THE EFFECT OF DIFFUSING ATOMIC HYDROGEN ON THE POTENTIAL OF POLARIZED IRON AND ELECTRODEPOSITS ON IT

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Atomic hydrogen is an intermediate product in the electrochemical liberation of hydrogen. Thus, a study of the effect of an artificially increased atomic hydrogen concentration at an electrode surface on the process mechanism makes it possible to decide on the reaction mechanism of cases.

In this investigation, the atomic hydrogen concentration was increased by diffusion of atomic hydrogen formed by cathode polarization on one side of a membrane of Armco iron to the other side, which was the electrode being investigated. The measurements were made in an NaOH solution at the stationary electrode potential, when the strength of cathode polarizing current equaled zero, and, at various cathode polarizations $\underline{i}$.

The curves given in the figures show the change in overvoltage η with time at various cathode polarizations with and without diffusion (I is the hydrogen diffusion rate in electrical units). The black circles indicate values of η in the absence of diffusion and white ones – with it.

Figure 1, shows that the diffusing atomic hydrogen displaced the stationary potential of iron, φ_{st}, equal to -0.06 v with respect to a hydrogen electrode, by 60-70 mv towards the negative side. It was observed that when anode polarization (C) was applied to the iron electrode for a short time, the diffusing hydrogen continued to be liberated although the potential of the iron electrode was more positive than a reversible hydrogen electrode. This indicated slow ionization of the adsorbed hydrogen, $H_{ads} + OH^- \rightarrow e + H_2O$. When anode polarization ceased the displacement of the stationary potential usually increased in a negative direction. With cathode polarization of the iron, the diffusing hydrogen increased η. If η were increased due to cathode polarization, then there was a smaller increase in η in the presence of atomic hydrogen. With cathode polarization greater than that shown in the graph, atomic hydrogen had no effect at all on η. With a further increase in η, the diffusing atomic hydrogen lowered it by several millivolts.

To confirm the possibility of reversing the sign of the effect of atomic hydrogen on η on iron, we slightly poisoned the iron with lead, which increased the η of such an electrode to 50-90 mv above that of one of pure iron (Fig. 2). On such an electrode, atomic hydrogen increased the overvoltage at low values of η and decreased the overvoltage at high values, while the hydrogen had no effect at average η.

If iron were strongly poisoned with mercury and, thus, its η rose by 250-350 mv, at high values of η on such electrodes the diffusing hydrogen lowered η by 150-250 mv (Fig. 3). This corresponds to an acceleration of hydrogen liberation by a factor of 10-100. However, with a fall in η, this effect decreased and at low values of η, atomic hydrogen increased the latter.*

A reverse in the sign of the effect of atomic hydrogen on η was also observed on nickel, 10^{-4} cm thick, electrodeposited on the iron electrode being investigated (Fig. 4). At high η, atomic hydrogen lowered the overvoltage and at low η, it raised the overvoltage. However, in the case of nickel this effect equaled 5-15 mv. A similar effect of atomic hydrogen on η on nickel was observed in an H_2SO_4 solution.

*S. D. Levina carried out the first experiments to elucidate the effect of diffusing hydrogen on the stationary potential of iron poisoned with mercury in an alkali solution.

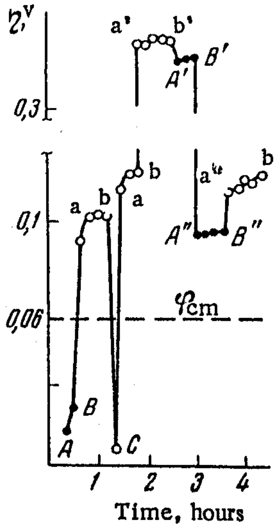

Fig. 1. The effect of diffusing hydrogen on the potential of iron in 1 N NaOH at various polarizations. AB) $i = 0$, $I = 0$; ab) $i = 0$, $I = 0.8 \cdot 10^{-3}$ a/cm^2; C) (anode polarization) a'b') $i = 4 \cdot 10^{-3}$ a/cm^2, $I = 8 \cdot 10^{-4}$ a/cm^2; A'B') $i = 8 \cdot 10^{-4}$ a/cm^2, $I = 0$; A"B") $i = 8 \cdot 10^{-6}$ a/cm^2, $I = 0$; a"b") $i = 8 \cdot 10^{-6}$ a/cm^2, $I = 4 \cdot 10^{-3}$ a/cm^2.

In the case of electrodeposits of zinc and tin (Fig. 5), we were limited to measurements at low η values due to the solution of these metals in alkali and did not observe a reversal of the sign of the effect of atomic hydrogen on η. Diffusing hydrogen always lowered η on zinc and tin. The higher the value of η, the greater was its decrease.

