Relationship between the reactions of hydrogen sorption/desorption and methanol oxidation on bifunctional Ni/Pd electrode in alkaline solution

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Abstract The present paper is aimed at studying the influence of the hydrogen sorption/desorption process occurring on the layered nickel–palladium (Ni/Pd) electrode on the kinetics of the reaction of methanol oxidation in strong alkaline KOH solution. The electrodes were prepared by chemical deposition of a thin layer of porous palladium on a nickel foam support. A scanning electron microscope was used for studying the morphology of both the nickel support and the porous palladium layer. The mechanism of the anodic desorption of hydrogen changes depending on whether or not 6 M KOH electrolyte is admixed with methanol. It was shown that, in the first cycle of the cyclic voltammetry (CV) measurements, the anodic peak current and peak charge related to the oxidative desorption of hydrogen significantly decrease due to the presence of methanol in KOH. This effect is attributed to the obstacles in hydrogen sorption due to the formation of a passivating layer on the Pd surface composed of both adsorbed methanol molecules and the intermediate products involving adsorbed CO. On the other hand, hydrogen desorbing from Pd electrode exerts influence on the kinetics of the reaction of methanol oxidation. Ni/Pd electrode undergoes considerable reactivation due to the potentiostatic saturation with hydrogen at -1.1 V, followed by the ease in hydrogen desorption. The CV measurements proved that, after such a treatment, the peak of hydrogen desorption partially overlaps the double peak of methanol oxidation and, in consequence,

the rate of methanol oxidation is enhanced. The positive effect of hydrogen releasing from the electrode on the kinetics of the reaction of methanol oxidation is ascribed to the anti-poison behavior consisting in the reaction of hydrogen radicals with intermediates adsorbed on the Pd surface.

Keywords Nickel foam · Palladium · Ni/Pd-layered electrode · Hydrogen electrosorption · Methanol oxidation · Cyclic voltammetry · Alkaline solution

Introduction

Due to the rising costs of fossil fuels in recent years, a great attention has been focused on the development of alternative sources of energy such as nickel–metal hydride batteries [1, 2] and methanol fuel cells [3–5], which can be used to power electric vehicles and portable electronic devices.

Hydrogen and methanol, which are easily oxidized to products like H_2O and CO_2 , have attracted much attention as potentially clean and effective fuels. One of the main problems to be overcome for the common use of new energy carriers, like hydrogen and methanol, is the too low electrochemical activity of electrode materials used in the processes of hydrogen storage and methanol oxidation. A very important factor influencing the electrode activity is also the physicochemical property of the electrode support/current collector, which should represent the high specific surface area, good electrical conductivity, and low weight. It is well known that metals such as platinum, palladium, and their alloys exhibit high activity in the processes of hydrogen sorption/desorption [6–13]. Recently, an increasing attention has been paid on

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palladium and palladium-based electrodes due to their high electroactivity and lower price in comparison with platinum. It has been shown in many works [9–13] that hydrogen can be electrochemically stored (cathodically sorbed) in palladium and palladium alloys at room temperature and under atmospheric pressure and then easily recovered (anodically desorbed). It has been reported by Czerwiński et al. [9, 10] that the palladium limited volume electrodes (Pd-LVE), consisting of a thin layer of Pd deposited on a gold support, exhibit high specific volume capacity of hydrogen with an H/Pd ratio around 0.7. A similar value was also found for nickel foam/palladium composite electrodes in alkaline solution [11–13]. In the last few years, many papers have been devoted to the oxidation of small organic molecules, like methanol [3, 4, 14–22], ethanol [4, 16, 20, 23–27], and formic acid [20, 28–31], on palladium and palladium composite electrodes. From the aforementioned papers, a conclusion can be drawn that palladium is a good catalyst for oxidation of small organic molecules with the electroactivity comparable to the platinum catalysts. Additionally, Yépez and Scharifker [32] have reported the results indicating that hydrogen occluded in the bulk of the electrode increases the activity of a palladium catalyst in the electrooxidation process of formate present in 0.5 M KOH solution by reacting with the adsorbed CO poison and therefore regenerating the catalyst surface. A similar activating influence of hydrogen on the activity of PdPtRu-coated Pd electrode has been found by Yépez and Pickup [33] for the process of methanol oxidation in 0.5 M H₂SO₄.

In this paper, we present new experimental data concerning the electrochemical behavior of Ni/Pd-layered electrodes in the processes of simultaneous hydrogen sorption/desorption and methanol oxidation. The electrochemical features of these electrodes were investigated in a strong alkaline solution of 6 M KOH using cyclic voltammetry technique. The reactivation of the Ni/Pd electrode via the stripping process of adsorbed methanol oxidation products occurring in 6 M KOH solution was also examined.

