# THE PROBLEM OF THE INCREASE IN HYDROGEN OVERPOTENTIAL ON IRON DURING CATHODIC POLARIZATION IN ALKALINE SOLUTIONS

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(UDC 541.13)

During the cathodic polarization of an iron electrode with a current of 20-200 mA/cm$^2$ in 1N solutions of LiOH, KOH, $(CH_3)_4OH$, an increase in the hydrogen overpotential takes place with time. It is caused by adsorption of impurities from the electrolyte solution which enable the penetration of hydrogen inside the metal.

In several investigations [1-3], devoted to the electrochemical behavior of the iron electrode in alkaline solutions, an increase in hydrogen overpotential was observed with time during polarization of the electrode at high current densities. It was proposed [1, 2] that this could be connected with the penetration of the electrode by hydrogen or by the formation of iron hydride. In some investigations [4, 5-9], the introduction of hydrogen atoms into the metal was observed only in the case when impurities were in the solution or in the iron. However, the formation of iron hydride during this was not observed [6, 7, 10]. It was considered [3, 11] at low temperatures that it was possible to form iron hydride or an alloy of the alkali metal with the surface atoms or iron. The formation of intermetallic compounds of the alkaline cation with the material or the cathode from Ag, Pb, Zn, Al was shown in other works [12, 13].* However, the possibility of the formation of an iron compound of the alkaline cation has not been indicated in the literature up to the present time.

Since in various investigations the reasons for the increase in hydrogen overpotential have been treated differently, we carried out the present work. We used the method of polarization curves, the method of the fall in potential after switching off the current using an electrometric amplifier U1-2 and an electron oscillograph ENO-1 and the method of measuring the capacity using alternating current (frequency 800 cps). The measurements were carried out on pure iron after zone melting and annealing in an atmosphere of hydrogen for 4-5 h at 600°C. The electrode was sealed into a glass tube under vacuum ($3\text{-}5 \cdot 10^5$ mm Hg). In individual experiments, the nonworking part of the surface of the electrode was covered with polystyrol. The measurement of potential was carried out relative to a mercury oxide electrode in the same solution at +20°C. A solution of LiOH was prepared by decomposition of a lithium amalgam in Teflon vessels, and a solution of $N(CH_3)_4OH$ from doubly recrystallized $N(CH_3)_4I$ salt by exchange reaction with freshly prepared silver oxide. The solution of caustic soda was prepared from chemically pure NaOH, the solution of caustic potash from chemically pure potassium hydroxide from Czechoslavakian production. Before the experiment, the electrode was polarized for 40-60 min with $i_c$ = 8-10 mA/cm$^2$. Special attention was paid to the purity of the solutions. This was carried out first on a platinum grid with $i_c$ = 4 mA/cm$^2$ for 4-5 days and afterwards on an iron electrode with $i_c$ = 100-150 mA/cm$^2$ for 4 h. Checking experiments were carried out in polystyrol vessels without contact of the solution with glass so that the latter could have no marked influence on the hydrogen overpotential during prolonged contact of the alkaline solution with glass.

## EXPERIMENTAL RESULTS

There was practically no increase in hydrogen overpotential with time in carefully purified 1N solutions of LiOH, NaOH, KOH and $N(CH_3)_4OH$ when the electrode was held for 1 h at $i_c$ = 100 mA/cm$^2$ (for inorganic alkalies

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*In the article by I. G. Bardina and Z. A. Iofa (Izv. vuzov, Khimiya i khimich. tekhnologiya, 5, No. 6, 916,(1962)) by error it was not indicated that the conclusion about the possibility of the influence of the formation of alloys of Zn with Na on the hydrogen overpotential was made on the basis of work which was carried out in the laboratory of B. N. Kabanov under his direction (see [12]).

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M. V. Lomonosov State University, Moscow. Translated from Élektrokhimiya, Vol. 2, No. 9, pp. 1000-1005, September, 1966. Original article submitted September 21, 1965.

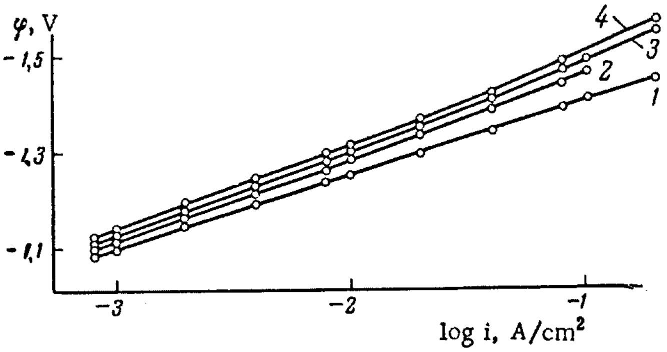

Fig. 1. Polarization curves recorded on zone melted iron in carefully purified 1N solutions of: 1) LiOH; 2) NaOH; 3) KOH; 4) $N(CH_3)_4OH$.

