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In-situ TEM and Atomic-Resolution STEM Study of Highly Active Partially Ordered Cu_3Pt Nanoparticles used as PEM-Fuel Cells Catalyst

Goran Dražić[1], Marjan Bele[1], Andraž Pavlišič[1], Primož Jovanovič[1], Milena Zorko[1], Nejc Hodnik[2], Barbara Jozinovič[1], Miran Gaberšček[1]

[1.] Laboratory for Materials Chemistry, National Institute of Chemistry, Ljubljana, Slovenia
[2.] Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Ljubljana, Slovenia

The efficiency of harvesting the energy in proton exchange membrane fuel cells (PEM-FC), like in all other types of fuel-cells, is mainly limited by the activity of the cathode catalyst for oxygen reducing reaction (ORR). Various catalysts, such as noble metals, intermetallic alloys, carbon-based supports, metal chalcogenides and carbides, are used to reduce the ORR temperature and achieve maximum reaction efficiency [1]. The main problem is slow adsorption and reaction kinetics, so searching for more efficient catalysts is one of the main challenges in the field of fuel cells. Among the most promising materials are C-supported Pt-based catalysts [2, 3]. In order to reduce the price of the material, Pt has been alloyed with various transition metal elements. In many cases not only the expected mass activity of the catalyst is improved, but also its specific activity is enhanced due to crystal lattice strains and the ligand effects through the d-band center shift induced by the transition elements [4, 5]. In the case of C-supported $CoPt_3$ particles it has been recently shown that the electrocatalytic activity can be radically increased through core-shell structural ordering of intermetallic nanoparticles [5].

Using a novel, modified sol-gel method the ordered (Pm3-m) Pt-Cu nanoparticles for catalytic oxygen reduction reaction applications were prepared. Tailoring specific parameters like chemical composition, degree of ordering, presence of Pt rich layer at the surface of the nanoparticles and appropriate embedding in carbon matrix the material obtained exhibits a 5-fold improvement of mass activity and a 9-fold improvement of specific activity compared to the Pt/C benchmark. These values exceed markedly the US Department of Energy target for 2017.

To understand the processes and chemical reactions taking place during the synthesis of the catalyst material, *in-situ* heating experiments were performed in transmission electron microscope. The formation of spherical Cu_3Pt particles was followed from the room temperature to 800 °C. In Figure 1 an example of the evolution of catalyst material from precursors from room temperature to 800 °C is displayed. The chemical composition of catalyst particles, densely populated on carbon support and with an average size between 20-50 nm, was determined with EDXS. Phase composition was examined with electron diffraction and XRD.

Detailed analysis of Cu-Pt particles prepared at different conditions showed a core-shell type of alloy. The core consisted of disordered Fm3-m cubic phase where Pt and Cu atoms are statistically distributed inside the spheres. Around this disordered core, an ordered Pm3-m shell could be formed during the annealing procedures. Furthermore, consistently with previous reports on similar alloy systems [5] the existence of a Pt-rich outer layer, 1- 2 nm thick, called skin, can be demonstrated on the surface of particles (Figure 1c). It is possible that additional effects besides Pt skin and ordered phase could be present. We observe some twinning and other crystallographic defects like dislocations that could

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contribute to the strain of the surface platinum and hence to the very high specific activity. The presence of ordered Cu_3Pt Pm3-m phase and Pt-rich skin was proved with an atomic-resolution Cs corrected STEM. In Figure 2 cross-sections of different Cu-Pt particle are shown.

The influence of the synthesis conditions on the formation of ordered Pm3-m structure and Pt-rich skin will be explained in detail and the impact of those parameters on the final properties will be discussed.

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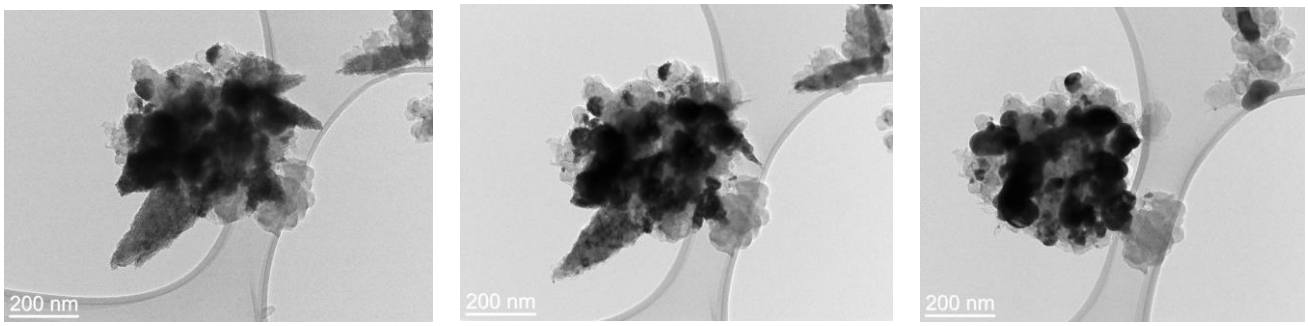

Figure 1. In-situ heating experiment: evolution of the Cu_3Pt based catalyst material

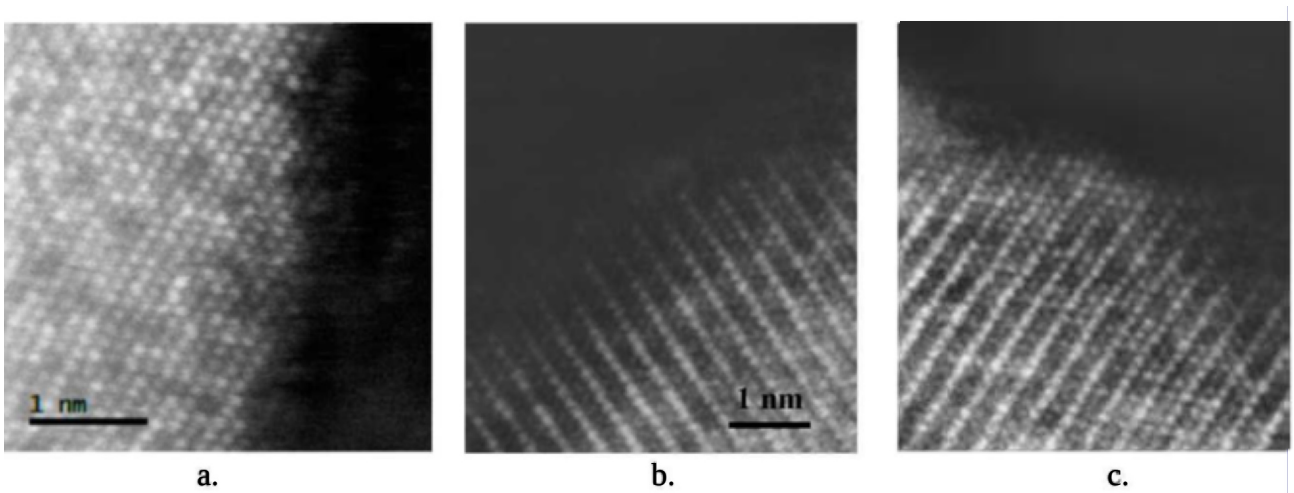

Figure 2. Cs corrected HAADF-STEM images of Cu_3Pt particles with a) disordered Fm-3m structure, b) ordered Pm-3m structure and c) ordered Pm-3m structure with Pt skin on the surface. The atomic columns with a brighter contrast correspond to Pt.

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