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CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

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*STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE,  
ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE*

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*Udruženje Inženjera Srbije za Koroziju i Zaštitu Materijala*



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## Formic acid electrooxidation on Ni-supported platinum thin film catalyst

### *Oksidacija mravlje kiseline na platinskim katalizatorima na Ni nosaču*

Dragana L. Milošević<sup>1,\*</sup>, Sanja I. Stevanović<sup>1</sup>, Nebojša D. Nikolić<sup>1</sup>, Dušan V. Tripković<sup>1</sup>

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#### **Abstract**

Pollution caused by the usage of fossil fuels is a consequence of industrialization, urbanization, and technological development, having a huge impact on the environment and human health. Thus, one of the biggest challenges that currently confront not only the scientific community but also humanity is reducing the use of fossil fuels, as well as the production and consumption of energy using renewable energy sources. In the last decades, small organic molecules such as methanol, ethanol and formic acid have attracted attention due to their properties that make them convenient for use in fuel cells. Among other precious metals, Pt is the most investigated as a promising catalyst for the anodic electrooxidation reaction of small organic molecules. However, high price, scarceness and susceptibility to poisoning are some of the limiting factors for the commercial use of pure Pt. There are two ways to mitigate those problems: lower the content of a noble metal present or make the catalyst more active for the particular reaction. To address the first problem nanocatalyst, produced by the deposition of platinum onto high surface area supports were introduced. A far greater challenge is to modify the catalyst to make it not just more active, but more stable as well, for a particular reaction. It is now well known that bimetallic catalysts fulfill these requirements quite well, and currently, they are widely used in many catalytic and electrocatalytic processes. In this study, a thin Pt film was electrochemically deposited on nickel support (Pt/Ni) and afterward subjected to the controlled thermal treatment in an attempt to reduce the proneness of Pt to poisoning species (CO) and therefore improve its catalytic performance at low potentials in the formic oxidation reaction. All produced catalysts were electrochemically characterized using cyclic voltammetry and oxidation of CO monolayer, while the influence of thermal annealing on the morphology was monitored using an atomic force microscope (AFM). Finally, catalyst performance was tested in a formic acid electrooxidation reaction. The obtained results clearly show that the exceptional activity for formic acid electrooxidation, measured on annealed Pt/Ni is a direct consequence of the nature of the substrate which manifests itself after controlled heat treatment through surface reconstruction and bifunctional effect.

**Keywords:** Pt thin films; Ni support; thermal treatment; electrooxidation; formic acid

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### **Izvod**

Zagađenje izazvano upotrebom fosilnih goriva posledica je industrijalizacije, urbanizacije i tehnološkog razvoja i ima ogroman uticaj na životnu sredinu i zdravlje ljudi. Dakle, jedan od najvećih izazova sa kojima se trenutno suočava ne samo naučna zajednica već i čovečanstvo jeste smanjenje upotrebe fosilnih goriva, kao i proizvodnja energije korišćenjem obnovljivih izvora energije. Poslednjih decenija mali organski molekuli poput metanola, etanola i mravlje kiseline privukli su pažnju zbog svojih svojstava koja ih čine pogodnim za upotrebu u gorivnim ćelijama. Među ostalim plemenitim metalima, Pt je najviše istraživana kao potencijalni katalizator za reakciju anodne elektrooksidacije malih organskih molekula. Međutim, visoka cena, iscrpljivi resursi i podložnost formiranja ometajućih nusprodukata tokom reakcije oksidacije (CO) su neki od ograničavajućih faktora za komercijalnu upotrebu čiste platine kao katalizatora. Postoje dva načina da se ti problemi ublaže, poput smanjenja sadržaja prisutnog plemenitog metala ili poboljšanja aktivnosti katalizatora za određenu reakciju. Da bi se rešio prvi problem, napravljeni su nanokatalizatori, proizvedeni taloženjem platine na nosače velike površine. Daleko veći izazov je modifikovati katalizator kako bi bio ne samo aktivniji, već i stabilniji za određenu reakciju. Dobro je poznato da bimetalni katalizatori dosta dobro ispunjavaju ove zahteve, a trenutno se široko koriste u mnogim katalitičkim i elektrokatalitičkim procesima. U ovoj studiji, tanak film platine je elektrohemijski nanesen na podlogu od nikla (Pt/Ni) i nakon toga podvrgnut kontrolisanom termičkom tretmanu u pokušaju da se ublaži trovanje platine sa CO i stoga poboljšaju njegove katalitičke performanse na nižim potencijalima u reakciji oksidacije mravlje kiseline. Svi proizvedeni katalizatori su elektrohemijski okarakterisani primenom ciklične voltametrije i oksidacije CO monosloja, dok je uticaj termičkog tretmana na morfologiju praćen pomoću atomskog mikroskopa (AFM). Performanse katalizatora su testirane u reakciji elektrooksidacije mravlje kiseline. Dobijeni rezultati jasno pokazuju da je izuzetna aktivnost za elektrooksidaciju mravlje kiseline, izmerena na termički tretiranom Pt/Ni, direktna posledica prirode nosača koja se manifestuje posle kontrolisanog termičkog tretmana kroz rekonstrukciju površine i bifunkcionalni efekat dobijen prisustvom nikla na površini.

**Ključne reči:** Pt tanki filmovi; Ni nosač; termička obrada; elektrooksidacija; mravlja kiselina

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