THE MECHANISM OF ACTIVATION OF AN IRON ELECTRODE BY SMALL ADDITIONS OF NICKEL OXIDES

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It is well known that an iron electrode tends to become passive in alkaline solutions. This tendency is very pronounced when the metal is quite free from impurities, and shows itself, not only by restricting the anodic dissolution of iron, but also by restricting the extent of the anodic process in repeated cycles of cathodic and anodic polarization. Certain additives have a marked effect on the electrochemical behavior of the iron electrode. Some of these (oxides of Mn, Cr, Ca, Al, Ti, V, and others) increase the anodic passivation, while others prevent rapid onset of passivation and stabilize the capacity for anodic dissolution in repeated cycles of cathodic and anodic polarization. Additives of this second type include sulfur, oxides of As, Sb, Ni, Cu, and others. The action of some of these additives has been specially investigated, and, as a result of this, the mechanism of the poisoning of the iron electrode by manganese and calcium, for instance, is more or less understood. According to Lyzlov [1], the action of manganese and calcium oxides on the iron electrode is due to the close interaction of iron hydroxide with the additive. The hydroxides of iron and of the additives form isomorphous mixtures which are not subject to cathodic reduction, so that an iron electrode, which has been anodically oxidized in the presence of these additives, cannot be converted back to its original active state by cathodic polarization, and thus loses its electrochemical activity. However, the mechanisms of the effects of most of the above mentioned additives, particularly those of the activating type, have not been explained.

This paper deals with an investigation of the activation of the iron electrode in alkaline solution by small amounts of hydrated nickel oxide. We made a special study of an iron powder electrode, which, in its initial state, contained 6.5% of Fe metal, 55.7% of Fe_3O_4, and 37.8% of FeO. This material was prepared by reduction with hydrogen, at 600°, of iron oxide obtained by decomposing $FeSO_4$ or $Fe(NO_3)_3$ at 700° and washing out any residual undecomposed salt. The $FeSO_4$ and $Fe(NO_3)_3$ were made from pure carbonyl iron and chemically pure acids. Spectrographic analysis showed that the carbonyl iron contained traces of Ni, Ca, Ti, Cr, Mo, and Si, but was free from Mn, Al, Mg, V, W, and S. The nickel was added to the iron as a saturated solution of $NiSO_4$, which was carefully mixed with the iron powder. The electrode was made up by compressing the iron powder in an armco cylinder. $Ni(OH)_2$ was precipitated on the iron particles when the electrode was immersed in NaOH solution. Electrochemical measurements were carried out in a glass cell with separate anodic and cathodic compartments, and the electrode under investigation was placed between two auxiliary nickel/nickel oxide electrodes used for producing polarization from an external current source. The cell was connected to a gas-measuring buret. The electrolyte was 5 N NaOH (chemically pure). The potential was measured with respect to a mercury/mercury oxide electrode in the same alkaline electrolyte by a compensation method.

HYDROGEN OVERVOLTAGE

The hydrogen overvoltage at iron electrodes, with and without added nickel, was measured after prolonged cathodic polarization (not less than 12 hours) at a current density of $1.2 \cdot 10^{-2}$ amp/cm^2 of apparent electrode surface ($4.3 \cdot 10^{-2}$ amp/g Fe). In some experiments, before measurement of the hydrogen overvoltage, the extent of cathodic reduction of the electrode was checked by measuring the hydrogen evolution rate at the given current. Fig. 1 shows the effects of adding different amounts of $Ni(OH)_2$ on the hydrogen overvoltage at an iron powder electrode in 5 N NaOH. A small reduction in hydrogen overvoltage under the influence of $Ni(OH)_2$ was observed at high current densities.

