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Abstract

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SEPARATION OF HYDROGEN ISOTOPES ON A PALLADIUM CATHODE

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A number of works have been devoted to the electrochemical separation of hydrogen isotopes ($^{1-5}$). However, the experimentally obtained data cited in the literature on the values of the separation coefficient S show a large scatter. The published theoretical works ($^{6-9}$) do not explain sufficiently convincingly the regularities in the change of the value of S under various electrolysis conditions. In a series of works carried out in the electrochemistry laboratory of the L. Ya. Karpov Institute (^{1,10}), a dependence of S on the potential was found for metals that adsorb hydrogen. It was concluded that the separation coefficient is connected in a very complex way with the electrochemical process, the kinetics and mechanism of which depend on the state of the electrode surface. On the surface of cathodes made of Fe, Ni, Pt, and Pb there is hydrogen, the form of whose bond with the surface, depending on the treatment of the specimen and the electrolysis conditions ($^{11-13}$), determines the energetic properties of the surface.

The aim of the present work was to clarify the influence of the properties of the surface layers of hydrogen on the electrode on the value of S. A palladium cathode was used in the work, concerning which the following is known: 1) measurements of the overvoltage on palladium, carried out in the appropriate manner, give information on the activity of the hydrogen located on the surface (see (^{14})); 2) the centers of discharge and recombination on the surface of palladium are spatially separated (^{15,16}); 3) the rate of isotopic exchange occurring on the electrode surface between palladium hydrogen and the alkaline electrolyte is 10^{-4}—10^{-5} a/cm^2; this makes it possible to consider that the reactions of isotopic exchange on a palladium cathode, already at electrolysis currents of the order of 10^{-3} a/cm^2 in alkaline solutions, do not affect the value of S (^{17}).

We measured the separation coefficient of the isotopes tritium and protium.* The electrode under study was made from palladium foil. The current-carrying platinum wire was sealed with polyethylene. The anode was the outer wall of a palladium test tube. The test tube was saturated from within with hydrogen. With such an arrangement, the anodic reaction was the reaction of hydrogen ionization, which excluded the entry of oxygen into the apparatus.

To characterize the electrode, so-called "fast" oscillographic overvoltage curves

Fig. 1

Figure 1: Fig. 1

were taken (over 1.5 sec the current changed by 3 orders of magnitude). These curves were recorded by connecting the cell in series to a discharging capacitor charged to 4 kV. The capacitor discharged through an auxiliary resistance of 160 kΩ. When the capacitor was discharged through the cell, a current passed whose strength varied exponentially with time. The influence of the emf of the cell obviously could not distort the exponentials, at least over an interval of 4 orders of magnitude, owing to the comparatively small polarizability of the electrodes. The change in overvoltage was recorded on an ÉNO-1 low-frequency oscillograph.

The method described made it possible to distinguish with great clarity— to distinguish the constituent components of the total overvoltage on palladium, η_1 and η_2, and to reveal their relation to the separation coefficient*.

Simultaneous measurements of the overvoltage and of the coefficient S were carried out. Both quantities depend strongly on the treatment of the electrode and on the method of saturating the electrode with hydrogen. Both can change the ratio between the number of recombination centers and discharge centers on the electrode surface, which leads to a change in the total value of the overvoltage and in the value of S on it (see also ([19])). By applying certain methods of surface polarization, one can change the ratio of the quantities η_1 and η_2 without changing the total overvoltage, which also leads to a change in S.

Fig. 1. Cathodic and anodic overvoltage curves. **A**—on electrodes without preliminary anodic treatment after saturation with a constant current of 50 ma/cm^2. —on the cathode after saturation with a current of 50 ma/cm^2, with constant current (curve 1) and with interruptions (2). —with saturation of the electrode by alternating current (cathodic pulse -50 ma/cm^2, anodic $+3$ ma/cm^2) and decay curve 3 ($t = 1.4$ sec). —on an activated palladium electrode.

If the palladium plate is not subjected to strong oxidation by preliminary anodic polarization, then on such an electrode, under cathodic polarization, an increase of the overvoltage with time is observed. From the initial to the stationary state the curve shifts into the cathodic region

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* The analysis of the tritium concentration was carried out with the aid of an internally filled Geiger-Müller counter, both in the electrolytic hydrogen and in the hydrogen obtained upon complete decomposition of the electrolyte water ([10]).

* η_1 is the component of the overvoltage associated with the slowness of the

Fig. 2

Figure 2: Fig. 2

discharge stage of the hydrogen-evolution process; η_2 is the component of the overvoltage associated with the activity of the hydrogen present on the surface.

by 100-200 mV. The oscillographic overvoltage curves recorded after attainment of the steady state (Fig. 1A) show the presence of large values of η_2 (curve 1). The form of the anodic ionization curve of hydrogen, recorded on the same surface, shows (see the initial portion of curve 2 in Fig. 1A) that a considerable amount of active hydrogen is present on the electrode. On such electrodes the separation coefficient is $S = 6.5 \div 11$.

