

## Enhanced Activity of Polycrystalline Palladium Decorated by Ru Nanoislands for Hydrogen Evolution in Alkaline Medium

Milutin Smiljanić<sup>1</sup>, Zlatko Rakočević<sup>1</sup>, Jelena Potočnik<sup>1</sup>, Svetlana Štrbac<sup>2,\*</sup>

<sup>1</sup> INS Vinča, Laboratory of Atomic Physics, University of Belgrade, Mike Alasa 12-14, 11001 Belgrade, Serbia

<sup>2</sup> ICTM-Institute of Electrochemistry, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

\*E-mail: [sstrbac@tmf.bg.ac.rs](mailto:sstrbac@tmf.bg.ac.rs)

Received: 2 April 2019 / Accepted: 10 May 2019 / Published: 10 June 2019

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Hydrogen evolution reaction (HER) was studied on polycrystalline Pd, Pd(poly), decorated by spontaneously deposited Ru nanoislands below full coverage. Surface features of as-prepared bimetallic Ru/Pd(poly) electrodes were explored by Field Emission Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometer. Electrochemical properties and hydrogen evolution activities of obtained electrodes were investigated in an alkaline electrolyte by Cyclic and Linear Sweep Voltammetry, respectively. It was found that the activities of bimetallic Ru/Pd(poly) electrodes for HER significantly exceeded the activity of bare Pd(poly) and approached the activity of Pt, which is the most active material for this reaction. This enhancement was explained by the favorable influence of the electronic interaction between Pd substrate and Ru nanoislands on the adsorption of the reactive H species.

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**Keywords:** palladium, ruthenium, FESEM, hydrogen evolution, alkaline solution

### 1. INTRODUCTION

According to some estimations, fossil fuels will have to be abandoned as the main energy sources in the next 100 years [1,2], hence the question of renewable and green energy has emerged as one of the critical issues of the modern society. In that respect, great efforts are being invested in research related to fuel cells, which are regarded as the most important stationary and mobile power sources [3,4]. The need of CO<sub>2</sub>-free energy cycle in such electrochemical devices promotes hydrogen over small organic molecules as the most convenient energy carrier and fuel for fuel cells. Unfortunately, the application of H<sub>2</sub> suffers from several issues, one of the most important being related to its sustainable production [5]. As a green alternative to the current H<sub>2</sub> production that comes mainly from various hydrocarbons [5], high purity and truly renewable H<sub>2</sub> can be produced by water

electrolysis [6,7]. State of the art catalysts for H<sub>2</sub> evolution are based on platinum on which hydrogen evolution reaction (HER) occurs at lower overpotentials [8,9]. As platinum is scarce and expensive there is an ongoing quest for the other electrode materials with comparable activity. In this sense, Pd meets the demands to be sufficiently active for H<sub>2</sub> evolution but more abundant than Pt [10-12]. Viable route to further enhance the activity of Pd in order to approach that of Pt, is its modification by foreign metal deposition, with the aim to trigger the electronic interaction between two metals in contact [13-15]. The main role of the electronic interaction is to favorably modulate the binding energy of the H intermediate species as the main parameter which determines the activity of certain material for HER.

Among many foreign metals to be used for Pd modification, Ru is an interesting member of platinum group metals. Ru is already recognized in water splitting as one of the state-of-the-art catalysts for anodic O<sub>2</sub> evolution [6,16]. At the same time, different Ru-based nanomaterials have shown very promising activity for HER [17-19], and Ru has already been used as a foreign metal to enhance the activity of different metals including Ni [20,21], Pt [22] and Pd [23-25]. Studies of different Ru-Pd nanoparticles have shown that the addition of Ru resulted in enhanced activity for HER with respect to parent Pd materials [23-25]. In general, observed enhancement was explained by tuning of the hydrogen binding energy due to the presence of Ru.

In the present contribution, hydrogen evolution reaction was studied on model bimetallic Ru/Pd(poly) electrodes prepared by the spontaneous deposition of Ru on polycrystalline Pd electrode. The influence of Ru coverage on H<sub>2</sub> evolution activity was investigated simply by controlling the deposition time. Surface characterization of as-prepared bimetallic electrodes was performed by Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer (FESEM-EDS). Electrochemical properties and HER activities of Ru/Pd(poly) electrodes were investigated in an alkaline electrolyte by voltammetric techniques. Obtained enhancement of HER activity was discussed on the basis of the electronic interplay between Pd substrate and Ru deposit and compared with the activity of Pt.

