DTU Library

Advanced Electron Microscopy Study of Platinum Alloy Nanoparticles

Deiana, Davide; Hernandez-Fernandez, Patricia; Strebel, Christian Ejersbo; McCarthy, David Norman; Stephens, Ifan; Chorkendorff, Ib; Wagner, Jakob Birkedal; Hansen, Thomas Willum

Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

DTU Cen
Center for Electron Nanoscopy

Center for Individual Nanoparticle Functionality

DTU

Advanced Electron Microscopy Study of Platinum Alloy Nanoparticles

D. Deiana[1], P. Hernandez-Fernandez[2], C. Strebel[2], D.N. McCarthy[2], I.E.L. Stephens[2], I. Chorkendorff[2], J.B. Wagner[1] and T.W. Hansen[1]

[1] Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Lyngby, Denmark
[2] Center for Individual Nanoparticle Functionality, Technical University of Denmark, DK-2800 Lyngby, Denmark

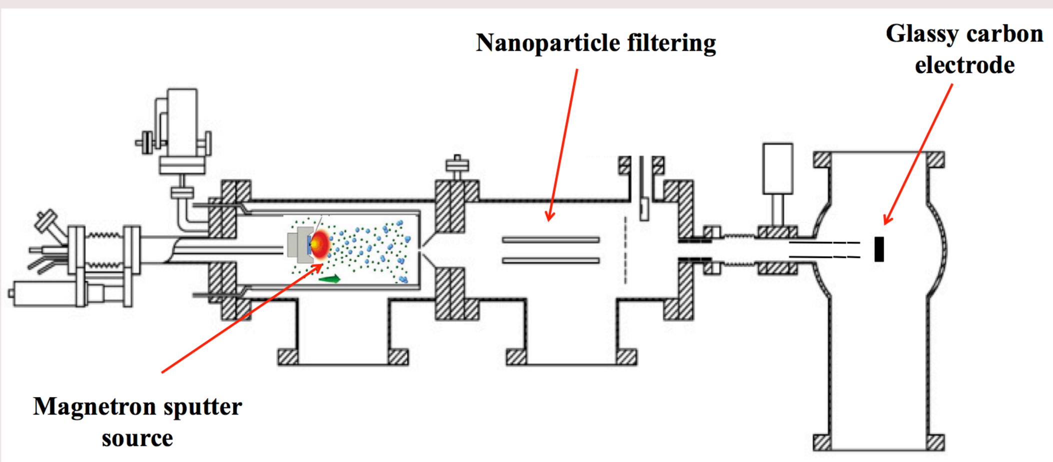
Motivation

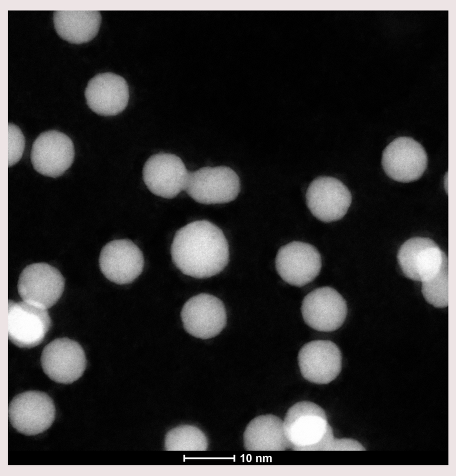
The major limitation of proton exchange membrane fuel cell technology is the high cost due to the high loading of Pt used to catalyse the oxygen reduction reaction (ORR) at the cathode. Alloying nanoparticles of Pt with less noble late transitions metals has been found to enhance the ORR [1]. Furthermore,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

Pt_3Y 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 Pt_xY electrocatalyst in the more relevant form of nanoparticles.

Synthesis of PtY nanoparticles

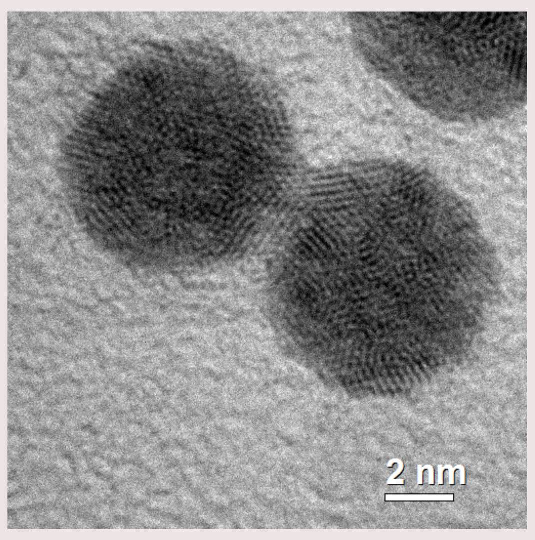
Well defined Pt_xY nanoparticles are prepared at DTU CINF laboratories using a Magnetron cluster source. This technique allows to fine control parameters such as particle size, coverage and density.



