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Stability of Octahedral-Shaped Pt-Ni Nanoparticles for Electrochemical Oxygen Reduction

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Abstract Text:

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 combine the DMF-based synthesis with a thermal post-treatment as annealing step toward an improved PtNi alloy structure with higher stability. The study is primarily based on the morphological investigations by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) combined with energy dispersive X-ray analysis (EDX), both ex situ as well as in situ mode, to gain insights into the structure-activity-stability relationship.

In detail, based on a previous work [7], we exposed octahedral PtNi particles (supported on carbon) to a post-treatment in hydrogen using a tubular furnace. First off all, an increased annealing temperature results in a better defined PtNi alloy – proven by XRD. Whereas after 300°C mainly octahedral NPs were present, a complete loss of shape was observed after annealing at 500°C, where nearly spherical particles resulted. Additionally, the morphological changes during heating were also observed in situ using a TEM heating nano-chip (i.e. heating in vacuum). Both annealing in hydrogen as well as in vacuum show indications for Pt diffusion to (111) facets before the octahedral shape collapsed. 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.

References

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

[2] H. A. Gasteiger, N. M. Marković, *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.

[7] M. Ahmadi et al., ACS Nano 7 (2013) 9195-9204.