## 2. EXPERIMENTAL

### 2.1. Preparation of bimetallic Ru/Pd(poly) electrodes

Polycrystalline Pd electrode (geometric area 0.196 cm<sup>2</sup>) was used as the working electrode and the substrate for Ru deposition. Maintenance of the purity of the Pd electrode was accomplished by electrochemical polishing in the mixture of 0.5 M LiCl and 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub> dissolved in methanol [26,27]. Spontaneous deposition of Ru was performed via immersion of Pd(poly) into 10<sup>-3</sup> M RuCl<sub>3</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub> solution at an open circuit potential (OCP) during the selected times of 3 and 30 minutes. Changes of OCP during Ru deposition were recorded by chronopotentiometry measurements as reported previously [28]. According to the OCP curve, chosen deposition time of 3 min corresponds to the lower deposition rate, after the initial fast deposition. Deposition time of 30 min corresponds to the plateau on the OCP curve indicating the stationary state when the coverage of the deposited Ru achieved its saturation value. After deposition, electrodes were removed from the depositing solution, copiously rinsed with Milli-pure water and protected by a drop of water before being subjected to the

further characterization in order to minimize possible changes in the surface composition due to the air exposure.

## 2.2. FESEM-EDS characterization of Ru/Pd(poly) surfaces

For FESEM and EDS measurements, FEI Scios 2 microscope with Energy Dispersive X-ray Spectrometer was used for morphology studies and for analysis of particle distribution over the electrodes surfaces. Electron beam voltage used for X-ray excitation was 5 kV and the spectrum acquisition time, together with elemental mapping, was 20 min. Freshly prepared electrodes were analyzed at the pressure of  $3.5 \times 10^{-4}$  Pa.

## 2.3. Electrochemical measurements

Electrochemical measurements were performed in standard three electrode setup, with Pd(poly) (bare or modified), Ag/AgCl, 3M KCl and platinum wire as the working, reference and auxiliary electrode, respectively. Measurements were performed in deoxygenated 0.1 M NaOH solution. Cyclic Voltammetry (CV) was used for the characterization of the electrodes, while Linear Sweep Voltammetry (LSV) was used for the evaluation of their activities for H<sub>2</sub> evolution. Potential of -0.5 V was applied during 15 minutes before each CV or LSV measurement in order to stabilize Ru deposit. Each electrochemical measurement was performed in a separate experimental setup, which provided good reproducibility of the results. Special care was devoted to minimize the influence of glass corrosion on apparent electrocatalytic activity [29,30] by reducing the time of glassware contact with the alkaline solution. In addition, thorough cleaning of the glassware was applied between each measurement.

## 2.4. Chemicals

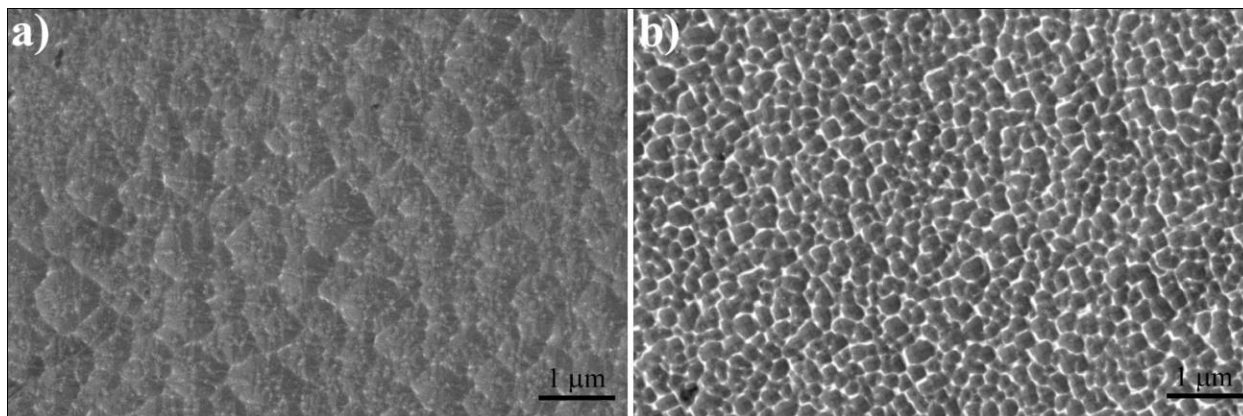
Solution for electrochemical polishing was prepared using methanol (Merck), LiCl (Fisher Chemicals) and Mg(ClO<sub>4</sub>)<sub>2</sub> (Fisher Chemicals). Depositing Ru solution was prepared from RuCl<sub>3</sub>·xH<sub>2</sub>O (Merck) and suprapure H<sub>2</sub>SO<sub>4</sub> (Merck), while the electrolyte solution was prepared from NaOH pellets (Merck). All solutions (except non-aqueous polishing bath) were diluted by Milli-Q water (18 MΩ cm). Deoxygenation of the electrolyte solution during electrochemical experiments was ensured by the constant flow of the high purity nitrogen (Messer, 99.999%).

