

## ACTIVITY OF PALLADIUM ELECTRODE IN ALKALINE MEDIUM

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Palladium, and palladium containing electrodes of fuel cells may be regenerated by electrochemical oxidation and reduction. We found that the charge produced by the Pd-electrode during its catalytic activity is dependent on the initial hydrogen content in palladium. The value of this charge passes through a maximum. The following interpretation of the mentioned dependence is proposed: *I.* Increase in the active area of the electrode by *I.* subsequent reduction of oxides which are reduced only with difficulty, and *2.* the passage of hydrogen through the superficial layers of Pd. *II.* By change of the reaction mechanism on the Pd-electrode with optimum content of hydrogen. However, if the amount of hydrogen is increased to a value enabling the formation of  $\beta$ -phase of Pd, the drop in catalytic activity of Pd occurs again.

During the investigations of the time dependence of the activity of palladium anode in a fuel cell and the methods of a suitable regeneration of the electrode, we found that the time during which the electrode behaves as a catalytically active electrode is dependent on the content of hydrogen in palladium. The process of deactivation was followed in the system Pd-9M-KOH-1M-HCOOH. The viewpoints of various authors on the explanation of the causes of the deactivation of the catalytic electrode may be divided into two groups.

The first is based on the assumption that the pure surface of the electrode forms catalytically active atoms, and that deactivation is caused by adsorbed particles which block the active sites. These particles may be impurities from the solution, intermediates of dehydrogenation or anodic oxidation in the main reaction path, or the products of side reactions. From this conception the determination of the roughness factor of the surface follows logically, which determines the true area of the electrode from the amount of the adsorbed hydrogen. It is supposed that all atoms on the free surface are active. The activation of the electrode (for example by alternating oxidation and reduction) denudes the active sites. The blocking particles are either oxidised or they undergo desorption. During the activation the surface area of the electrode usually increases<sup>1-3</sup>. The second group of authors<sup>4,5</sup> base their considerations on the point of view that the active sites on the electrode have first to be created by the reduction of the palladium metal. These sites have a higher energy level and they disappear gradually by recrystallisation or re-orientation, or also by the blocking of active sites by strongly adsorbed particles<sup>5</sup>. In the case of palladium when hydrogen enters the electrode and then leaves it again the formation of pores and cracks takes place. Additional active sites can be formed on the damaged crystals of the electrode material<sup>6-9</sup>.

However, the final loss of the electrode activity is caused by its covering by non-stoichiometrical oxides or  $\text{OH}^{\cdot}$  radicals after a sufficiently positive potential has been attained<sup>1,10,11</sup>. The adsorption of the blocking particles leads to an anodic shift of the potential if a constant current passes through the electrode. And here it was found that the time during which the electrode potential attains a value at which its final deactivation takes place, is dependent on the initial hydrogen content in the palladium. The fact that the presence of hydrogen in the electrode has an effect on the course of electrochemical reactions has already been observed by a number of authors<sup>4,12-14,15</sup>, but from other points of view.

### EXPERIMENTAL

*Electrodes.* All measurements were carried out with a single palladium electrode of  $5.0 \times 0.3 \times 0.02$  cm size, sealed in a polyethylene bag 4.8 cm long, *i.e.* its uncovered active part was  $0.2 - 0.3$  cm. The corners of this part were rounded and the edges were also round. Its area was  $0.1 \text{ cm}^2$ . The electrode was palladium coated in acidified palladium(II)chloride solution for 3 minutes at a current intensity of 50 mA. The determination of the roughness factor of the surface on the basis of the quantity of the hydrogen adsorbed (as in the case of Pt electrodes) is not possible because hydrogen is soluble in palladium. However, for the sake of completeness the values of charges corresponding to hydrogen oxidation are given. These values were obtained on integration of the current peak of hydrogen oxidation during periodical potentiodynamic measurement in the potential range  $+150 \text{ mV} - +1200 \text{ mV}$  and at a linear potential sweep at a rate of  $3.7 \text{ mV s}^{-1}$  (Fig. 1). 1. freshly prepared electrode (after 2 days)\* 24.0 mC; 2. electrode was used for measurement for one month 2.6 mC; 3. for 3 months 2.2 mC; 4. for 5 months 2.0 mC; 5. for 12 months 1.6 mC.

