# EFFECT OF CARBON MONOXIDE ADSORPTION AND THE FORMATION OF IRON CARBIDES ON THE ELECTROCHEMICAL BEHAVIOR OF THE IRON ELECTRODE IN ALKALINE SOLUTIONS

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It has been shown in a number of papers [1-3] that carbon monoxide is chemisorbed on iron from acidic solution, increasing the supertension of hydrogen ion discharge reactions and the ionization of iron. The effect of carbon monoxide on iron in alkaline solutions has not been thoroughly studied. Little attention has been paid also to the effect of carbide and cementite formation on the behavior of an iron powder electrode in alkaline solution. This problem is important in battery manufacture, in connection with the reduction of iron oxides or the oxide mass with technical hydrogen containing carbon monoxide, or with carbon black.

Experiments have shown that in a 5N KOH solution saturated with carbon monoxide the supertension of hydrogen liberation is reduced by 15-20 mV in the case of solid iron and by ~ 30 mV in the case of an iron powder electrode. A small reduction is apparently related to a small adsorption of carbon monoxide, which in turn is caused by the fact that, in the adsorption, the competing effect not only of water molecules but also of $OH^-$ ion adsorption must be overcome. A similar effect is noticed with a ruthenium electrode [4].

At elevated temperatures carbon monoxide forms iron carbides. When heated for 5-6 h at 600°C in a carbon monoxide atmosphere, iron powder is completely converted to cementite ($Fe_3C$). The rate of this reaction increases with temperature [5, 6].

Potentiostatic curves were taken on iron powder electrodes, as well as curves of the differential capacity of the double layer, and charge-discharge curves. The temperature of the experiments was 25° ± 1°; the potentials are given with reference to the mercury-oxide electrode in the same alkaline solution. The iron powder was obtained by reduction of iron oxide at 600° in a pure hydrogen atmosphere. Electrode I was obtained by pressing this powder onto an iron conductor. Electrodes II were prepared from pure iron powder, which was tempered 3 h at 800° in a mixture of $CO + H_2$ (1 : 4) and then placed into iron lamellas.*

The different behavior of electrodes I and II can be seen from the potentiodynamic curves in Fig. 1. Table 1 gives the peak potentials of anodic and cathodic potential scans on the potentiodynamic curves (in mV), current density maxima on i, $\varphi$-curves (in mA), capacities of reaction yield Q (in C/g), and the hydrogen liberation potentials $\varphi_H$ at $i = 8.6$ mA/cm$^2$ (extrapolated for curve (2) in Fig. 1).

For the pure iron electrode (electrode I) the first anodic peak appears at $\varphi_1 = 820$ mV, corresponding to the process $Fe \rightarrow Fe^{2+}$; this peak is twice as high and the yield of this reaction is twice that of the second anodic process, corresponding to the reaction $Fe^{2+} \rightarrow Fe^{3+}$. On the other hand, in the case of the iron powder electrode tempered in a carbon monoxide atmosphere, the first peak is significantly reduced and the second increased, and the poten-

TABLE 1

| Electrode | $\varphi_1$ | $i_1$ | $Q_1$ | $\varphi_2$ | $i_2$ | $Q_2$ | $\varphi_3$ | $i_3$ | $Q_3$ | $\varphi_4$ | $i_4$ | $Q_4$ | $\varphi_H$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | –820 | 70 | 53 | –600 | 40 | 28 | –1010 | 43 | 27 | –1120 | 10 | — | 1200 |
| II | –820 | 14 | 6,12 | –480 | 45 | 54 | –980 | 19 | 4,1 | –1150 | 49 | 4,3 | –1140 |

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* Iron powder tempered in a carbon monoxide atmosphere cannot be pressed.