# 3. RESULTS AND DISCUSSION

## 3.1. FESEM-EDS characterization

Figure 1 shows high resolution FESEM images of bare Pd(poly) surface and of bimetallic Ru/Pd(poly) electrode obtained after 30 minutes of Ru deposition. Image of bare Pd(poly), Figure 1a, shows that Pd grains are homogeneously distributed over the surface. Similarly, image from Figure 1b shows grainy structure of bimetallic Ru/Pd(poly) surface consisting of Ru deposited on top of

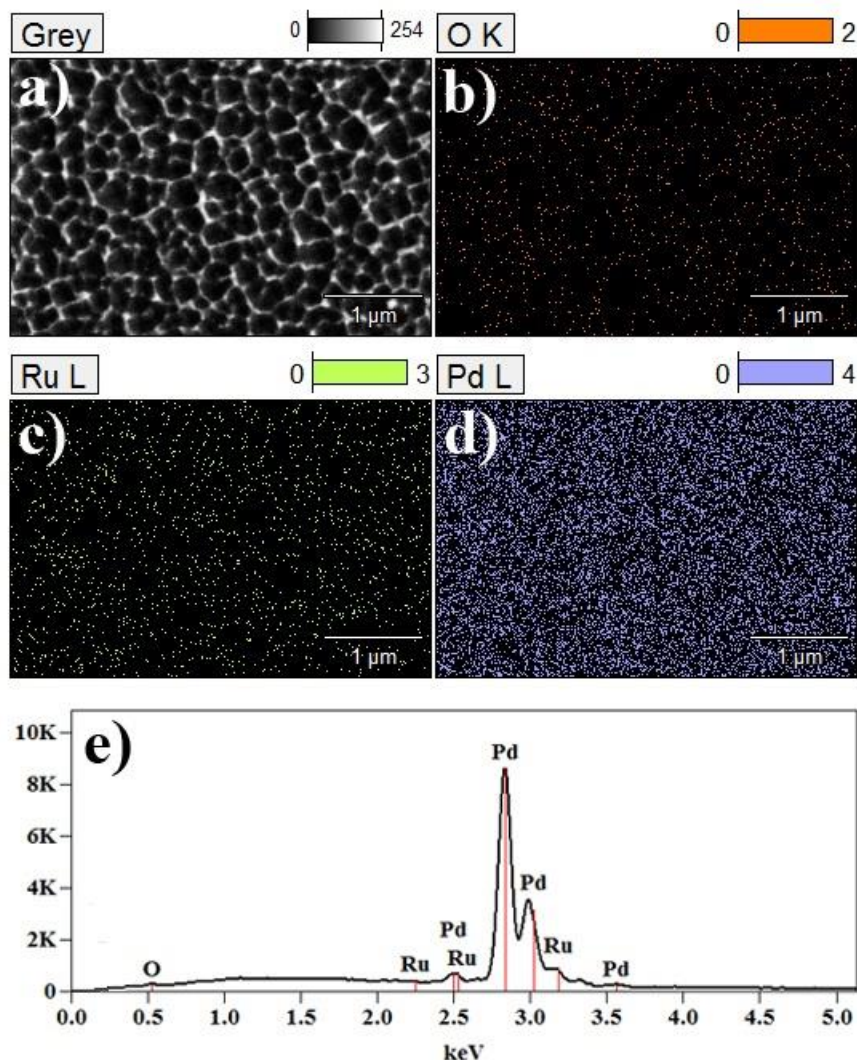
underlying Pd grains with clearly highlighted grain boundaries. Comparing the size of grains from Figures 1a and b, it appears that they are considerably larger in the case of bare Pd than in the case of Ru/Pd(poly) surface. This indicates that spontaneous deposition of Ru occurs predominantly on the edges of Pd grains making the boundaries between the grains more emphasized. Deposition of Ru on top of Pd grains seems to occur as well but to a lesser extent.



