VOLTAMMETRIC STUDY OF AN IRON ELECTRODE IN ALKALINE ELECTROLYTES

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Summary

The electrochemical behaviour of a pure iron electrode was studied by cyclic voltammetry in solutions of KOH containing LiOH, Na_2S or SeO_2. The maximum charge delivered by the electrode in one cycle was observed in the concentration ranges 1.1 - 2.4 M KOH and 10^{-4} - 10^{-3} M Na_2S. Sulphide ions enhance the anodic reaction, while LiOH enhances the cathodic reduction of $Fe(OH)_2$. The effect of SeO_2 is similar to that of Na_2S, but it is considerably weaker; its advantage compared to the sulphide is that the reduction of $Fe(OH)_2$ is better separated from the hydrogen evolution peak, thus improving the charging efficiency.

Introduction

Oxidation and reduction processes taking place on an iron electrode in alkaline media are important from the point of view of alkaline accumulators, and many authors have dealt with the reaction mechanism, influence of additives, etc. The oxidation of iron proceeds in two main steps, the first of which is [1 - 7]

$$Fe + 2OH^- = Fe(OH)_2 + 2e^- \tag{1}$$

and this may be accompanied by a preceding electrochemical desorption of hydrogen which was adsorbed onto the electrode during the cathodic process [2, 8, 9]. According to some authors [8, 10], eqn. (1) involves the following partial steps in conjunction with the adsorption of OH^- ions:

$$Fe + OH^- = Fe(OH)_{ads} + e^- \tag{2}$$

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$$Fe(OH)_{ads} + OH^- = Fe(OH)_2 + e^- \tag{3}$$

Most authors agree that the formation of $Fe(OH)_2$ is conditioned by the formation of a soluble intermediate product, $HFeO_2^-$.

Even during the first cycle, the second oxidation step of the iron electrode involves the formation of δ-FeOOH and, during further cycling, more and more magnetite, whose formation is strongly enhanced by the addition of LiOH into the KOH electrolyte [1, 11] or in pure LiOH solution [6]. According to Dibrov and co-workers [4], magnetite appears in a hydrated form

$$3Fe(OH)_2 + 2OH^- = Fe_3O_4 \cdot 4H_2O + 2e^- \tag{4}$$
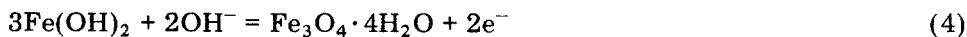
The standard potential of this reaction is $E^\circ = -0.66$ V, which can be compared with the potential of the second step on the discharge curves [1 - 3, 11] (the overpotential is only 0.1 - 0.2 V).

The influence of additives can most readily be studied by cyclic voltammetry with a stationary or rotating disc electrode. Sulphide ions which are irreversibly adsorbed onto iron enhance its anodic dissolution and also the discharge capacity of porous iron electrodes; their absence causes the iron electrode to passivate [1, 12, 13]. This phenomenon was studied recently from the point of view of the solubility of the passivation layer in the presence of S^{2-} ions [14]. A comparison was also made with the effect of selenium [15], which was claimed to improve the cycle life of smooth iron electrodes (i.e., the discharge capacity did not drop during several cycles) and increase the hydrogen overpotential on iron.

Of other additives, the most common is LiOH, which to some extent permits lower concentrations of KOH without loss of the discharge capacity [16] and improves the cycle life of porous iron electrodes [17, 18].

With an increasing concentration of KOH, the discharge capacity of porous Fe electrodes increases [16, 19] and the charging efficiency (i.e., the separation of the charging reaction from the evolution of hydrogen) improves [20]. Alexandrova et al. [21] found that the voltammetric peak due to dissolution of iron was highest in 5 - 6 M KOH, whereas Muralidharan [22] found anomalous, obtuse voltammetric peaks at elevated concentrations of NaOH (6 M or more). Disagreement between the published data is most often found in the measured peak potentials.

The aim of the present work was to study the influence which the solution composition has on the voltammetric curves from a pure Fe disc electrode and to obtain information relevant to Ni–Fe battery negative electrodes.

