IONIC ADSORPTION PROCESSES ON PALLADIUM

I. THE ADSORPTION OF THE IONS OF SODIUM SULFATE FROM ACIDIFIED SOLUTIONS

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UDC 541.13

Palladium is one of the active catalysts for a number of electrochemical reactions involving organic and inorganic substances. Surface active ions have a substantial effect upon the activity and selectivity of the palladium's action. This has been shown, in particular, when the effect of the anions Cl^-, Br^-, and I^- and that of the cations Cd^{2+}, Zn^{2+}, Cr^{3+}, and Ni^{2+} upon hydrogen adsorption and upon the hydrogenation rate of certain organic compounds was investigated [1]. Quantitative data are required concerning the adsorption of cations and anions under various conditions, the strength of their bond with the surface, and the mutual effect of adsorbed ions and electrochemically active gases, if one wants to harness ionic adsorption processes on the catalyst surface for the sake of changing its catalytic properties. For palladium such data are practically nonexistent.

The present investigation is concerned with ionic adsorption on palladium as a function of various factors. In the first communication, results are reported on the adsorption of the ions Na^+ and SO_4^{2-} as function of the potential of palladium; these were obtained with the radiotracer method. The choice of these ions was dictated by their low surface activity on platinum and other metals of the platinum group and, thus, by the possibility of studying the adsorptive properties of palladium and the position of its zero-charge potential in the absence of specific adsorption of ions.

Electrolytic palladium deposits served as electrodes. They were obtained on smooth platinum (which had been pretreated in HCl under anodic polarization and then in H_2SO_4 under cathodic polarization) from 1-% $PdCl_2$ solution at pH 1 under two sets of conditions: method I and method II. These were the same during the first 160 min. The current density was alternated in the following manner: 10 min at 8 mA/cm^2, 30 min at 4 mA/cm^2, etc. During the final 20 min, the polarization was done with a current of 8 mA/cm^2 in method I, and with a current of 1.5 mA/cm^2 in method II. When the plating was completed, the deposits were washed with twice-distilled water, cathodically polarized in 0.1 N H_2SO_4 (2 h) under hydrogen evolution, again washed in twice-distilled water under a hydrogen atmosphere, and kept therein under an air atmosphere until used. The true surface area of the electrodes was measured periodically as in [2], in terms of the quantity of adsorbed hydrogen which corresponds to part "c" of the charging curve (curve 3 of Fig. 3). It was assumed that one hydrogen atom is adsorbed per palladium atom, and that the number of palladium atoms per cm^2 of surface is $1.33 \cdot 10^{15}$. It was shown in [2] that measuring the surface area of palladium powders by this method gives values coinciding with those obtained by the BET method. It is possible, however, that for electrolytic palladium the values for the true surface area are somewhat too high.

The measured true surface area of the deposits strongly decreased with time, and did so differently for deposits obtained by different methods. The sharpest change in surface area for deposits obtained by method I occurred during the first 10-12 days, that for deposits obtained by method II during the first 20-25 days after their formation (Fig. 1). Such changes in the surface area can be explained by recrystallization of the deposits, which occurs at a different rate depending on their structure, which in turn is determined by the method of plating. Hydrogen dissolved in the bulk of the palladium, which is removed from it while it is kept in an air atmosphere, may play a decisive role. This is confirmed, in particular, by exaggerated values for the double-layer capacity (150-300 μF/cm^2) which can be obtained on freshly deposited palladium

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 6, No. 7, pp. 1057-1060, July, 1970. Original article submitted August 13, 1969.

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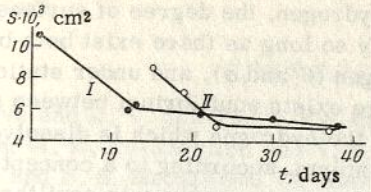


Fig. 1

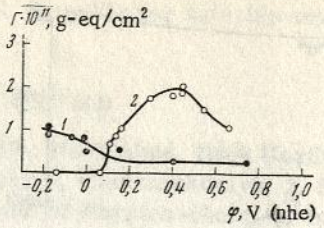


Fig. 2

Fig. 1. The variation of the true surface area of palladium electrodes with time: I) method I, II) method II.

