

Mass-selected nanoparticles of Pt_xY as model catalysts for oxygen electroreduction

A team of researchers from DTU Physics, DTU CEN, and SLAC National Laboratory have demonstrated the superior performance of nanoparticles of Pt_xY as catalysts for oxygen electroreduction.

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Polymer electrolyte membrane fuel cells (PEMFCs) hold promise as a potentially zero-emission alternative source of power for automotive vehicles. Moreover, in comparison to batteries, they provide much longer driving ranges and faster refuelling times. Even so, the widespread uptake of PEMFC's has been hampered by the need for high loadings of platinum catalysts at the cathode, where oxygen reduction takes place. Even using current state-of-the-art technology, it would not be possible to scale up PEMFC production to make a global impact, i.e. to the terawatt level.

Arguably, the most viable route towards decreasing the platinum loading is to employ alloys of platinum with other metals as catalysts for oxygen reduction. Most researchers have focused on alloys of platinum with late transition metals, such as nickel, cobalt, copper or iron. Even so, the long term stability of these catalysts is typically compromised by their tendency to degrade via dealloying. The dealloying results in the segregation of the less noble late transition metal to the surface of the catalyst, which subsequently dissolves in the acidic electrolyte.

In 2009, a team of researchers from Center for Individual Nanoparticle Functionality (CINF) at DTU Physics discovered a new alloy for oxygen reduction, platinum-yttrium¹. Not only was this new alloy more active than the other alloys of platinum and early transition metals, but it could potentially be much more stable. The exceptionally strong bond between platinum and yttrium should prevent dealloying. However, platinum-yttrium was first tested in bulk polycrystalline form. However, in a real fuel cell it would have to be implemented in nanoparticulate form, i.e. with a high ratio of surface atoms to the catalyst core. This turned out to be a highly challenging task, simply because platinum is a noble metal, and can be reduced to the metallic form easily, whereas yttrium is highly oxophilic and hence extremely challenging to reduce.

Nonetheless, as reported in the *** issue of Nature Chemistry, researchers from DTU Physics have now managed to synthesise nanoparticles of the platinum yttrium alloy. They achieved this by using a physical method, involving magnetron sputtering; the advantage of this synthesis route is that it allows a high degree of control over the nanocatalyst produced, with a well-defined size and composition. This in turn, allows for scientific insight into the relationship between the structure and functionality of the particles.

¹ Nature Chemistry 1, 552 - 556 (2009): "Alloys of platinum and early transition metals as oxygen reduction electrocatalysts" by J. Greeley et al.

The particles were characterised using a large number of spectroscopic and imaging techniques. The most active catalysts exhibited a high mass activity of 3.05 A/mg Pt, a factor of five improvement over commercial platinum catalysts measured in the same manner. Moreover, the new catalyst retained 63% of its initial activity in an extended stability test.

It turns out that the catalyst forms a Pt overlayer at the surface, as the yttrium will leach out from the first nanometer of the catalyst surface. X-ray absorption spectroscopy measurements (carried out at SLAC National Laboratory, in California), showed that the effect of alloying was to induce compressive strain onto the nanoparticles. This in turn, led to improved catalytic activity for oxygen reduction, relative to pure platinum catalysts, due to a mildly weaker bond between the platinum surface atoms and the hydroxyl reaction intermediates.

In summary, the results demonstrate a proof-of-principle that platinum-yttrium nanoparticles can be synthesised and are highly active for the oxygen reduction reaction. There is further potential for even higher, record-setting performance if the particle size and composition can be optimised. The physical origin of the activity enhancement has been identified: it is due to the formation of a core-shell structure with a compressively strained outer Pt shell. The next challenge in order for this promising material to find its way into fuel cell applications will be the development of a chemical synthesis method that allows for production of the catalyst in large quantities.