Various catalysts, such as noble metals, intermetallic alloys, carbon-based supports, metal chalcogenides and carbides, are used to reduce the oxygen reducing reaction temperature and achieve maximum reaction efficiency in proton exchange membrane fuel-cells. 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. 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. In the case of C-supported CoPt₃ particles it has been recently shown that the electrocatalytic activity can be radically increased through core-shell structural ordering of intermetallic nanoparticles. 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. 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 the existence of a Pt-rich outer layer, 1-2 nm thick, called skin, can be demonstrated on the surface of particles. 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 contribute to the strain of the surface platinum and hence to the very high specific activity. The presence of ordered Cu-Pt Pm3-m phase and Pt-rich skin was proved with an atomic-resolution Cs corrected STEM. In Figure 2 cross-sections of 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.

Acknowledgement: The work was financed through the P2-0148 research program by Slovenian Research Agency.
Fig. 1: STEM images (a. BF-STEM, b. ADF-STEM) of Cu₃Pt nanoparticles.

Fig. 2: HAADF-STEM images of a. Cu₃Pt nanoparticle with ordered Pm3-m structure. At the surface of the particle 2nm thick Pt rich skin is present. b. Atomic resolution image of the Pt rich skin layer at the surface.