

STUDY OF IRON OXIDE ELECTRODES IN AN ALKALINE ELECTROLYTE

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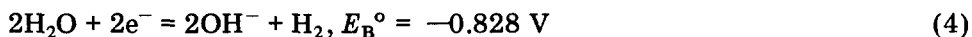
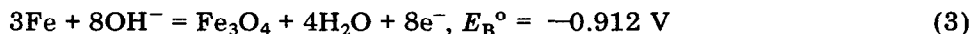
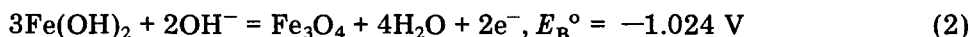
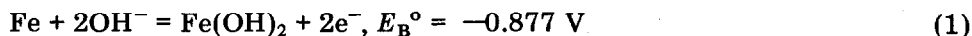
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Summary

Electrodes were prepared by pressing a mixture of iron oxides with a conducting component and a plastic binder, and their electrochemical behaviour in aqueous KOH solution was studied with regard to the influence of doping agents, impurities, and other factors. The discharge capacity of the electrodes was substantially enhanced by adding a conducting component such as acetylene black, and decreased when impurities in the iron oxides, mainly manganese, were present. Of the doping agents, sulphide ions proved most effective in increasing the discharge capacity.

Introduction

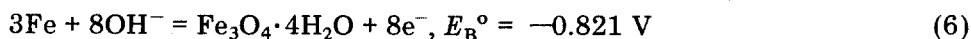
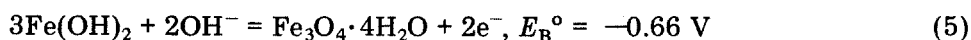
The electrochemical reduction of iron oxides in strongly alkaline medium is of practical significance for alkaline Ni-Fe accumulators. The main reactions of interest and their standard potentials [1 - 3] are:



Here, the values of E_{B}° correspond to systems with a unit activity of OH^- ions; they suggest that (a) the iron electrode is unstable in alkaline solution, (b) magnetite behaves as a very strong (*i.e.*, stable) complex compound which is very difficult to reduce in aqueous medium to $\text{Fe}(\text{OH})_2$ or Fe. On the other hand, there is general agreement in the relevant literature that magnetite is one of the products of the discharge reaction that can easily be reduced back to iron. This was elucidated by Dibrov *et al.* [4], who assumed that electrochemical oxidation of iron in strongly alkaline medium leads to

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hydrated magnetite, $\text{Fe}_3\text{O}_4 \cdot 4\text{H}_2\text{O}$, *i.e.*, reactions (2) and (3) should be written as



The standard free energy (of formation) for the hydrated magnetite is $\Delta G^\circ = -1894 \text{ kJ mol}^{-1}$, which is less in absolute value than the sum of the standard free energies for Fe_3O_4 , $-1014 \text{ kJ mol}^{-1}$, and $4\text{H}_2\text{O}$, $948.8 \text{ kJ mol}^{-1}$. Hence, hydrated magnetite is less stable than natural magnetite: it can be reduced well before the evolution of hydrogen.

Nevertheless, owing to its good electronic conductivity, chemical stability, and natural abundance, natural magnetite has been the subject of extensive electrochemical research. The experimental findings [5 - 7] substantiated the theoretical expectation that only a fraction of the cathodic reduction current can be utilized for reduction of natural magnetite in NaOH solutions, the remainder being consumed in the evolution of hydrogen; elevated temperatures (70 - 90 °C) were found to facilitate the reduction. Dugleux *et al.* [8, 9] discovered that a slight reduction of synthetic magnetite, *e.g.*, by hydrogen at elevated temperatures (250 - 600 °C) considerably facilitates its electrochemical reduction, and that its electrochemical behaviour depends on the impurity content and mode of preparation. Practical studies were carried out, *e.g.*, by Flerov *et al.* [10, 11], who made pressed electrodes from the product of partial reduction of Fe(III) oxide with carbon black: after several cycles the utilization of iron was near to 20% and increased after the addition of powdered Cu or graphite, but not after the addition of nickel flakes. Similar electrodes prepared by Teplinskaya *et al.* [12] from pure synthetic magnetite had no significant capacity. The use of pulverized and purified magnetite ore as active material for iron electrodes was proposed by Sentemova *et al.* [13], but no details about admixtures were given. Novakovskii *et al.* [14] pointed out the difference between magnetite formed in aqueous medium of NaOH + LiOH in iron accumulator electrodes, which is easily reducible according to