Experimental

Bifunctional layered Ni/Pd electrodes were prepared by chemical deposition of thin layer of palladium onto nickel foam (produced by Nitech, thickness 1.6 mm, density 500 g cm⁻² and porosity higher than 95 %). After cleaning in acetone, Ni foam pieces (5 × 10 mm in dimension) were immersed in a solution of 0.11 M PdCl₂ in 1 M HCl for 5 min. The amount of Pd deposit was calculated from direct UV–VIS measurements (Multispec 1500 Shimadzu) of Pd and Ni ions concentrations in the electroplating solution before and after deposition of palladium on the Ni foam as well as electrode weighting before and after Pd electrolysis. The amount of hydrogen absorbed in the Pd layer deposited on Ni foam was calculated from cyclic voltammograms, taking into account the charge of

the anodic peak corresponding to the reaction of hydrogen oxidation. The morphology of the nickel foam and two-layer Ni/Pd electrodes were examined by scanning electron microscopy (SEM) analysis (Hitachi S-3400 N).

The reactions of methanol oxidation and hydrogen sorption/desorption into/from the working Ni/Pd electrode were measured at ambient temperature by cyclic voltammetry (CV) method and potentiostatic method using a potentiostat–galvanostat PGSTAT30 AutoLab (EcoChemie B.V.). The CV measurements were carried out in a three-electrode cell in deaerated 6 M KOH with and without addition of 0.1 M CH₃OH. A Hg/HgO/6 M KOH was used as the reference electrode. All potentials throughout the paper are referred to this electrode. Platinum gauze was used as a counter electrode. The CV measurements were carried out with potential scan rates of 1 and 10 mVs⁻¹ in the potential range -1.1↔0.3 V. The measurements were started from the rest potential of the electrode and the potential was changed in the negative direction (cathodic polarization) to reach -1.1 V; after the reversal of polarization, the potential was increased until the limit potential of +0.3 V was attained. At this moment, polarization was again reversed. Before starting the CV measurements, electrodes were electrochemically activated by cycling (10 cycles) in the potential range between -1.1 V and 0.3 V in KOH solution to attain a steady-state behavior. Such a treatment allowed us to enhance the electrochemical activity of examined electrodes in the process of sorption/desorption of hydrogen as compared to non-activated electrodes examined in our previous work [11].

The process of hydrogen sorption was carried out in such a way that, after reaching the potential of -1.1 V in the second cycle, hydrogen saturation of Ni/Pd electrode was performed for 15 min followed by potential scanning in the positive direction.

The reactivation of the Ni/Pd electrode coated with adsorbed methanol and the products of its oxidation was carried out using the following procedure. After completing 50 cycles performed in 0.1 M CH₃OH /6 M KOH solution in the potential range -1.1↔0.3 V, this solution was replaced in electrolytic cell with 6 M KOH free of methanol, in which two complete cycles were then recorded in the potential range -1.1↔0.3 V with a scan rate of 1 mVs⁻¹.

To confirm the positive influence of absorbed hydrogen on the activity of Pd catalyst in methanol oxidation process, the separate CV measurements were performed in 0.1 M CH₃OH/6 M KOH solution in the potential range -0.85↔0.3 V.

The potentiostatic measurements were carried out in a three-electrode cell in 6 M KOH solution with and without addition of methanol at -0.3 V. In order to study the influence of hydrogen occluded in Ni/Pd electrode on the methanol oxidation process before potentiostatic polarization at

−0.3 V Ni/Pd, the electrode was saturated with hydrogen at −1.1 V for 15 min.

Results and discussion

Characterization of Ni/Pd electrode by scanning electron microscopy

Figure 1 shows SEM micrographs for nickel foam. As can be seen in Fig. 1a, the nickel surface is very flat and only grain boundaries are visible at a high magnification. The nickel skeleton represents an open-pore structure composed of holed cells linked to each other (Fig. 1b). These cells are built of concave ribbons with sharp edges. Upon coating the nickel foam support with palladium, a porous layer is formed onto the nickel surface (Fig. 2a). The porous grains of Pd layer are mostly 0.1–1 μm in diameter. On viewing the palladium layer under a higher magnification, one can see that each palladium grain is composed of porous aggregates consisting of particles even smaller than 50 nm. This implies that the Ni/Pd porous electrode has the desired high electro-catalytic activity in the hydrogen sorption/desorption reaction. The tightness of Pd layer coating a Ni support was checked by recording CV curves in the potential range −1.1↔0.55 V (not shown here). As shown in our previous papers reporting on nickel foam electrode [34, 35], the limit value of 0.55 V in 6 M KOH solution is high enough to record the anodic peak associated with the $\text{Ni}(\text{OH})_2 \rightarrow \text{NiOOH}$ transformation. The lack of the peak at about

