

**ELMINA**  
**ELMINA** 2022

**SECOND INTERNATIONAL CONFERENCE  
ON ELECTRON MICROSCOPY OF  
NANOSTRUCTURES**

**ДРУГА МЕЂУНАРОДНА КОНФЕРЕНЦИЈА  
О ЕЛЕКТРОНСКОЈ МИКРОСКОПИЈИ  
НАНОСТРУКТУРА**



August 22<sup>nd</sup>–26<sup>th</sup>, 2022, Belgrade, Serbia  
22–26. август 2022. Београд, Србија

**SECOND INTERNATIONAL CONFERENCE**

# **ELMINA 2022**

Serbian Academy of Sciences and Arts, Belgrade, Serbia  
August 22nd-26th, 2022  
<http://elmina.tmf.bg.ac.rs>

## **Program and Book of Abstracts**

Organized by:  
**Serbian Academy of Sciences and Arts**  
and  
**Faculty of Technology and Metallurgy, University of Belgrade**

Endorsed by:  
**European Microscopy Society**  
and  
**Federation of European Materials Societies**

**Title:** SECOND INTERNATIONAL CONFERENCE  
ELMINA 2022  
Program and Book of Abstracts

**Publisher:** Serbian Academy of Sciences and Arts  
Knez Mihailova 35, 11000 Belgrade, Serbia  
Phone: +381 11 2027200  
<https://www.sanu.ac.rs/en/>

**Editors:** Velimir R. Radmilović and Vuk V. Radmilović

**Technical Editor:** Vuk V. Radmilović

**Cover page:** Raša Hindawi

**Copyright:** © 2022 Serbian Academy of Sciences and Arts

**Printed in:** Serbian Academy of Sciences and Arts  
Knez Mihailova 35, 11000 Belgrade, Serbia  
Phone: +381 11 2027128  
[stamparija@sanu.ac.rs](mailto:stamparija@sanu.ac.rs)  
Circulation: 55 copies.

## **Cu<sub>upd</sub>@Pd/C and Pd-Cu/C Nanocatalysts for Electrochemical Ethanol Oxidation in Alkaline Solution**

Maja D. Obradović<sup>1</sup>, Jelena R. Rogan<sup>2</sup>, Uroš Č. Lačnjevac<sup>3</sup>, Aleksandra Gavrilović-Wohlmuther<sup>4</sup>, Vuk V. Radmilović<sup>2</sup>, Velimir R. Radmilović<sup>2,5</sup>, Snežana Lj. Gojković<sup>2</sup>

1 University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia.

2 University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia.

3 University of Belgrade, Institute for Multidisciplinary Research, Belgrade, Serbia.

4 Schoeller-Bleckmann Nitec GmbH, Ternitz, Austria.

5 Serbian Academy of Sciences and Arts, Belgrade, Serbia.

Easy storage and handling, high energy density, wide availability, and low toxicity are the features of ethanol that make direct ethanol fuel cells the most promising among all alternative power sources [1,2]. Unfortunately, the ethanol oxidation reaction (EOR), taking place at the anode, is slow and incomplete even on the best available catalysts known to date. Pure Pt and Pd are not capable of catalyzing the oxidation of ethanol through a total oxidation pathway [2]. However, Pt and Pd are necessary catalyst constituents in providing efficient adsorption of ethanol, which is the first reaction step in ethanol oxidation. The activity of Pd and Pt for alcohol oxidation can be enhanced by adding a co-catalytic element, mainly oxophilic metal (either d- or p-metals), or compounds such as oxides [3]. Therefore, the Pd nanoparticles supported on carbon black (Pd/C) and decorated by Cu sub-monolayers by underpotential deposition (Cu<sub>upd</sub>@Pd/C), as well as alloyed Pd-Cu nanoparticles (Pd-Cu/C) were investigated for the EOR in an alkaline solution.

