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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Catalytic Activity of Electrolytic Palladium Deposits on Porous Nickel Substrates

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Abstract—Catalytic activity of palladium layers in reduction of atmospheric oxygen and oxidation of methanol and ethanol in an alkaline medium was studied for electrolytic palladium deposits on porous nickel substrates by cyclic voltammetry on a rotating disk electrode.

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It is known that the catalytic activity of palladium is frequently comparable with that of platinum, which makes palladium promising as an electrocatalyst for fuel cells. A particular attention is paid in development of new palladium catalysts to the nature and state of substrates on which palladium is deposited and to the method of deposition of the metal. Use of nickel as a catalyst in fuel cells is promising because of its high corrosion resistance and comparatively low cost. Of particular interest in this case are deposits with large roughness factor and good mechanical strength.

The problem of application of pure electrolytic deposits of nickel as electrocatalysts has been little discussed in the literature. Use of electrochemically obtained highly porous metallic nickel matrices with large roughness factor and good mechanical resistance as Raney electrodes was mentioned in [1]. The possibility of using hollow nickel spheres constituted by needle-like nickel particles as catalysts in methanol and ethanol oxidation in an alkaline medium was noted in [2]. In [3-6], particles of metallic nickel were dispersed in conducting polymeric films when fabricating active catalysts for methanol oxidation. It is known that nickel favors an increase in catalytic activity when used as a substrate for double (Pt-Ru/Ni) [7] and triple (Pt-Ru-Ni/C) catalysts [8-11] and in the form of oxides [12].

It has been shown [13–16] that palladium catalysts exhibit a higher activity and stability in ethanol oxidation in alkaline solutions, compared with platinum catalysts. Use of such oxides as NiO, CeO₂, Co_3O_4 , and Mn_3O_4 as substrates for palladium catalysts improves their activity in reactions of ethanol oxidation. The improved activity is due to their increased resistance to poisoning by products of these reactions, introduced into the catalysts.

Palladium catalysts deposited on various substrates, as well as double and triple palladium-containing catalysts, exhibit a sufficient activity in methanol and ethanol oxidation in alkaline solutions [13–28]. Fabrication of palladium catalysts by electrochemical reduction of various complex compounds of palladium(II) on electrically conducting substrates has been comparatively rarely reported in the literature, although it has been shown [29] that this method has a number of advantages in the case of deposition of small controlled amounts of palladium.

The goal of our study was to obtain porous nickel deposits by procedures suggested in the literature and to electrochemically deposit catalytic layers of metallic palladium onto these substrates from solutions of glycinate-chloride complexes of palladium(II). The catalytic activity of the electrodes was evaluated by the rates of reduction of atmospheric oxygen and oxidation of alcohols (methanol and ethanol) in an alkaline aqueous solution.

EXPERIMENTAL

We used the following reagents: NiSO₄, CuSO₄, and NiCl₂ of analytically pure grade; NH₄Cl and NaCl of chemically pure grade; H₃BO₃ of analytically pure

grade; and KOH of chemically pure grade. The study was performed in a hermetically sealed three-electrode electrochemical cell with separated cathode and anode spaces. Prior to carrying out an experiment, we kept the cell in concentrated sulfuric acid and then washed it with twice-distilled water. All the solutions used in the study were prepared from twice-distilled water. A glassy graphite rotating disk electrode with an area of 0.07 cm^2 served as the cathode. A layer of porous nickel was formed on this electrode by the electrochemical methods described in [1, 30], and then palladium was deposited. A platinum wire sealed in a glass tube served as the auxiliary electrode. A calomel electrode in a saturated KCl solution (sat.c.e) was used as reference. All the potentials are given relative to this electrode. The study was carried out at a temperature of $18 \pm 2^{\circ}$ C in the atmosphere of argon.

The measuring setup comprised a PI-50-1.1 potentiostat, PR-8 programming unit, and X–Y recorder. The study was performed in various modes: galvanostatic, potentiostatic, and potentiodynamic at various potential sweep rates. The voltammetric curves recorded by the self-recorder were digitized with Windic program and processed with OriginPro software. Pulsed galvanostatic curves were recorded with a Grafit-2 electronic self-recorder.