and natural magnetite or that prepared at elevated temperatures, which is difficult to reduce electrochemically. Magnetite of unspecified origin was used by Soviet authors [15, 16] to prepare pressed or rolled accumulator electrodes bonded with polyethylene. The common electrode material referred to by some authors as "iron by hydrogen" [17] is essentially a mixture of magnetite and iron.

The higher oxide of iron, Fe_2O_3 , seems less suitable as active material: its electrochemical reduction in alkaline medium proceeds sluggishly at a low current efficiency, since it is a nonconductor and its reduction requires either direct contact with a metal electrode or dissolution in the form of FeO_2^- anions and their transport to the electrode. The contact can be improved by powdered graphite [18]; the pure oxide may be reduced to

some extent in strongly alkaline medium [18, 20], in which it is slightly soluble, but not in weakly alkaline or neutral [8, 18, 19] solutions.

The electrochemical behaviour of iron oxides is strongly influenced by impurities, of which Mn is the most common. Thus, the presence of as little as several hundredths of 1% of Mn, Ca, Mg, Al, Ti, Cr, or V in the iron-active material may render the iron electrode practically useless [21] owing to increased overpotential for reduction of iron oxides and decreased overpotential for evolution of hydrogen.

The effect of Mn was studied in detail: it enhances the anodic dissolution of Fe to $\text{Fe}(\text{OH})_2$, but considerably hinders the back reduction, whereas the hydrogen overpotential is not affected [22]. Normal functioning of the iron electrode mostly requires the addition of S^{2-} ions to the electrolyte (or FeS to the active material), which are irreversibly adsorbed on iron, accelerate its anodic dissolution, and thus increase the discharge capacity; their absence causes the iron electrode to passivate [23 - 25]. Other additives were tested with the aim of lowering the self-discharge and/or increasing the charging efficiency of the iron electrode [26 - 28]; LiOH permits the concentration of KOH to be reduced without impairing the electrode capacity [29] and improves its cycle life [30].

The present work is devoted to the study of various iron oxides and originates from the possibility of their use as electrode materials in alkaline electrolyte.

Experimental

Materials

The following materials were used for the preparation of laboratory iron oxide electrodes:

(a) So-called polishing black (VCHZ Synthesia, Pardubice-Semtin, CSSR), which is a by-product of the chemical reduction of nitrobenzene with coarsely powdered iron; its chemical composition can be written as $\text{FeO} \cdot n\text{Fe}_2\text{O}_3$, where $n \approx 20$.

(b) Iron oxide pigments (Moravian Chemical Works, Pterov, CSSR) "fepren B-91" (Fe_3O_4 , black), "fepren TP-303" (Fe_2O_3 , red-brown), and "black 9/P" (Fe_3O_4).

(c) Commercial $\alpha\text{-Fe}_2\text{O}_3$ (Lachema, Brno).

(d) Commercial $\alpha\text{-Fe}_2\text{O}_3$ "Bayferrox WF 1352" (Bayer, Leverkusen).

(e) Synthetic Fe_3O_4 (Lachema, Bohumin) prepared by precipitation of a solution of FeSO_4 with NH_3 and oxidation with NH_4NO_3 at 95 - 100 °C; approximate composition $1.2 \text{Fe}_2\text{O}_3 \cdot \text{FeO}$.