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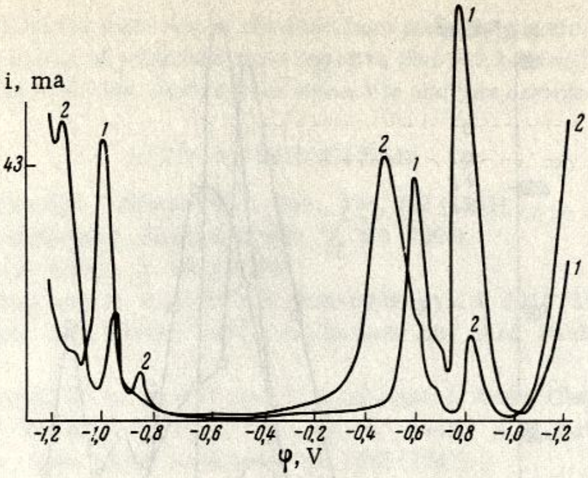

Fig. 1. Potentiodynamic i, $\varphi$-curves (anodic curves from $-1.2$ to $-0.2$ V from right to left, and cathodic curves from $-0.2$ to $-1.2$ V) in 5N KOH: (1) on a pure iron powder electrode, cathodic polarization 18 h, i = 10 mA/cm$^2$ (electrode I); (2) on an iron powder electrode tempered in a mixture of CO + $H_2$ (1 : 4), cathodic polarization 1 h, i = 10 mA/cm$^2$ (electrode II), potential scanning rate 0.5 V/h.

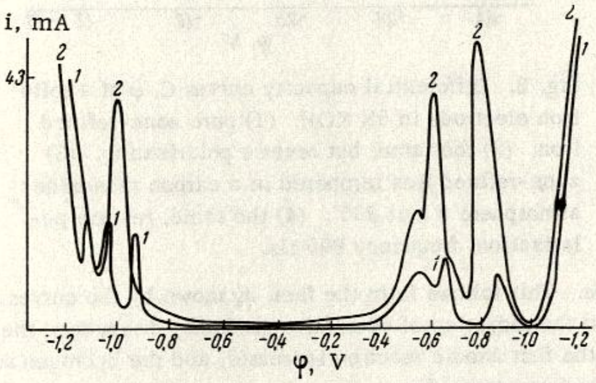

Fig. 2. Potentiodynamic i, $\varphi$-curves in 5N KOH: (1) after one charge-discharge cycle, cathodic polarization 18 h, i = 10 mA/cm$^2$, (2) after nine charge-discharge cycles on electrode II (see Fig. 1), cathodic polarization 44 h, i = 10 mA/cm$^2$.

tial of the latter is shifted for 120 mV towards more positive values. These peculiarities explain the observation that, in the discharge of the iron powder electrode tempered in a carbon-monoxide containing atmosphere, in the first cycles the technological capacity of the first process is very small, and that the technological capacity of the second anodic process is significantly increased. In the cathodic potential region the i, $\varphi$-curve for electrode II shows two maxima as in the case of electrode I, which correspond to the reactions $Fe^{3+} \rightarrow Fe^{2+}$ and $Fe^{2+} \rightarrow Fe$, respectively. In the case of electrode II an additional inflection of the curve can be seen in the anodic part before $\varphi_2$ at $\varphi = -620$ mV and another weak maximum in the cathodic scan at $\varphi = -860$ mV, corresponding apparently to the reduction of iron carbides and cementite. The reduction of the hydrogen supertension by 60 mV in the case of electrode II and an increase of the supertension of reaction $Fe^{2+} \rightarrow Fe$ by 30 mV leads to a low current yield of the latter reaction at electrode charge and to a preferential evolution of hydrogen. In the case of iron powder electrodes tempered in a carbon monoxide atmosphere, consisting entirely of $Fe_3C$, the peculiarities indicated above are more strongly pronounced.

