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Author(s)	KOROVIN, N. V.; ULKO, N. G.; KONSTANTINOVA, G. S. et al.
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HYDROGEN SORPTION BY PALLADIUM BLACK AND PALLADIUM OSMIUM CATALYSTS DURING ELECTROOXIDATION OF HYDRAZINE

By

N. V. KOROVIN,*) N. G. ULKO,*) G. S. KONSTANTINOVA*) and B. N. JANCHUK*)

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Abstract

By taking the charging curves after hydrazine electro-oxidation (followed by repeated rinses) on palladium black and palladium osmium catalysts, it has been established that in hydrazine electro-oxidation these catalysts sorb hydrogen.

The quantity of hydrogen sorbed can increase with anodic polarization. Hydrogen is found to be present in the catalysts after hydrazine electro-oxidation at high positive potentials (up to 1.0 v on the RHE scale in the same solution).

Hydrogen is known to be sorbed by palladium during the cathodic polarization[1~3] or during the dehydrogenation of an organic compound.[4] This is usually oxidized and removed from the palladium at anodic potentials below 0.3 v[5] on the RHE scale in the same solution.

It was shown[6,7] that hydrogen can also be sorbed by palladium in the course of anodic oxidation of hydrazine. In the case of hydrazine electro-oxidation in an alkaline solution on one side (contact side) of a palladium membrane, it was stated that the potential of the other side (diffusion side) shifts towards negative values. Further, the charging curves taken of the membrane after conducting the hydrazine electrooxidation (followed by repeated rinses) have shown that the palladium contains hydrogen whose quantity increases with increase in the anodic polarization of the hydrazine electro-oxidation. Similarly, in case of anodic polarization of both sides of the membrane, the contact side in an alkaline solution containing hydrazine and the diffusion side in the background alkaline solution, the current value on the diffusion side increases with increase in the anodic polarization of the contact side.

It was assumed previously[6,7] that the hydrogen sorbed by palladium is

*) Moscow Power Institute, Moscow, USSR.

the intermediate product of the hydrazine electrooxidation which may be expressed as

$$N_2H_4\,(ads) + n\,OH^- \longrightarrow N_2(ads) + n\,H_2O + (4-n)\,H\,(ads) + ne^- \qquad (1)$$

Reaction (1) would be the summary of a series of elementary steps and hence involves several intermediates *e.g.*, radicals such as N_2H_3, N_2H_2 and N_2H which eventually decompose into nitrogen and hydrogen. The hydrogen thus adsorbed on palladium is anodically oxidized on the contact side and also penetrates into and diffuses through the membrane and then is oxidized at the diffusion side.

Hydrogen sorption during hydrazine electrooxidation on palladium, palladium coated with palladium black and palladium-osmium was investigated in the present work.

Method of Investigation

The palladium black electrodes were prepared as follows; palladium was deposited onto a smooth palladium from an 1% palladium chloride solution in 1M hydrochloric acid with the current density of 10 ma/cm^2, at 18–20°C. The palladization continued for 2 hours to obtain a sufficiently thick palladium laver so that the influence of the base metal should be minimized. The real surface area of the electrodes was 10^4 cm. Palladium-osmium electrodes were prepared by first palladizing a platinum plate for 2 hours and, after repeated rinses with redistilled water, cathodizing in an osmium complex salt solution; a platinum wire served as the anode. Osmium was deposited for 3–4 minutes with the current density of 0.5 ma/cm^2.

Hydrogen sorption during the hydrazine electrooxidation was studied by the method of the charging curves which were taken after contact of the electrode with hydrazine or after hydrazine electrooxidation followed by repeated rinses of the cell and the electrode. The hydrazine electrooxidation was carried out at a constant potential which was maintained by means of a potentiostat. The charging curves were taken by means of a potentiometric recorder.

Prior to every experiment the electrodes (except the palladium-osmium electrode, see later) were anodically treated in the following way: the cell was filled with 1M KOH solution and the working electrode was polarized at +1.5 v for 10 min by means of a potentiostat, in order to oxidize impurities and admixtures which may happen to be adsorbed on the electrode surface. Oxides may be formed during the anodic treatment but these are easily reduced with the subsequent introduction of hydrazine. Thus after the anodic

treatment (and after the alkaline solution was substituted by the hydrazine solution) the electrode surface is considered clean and indeed possessed of an increased catalytic activity.

Only palladium and palladium black electrodes were anodically treated. Analogous treatment of palladium-osmium electrodes was not possible because of dissolution of osmium which commenced at potentials more positive than 0.9 v.

All the experiments were carried out in alkaline medium. The alkaline solution was prepared from recrystallized c.p. grade KOH and redistilled water. Hydrazine solution was prepared just before the experiment. An amount of c.p. grade hydrazine hydrate solution was dis-solved in 100 mℓ of 1M KOH to make 1M hydrazine solution. The solution was carefully stirred and introduced into the cell immediately after the anodic treatment.