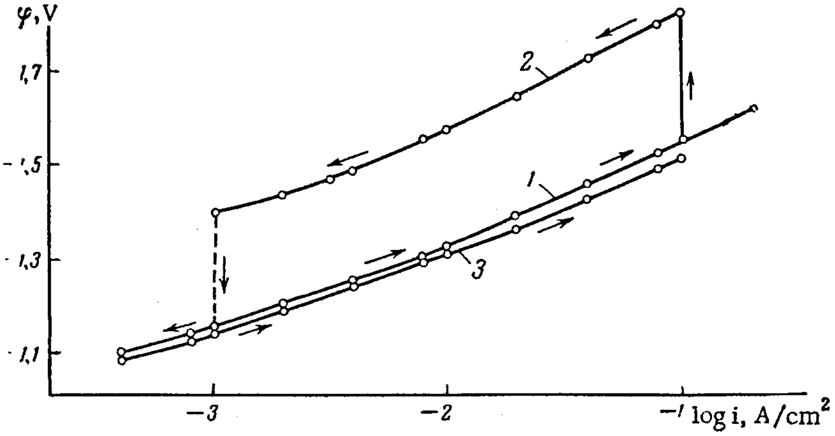

Fig. 2. Polarization curves recorded on iron in insufficiently purified 1N solution of NaOH: 1) without holding, 2) after holding the electrode at a current density of 100 mA/cm² for 90 min, 3) return path of curve 2.

the increase in overpotential $\Delta\eta$ = 10-15 mV, for $N(CH_3)_4OH$, $\Delta\eta$ = 15-18 mV after 1 h). Figure 1 gives polarization curves $\varphi - \log i$ for iron in the indicated solutions. As can be seen from the curves, the hydrogen overpotential increases in the order of cations $Li^+$, $Na^+$, $K^+$, $N(CH_3)_4^+$ i.e., with increase in size of cation which is in agreement with a previous investigation [14]. If the electrolyte was insufficiently purified (purification was carried out only on platinum with $i_c$ = 4 mA/cm²), then the overpotential with $i_c$ = 100 mA/cm² after an hour increases to 200-300 mV. During this, this increase mainly occurred after the first hour and with further polarization the increase in overpotential was strongly retarded and after two hours was practically stopped. After this, with decrease in $i_c$, the $\varphi - \log i$ curve in a definite region is placed above the initial one recorded without holding at high values of $i_c$ (see curve 2 Fig. 2); however with $i_c = 6 \cdot 10^{-4}$-$10^{-3}$ mA/cm², the cathodic potential rapidly decreased and the curve practically agreed with the initial curve 1. During polarization of the electrode with a lower current density (25 - 50 mA/cm²), there is also observed an increase in hydrogen overpotential with time and its limiting value reaches the value corresponding to curve 2.

Figure 3 gives curves for the fall in potential recorded in insufficiently purified 1N NaOH solution on iron. Before switching off the current the electrode was polarized cathodically at various current densities for 90 min, except for curve 7 which was recorded directly after the recording of curve 1 without preliminary prolonged cathodic polarization. On the curves, except for curves 6 and 7, there is a clear step at a potential of −1.4- −1.45 V. The current density $i_c$ of the preliminary polarization has little effect on the potential of the step and changes only the length of the step and therefore the quantity of electricity Q corresponding to the step; this is as follows:

| $i_c$, mA/cm² | 10 | 25 | 50 | 100 | 150 |
|---|---|---|---|---|---|
| $Q \cdot 10^2$, coulombs/cm | 1.5 | 4.9 | 5.8 | 7.0 | 8.2 |