Porous nickel was electrochemically deposited onto a glassy graphite disk electrode in two ways. By the method described in [1], nickel was deposited from a solution of composition 0.2 M NiCl₂ + 2 M NH₄Cl in the galvanostatic mode in the course of 100 s at a current density of 0.1 A cm⁻². The mass of the deposited nickel was about 3 mg cm⁻². Under these conditions, highly porous metallic matrices with large roughness factor and high mechanical strength are formed [1]. In what follows, we designate nickel produced by this method as Ni.

The procedure described in [30] was used to deposit a Ni–Cu alloy from a solution of composition 1 M NiSO₄ + 0.01 M CuSO₄ + 0.5 M H₃BO₃ in the potentiostatic mode at a potential E = -0.8 V by passing about 0.05 C cm⁻² of electricity. Further, copper was anodically etched-out in the same solution at a potential E = +0.5 V, and the amount of passed electricity was used to calculate the mass of dissolved copper. The Ni : Cu ratios in alloys obtained at different deposition potentials, reported in [30], were used to evaluate the composition of the alloy obtained upon etching-out of copper. This alloy contained approximately equal amounts (300 µg cm⁻²) of nickel and copper. In what follows, we designate the substrate produced by this method as Ni–Cu.

To characterize the roughness of nickel substrates, we estimated their capacitance, as it was done in [31]. For this purpose, we measured pulsed galvanostatic *E*,*t* curves. The height of galvanostatic pulses was varied in the range 1–15 μ A, and values of the derivative $(dE/dt)_{t=0}$ were determined from the initial portions of the *E*,*t* curves. Then, the capacitance *C* (F cm⁻²) was calculated by the equation

$$C = -\frac{I/S}{(dE/dt)_{t=0}},$$
(1)

where *I* is the current (A), and *S*, size of the visible electrode surface ($S = 0.07 \text{ cm}^2$).

The observed constancy of the electrode capacitance in the galvanostatic pulse range we used indicates that the values of the capacitance correspond to charging of the electric double layer and are not complicated by occurrence of Faraday processes. Large values fluctuating in the range 2–4 mF cm⁻² were obtained for the capacitance of nickel electrodes, which confirms that highly porous nickel substrates are obtained.

On porous Ni substrates, we measured cyclic voltammetric (CVA) curves in a 1 M KOH solution. Figure 1 shows voltammograms obtained on a nickel electrode at various potential sweep rates. The arrows show the directions of potential variation. It can be seen in Fig. 1 that the CVA curves show at positive potentials (>+0.4 V) peaks corresponding, according to [4], to the process of nickel recharging at the electrode, to which the following reaction may correspond:

$$Ni(OH)_2 + OH^- = NiOOH + H_2O + e.$$

The nickel recharging peaks obtained at various electrode rotation speeds (from 350 to 1490 rpm) were independent of the disk rotation speed. This means that the process of nickel recharging is not controlled by diffusion from solution. On plotting the dependence of the logarithm of the peak current, $\ln I_p$, on the logarithm of the potential sweep rate, $\ln v$, and that of the peak potential E_p on the logarithm of the potential sweep rate, $\ln v$, and that of the peak potential E_p on the logarithm of the potential sweep rate, $\ln v$, we found that $\ln I_p$ linearly depends on $\ln v$, with a slope ratio of approximately 0.6. There also exists a linear relationship between E_p and $\ln v$. This indicates that the process occurring at the electrode is irreversible.