The reference electrode was a dynamic hydrogen electrode. The blackened platinum cathode area was  $20 \text{ cm}^2$  and the current was 0.4 mA. It was located in its own vessel with Pt anode and connected by means of an electrolytic bridge and Luggin capillary with a measuring system. It was filled with a 9M-KOH solution; all measured values are referred to the hydrogen electrode in the same basic solution. The current of the reference electrode was always connected for at least one hour before the measurement proper. The auxiliary electrodes were made of platinum metal sheet of an area from 20 to  $100 \text{ cm}^2$ .

*Metallization and electrolytic baths.* Platinum bath: 3 g of  $\text{H}_2\text{PtCl}_6$  in 100 ml of 1M-HCl, temperature approx.  $25^\circ\text{C}$ , current  $25 \text{ mA cm}^{-2}$ . Palladium bath: 3 g  $\text{PdCl}_2$  in 100 ml of 1N- $\text{H}_2\text{SO}_4$ , temperature approx.  $25^\circ\text{C}$ , current  $50 \text{ mA cm}^{-2}$ . *Vessels.* For measurements of the fundamental solution alone a glass vessel was used. Chronopotentiometric measurements were carried out in polyethylene vessels and potentiodynamic measurements in a teflon vessel. All vessels were adjusted for a three-electrode system. Anodes and cathodes were located in partly separated compartments provided with independent gas bubbling.

Oxygen was eliminated from the solutions by bubbling argon through them. The argon used contained 9 to 18 p.p.m. of oxygen. All solutions were prepared with redistilled water. During the second distillation potassium permanganate and KOH were added.

Potassium hydroxide for the preparation of solutions was of a special brand. It was an intermediary product from that production phase (Spolek pro chemickou a hutní výrobu) preceding

\* Before the first measurement the electrode was kept in redistilled water for 48 hours. Completely fresh electrode changes too rapidly and the results of measurements are not reliable.

the adjustment of the solution before granulation. We found that when common KOH a.g. is used, a small current peak appears in the double-layer region. Formic acid a.g. was dosed slowly (getting warm) into measuring cells and correction was done for the decrease of KOH. All measurements were carried out in 9M-KOH or 9M-KOH + 1M-HCO<sub>2</sub>K at 20 ± 2°C.

Polyethylene used for the construction of the electrodes and vessels was checked in the following manner: No difference was observed in potentiometric curves obtained with the special KOH solution, and the same basic solution (100 ml) in which a piece of polyethylene (1 g) was boiled and then allowed to stand for 24 hours. The measurement was carried out in a glass vessel with Pt electrode sealed in glass.

**Apparatus and connection.** Galvanostatic measurements were carried out in the usual manner, according to the scheme in Fig. 2a. The output was recorded with a Regula recorder preceded by a transistor amplifier of our own construction. The parasitic current at the input of the amplifier was 0.5 ± 0.3 μA.

During potentiometric measurements (Fig. 2b) a transistor potentiostat of our own construction was utilised. The parasitic current in the circuit of the reference electrode was maximum 1 μA; maximum attainable current and potential values were 100 mA and 10 V. The courses of the curves were recorded by a X,Y-recorder BAK II Aritma.

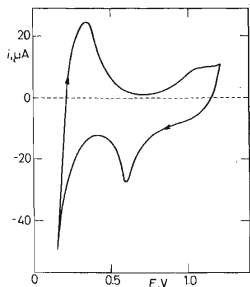


FIG. 1

Potentiodynamic Curve of the Stabilised Pd Electrode

9M-KOH, 20 ± 2°C,  $\Delta E/\Delta t = 3.7 \text{ mV s}^{-1}$ ; from +150 mV to +1200 mV and back.

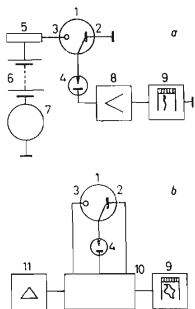


FIG. 2

Scheme of Circuits: a) for galvanostatic measurements, b) for potentiodynamic measurements

1 vessel; 2 working electrode; 3 auxiliary electrode; 4 reference electrode (dynamic hydrogen electrode); 5 resistance determining the current; 6 source of direct current; 7 microammeter; 8 amplifier; 9 recorder; 10 potentiostat with a built-in decade of output resistance; 11 source of the potential of triangular course.