**Figure 1.** FESEM images of: a) bare Pd(poly) surface and b) Ru/Pd(poly) surface obtained after 30 min deposition.

In order to confirm that the surface of Pd is successfully decorated by spontaneously deposited Ru, EDS elemental mapping was performed and the obtained results are presented in Figure 2. The chosen micro-area of Ru/Pd(poly) surface is shown in Figure 2a, corresponding EDS elemental mapping of the Ru/Pd(poly) surface is given in Figure 2(b-d), while EDS spectrum is depicted in Figure 2e. Besides Pd and Ru as the main surface constituents, the presence of oxygen on the surface of the sample is also noticed. Oxygen, ruthenium and palladium are presented with different colours in Figure 2(b-d): O (orange), Ru (green) and Pd (purple). Figure 2c confirms that Ru is deposited preferentially onto the Pd grain edges, as well as on their surface but to the lesser extent. On the basis of EDS analysis, the island growth of Ru onto Pd substrate is observed. Typical EDS spectrum, Figure 2e, collected from the observed area in the energy range of 0.2 keV to approximately 3.7 keV, confirmed the presence of O, Ru and Pd on the sample surface.

It is interesting to complement FESEM analysis of the Ru/Pd(poly) surface with the atomic force microscopy (AFM) imaging of the same system given in details in ref. [28]. On both larger (FESEM) and lower (AFM) imaging scale, it is clear that Pd substrate consists of crystallites and that Ru deposition occurs on edges as well as on top of Pd grains. Surface coverage estimated from phase AFM images for 3 and 30 minutes Ru deposition was  $(30 \pm 5)\%$  and  $(50 \pm 5)\%$ , respectively [28].



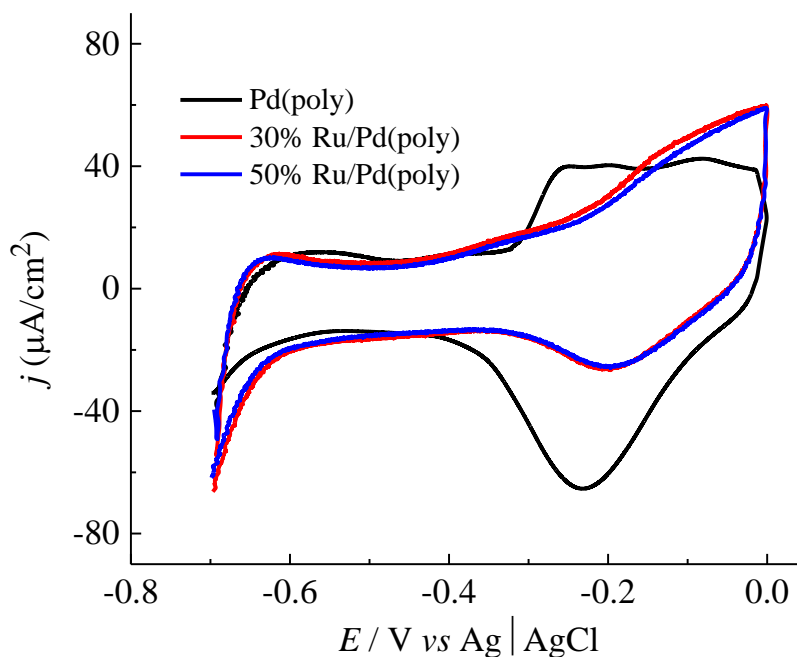
**Figure 2.** FESEM-EDS characterization of bimetallic Ru/Pd(poly) electrode surface: a) FESEM micrograph; (b-d) corresponding EDS elemental mapping of O, Ru and Pd, respectively; e) EDS spectrum of the sample.

### 3.2. Cyclic Voltammetry characterization

Electrochemical characterization of bimetallic Ru/Pd(poly) electrodes was performed by cyclic voltammetry in 0.1 M NaOH solution. Collected CVs are presented in Figure 3 together with the CV of bare Pd(poly) electrode. Potential window between -0.70 V and 0.0 V was chosen by taking into account the main electrochemical characteristics of Pd substrate. Negative potential limit of -0.70 V was set to be considerably higher than the equilibrium potential for hydrogen evolution (-0.98 V vs. used Ag/AgCl reference electrode in 0.1 M NaOH) in order to avoid excessive absorption of hydrogen. Positive potential limit of 0.0 V was set high enough to include the onset of Pd surface oxidation but not too high in order to avoid the formation of high valence Pd-oxides and a possibility of electro-dissolution of Pd [31].

