



**PETI MEĐUNARODNI SIMPOZIJUM O  
KOROZIJI I ZAŠTITI MATERIJALA,  
ŽIVOTNOJ SREDINI I ZAŠTITI OD  
POŽARA**

**KNJIGA RADOVA**

**FIFTH INTERNATIONAL SYMPOSIUM  
ON CORROSION AND MATERIALS  
PROTECTION, ENVIRONMENTAL  
PROTECTION AND PROTECTION  
AGAINST FIRE**

**PROCEEDINGS**

**Bar, 26-29. septembar 2023. godine**

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ZAŠTITU MATERIJALA I ZAŠTITU ŽIVOTNE SREDINE

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CIP - Каталогизacija u publikaciji  
Национална библиотека Црне Горе, Цетиње

ISBN 978-9940-9334-4-9  
COBISS.CG-ID 27476484

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## Ispitivanje stabilnosti PtZn/C katalizatora za reakciju elektrooksidacije metanola, etanola i mravlje kiseline

### Stability tests investigations for PtZn/C catalyst in methanol, ethanol and formic acid electrooxidation reaction

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#### Izvod

*PtZn katalizator deponovan na ugljenik razvijene površine Vulcan XC-72R sintetizovan je polirol metodom uz pomoć mikrotalasne pećnice i testiran za reakciju elektrooksidacije metanola, etanola i mravlje kiseline u sumpornoj kiselini. Pore enje stabilnosti PtZn/C katalizatora za reakciju elektrooksidacije metanola, etanola i mravlje kiseline dobijeno je produženim cikliziranjem. Fizičko-hemijska svojstva dobijenih katalizatora su okarakterisana transmisivnom elektronskom mikroskopijom (TEM), termogravimetrijskom (TGA) analizom i energetska disperzivnom spektroskopijom (EDS). Prema TEM analizi, PtZn/C katalizator ima male estice prilično velike izmeću 1 i 2 nm. TGA analiza je pokazala 27,68 tež. % metala za PtZn/C katalizator. Hemijski sastav PtZn/C katalizatora je pokazao da je odnos Pt:Zn u katalizatoru 87 tež.% : 13 tež.%. Dodavanje Zn u Pt značajno poboljšava aktivnost za oksidaciju metanola i etanola u pore enju sa Pt/C referentnim katalizatorom. Testovi stabilnosti su potvrdili da su PtZn/C katalizatori najstabilniji za reakciju elektrooksidacije metanola. U ovisnosti od visoke katalitičke aktivnosti i dobre stabilnosti u reakciji oksidacije metanola sintetizovanog katalizatora mogu se pripisati veoma efikasnoj mikrotalasnoj sintezi i dobro izbalansiranom sadržaju Zn kao legirajućeg metala.*

**Keywords:** Platinski katalizatori; metanol; etanol; mravlja kiselina;

#### Abstract

*PtZn catalyst material deposited on high surface area carbon Vulcan XC-72R was synthesized by microwave-assisted polyol method and tested for methanol, ethanol and formic acid electrooxidation reaction in sulphuric acid. The comparison of the stability behaviour of the PtZn/C catalyst for the methanol, ethanol and formic acid electrooxidation reaction were obtained from prolonged cycling. Physicochemical properties of obtained catalysts were characterized by transmission electron microscopy (TEM), thermogravimetric*

*(TGA) analysis and energy dispersive spectroscopy (EDS). According to TEM analysis PtZn/C catalyst have small particles of rather similar size between 1 and 2 nm. TGA analysis revealed 27.68 wt. % of metals in PtZn/C catalyst powder. The chemical composition of the PtZn/C catalyst was showed that the Pt:Zn ratio for the PtZn/C catalyst is 87 wt.% : 13wt.%. Addition of Zn to Pt significantly improves methanol and ethanol oxidation activity in comparison to Pt/C benchmark catalyst. Long term stability tests confirmed that PtZn/C catalysts are notably less poisoned for the methanol electrooxidation reaction. The observed high catalytic activity and good stability in the methanol oxidation reaction of synthesized catalyst can be ascribed to the very efficient microwave synthesis and well-balanced content of Zn as alloying metal.*