Nanocatalysts Pd/C and Pd-Cu/C were synthesized by a borohydride reduction method [4] and characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Total metal loadings of the Pd/C and Pd-Cu/C catalysts, determined by TGA measurements, were 8.0 mass% and 15.0 mass%, respectively. The average atomic ratio between Pd and Cu in the Pd-Cu/C catalyst was calculated to be 0.83:0.17 by energy dispersive X-ray spectroscopy (EDS). Taking into account the total metal loading, the Pd-Cu/C catalyst contained 12.4 mass% of Pd. The XRD patterns of the Pd/C and Pd-Cu/C powders are displayed in Fig. 1a) and 1b). The overall peak positions corresponding to Pd diffraction planes are shifted toward higher angles in the presence of Cu atoms, indicating alloyed structure of the Pd-Cu catalyst. The XRD analysis did not reveal the presence of pure copper metal or oxide phases in Pd-Cu/C. TEM characterization of the Pd/C and Pd-Cu/C powders indicated nanosized structure with mean diameters of 3.7 nm and 2.5 nm, respectively (Fig. 1c, d, e, f and g).

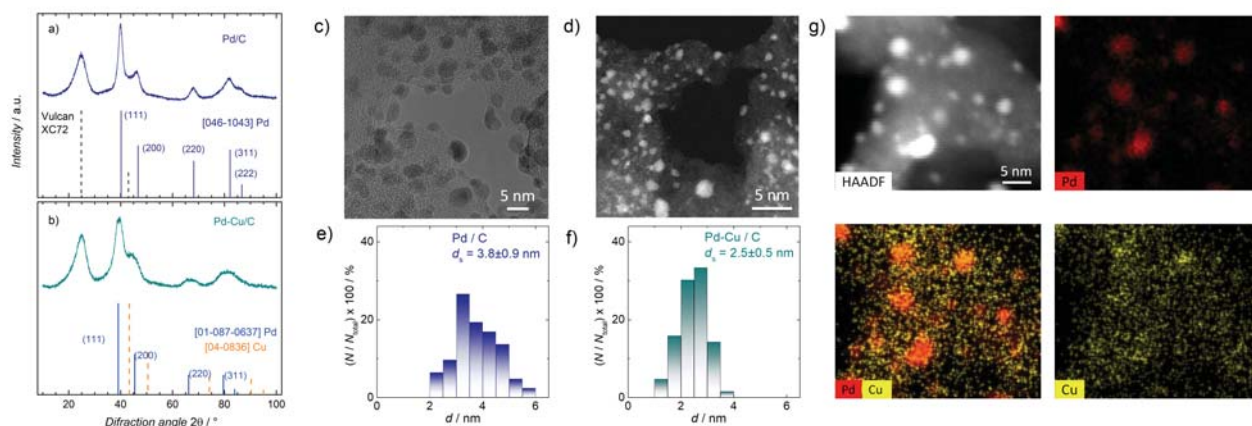
In addition, the Pd/C catalyst was decorated by Cu<sub>upd</sub> in an acid solution with various surface coverages (up to 0.5). The catalysts were electrochemically characterized by cyclic voltammetry (CV) and CO<sub>ads</sub> stripping in acid and alkaline solutions. A decreased hydrogen adsorption/desorption charge in CVs and increased currents in the potential region of hydroxide adsorption/desorption (Fig. 2a-d) indicate the presence of metallic Cu on the bimetallic catalyst surface. The electrochemically active surface area (ECSA) was estimated from the charge under the CO desorption peak in the alkaline solution and used for determining specific and mass activity for the EOR. As shown in Fig. 2a-d, the onsets of CO desorption on the Cu<sub>upd</sub> decorated and alloyed surfaces are negatively shifted compared the pure Pd surface. This indicates that Cu atoms provide oxygen-containing species at adjacent Pd sites at a lower potential than that achieved on pure metals.