Experimental

The 0.55 cm dia. rotating iron disc electrode was made from a 99.999%-pure Fe cyclinder (VEB Pure Metalle, Freiberg/SA, GDR) according to Beran and Opekar [23]. The counter electrode consisted of a nickel foil of 1 cm^2 area, and the reference electrode was Hg/HgO in 5 M KOH. The 50 ml

electrolyte was a solution of KOH, with additives in later experiments. All were placed in a cylindrical cell of 5 cm dia.

Comparative measurements were made on rectangular electrodes of about 1 cm^2 in area cut from a 0.9 mm thick mild steel sheet. Analysis by emission spectrometry gave C 0.40%, Mn 0.41%, Si 0.012%, P 0.070%, S 0.011%, Ni 0.021%, Cu 0.037%, and trace impurities (Ca, Mo, V, W, Co, Ti, Al, Sn, and Sb) below 0.01%.

Before every measurement, the disc electrode was polished with a 7/0 grade metallographic paper to a mirror-like finish then rinsed with distilled water several times. The solution was deaerated for 30 min with nitrogen. During the tests the electrode potential was controlled by a potentiostat coupled to a saw-tooth voltage generator and the voltammograms were recorded on an X–Y recorder. The sweep rate was 100 mV s^{-1} (the rate at which the peaks on the curves were most distinct) and the temperature was maintained at 24 ± 1 °C.

The electrode was immersed in the solution in the open-circuit-state. At the moment of switching on the recorder the initial potential was 0.0 V (Hg/HgO) which then began to change at the rate indicated toward negative values; pseudostationary curves were obtained after several (usually nine) cycles. The length of time during which the electrode was immersed in the electrolyte (up to several minutes) on open-circuit had no influence on the voltammograms after the 9th cycle. All potential values are given against the Hg/HgO reference electrode in 5 M KOH.

Results

Influence of KOH concentration
The concentration range investigated was 0.014 - 9.22 M KOH. Typical voltammograms are shown in Fig. 1(a) for a non-rotating electrode and in Fig. 1(b) for an electrode rotating at 37 Hz; all of the curves correspond to the 10th cycle. Their form is similar to that published by Burke and Lyons [9], who used solutions of NaOH as the electrolyte. At a concentration of 4.8 M KOH or higher, four anodic peaks (A_1 - A_4) and two cathodic peaks (C_1 and C_2) are observed; at lower concentrations the peaks A_2 and A_4 disappear. The peaks A_3 and C_1 increase with the number of cycles; their dependence on the KOH concentration passes through a maximum in the region 1.1 - 2.4 M, corresponding to the maximum charge delivered by the electrode during one cycle. Detailed data are summarized in Table 1, from which the changing character of the dependence of the peak height on the rotation rate can also be seen.

By a suitable choice of the limiting anodic potential (Fig. 2) it can be shown that the peak C_1 is related to A_3 and the peak C_2 is related to both A_1 and A_2. Thus, the couple C_1–A_3 belongs to one redox system and the triad C_2–A_1, A_2 to another.
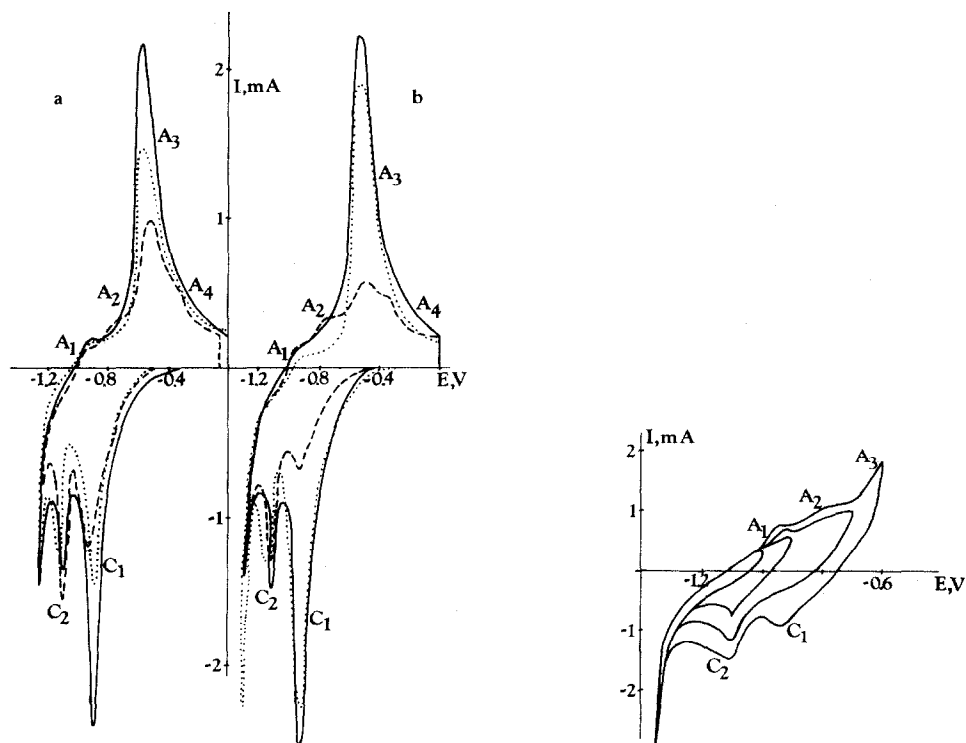
Fig. 1. Voltammograms of iron at various electrolyte concentrations: ⋯⋯, 0.1 M KOH; ———, 1 M KOH; - - -, 5 M KOH. (a) Electrode stationary, (b) rotating at 37 Hz.