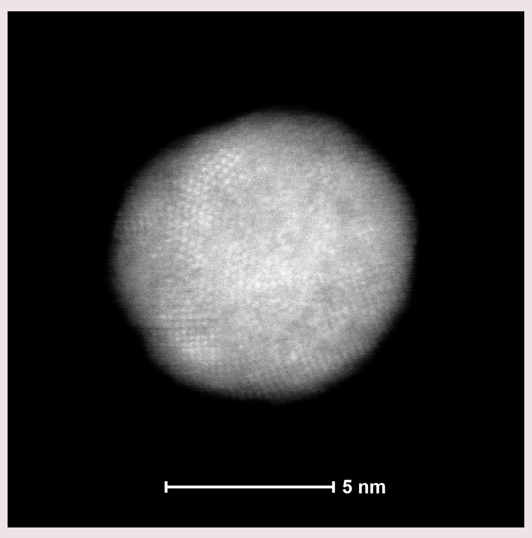


Electron Microscopy Analysis

High Resolution TEM/STEM imaging indicates a polycrystalline form of the nanoparticles.



HR-TEM image, 200 kV

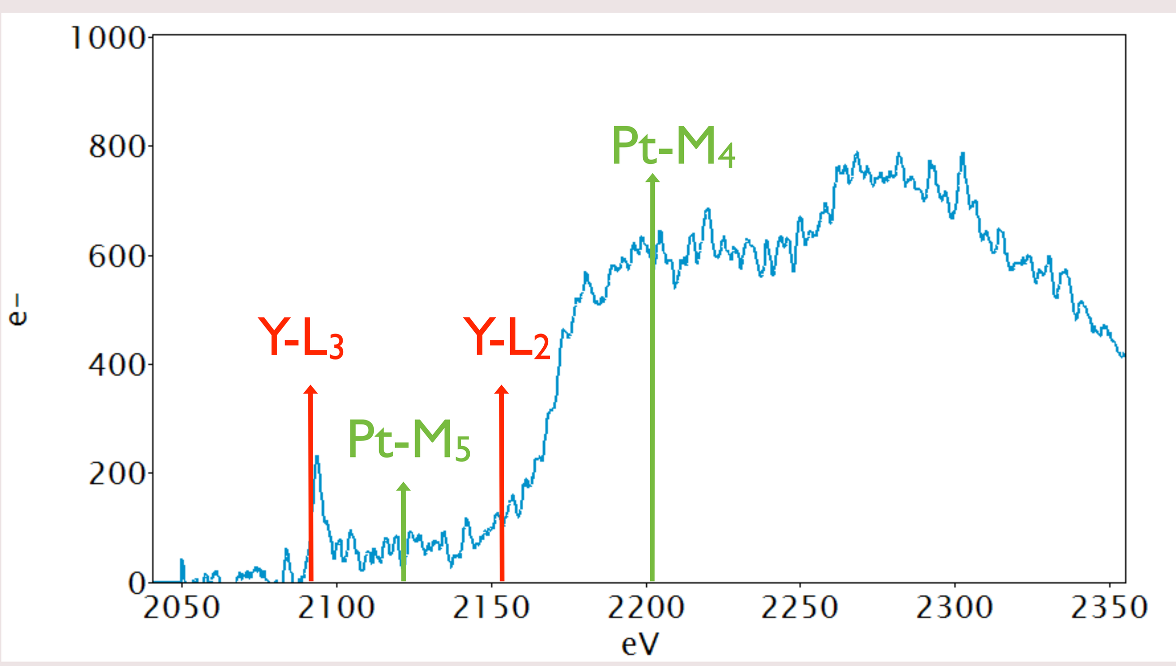


HAADF HR-STEM image
120 kV C_s probe-corrected

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.

