



Electrochemical oxidation of ethanol on palladium-nickel nanocatalyst in alkaline media



M.D. Obradović^a, Z.M. Stančić^b, U.Č. Lačnjevac^c, V.V. Radmilović^d,
A. Gavrilović-Wohlmuther^e, V.R. Radmilović^{b,f}, S.Lj. Gojković^{b,*}

^a Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

^b Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

^c Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1, 11030 Belgrade, Serbia

^d Innovation Center, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

^e Centre of Electrochemical Surface Technology, Viktor-Kaplan-Strasse 2, A-2700 Wiener Neustadt, Austria

^f Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia

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ABSTRACT

Pd-Ni/C catalyst was synthesized employing a borohydride reduction method. The high area Ni was first dispersed on the carbon support and then modified by Pd nanoparticles. Transmission electron microscopy confirmed relatively even distribution of Ni across the carbon support with discrete palladium particles of about 3.3 nm mean diameter on it. Cyclic voltammetry confirmed the presence of Ni on the catalyst surface. The activity of the Pd-Ni/C catalysts for ethanol oxidation reaction (EOR) in alkaline solution was tested under the potentiodynamic and potentiostatic conditions and the results were compared to those obtained on the Pd/C catalyst. It was found that Pd-Ni/C is more active for the EOR compared to Pd/C by a factor up to 3, depending on the type of experiments and whether specific activity or mass activity are considered. During the potentiodynamic stability test an interesting phenomenon of activation of Pd-Ni/C catalyst was observed. It was found that maximum activity is attained after fifty cycles with the positive potential limit of 1.2 V, regardless of whether they were performed in the electrolyte with or without ethanol. It was postulated that potential cycling of the Pd-Ni surface causes reorganization of the catalyst surface bringing Pd and Ni sites to a more suitable arrangement for the efficient ethanol oxidation.

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1. Introduction

Direct alcohol fuel cells (DAFCs) are recognized as promising power sources for portable electronic devices and electric vehicles [1]. Although DAFC driven by methanol oxidation in acidic media is the most common and commercially available [2], ethanol as a fuel attracts increasing attention because it can be produced from fermentation of biomass [3], it is a low-toxic liquid and its crossover through the polymer membrane is lower than that of methanol [4]. In acidic media ethanol can be oxidized only on Pt-based catalysts, but the reaction is rather sluggish for efficient operation of direct ethanol fuel cells (DEFC) [1]. However, in alkaline media ethanol oxidation reaction (EOR) is faster [5,6], and interestingly, Pd shows greater activity for the EOR in this environment than Pt [7–10].

This shows opportunity of the development of DEFC since Pd is less expensive than Pt [11] and the development of anion exchange membranes [12] is in progress. In addition, numerous metals are stable in alkaline media and can be used for designing bi- and tri-metal catalysts [9,10,13].

Higher activity of Pd compared to that of Pt for the EOR is attributed to its more oxophilic nature [6] that facilitates oxidative desorption of intermediate species. The same rationale is behind introducing Ni in electrocatalysts for the EOR. Although Ni itself is not active for the EOR at the potentials relevant for DEFC operation [14], various Pd-Ni electrocatalysts exhibited enhanced activity and greater tolerance to catalyst poisoning compared to pure Pd [15–24].

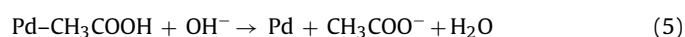
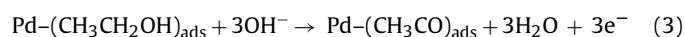
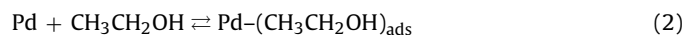
Shen and Xu [13] were the first to report that the EOR on Pd-NiO/C commences at 150 mV lower potential than on Pd/C and even 250 mV lower potential than on Pt/C catalysts. Higher activity and decreased poisoning of Pd-NiO/C compared to the Pt-NiO/C electrocatalyst for the EOR was reported by Hu et al. [15]. Neg-

* Corresponding author.

E-mail address: sgojkovic@tmf.bg.ac.rs (S.Lj. Gojković).

actively shifted onset potential and doubled peak current density in potentiodynamic conditions for core-shell Ni-Pd/C compared to Pd/C was found by Zhang et al. [20]. High activity and excellent stability in potential cycling conditions were found for Pd supported on Ni foam in the study by Wang et al. [16]. Pd-Ni/C catalysts with various ratios of Pd and Ni were also investigated [17,18,22,24]. Irrelevant of the method of preparation and the structure, all studies show that the catalysts containing between 50 and 60 at.% of Ni are the most active and stable. In the work by Dutta and Datta [24] clear correlation between the alloying degree and the activity was established as the more alloyed Pd–Ni particles were more active. The same influence of the metal alloying was found by Ahmed and Jeon [22]. In the Pd-Ni/C catalysts investigated by Shen et al. [17] and Zhang et al. [18] Pd and Ni did not alloy well, but their performance was still improved compared to Pd/C. These results suggest that the capacity of Ni to generate OH_{ads} species at lower potential and facilitate the oxidative desorption of intermediates in the EOR is crucial for the enhanced activity of Pd, although the ligand and strain effects also contribute. The insertion of substitutional Ni atoms into the Pd crystal lattice causes a contraction of the Pd lattice because of a smaller Ni radius (135 pm for Ni and 140 pm for Pd). This causes a downshift of the Pd d-band center and consequently leads to weaker bonding with adsorbates such as poisoning intermediates in the EOR. In addition, since Pd has a higher ionization energy than Ni (8.34 eV compared to 7.63 eV, respectively), Ni atoms become positively charged, which facilitates the formation of oxides on Ni [24].