Fig. 2. Effect of changing the limiting anodic potential on the voltammogram of iron in 4.85 M KOH starting at −1.35 V.

TABLE 1

Height of peak A_3 as a function of KOH concentration and rotation frequency of the disc electrode in the 10th cycle

KOH conc. (mol l^{-1})	Peak height (mA)		
	0 Hz	25 Hz	37 Hz
0.014	0.38	0.54	0.85
0.122	1.45	1.73	1.90
0.55	1.82	2.04	2.04
1.09	2.16	2.08	2.20
2.37	2.18	1.38	1.13
4.85	0.95	0.65	0.57
7.50	0.90	0.56	0.48
9.22	0.55	0.50	0.50

The voltammetric curves obtained on the mild steel sheet electrodes in 5 M KOH differed from those obtained on the Fe disc in the same electrolyte in that the peak C_2 was relatively smaller (compared with C_1).
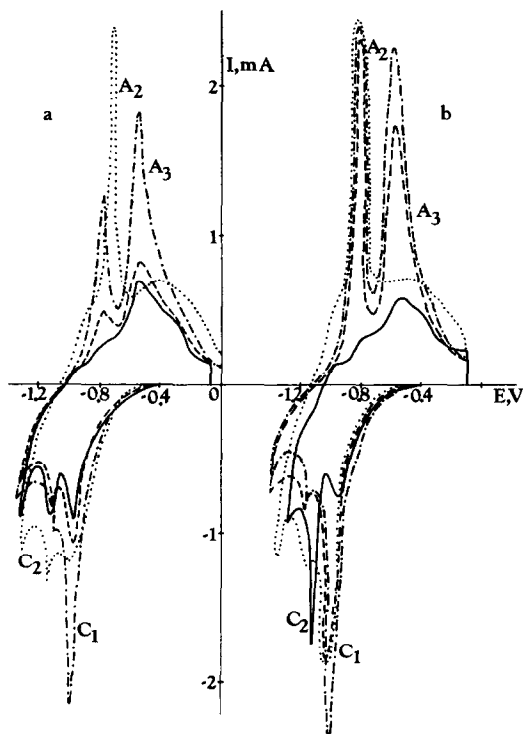
Fig. 3. Effect of sulphide ions on the voltammograms of iron in 4.85 M KOH: ——, pure electrolyte; - - - -, 8×10^{-6} M Na_2S: — · —, 1.6×10^{-4} M Na_2S; · · · · ·, 3.2×10^{-2} M Na_2S added. (a) Electrode stationary, (b) rotating at 25 Hz.