Fig. 1 a, b SEM micrographs for nickel foam

Fig. 2 a, b SEM micrographs for palladium coating on nickel foam support

0.4 V on CV curves for Ni/Pd electrode proves the Pd layer to be impermeable to electrolyte to reach a Ni sublayer.

Cyclic voltammetry measurements at a scan rate of 10 mVs^{-1}

Cyclic voltammograms recorded for Ni/Pd electrode in the potential range of −1.1↔0.3 V with the potential scan rate of 10 mVs^{-1} in 6 M KOH are presented in Fig. 3. In the first cycle, the potential of electrode was scanned in the negative direction, starting at the rest potential of −0.03 V. The reactions of hydrogen adsorption/absorption occur within a small cathodic peak at about −0.7 V and a cathodic wave commencing at about −0.85 V followed by the increase in current on scanning to more negative potentials. The oxidation of sorbed hydrogen takes place within the oxidation peak at −0.58 V after the reversal of polarization. As the potential increases further, the oxidation of Pd surface occurs to form the surface palladium oxides. After the next reversal of polarization, the reduction of Pd oxides takes place within a cathodic peak noted at around −0.20 V. The character of CV curves in this figure is the same as those recorded in alkaline solution for the Pd-LVE prepared by electrodeposition of a thin layer of palladium on the gold support [10]. In the second cycle, after the potentiostatic saturation of Ni/Pd electrode with hydrogen for 15 min at a constant potential of −1.1 V followed by scanning in the positive direction (anodic polarization), a huge anodic peak corresponding to the recovery of sorbed hydrogen is 160 mV shifted to more positive potentials as compared to that in the first cycle, whereas the peak current and peak

Fig. 3 Cyclic voltammograms recorded in 6 M KOH for Ni/Pd electrode. In the second cycle, after the potential of electrode was linearly decreased from the rest value down to -1.1 V, the potentiostatic saturation of electrode with hydrogen for 15 min was performed and then the second cycle was completed. Scan rate, 10 mV s^{-1}

charge are 2.4- and 4.2-fold higher, respectively, than those recorded in the cycle before the potentiostatic sorption (Table 1). The value -1.1 V of lower limit potential, positioned below the equilibrium potential of the H_2/H^+ reaction, was chosen purposely to overcome the overpotential of the sorption reaction and, in consequence, to allow the insertion reaction of hydrogen into the palladium electrode to occur effectively. During potentiostatic polarization of Ni/Pd electrode at a constant potential of -1.1 V (Fig. 3, cycle 2), a successively increasing amount of adsorbed/absorbed hydrogen diffuses from the outer layer of palladium into the palladium bulk where it is stored, forming α - and/or β -phase. Thus, after the reversal of polarization, the anodic process of hydrogen desorption occurs first from the outer layers of palladium, followed by diffusion from the bulk of the electrode to its surface layer to be desorbed. This fact has a significant influence on the mechanism of these processes, i.e., on the potential of hydrogen desorption and on the time needed for releasing–desorbing all the occluded hydrogen from the electrode. Such a mechanism of hydrogen desorption is responsible for 160 mV shifting the anodic peak maximum to more positive potentials. It has been shown previously in detail [13] that the potential shift and asymmetry of CV peak are greatly dependent on the scan rate used. On the other hand, a higher increase in the peak charge indicates that the reaction of hydrogen oxidation occurs in a wider range of potential.

At this point, it is reasonable to remind that in alkaline solutions the amount of electrooxidized hydrogen from the Pd electrode can be calculated only based on the charge of anodic peak due to the overlapping of the cathodic currents arising from hydrogen adsorption/absorption and hydrogen evolution on the CV curves during the negative scanning.

As has been shown in [11], the amount of hydrogen gas produced at the Pd surface, e.g., due to lowering the potential of hydrogen sorption from -1.1 to -1.25 V in the region where hydrogen absorption into Pd electrode is accompanied by hydrogen evolution, has insignificant contribution to the charge of the anodic peak of hydrogen recovery. This result is consistent with measurements performed with and without removal of gaseous hydrogen dissolved in the electrolyte [8], which evidenced that the oxidation of hydrogen from the solution has no noticeable influence on the total charge calculated from the oxidation peak used for the calculation of the amount of absorbed hydrogen. The same conclusion has been drawn from measurements carried out by Lawson et al. [36] who reported no difference between the D/Pd ratios calculated from the anodic charge for the cases when instantly after the cathodic reaction of deuterium absorption accompanied with the violent generation of copious amounts of D_2 gas the solutions were or were not degassed by purging with N_2 stream. Our recent CV measurements for Ni/Pd electrodes (curves not shown here) in 6 M KOH solution confirmed that the difference between the anodic peak charges of hydrogen oxidation is negligible if CV curve is recorded instantly after the potentiostatic saturation of the electrode with hydrogen at -1.1 V for 15 min and after the subsequent multiple exchange of a solution containing molecular hydrogen for a blank one free of dissolved hydrogen. All the aforementioned results prove unequivocally that hydrogen generated at the electrode surface and in turn diffusing to the bulk of electrolyte has unimportant contribution to the anodic charge arising from the oxidation of hydrogen undergoing desorption from Pd electrode.

