Role of copper and gold in improvement of the electrochemical oxygen reduction on palladium nanoparticles in alkaline solution

Maja Obradović[1], Uroš Lačnjevac[2], Vuk Radmilović[3], Aleksandra Gavrilović-Wohlmuther[4], Jelena Rogan[3], Sanja Stevanović[1], Velimir Radmilović[5], Snežana Gojković[3]

[1] *University of Belgrade – Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, Belgrade, Serbia*

[2] *University of Belgrade – Institute for Multidisciplinary Research, Kneza Višeslava 1, Belgrade, Serbia*

[3] *University of Belgrade – Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia*

[4] *Schoeller-Bleckmann Nitec GmbH, 2630 Ternitz, Austria*

[5] *Serbian Academy of Sciences and Arts, Knez Mihailova 35, Belgrade, Serbia*

Carbon supported nanocatalysts Pd/C, Pd-Cu/C and Pd-Cu-Au/C were synthesized using a borohydride reduction method and characterized by energy-dispersive X-ray spectroscopy, X-ray diffraction, and transmission electron microscopy. Crystallite size of ≤3 nm and low Cu and Au contents were found for Pd-Cu and Pd-Cu-Au catalyst; 8.2 at.% Cu and 4.4 at.% Au for Pd-Cu-Au/C and 17 at.% Cu for Pd-Cu/C catalyst with alloy structure [1].Thin layers of synthesized catalysts, supported on a glassy carbon rotating disk electrode, were examined for the electrochemical oxygen reduction reaction (ORR) in an O_2 saturated 0.1 M NaOH solution and compared with a commercial Pt/C. The electrochemically active surface area (EASA) was determined from CO_{ads} stripping voltammetry in deaerated 0.1 M NaOH solution [1], both initially and after a short stability test consisting of 500 potential cycles in N_2 and O_2 saturated solution (Fig. 1a). In addition, thin layers of Pd-Cu/C and Pd-Cu-Au/C catalysts were subjected to a short acid treatment, which resulted in the removal of surface Cu atoms and the production of Pd@Pd-Cu/C and Pd-Au@Pd-Cu-Au/C skin catalysts. Examination of the ORR kinetics showed first-order kinetics with respect to O_2, with nearly four electrons transferred per O_2 molecule on all catalysts. Bimetallic and trimetallic catalysts were more active for ORR than monometallic Pd/C and Pt/C catalyst with the highest specific activity (SA) achieved on skin-type catalysts (Fig. 1b). This indicates that the Cu atoms just beneath the surface of the nanoparticles are crucial for the high activity. The skin-type catalysts also exhibited higher activity after the stability test (Fig. 1b and 1c). The catalyst with the highest SA and mass activity (MA) after the stability test was skin-type Pd-Au@Pd-Cu-Au catalyst. Therefore, it was concluded that Pd-Au skin contribute to the stability during the ORR, as it was reported for Pt-Au skin catalyst [2].

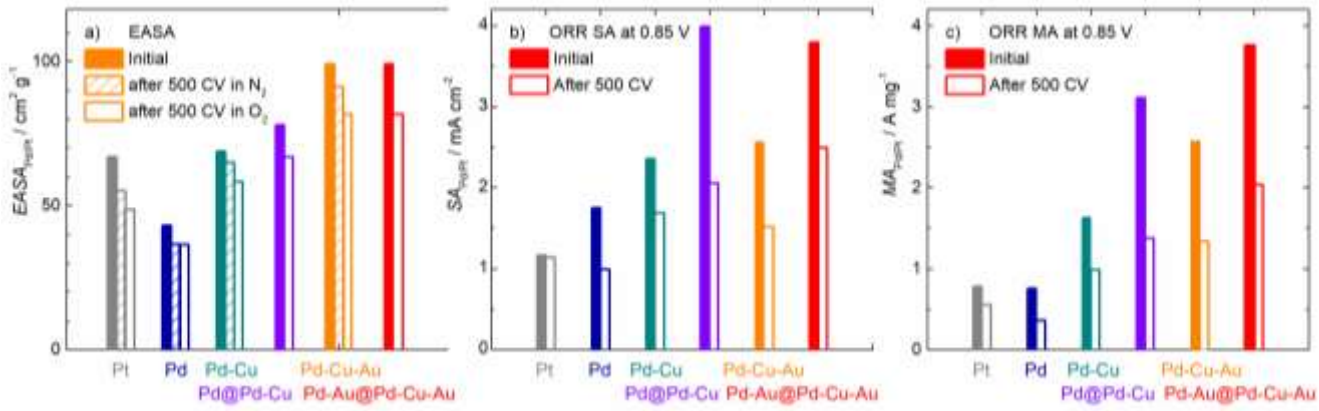

Figure 1. a) EASAs of investigated catalysts, their b) specific activity and c) mass activity for the ORR at the potential of 0.85 V. Specific and mass activity were calculated per area/mass of Pd or Pt

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