Influence of sulphide ions

The concentration range studied was 8×10^{-6} - 3.2×10^{-2} M Na_2S with the use of 4.85 or 1.09 M KOH. Representative voltammograms are shown in Figs. 3(a), (b) and 4(a), (b). There is a dramatic increase of the peak A_2; the neighbouring peak A_1 is completely overlapped by A_2. The effect of Na_2S is much more marked at the higher KOH concentration (Fig. 3(a), (b)), where the peaks A_3 and C_1 are also very sensitive to the addition of sulphide. The electrode, once "activated" with Na_2S, remains active even when the electrolyte is replaced by a pure KOH solution.

Similar results were obtained with the mild steel electrodes where, however, peak C_2 disappeared after addition of sulphide.

Influence of LiOH and other additives

The addition of LiOH to 0.1 - 1.0 M KOH manifests itself by a decrease of the anodic peak A_3 and of the conjugated peak C_1 (Table 2). The effect diminishes with increasing concentration of KOH (at constant LiOH), suggesting that the ratio of LiOH to KOH is the controlling factor. Peak C_2, however, behaves differently: it increases with the addition of LiOH, espe-
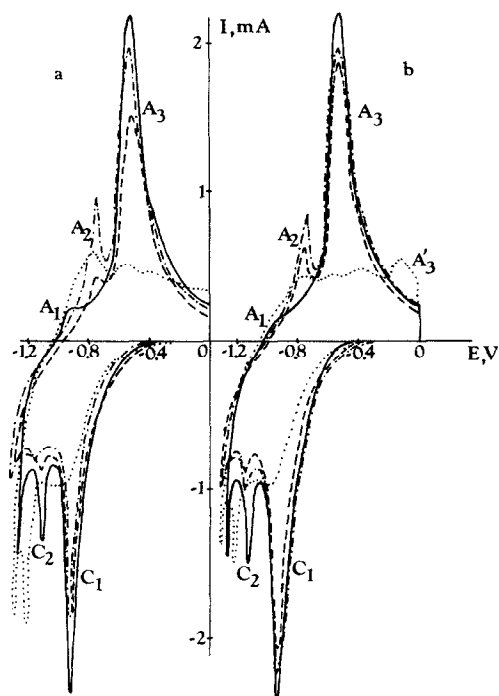
Fig. 4. Effect of sulphide ions on the voltammograms of iron in 1.09 M KOH: ————, pure electrolyte; - - - -, 8×10^{-6} M Na_2S; — · —, 1.6×10^{-4} M Na_2S; ·····, 3.2×10^{-2} M Na_2S added. (a) Electrode stationary, (b) rotating at 25 Hz.

TABLE 2

Heights of the peaks A_3, C_1, and C_2 at various concentrations of KOH and their changes after addition of 30 g l^{-1} of LiOH. H_2O (in parentheses)

KOH conc. (mol l^{-1})	A_3 (mA)	C_1 (mA)	C_2 (mA)
0.122	1.45 (0.80)	1.50 (0.85)	0.95 (1.02)
1.09	1.90 (1.30)	2.45 (1.65)	2.40 (2.85)
4.85	0.95 (1.0)	0.95 (1.0)	0.60 (0.80)

cially in concentrated KOH. This supports the view that the addition of LiOH promotes the reduction of $Fe(OH)_2$ [17] (*cf. Assignment of the peaks*).