Table 1 Dependence of the methanol oxidation peak current and peak charge on the hydrogen sorption/desorption reaction conditions

Figure	Cycle no.	Scan rate [mV/s]	Peak current of H ₂ oxidation [mA]	Ratio of peak current of H ₂ oxidation of cycle 2 to cycle 1 [%]	Peak current of CH ₃ OH oxidation [mA]	Ratio of peak current of CH ₃ OH oxidation of cycle 2 to cycle 1 [%]	Peak charge of H ₂ oxidation [C]	Peak charge of CH ₃ OH oxidation [C]	Total anodic peak charge [C]	Ratio of total anodic peak charge of cycle 2 to cycle 1 [%]
3	1	10	59.5	2.4	—	—	0.98	—	0.98	4.2
	2		145.0		—		4.08	—	4.08	
4	1	10	22.0	5.0	24.1	1.6	0.47	0.43	0.90	4.4
	2		110.1		38.0		—	—	3.95	
5	1	1	14.9	1.0	—	—	2.26	—	2.26	1.0
	2		14.7		—		2.28	—	2.28	
6	1	1	2.4	3.1	15.5	1.0	0.42	4.06	4.48	1.4
	2		7.4		15.9		—	—	6.18	

In order to answer a question of the influence of hydrogen stored at the subsurface layer of Pd electrode on the kinetics of methanol oxidation, the CV measurements were repeated using 6 M KOH solution containing 0.1 M CH₃OH. As seen in Fig. 4, CV curves are noticeably altered after the KOH solution is admixed with methanol. In the first cycle, after the completed cathodic scanning, the anodic peak of hydrogen desorption at -0.58 V is followed by a new anodic peak at -0.15 V, with a precedent shoulder at -0.25 V. The latter peak is associated with the reaction of methanol oxidation occurring in the potential range of the formation of Pd oxide [9, 11–13, 16, 19]. A characteristic feature of the reaction of methanol oxidation is a sharp anodic peak, related to the reactivation of the electrode surface, appearing abruptly at -0.25 V during the negative scanning. The comparison of CV curves presented for the first cycle in Figs. 3 and 4 leads to the conclusion that the presence of methanol in KOH solution gives rise to a significant decrease in the anodic peak current and peak charge related to the oxidation of hydrogen. As can be seen from Table 1, the respective values recorded in the first cycle in the KOH/methanol solution for the peak at -0.58 V are 2.7 and 2.1 times lower than those measured in the KOH solution free of methanol. It means that after adding methanol to KOH electrolyte, the Ni/Pd electrode becomes less active in the reaction of hydrogen sorption/desorption. Because this reaction takes place at potentials lower than the potential of the methanol oxidation reaction, it is reasonable to assume that methanol adsorbed at the electrode surface blocks catalytic Pd sites and, in consequence, results in a considerable deterioration of the Ni/Pd electrode activity towards hydrogen sorption/desorption. A twice lower value of cathodic current noted at -1.1 V in KOH/methanol solution (Fig. 4) as compared to that for the methanol-free solution (Fig. 3) indicates that a smaller amount of desorbed hydrogen can be attributed to the cathodic reaction of hydrogen sorption being hindered due to the methanol adsorbed on the Pd surface.

In the second cycle carried out in KOH/methanol solution, the situation changes strikingly. As seen from Fig. 4, after the potentiostatic sorption of hydrogen, the amount of hydrogen desorbed from Ni/Pd electrode increases significantly, similar to the case observed in pure KOH solution. The main peak involving hydrogen desorption is only 30 % lower than that noted in the second cycle in KOH solution (Fig. 3), whereas the ratio of the peak currents measured for the second and first cycle in KOH/methanol solution is twice that measured in KOH without methanol. This comparison shows clearly that the electrode is capable of easily recovering its activity towards hydrogen sorption upon cathodic polarization despite the presence of methanol in the electrolyte. A not-less-interesting feature is that, due to the presence of methanol, the peak of hydrogen oxidation in the second cycle becomes wider and 110 mV shifted towards the positive potentials (Fig. 4) as compared to that noted in KOH solution (Fig. 3).