An increase in η under the action of diffusing hydrogen was always observed on electrodeposited copper (Fig. 6). The results obtained confirm the data of Gerischer and Mehl [1] who observed a decrease in current on a copper electrode in the initial period after applying cathode polarization to the electrode at constant potential. This phenomenon is connected with the increase in the atomic hydrogen concentration on the electrode surface during the passage of a current and equally with the increase in overvoltage at a constant current strength under the effect of diffusing hydrogen.

We may conclude from the experimental data obtained, that an increase in the atomic hydrogen concentration on an electrode surface may both retard

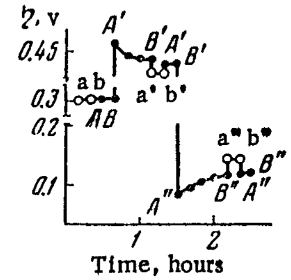

Fig. 2. The effect of diffusing hydrogen on the potential of iron poisoned with lead in 5 N NaOH at various polarizations. AB) $i = 8 \cdot 10^{-5}$ a/cm^2, $I = 0$; ab) $i = 8 \cdot 10^{-5}$ a/cm^2, $I = 2{,}2 \cdot 10^{-3}$ a/cm^2; A'B') $i = 8 \cdot 10^{-4}$ a/cm^2, $I = 0$; a'b') $i = 8 \cdot 10^{-4}$ a/cm^2, $I = 2{,}5 \cdot 10^{-3}$ a/cm^2; A"B") $i = 8 \cdot 10^{-6}$ a/cm^2, $I = 0$; a"b") $i = 8 \cdot 10^{-6}$ a/cm^2, $I = 2 \cdot 10^{-3}$ a/cm^2.

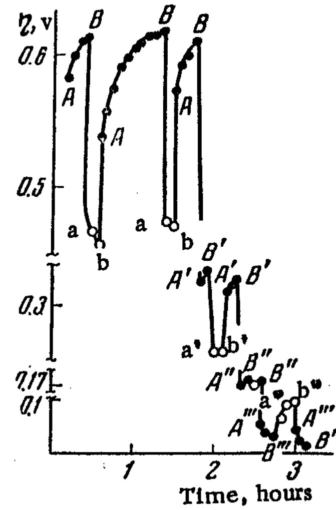

Fig. 3. The effect of diffusing hydrogen on the potential of iron poisoned with mercury in 1 N NaOH at various polarizations. AB) $i = 8 \cdot 10^{-4}$ a/cm^2, $I = 0$; ab) $i = 8 \cdot 10^{-4}$ a/cm^2, $I = 4 \cdot 10^{-3}$ a/cm^2; A'B') $i = 8 \cdot 10^{-6}$ a/cm^2, $I = 0$; a'b') $i = 8 \cdot 10^{-6}$ a/cm^2, $I = 4{,}8 \cdot 10^{-3}$ a/cm^2; A"B") $i = 8 \cdot 10^{-7}$ a/cm^2, $I = 0$; a"b") $i = 8 \cdot 10^{-7}$ a/cm^2, $I = 3 \cdot 10^{-3}$ a/cm^2; A'''B''') $i = 0{,}1 = 0$; a'''b''') $i = 0$, $I = 4{,}5 \cdot 10^{-3}$ a/cm^2.

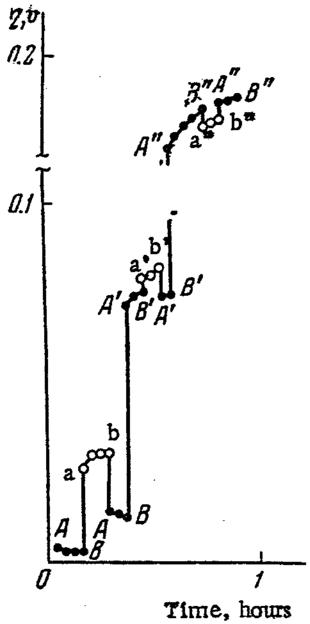

Fig. 4. The effect of diffusing hydrogen on the potential of nickel electrodeposited on iron in 1 N NaOH at various polarizations. AB) $i = 0$, $I = 0$; ab) $i = 0$, $I = 1.2 \cdot 10^{-3}$ a/cm²; A′B′) $i = 8 \cdot 10^{-6}$ a/cm², $I =$ a′b′) $i = 8 \cdot 10^{-6}$ a/cm², $I = 1.2 \cdot 10^{-3}$ a/cm²; A″B″) $i = 8 \cdot 10^{-5}$ a/cm², $I = 0$; a″b″) $i = 8 \cdot 10^{-5}$ a/cm², $I = 1.6 \cdot 10^{-5}$ a/cm².

