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Effect of Electron Dose on Imaging of Ni@Pt Nanoparticles for Fuel Cells

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The widespread applications of fuel cell devices require electrocatalysis cost reduction. Especially a decrease of Pt loading of catalyst layers (CL) is an effective strategy for such a goal i.e., use less than 0.1 g/kW of Pt [1]. As a consequence the development of new Pt-based catalysts, with stability, superior electrocatalytic activity and improved active surface area utilization is very important. As for the catalytic activity, core-shell catalysts have been recently under intense investigation. The specific and mass activity of these Pt monolayer electrocatalysts for the oxygen reduction reaction (ORR) can be several times higher than that of commercial Pt/C materials [2]. In this work, the structural characterization is done by means of transmission electron microscopy with the objective to determine shape and atomic distribution of Pt for different loadings (0-30%) on a Ni core basis. In all cases the electron dose rate has been kept in the range 20-100 $e^-/Å^2s$ in order to avoid surface rearrangement by interaction with the electron beam. Depending on the particle position in the supporting film, the dose rate needs to be varied in order to avoid sample vibration that can affect the final results. The TEAM 05 has been used for this work, the dose rate in this microscope can be varied by adjusting the beam position through the monochromator setting. In all cases TEM is used and a focal series reconstruction procedure (EWR) is used to recover both phase and amplitude images that provide information of the spacing between atomic planes and the chemical nature of the corresponding atomic columns.

Figure 1 shows XPS spectra for the different Pt coverage loadings under investigation. The spectra show a rather homogeneous core distribution for all catalysts with a clear increase of the Pt 4f core level response as the Pt loading becomes higher. Figure 2 shows a sequence of experimental images (dose rate 60 $e^-/Å^2s$) and the resulting EWR phase image for a nanoparticle with 30 % Pt coverage. The phase image recovers lattice spacings, atomic nature of the columns and provides an increased contrast as compared to the experimental images. Figure 3 shows the same image together with a preliminary analysis of the recovered phases on an atomic column basis. Ni and Pt have a very different scattering factors and to a first approximation the measured intensities (recovered phase) can be related used to evaluate chemical content. Fig. 3c shows differences in spacing and chemical nature of several columns in the atomic line shown in Fig. 3a. Fig 2b shows also the intensities in the whole particle and allows a description of the elemental distribution. Accordingly, Pt is seen to cover partially the surface of this particle. Figure 4 shows a similar set of results but for a particle with nominally 10 % Pt loading coverage. The dose rate is 50 $e^-/Å^2s$ in this case. There is a difference in the number of high intensity spots in the phase images that reflects the processing and desired nominal Pt coverage. Although fully quantitative results are difficult to obtain the technique in use shows compositional differences in the investigated nanoparticles. Additionally the rather low dose rate reduces beam sample interaction allowing a more precise characterization of the shape and exposed surfaces.

References:

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[2] R.R. Adzic et al. Science 109 (2005) 22701-22704. S.J. Hwang et al. JACS 1434 (2012) 19508.

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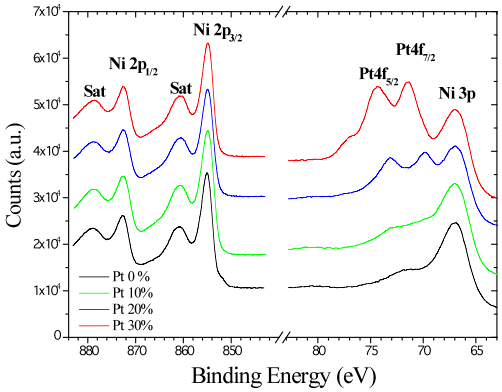

Fig. 1. XPS spectra of Ni2p, Ni2p-sat and 3p-Pt4f electronic core level for different Ni@Pt core-shell catalysts with different Pt loading coverages.