Fig. 4 Cyclic voltammograms recorded in 0.1 M CH₃OH/6 M KOH for Ni/Pd electrode. In the second cycle, after the potential of electrode was linearly decreased from the rest value down to −1.1 V, the potentiostatic saturation of electrode with hydrogen for 15 min was performed and then the second cycle was completed. Scan rate, 10 mV s^{−1}

As a consequence, the peak associated with the reaction of methanol oxidation is almost hidden from view. Because the superposition of these peaks is incomplete, one can notice that the current of the residual peak of methanol oxidation emerging at the right side of a huge peak of hydrogen oxidation is 60 % higher than the peak of methanol oxidation in the first, whereas the depassivation peak recorded during the scan towards negative potentials remains unchanged (Table 1). This feature suggests that hydrogen released from the Pd surface in the potential range of methanol oxidation enhances the anti-poison ability of the Pd catalyst.

For better understanding of the mechanism of the process of hydrogen sorption/desorption followed by methanol oxidation, it should be realized at this point that the potentiostatic sorption of hydrogen in KOH/methanol solution in the second cycle at −1.1 V occurred on/in the Pd surface on which methanol and incompletely oxidized carbonaceous species were adsorbed during the positive scan in the first cycle. The anodic peak seen in Fig. 4 at −0.32 V, corresponding to the oxidation reaction of hydrogen in the second cycle, is broader and 160 mV positively shifted as compared to that in Fig. 3, whereas the peak current is only about 30 % lower in comparison with the peak observed during the process taking place in the KOH solution without methanol (Fig. 3). This observation suggests that hydrogen desorption occurs at some overpotential due to the changes in the chemical structure of the surface of Pd electrodes resulting from the presence of residual passivating species. On the other hand, owing to this overpotential, the maximum rate of hydrogen desorption is moved to the potential region of methanol oxidation. A not-less-interesting result is

that the ratio of the hydrogen desorption peak currents measured in the second and first cycle, which amounts 5.0 for KOH/methanol solution, is twice that calculated for the peaks recorded in pure KOH solution (Table 1). These calculations prove that despite the presence of CH₃OH and the products of its oxidation adsorbed on the surface of Ni/Pd electrode, the potentiostatic uptake of hydrogen at a constant potential of −1.1 V proceeds effectively.

On searching for the explanation of the positive effect of hydrogen releasing from the electrode on the kinetics of the reaction of methanol oxidation, it is important to notice that the peak of methanol oxidation in the second cycle (Fig. 4) begins before the peak of hydrogen oxidation is completed. It means that active hydrogen atoms desorbing at the interface of the electrode/KOH–methanol solution can be involved in the reaction of methanol oxidation and, in consequence, bring about the decrease of the poisoning effect on the electrode surface. The results obtained in this work show that the reactivation process of the electrode surface occurring during the electrosorption of hydrogen has a positive influence on the activity of Ni/Pd catalyst in the process of methanol oxidation. In consistency with the mechanism of methanol oxidation proposed for Pd/PdPtRu electrode [33], one can assume that also in the case of Ni/Pd electrode examined by us in strongly alkaline solution admixed with methanol, active hydrogen (H[•]) stored at the surface of Pd layer deposited onto nickel foam carrier takes part in the removal of CO species poisoning Pd sites:

Cyclic voltammetry measurements at a scan rate of 1 mVs^{-1}

Figures 5 and 6 depict the cyclic voltammograms recorded for Ni/Pd electrode in the same solutions as regarded earlier but at ten times lower the potential scan rate of 1 mVs^{-1} . As can be seen in Fig. 5, where CV curves recorded in pure KOH solution are presented, in the first cycle the anodic peak of hydrogen desorption at -0.68 V is fourfold lower than that noted at a higher scan rate (Fig. 3; Table 1). The potentiostatic sorption of hydrogen in 6 M KOH at -1.1 V has only a slight influence on the amount of hydrogen released from Ni/Pd electrode at the potential scan rate of 1 mVs^{-1} , and the anodic peak at -0.68 V remains almost unchanged in the second cycle. This observation allows inferring that lower potential scanning ensures complete saturation of Ni/Pd electrode with hydrogen during the potentiodynamic run proceeding in the potential range from -0.85 to -1.1 V where the cathodic peak associated with the hydrogen adsorption/absorption appears. In other words, despite the cathodic polarization at the potential of -1.1 V for 15 min , no more hydrogen can be stored in Ni/Pd electrode [13].