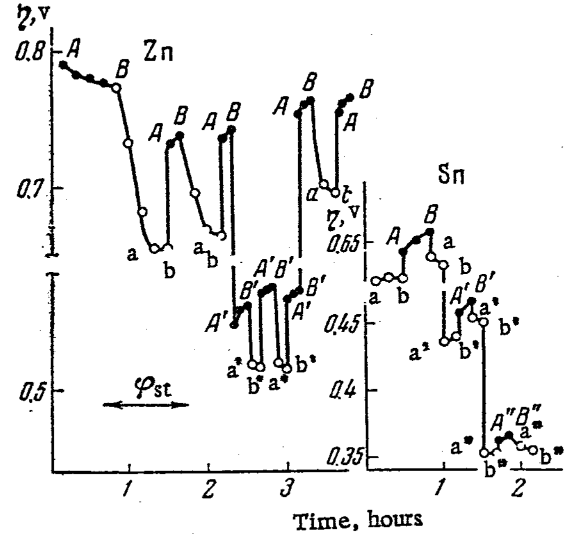

Fig. 5. The effect of diffusing hydrogen on the potentials of zinc and tin electrodeposited on iron in 1 N NaOH at various polarizations. AB) $i = \pm 8 \cdot 10^{-4}$ a/cm², $I = 0$; ab) $i = 8 \cdot 10^{-4}$ a/cm², $I = 1.6 \cdot 10^{-3}$ a/cm²; A′B′) $i = 8 \cdot 10^{-5}$ a/cm², $I = 0$; a′b′) $i = 8 \cdot 10^{-5}$ a/cm², $I = 1 \cdot 10^{-3}$ a/cm²; A″B″) $i = 2 \cdot 10^{-5}$ a/cm², $I = 0$; a″b″) $i = 2 \cdot 10^{-5}$ a/cm², $I = 7 \cdot 10^{-4}$ a/cm².

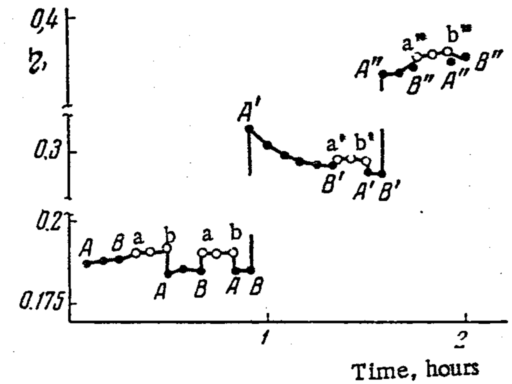

Fig. 6. The effect of diffusing hydrogen on the potential of copper deposited on iron in 1 N NaOH at various polarizations. AB) $i = 8 \cdot 10^{-5}$ a/cm², $I = 0$; ab) $i = 8 \cdot 10^{-5}$ a/cm², $I = 3.2 \cdot 10^{-3}$ a/cm²; A′B′) $i = 8 \cdot 10^{-4}$ a/cm², $I = 0$; a′b′) $i = 8 \cdot 10^{-4}$ a/cm², $I = 3.2 \cdot 10^{-3}$ a/cm²; A″B″) $i = 2.8 \cdot 10^{-3}$ a/cm², $I = 0$; a″b″) $i = 2.8 \cdot 10^{-3}$ a/cm², $I = 2.8 \cdot 10^{-3}$ a/cm².

and accelerate the electrochemical liberation of hydrogen [2], with the retarding effect of atomic hydrogen decreasing with increasing values of η while at high η atomic hydrogen accelerates the electrochemical liberation of hydrogen.

The increase in η under the effect of diffusing hydrogen, corresponding to the reducing properties of atomic hydrogen, is always connected with the slow elimination of adsorbed hydrogen from the electrode surface by recombination or electrochemical desorption. Furthermore, it is also connected with an increase in the ionization of the adsorbed hydrogen caused by an increase in its concentrations: $H_{ads} + OH^- \rightarrow e + H_2O$. We showed by special experiments that on pure iron the discharge rate in an alkali solution is in all cases of the same order as elimination [3].

With a slow discharge mechanism a decrease in η, corresponding to the oxidizing properties of atomic hydrogen, is always connected with an acceleration of electrochemical desorption, $H_{ads} + H_2O + e \rightarrow H_2 + OH^-$, and a retardation of the reverse reaction.

We determined quantitatively the fall in overvoltage $\Delta\eta$ in relation to the diffusion rate of atomic hydrogen on iron poisoned with mercury in 1 N NaOH at various values of η. In agreement with theory, it was established that at a constant ratio, I/i, between the diffusion rate of the hydrogen (I) and the strength of the current passing through the electrode (i), the fall in overvoltage at first increases with an increase in η, and then becomes constant. It is interesting to note that in this case $\Delta\eta$ was greater than would have been expected from theory [2]:

$$\Delta\eta_{\text{theor}} = b \lg \frac{i}{i - I},$$

considering that all the diffusing hydrogen participated in electrochemical desorption and that electrochemical desorption proceeded reversibly. We cannot as yet explain this interesting phenomenon.

LITERATURE CITED

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