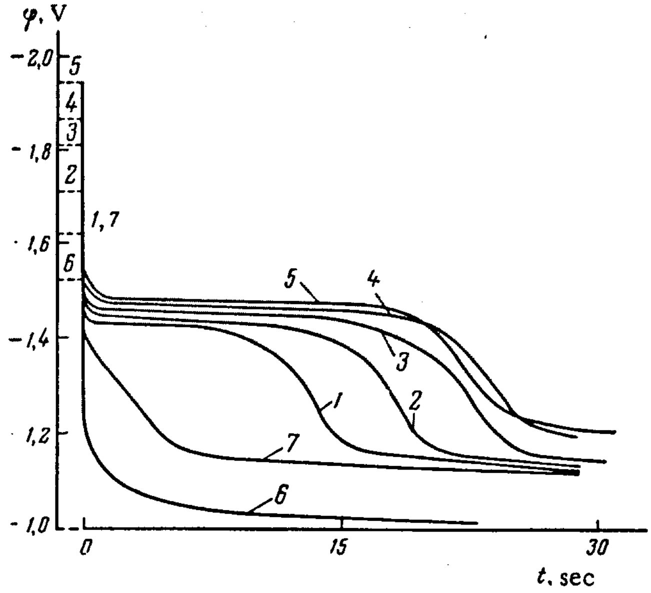

Fig. 3. Curves for the change in potential on iron in insufficiently pure (curves 1-5 and 7) 1N NaOH solution after cathodic polarization (mA/cm$^2$) for 90 min: 1) $i_C$= 10, 2) 25, 3) 50, 4) 100, 5) 150, 6) 100 (solution carefully purified), 7) recorded without polarization.

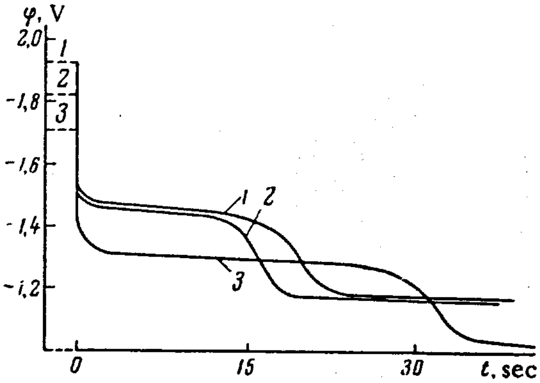

Fig. 4. Curves for the fall in potential on iron: 1N NaOH, 2) 1N LiOH, 3) 1N $N(CH_3)_4OH$ after polarization of the electrode at $i_C$ = 100 mA/cm$^2$ for 90 min.

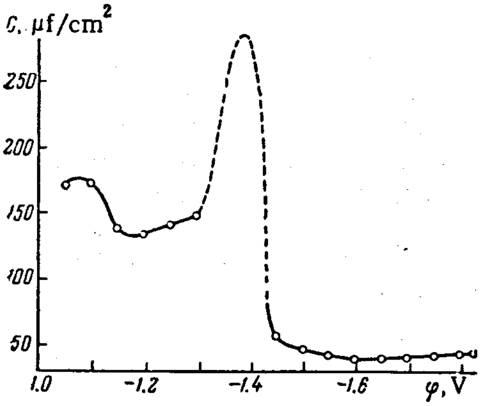

Fig. 5. Curve for the differential capacity on iron with increased hydrogen overpotential in 1N KOH (parallel system for resistance and capacity).

In carefully purified 1N solutions of LiOH, NaOH, KOH, $N(CH_3)_4OH$, when prolonged polarization at $i_C$ = 100 mA/cm$^2$ results only in a slight increase in overpotential, the latter after switching off the current very rapidly falls without a step (see curve 6, Fig. 3).

Comparing Figs. 2 and 3 it can be noted that the potential at the end of the step (−1.4 V) on the curves corresponds to the potential on the polarization curve at which a rapid decrease in overpotential for hydrogen begins. The step in the cathodic potential on the curves recorded in insufficiently purified 1N solutions of NaOH is at the same potential as in the case of 1N LiOH (Fig. 4). In 1N KOH the step is also observed at these potentials (−1.45 V). For $N(CH_3)_4OH$, it is at approximately 150 mV more positive (curve 3).

On the curve for the differential capacity Fig. 5, obtained on iron in insufficiently purified 1N KOH solution, a maximum in capacity is observed at a potential of −1.4 V (it is shown as a dotted line because the height of the peak depends on the rate of recording of the $C-\varphi$ curve). At more negative potential (−1.4-1.8 V) the capacity is relatively small at about 40 $\mu f/cm^2$ and is almost independent of potential. Figure 6 gives the curves of the differential capacity in carefully purified 1N solutions of KOH, LiOH, and $N(CH_3)_4OH$. The curves were calculated from an equivalent scheme proposed in ref. [15]. In the present case, C is the pseudo-capacity connected with adsorbed hydrogen on the surface of the electrode. On the $C-\varphi$ curves, both for an LiOH solution and also for KOH there is a maximum at a potential of −1.38- −1.35 V, corresponding to the potential of the end of the step on the $\varphi$-t curve; the maximum of the capacity in $N(CH_3)_4OH$ is displaced in the direction of more positive values of potential and corresponds to $\varphi$ = −1.26 V.

