Structure of bimetallic PtCu/C nanocatalysts studied by ASAXS and EXAFS

N. V. Bulat (a), L. A. Avakyan (a), V. V. Pryadchenko (a), D. B. Shemet (a), V. E. Guterman (b), L. A. Bugaev (a)

bulat@sfedu.ru

(a) Southern Federal University, Department of Physics, Zorge Str. 5, RU-344090 Rostov-on-Don, Russia,
(b) Southern Federal University, Department of Chemistry, Zorge Str. 7, RU-344090 Rostov-on-Don, Russia

Platinum-containing nanocomposite electro-catalysts are perspective for oxygen reduction reaction in low-temperature fuel cells. Today the use of environmentally friendly hydrogen energy is restrained by the high cost of pure platinum electrochemical catalysts. To solve this problem, the synthesis of electro-catalysts containing bimetallic nanoparticles with copper core and platinum shell structure was proposed, so that the content of platinum and the cost of the material is reduced [1].

Knowledge of structure of nanoparticles is necessary for a detailed understanding of the nanoscale processes and their relationship with the catalytic properties. Information about nano- and sub-nano scale (atomic) structure of such materials can be obtained by various of methods, involving X-ray radiation: anomalous small-angle X-ray scattering (ASAXS) [2], X-ray absorption spectroscopy (XAS). Extinguishing feature of ASAXS method is the possibility of extraction of contributions from X-ray scattering on atoms of particular type from all scattering processes in multicomponent system due to the energy dependence of atomic factor. The contributions from scattering on platinum and on copper atoms were extracted by two methods: 1) subtraction of two diffraction curves corresponding to different pairs of energy points and 2) solving of the system of linear algebraic equations corresponding to three or more energy points. After that the information about the structure can be extracted by direct fitting of the obtained anomalous small-angle curves. The equivalence of these two approaches for the studied materials was shown in this work. Also, size distributions of platinum and copper nanoparticles' components were obtained. X-ray absorption spectroscopy is very sensitive to local atomic structure of X-ray absorbing atoms. The analysis of the extended X-ray absorption fine structure (EXAFS) provides interatomic distances and coordination numbers averaged over all positions of the absorbing atom in all nanoparticles [3, 4].

The performed EXAFS analysis near platinum and copper absorption edges made it possible to determine average interatomic distances and average coordination numbers (Pt-Pt, Cu-Cu, Pt-Cu, Cu-Pt), which allowed to construct 3D models of the average nanocluster for each considered electro-catalyst. These cluster models were verified and complemented by size distributions and structural information obtained from ASAXS.

The formation of a core-shell structure for samples were established at certain treatment conditions. After intense thermal treatment the core-shell structure transforms to partially ordered alloy structure.

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