**Keywords:** *Platinum Catalysts; Methanol; Ethanol; Formic acid;*

## **Introduction**

Fuel cells, as sources of green energy, can be a very good replacement of fossil fuels with the aim of ensuring the path to sustainable development. Platinum (Pt) is frequently utilized as an anodic catalyst in polymer electrolyte membrane fuel cells (PEMFC) [1,2]. PEMFCs are currently high-priority technologies because they can provide electricity for vehicles such as cars, buses, and heavy-duty trucks and also for small power devices such as laptops and mobile phones. Especially compared to combustion engines, fuel cells have numerous advantages; first of all, they produce energy through an electrochemical process rather than combustion, thus providing greater efficiency than internal combustion engines and do not release air pollutants that create smog. However, the most difficult concerns in the fuel cell sector are cost, efficiency, and lifetime. Because platinum is the most expensive component of PEMFCs, it is most important to produce catalysts with higher activity and stability while reducing the content of expensive platinum. Also, pure Pt-based catalysts are easily occupied by strongly adsorbed species such as CO<sub>ads</sub> intermediate produced by methanol, ethanol and formic acid (common fuels in PEM fuel cells) oxidation during the electrocatalytic reaction. Effective ways to solve the problem of poisoning Pt and decrease cost of catalyst production are to alloy Pt with cheaper metals such as Sn, Mo, Zn, Fe, Co, Au, Bi, Ni [3,11]. These metals can improve catalyst activity by facilitating the oxidation of highly adsorbed species blocking the platinum surfaces formed during the oxidation reaction of highly adsorbed carbon intermediates at much lower potentials compared to platinum. In this work PtZn/C catalyst was synthesized by microwave-assisted polyol method and its electrochemical activity and stability was tested for methanol, ethanol and formic acid electrooxidation reaction.

## Experimental

### Catalyst preparation

PtZn nanoparticles were synthesized by microwave assisted polyol method. To obtain the PtZn/C catalyst, 0.5 ml of 0.05 M  $\text{H}_2\text{PtCl}_6$  solution was mixed with 0.5 ml 0.05 M  $\text{ZnSO}_4$  solution and 25 ml of ethylene glycol in a 100 ml erlenmeyer flask. The reduction reaction was carried out by microwave irradiation at 700 W for 90 s. After microwave heating, the colloidal solution was mixed with 20 ml of Vulcan XC-72R carbon water suspension and 150 ml 2 M  $\text{H}_2\text{SO}_4$  for 3 h. The final suspension was filtered by vacuum pump and the solid residue was rinsed with high purity water. The solid product was dried for 3h in an  $\text{N}_2$  atmosphere at 160  $^\circ\text{C}$ . Catalyst metallic loading was adapted to 20 mass %.

### Physicochemical characterisations

PtZn/C catalyst was examined by the thermogravimetric (TGA) and differential thermal (DTA) analyses performed in the range of 30-1000  $^\circ\text{C}$  range on a SDT Q600 TGA/DSC instrument (TA Instruments). The chemical composition of the PtZn/C catalyst was obtained by a scanning electron microscope (SEM) Tescan VEGA TS 5130 MM supplied with energy-dispersive X-ray spectroscopy (EDS) detector INCAPentaFET-x3, Oxford Instruments. Transmission electron microscope (TEM) JEM-1400 with an accelerating voltage of 120 kV was employed for detailed characterization of the morphology of the produced catalyst.

### Electrochemical characterisations

The electrocatalytic activity of PtZn/C catalyst was examined in 0.5 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{CH}_3\text{OH}$ , 0.5 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{C}_2\text{H}_5\text{OH}$  and 0.5 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{HCOOH}$  solutions. Catalyst stability was examined by long-term potential cycling. The specific catalyst activities are normalized in relation to the values of platinum mass loading.

