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Exploring the local composition of novel well defined size-selected Pt alloy nanocatalysts for Oxygen Reduction

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Motivation
The major limitation of proton exchange membrane fuel cell technology is the high cost due to the high loading of Pt used to catalyse the oxygen reduction reaction (ORR) at the cathode. Allowing nanoparticles of Pt with less noble late transitions metals has been found to enhance the ORR [1]. Furthermore, the alloy catalysts are cheaper compared to the currently used expensive catalysts.

Pt₃Y has been identified on the basis of density functional theory calculations as being a catalyst that is both active and stable. Subsequent experiments on smooth, polycrystalline electrodes confirmed these theoretical notions: the catalyst exhibited the highest activity ever reported for a polycrystalline surface prepared in this way [2]. Here we present an electron microscopy study of a model Pt₃Y electrolyte catalyst in the more relevant form of nanoparticles.

Synthesis of Pt₃Y nanoparticles
Well defined Pt₃Y nanoparticles are prepared at DTU CINF laboratories using a Magnetron cluster source. This technique allows to fine control parameters such as particle size, coverage and density.

Electron Microscopy Analysis
High Resolution TEM/STEM imaging indicates a polycrystalline form of the nanoparticles. Particle size distribution shows the narrow peak of the selected size (~7 nm).

Core-loss Spectroscopy
Fundamental insight of the alloy formation is needed in order to better understand the stability and activity of the catalyst. To extract the chemical information Electron Energy Loss Spectroscopy (EELS) has been used. Thanks to the aberration-corrected STEM, a bright small probe is positioned on the particle and the inelastic scattered electron spectra are collected in the post-column electron spectrometer.

Beam Damage
In the core-loss region of the EELS spectrum, Y and Pt present major features at high energy losses. In this region the signal is intrinsically low. This brings to the use of long exposure times for the spectrum collection (3x10 s for the core-loss spectrum). At such acquisition times the beam damage increases dramatically.

Low-loss Spectroscopy
Minor weak edges are present when acquiring the low-loss region of the EELS spectrum. Here, the signal intensity is very high, allowing the collection of the spectra with short acquisition times (200 ms for the following spectrum) and therefore reduce the beam damage. The drawback is the overlap of plasmon resonances of the nanoparticle elements and the carbon from the support.

Comparison between the low loss region of the C support and the PtₓY particle on top of the C layer.

By placing the STEM probe on particles sitting on the border of the carbon support it is possible to obtain low loss spectra without carbon components. The five different spectra acquired on different (but same size) particles show a consistent shape of the low loss region for the PtₓY alloy nanoparticles.

Conclusion and Outlook
In this study we have been able to recognise the low loss PtₓY feature from the pure Pt one. The use of the low loss part of the EELS spectrum allows us to reduce the acquisition times and hence limit the electron beam damage. This condition will be used in future for chemical composition mapping in non-homogeneous alloy nanoparticles.

References