The i, $\varphi$-curves for electrode II after several charge-discharge cycles are shown on Fig. 2. From the curves it can be seen that a deep discharge leads to breakdown on the cementite and to gradual restoration of the normal

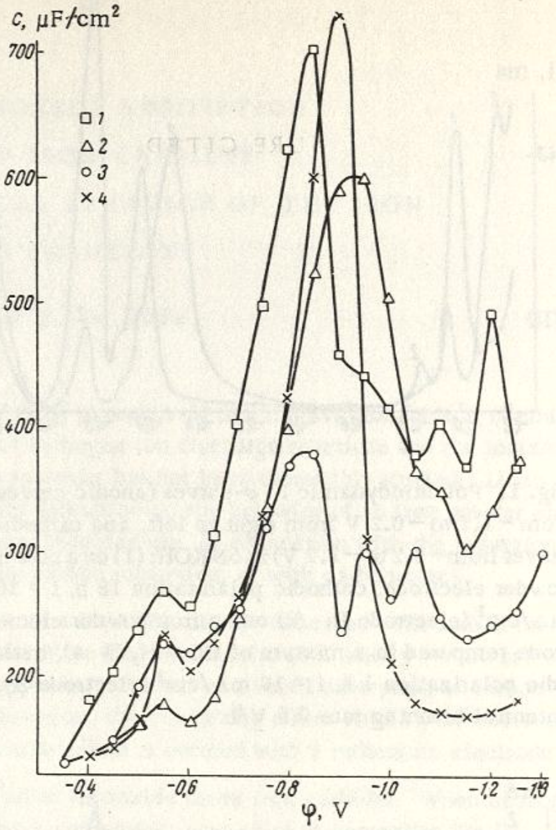

Fig. 3. Differential capacity curves C, $\varphi$ of a solid iron electrode in 5N KOH: (1) pure zone-refined iron; (2) the same, but reverse polarization; (3) zone-refined iron tempered in a carbon monoxide atmosphere 3 h at 800°; (4) the same, reverse polarization, frequency 800 Hz.

properties of the iron electrode. This follows from the fact, as shown by the curves in Fig. 2, that with cycling the cathodic peak corresponding to the reduction of cementite gradually disappears, the peak of the second anodic reaction decreases, the peak of the first anodic reaction increases, and the hydrogen supertension increases to a value approaching the value of a pure iron electrode.

The curves on Fig. 3 represent the differential capacity of the double layer, taken on a pure zone-refined iron wire (curves (1) and (2)), and on a wire tempered in a carbon monoxide atmosphere (curves (3) and (4)). Curves (1) and (2) show two peaks in the cathodic potential region, corresponding to the different bond energies between the adsorbed hydrogen and the iron: the higher peak in the anodic region is connected with the adsorption of $OH^-$-ions and with the reaction $Fe \rightarrow Fe^{2+}$ taking place; the lower peak corresponds to the reaction $Fe^{2+} \rightarrow Fe^{3+}$. The height of this peak is strongly reduced after formation of a passive film, which appears during the first anodic process and which interrupts the course of this process [7].

In reverse polarization from anodic to cathodic potentials (curve (2) in Fig. 3) the capacity is somewhat reduced, the higher peak is shifted by 80 mV towards the negative side, and, because of the preservation of the passivating film, the peaks in the cathodic region completely disappear.

The capacity of the second electrode (curve (3)) is reduced over the whole course of the normal polarization curve. The peaks in the cathodic region, corresponding to different energies of the hydrogen-metal bond, disappear. Two new peaks appear at $\varphi = -0.950$ V and $-1.050$ V, the nature of which is not yet explained. The reverse polarization in the anodic region coincides with the direct polarization; however, the peak corresponding to

$$Fe^{2+} \rightarrow Fe$$

is considerably higher. This is related to the oxidation of carbides in anodic polarization and the formation of an additional ferrous-oxide layer on the surface. The capacity in the cathodic potential region is strongly reduced because of the absence of adsorbed hydrogen.

The C, $\varphi$-curves shown confirm the basic results obtained from potentiodynamic curves. They also confirm that in anodic polarization in the region of potentials more negative than −0.2 V, with reference to the mercury-oxide electrode in the same alkaline solution, oxidation of cementite and iron carbides takes place.

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