloys are the state of the art [1, 2]. Following a study by Stamenkovic et al. in 2007 [3] several groups dealt with octahedral shaped nanoparticles (NPs) during the last decade to enhance both specific and mass activity [4]. Well-defined octahedral shaped NPs can be obtained e.g. by solvothermal synthesis using DMF as solvent and reduction agent [5]. Unfortunately, such PtNi octahedra show a major disadvantage in lacking of morphological stability during electrochemical cycling [6]. In the present work, we investigated thermal annealing of PtNi octahedra as approach toward an improved PtNi alloy structure with higher morphological stability. To investigate the morphological changes during heating, *in situ* TEM was applied in comparison to *ex situ* post-treatments in hydrogen. For *in situ* TEM a MEMS chip with 4 point measurement for precise temperature control was used.

Figure 1 shows an *in situ* TEM image series of PtNi1.5 octahedral NPs supported on carbon heated from room temperature (23 °C) to 600 °C, using 100 °C stepwise heating. At room temperature octahedral NPs as well as some small spherical NPs are observed (***Figure 1***A). Thermal annealing at 200 °C do not lead to significant changes (***Figure 1***B). At 300 °C and 400 °C (***Figure 1***C and D) the corners of the octahedra becoming rounded. At 500 °C and 600 °C (***Figure 1***E and F) the octahedral shape is lost and resulting in nearly spherical particles.

Additionally, samples annealed ex situ in hydrogen were also investigated by TEM, where similar morphological changes were observed. Thus, although the *in situ* and *ex situ* experiments were performed under different 'atmosphere', a similar behavior of the catalysts was observed. Accordingly, *in situ* heating TEM can actually be used as a proxy for the morphological changes of Pt-based nanoparticles. Furthermore, as shown by X-ray diffraction (XRD) a PtNi lattice contraction can be observed with increasing annealing temperature, indicating an improvement of the alloy structure. Indeed, a rather mild treatment in hydrogen can improve the alloy structure and, thus, lead to higher activity in ORR, whereas a complete PtNi alloying at higher temperatures is diminishing the ORR activity due to the loss of octahedral shape and, accordingly, {111} facets.

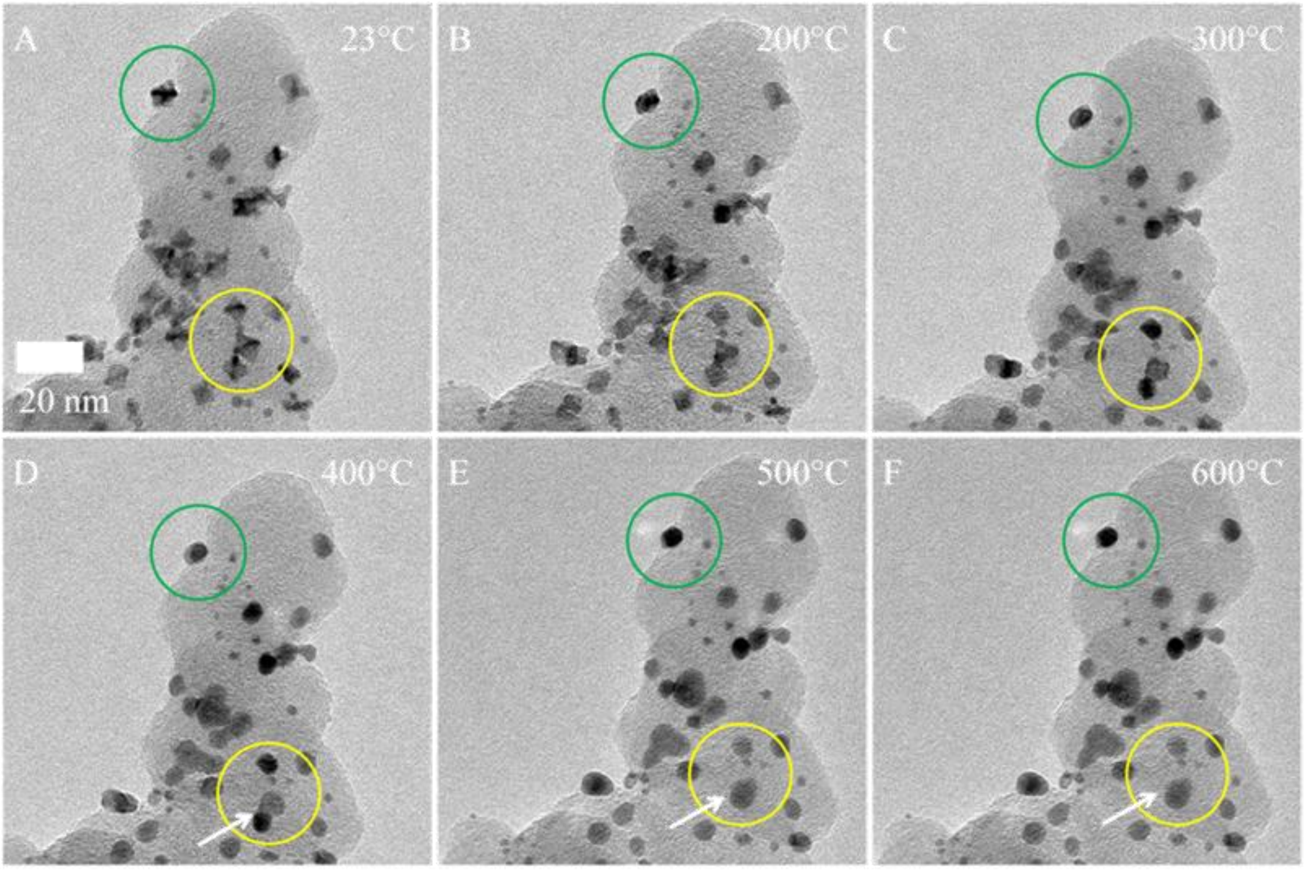

Figure 1. (A-F) TEM image series of $PtNi_{1.5}$ octahedral NPs under in situ thermal heating conditions from 23 °C to 600 °C. Green and yellow circles mark identical NPs at different temperatures. The arrows indicate coalescence of neighboring particles.

References

[1] Y. Bing et al., *Chem. Soc. Rev* **39** (2010) 2184-2202.

[2] H. A. Gasteiger, N. M. Markovic, *Science* **324** (2009) 3791.

[3] V. R. Stamenkovic et al., *Science* **315** (2007) 493.

[4] P. Strasser, *Science* **349**, 379-380 (2015).

[5] M. K. Carpenter et al., *J. Am. Chem. Soc.* **134** (2012) 8535-8542.

[6] L. Gan et al., *Science* **346** (6216) (2014) 1502-1506.

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