Fig. 2. The adsorption of Na^+ (1) and of SO_4^{2-} (2) as function of potential for palladium deposited by method II, form $1 \cdot 10^{-3}$ N $Na_2SO_4 + 1 \cdot 10^{-3}$ N H_2SO_4 solution.

from the slope of the double-layer portion of the charging curve. On old deposits the capacity has a normal value. For this reason deposits were used in the present work which had reached practically stable values of capacity and true surface area, and the adsorption was reckoned to a value of surface area that had been obtained on the day when adsorption was measured.

The adsorption was determined from the radioactivity of the electrode, correcting for the adhering film of solution [3]. The adsorption experiments were carried out in the following manner: the electrode was activated by alternate anodic and cathodic polarization in 0.01 N H_2SO_4, rinsed with twice-distilled water, transferred into the working cell with 0.001 N H_2SO_4, and cathodically polarized to hydrogen evolution for one hour. In a stream of pure argon the electrode potential was then displaced to the selected value and kept at this value until equilibrium was attained. The H_2SO_4 solution was then replaced by the salt solution without the access of air, and the electrode was kept at the same potential until a constant value for the adsorption of the ion studied was attained without current. In the range of potentials studied, no changes in the adsorption of Na^+ and SO_4^{2-} ions were observed after 15 min to 2 h. After keeping the electrode at the equilibrium adsorption value it was lifted from the solution, and the radioactivity of the entire surface was measured on it. Then it was washed free of the adsorbed ions under defined conditions and used for the subsequent experiment following the same order of operations. There proved to occur no perceptible dissolution of palladium in Na_2SO_4 solution at pH 2-3 during the time of the experiments, nor any change in the true surface area of the electrode.

The adsorption activity of palladium deposits toward the ions of sodium sulfate strongly depends on the length of time for which they were stored after plating. The most significant change in activity is observed during the first 1.5-2 months; i.e., it occurs over a longer time than the change in their true surface area. The reasons for this drop in adsorption activity of palladium were not studied in the present work.

It is known from literature data that the adsorption activity of palladium toward hydrogen strongly depends on the way in which it was prepared [4-6]. It is seen from Figs. 2 and 3 that this is also true in the adsorption of the ions of sodium sulfate. The basic behavior characterizing the change in adsorption of cations and anions with potential and, hence, with charge and surface state remains the same between deposits obtained by the two methods; however, there are notable differences in the quantities adsorbed and in the details of the shape of the curves. Thus, for the deposits obtained with a low final current density (Fig. 2), the adsorption values are appreciably lower than for deposits obtained with a higher current density (Fig. 3).

From the shape of the curves of Figs. 2 and 3 it is seen that the change in slope and the appearance of extrema on the adsorption curves take place at approximately the same potential regions where a change in the slope of the charging curve is observed (curve 3 of Fig. 3)* which is characteristic of a change in the surface state of the electrode. Since the latter is linked to the variation in the degree of coverage of the palladium surface by adsorbed hydrogen or oxygen, one can assume that the adsorption properties of palladium toward the ions of sodium sulfate are directly linked to changes in its surface state due to the adsorption of these gases. An analogous situation was observed for platinum [7-9].

*The curve is turned 90° against its usual representation.

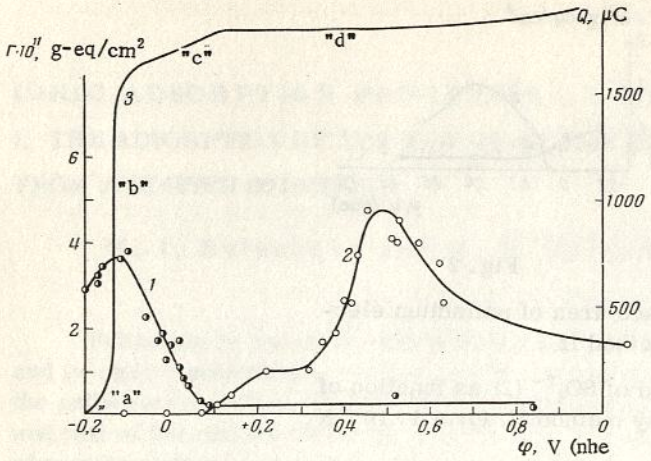


Fig. 3. The adsorption of Na^+ (1) and of SO_4^{2-} (2) as function of potential for palladium deposited by method I, from $1 \cdot 10^{-3}$ N $Na_2SO_4 + 1 \cdot 10^{-3}$ N H_2SO_4; 3) the charging curve in 0.1 N H_2SO_4.