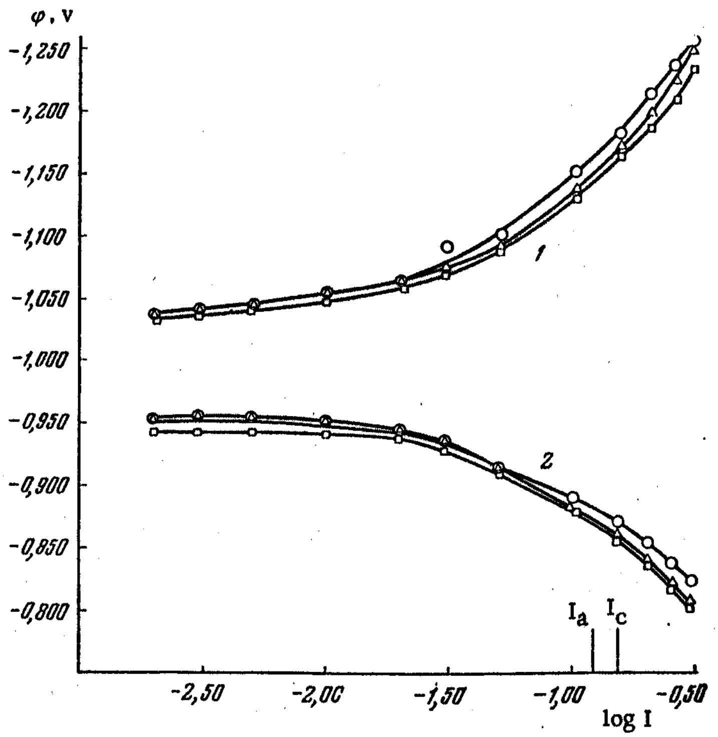

Fig. 1. Hydrogen overvoltage at iron electrode, 1) for hydrogen evolution and 2) for the first anode process: ○ — ○ without additive; △ — △ with 0.3% Ni added; □ — □ with 1% Ni added. I is in amp.

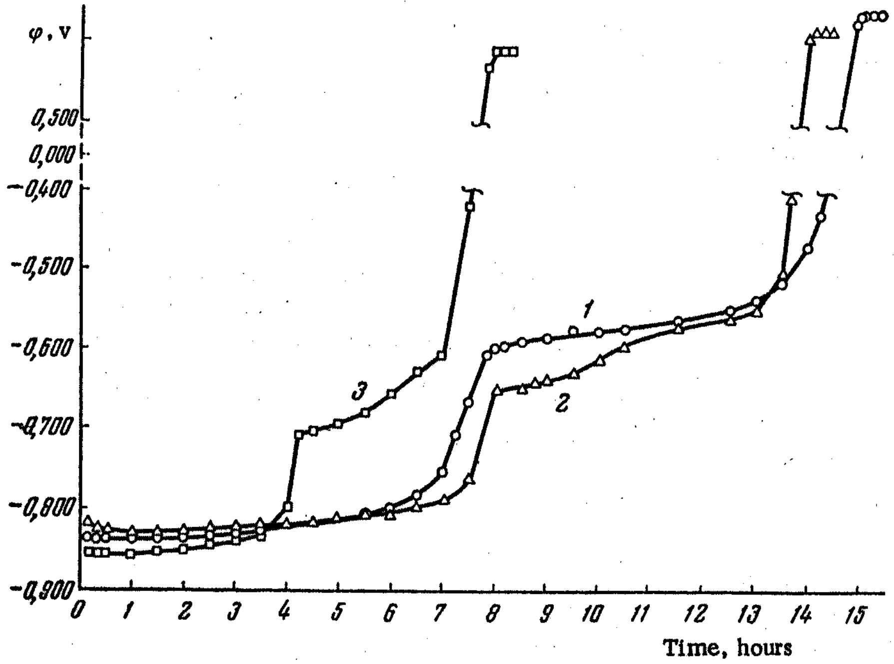

Fig. 2. Heavy discharge of iron electrode. Cycle 5. 1) Without additive; 2) with 0.3% Ni added; 3) with 1% Ni added.