When KOH solution contains methanol (Fig. 6), in the first cycle the anodic peak of hydrogen desorption at -0.68 V is ninefold lower than that noted at a higher potential scan rate (Fig. 4; Table 1). The process of methanol oxidation occurs within two peaks, of which the larger and sharper one at -0.18 V and incompletely shaped peak at -0.33 V are 42 and 20% lower than the respective peaks recorded at a scan rate of 10 mVs^{-1} . The increase of the flattened peak at -0.33 V in relation to the one at -0.18 V is indicative of the enhancement of the rate of reaction preceding the main reaction of methanol

oxidation. Although it is beyond doubts that methanol oxidation assisted by active hydrogen undergoing desorption is a two-step process, further investigations are needed to elucidate thoroughly the mechanism of this process. The anodic peak of depassivation observed in Fig. 6 at -0.18 V during the negative scanning is very sharp and its current value is three times higher than that noted at a tenfold-higher scan rate (Fig. 4). This feature indicates that the reactivation of Ni/Pd catalyst occurs with higher efficiency at a lower scan rate. The other change resulting from the decrease in scan rate is that after the cathodic polarization at the potential of -1.1 V for 15 min , the peak of hydrogen desorption becomes threefold higher and is positioned at a potential around 150 mV more positive than the corresponding peak recorded without the potentiostatic sorption of hydrogen. As compared to the phenomenon observed for the process occurring in KOH/methanol solution at the potential scan rate of 10 mVs^{-1} (Fig. 4), the anodic peak of hydrogen desorption observed on CVs in Fig. 6 only a little superposes on the peak associated with the reaction of methanol oxidation. This is probably the reason that the difference in the peak intensities of methanol oxidation in the first and second cycle are less pronounced than in the situation shown in Fig. 4 where the reaction of hydrogen desorption covers almost the whole region of methanol oxidation. The difference in the peak intensities and charges of methanol oxidation in the first and second cycle measured with a scan rate of 1 mVs^{-1} (Fig. 6) is a consequence of involvement of desorbing hydrogen in the reaction of methanol oxidation.

For a slower scan rate of 1 mVs^{-1} (Fig. 6), a great part of hydrogen stored in the electrode (Pd layer) during the potentiostatic cathodic treatment may undergo desorption due to

Fig. 5 Cyclic voltammograms recorded in 6 M KOH for Ni/Pd electrode. In the second cycle, after the potential of electrode was linearly decreased from the rest value down to -1.1 V , the potentiostatic saturation of electrode with hydrogen for 15 min was performed and then the second cycle was completed. Scan rate, 1 mVs^{-1}

Fig. 6 Cyclic voltammograms recorded in 0.1 M CH₃OH/6 M KOH for Ni/Pd electrode. In the second cycle, after the potential of electrode was linearly decreased from the rest value down to -1.1 V, the potentiostatic saturation of electrode with hydrogen was performed for 15 min and then the second cycle was completed. Scan rate, 1 mVs^{-1}

the non-electrochemical reaction (the hydrogen recombination governed by the Tafel reaction) [10, 13] before the reaction of methanol oxidation starts. This path of desorption is of less importance if the potential scanning is faster because a shorter time is allowed for the recombination process to take place. This fact is the reason for the less pronounced enhancement of activity of Pd catalyst in the reaction of methanol oxidation at 1 mVs^{-1} (Fig. 6) in comparison with that revealed on the CV curves recorded with a tenfold higher scan rate of 10 mVs^{-1} (Fig. 4) when the reaction of methanol oxidation starts to occur at the electrode in which much more hydrogen is still preserved. In other words, the smaller increase in the current for a scan rate of 1 mVs^{-1} (Fig. 6) results from a lower amount of hydrogen present in the electrode in the potential region where the process of methanol electrooxidation occurs. From this comparison, one can infer that the degree of the reactivation of Pd catalyst by hydrogen occluded in the electrode and its activity in the process of methanol oxidation are directly dependent on the potential scan rate used.

In order to struggle through the difficulty in a strict comparison of the peak currents related to hydrogen and methanol oxidation due to the superposition of the peaks, the consideration of the anodic charges for both reactions seem to be worthy of attention to approach to the problem concerning the contribution of desorbing hydrogen to the kinetics of the reaction of methanol oxidation. As can be seen in Table 1, for the first cycle in KOH/methanol solution, the anodic charges for hydrogen oxidation (column 8) are comparable for scan rates of 10 mVs^{-1} (0.47 C) and 1 mVs^{-1} (0.42 C), whereas the same change in scan rate results in a ninefold increase in charge for methanol oxidation (column 9). The remarkably

much higher increase in charge for the methanol-containing solution due to ten times slower scan rate is understandable because of lower reaction rate of methanol oxidation as compared to hydrogen oxidation. Moreover, the ratio of total anodic peak charges in cycles 2 and 1 is higher for the KOH solution admixed with methanol than for pure KOH solution (last column). This change is especially pronounced for a lower scan rate. These results, being consistent with earlier calculations based on the changes in peak currents, prove that the kinetics of methanol oxidation is considerably enhanced by active hydrogen, which during desorption gives rise to the reactivation of the palladium surface due to cleaning the catalytic sites for methanol oxidation.