The source of a triangular potential was a polarograph LP 55 Laboratorní přístroje. For all measurements in this paper a single rate of triangular potential sweep  $\Delta E/\Delta t = 3.7 \text{ mV s}^{-1}$  was used. The saturation of palladium with hydrogen was carried out galvanostatically with a  $20 \mu\text{A}$  current, in the basic  $9\text{M-KOH}$  solution, under simultaneous mild bubbling with argon. The unrinsed electrode was then transferred quickly into the measuring vessel.

### RESULTS OF MEASUREMENTS

In Fig. 3 the values of the charge  $Q_{\text{ox}}$  produced by oxidation of formate on the palladium electrode (at a constant current of  $20 \mu\text{A}$ ) over the whole period of electrode catalytic activity are presented in dependence of the amount of hydrogen  $Q_{\text{H}}$  contained in palladium before the beginning of the oxidation cycle. It is important to stress the experimental conditions under which the dependence was measured. Each measurement, *i.e.* each oxidation cycle ended with the loss of the electrode's catalytic effect, *i.e.* by the transition to the potential of the oxygen evolution. The electrode maintained this value for 30 minutes. The  $Q_{\text{H}}$  value given in millicoulombs represents a charge necessary for the oxidation of hydrogen contained in the palladium electrode. For the sake of clearness two partial experiments are shown in Fig. 4. The curve in Fig. 3 is composed from the results of such experiments. Only the measurement of  $Q_{\text{ox}}$  at  $Q_{\text{H}} = 0$  is presented independently. The values of  $Q_{\text{ox}}$  were found  $Q_{\text{ox}} \rightarrow 10^{-3}$  to  $6 \cdot 10^{-3} \text{ C}$ ; however, the average value is  $2 \cdot 10^{-3}$  to  $3 \cdot 10^{-3} \text{ C}$ .

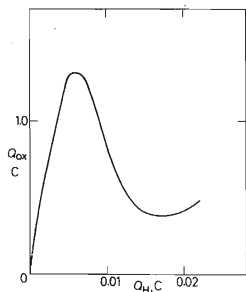


FIG. 3

Dependence of Produced Charge  $Q_{\text{ox}}$  by the Palladium Electrode in the Steady State at Constant Current Intensity  $20 \mu\text{A}$  on Hydrogen Content in Pd, Determined by the Charge  $Q_{\text{H}}$

$9\text{M-KOH} + 1\text{M-HCOO}^-$ ,  $20 \pm 2^\circ\text{C}$ , under argon.

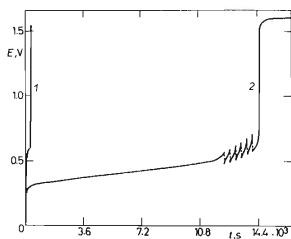


FIG. 4

Two Examples of the Course of Galvanostatic Curves of Pd Electrode, from which Charges  $Q_{\text{ox}}$  were Determined for the Dependence in Fig. 3

$9\text{M-KOH} + 1\text{M-HCOO}^-$ , under argon,  $20 \pm 2^\circ\text{C}$ ; 1  $Q_{\text{H}} = 0$ ; 2  $Q_{\text{H}} = 0.6 \text{ mC}$  (30 s).

The magnitude of the produced charge  $Q_{ox}$  is also dependent on the magnitude of the oxidation current at constant  $Q_H$  (in our case  $Q_H = 3$  mC). This dependence is shown in Fig. 5. With increasing current density  $Q_{ox}$  also increases at the beginning and the changes of  $Q_{ox}$  caused by the presence of hydrogen in palladium become negligible. Therefore we chose a  $20 \mu\text{A}$  current for our experiments, *i.e.* the weakest current at which the error caused by parasitic currents of the input circuits of the potentiostat and the amplifier (Fig. 2a, b) does not exceed 5%, but has an average value of about 2%. The current density of  $20 \mu\text{A}$  corresponds approximately to the current density of  $2 \text{ mA cm}^{-1}$  on the electrode with a very coarse and porous surface, such as are used in fuel cells.

In Fig. 1 the potentiodynamic curve for Pd-electrode in the basic solution of 9M-KOH is shown at a rate of the triangular potential sweep of  $3.7 \text{ mV s}^{-1}$ , in the potential interval from  $+150 \text{ mV}$  to  $+1200 \text{ mV}$ . The curve for a solution also containing  $1\text{M-HCOO}^-$  is shown in Fig. 6.