All solutions were made using Merck p.a. reagents and high purity water. Before each experiment the electrolytes were purged with nitrogen. AUTOLAB potentiostat / galvanostat PGStat 128N (ECO Chemie, The Netherlands) was employed for electro-chemical measurements.

## Results and discussion

Recognized as catalysts with great potential for the methanol, ethanol and formic acid electrochemical oxidation, PtZn/C catalyst has been successfully synthesized by the microwave synthesis process. PtZn/C catalyst was analysed by the TGA/DTA analysis, and EDX examination. The results for TGA and EDX were presented in Table 1.

Table 1. TGA and EDS analyses for PtZn/C catalyst.

Catalyst	Metal content from TGA (mass %)	The Pt:Zn atomic ratios	
		Nominal (mass %)	EDS (mass %)
PtZn/C	27.68	75 : 25	87 : 13

TGA analysis determined the 27.68 wt. % of metals in the PtZn/C catalyst powder. The residual mass shows slightly higher value in comparison to the nominal value and it can be attributed to the presence of ZnO in the catalyst which can increase the reaction extent during the heating procedure. According to EDS analysis obtained ratio of metals is 87 wt.% : 13wt.% (Pt:Zn).

A TEM investigation was performed to measure the particle size of the produced catalyst. According to the TEM study, the particle sizes of PtZn/C catalyst was fairly similar, the observed catalyst particles have diameters of  $1.63 \pm 0.3$  nm. TEM image and particle size distribution histogram is presented in Figure 1.

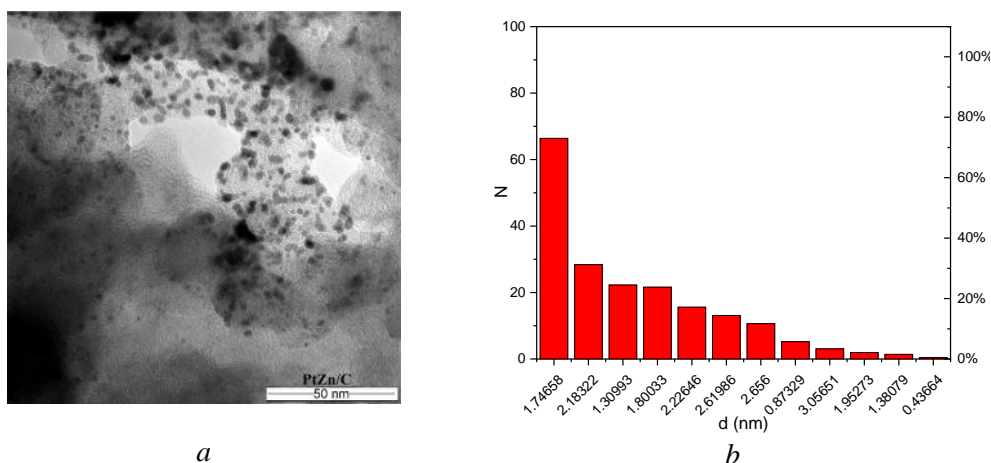


Figure 1. TEM image (a) and particle size distribution (b) of PtZn/C catalyst.

The electrochemical behavior of the PtZn/C catalyst was determined using cyclic voltammetry studies. Cyclic voltammetry experiments are made on untreated, as-prepared catalysts since Sn and Zn dissolve at potentials over 0.4 V versus SCE, while at those potentials, their oxide is stable [12-13]. Figure 2 shows the basic voltammograms of a PtZn/C catalyst with the well-developed hydrogen adsorption/desorption region (Fig3b). The obtained voltammograms of PtZn/C catalyst are in agreement with voltammograms that has been reported in the literature for platinum catalysts synthesized in the similar procedure [14-15].