For palladium, which absorbs large quantities of hydrogen, the degree of surface coverage remains unity so long as there exist both bulk phases of hydrogen (β and α), and under stationary conditions there exists equilibrium between adsorbed hydrogen and the hydrogen which is dissolved in the bulk of palladium, according to a concept advanced in [5, 10]. Since in our experiments equilibrium conditions prevailed between electrode and solution, we can analyze the adsorption and desorption of the ions and of hydrogen for the same potential regions. It is convenient to carry out such an analysis starting from the potential of zero charge.

The potential of zero charge of palladium in acidified solution of sodium sulfate, which corresponds to the intersection of the adsorption curves for cation and anion [3], is 0.10 V for both types of deposit.* It follows from a comparison with the charging curve (Fig. 3) that it refers to a surface still covered with adsorbed hydrogen, a fact which is also confirmed by the high (~ 300 $\mu F/cm^2$) value of the double-layer capacity as calculated from the charging curve in the potential region from 0.1 to 0.2 V. With increasing negative charge the adsorption of cation increases (curve 1 of Fig. 3) for the entire potential range corresponding to the presence of the α-β transition (segment b of curve 3 in Fig. 3), but it falls off again in the region of the β-phase (segment a). The distinct maximum in Na^+ adsorption developing on the curve for the palladium deposit obtained by method I is analogous to the maximum first observed on platinum in the same potential range [9]. On a positively charged palladium surface the adsorption of cations is very low, for reasons not yet understood.

There is practically no adsorption of SO_4^{2-} ions over the entire potential range corresponding to high negative surface charges. Near the null point and at low negative charge densities adsorption becomes apparent, and it begins to rise at positive charge densities, which favor the adsorption of anions; it rises differently for the two types of deposit. The change in slope of the adsorption curve 2 corresponds to a change in the degree of coverage of the palladium surface with adsorbed gases, as can be seen when comparing the values of double-layer capacity calculated from the charging curve with those calculated from the adsorption curve. The capacity calculated from the adsorption curve is 6-7 $\mu F/cm^2$ in the potential range from 0.1 to 0.2 V, while that calculated from the charging curve on the same deposit is 280 $\mu F/cm^2$. At more positive potentials high values of capacity are obtained (25 to 30 $\mu F/cm^2$ for the potential range from 0.30 to 0.43 V) by calculation from the adsorption curve, and like values are obtained from the charging curve up to even higher potentials (0.55 V). From this it can be concluded that the adsorption of SO_4^{2-} ions occurs up to 0.2 V on a surface still covered with adsorbed hydrogen, but up to 0.43 V, when the degree of hydrogen coverage falls to zero, it occurs on a pure palladium surface which has different adsorption properties.

At potentials above 0.5 V the adsorption of anions decreases, which is explained by the fact that they are displaced by adsorbed oxygen which forms dipoles with the palladium similarly as assumed for platinum [7, 8]. This is reflected in an increase in capacity as calculated from the charging curve. The slower desorption of anions at potentials above 0.6 V may be due, either to a decrease in the effective dipole moment of the bond of oxygen with palladium with increasing degree of surface coverage, or to the fact that oxygen begins to adsorb on surface sites not occupied by anions. The latter hypothesis requires the presence of two forms of adsorbed oxygen with different adsorption energies. This needs further investigation.

The data on the desorption of Na^+ cations and SO_4^{2-} anions from the palladium surface in water or sulfuric acid of different concentrations show that the strength of their bond with the palladium is relatively low even in the presence of oxygen. The data on the adsorption and desorption of these ions allow one to conclude that their bonding with the palladium surface is close to an electrostatic bonding.

*All potentials are given against the normal hydrogen electrode.

We express our great gratitude to Academician A. N. Frumkin for valuable remarks in the discussion of the results of this work.

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