INVESTIGATION OF THE HYDROGEN EVOLUTION REACTION AT TUNGSTEN IN ACIDIC SOLUTIONS

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Earlier [1] the hydrogen evolution reaction was investigated in alkaline solutions, and in the present work the investigation has been extended to acidic solutions. The experimental procedure was described in detail in [1]. In order to free the surface from oxides, Bockris and co-workers heated the electrode in an atmosphere of hydrogen [2-4] and in molten sodium nitrite [5, 6] and then transferred it to the cell without contact with air. Trchunyan and Antropov [7] recorded the polarization curves at various pH values on a tungsten filament which was heated directly in the cell in an atmosphere of hydrogen. The measurements showed that the overpotential is independent of pH in the region between pH 0.1 and 3.6. Ammosse and Barbier [8] made measurements in a phthalate buffer solution without previous reduction of the surface. The curves are complex in form, and a significant increase in overpotential is observed in the region between pH 5 and pH 6. The data published in [2-8] and the conclusions reached by the authors about the reaction mechanism are summarized in Fig. 1. As seen, the results are contradictory. We note that for different electrodes of the same tungsten wire subjected to the same pretreatment [1] we observed almost the same spread in alkaline solutions as the discrepancy between the data obtained by the authors in [3-8]. No data were given in [3-8] about the behavior of the electrodes with time over any considerable period, while in [2] it was mentioned that there was a strong variation in η during the first 2 h.

In the first experiments we reduced the surface electrochemically, for which purpose the electrode was held in acid at a high cathodic current density before the measurements. Here there was a decrease in the overpotential during the reduction process, an increase in the potential with time on passing to lower current densities, and appreciable hysteresis in the forward and reverse curves. These effects amounted to several tens and in some cases more than a hundred millivolts and intensified with increase in the current density during the preliminary polarization right up to the highest current density which we investigated (10 A/cm^2).* The typical pattern of such changes is given in Fig. 2. Tens of experiments of this kind showed clearly that almost any of the published data could be reproduced in respect of both the magnitude of the overpotential and the form of the curve if suitable reduction conditions and experiment lengths were chosen. However, the values obtained in this way relate to some unspecified state of the surface and are unstable with time. The described phenomena due to change in the state of the surface can be explained by oxidation of the tungsten by the oxygen of a water molecule after electrochemical reduction. The oxidation takes place as follows:

$$W + 2H_2O = WO_2 + 2H^+ + 4e. \tag{1}$$

The standard equilibrium potential of reaction (1) lies in the cathodic region and is equal to −119 mV [9], and in this case the deposition of oxygen takes place at a potential 150-200 mV more negative. A similar effect arises in the case of a series of metals, such as platinum, gold, silver, and others [10]. As a result of electrochemical reduction the surface evidently arrives at a state where the deposition of oxygen is facilitated.

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*For polarization with such a high current density we used a special auxiliary anode, separated from the cathode compartment by a closed large-diameter tap (the anode 4 in Fig. 1 in [1]).

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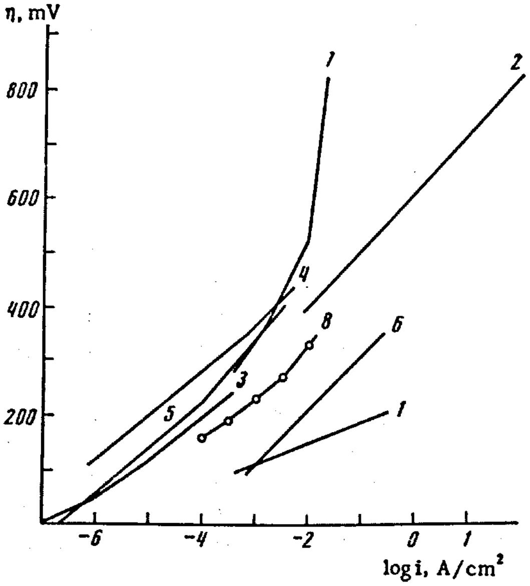

Fig. 1

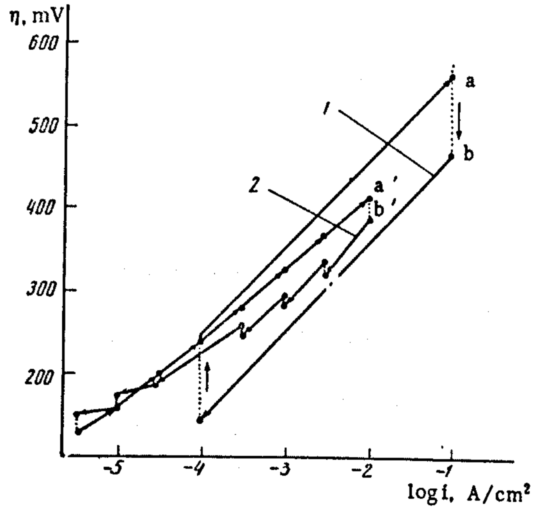

Fig. 2

Fig. 1. Results from polarization measurements and reaction mechanisms proposed by the following authors: 1) Bockris and Parsons [2], 1 N hydrochloric acid, slow recombination; 2) Bockris and Azzam [3], 5 N hydrochloric acid, slow discharge or slow electrochemical desorption at $i > 10$ A/cm^2; 3) Bockris, Azzam, and Hug [4], 0.1 N hydrochloric acid, slow electrochemical desorption; 4) Bockris and Koch [5], 0.5 N hydrochloric acid, slow electrochemical desorption; 5) Bockris and Srinivasan [6], 0.5 N sulfuric acid, slow electrochemical desorption; 6) Trchunyan and Antropov [7], sulfuric acid, pH = 0.1, slow recombination; 7) Ammosse and Barbier [8], potassium phthalate, hydrochloric acid, pH = 3; 8) our data, 1 N sulfuric acid.