Small controlled amounts of metallic palladium were deposited onto porous nickel substrates from a



Fig. 1. CVA curves obtained on a nickel electrode at various potential sweep rates. (*I*) Current and (*E*) potential; the same for Figs. 2–6. Potential sweep rate (V s⁻¹): (*I*) 0.05, (*2*) 0.02, and (*3*) 0.01; the same for Fig. 5.

solution containing 5×10^{-4} M of glycinate-chloride complexes of palladium(II), Pd(Hgly)₂Cl₂. As shown in [32], palladium is deposited from these solutions with a 100% current efficiency. Palladium was deposited onto a rotating electrode in the potentiodynamic mode, with the potential varied from +0.15 to -0.25 V at a potential sweep rate of 0.005 V s⁻¹. At different numbers of potential scanning cycles, we obtained electrodes with different contents of metallic palladium (from 6 to 390 µg cm⁻²).

On electrodes with various catalytic layers, we measured cyclic voltammograms in a 1 M KOH solution and studied the catalytic activity of these electrodes in reduction of atmospheric oxygen and oxidation of methanol and ethanol in an alkaline medium.

Prior to measuring cyclic voltammograms on all palladium electrodes, we preliminarily cleaned the surface of palladium by cycling the electrode potential for 20 min in the range from hydrogen evolution potentials to oxygen evolution potentials, as described in [29]. Then we measured CVA curves at various potential sweep rates (0.05, 0.02, and 0.01 V s⁻¹) in the range 0-1.3 V relative to a reversible hydrogen electrode in the same solution. The CVA curves measured on a palladium electrode in this range of potentials make it possible to evaluate the true palladium surface area by the quantity of electricity consumed for removal of a monolayer of atomic oxygen adsorbed on the palladium surface. This can be



Fig. 2. CVA curves obtained in a 1 M KOH solution. (1) Glassy graphite, (2) Ni–Cu, and (3) Pd/Ni–Cu.

done because, as shown in [33], a monolayer coverage of the palladium surface by adsorbed oxygen atoms is obtained at a potential of 1.3 V relative to the equilibrium hydrogen electrode in the solution under study. The method in which the true surface area of palladium is found from removal peaks of a monolayer of adsorbed oxygen atoms is frequently employed in studies performed on palladium electrodes [34, 35].

Figure 2 shows CVA curves obtained at a potential sweep rate of 0.05 V s⁻¹ on a glassy graphite electrode (curve *I*), glassy graphite electrode coated with porous nickel (Ni–Cu) (curve 2), and palladium electrode with a porous nickel substrate (Pd/Ni–Cu) at a palladium content of 216 μ g cm⁻² (curve 3). It can be seen that no electrochemical process occurs on the glassy graphite electrode in a wide range of potentials. On the Ni–Cu electrode, charging of the capacitance of the double electric layer on well developed surface is observed, and on the palladium Pd/Ni–Cu electrode, clearly pronounced peaks of adsorption–desorption of atomic hydrogen and oxygen appear at potentials in the range under study.

The adsorption–desorption peaks of hydrogen and oxygen become more pronounced with increasing content of palladium in a catalytic layer and on passing from the Pd/Ni–Cu electrode to Pd/Ni at the same content of palladium, which indicates that the active surface areas of palladium are different on these electrodes.

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Pd content, $\mu g \text{ cm}^{-2}$	<i>Q</i> ₀ , μC	<i>n</i> _{Pd}	$S_{\rm true},{\rm cm}^2$	D, %	K	d, μm
Pd/Ni–Cu electrode						
216	470	1.4×10^{15}	1.12	1.5	16	1.0
124	600	1.8×10^{15}	1.42	3.6	20	0.46
90	230	0.7×10^{15}	0.54	1.7	8	0.88
Pd/Ni electrode						
389	1900	5.9×10 ¹⁵	3.97	3.7	43	0.51
175	1080	3.2×10 ¹⁵	2.58	5.1	36	0.35
49	400	1.2×10^{15}	0.87	5.8	10	0.29
6	100	0.3×10 ¹⁵	0.24	9.8	3	0.13

Parameters characterizing the active surface area of catalytic palladium layers on various porous nickel substrates

For all of the palladium electrodes obtained, we determined from the area under the removal peak of a monolayer of adsorbed oxygen (shaded region in Fig. 2) in cyclic voltammograms measured in 1 M KOH at various potential sweep rates the quantity of electricity Q_0 consumed for removal of a monolayer of atomic oxygen adsorbed on the surface of palladium, number n_{Pd} of surface palladium atoms, true surface area S_{true} of palladium, roughness factor K of the electrode, variance D (%) of the size of palladium particles, and average size d of palladium particles in the catalytic layer. This was done as described in [29]. The table lists values of these parameters, found for the palladium electrodes under study.