Obtained CV of bare Pd(poly) electrode is in good agreement with previous reports [28,31], showing OH<sup>-</sup> adsorption in the potential range between -0.45 V and -0.33 V, the formation of PdO at

higher potentials in the forward scan, and a peak centred at -0.23 V originating from the PdO reduction in the backward scan. In the low potential region the onset of hydrogen absorption can be observed at the potential of -0.55 V (see detailed analysis of hydrogen absorption/evolution in ref. [32]).



**Figure 3.** Cyclic voltammograms of bare Pd(poly) and bimetallic Ru/Pd(poly) electrodes recorded in 0.1 M NaOH at a sweep rate of  $50 \text{ mV s}^{-1}$ .

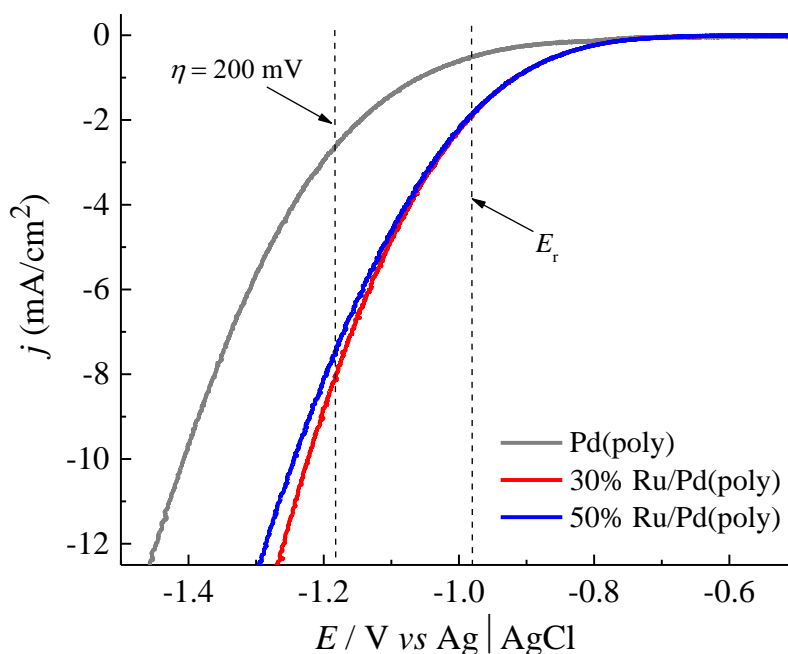
Spontaneous deposition of Ru on Pd(poly) provoked notable changes in the CV profiles of bimetallic electrodes with respect to Pd(poly). In the forward scan, Pd oxide formation peak is suppressed by the presence of Ru, and this suppression is only slightly more pronounced with the increase of Ru coverage from 30% to 50% [28]. Accordingly, in the reverse scan corresponding Pd-oxide reduction peak is suppressed and slightly shifted to more positive potentials due to the presence of Ru. Onset of hydrogen absorption is shifted to slightly more positive potentials with respect to bare Pd(poly) (for  $\sim 50 \text{ mV}$ ), meaning that the presence of Ru promotes this process. This is in accordance with reports on enhanced hydrogen absorption into Ru-Pd alloys with high Pd content [33,34], which is explained by the changes of the electronic structure upon alloying. This points out that there is also the electronic interaction between Pd substrate and spontaneously deposited Ru, which is expected to play an important role in the activity of bimetallic Ru/Pd(poly) electrodes towards HER. Moreover, such an interaction has been verified by X-ray photoelectron spectroscopy in our previous report [28] through the down shift of Pd 3d binding energies due to the presence of spontaneously deposited Ru. Besides, the detailed analysis of the surface composition of as-prepared Ru/Pd(poly) electrode by XPS showed that Ru is deposited as a mixture of metallic Ru and different RuOx species [28]. However, changes in the composition of the Ru deposit are expected in the electrolyte solution due to the applied potential. Current drop/rise in the CVs of bimetallic electrodes in the low potential region and widening of the double layer up to the potential of -0.45 V are the only features that may be associated with the Ru oxidation/reduction that mostly occurs parallel with the hydrogen related processes

[35,36]. Before recording of the HER polarization curves, bimetallic electrodes were subjected to the potential holding at -0.50 V, which led only to the partial reduction of RuOx species.