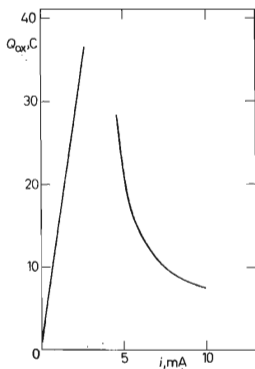


FIG. 5

Values of  $Q_{ox}$  Charge Produced by Pd Electrode (in Stabilised State) in Dependence on the Value of the Constant Current

Galvanostatic connection was used. 9M-KOH + 1M-HCOO<sup>-</sup>,  $20 \pm 2^\circ\text{C}$ ,  $Q_H = 3$  mC. In the region of the maximum of the curve the measurements were unreliable.

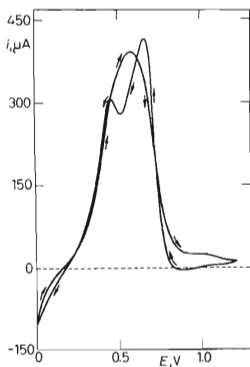


FIG. 6

Potentiodynamic Curve of the Stabilised Pd Electrode

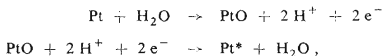
9M-KOH + 1M-HCOO<sup>-</sup>,  $20 \pm 2^\circ\text{C}$ ,  $\Delta E/\Delta t = 3.7 \text{ mV s}^{-1}$ ; from  $+150 \text{ mV}$  +  $+1200 \text{ mV}$  and back.

The charge  $Q_H$  obtained by oxidation of hydrogen present in palladium depends linearly on the charge  $Q_{red}$  which corresponds to the cathodic charge, which passed through the electrode during the preceding hydrogen evolution on the electrode (constant current  $20 \mu A$ ). The ratio of charges  $Q_H/Q_{red}$  was obtained  $0.60 \pm 0.05$ . We explain this by the diffusion of hydrogen into the electrolyte and into the palladium connector to the electrode.

The electrode immersed for 20 minutes in the solution of  $9M-KOH + 1M-HCOO^-$  and rinsed with water produces an oxidation current peak at potentiodynamic measurement in  $9M-KOH$ , corresponding to 5 mC to 10 mC. The surface of the electrode is strongly porous, however, and a mere rinsing does not guarantee a perfect elimination of the formate solution.

## DISCUSSION

In references<sup>1-3</sup> the loss of catalytic activity is explained by the adsorption of some substance on the active surface of the electrode. Impurities come into consideration first. It is known that the results of voltametric measurements of hydrogen electrode differ when distilled and redistilled water are used. Similar impurities may also be supposed in substances used for the preparation of solutions. Another source of substances capable of blocking the active sites on the electrode surface are the products of side-reactions, mainly dehydrogenated particles containing carbon and formed in the course of the main reaction<sup>1,6</sup>. These substances occur only on the surface of the electrode. However, the loss of activity of the platinum metal surface may also be explained in a different manner, as shown by some more recent studies. Their authors suppose that the activity of the surface of the electrode is small or none. It is acquired only on oxidation and reduction of the platinum metal, as mentioned by French and Kuwana, Sawyer and Seo<sup>4,5</sup>, and others:



where  $Pt^*$  means platinum in active state. The loss of activity ( $Pt^* \rightarrow Pt$ ) is ascribed to the transition of platinum from a high energetic level to a thermodynamically more stable state by surface migration and recrystallisation. The authors admit that the electrode may be deactivated parallelly by chemisorbed substances.

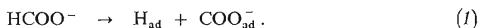
When considering both mentioned explanations it becomes evident that active sites on platinum metal either exist and are gradually blocked by the adsorbed substance (which is desorbed on oxidation of the electrode), or they must be first formed by reduction of the oxide, upon which they degenerate even in the absence of adsorption. In both cases the active state of the electrode may be attained by its oxidation, followed by reduction. If considering that in experimental work it is difficult to eliminate safely the effect of impurities and that for the covering of  $1 \text{ cm}^2$  of the electrode area only approximately  $10^{-9}$  mol of substance are necessary, the conclusion can be drawn that the determination of the ratio of deactivation caused by the blocking of the electrode's surface and that caused by energetic degradation of active sites is rather problematic.

