

Pt₅Gd as a highly active and stable catalyst for oxygen electroreduction

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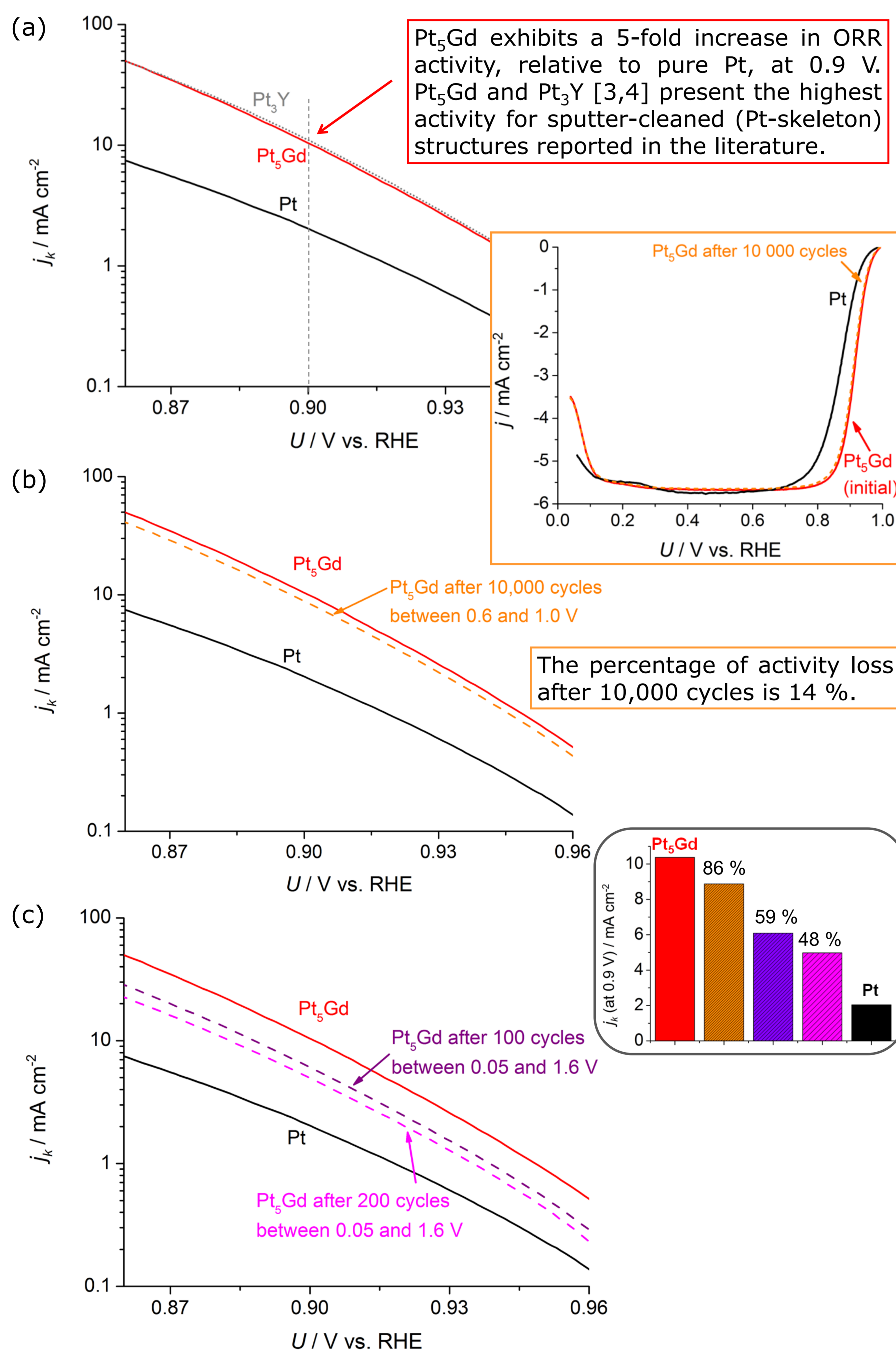
Motivation

