P-53

Nano-structured Pt embedded in the acidic salts of heteropolymolybdate matrices: MS XAFS study

A. Witkowska[1]*, S. Dsoke[2], R. Marassi[2] and A. Di Cicco[3]

[1]*Department of Solid State Physics, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland*
[2]*Chemistry Department, University of Camerino, I-62032 Camerino (MC), Italy*
[3]*School of Science and Technology, Physics Division, University of Camerino , I-62032 Camerino (MC), Italy*

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*e-mail: agnieszka@mif.pg.gda.pl

In the contribution, X-ray absorption spectroscopy (XAS) study combined with TEM and XRD analysis of a novel Pt-based catalyst operating at low temperature fuel cells (FCs) is presented. Low temperature fuel cells generally utilize solid polymer electrolytes and they are a promising class of compact devices representing a future alternative to fossil fuels based engines. Up to now one of the most challenging goals in development of these type of FCs is to accelerate too slow oxygen reduction reaction (ORR) and limit the requested amount of Pt in the catalyst [1,2]. A significant decrease of the Pt loading during the last two decades accompanied by tangible improvements of power density has been achieved [3]. The result has been obtained mainly by diminishing the metal grain size to the nanometric scale and by improving homogeneity of the nanocatalysts dispersion on a support.

Innovation in the case of the considered catalyst resides in the use of a porous inorganic matrix of acidic heteropolymolybdate salts of composition $X_{2.5}H_{0.5}YMo_{12}O_{40}$, where X = Cs, Rb and Y = P, Si as a catalyst support [4,5]. The meso-microporous matrix is characterized by good stability, insolubility in water, and exhibits high acidity (proton availability and mobility). To prepare electrocatalysts, the platinum ions were introduced using electrochemical method to the heteropolyacid salts and then were reduced using an H_2/Argon stream at 300ºC. Most of the Pt metallic nanoparticles created during the reduction process were embedded into a support pores which size can be controlled by the kind and content of cation used. Thus, the desired/optimal Pt nanoparticle size can be precisely defined by the proper heteropolyacid salt composition.

Presented results show the relation between the matrix composition and the size of the obtained metallic Pt nanoparticles determined mainly by mean of multiple-scattering extended X-ray absorption fine structure (MS EXAFS) analysis [6] (using two- and three-body configurations degeneracies as shown in Figure 1 and relation between the first shell mean distance and coordination number introduced in [7]). TEM and XRD-extracted nanoparticle diameters are also presented and compared with XAFS results. Accuracy and sensibility of the applied techniques and approaches in micro- and nanoscopic structural analysis of these novel low-Pt content catalysts are discussed.

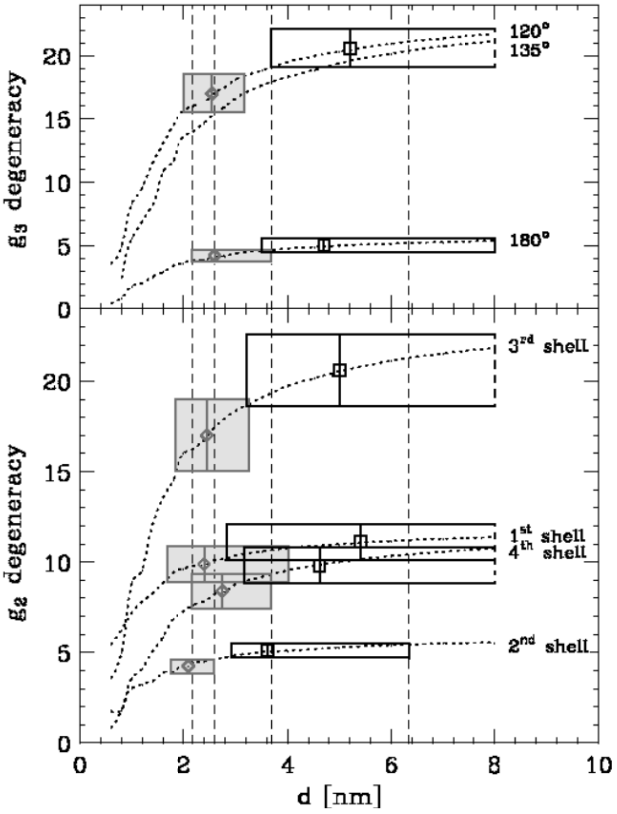

Figure 1. Pt nanoparticles size determination performed on the base of model calculations (doted lines) and MS EXAFS analysis for: $5\%Pt^{IV}$-$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ catalyst (d_{ave}= 2.4(2)nm) – diamond and gray uncertainty box; $5\%Pt^{IV}$-$Rb_{2.5}H_{0.5}PMo_{12}O_{40}$ catalyst (d_{ave} = 5.0(1.3)nm) – square and white uncertainty box.

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