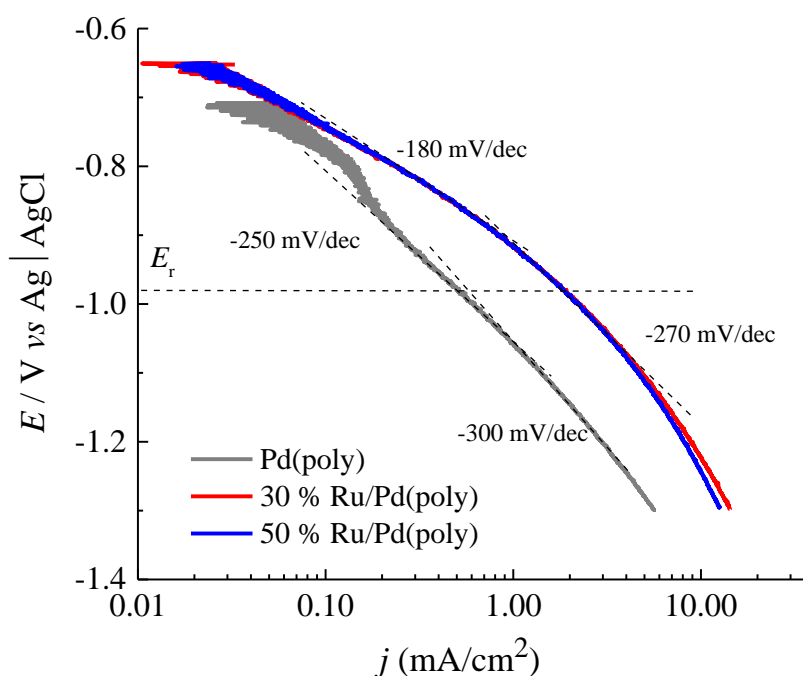
Investigation of the HER catalysis requires a proper estimation of the electrochemically active surface area (EASA) of the Ru/Pd(poly) electrodes, which must be defined in order to provide straightforward comparison of their activities. EASA values of Ru/Pd(poly) electrodes cannot be determined from cyclic voltammetry due to several reasons. Although both Pd and Ru adsorb hydrogen,  $H_{\text{upd}}$ , charge corresponding to this process cannot be used for EASA calculation of bimetallic Ru/Pd(poly) electrodes. It is well-known that Pd absorbs large amount of H which overlaps and dominates over  $H_{\text{upd}}$  process [37,38], and thus evaluation of EASA of Pd electrodes from CV using  $H_{\text{upd}}$  charge is impossible. Similarly, in the case of Ru electrodes, overlapping of hydrogen and oxygen adsorption regions as well as the absorption of certain amounts of hydrogen also prevent the application of  $H_{\text{upd}}$  charge as a tool for the determination of EASA [35,37,39]. Besides, Pd-oxide reduction peak cannot be used for EASA determination since there is no reduction peak corresponding to the deposited Ru to complement such an analysis and to give an overall EASA. Therefore, CO stripping voltammetry stands out as the most appropriate method for calculation of the EASAs of Ru/Pd(poly) electrodes [28]. Taking into account the charge of  $424 \mu\text{C cm}^{-2}$  for a full monolayer of CO on Pd [27,30], EASA values for bare Pd(poly), 3 min Ru/Pd(poly) and 30 min Ru/Pd(poly) electrodes of  $0.21 \text{ cm}^2$ ,  $0.209 \text{ cm}^2$  and  $0.205 \text{ cm}^2$  were obtained. These values will be used for the calculation of the current densities for the HER polarization curves.