OVERVOLTAGE FOR ANODIC PROCESSES AT IRON

The overvoltage for the anodic dissolution of iron (anodic process I) was little affected by the presence of nickel oxides (Fig. 1); but the potential for the further oxidation to ferric oxide (anodic process II) of the $Fe(OH)_2$, formed by process I, was greatly affected by the presence of nickel oxides in the electrode (Fig. 2). The presence of nickel oxides considerably facilitated this second process. For instance, with an anode current density of $3.5 \cdot 10^{-2}$ amp/ g Fe, the process $Fe^{2+} \rightarrow Fe^{3+}$ occurred at −0.6 to −0.54 v relative to a mercury/ mercury oxide electrode in the absence of Ni, at −0.65 to −0.55 v with 0.3% Ni as $Ni(OH)_2$, and at −0.70 to −0.60 v with 1% Ni. The oxygen evolution potential, after heavy anodic oxidation of the iron electrode, was also considerably reduced by the presence of nickel oxides and, at the above current density, was 0.643 v in the absence of Ni, 0.615 v with 0.3% Ni, and 0.581 v with 1% Ni (Fig. 2).

OVERVOLTAGE FOR THE CATHODIC REDUCTION OF IRON OXIDES

Addition of nickel oxides had a particularly marked effect on the overvoltage for reduction of anodically oxidized iron. A comparison of the reduction curves shown in Fig. 3 indicates that iron oxides, formed on iron by anodic polarization in the presence of $Ni(OH)_2$, were reduced at a considerably lower overvoltage. It is interesting to note that the presence of Ni did not facilitate primary cathodic reduction of the initial iron oxides, on which the $Ni(OH)_2$ was deposited as described above and was distributed mechanically. Only after further operation of the electrode, when the $Fe(OH)_2$ formed by anodic dissolution of metallic iron had been able to react intimately with the $Ni(OH)_2$ present on the electrode, was there any marked facilitation of cathodic reduction of the oxides formed. The effects of $Ni(OH)_2$ on hydrogen evolution, reduction of iron oxides, and anodic dissolution of iron, as described above, correspond to the effects of additives in activating an iron electrode, as widely used in practice. In fact, owing to the considerable reduction in overvoltage for cathodic reduction of iron oxides under the influence of added $Ni(OH)_2$, and owing to the absence of any marked effect by the latter on the hydrogen overvoltage, the charging of an iron electrode in the presence of $Ni(OH)_2$ occurred effectively (Fig. 4) at a less negative potential (Fig. 5). The increase in the iron content of the electrode, produced by reduction to the metallic state during charging, increased the technological capacity of the electrode obtained by oxidation of the metal*.

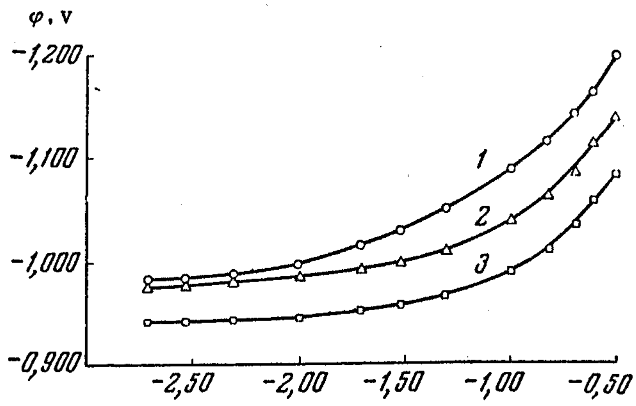

Fig. 3. Overvoltage for the cathodic reduction of oxides at an iron electrode. Cycles 12 - 13. 1) Without additive; 2) with 0.3% Ni added; 3) with 1% Ni added. I is in amp.

Thus, the used of added $Ni(OH)_2$ considerably speeds up, in practice, the so called forming process of the iron electrode of an alkaline accumulator.