The impurity contents are given in Table 1. Poly(tetrafluoroethylene) "Fluon CD-1" (ICI, Great Britain) was used as binder, and acetylene black P 1042 (VEB Stickstoffwerke Piesteritz, GDR) or powdered graphite (GDR) was used as conducting component.

TABLE 1

Impurity levels in iron oxides used as active materials, determined by spectrographic analysis and, in parentheses, from chemical analysis

Substance	Mn (%)	Mg (%)	Al (%)	Ti (%)	Other (0.01 - 0.1%)
Polish. black	0.1 - 1 (0.19)	0.01	0.01 - 0.1	not found	-
Fepren B-91	0.01 - 0.1 (0.03)	0.001 - 0.01	not found	not found	Na
Bayferrox	0.01 - 0.1 (0.01)	0.001 - 0.01	0.1 - 1	0.001 - 0.01	Zn*
Magnetite 9/P	0.01 - 0.1	0.001 - 0.01	0.01 - 0.1	0.01 - 0.1	Ca, Cu
α -Fe ₂ O ₃ (Lachema)	0.1	0.001 - 0.01	0.1	not found	Ba, Ca, Cr, Cu, Mo, Pb, Sn, W, Zn**
Fe ₃ O ₄ (Lachema)	0.1 - 1	0.01 - 0.1	0.001 - 0.01	0.001 - 0.01	Ca, Na, Si, Zn
Fepren TP-303	0.01 - 0.1	0.001 - 0.01	not found	0.1 - 1	Na

*0.1 - 1% Na.

**About 1% Na and K.

Electrode preparation

Laboratory electrodes were prepared by pressing the electrode mix at 100 MPa in the form of a disc of 31 mm dia. and about 2 mm thickness, wrapped in a fine nickel gauze (0.1 mm mesh size). The electrode mix contained 2.8 g of the active material (Fe oxide), 0.33 g of powdered PTFE and 0.18 g of acetylene black (unless otherwise indicated). The electrodes had nickel gauze (1.3 mm mesh size) current leads on either side; the counter-electrode was a nickel foil folded so as to surround the test electrode, the separator was a perforated and corrugated poly(vinylchloride) foil, the electrolyte was 7 M KOH (density 1.3 g cm^{-3}), and the reference electrode was Hg/HgO filled with 4.5 M KOH (density 1.2 g cm^{-3}). The only additive used in the electrolyte was about 0.02 M Na_2S (added usually before the first cycle); additives (doping agents) in the active material were as given and discussed below.

Some electrodes were made with the addition of Teflonized acetylene black [31] containing 35 - 75% PTFE rather than with separate additions of acetylene black and PTFE. The optimum proportion was 55 - 65% PTFE and 45 - 35% acetylene black; this mixture was added to powdered iron oxide so as to obtain 10% PTFE in the electrode mix.

The test electrodes were usually charged with a current of 100 mA for 16 h (overnight), corresponding roughly to twice the available capacity, and discharged with 150 mA (*i.e.*, 10 mA cm^{-2}) at the laboratory temperature. The time of discharge was determined from the inflection point between the first and second discharge steps, corresponding to about -0.8 V versus Hg/HgO. Sometimes the second discharge step (to $-0.5 \pm 0.1 \text{ V}$) was also followed. The current was supplied by a stabilized d.c. current source and the discharge curves were recorded with pen recorders. The discharge capacity was expressed in per cent. of the theoretical ($\% C_t$) referred to reaction (1).

Results and discussion

In spite of a low electrical resistance (1 - 15 Ω) electrodes pressed from a mixture of powdered Fe_3O_4 and PTFE were practically inactive: a negligible discharge capacity was obtained even after repeated cycling. It is probable that the electrical conductivity of magnetite decreases during the initial reduction (FeO is a nonconductor) and inhibits further reduction to iron. This adds to the difficult reduction of magnetite mentioned in the Introduction.