### 3.3. Hydrogen evolution reaction on Ru/Pd(poly) electrodes

Polarization curves for HER on Pd(poly) and on bimetallic Ru/Pd(poly) electrodes recorded in 0.1 M NaOH solution are presented in Fig. 4. For bare Pd(poly) electrode, current densities start to drop below zero at potentials far more positive than the equilibrium HER potential (-0.98 V) due to the hydrogen absorption [31,32]. At equilibrium potential for hydrogen evolution, current density on Pd(poly) electrode reaches  $-0.5 \text{ mA cm}^{-2}$ , and at more negative potentials  $\text{H}_2$  evolution and hydrogen absorption occur simultaneously. In the case of Ru/Pd(poly) electrodes, the onset of hydrogen absorption is placed at more positive potentials and this process proceeds more rapidly with respect to bare Pd(poly). Current density of  $-1.90 \text{ mA cm}^{-2}$  is reached on the equilibrium HER potential, which is notably higher than for the bare Pd(poly). Again, this observation of the promoted H absorption due to the presence of Ru is in accordance with the previous reports about Ru-Pd alloys [33,34]. At potentials more negative than the equilibrium one, hydrogen evolution start to take place together with hydrogen absorption. Both Ru/Pd(poly) electrodes are notably more active than bare Pd(poly), between which the one with 30% Ru coverage shows slightly higher activity than the one with 50% Ru coverage. At the overpotential of 200 mV, current densities of  $-2.6 \text{ mA cm}^{-2}$  and  $-8.0 \text{ mA cm}^{-2}$  are reached for HER on Pd and 30% Ru/Pd(poly) electrodes, respectively, showing threefold increase of the activity due to the presence of Ru.



**Figure 4.** Polarization curves for hydrogen evolution reaction on Pd(poly) and on bimetallic Ru/Pd(poly) electrodes recorded in 0.1 M NaOH at a sweep rate of  $10 \text{ mV s}^{-1}$ . Current densities are calculated by using EASA values.



**Figure 5.** Tafel plots for HER on Pd(poly) and Ru/Pd(poly) electrodes derived from polarization curves given in Figure 4.

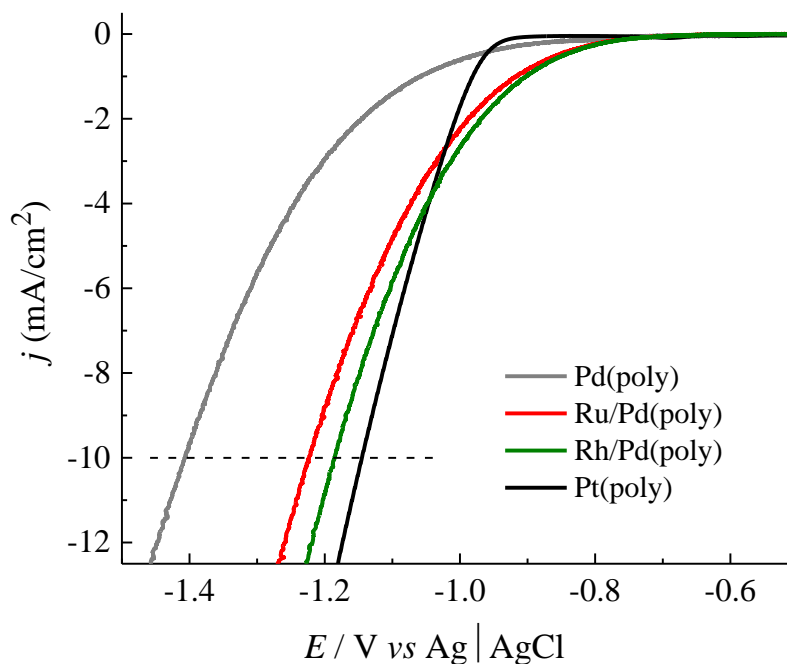
Apart from standard Volmer, Tafel and Heyrovsky steps, consideration of HER mechanism on Pd-based electrodes involves the steps of direct and indirect hydrogen absorption as this process overlaps with  $\text{H}_2$  evolution [32,40]. Volmer step implies the adsorption of H intermediate through the discharge of water molecules in alkaline media. In the following step, hydrogen can be absorbed into bulk Pd (indirect absorption) and/or it can undergo either Tafel or Heyrovsky steps to form gaseous  $\text{H}_2$



product. Concurrently, direct absorption of hydrogen into Pd can occur without previous adsorption step.

