

## **Pt Nanoparticles by EELS and ab initio calculations**

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A great effort in material research for fuel cell reactions is devoted to explore novel materials, to increase tolerance to poisonous species, to reduce the cost of electrocatalysts and to decrease the Pt loading [1-3]. Improvement of Pt activity for electrocatalytic reactions can be accomplished by modifying and/or alloying Pt nanoparticles with other metals [4, 5]. Another route is to modify platinum with a chalcogenide. In this connection, this work focuses on the development of materials used as electrocatalysts through a synthesis procedure with sulphur- platinum. The traditional synthesizing approaches have not been successful in producing high quality core-shell type nanoparticles. These difficulties are due to several factors including random nucleation processes and inhomogeneous growth of the heterometallic component on top of the seeding host nanomaterials [6]

Over the last two decades high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM), combined with nanometer resolution electron diffraction, electron energy-loss spectroscopy (EELS), energy-dispersive X-ray (EDX) spectroscopy (the so called analytical electron microscopy, AEM) and energy-filtering transmission electron microscopy (EFTEM) have become the major techniques for direct structural and analytical investigation of ultrafine particles [7].

In this work we have focused in the study of PtS nanoparticles by Low-Loss Electron Energy Loss Spectroscopy (EELS), as well as ab initio calculations. EELS

spectra were acquired using a Gatan Parallel Electron Energy Loss Spectrometer (PEELS model 766). The resolution of the spectra was determined by measuring the full width at half-maximum (FWHM) of the zero loss peak and this was typically close to 1.4 eV, when the TEM was operated at 200 kV.

Figs. 1a and 1b show the energy loss function  $\text{Im}[-1/\epsilon]$ , from experimental (EELS) and numerical calculations (Wien2k) respectively, for Pt nanoparticles. Comparison of the experimental and calculated spectra is indeed quite acceptable, as long as peak positions are concerned. Calculated peaks B and C, with energies 24.8.0 eV and 38.0 eV come from plasmon excitations, as deduced from Fig. 2, where we have plotted the calculated real part of the dielectric function  $\epsilon_1$ , crossing the energy axis with positive slope twice, at 25.2 eV and 35.5 eV. Corresponding peaks in experimental EELS (Fig. 1a) are found at 24.6 eV and 32.4 eV, respectively. The peak A comes from interband transitions at 13.6 eV from numerical calculations and corresponding to 12.4 eV from experimental results. The peak D comes from O<sub>2,3</sub> ionization edge. Fig. 3 shows the Kramers-Krönig derived imaginary part of the experimental dielectric function  $\epsilon_2$  and theoretical calculations. Fig. 4 shows more structure that imaginary part of the experimental dielectric function  $\epsilon_2$ . Our calculations are in good agreement with the experiment in both shape and energy position. The numerical calculations offer then, a great help in the EELS spectra interpretation.

#### References

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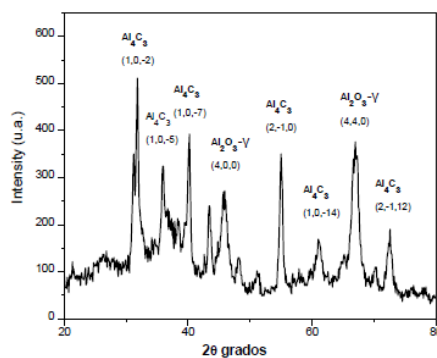


Figure 1. X-Ray diffraction pattern from the sintered mixture Al-C 4h MM and 2h sintering.

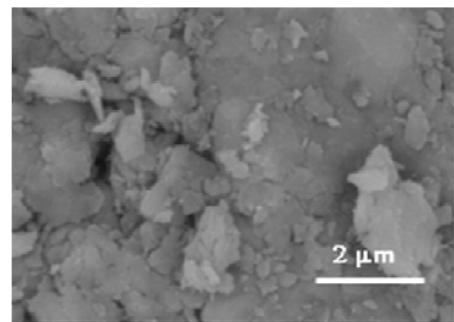


Figure 2. Backscattered image from the sintered mixture Al-C 4h MM and 2h sintering.

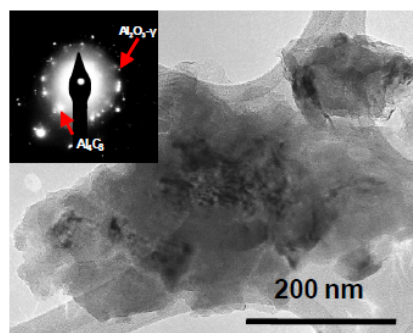


Figure 3. TEM bright field image and SADP from a particle of the sintered mixture Al-C.

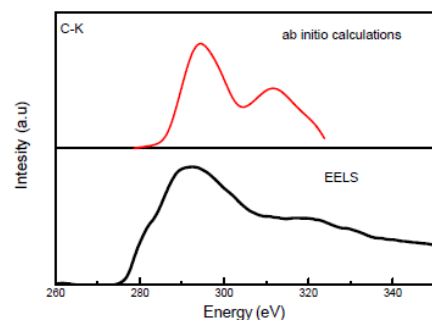


Figure 4. Experimental and calculated C-K ionization edge.