Experimental Results

Previous investigations[6,7] have shown that potential of a smooth palladium electrode in a hydrazine solution is close to that of the reversible hydrogen electrode. However, we failed to detect hydrogen in bulk of the palladium after its contact with hydrazine. Analogous experiments on palladium black electrode are of interest since its capacity for hydrogen sorption would be much higher than that of smooth metal.

Introduction of hydrazine to the palladium black electrode following an anodic treatment causes a sharp shift in the potential towards negative values (the potential shift occurs within fractions of a second, Fig. 1 curve 1). Stationary hydrazine potential (the rest potential) on palladium black electrode is more negative than that on smooth palladium under the same condition. However, reversible hydrogen potential value is not reached in both cases.

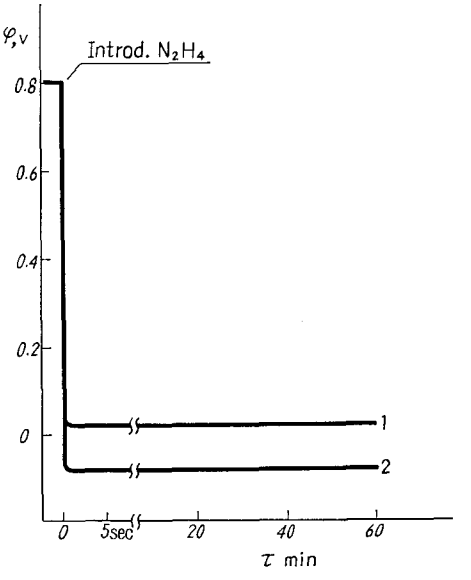

Fig. 1. Potential shift with hydrazine introduction onto the electrode surface.

1) Palladium black electrode
2) Palladium-osmium electrode

The charging curves taken of the

smooth palladium after it is brought into contact with hydrazine solution have not shown a formation of firmly sorbed particles (hydrogen) which also did not take place by simply keeping the palladium black electrode in a hydrazine solution at the rest potential. Thus, hydrogen does not penetrate into the bulk of palladium at the rest potential; probably only a weak physical adsorption of hydrogen takes place in this case. In contrast with this, the charging curves taken on palladium black electrode after hydrazine electrooxidation (followed by repeated rinses of the cell and the electrode) had the shapes analogous to those taken after saturating the palladium with hydrogen (not shown). In Fig. 2 (curve 1) the quantity of particles sorbed by palladium black electrode during the hydrazine electrooxidation is given against the potential of the anodization.

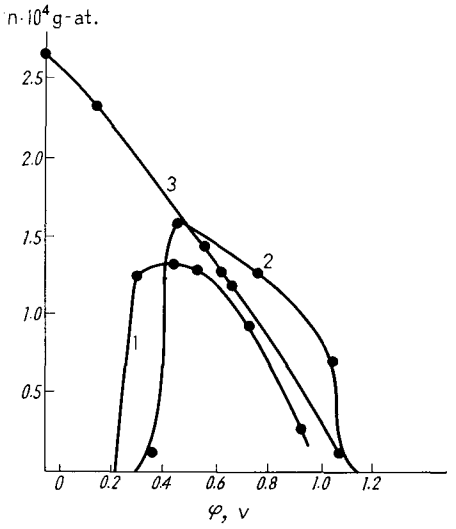

Fig. 2. Quantity of sorbed hydrogen versus potential of hydrazine electrooxidation.
1) On palladium black electrode
3) On palladium-osmium electrode
2) On smooth palladium electrode

However, it has been established[7] that smooth palladium sorbs just hydrogen as the charging curves has taken on diffusion side of a palladium membrane, when another particle absence exupt hydrogen.

An analogous curve for smooth palladium is also given in Fig. 2 for comparison (Curve 2, obtained in 0.3 M N_2H_4 solution). The two curves are analogous in shape and only slightly shifted from each other. Thus, one may conclude the hydrazine electrooxidation to be accompanied by hydrogen sorption.

The increase in the amount of hydrogen sorbed in palladium with increasing polarization of the hydrazine electrooxidation should be due to increased rate of reaction (1). At more positive potentials, however, the hydrogen content decreases than that at the maximum as stated by JANCHUK and KOROVIN[8]. This is mainly due to oxygen or OH radical sorption on the palladium and, owing to this, the hydrazine electrooxidation now follows another mechanism:

$$OH^- \rightleftharpoons OH\,(ads) + e^- \qquad (2)$$

$$OH\,(ads) + N_2H_4 \longrightarrow N_2 + 4\,H_2O \qquad (3)$$

Thus, in this case the hydrazine electrooxidation is not accompanied by hydrogen sorption.