The addition of SeO_2 to the electrolyte has a similar effect to that of Na_2S, but it is much weaker, as can be seen from Figs. 5 and 6, corresponding to 1 M and 4.5 M KOH, respectively. It is remarkable that no effect of SeO_2 can be observed during the first few cycles. A pseudo-stationary state is reached after about nine cycles and an increase in the heights of the peaks A_2, A_3 and C_1 compared with those in a pure KOH solution is apparent. The concentration of SeO_2 in solution is, however, about three orders of magnitude higher than that of sulphide at a comparable increase in the peak height.
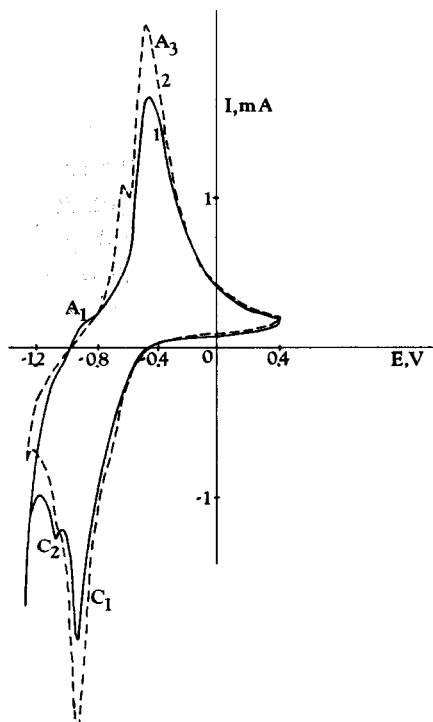
Fig. 5. Effect of SeO_2 on the voltammograms of iron in 1 M KOH: 1, pure electrolyte; 2, 0.02 M SeO_2 added. Electrode stationary, pseudostationary state.
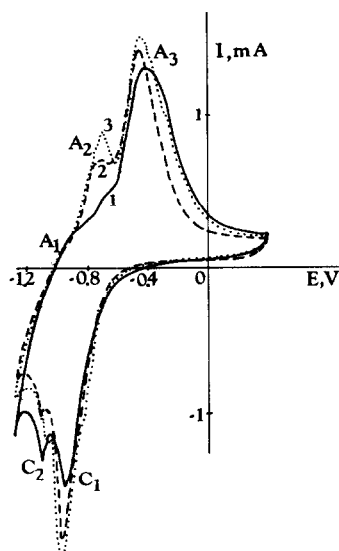
Fig. 6. Effect of SeO_2 on the voltammograms of iron in 4.5 M KOH: 1, pure electrolyte; 2, 3.8×10^{-3} M SeO_2; 3, 0.02 M SeO_2 added. Electrode stationary, pseudostationary state.

At a concentration of 0.02 M SeO_2 a limiting height for A_2 and C_1 is attained. The effect of selenium persists after replacing the electrolyte by a pure KOH solution.

Qualitatively, similar voltammetric curves were obtained on the mild steel electrodes, except that peak C_2 disappeared after the addition of SeO_2.

Discussion

Assignment of the peaks

The position of the peaks on the potential scale, their relative orders of magnitude, and their behaviour during cycling as observed by different authors, are shown in Fig. 7.

There is general agreement that the voltammograms of iron in strongly alkaline media involve two conspicuous peaks, an anodic and a cathodic one (A_3 and C_1 in Fig. 1): both increase with the number of cycles up to a limit. These are indicated by arrows in Fig. 7; their potentials vary appreciably

A   B C

[7]	10 M KOH Fe unspec.; 10 mV/s
[2]	5.6 M KOH Fe powder; 0.5 mV/s
[6]	1 M LiOH 99.98% Fe; 14 mV/s
[25]	0.1 M NaOH 99.97% Fe; 40 mV/s
[20]	4.5 M KOH por. FeCO; 0.1 mV/s
[27]	0.05 M NaOH 99.95% Fe; 10 mV/s
[24]	1 M KOH spectr.Fe; 100 mV/s
[8]	5 M KOH 99.995% Fe; 10 mV/s
[21]	5 M KOH ARMCO Fe; 20 mV/s
[18]	5 M KOH 99.99% Fe; 100 mV/s
[22]	1 M NaOH 99.95% Fe; 200 mV/s
[9]	1 M NaOH 99.998% Fe; 40 mV/s
[26]	5 M KOH ARMCO Fe; ? mV/s
this work	5 M KOH 99.999% Fe; 100 mV/s