In order to complete the picture of the properties of palladium let us present the following data<sup>1,17,18,24</sup>: palladium crystallises in cubic system, phase centered, with a lattice constant 3.883 Å; if the hydrogen content in palladium increases to the value of 0.9 at % H the lattice constant also increases up to 3.894 Å at 30°C; within this interval the so-called  $\alpha$  phase exists; if the hydrogen content in palladium is further increased,  $\beta$ -phase is formed of the composition PdH<sub>0.6</sub>, also cubic and phase centered, with a lattice constant<sup>17</sup> 4.017 Å, which can dissolve additional hydrogen.

In the palladium surface, in a very thin layer, both sites with H<sub>ad</sub>, and  $\alpha$ - and  $\beta$ -phases may exist simultaneously<sup>19,20</sup>. We must start from these facts in our attempt to explain the relationship (Fig. 3) which we found.

It is known that on platinum electrodes a part of the so-called hardly reducible oxides remains after their reduction. These are probably oxides which have formed several layers on the electrode. During the reduction a layer of metal is formed on their surface which shields (electrically) the underlying layers of oxides and prevents their reduction. This is dependent on the rate diffusion of the adsorbed – and in the case of palladium also of the absorbed – hydrogen to the oxides enclosed in the metal. This explains how a small amount of hydrogen introduced into palladium can increase the number of active sites through the reduction of the enclosed oxides. We suppose that the shielding layer of the metal is decomposed on the basis of large volume changes. A similar possibility, *i.e.* the increase of the active surface of the electrode or the increase of the number of active sites, enables the penetration of hydrogen through the electrode surface. During this process appreciable volume changes take place causing cracks in the metal. New active sites appear on these cracks. However, there exists another possible process leading to the formation of the maximum on the curve in Fig. 3.

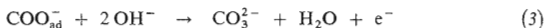
*Electrode without hydrogen.* The palladium electrode was first oxidised at 1.2 V and reduced at 0.5 V in pure basic KOH solution and then transferred into a solution of alkaline formate and charged with a weak constant anodic current. On this electrode dehydrogenation and adsorption of the products<sup>1,2,8</sup> takes place



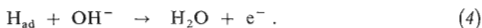
The adsorbed hydrogen partly passes into palladium



and the reaction continues on the liberated sites (1). However, the transition H<sub>ab</sub> → H<sub>ad</sub> is no longer possible at these sites because the particle COO<sub>ad</sub><sup>-</sup> prevents the formation of H<sub>ad</sub> irrespective of whether hydrogen comes from the solution or from deeper layers of palladium. Only when the potential is about +580 mV and when oxidation of COO<sub>ad</sub><sup>-</sup> begins



does the transition of hydrogen  $\text{H}_{\text{ab}} \rightarrow \text{H}_{\text{ad}}$  take place at the liberated sites followed by its oxidation



At this potential of the electrode another process takes place which prevents both adsorption and dehydrogenation of the formate, *i.e.*



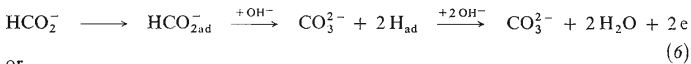
or the formation of non-stoichiometrical oxides.

Such an electrode rapidly loses its catalytic activity for formate oxidation, and under galvanostatic conditions potential of the electrode changes to +1600 mV. The experimental values of the charge  $Q_{\text{ox}}$  of the electrode without hydrogen are maintained at approximately 2–3 mC (Fig. 4, curve 1). If we suppose that no other reactions take place on the electrode, then the charge in mC necessary for the oxidation of  $\text{H}_{\text{ad}}$  adsorbed on the whole surface of the electrode is 0.5 to 3 mC. This is a value comparable to that determined from the area of the current peak for the oxidation of hydrogen, taken from the  $i$ - $E$  curve in pure KOH solution, at periodic sweeping between potentials +150 mV to +1200 mV, when the increase of the potential from +150 mV to +650 mV lasts 2 minutes and 15 s (Fig. 1). The average value of this charge varies over a long time interval (a year) within the 0.9 to 2.5 mC range. This comparison should be considered with appreciable reserve, but even so it is important for us, because we cannot determine the immediate active area of the palladium electrode. It supports the view that the charge  $Q_{\text{ox}}$  of hydrogenless electrode is composed predominantly of the charge necessary for the oxidation of the adsorbed formate, *i.e.* dehydrogenation reaction (1) takes place on the active sites of the palladium, all  $\text{H}_{\text{ad}}$  is transformed to  $\text{H}_{\text{ab}}$ , and  $\text{COO}_{\text{ad}}^-$  only remains on the electrode. Direct potentiodynamic measurement of  $Q_{\text{ox}}$  electrode covered by formate at  $Q_{\text{H}} = 0$  gives higher values between 5 mC and 10 mC, but the measured values are dubious.

