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ADATOMS INFLUENCE ON OVERVOLTAGE OF HYDROGEN

By

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Abstract

It has been shown that the treatment of electrodes with the surface skeleton catalyst with the solutions of nitrates of heavy metals caused the considerable decrease overvoltage of hydrogen evolution. It has been found that during the treatment the adsorption of heavy metals on the surface and the electroreduction of nitrate-ions occured. The mechanism of activation due to the decrease of the binding energy of the hydrogen atoms with the surface in the presence of heavy metals has been offered.

Recently much attention has been paid to the study of influence of adatoms of various metals on activity and properties of catalysts of chemical and electrochemical reactions.[1~9,13] Thus in the works of D. V. Sokolskii and G. D. Zakumbaeva the influence of adsorption of different ions on the velocity of heterogeneous reactions was shown.[1] Despic and his collaborator got considerable catalyst effect on electrooxidation of formic acid on platinum and rhodium in the presence of adatoms Pb, Bi, and Cd.[2] There are data on the influence of cations Zn^{2+}, Cd^{2+}, Tl^{+} on the electroreduction of carbon dioxide and organic compounds,[4] and adatoms of silver, tin, bismuth and thallium on the electrooxydation of methanol and formic acid.[5,7]

The works[1,6~9] show that the adsorption of adatoms on electrode considerably influence the hydrogen adsorption. This paper presents the results of the study of the influence of adatoms of cadmium, lead, mercury, bismuth and tallium on the adsorption of hydrogen and on the electrocatalyst properties of nickel. Unlike most of the works[1~9] in which cations were introduced in working solutions, in our laboratory we treated electrodes by immersion in salt solutions before studying its catalyst activity.

Electrocatalyst was prepared by leaching of the surface alloy Ni-Zn formed by electrodeposition zinc on nickel foil followed by heat treatment.[10,11]

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Electrodes before adsorption had the roughness factor of 6440. The roughness factor of Pt/Pt electrode used for comparison equaled 6000.

The electrocatalyst cleaned from alkali was treated by immersion in salt solutions of different concentration $3 \cdot 10^{-4} - 1$ M for certain time. In the process of treatment, solution pH changes and changes of electrode potential referred to silver chloride electrode were observed. After treatment the electrode was thoroughly cleaned from salt solution. The activity of electrocatalysts was estimated by making up of cathode $\varphi/\log i$ curves of the hydrogen evolution in 6 M KOH under the temperature of 25°C. The adsorption capacity with respect to hydrogen was estimated by a potentiodynamic method. The sweep rate was 2 mV/s. Before making up the potentiodynamic curves electrochemical treatment[14] was given to the samples. The electrode for comparison was a murcury oxide electrode in 6 M alkali solution. Potentials were re-estimated by the scale of the hydrogen electrode (φ_r) in the same solution. The alkali of high purity type was used. The amount of metal adsorbed on the surface of skeleton electrocatalyst was established by spectral analysis. As follows from Fig. 1, the treatment of electrodes with the surface skeleton catalyst by the solutions of nitrates of cadmium, thallium, lead, murcury and bismuth causes the decrease of overvoltage of hydrogen evolution. The greatest effect of overvoltage decrease is observed as the result of treatment by salts of cadmium and thallium. In addition to it the slopes of $\varphi/\log i$ curves of the evolution of hydrogen on the treated electrodes were than on untreated ones. Thus in case with cadmium adatoms Tafel coefficient decreases from 0.06 to 0.027 V. The similar shape of curves ($b=0.03$) is obtained

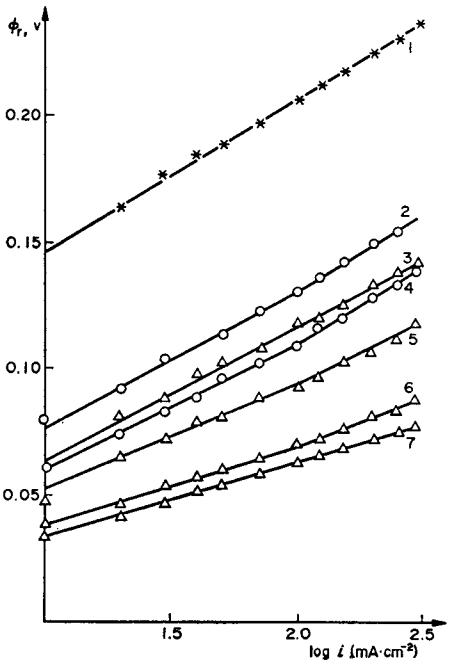

Fig. 1. Plots of $\varphi/\log i$ for the cathode evolution of hydrogen under the temperature of 25°C in 6 M KOH on the surface of skeleton nickel without treatment (1) and treated by solutions.

$Bi(NO_3)_3$-(2): $Pb(NO_3)_2$-(3):
$Hg(NO_3)_2$-(4): $TlNO_3$-(5):
$Cd(NO_3)_2$-(6): Pt/Pt-(7).

for Pt/Pt electrode (curve 7).