To counteract the drop in conductivity during the initial reduction, powdered magnetite was blended with a conducting component. Powdered graphite may be used, but acetylene black is more suitable since its addition leads to an increase in porosity and, hence, discharge capacity. The optimum ratio of the components was shown experimentally to be that given above, *i.e.*, approximately 85% oxide + 5% acetylene black + 10% PTFE. The

cohesion of the pressed electrode discs was not as good as with nickel oxide electrodes bonded with PTFE, therefore the fine nickel gauze envelope was employed.

Another necessary condition for good functioning of the iron electrodes is that passivation of iron must be suppressed by adding 0.5 - 2% powdered FeS to the electrode mix or, better, S^{2-} ions (e.g., 0.02 M Na_2S) to the electrolyte. These are irreversibly adsorbed on to the Fe electrode as soon as the oxide is reduced to the metal [23], and can be removed only by polarizing the electrode to the potential of oxygen evolution.

The measured discharge capacity often could not be reproduced well. The main reason is probably that the ohmic contacts between the current collector and the active material and between the individual active material particles were variable. This caused variations in the discharge capacity between electrodes of the same composition as well as with the same electrode during cycling. The measured values are summarized in Table 2 and three typical discharge curves are shown in Fig. 1.

The discharge capacity in the first step depends, under otherwise identical conditions, on the content of impurities in the active material, as seen by comparing the contents of Mn, Mg, Al, and Ti given in Table 1 with the discharge capacities to -0.8 V given in Table 2. This is in agreement with the findings of Soviet and Japanese authors working with pressed [21] and sintered [32] iron electrodes. It is remarkable, however, that the discharge capacity measured to a cut-off potential of -0.5 V (Hg/HgO) is not much affected by the Mn content. Thus, admixture of manganese, e.g., in commercial Fe_2O_3 increases the second discharge step at the expense of the first, whereas admixture of titanium in Fepren TP 303 suppresses both steps (Fig. 1). Indeed, manganese has been reported [22] to promote the formation of $Fe(OH)_2$ by reaction (1) and hinder its reduction, hence reaction (5) becomes relatively more important.

Various authors have found that the performance of iron electrodes can be improved by the addition of some form of copper [10, 17], mercury

TABLE 2
Discharge tests of different active materials

Material	C_t to -0.8 V (%)	C_t to -0.5 V (%)
Fepren B-91	32 - 38 (0)*	47 - 57 (6)
Bayferrox	37 - 43	60 - 68
Magnetite 9/P	17 - 22	32 - 39
Polish. black	20 - 30 (0 - 10)	40 - 50 (20 - 40)
α - Fe_2O_3 (Lachema)	21 - 24	40 - 50
Fe_3O_4 (Lachema)	17 - 21 (0)	45 - 51 (20 - 22)
Fepren TP-303	8 - 11	15 - 22

*Values in parentheses refer to absence of S^{2-} ions in the electrolyte. The initial formation cycles, which gave lower values, are not included.

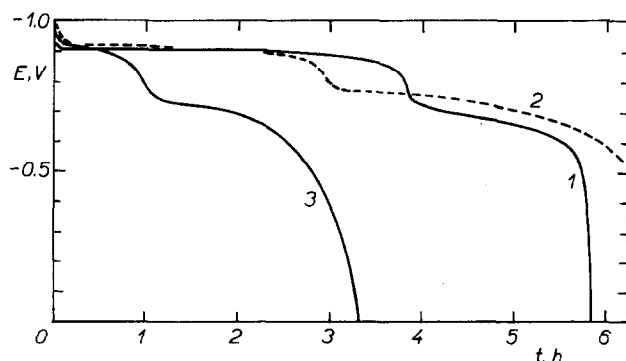


Fig. 1. Discharge curves for different active materials after two or more cycles at discharge currents of 150 mA. 1, Fepren B-91; 2, $\alpha\text{-Fe}_2\text{O}_3$ (Lachema); 3, Fepren TP-303. For other conditions see Experimental.

