

# Synchrotron Based Structural Investigations of Mass-Selected Pt<sub>x</sub>Gd Nanoparticles and a Gd/Pt(111) Single Crystal for Electrochemical Oxygen Reduction

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The sluggish kinetics of the oxygen reduction reaction (ORR) hinders the commercialization of proton exchange membrane fuel cells (PEMFC). The ORR activity is enhanced by alloying Pt with late transition 3d metals (i.e. Fe, Co, Ni, and Cu)<sup>1</sup>. However, these compounds tend to degrade in a fuel cell by dealloying. An alternative approach is to alloy Pt with rare-earth elements. Their highly negative alloying energy may provide them with kinetic stability against dealloying under reaction conditions. A recent publication from our group reported the high ORR activity and stability of polycrystalline Pt<sub>5</sub>Gd<sup>2</sup>. In this work, we present the experimental results of mass-selected Pt<sub>x</sub>Gd nanoparticles synthesized by gas aggregation after sputtering of an alloy target in an ultrahigh vacuum (UHV)<sup>3</sup>. Pt<sub>x</sub>Gd nanoparticles with nominal sizes of 3, 5, 7, and 9 nm were selected using time-of-flight mass filtering and deposited on glassy carbon (GC) disk electrodes. Rotating ring disk electrode (RRDE) measurements in 0.1 M HClO<sub>4</sub> were used to measure the activity in comparison to pure Pt<sup>4</sup>. The ORR specific activity increases with the nanoparticle size; a maximum mass activity is achieved with the 7 nm sample, ~3.6 A/mg Pt at 0.9 V. X-ray absorption spectroscopy measurements suggest that the high ORR activity is due to a compressive strain exerted by the alloy core onto the Pt overlayer at the surface.

The structure formed on these types of alloys<sup>2</sup> is further elucidated using a Gd/Pt(111) single crystal. The alloy was prepared in UHV by depositing 150 Å of Gd followed by annealing, thus simulating a bulk single crystal. It was characterized in vacuo using low energy electron diffraction, ion scattering spectroscopy, X-ray photoelectron spectroscopy and temperature programmed desorption of CO. Subsequently, the crystal was transferred to an electrochemical cell, where a 1 nm thick Pt overlayer was formed; this constitutes the active phase for oxygen reduction. Using synchrotron based grazing X-ray diffraction, we determine the structure of the alloy and the Pt overlayer. The diffraction contributions from the Pt overlayer is separated from the Pt<sub>5</sub>Gd alloy, and the analysis of both diffraction patterns are presented.

By investigating such well-defined structures, we gain valuable scientific insight into the relationship between their structure and functionality. On the basis of this insight, we can develop even better catalysts for oxygen electroreduction.

## References

1. Chen, C. *et al.* Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces. *Science* **343**, 1339–1343 (2014).
2. Escudero-Escribano, M. *et al.* Pt<sub>5</sub>Gd as a Highly Active and Stable Catalyst for Oxygen Electroreduction. *J. Am. Chem. Soc.* **134**, 16476–16479 (2012).
3. Velazquez-Palenzuela, A. *et al.* The enhanced activity of mass-selected Pt<sub>x</sub>Gd nanoparticles for

oxygen electroreduction. *J. Catal.* [in press] (2015). doi:10.1016/j.jcat.2014.12.012

4. Perez-Alonso, F. J. *et al.* The Effect of Size on the Oxygen Electroreduction Activity of Mass-Selected Platinum Nanoparticles. *Angew. Chem. Int. Ed.* **51**, 4641–4643 (2012).