## DISCUSSION OF RESULTS

According to our data, an increase in hydrogen overpotential on iron with time results from two causes: precipitation of impurities found in the electrolyte solution on the surface of the iron and increase in concentration of absorbed hydrogen under the influence of the catalytic action of these impurities on the penetration of hydrogen into the depth of the metal. The poisoning of the active centers on the surface of the iron results in a decrease of

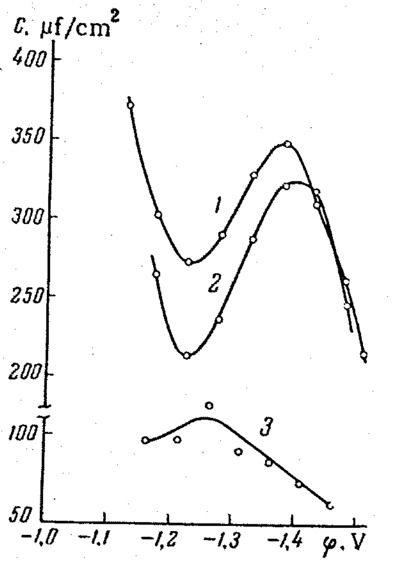

Fig. 6. Curves for differential capacity on iron: 1) 1N KOH, 2) 1N LiOH; 3) 1N $N(CH_3)_4OH$.

the concentration of atomic hydrogen on the surface of the metal and an increase of the hydrogen overpotential. Values of the differential capacity in the region of $\varphi = -1 - -1.4$ V obtained in a pure solution of alkali are 2-3 times higher than the values of the capacity in an unpurified solution (Figs. 5 and 6).

The following experiments also show the considerable influence of the purity of solution on the hydrogen overpotential. When 1 ml unpurified solution is added to 24 ml of pure 5 N KOH solution, an increase in overpotential with time occurs at a rate of 40-50 mV/h. Earlier, Past [16] noted the influence of the material of the cell on the increase of hydrogen overpotential with time at low polarization currents. We attempted to simulate possible impurities in 1N KOH solution. With this aim, $Na_3AsO_3$ up to $2.5 \cdot 10^{-5}$N concentration was added to the electrolyte. During this, an increase in hydrogen overpotential occurred of 100-120 mV/h and a step in the potential was observed on the curve at $\varphi = -1.4$ V. A similar phenomenon was noted in ref. [3] during the poisoning of the electrode with mercury. As is well known, arsenic and mercury are good promoters of hydrogen penetration. During the appearance of the surface of the electrode of these or some other materials which catalyze the introduction of hydrogen into the metal, an increase occurs in the concentration of absorbed hydrogen and an increase in its pressure in the surface layers of the metal. As a result of this, there is a displacement of the equilibrium potential of the hydrogen electrode in the direction of more negative values and the observed hydrogen overpotential increases. The latter was noted in the work of Frumkin and Aladzhalova [17] for the palladium electrode.

On iron, with an increase in hydrogen overpotential in the range of potentials from −1.85 to −1.5 V, the degree of coverage of the surface of the iron by hydrogen ($\theta$) changes little (Fig. 5). In this region of potentials the values of the capacity are close to the capacity of the double layer. At more positive potentials, $\theta$ decreases and the capacity increases. Only with strong changes in the degree of coverage with potential (in the region of the maximum on the curve of Fig. 5) does hydrogen begin to be removed from the metal, ionizing on the surface and causing a step in the potential on the curves. The potential of the step on the curves coincides with the potential of the maximum on the curves for differential capacity. The peak on the curve to a first approximation corresponds to the point of inflection on the adsorption isotherm for hydrogen on iron and reflects the maximum change in concentration of adsorbed hydrogen with potential [18]. The hydrogen cannot completely be removed from the metal in the time for recording the charge curve. This can be seen from Fig. 3 (curve 6 was recorded immediately after the fall in potential).

In 1N solution of $N(CH_3)_4OH$, the maximum change in $\theta$ is observed at a potential of −1.25 V. This potential corresponds to the end of the step on the potential curve. The lower values of capacity and $\theta$ in this case compared with the inorganic alkalies is obviously connected with the specific adsorption of the organic cation.

An increase in hydrogen overpotential on account of the formation of intermetallic compounds of the alkali metal with iron is not very probable. In the case of the formation of such compounds, we would expect to observe a dependence of the cathodic potential of the step on the curves on the nature of the alkaline cation and we should not observe a step at all in the case of the $N(CH_3)_4^+$ cation, because, in this case, it is difficult to propose the formation of a compound between iron and the organic cation. The methods used in this work, however, did not allow us to establish the formation of the phase compounds of iron with hydrogen (iron hydrides).

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