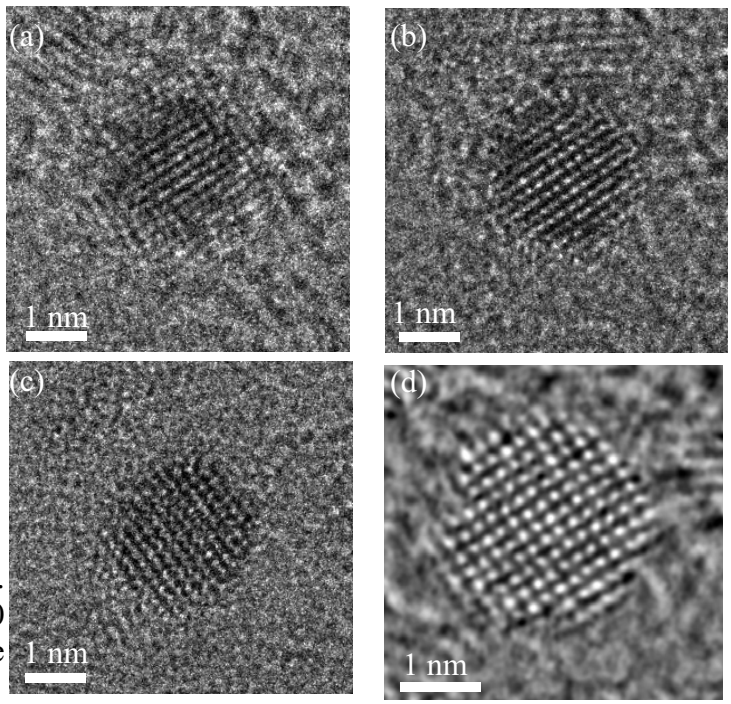

Fig. 2. Ni@Pt nanoparticle 30 % Pt loading. Experimental images at a defocus of (a) 220 nm (b) 0 nm and (c) -165 nm. (d) Phase image after EWR.

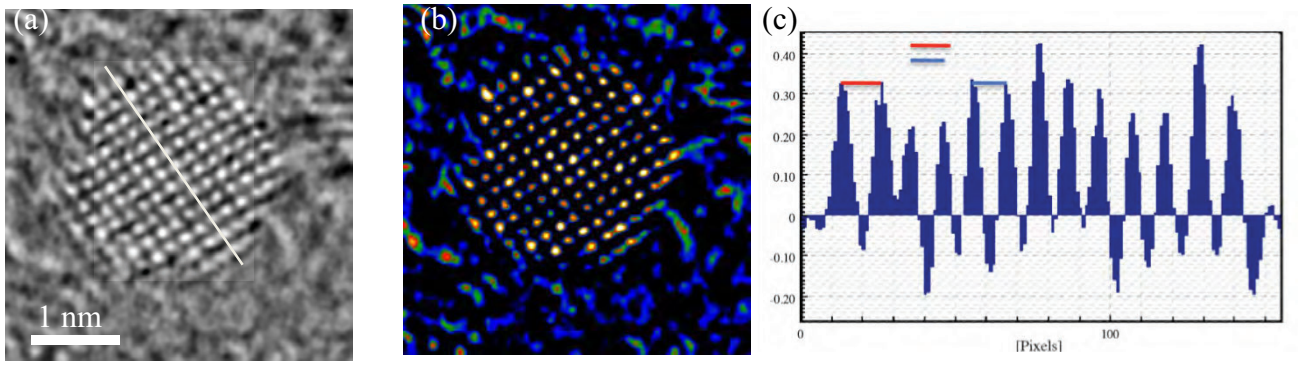

Figure 3. Ni@Pt nanoparticle with a 30% Pt coverage. (a) Phase image in gray and (b) color tones (c) line profile across line in (a). The phase image intensity suggests the relative abundance of Pt as well as a locally different lattice spacing.

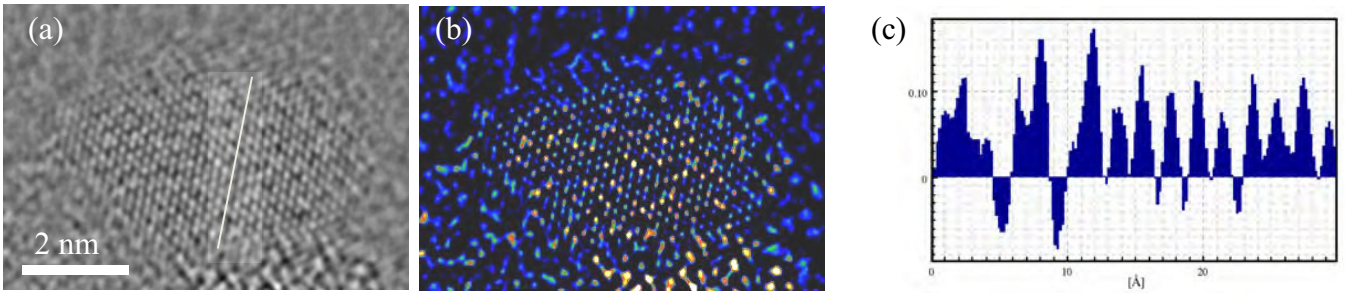

Figure 4. Ni@Pt nanoparticle with a 10% Pt coverage. (a) Phase image in gray and (b) color tones (c) line profile across line in (a).

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