The activity of the Pd/C, Cu<sub>upd</sub>@Pd/C and Pd-Cu/C nanocatalysts for EOR was investigated in 0.1 M NaOH under potentiodynamic (Fig. 2e) and potentiostatic conditions (Fig. 2f). The Pd/C with a Cu<sub>upd</sub>

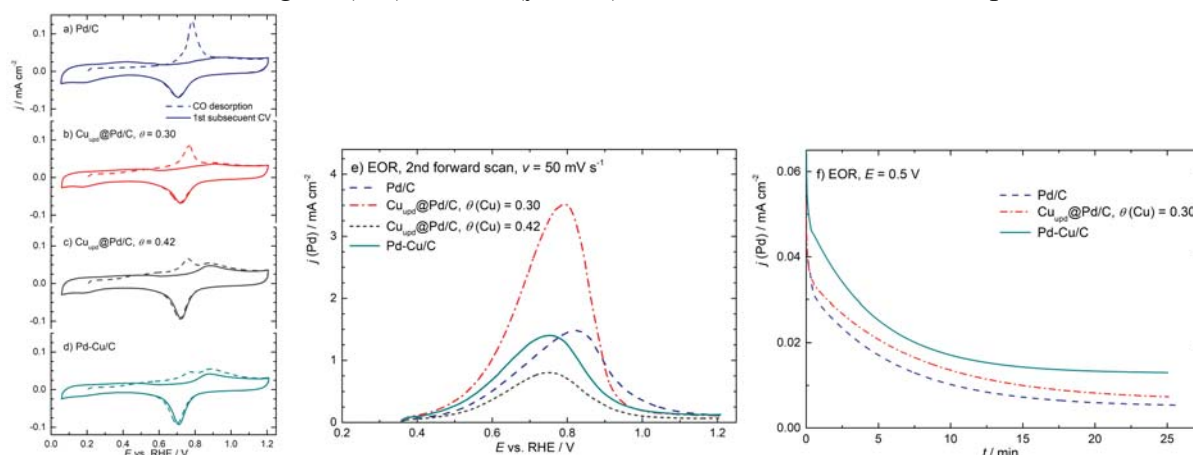
coverage of 0.30 and Pd-Cu/C exhibited lower onset potentials and up to a 2.5-fold increase in EOR activity with respect to Pd/C (calculated per Pd ECSA). However, with a further increase in coverage, the positive effect of Cu<sub>upd</sub> disappeared, and the activity even decreased. Although the EOR currents are higher on Cu<sub>upd</sub>@Pd/C than Pd-Cu/C nanoparticles in potentiodynamic measurement (Fig. 2e), the potentiostatic curves show that the highest EOR currents are observed on the Pd-Cu alloy nanoparticles (Fig. 2e). This is indicative of their higher stability compared to the Cu<sub>upd</sub>-modified nanoparticles.

## References:

- [1] E. Antolini, Journal of Power Sources 170 (2007) p. 1.
- [2] N.S. Marinkovic, M. Li, R.R. Adzic, Topics in Current Chemistry 377 (2019) p. 11.
- [3] L. Ma, D. Chu, R. Chen, International Journal of Hydrogen Energy 37 (2012) p. 11185.
- [4] M.D. Obradović, J.R. Rogan, U.Č. Lačnjevac, A. Gavrilović-Wohlmuther, V.V. Radmilović, V.R. Radmilović, S.Lj. Gojković, Applied Catalysis B: Environmental 189 (2016) p. 110.
- [5] The authors acknowledge funding from the Science Fund of the Republic of Serbia (the grant No 7739802), the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contracts No. 451-03-68/2022-14/200135 and 451-03-68/2022-14/200026) as well as the Serbian Academy of Sciences and Arts (Contract No. F141).



**Figure 1.** XRD patterns of a) Pd/C and b) Pd-Cu/C; TEM images and corresponding particle size distribution of Pd (c and e) and Pd-Cu nanoparticles (d and f); g) EDS elemental mapping showing Pd (red) and Cu (yellow) distribution in Pd-Cu/C sample.



**Figure 2.** Stripping voltammograms of CO<sub>ads</sub> (dashed lines) and the first subsequent voltammograms (solid lines) of a) Pd/C; b) Cu<sub>upd</sub>@Pd/C,  $\theta$  (Cu) = 0.30; c) Cu<sub>upd</sub>@Pd/C,  $\theta$  (Cu) = 0.42 and d) Pd-Cu/C in 0.1 M NaOH at the scan rate of 20 mV s<sup>-1</sup>; e) Potentiodynamic polarization curves and f) chronoamperometric curves for the EOR in 0.1 M NaOH + 0.5 M ethanol solution.