To substantiate this conclusion, additional experiments have been made at a scan rate of 10 mVs^{-1} . Figure 7 shows the CV curves recorded without the potentiostatic sorption of hydrogen for the Ni/Pd electrode in 0.1 M CH₃OH/6 M KOH solution with a scan rate of 10 mVs^{-1} . The first cycle was performed in a narrow potential range of $-0.85 \leftrightarrow 0.3$ V, thus preventing the process of hydrogen electrosorption to occur, whereas the second cycle was recorded after moving the lower limit potential down to -1.1 V (without stopping at this potential), thus allowing for the process of sorption/desorption of hydrogen to take place. From Fig. 7, it is clearly seen that, as compared to the first cycle, during anodic polarization the peak charge of the methanol oxidation measured in cycle 2 is 14.4 % higher in the potential range $-0.45 \leftrightarrow 0.0$ V when the Ni/Pd electrode is scanned down to -1.1 V. This fact confirms the earlier statement that hydrogen radicals coming into the reaction with intermediates of methanol oxidation bring about the reactivation of catalytic sites on Pd surface.

Fig. 7 Cyclic voltammograms recorded for Ni/Pd electrode in 0.1 M CH₃OH/6 M KOH in the potential range $-0.85 \leftrightarrow 0.3$ V (cycle 1) and $-1.1 \leftrightarrow 0.3$ V (cycle 2). Scan rate, 10 mV s^{-1}

The next proof supporting the obtained results arises from new potentiostatic experiments shown in Fig. 8. This figure relates to hydrogen-free Ni/Pd electrode and for Ni/Pd electrode saturated with hydrogen in 6 M KOH solution without (curves a and b, respectively) and with addition of methanol (curves c and d, respectively). Hydrogen sorption was carried out at a potential of -1.1 V for 15 min. After this time elapsed, the potentiostatic polarization of examined electrodes was immediately carried out at the potential of

-0.3 V at which stored hydrogen is still present in the electrode (Pd layer), and simultaneously the process of methanol electrooxidation occurs (note that the maximum of hydrogen desorption peak is about 0.2 V shifted towards positive potentials for KOH solution admixed with methanol; see Figs. 4 and 6). From a comparison of recorded curves in blank KOH solution, it can be seen that the anodic charge calculated for Ni/Pd electrode saturated with hydrogen (0.1 C, curve b) is five times higher than for Ni/Pd

Fig. 8 Potentiostatic curves recorded at -0.3 V in 6 M KOH for hydrogen-free Ni/Pd electrode (curve a) and hydrogen-saturated Ni/Pd electrode (curve b) and in 0.1 M CH₃OH/6 M KOH for hydrogen-free Ni/Pd electrode (curve c) and hydrogen-saturated Ni/Pd electrode (curve d). Saturation of electrode with hydrogen at -1.1 V for 15 min

hydrogen-free electrode (0.02 C; curve a). This effect results from hydrogen desorption (oxidation) process. In the case of KOH solution containing 0.1 M CH_3OH , the calculated anodic charge for methanol oxidation for Ni/Pd hydrogen free electrode (4.60 C; curve c) is 230 times higher than the respective anodic charge measured for 6 M KOH solution not admixed with methanol (0.02 C; curve a). This enhancement arises exclusively from the reaction of methanol oxidation. It is worth noting that in the case when Ni/Pd electrode is at first saturated with hydrogen and then polarized at -0.3 V in the 0.1 M $\text{CH}_3\text{OH}/6$ M KOH solution, the calculated total anodic charge consisting of both hydrogen desorption charge and methanol oxidation charge is 16.5 % higher (5.36 C; curve d) than for the hydrogen-free electrode subjected to potentiostatic polarization at -0.3 V in electrolyte containing methanol (curve c). Moreover, the total anodic charge recorded for the electrode saturated with hydrogen in a solution containing methanol (5.36 C; curve d) is still much higher than the sum of methanol oxidation charge at hydrogen-free electrode (4.60 C; curve c) and hydrogen desorption charge for hydrogen stored in the electrode in methanol-free electrolyte (0.10 C; curve b). The obtained potentiostatic results clearly prove that hydrogen stored in the Pd layer of Ni/Pd electrode is noticeably favorable to the activity of the palladium catalyst in the process of methanol electrooxidation. Active hydrogen (H^*) present at the subsurface regions of Pd layer deposited onto nickel foam carrier is involved in the reactivation of the palladium catalyst due to the removal of poisoning CO species being intermediate products of methanol oxidation

and thereby has a positive influence on the kinetics of the regarded process.