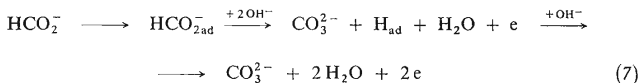
*Electrode with optimum of hydrogen.* The optimum amount of hydrogen  $Q_{\text{H}}$  at which maximum  $Q_{\text{ox}}$  is attained is 6 mC (Fig. 3). On the basis of the considerations from the preceding section it is possible to estimate approximately that the charge for the oxidation of  $\text{H}_{\text{ad}}$  is approximately 2 mC, and for the oxidation of  $\text{H}_{\text{ab}}$  it is 4 mC. If this electrode is immersed in a solution of alkaline formate, the dehydrogenation reaction can no longer be expected (1). The sum of the charges for the oxidation of hydrogen in the electrode, *i.e.* 6 mC, and gradual occupation of the sites and the oxidation of these particles (see reactions (1), (3), (4)) cannot give the value 1.3 C. Therefore, another reaction should be admitted, of which we assume the following featu-



res: 1. it is an oxidation of formate; 2. the main reaction is not dehydrogenation at which  $\text{COO}_{\text{ad}}^-$  is formed which strongly blocks the active sites of the electrode; 3. a weak adsorption of the anion  $\text{HCOO}^-$  may be expected. The following schemes are most suitable for these suppositions<sup>10,23</sup>:

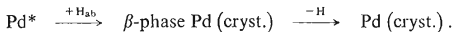


or



However, reaction (1) cannot be completely excluded; in this case, as a side reaction, it gradually deactivates the electrode.

*Electrode with a higher content of hydrogen.* In the preceding case hydrogen covered the electrode and formed roughly a 0.3 at % solution of hydrogen in palladium. If its content is increased, conditions suitable for the formation of hydride  $\text{PdH}_{0.6}$ <sup>17,18</sup> are gradually formed on the surface of the electrode.  $\text{PdH}_{\text{ad}}$ ,  $\alpha$ -phase, and  $\beta$ -phase of palladium may coexist simultaneously<sup>19,20</sup> on the palladium surface and the area formed by hydride will increase with increasing hydrogen content. We believe that the hydride loses its dehydrogenation ability and catalytic activity. The susceptibility of palladium ( $\chi \approx 6 \cdot 10^{-4}$ ) decreases with the increasing hydrogen content in palladium up to the value 0.6 at. H per 1 at. Pd, and does not further change substantially. It is supposed that hydrogen dissolved in Pd is ionised and that the electrons fill the *d*-bands of palladium, thus changing its properties<sup>21,22</sup>. Should we now return to the idea that active  $\text{Pd}^*$  is created by reduction of oxide and that it is either atomic Pd or rather an unsufficiently or irregularly developed microcrystalline form<sup>5</sup>, then conditions are given for the loss of the electrode's activity on the basis of the following mechanism:



This is in agreement with our experimental experience.

The three courses mentioned of the dependence of  $Q_{\text{ox}}$  on the hydrogen content in palladium *i.e.* 1. additional reduction of hardly reducible oxides and the increase of the active area of the electrode following from it; 2. the increase in the area of the electrode caused by the destruction of surface layers of the electrode due to the hydrogen concentration changes in palladium; 3. deactivation of palladium by the dissolved hydrogen, cannot be distinguished from one another or any of them eliminated. Neither we are able to determine their share in the course of  $Q_{\text{ox}}$ . On the contrary, we

consider it as demonstrated that the hydrogen dissolved in palladium determines the mechanism of oxidation on palladium in an alkaline medium. This effect is especially striking at a low anodic current intensity.

From the point of view of the use of palladium for the electrodes of fuel cells we have come to the conclusion that palladium alone in an alkaline medium is not suitable as a catalyst because it very easily loses its activity and the time of its activity is strongly limited without frequent or automatic regenerations of the fuel-cell electrode.

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