Proton exchange membrane fuel cells (PEMFCs) are a potentially zero emission source of power, which are expected to play a key role in a future society based on sustainable energy. The main obstacle to the development of PEMFCs as a commercially competitive reality is the high overpotential required for the oxygen reduction reaction (ORR) to proceed at an adequate rate. In order to improve the kinetics for the ORR and reduce the Pt loading, there is a need to develop novel catalysts with enhanced activity and long-term stability under operating conditions, which can be achieved by alloying Pt with other metals [1-4]. Alloys of Pt and early transition metals, such as Pt₃Y [3,4], have shown very promising activity for the ORR. Furthermore, alloys of Pt with early transition metals or rare earths are exceptionally stable [4]; this should provide them with the kinetic stability to prevent dealloying under fuel cell reaction conditions, unlike alloys of Pt and late transition metals.

Herein, we investigate the activity and stability of Pt₅Gd, using a combination of electrochemical measurements, angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and density functional theory (DFT) calculations.

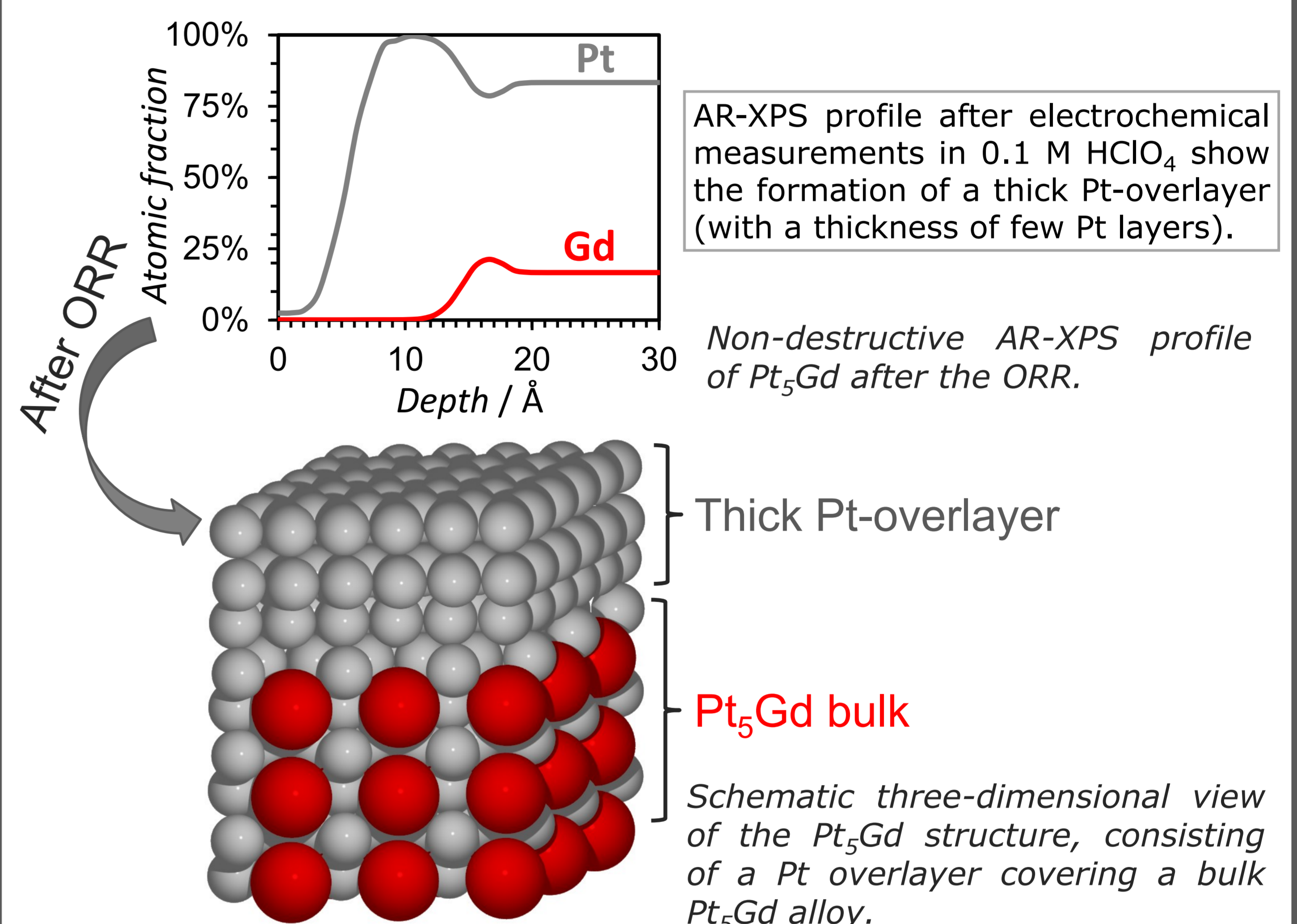
Electrochemical measurements: ORR activity and stability