Stripping voltammetry measurements

Figure 9 presents CV curves recorded in KOH solution free of methanol. Prior to these measurements, long-term cycling of Ni/Pd electrode was performed in 6 M KOH+0.1 M CH_3OH solution in the potential range $-1.1 \leftrightarrow 0.3$ V using a scan rate of 1 mVs^{-1} . Upon cyclization, all of the reactions involved in the consecutive process of hydrogen sorption/desorption and methanol oxidation/reduction were allowed to occur. As mentioned in “Experimental”, after finishing 50 cycles, KOH/methanol solution was removed from the electrolytic cell and repeatedly filled with pure KOH solution in which further CV measurements were performed. As can be seen in Fig. 7, after starting the CV measurements at the rest potential of the electrode (-0.65 V), the cathodic scanning proceeds typically until the potential of -1.1 V was attained. After the reversal of polarization, the anodic peak corresponding to hydrogen desorption is recorded at about -0.62 V, and on further increase in potential a small peak appears at -0.33 V. This peak agrees well with the position of the first peak (positioned at a more negative potential) involved in the process of methanol oxidation (Fig. 6). Based on this observation, it is reasonable to assume that the peak at -0.33 V arises from the oxidation of adsorbed methanol and intermediate products of methanol oxidation strongly bounded to the Pd surface of Ni/Pd electrode. Such an assumption is justified by the fact that the

Fig. 9 Cyclic voltammograms recorded in 6 M KOH solution for Ni/Pd electrode after the precedent 50 cycles performed in the potential range $-1.1 \leftrightarrow 0.3$ V in 0.1 M $\text{CH}_3\text{OH}/6$ M KOH solution. Scan rate, 1 mVs^{-1}

peak related to hydrogen desorption in the first cycle (Fig. 9) is 60 mV shifted towards positive potential and its intensity is over fivefold lower compared to that recorded in the first cycle for clean Ni/Pd electrode in KOH solution (Fig. 5). This result confirms the aforementioned statement that hydrogen sorption is being hindered by methanol adsorbed on the Pd surface. A slight cathodic peak noted at -0.1 V in Fig. 9 arises from the reduction of palladium oxides formed in the positive run due to the potential polarization up to $+0.3$ V. In the second cycle, the anodic peak of hydrogen desorption is three times higher and a slight peak of methanol oxidation disappears completely. This feature proves that the surface of Ni/Pd electrode is reactivated in the first cycle due to the removal of the passivating layer.

Conclusions

It was shown that the reaction of methanol oxidation can proceed on Ni/Pd electrode in a strong KOH solution and that the rate of this reaction depends on the activity of the electrode in the preceding reaction of hydrogen sorption/desorption. Based on the results of cyclic voltammetric measurements, it was found that the kinetics of the reaction of hydrogen sorption/desorption into/from Ni/Pd electrode changes after admixing with methanol to KOH solution.

Adding methanol to KOH solution gives rise to the decrease in anodic charge associated with the oxidation of hydrogen stored in Ni/Pd electrode during the cathodic polarization. Such a behavior is related to a screening effect of passivating layer formed on the Pd surface. This layer, composed of adsorbed methanol as well as not completely oxidized carbonaceous species, covers the palladium surface on/in which the potentiostatic hydrogen sorption occurs. After the potentiostatic saturation of electrode with hydrogen, the process of hydrogen desorption is considerably enhanced. Due to shifting of the peak of hydrogen oxidation towards positive potentials, the anodic peaks of hydrogen desorption and methanol oxidation partially superpose on each other. As a consequence, the rate of the hydrogen-assisted reaction of methanol oxidation increases markedly. It is likely that hydrogen radicals coming into the reaction with intermediates of methanol oxidation bring about the reactivation of catalytic sites on Pd surface.

The CV measurements showed that hydrogen desorbing from the Pd phase contributes to electrode reactivation after the process of methanol oxidation. The influence of hydrogen on both the kinetics of the reaction of methanol oxidation and electrode reactivation depends on the potential scan rate used. A double peak revealed on CV curves indicates that the reaction of methanol oxidation is a two-step process. The separation of peaks is more pronounced on CV curves recorded at a lower scan rate. Further experimental works

are expected to close the explanation of the reasons for this phenomenon.

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