[17], nickel [25], or other substance. Therefore, we experimented with electrodes made from polishing-black and Fepren B-91 doped with a suitable metal compound; Na_2S was added to the electrolyte when the electrode material did not contain any sulphide. The active material was doped:

(a) By adding 0.5 - 2% of dry, powdered FeS.

(b) By adding 5 - 10% of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in water to form a paste with the oxide, which was dried and made alkaline with a stoichiometric quantity of KOH solution, washed with water, again dried, and milled (resulting content of $\text{Ni}(\text{OH})_2$ 1.65 - 3.3%). For comparison, the procedure was repeated without washing with water or the addition of KOH. As another alternative, nickel sulphate in powdered form was added to the active material.

(c) By adding 2.5% of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 5% of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, or 2.5% of HgSO_4 in dissolved form, and drying (final content 1.4% of $\text{Cu}(\text{OH})_2$ or 1.8% of HgO after immersing in the KOH electrolyte).

(d) By soaking with a solution of CuCl_2 and NiSO_4 and precipitating with Na_2S (final content 0.28 - 2.8% of CuS and 0.16 - 1.6% of NiS).

The addition of FeS had a similar effect on the electrode capacity as the addition of Na_2S to the electrolyte, although, with Fepren B-91, the latter was more efficient. The addition of metal salts without subsequent precipitation with KOH or Na_2S had either a negative or zero effect on the iron oxide electrode — probably because precipitation took place only after immersion of the pressed electrode in the electrolyte when its pores became more or less clogged by the voluminous metal hydroxides. The treatment of polishing black with a solution of NiSO_4 , precipitating with KOH, washing, drying, and milling, gave a material which, in the form of electrodes, had the same capacity as the undoped polishing black. When the doping procedure was repeated without washing with water, the results were better, probably because Na_2SO_4 , formed during doping, was leached when the electrode was cycled, thus increasing the pore volume. (An opposite effect took place

when the voluminous acetylene black was partly or entirely replaced by the more compact powdered graphite, causing a decrease in the discharge capacity.)

Doping with CuS and NiS simultaneously had a similar effect to doping with FeS (or Na₂S), their lower content (about 0.2%) being preferable. It should be noted that some FeS may be formed during the doping procedure as a result of a surface reaction of the iron oxide with Na₂S. This, however, was found to be less significant than adsorption of S²⁻ ions on metallic Fe [23]. Doping with CuS or NiS separately did not give satisfactory results.

Experiments with polishing black showed that doping with S²⁻ ions alone has a favourable effect, shifting the discharge curves to more negative potentials, increasing appreciably the discharge capacity, and lowering the overpotential of anodic dissolution of iron. The S²⁻ ions adsorbed on the reduced metallic iron are not oxidized unless the potential of Fe reaches the value for the evolution of oxygen [12, 26]. This must, therefore, be avoided to preserve the electrode performance.

Soviet authors [25], who used an iron ore reduced with hydrogen at 600 - 700 °C as active material, found a positive, although not very pronounced, effect of doping with a solution of NiSO₄ (lowering the overpotential for cathodic reduction of iron oxides and a moderate increase in the discharge capacity). Our negative results may be due to using another starting material.

Fepren B-91 gave similar results to polishing black in respect of the effect of doping agents, but its discharge capacity was higher owing to its higher degree of purity. It also has much finer particles (50% of particles up to 1 μm according to sedimentation analysis) than polishing-black (50% of particles up to 6 μm) and a correspondingly higher surface area available for adsorption. The addition of powdered FeS to this material was therefore less efficient than the addition of Na₂S to the electrolyte.

Conclusions

It may be concluded that the purity of the active material, especially the absence of Mn, and the presence of adsorbed S²⁻ ions are two basic conditions for the high performance of iron oxide electrodes. Doping with sulphides of Ni, Cu, or Hg does not bring any advantage over doping with FeS or Na₂S. Doping with salts or hydroxides of Ni, Cu, or Hg cannot be recommended.

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