The electrocatalytic activity of the electrode depends on the concentration of the solution in which it was treated and on the time of treatment. The catalyst electrode reaches its constant activity after treatment in concentrated solutions during 30-40 minutes (Fig. 2). After electrode treatment by the solutions of heavy metals nitrates, its potential becomes more positive, besides the increase of pH of solutions of nitrates is observed (Fig. 3). There is a correlation between the electrode potential change in the process of treatment and the subsequent change of its electrocatalitic activity: the

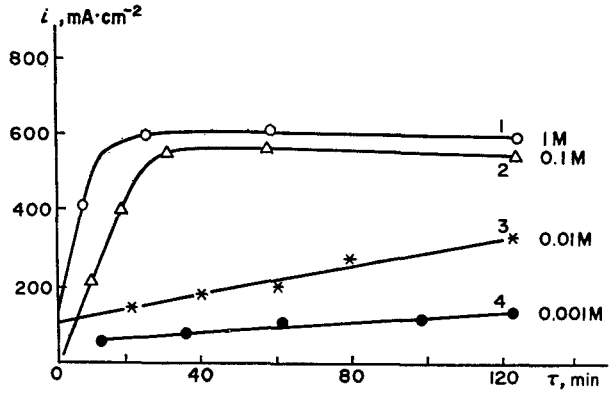

Fig. 2. Dependence of the rate of the cathode evolution of hydrogen under $\varphi_r = -0.15$ V and 25°C on the time of treatment of electrode in solution $Cd(NO_3)_2$.

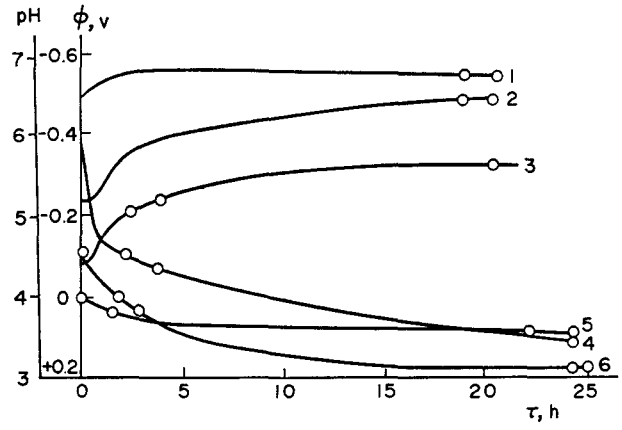

Fig. 3. The change of pH of solutions of nitrate of cadmium 0.01 M (1), 0.1 M (2), 1 M (3) and of electrode potential in the same solutions 0.01 (4), 0.114 (5), 1 M (6) in respect to the time of treatment.

greater the potential change the greater is its activity change.

In the process of treatment by solutions of nitrates adsorption process may take place on the surface of nickel. Spectral analysis found the presence of heavy metals on the surface of nickel catalyst. For example: depending on the conditions of treatment the cadmium content changed from 0.1 to 15 wt. %, and of lead — from 0.25 to 6.2 wt.%. Assuming a monolayer adsorption the corresponding coverage of the surface will make up 0.0013–0.19 of monolayer for Cd adatoms and 0.0017–0.043 of monolayer for lead.

Fig. 4 shows the dependence of Ni electrode activity on the coverage by cadmium. As is seen, the previously observed almost directly-proportional dependence has a weakening character under high degrees of coverage.

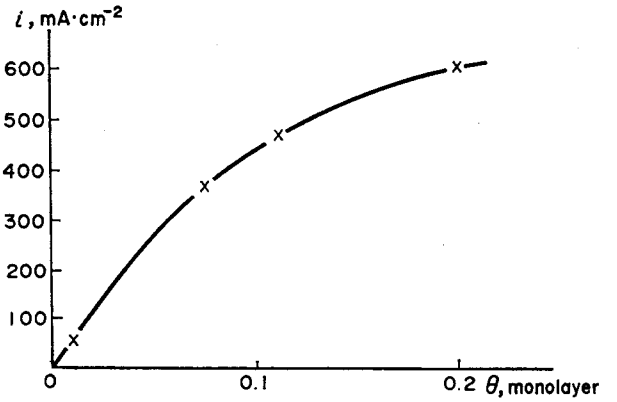

Fig. 4. Dependence of the rate of the reaction of cathode evolution of hydrogen on the coverage of the Ni electrode by cadmium ($\varphi_r = -0.15$ V; 25°C).

As is seen from potentiodynamic curves (Fig. 5), after treatment of electrocatalyst by adatoms of cadmium the decrease of the peak current and the displacement of maximum current to the region of electronegative potentials take place, pointing to the decrease of the adsorption capacity of hydrogen on the nickel surface and to the change of energy state of adsorbed hydrogen.

Besides, the amount of weakly bound hydrogen remains practically constant. The decrease of the amount of strongly bound hydrogen is really observed.