Introduction of osmium in small amounts changes the behaviour of the palladium black. The charging curve obtained with the palladium-osmium electrodes (Fig. 3 curve 2) was analogous in shape to those obtained with palladium black electrodes (Fig. 3, curve 1), indicating that the former electrodes

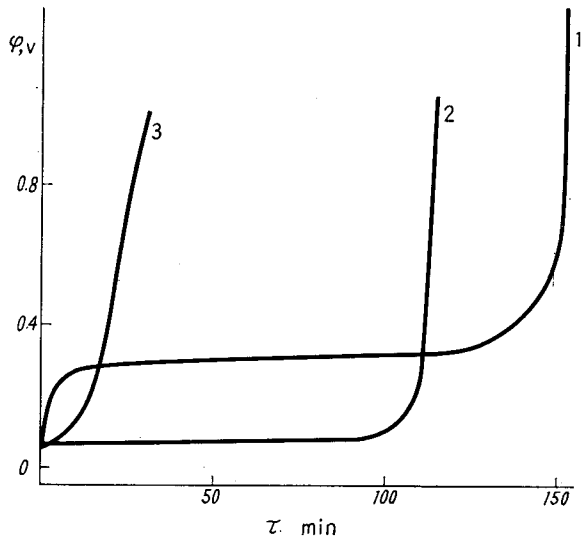

Fig. 3. Charging curves.
1) On palladium black electrode
2) On palladium-osmium electrode
3) On osmium electrode

are only partially covered with osmium. It was however found that the flat portion A on the charging curve decreases, or even disappears completely (curve 3), with increasing osmium deposition. Further, as seen from Fig. 1 (curve 2), the rest potential of the palladium-osmium electrode in a hydrazine solution is 60 mv more negative than RHE potential.

When a stationary rest potential is established after a long-time exposure of the electrode to the hydrazine solution (Fig. 4) the sorbed particles were found on the surface and/or in the bulk of the electrode. The charging curves, one taken after keeping the palladium-osmium electrode in an alkaline hydrazine solution at the rest potential ($\varphi = -60$ mv, curve 1) and the other at the same potential for the same duration in a pure alkaline solution (curve 2, were very similar in shape and their comparison indicated that the quantities of the substance sorbed in both the solutions are very close to each

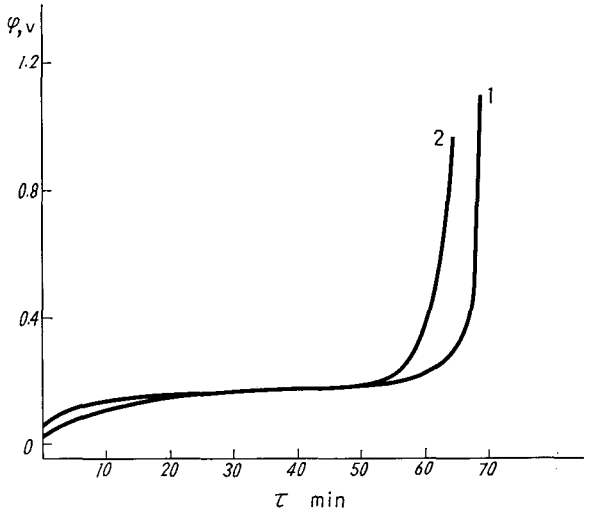

Fig. 4. Charging curves of palladium-osmium electrode.
1) After standing in 1M N_2H_4+1M KOH at a rest potential
2) After exposure in 1M KOH at the same potential as 1)

other. A similar comparison was also possible between charging curve of the palladium-osmium electrode after hydrazine electrooxidation and that after cathodic saturation with hydrogen in the pure alkaline solution. These facts clearly demonstrate that the substance sorbed by the electrode in a hydrazine solution are hydrogen. Figure 4 also indicates that hydrogen is removed at the same potential, *i.e.*, energies of the bond between hydrogen and the electrode surface in both cases are practically equal.

Such a similarity of curves shows, in our opinion, that hydrogen adsorbed in the bulk of the palladium-osmium electrode in case of its contact with hydrazine is formed not at the expense of hydrazine dehydration but at the expense of water molecules which discharge just as in the background solution

$$H_2O + e^- \longrightarrow H\,(ads) + OH^- \qquad (4)$$

Thus, hydrogen may be adsorbed on the palladium-osmium electrode both by reactions (1) and (4). Here, the rate of reaction (4) and the quantity of hydrogen sorbed must decrease with the increase of anodic polarization; as experiments have shown hydrogen sorption by reaction (4) in the background solution is possible only at potential below +0.15 v. However, in the case of the hydrazine electrooxidation on palladium-osmium catalysts, hydrogen is sorbed at potentials up to 1.0 v (Fig. 2, curve 3). Hence, hydrogen generated

at more anodic potentials may be formed through the hydrazine electro-oxidation.

The decrease in the amount of hydrogen adsorbed in the bulk of the catalyst with further increase in the anodic polarization of hydrazine electro-oxidation may be due to both the decrease in the rate of reaction (4) and oxygen deposition on the metal, which causes hydrazine oxidation by reactions (2) and (3). Oxygen deposition on osmium is known to begin at more negative potentials than on palladium and platinum.

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