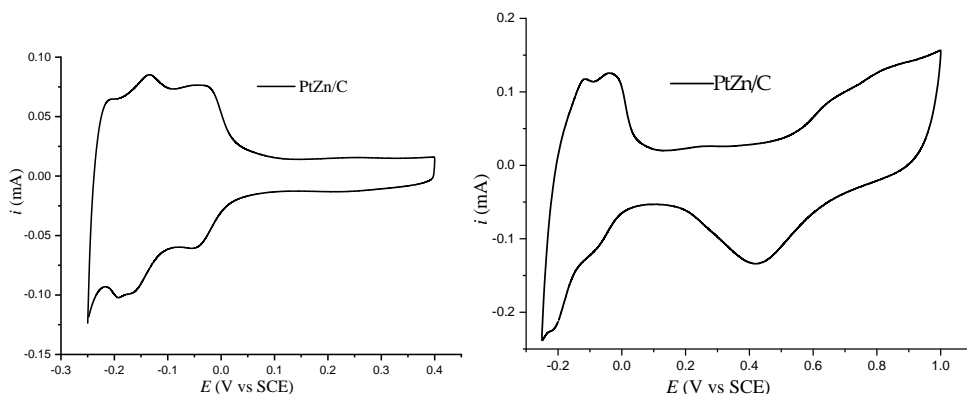
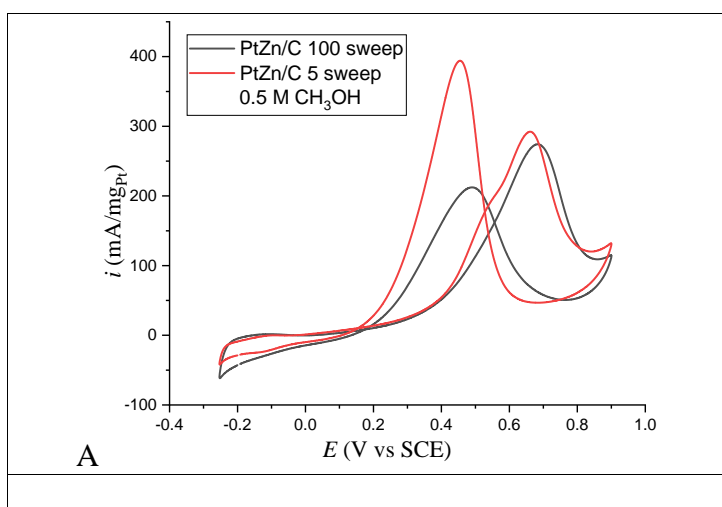


Fig. 4: Cyclic voltammograms of PtZn/C catalyst in 0.5 M  $H_2SO_4$ ,  $v = 50 \text{ mV/s}$ .

### Methanol oxidation

The activity of the *as prepared* PtZn/C catalyst for methanol, ethanol and formic acid oxidation reactions was evaluated from potentiodynamic measurements (Fig. 3A, B and C respectively).