It can be seen in the table that, as the content of palladium in a catalytic layer increases, the roughness coefficient of the palladium electrode markedly grows and the variance of the size of palladium particles slightly decreases. The largest variance (D = 9.8%) is observed for the electrode with the lowest content of palladium (6 µg cm⁻²). The average diameter of palladium particles in the catalytic layers varies from 0.1 to 1 µm, depending on the palladium content of the electrode and on a substrate. Finer palladium particles (d = 0.13 µm) were obtained on a porous Ni substrate at the lowest content of palladium (6 µg cm⁻²).

The reaction in which atmospheric oxygen is reduced on palladium catalytic layers was studied in a nondearated 1 M solution of KOH on a rotating electrode at various rotation speeds (from 730 to 3500 rpm). Voltammetric curves were measured with the potential varied from +0.10 to -0.60 V at a constant potential sweep rate (0.01 V s⁻¹).

Figure 3 shows voltammetric curves for reduction of molecular oxygen on Pd/Ni electrodes with various palladium contents at an electrode rotating speed of 1100 rpm. The same figure presents a similar curve obtained on a porous NI substrate (curve 1). It can be seen that the porous nickel electrode does not catalyze the reaction of reduction of molecular oxygen, whereas on Pd/Ni electrodes, oxygen reduction currents are observed at potentials in the range under study. The catalytic activity on Pd/Ni electrodes grows as the content of palladium increases and, simultaneously, so does the true surface area of palladium in the catalytic layer (see table).

The reduction currents of molecular oxygen on Pd/ Ni electrodes increase with the rotation speed of the disk electrode, and the corresponding dependences of the reduction currents on the disk rotation speed are linear in the Levich–Koutecky coordinates, which indicates that the process under study occurs under diffusion-kinetic control [29].

We studied the catalytic activity of the palladium catalysts we obtained in the reactions of methanol and ethanol oxidation in an alkaline medium. We measured CVA curves in a 1 M KOH solution with addition of 1 M of methanol or ethanol at different potential sweep rates (0.05, 0.02, and 0.01 V s⁻¹) in a wide range of variation of the potential on the glassy graphite electrode, porous nickel Ni–Cu and NI substrates, and also on Pd/Ni–Cu and Pd/Ni palladium electrodes. No

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Fig. 3. Voltammetric curves for reduction of atmospheric oxygen on Pd/Ni electrodes with various palladium contents. Palladium content ($\mu g \text{ cm}^{-2}$): (1) 0, (2) 6, (3) 49, (4) 175, and (5) 389.



Fig. 5. CVA curves for oxidation of ethanol on a Pd/Ni electrode at various potential sweep rates. Solution composition: $1 \text{ M KOH} + 1 \text{ M C}_2\text{H}_5\text{OH}$; palladium content 49 µg cm⁻²).

oxidation of methanol in the alkaline solution was observed on the glassy graphite electrode and porous nickel substrates in the whole potential range under study. The Ni–Cu and Ni electrodes catalyze the process of ethanol oxidation in the alkaline medium at high positive potentials (>+0.5 V).

Figure 4 shows that, in ethanol oxidation on a nickel substrate in an alkaline medium, there occurs superposition of two processes: oxidation of ethanol and recharging of nickel. It can be seen that the



Fig. 4. CVA curves obtained on a nickel electrode in solutions of different compositions. Potential sweep rate 0.05 V s^{-1} . (1) 1 M KOH and (2) 1 M KOH + 1 M C₂H₅OH.