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*It should be noted, however, that the metallic iron content of the charged electrode does not in itself provide a unique value for the technological capacity which can be obtained in the following anodic process, since the kinetics of the anodic passivation of metallic iron depends on a number of factors, which will be considered separately.

DISCUSSION OF RESULTS

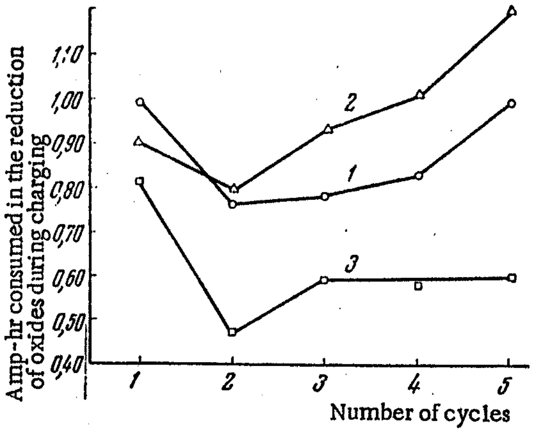

Fig. 4. Current consumption in forming an iron electrode by charging: 1) without additive; 2) with 0.3% Ni added; 3) with 1% Ni added.

The phenomena associated with the addition of $Ni(OH)_2$ to an iron electrode, as described above, indicate that the action of the nickel is effective when the electrode is in the oxidized state and, consequently, when the main role in the processes occurring on it is played by the iron oxides which are forming. Indeed, the most pronounced effects were observed in the cathodic reduction and subsequent anodic oxidation of the $Fe(OH)_2$ formed, whereas there was no significant change in the anodic dissolution of metallic iron and the liberation of hydrogen at metallic iron. It is particularly interesting that, contrary to the natural behavior of a pure iron electrode on standing in alkali without current, the iron electrode containing $Ni(OH)_2$ evolved hydrogen more quickly in the discharged state than when charged (Fig. 6).

All these results induced us to turn our attention to the system $Fe(OH)_2 - Ni(OH)_2$. It is well known that these substances form a series of solid solutions, as would be expected from their similar crystalline structures and almost identical lattice parameters [2]. We prepared a series of mixed $Fe(OH)_2 - Ni(OH)_2$ deposits by adding alkali to mixed solutions of the sulfates of these metals, with different Ni/ Fe ratios (from 0.3 to 10% Ni); we also added $FeSO_4$ solution to NaOH solution containing previously precipitated $Ni(OH)_2$ in suspension. In this latter case, precipitation of $Fe(OH)_2$ was carried out in the presence of previously formed $Ni(OH)_2$ particles, so that the conditions were very similar to those for the anodic formation of $Fe(OH)_2$ on an electrode containing added $Ni(OH)_2$.

X-ray investigation of these precipitates* showed that a more disperse $Fe(OH)_2$ deposit was obtained in the presence of $Ni(OH)_2$, and that the degree of dispersion was greater the larger the amount of additive. There was also some distortion in the presence of small amounts of additive, and there was some change in the $Fe(OH)_2$ lattice parameters. The oxidation products from these precipitates, after aging in the mother liquor, were δ - Fe_2O_3 and α-FeOOH, and these also showed higher dispersion in the presence of $Ni(OH)_2$. Another change in the properties of $Fe(OH)_2$, under the influence of added $Ni(OH)_2$, was that it acquired the ability to decompose water at a considerable rate, with evolution of hydrogen. The volume of gas evolved was higher the greater the amount of $Ni(OH)_2$ added (over the range investigated – up to 10% Ni). When air was admitted, gas evolution