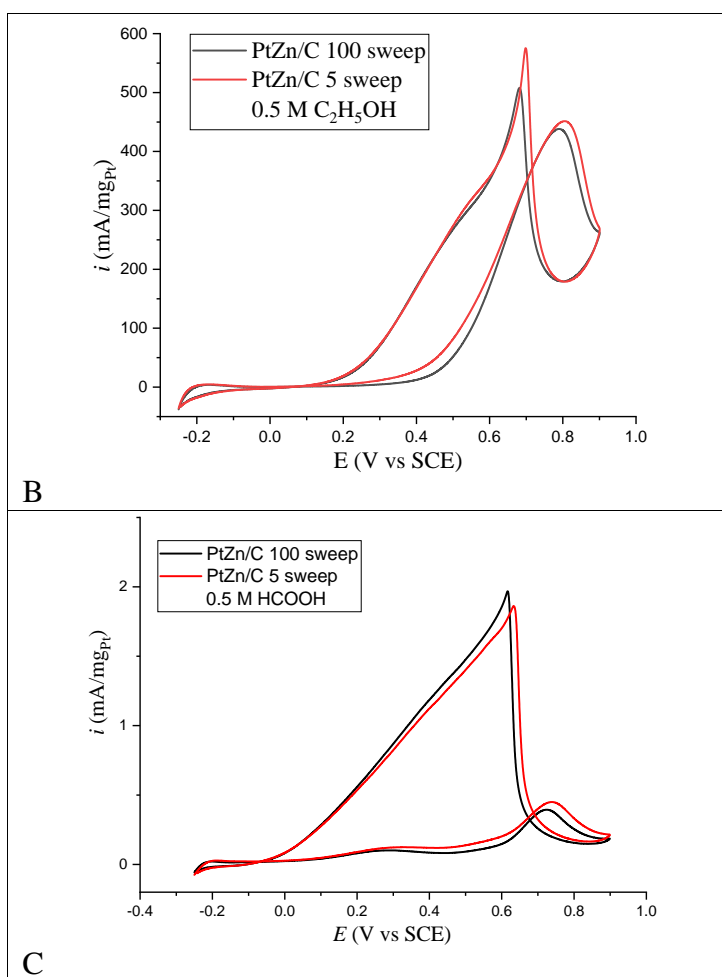


Fig. 3. Potentiodynamic measurements of the as prepared PtZn/C catalyst for A) 0.5 M CH<sub>3</sub>OH, B) C<sub>2</sub>H<sub>5</sub>OH and C) HCOOH electrooxidation reactions. Red line represents 5<sup>th</sup> sweep of electrooxidation reaction while black line represents 100<sup>th</sup> sweep for the same reaction.

Based on the electrochemical tests related to the PtZn/C catalyst efficiency for methanol, ethanol and formic acid electrooxidation, the performances of the catalyst were compared with the corresponding Pt/C catalysts synthesized by the same procedure and presented in Table 2.

Table 2. Summary of maximum forward activity expressed in mass activity for synthesised PtZn/C and Pt/C benchmarked catalyst.

Catalyst	$J_{max}$ (mA/mgPt) for PtZn/C catalyst	$J_{max}$ (mA/mgPt) for Pt/C catalyst
methanol oxidation	292.46	160
ethanol oxidation	451.22	360.50
formic acid oxidation	450.03	720

Electrocatalytic stability of the PtZn/C catalysts for methanol, ethanol and formic acid oxidation reactions was examined by prolonged cycling. Analyzing the CVs from Fig.3 it can be noticed that for methanol oxidation reaction PtZn/C, peak current in forward (anodic) scan is higher than in reverse (cathodic) scan. Since the peak in reverse scan is due to removal of intermediates formed during the forward scan than the ratio between peak currents in the forward and backward scan ( $j_f/j_b$ ) can be used to define the catalyst tolerance to carbonaceous species [16-18]. As a matter of fact, a higher ratio corresponds to a lower  $j_b$  peak, which suggests that less unwanted CO molecules adsorbed on the catalyst surfaces. This ratio is highest for PtZn/C catalysts for methanol electrooxidation reaction and suggests higher resistance versus poisoning intermediate products. All values for  $j_f/j_b$  ratio are summarized in Table 3.

Table 3. Summary values of  $j_f/j_b$  of PtZn/C catalyst for methanol, ethanol and formic acid electrooxidation reactions.

Catalyst	$j_f/j_b$ for PtZn/C catalyst
methanol oxidation	1.11
ethanol oxidation	0.87
formic acid oxidation	0.20

## Conclusions

The focus of this research was the synthesis of PtZn/C catalysts with enhanced efficiency for the methanol, ethanol and formic acid electrooxidation reaction. In this work carbon-supported PtZn catalysts were successfully synthesized by the microwave-assisted polyol procedure. The results from cyclic voltammetry experiments indicate enhanced catalytic activities for methanol and ethanol oxidation reaction and improved resistance ability to CO inhibition, after addition of Zn to Pt catalyst. It should also be noted that the PtZn/C catalyst shows better activity for methanol and ethanol oxidation reaction compared to the same synthesized Pt/C catalyst. This implies that synergistic effects are achieved between Pt and Zn atoms.

## Acknowledgments

This work was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (contract No 451-03-47/2023- 01/200026) and by the Science Fund of the Republic of Serbia under grant No 7739802

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