Tafel plots obtained from the HER polarization curves (Figure 4) are presented in Figure 5. Unusually high values of Tafel slopes appear as a consequence of simultaneous absorption and evolution of hydrogen. For bare Pd(poly), at lower overpotentials the slope is  $-250$  mV/dec, while at higher overpotentials it is  $-300$  mV/dec. For both 30% and 50% Ru/Pd(poly) electrodes, values of  $-180$  mV/dec and  $-270$  mV/dec for Tafel slopes were obtained at higher and lower overpotentials, respectively. These values cannot be used to directly propose possible HER mechanism due to the simultaneous hydrogen absorption, but lower Tafel slopes obtained for bimetallic Ru/Pd(poly) electrodes with respect to Pd(poly) confirm the faster kinetics of both hydrogen evolution and absorption processes. In the case of Pd electrodes, HER mechanism was proposed to follow Volmer-Tafel route at lower overvoltages, while at higher overpotentials Heyrovsky step can be involved [41,42]. It can be assumed that the presence of spontaneously deposited Ru increases the rate of the reaction by lowering of the adsorption energy of H intermediate species through the electronic interaction. Slight decay in the HER activity of bimetallic electrodes that occurs with the increase of Ru coverage from 30% to 50% can be explained by the weakening of the electronic interaction. In the terms of HER mechanism on Ru/Pd(poly) electrodes, most likely it remains the same as on bare Pd(poly), but with faster discharge step. Besides, since hydrogen absorption is also enhanced by the presence of Ru, it can be proposed that it takes place via indirect pathway in which H species are first adsorbed on the surface of Ru/Pd(poly) electrodes and then absorbed into the bulk material.

Since Ru/Pd(poly) electrodes have shown significant catalytic effect for HER, it is interesting to compare their activity with parallel Rh/Pd(poly) system, which is also very active for HER [32].



**Figure 6.** Comparison of HER activities of Pd(poly), Ru/Pd(poly), Rh/Pd(poly) and Pt(poly) electrodes. Polarization curves were recorded in 0.1 M NaOH at a scan rate of 10 mV/s.

Such comparison between these two bimetallic systems is illustrated in Figure 6. Besides, the activities of bare Pd(poly) as substrate electrode and of bare Pt(poly) as the benchmark catalyst for HER are also presented. It is obvious that bare Pd(poly) is notably less active than Pt(poly) for HER in alkaline media, as well as that the deposition of either Ru or Rh leads to a significant enhancement of the initial activity of Pd substrate. For such bimetallic systems consisting of Pd(poly) electrode decorated with the deposited either Ru or Rh nanoislands, the electrodes which were taken for comparison were the ones with the highest HER activity, namely 30% Ru/Pd(poly) and 50% Rh/Pd(poly) [32]. In the following text they will be referred to as Ru/Pd(poly) and Rh/Pd(poly). Between these two bimetallic systems, Rh/Pd(poly) is shown to be slightly more active for HER than Ru/Pd(poly). Apart from the sole nature of two foreign metals, the explanation for this trend can be found in the particularly strong electronic interaction between Pd substrate and Rh islands [43], which resulted in favourable energetics of hydrogen adsorption and high HER activity [32]. More importantly though is that both Ru/Pd(poly) and Rh/Pd(poly) electrodes exceeded the activity of bare Pt(poly) in the low overpotential region. At higher overpotentials, Pt(poly) becomes more active than bimetallic electrodes, but still the difference in the activities between Pd(poly) and Pt(poly) electrodes is significantly reduced in the presence of spontaneously deposited Ru or Rh. For example, at the current density of  $-10 \text{ mA cm}^{-2}$ , the difference between the corresponding potentials on HER polarization curves for Pd and Pt electrodes equals 250 mV. This substantial gap is reduced to only 80 mV and 40 mV between polarization curves for HER on Pt(poly) and on Ru/Pd(poly) or Rh/Pd(poly) electrodes, respectively, at the same current density. This comparison proves that the addition of foreign metals, such as Ru, to Pd(poly) electrodes is a promising way to obtain highly active Pd-based materials for HER which could serve as appropriate substitute for the state of the art Pt-based catalysts.

#### 4. CONCLUSIONS

In this work, we have demonstrated that the addition of Ru nanoislands on Pd(poly) substrate by spontaneous deposition significantly enhances its activity for HER in alkaline solution. FESEM-EDS characterization of bimetallic Ru/Pd(poly) electrodes revealed that grainy surface of Pd(poly) is successfully decorated by Ru islands, which are predominantly deposited on the edges of Pd crystallites and to the lesser extent on top of Pd grains. Significant enhancement in HER activity was ascribed to the electronic interaction between deposited Ru and Pd substrate, which facilitates the adsorption of H intermediate species as the first step in HER mechanism. Based on the results presented in this work, bimetallic Ru/Pd catalysts can be regarded as a promising alternative for Pt-based materials in HER catalysis.

#### ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Science of the Republic of Serbia; project N° 45005.

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