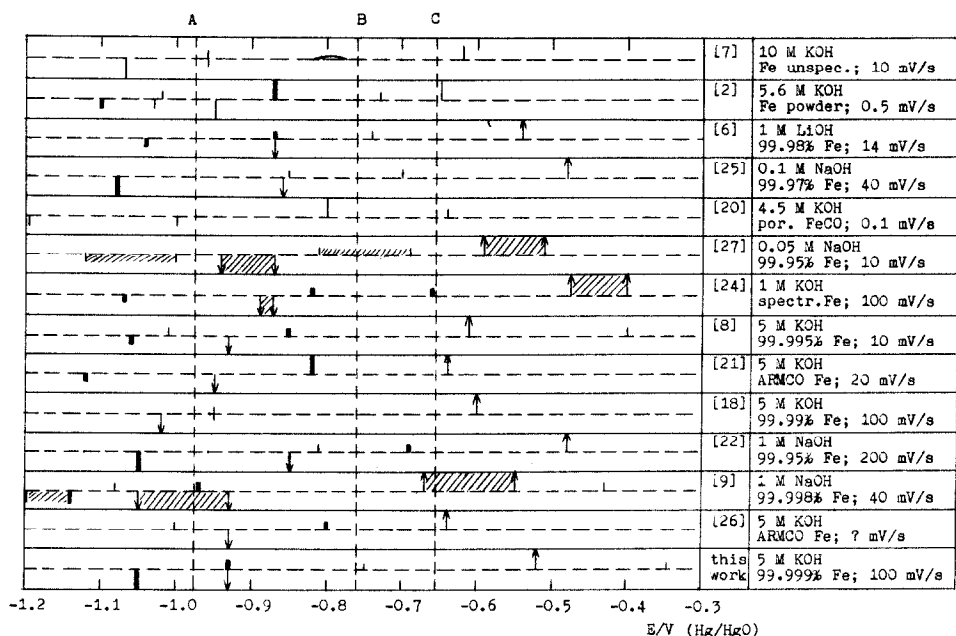-1.2   -1.1   -1.0   -0.9   -0.8   -0.7   -0.6   -0.5   -0.4   -0.3

E/V (Hg/HgO)

Fig. 7. Comparison of voltammetric data of various authors. Anodic and cathodic peaks are symbolized in the upper and lower halves of each band, respectively. Arrows pointing upwards and downwards indicate conjugated peaks growing with the cycle number. Other peaks are denoted by short vertical lines whose lengths indicate the relative orders of magnitude of the peaks. Thick lines denote conjugated peaks. Shaded areas denote variability of the potentials. All potential values were recalculated against Hg/HgO electrode in 5 M KOH. Dashed vertical lines denote the equilibrium potentials for the systems: A, Fe/Fe(OH)$_2$; B, Fe(OH)$_2$/Fe$_3$O$_4 \cdot 4H_2O$; C, Fe(OH)$_2$/FeOOH.

(anodic from -0.67 to -0.40 V, cathodic from -1.15 to -0.85 V). The best agreement between the peak potentials was achieved by Alexandrova et al. [21] and Eronko et al. [26], who used the same sort of iron (ARMCO) and the same method of pretreatment of the Fe electrode. The reasons why the peak potentials vary are not always clear; variations are sometimes observed even within a single published work (cf. shaded areas in Fig. 7). A suitable additional characteristic is the behaviour of the peaks during cycling.

The peaks A$_3$ and C$_1$ (Fig. 1) appear relatively small on the first cycle, but they increase with the number of cycles, evidence for thickening of the formed oxide film. This is a general phenomenon in cyclic polarization of smooth metal electrodes which may be attributed to both an increase in the roughness factor and three-dimensional film growth processes [25]. We observed that the growth essentially stopped after about ten cycles, but according to some authors it may continue very slowly even after twenty cycles [9, 24, 27].

Although the peak potentials are variable, it can be inferred from Fig. 7 that peak A$_3$ always lies in the region where oxidation of Fe(OH)$_2$ (either to Fe$_3$O$_4$ or to FeOOH) takes place; the conjugated peak C$_1$ logically corre-

sponds to the back reaction. The composition of the oxidation product may depend on the experimental conditions; the following compounds have been considered by various authors: $Fe(OH)_3$ or $FeOOH$ [6, 8, 9, 21, 22, 24, 26], Fe_2O_3 [6, 7, 25, 27], and Fe_3O_4 [2, 7, 25]. An inspection of Fig. 7 reveals that the formation of the magnetite at peak A_3 is more probable than $FeOOH$ in refs. 2, 9, 21, 26, where the peak potential lies too close to the equilibrium potential for the $Fe(OH)_2/FeOOH$ system (the over-potential being almost equal to zero).

