MECHANISM OF THE IONIZATION OF HYDROGEN ON TUNGSTEN CARBIDE

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In experiments [1] at a platinum electrode, it was shown that the ionization of hydrogen can take place both with the intermediate dissociation of a hydrogen molecule

$$H_2 \rightarrow 2H_{ads} \rightarrow 2H^+ + 2e, \quad (1)$$

and with electron transfer before dissociation, for example

$$H_2 \rightarrow (H_2^+)_{ads} + e; \quad (H_2^+)_{ads} \rightarrow 2H^+ + e. \quad (2)$$

In [2] it was established that the reaction involved in the ionization of hydrogen on tungsten carbide is of first order with respect to molecular hydrogen. Since tungsten carbide readily adsorbs hydrogen, and the adsorption changes slowly (linearly) with potential [3], it follows that the slow stage may be the first stage taking place by mechanism (1) or by mechanism (2). In order to determine the path by which the process in fact takes place, it was proposed in [1] to study the pH dependence of the rate of the process. According to mechanism (1), the rate at constant overvoltage should be independent of pH. For route (2) at constant overvoltage, the current density for the ionization of H_2 should depend on the activity of hydrogen ions, in accordance with the equation

$$i = ka_H^{\beta}, \quad (3)$$

where β is often close to 0.5.

We recorded the steady-state polarization curves for the ionization of hydrogen at a smooth rotating tungsten carbide electrode by the method described in [2]. The results for two independent series of experiments carried out at different electrodes are given in Fig. 1. The hydrogen ionization current decreased on going from 1 N H_2SO_4 to 1 N K_2SO_4, acidified with 10^{-2} and 10^{-4} N sulfuric acid. The current decreased by a factor of less than 2, however, for a change in the hydrogen ion concentration by four orders of magnitude. This shows that the slow stage of the process involved in the ionization of hydrogen on tungsten carbide is the adsorption with the dissociation of molecular hydrogen. The slight change in the rate with change in the composition of the solution may be due to a change in the state of the tungsten carbide surface with decrease in acidity, since this will evidently influence the rate of adsorption.

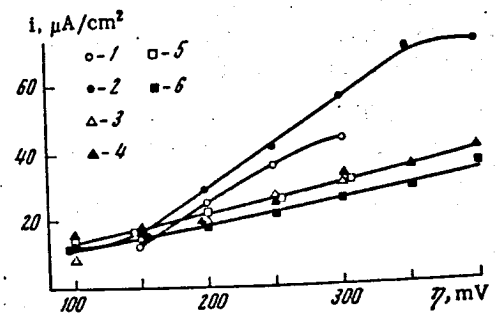


Fig. 1. Polarization curves for the ionization of hydrogen on tungsten carbide in solutions with different compositions: 1, 2) 1 N H_2SO_4; 3, 4) 10^{-2} N H_2SO_4 + 1 N K_2SO_4; 5, 6) 10^{-4} N H_2SO_4 + 1 N K_2SO_4. The dark circles refer to one series of experiments, and the open circles refer to the other.

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