The mechanism of the EOR on polycrystalline Pd was investigated by Fang et al. [25] using in situ FTIR spectroscopy. In the solutions with $\text{pH} < 13.3$ they detected acetate ions and CO_2 , but in more alkaline solutions the CO_2 band was absent. Interestingly enough, no trace of CO was detected even at pH 12. It was concluded that the cleavage of the C–C bond occurs only at lower pH values where a non-poisoning reaction path is likely to take place. Zhou et al. [26] also found that acetate is the main product and that CO_2 and carbonate ions appear only at potentials too high for DEFC application. However, they detected a weak signal of CO_{ads} suggesting that complete oxidation of ethanol might be achieved through an indirect pathway. In FTIR spectra for Pd black only the bands of acetate are observed. Liang et al. [27] investigated the EOR on Pd in a wide range of ethanol and hydroxide concentrations. Based on the polarization measurements of ethanol, acetaldehyde and potassium acetate oxidation, the authors suggested that the dissociative adsorption of ethanol proceeds rather quickly and that the rate-determining step is the removal of the adsorbed CH_3CO particles by the adsorbed hydroxyl on the Pd electrode. In the study of the EOR on Pd/C and Pd-Ni/C, Dutta and Datta [24] found acetate and carbonate ions as the final reaction products by using ion exchange chromatography. For the Pd/C catalyst, the acetate ions were predominant, while on the best performing $\text{Pd}_{37}\text{Ni}_{63}/\text{C}$ catalyst, carbonate ions slightly outbalanced acetate ions. DFT calculation by Cui et al. [28] confirmed that the dehydrogenation of ethanol is possible only in alkaline media where adsorbed OH species are abundant. The formation of acetaldehyde was predicted as the first step during the EOR, and it could be further oxidized. Based on these results, the following mechanism of the EOR on Pd in alkaline media has been proposed [27]:



For potentials below 0.6 V (RHE) it is suggested that the first stage in Pd oxidation, given by Eq. (1), is the rate determining step [29]. It is believed that Ni promotes the EOR on Pd by supplying adsorbed OH species at lower potentials, which influences the onset of the EOR. In addition, in the whole potential region, the OH species from the Ni sites facilitate the stripping of reaction intermediates, which recovers the Pd sites and thereby accelerates further oxidation of ethanol molecules [23].

In order to employ the beneficial effects of Ni on EOR activity of Pd-Ni catalysts, in this work we synthesized high surface area Ni on carbon support and modified it with Pd nanoparticles. Such a structure of the catalyst is different compared to conventional core/shell, alloyed or non-alloyed Pd-Ni nanoparticles. In this way Pd nanoparticles when immersed in an alkaline medium are surrounded by an abundance of OH groups attached to the Ni atoms. The Pd-Ni/C catalyst was characterized and its activity for the EOR in alkaline electrolytes was evaluated. The results were compared to those obtained on a Pd/C catalyst. The phenomenon of the activation of the Pd-Ni/C catalyst during the potential cycling was explored. It was found that the specific activity of Pd for the EOR can be doubled by the presence of Ni.

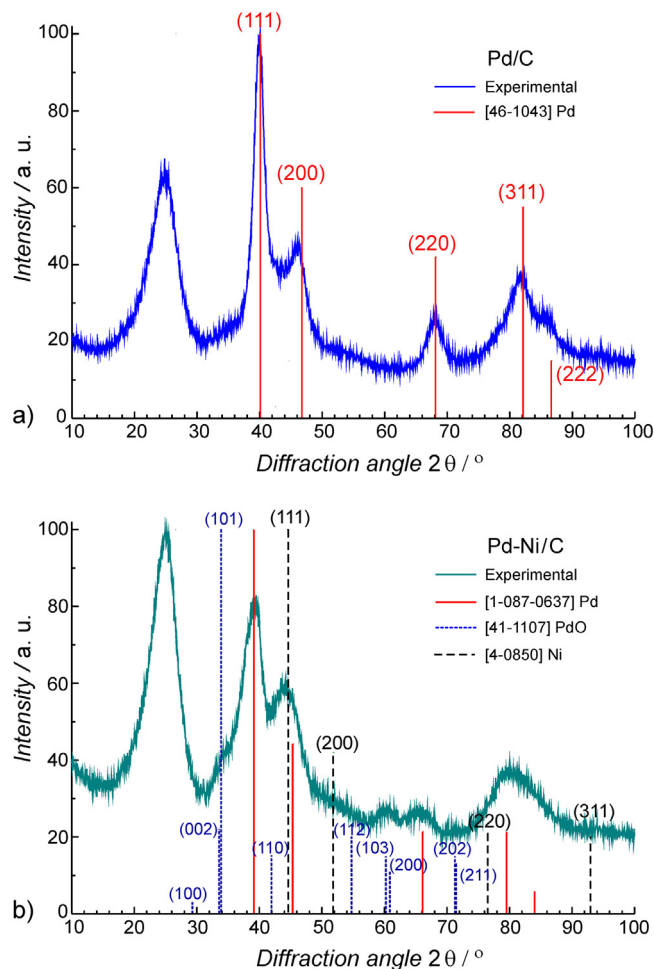


Fig. 1. XRD patterns of prepared catalysts: (a) Pd/C and (b) Pd-Ni/C. The lines represent 2θ positions and corresponding intensities of the diffraction peaks for Pd, PdO and Ni crystal structures according to the ICDD-PDF cards.

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