Studies with the ring-disc electrode revealed that Fe(III) species enter the solution in the region of peak A_3 [7]; therefore, the peak heights should depend on the rotation speed of the electrode. This is the case (Fig. 1(a), (b)), but the form of this dependence is governed by the concentration of KOH influencing the solubility products of the compounds in question.

From the 14 sets of data available (Fig. 7), the mean anodic and cathodic peak potentials were calculated as -0.547 ± 0.073 V (A_3) and -0.921 ± 0.059 V (C_1). The values found in the present work are -0.52 and -0.93 V.

There are two ill-developed anodic peaks or humps, A_1 and A_2, at more cathodic potentials than A_3. The curves in Fig. 2 suggest that the cathodic peak C_2 is conjugated with both of them, in accord with MacDonald and Owen [6]. There is a general agreement in the literature that the hump A_2, which is next to the peak A_3, corresponds to the reaction $Fe \rightarrow Fe(OH)_2$ (only the cited authors [6] assume the less probable reaction $Fe(OH)_2 \rightarrow Fe_3O_4$), hence the back reaction $Fe(OH)_2 \rightarrow Fe$ proceeds in the peak C_2. Confusion exists, however, regarding the hump A_1 (which is next to A_2 except for ref. 2): it has been attributed either to oxidation of adsorbed hydrogen [2, 8, 22, 25, 26] or to oxidation of iron [6, 24] or to both [7, 9], whereas some authors [20, 21, 27] did not observe this hump on their curves. Cnobloch *et al.* [2] first described a voltammetric peak due to oxidation of adsorbed hydrogen on an iron powder electrode at -1.0 V, *i.e.*, more cathodic than the $Fe/Fe(OH)_2$ equilibrium potential. This potential relation is also satisfied for the peaks described in refs. 8, 9, 26 (Fig. 7). Hence, the interpretation is plausible, whereas in refs. 22, 25 the first step in the oxidation of iron appears more probable than oxidation of hydrogen. This step should be formulated as $Fe \rightarrow FeOH_{ads}$ [9], contrasting with $Fe \rightarrow Fe(OH)_2$ proceeding in peak A_2.

The mean potential of the peak A_2 was calculated as -0.78 ± 0.09 V (from 12 of the sets of data) and that of C_2 as -1.07 ± 0.04 V (from 11 of the sets of data, *cf.* Fig. 7); the value for A_1 is -0.93 ± 0.10 V (from 9 of the sets of data). The respective values found in our work are -0.75, -1.05, and -0.93 V.

The fact that the peaks A_2 and C_2 do not increase with the number of cycles (sometimes they even decrease [6, 9, 25]) distinguishes them well from the peaks A_3 and C_1, and implies a "passivating" property of the Fe(II) hydroxide film formed: this probably has a low porosity and thus hinders the diffusion of ions necessary for its growth. The film is formed in concentrated KOH solutions probably by a dissolution–precipitation mechanism

[2, 7, 24]. By contrast, the "classical" passivation of iron occurs at more anodic potentials [28, 29] (the extrapolated value of the Flade potential being $E_F = -0.23$ V *versus* Hg/HgO in 1 M KOH) and is due to the formation of a non-porous film of Fe(III) oxides (*cf.* recent studies by ellipsometry [30] and Mössbauer spectroscopy [31]).

The fact that the peak C_2 obtained with the iron sheet electrode was relatively small can be attributed to the presence of Mn in the mild steel used hindering the reduction of $Fe(OH)_2$, as found in an earlier work [8].

Since the anodic charge corresponding to the humps A_1 and A_2 is considerably smaller than that corresponding to the peak A_3 (in the pseudo-stationary state after cycling), it is obvious that the latter cannot be due merely to one-electron oxidation of the film formed in the preceding steps, as suggested by most (and even recent [9]) authors. It is much more probable that the peak A_3 involves oxidation of both $Fe(OH)_2$ and Fe to Fe(III) [6, 27].

The hump A_4, which is more anodic than the peak A_3, is observed in concentrated solutions of KOH; it might correspond to the formation of a thermodynamically more stable Fe(III) species than that formed in the peak A_3 [8, 9]. A trace of this hump was observed in 1 M KOH [24], and other authors did not obtain it at all.