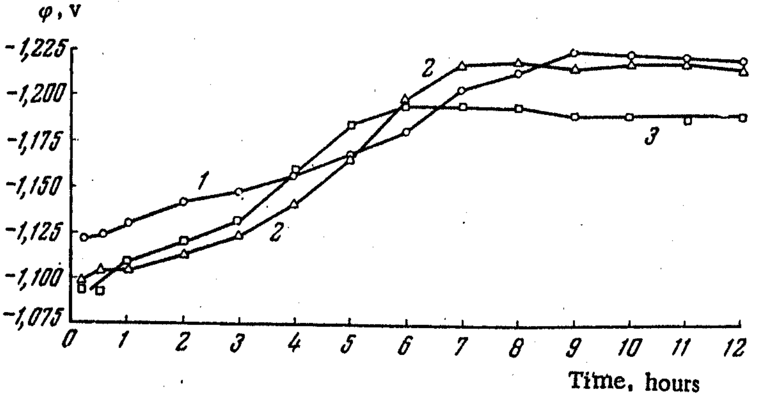

Fig. 5. Potential change during charging of an iron electrode. Cycles 1 - 13. 1) Without additive; 2) with 0.3% Ni added; 3) with 1% Ni added.

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* The X-ray investigation was carried out by N. N. Fedorova.

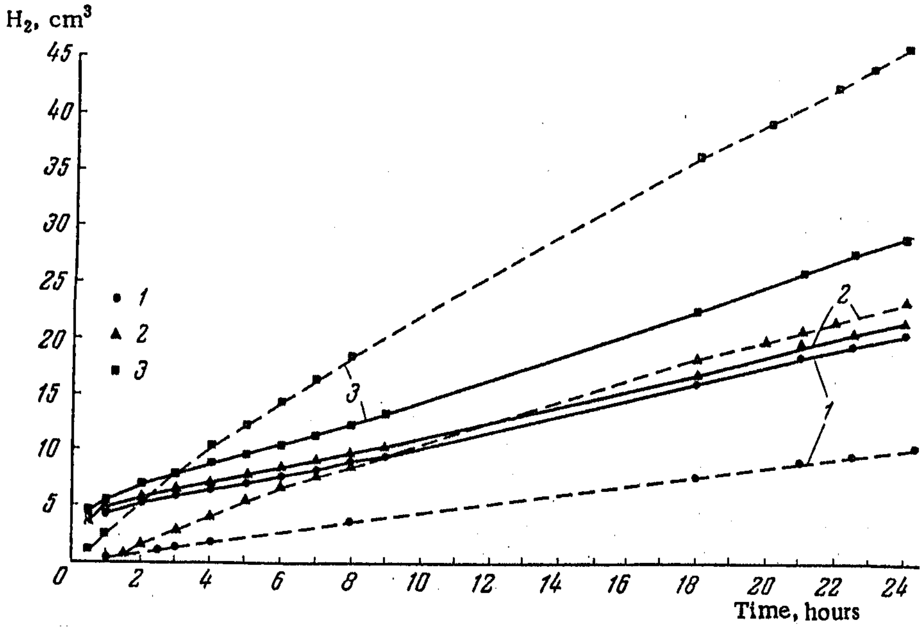

Fig. 6. Evolution of hydrogen at an iron electrode without current, in the discharged (———) and charged (------) states. 1) *without additive;* 2) *with* 0.3 % Ni added; 3) with 1% Ni added.

was observed even with small amounts of $Ni(OH)_2$ (0.3% Ni). This evidently fits in with the previous observation that an iron electrode containing $Ni(OH)_2$ evolved more hydrogen in the discharged state than when charged.

Thus,our experimental results indicate that the activation of an iron electrode by $Ni(OH)_2$ is mainly a result of the changes which occur in iron oxides formed in the presence of $Ni(OH)_2$, as the result of close interaction between the two materials. The $Fe(OH)_2$, formed under these conditions by anodic oxidation of metallic iron, is more highly dispersed, suffers some distortion of structure, and is more active with respect to electrochemical reduction and oxidation.

LITERATURE CITED

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2. G. Natta., Gazz. chim. ital. 58, 344, 597 (1928).