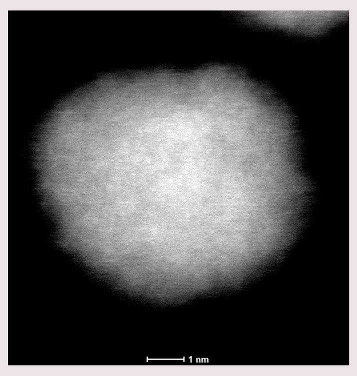


Core-loss spectrum of Pt_xY nanoparticle

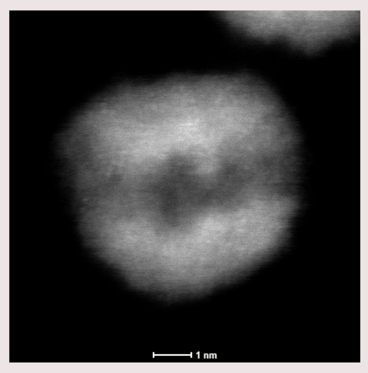
Edge	Energy (eV)
$Y\text{-}L_3$	2080
$Y\text{-}L_2$	2155
$Pt\text{-}M_5$	2122
$Pt\text{-}M_4$	2202

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.



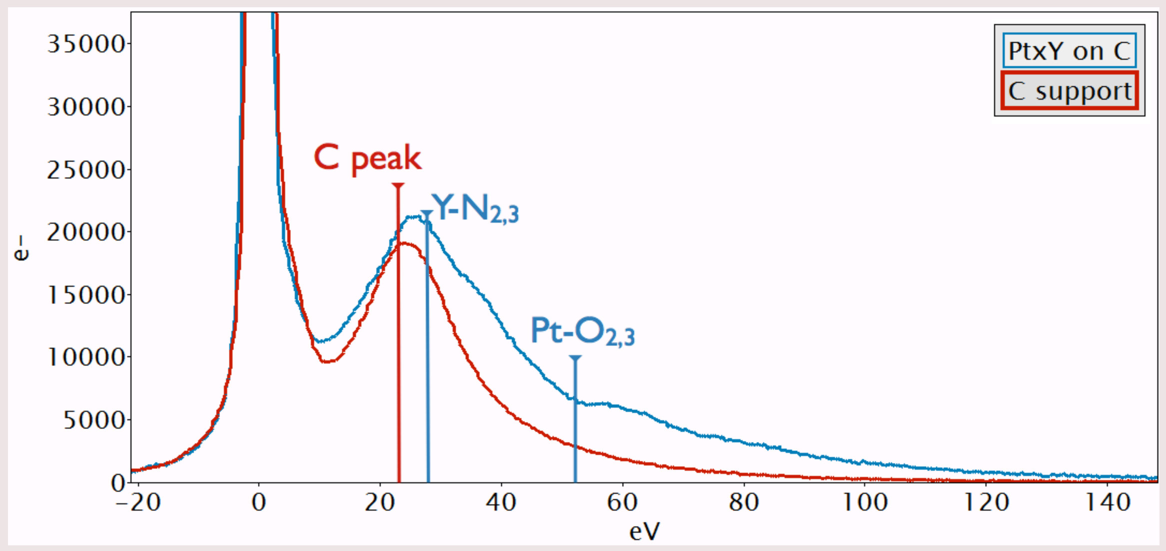
Before EELS acquisition



After EELS acquisition

Low-loss Spectroscopy

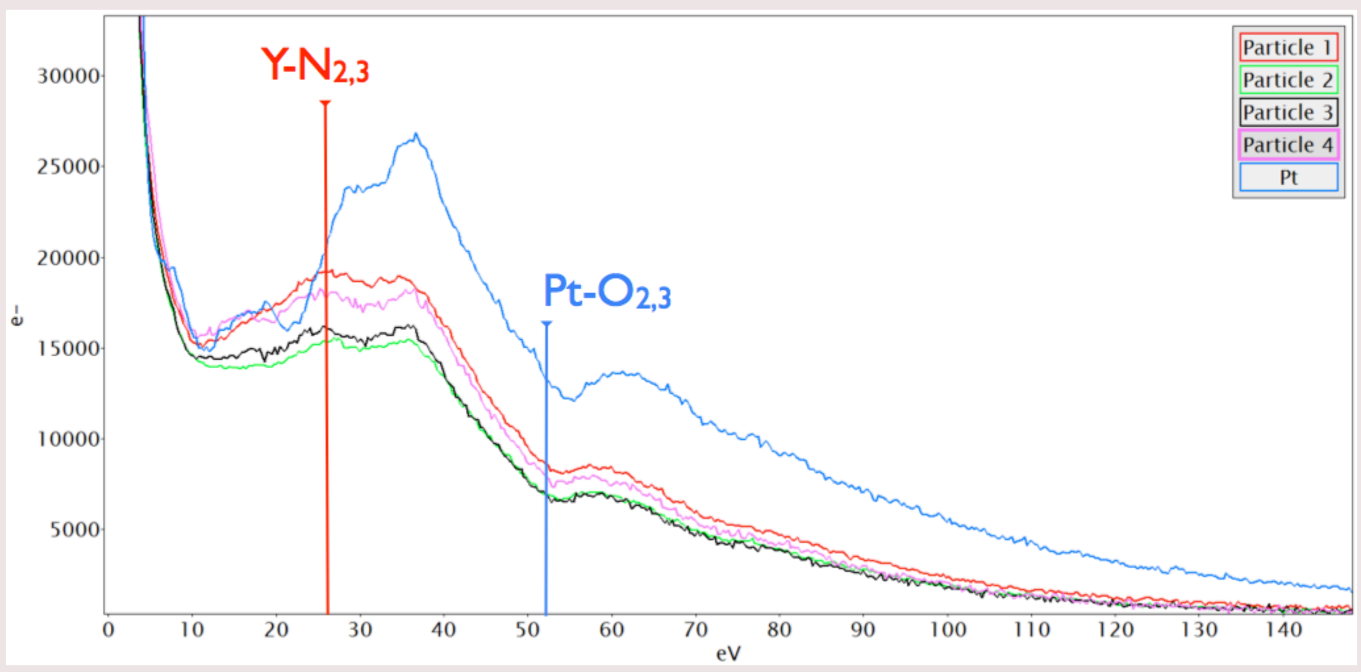
Minor weak edges are present when acquiring the low-loss region of the EELS spectrum. Here, the signal intensity is very high, allowing the collection of the spectra with short acquisition times (200 ms for the following spectrum) and therefore reduce the beam damage. The drawback is the overlap of plasmon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

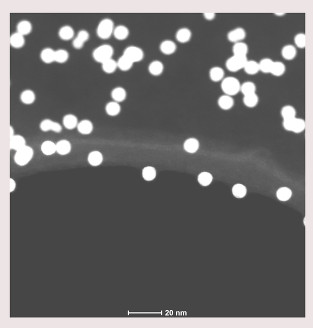


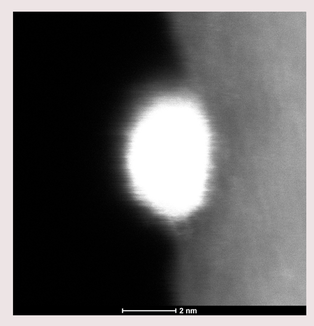
Edge	Energy (eV)
$Y\text{-}N_{2,3}$	26
$Pt\text{-}O_{2,3}$	52
C (π+σ)	~ 20

Comparison between the low loss region of the C support and the Pt_xY 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 Pt_xY.







The spectrum of a pure Pt nanoparticle [3] of the same size has been acquired and compared with the one of the platinum alloy. The difference in shape between the two is clearly visible, allowing the possibility to localise Y-rich region with respect to Pt-rich ones.

Conclusion and Outlook

In this study we have been able to recognise the low loss Pt-Y 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

[1] P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. Yu, Z. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney, and A. Nilsson, Nature chemistry, 6 (2010), 454–60.

[2] J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, and J. K. Nørskov, Nature chemistry, 7 (2010), 552–6.

[3] F. J. Perez-Alonso, D. N. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I. E. L. Stephens, J. H. Nielsen, and I. Chorkendorff, Angewandte Chemie, 19 (2012), 4641–4643.

Acknowledgement. *The Center for Individual Nanoparticle Functionality is supported by the Danish National Research Foundation. The A.P. Møller and Chastine Mc-Kinney Møller Foundation is acknowledged for their contribution toward the establishment of the Center for Electron Nanoscopy in the Technical University of Denmark.*