Rotating ring disk electrode (RRDE) assembly, 50 mV s⁻¹, anodic sweep, 23 °C, 1600 rpm, O₂-saturated 0.1 M HClO₄



Tafel plots showing the kinetic current density (j_k) of Pt₅Gd, Pt and Pt₃Y (a) as well as Pt₅Gd after 10,000 cycles between 0.6 V and 1.0 V (b) and after 100 and 200 cycles between 0.05 V and 1.6 V (c) as a function of the potential (U).

Angle-resolved XPS and DFT calculations



According to AR-XPS, the effect of alloying Pt would be to impose strain onto the Pt overlayer. In the absence of Gd in the first three atomic layers, there would be no ligand effect. DFT calculations suggest that a Pt overlayer on this structure would be compressed by 6 %, relative to Pt(111). This strain would result in an excessive weakening of the OH binding energy, relative to Pt(111), of ~0.3 eV. The compressive strain that would provide the optimal OH binding energy ~0.1 eV weaker than Pt(111), would be 2 % [5]. We speculate that strain relaxation takes place at this surface.

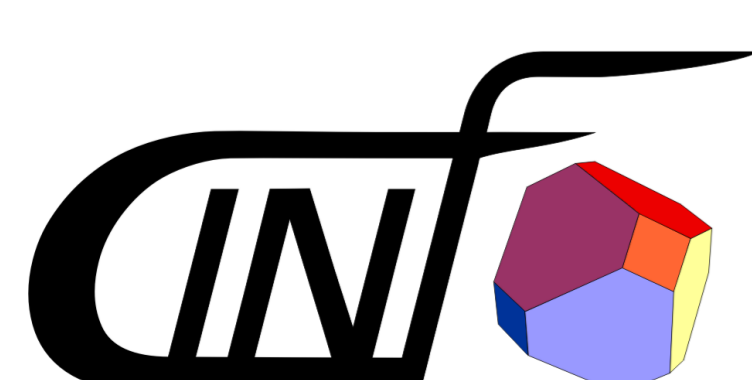
Conclusions and outlook

In summary, we present a novel highly active and stable electrocatalyst for the ORR. The activity of Pt₅Gd is similar to that obtained for Pt₃Y in previous studies, which was identified as the most active Pt-based polycrystalline alloy for the ORR. Moreover, Pt₅Gd electrodes are extremely stable, resistant to cycling to potentials as positive as 1.6 V. For all these reasons, we expect that alloying Pt with Gd and other rare earth metals will be a fruitful strategy towards the development of highly active and durable cathodes for PEMFCs.

References

- [1] Gasteiger, H.A.; Kocha, S.S.; Sompalli, B.; Wagner, F.T. *Appl. Catal. B* **2005**, *56*, 9.
- [2] Stamenkovic, V.R.; Fowler, B.; Mun, B.S.; Wang, G.; Ross, P.N.; Lucas, C.A.; Markovic, N.M. *Science* **2007**, *315*, 493.
- [3] Greeley, J.; Stephens, I.E.L.; Bondarenko, A.S.; Johansson, T.P.; Hansen, H.A.; Jaramillo, T.F.; Rossmeisl, J.; Chorkendorff, I.; Nørskov, J.K. *Nature Chem.* **2009**, *1*, 552.
- [4] Stephens, I.E.L.; Bondarenko, A.S.; Grønbjerg, U.; Rossmeisl, J.; Chorkendorff, I. *Energy Environ. Sci* **2012**, *5*, 6744.
- [5] Strasser, P. *et al. Nature Chem.* **2010**, *2*, 454.

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