If an electrode of this type is then polarized cathodically not with a constant current, but with an intermittent current having a frequency of interruption selected so that the effective current is, approximately, only 20% less than the constant current of the preceding experiment, then the overvoltage decreases and the curve shifts in the anodic direction by 50-150 mV. Comparison of curve 2 in Fig. 1B with curve 1 shows that the decrease in the total overvoltage under intermittent polarization occurs at the expense of the η_2 component. The value of S then increases by 1-2 units, to $7 \div 12$.

Fig. 2. Dependence of S on the method of polarization and on temperature. 1—polarization with alternating current 50 mA/cm^2 with an anodic pulse +3 mA/cm^2 (Fig. 1B); 2—polarization with intermittent current −50 mA/cm^2 (Fig. 1B); 3—polarization with constant current −50 mA/cm^2 (Fig. 1A).

If the electrode is polarized by superposing an alternating current, while maintaining an effective current density close to the preceding one by making the cathodic pulse exceed the anodic pulse by more than a factor of 10, an electrode is obtained for which the oscillographic overvoltage curve is shown in Fig. 1B. From decay curve 3 it is seen that on such an electrode the value of η_2 is small, while η_1 is considerably larger than in the other cases. The value of S for such an electrode lies within the range $15 \div 20$.

On an active surface of a palladium electrode a low value of the total overvoltage is obtained. Activation of the surface is achieved by alternating cathodic and anodic polarization with currents of low density (0.001 A/cm^2) and subsequent slight anodic oxidation of the metal. Figure 1G shows overvoltage curves for an activated electrode. Figure 1G shows the small value of the total overvoltage and of both its components. For electrodes with such surface treatment, $S = 3.5 \div 7$.

Figure 2 illustrates some results of separation experiments carried out at temperatures of 19 and 59°. In columns 1, 2, and 3 of experiment 1 and in columns 1 and 2 of experiment 2, the values of the coefficients obtained upon changing the temperature are given for electrodes with a large value of S (characterized by the curves in Fig. 1B). The values of the coefficients at 19-20°, as is seen from the figure, are higher than the values at 59-60°. With increasing temperature the value of S should decrease in accordance with the known expression $S = k\exp(\Delta E/RT)$ (^{20}).

On electrodes with large η_2, on which the influence of hydrogen on the value of the coefficient is substantial, an increase of S with increasing temperature is observed. This is seen from columns 4 and 5 of experiment 1 and columns 1 and 2 of experiment 3 in Fig. 2. The lowering influence of the temperature increase on the coefficient, of course, is present here as well, but it is outweighed by the increase in S, probably associated with acceleration of the desorption of hydrogen from the surface.

The question of the stage of the process responsible most unambiguously can be resolved ···

for the separation of hydrogen isotopes during electrolysis can be judged by analyzing the isotopic composition of the gas evolved from the electrode and of the gas absorbed in the bulk of the electrode metal.* It is obvious here that gas samples must be taken after stationary saturation of the cathode has been reached. According to the method we developed, the electrode saturated with hydrogen was removed from the electrolyte and immersed in liquid nitrogen. Then the frozen electrode with the remnants of electrolyte was placed in a precooled ampoule and evacuated. After thawing of the electrode and freezing out of the water, the ampoule was heated to 300°. The hydrogen released on heating was analyzed. The described procedure prevents losses of hydrogen during transfer of the electrode from the electrolytic cell to the analytical apparatus.

Table 1

Experiment No.	S gas—Pd volume	S gas—electrolyte	Experiment No.	S gas—Pd volume	S gas—electrolyte
1	1.46	6.5	5	1.3	8
2	1.15	7.5	6	1	15.6
3	1	9.6	7	1	19.8
4	1.1	9			

Note. 1, 2, 3, 4, and 5—electrodes with large η_2 (Fig. 1A); 6 and 7—electrodes with small η_2 (Fig. 1B).

From the data of Table 1 it is evident that the value of S at the recombination stage is close to unity. Taking this result into account, as well as the results of work (^{16}), it should be considered that the principal part of the kinetic separation coefficient on palladium must be attributed to the stage of rupture of the H—OH bond occurring during discharge of water molecules. Variations in the value of S on palladium are due, as experiment shows, to changes in the conditions of discharge of water molecules, which are determined by the state of hydrogen on the surface and by the character of adsorption of water on it.

A nonactivated electrode with high overvoltage, retaining a large chemical potential of hydrogen adsorbed on the surface (Fig. 1A), gives small and medium values of S. The same electrode, on the surface of which the chemical potential of adsorbed hydrogen has been lowered by applying anodic pulses, while the high overall value of the overvoltage remains (Fig. 1B), gives very high values of S. An activated electrode, on which both the chemical potential of adsorbed hydrogen and, along with this, the total overvoltage are lowered by the activation procedures described (Fig. 1G), gives small and the smallest values of S.

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* Earlier measurements of the isotopic composition of hydrogen absorbed by palladium (^{18}) are apparently less reliable.

Note: Figure translations are in progress. See original paper for figures.

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