Influence of sulphide ions

Our results indicate that in the presence of as little as 8×10^{-6} M Na_2S the peak A_2 (due to formation of $Fe(OH)_2$) is considerably increased (Figs. 3 and 4). With increasing concentration of Na_2S (up to 8×10^{-3} M) the peak A_3 and the conjugated peak C_1 also increase, and the potential of hydrogen evolution is shifted to more cathodic values. Since, however, peak C_2 (due to reduction of $Fe(OH)_2$) is shifted similarly, no improvement in the charging efficiency of the iron electrode can be expected.

When the concentration of Na_2S is increased above 8×10^{-3} M, the peak A_3 decreases, *i.e.*, the electrode loses its activity. A similar effect was observed by Shoesmith *et al.* [27], who attributed it to competitive adsorption of the highly polarized SH^- anions on the electrode surface; the rate of oxide growth is proportional to the total number of surface sites available for adsorption of OH^- anions. At a still higher Na_2S concentration (*e.g.*, 0.032 M) peak A_3' is formed, especially in 1 M KOH (Fig. 4), corresponding to the oxidation of S^{2-} ions to sulphur; under these conditions iron is oxidized to form the polymeric complex $(NaFeS_2)_n$ by a sequence of surface reactions [27].

The activation of the iron electrode by very low sulphide concentrations obviously cannot be elucidated by the formation of soluble Fe complexes, as assumed by Berger and Haschka [14]. Higher concentrations of sulphide were used by Shoesmith *et al.* [27], according to whom S^{2-} ions attack the Fe oxide film in a manner similar to Cl^- ions (*i.e.*, pitting attack). At the very low concentrations used by us, however, this explanation also seems to be unlikely. Since S^{2-} ions are strongly and irreversibly adsorbed in

the iron—electrolyte interface [12]and the solubility product for FeS is 4×10^{-19} compared with 1.8×10^{-15} for $Fe(OH)_2$ [32], sulphur is adsorbed in the form of FeS. This is responsible for some disorder in the structure of the anodic $Fe(OH)_2$ film, enhancing diffusion of ions and further growth of the film. The adsorbed FeS (indicated by the electrode activity) cannot be removed by rinsing with water and replacing the electrolyte by a pure KOH solution, but it can be removed by polishing with a wet metallographic paper.

Attempts to determine the adsorbed FeS film by the ESCA method failed, apparently due to a hydrated oxide film which formed in spite of precautions employed during the sample preparation (using electrodes from the mild steel sheet).

From the electrochemical point of view, FeS appears more stable than $Fe(OH)_2$, the Fe/FeS standard potential being equal to -0.97 V [32], compared with -0.877 V for $Fe/Fe(OH)_2$.

At low sulphide concentrations (up to 10^{-4} M) the peaks A_2, A_3 and C_1 increase when the electrode is set into rotation. This is probably caused by the higher transport rate of Na_2S to the electrode surface, since non-convective diffusion is too slow in highly diluted solutions.

Influence of selenium

Since the effect of Se (Figs. 5 and 6) is observable only after several cycles have elapsed, SeO_2 must first be reduced cathodically to selenide, which is the active form. Since the effect persists after replacing the electrolyte by a pure KOH solution (*cf.* the effect of sulphide), we are forced to assume that Se^{2-} ions are adsorbed onto the electrode surface, although our attempts to determine the possible FeSe film by the ESCA and SIMS methods (using samples from the mild steel electrodes) failed. The reason for this was probably the same as in the case of adsorbed sulphur. Any film of FeSe would be stable both chemically and electrochemically: its solubility product is 10^{-26} and the Fe/FeSe standard potential is -1.22 V [32].

In the presence of SeO_2 the cathodic peak C_2 due to reduction of $Fe(OH)_2$ is somewhat better separated from the evolution of hydrogen and almost fuses with the peak C_1 due to reduction of Fe(III) (Fig. 5 or 6). These circumstances would be favourable for the charging efficiency of (porous) iron electrodes. The effect Se has on the evolution of hydrogen is similar to that of sulphur and suggests a similar adsorption mechanism.

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