The more visible decrease of the surface hydrogen amount is observed under small degree of the surface coverage by adatoms (Fig. 6). While the activity increases almost proportionally to the degree of coverage (Fig. 4).

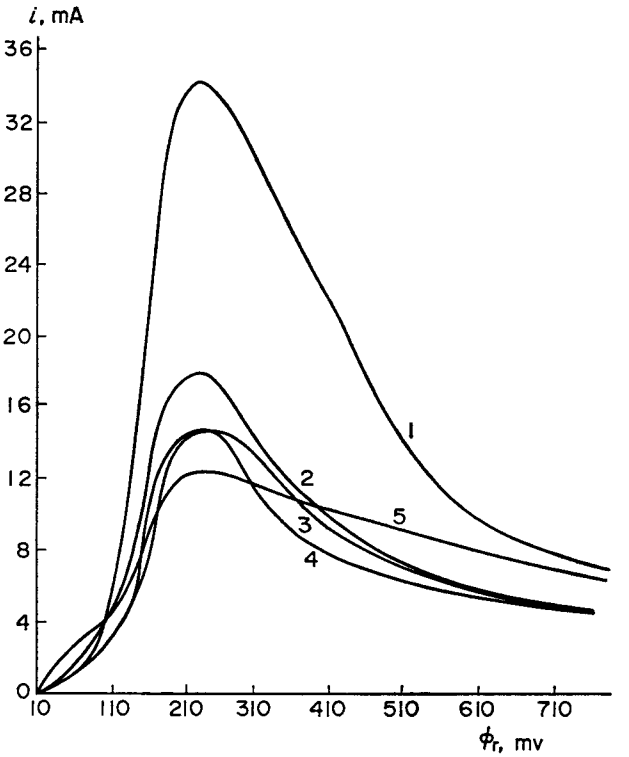

Fig. 5. Potentiodynamic curves of Ni-surface skeleton electrode (1) and modified by cadmium: 2–0.000127 monol. Cd; 3–0.077 monol. Cd; 4–0.112 monol. Cd; 5–0.19 monol. Cd.

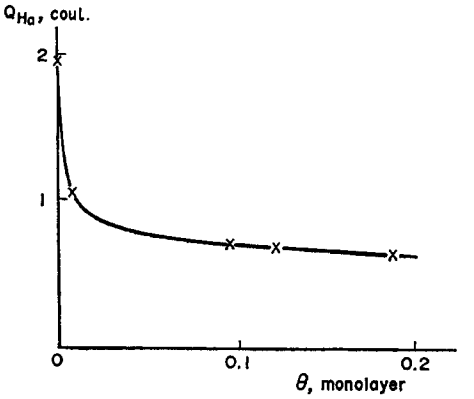

Fig. 6. Dependence of the hydrogen amount in catalyst on the coverage of cadmium adatoms.

The same result is obtained in case with electrocatalyst treated by salt of other heavy metals.

Thus when electrode is treated by salt solutions the adsorption of heavy metals take place. They can be adsorbed in the form of an ion or an atom and the displacement or oxidation of hydrogen atoms may take place. Heavy metals adsorption is one of the reasons for the electrode potential displacement in the region of positive side. Increase of solution pH can be stipulated by electroreduction of nitrate-ions[15] according to the scheme:

$$H_{ads}+H^{+}+NO_3^{-}\rightarrow NO_2+H_2O$$

$$2H_{ads}+H^{+}+NO_3^{-}\rightarrow HNO_2+H_2O$$

The electroreduction of nitrate-ions also leads to the electrode potential displacement toward positive side. These reactions to a certain degree influence the catalyst activity of the electrode. The increase of the latter under the influence of adatoms can be explained by specific state of adatoms on the surface of nickel. The electronic structure and the corresponding properties of adatoms differ from the electronic structure of heavy metals in metallic as well as in atomic condition. Between adatoms and nickel a chemical binding may appear. This influences the binding energy of adsorption particles in particular, as we see, the binding energy of adsorbed hydrogen.

It is possible to assume that the adsorption of adatoms of lead and cadmium followed by hydrogen displacement takes place first of all in the centers, characterized by the most strongly bound form of hydrogen, and the centers don't play the main role in the reaction of hydrogen evolution. Further adsorption of adatoms is followed by displacement of less strongly bound hydrogen and favours creation of new catalytically active centers, having the optimal binding energy of hydrogen with the surface of a metal and thus causes a noticeable growth of activity. As confirmation to the assumption of the creation of new catalyst active centres may serve the dependence of the rate of the cathodic evolution of hydrogen on the extent of all atoms coverage of the surface.

Thus it is possible to assume that after adsorption of atoms of heavy metals, having high overvoltage of hydrogen evolution, the binding energy of the hydrogen atoms with the surface of a catalyst may decrease and correspondingly the rate of reaction will increase on the catalyst for which the slow stage of the process of evolution of hydrogen is the removal of the latter from the surface.

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