Fig. 6. CVA curves obtained on Pd/Ni electrodes at a potential sweep rate of 0.05 V s⁻¹. Palladium content (μ g cm⁻²): (1) 44 and (2) 49. Solution composition: (1) 1 M KOH + 1 M CH₃OH and (2) 1 M KOH + 1 M C₂H₅OH.

process of ethanol oxidation occurs on the oxidized surface of nickel, in agreement with the data of [3, 4, 6]. In a reverse (cathodic) potential sweep, the voltammetric curve obtained in a solution with addition of ethanol shows a cathodic peak of nickel recharging.

In an alkaline solution with addition of ethanol, we measured CVA curves on a Ni electrode at various potential sweep rates. It was noted that the currents of ethanol oxidation peaks grow with increasing potential sweep rate, with the potentials of forward sweep peaks shifted to positive values. This is indicative of the irreversible course of the oxidation process. Voltammetric curves measured at various rotation speeds of the disk electrode demonstrated that the currents of the ethanol oxidation peaks are independent of the rotation speed and, consequently, the process of ethanol oxidation on the nickel electrode is not controlled by the diffusion from solution.

A catalytic process of methanol and ethanol oxidation in an alkaline solution was observed on all of the palladium electrodes we obtained. Comparison of the data in Figs. 4 and 5 demonstrates that catalytic oxidation of ethanol on palladium layers occurs at substantially more negative potentials, compared with the process on porous nickel substrates under the same conditions. Figure 5 shows CVA curves for ethanol oxidation, measured at different potential sweep rates on the Pd/Ni electrode. It can be seen that the curves obtained in an alkaline ethanolic solution on the palladium electrode exhibit a single peak of ethanol oxidation in a forward (anodic) potential sweep (peak at potentials of about -0.20 V) and a single peak of ethanol oxidation in a reverse (cathodic) potential sweep (peak at potentials of about -0.40 V). The currents of the peaks increase with the potential sweep rate, and the potentials of the peaks observed in a reverse (cathodic) potential sweep are more negative than those obtained in an anodic potential sweep. Similar voltammetric curves for ethanol oxidation in alkaline solutions on palladium catalysts supported by various substrates were reported, e.g., in [21, 26, 29].

The results we obtained can be explained as follows. The process of ethanol oxidation occurs in several stages to give several intermediate products. Ethanol is oxidized in alkaline solutions on a palladium electrode [37] via dissociative adsorption of ethanol at low potentials (the peak in the anodic potential sweep), which yields species of the intermediate oxidation product, acetaldehyde, strongly adsorbed on palladium. In the reverse (cathodic) potential sweep, the intermediate products of ethanol oxidation are converted into the final product, acetate ions.

The height of the peaks of ethanol and methanol oxidation depends on the content of palladium in the catalytic layer: as this content increases, the peaks become higher. The oxidation currents are also affected by the porous nickel substrate. The currents of ethanol and methanol oxidation on Pd/Ni electrodes exceed those on Pd/Ni–Cu electrodes at the same

content of palladium. On palladium electrodes with the same nickel substrates and close contents of palladium in the catalytic layer, the currents of methanol and ethanol oxidation are markedly different. The catalytic activity of palladium in oxidation of methanol in an alkaline medium substantially exceeds its catalytic activity in oxidation of methanol, as it can be seen in Fig. 6. Thus, catalytic layers produced by electrochemical deposition of palladium onto a porous nickel substrate can be recommended for use as catalysts for ethanol oxidation in an alkaline medium.

CONCLUSIONS

(1) Various methods for obtaining porous nickel deposits with large roughness coefficients were developed.

(2) It was shown that palladium with particle sizes of 0.1 to 1.0 μ m is formed in electrodeposition of metallic palladium onto porous nickel substrates from solutions of glycinate-chloride complexes of palladium(II).

(3) The catalytic activity of palladium electrodes in the reaction of reduction of molecular oxygen was determined.

(4) It was demonstrated that catalytic layers produced by electrochemical deposition of palladium onto porous nickel substrates can be recommended as catalysts for ethanol oxidation in an alkaline medium. They can be used as anode catalysts for direct ethanol fuel cells.

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