Fig. 2. Results from polarization measurements in 1N sulfuric acid during electrochemical reduction of the surface. The points show the variation in η with time for constant i: 1) reduction at current density 10^{-1} A/cm^2 for 3.5 h (section a, b); 2) reduction at 10^{-2} A/cm^2 for 12 h (section a', b'). The temperature was the same as in Fig. 3, 30°C.

In subsequent experiments we removed the oxide films from the surface by chemical dissolution in alkali during the cathodic polarization process, as in [1]. The effectiveness of the removal of the oxide film by treating the tungsten with alkali is demonstrated by the following qualitative test. Tungsten powder (specific surface are 0.95 m^2/g) does not react with 1 N sulfuric acid. After treatment with 1 N alkali for 1 min, however, it reacts vigorously with dilute acid releasing hydrogen, and passivation of the metal begins after approximately an hour.

Before the experiment the electrode was polished mechanically with a thoroughly washed quartz plate and then polarized cathodically in 1 N potassium hydroxide solution until stabilization of the surface had begun. A typical series of polarization curves in solutions containing K^+, SO_4^{2-}, and HSO_4^- ions in the region of pH values between 0.29 and 14 is given in Fig. 3. To a first approximation the ionic strength of the solution can be considered constant. The measurements were made in the order indicated by the figures. Curve 1 was recorded first in 1 N potassium hydroxide, the solution was then replaced by 1 N sulfuric acid and curve 2 was recorded (during replacement of the solution the electrode was kept in an atmosphere of hydrogen at a cathodic potential), and the acid was then diluted step by step with 1 N potassium sulfate solution and polarization curves 3-9 were recorded in the acidic solutions. After this 1 N potassium hydroxide solution was first added to the cathode compartment in small portions, and curves 10-11 were recorded in alkaline solutions. The measurements ended with the recording of the curve in 1 N potassium hydroxide solution. As a result of the use of this method in both acidic and alkaline solutions the hysteresis amounted to no more than 7 mV. With constant current density variations in η with time were hardly observed at all.

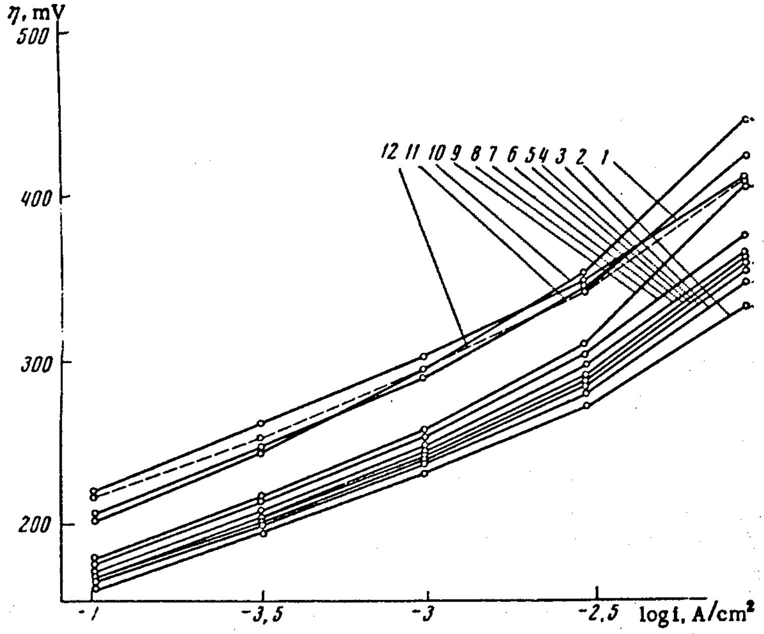

Fig. 3. Polarization curves for various pH values. Mixtures of 1 N H_2SO_4 and 1 N K_2SO_4 were used in the acidic solutions, and 1 N KOH and 1 N K_2SO_4 in the alkaline solutions. The curves were recorded in the order shown by the figures at the following pH values: 1) 14; 2) 0.29; 3) 1.05; 4) 1.53; 5) 1.8; 6) 2.37; 7) 2.66; 8) 2.99; 9) 3.28; 10) 12.23; 11) 12.91; 12) 14.

The measurements took 4-5 h, and in this time the state of the electrode surface did not change significantly. This follows from the fact that curves 1 and 12 coincide with an accuracy of 8 mV. The polarization curves 9 and 10 for $i \geqslant 10^{-2.5}$ A/cm² are evidently distorted by concentration polarization and ohmic losses.

As seen from Fig. 3, the overpotential in both acidic and alkaline solutions depends very little on the pH value. In acidic solutions the change in η amounts on the average to only 6 mV per pH unit with a current density of 10^{-4} A/cm² and to 17 mV with a current density of 10^{-2} A/cm². Impedance measurements which were carried out showed the presence of adsorption capacitance, and this indicates that the stage involving removal of the adsorbed hydrogen is irreversible. As for alkaline solutions [1], the slight dependence on pH indicates that a mechanism of rapid discharge and retarded recombination is most likely, and this agrees with the conclusions reached by Trchunyan and Antropov [7]. It is not, however, impossible that the observed slight dependence on pH corresponds to some involvement of electrochemical desorption in the process.

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