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Electrochemical generation of ferrate
Part 2: Influence of anode composition

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The influence of the composition of the anode on the anodic dissolution of iron based alloys in 10 M NaOH to give ferrate has been studied. It is shown that the current efficiency for ferrate formation increases significantly with the carbon content of the alloy. A silver steel with a carbon content of 0.90% initially gave a current efficiency greater than 70%, dropping to ~30% after an hour, in a cell with flat plate electrodes and using a current density of $1\,\text{mA cm}^{-2}$. In comparison, in the same conditions, an alloy with a carbon content of 0.08% showed a current efficiency dropping from 12 to 8%.

1. Introduction

Some of the very early papers on the electrosynthesis of metal ferrates by the anodic dissolution of iron or iron alloys in strong aqueous base mention that the yield of ferrate is sensitive to the exact composition of the anode [1, 2] and the carbon content was identified as important. Later, Tousek [3] obtained good yields of ferrate with a high carbon alloy (3.07% C). There has, however, been no systematic study of the influence of alloying elements on the efficiency of iron dissolution to ferrate. Hence, in this paper we report the study of a series of steels chosen to have a range of carbon contents.

Amongst later workers, there is general agreement that the oxidation of iron to ferrate takes place at a passivated iron surface in conditions where oxygen evolution is the competing reaction. Several papers have therefore discussed pretreatment of the iron/steel surface [4], the effect of cathodic polarization [2, 3, 5] or acid etching [6] before the electrolysis as well as current reversal [2] and a.c. modulation of the current [7, 8] during electrolysis in attempts to control the passivating oxide/hydroxide layer on the surface and minimize the drop in current efficiency generally observed with electrolysis time.

A convenient way to monitor the ferrate formed is to use its voltammetric response. Venkatadri *et al.* [9] have reported the voltammetry for the reduction of ferrate at an iron electrode while Beck *et al.* [6] have used a platinum cathode; both papers report well formed responses and suggest that ferrate undergoes an irreversible $3e^-$ reduction. On the other hand, Beck *et al.* [6] found, using a rotating iron disc electrode, that the limiting current was lower than expected and suggested that the cathodic reduction at iron is complicated by a chemical reaction between ferrate and the iron disc. During preliminary experiments, we found no evidence for such a complication and, in any case, we do not feel that the findings of Beck prevent the use of ferrate reduction on iron as a semi-quantitative method of *in situ* monitoring of ferrate formation.

2. Experimental details

Most of the equipment and procedures have been described in the previous paper [10]. The electrodes for the voltammetric experiments were stationary discs (diameter 5 mm) surrounded by an insulating sheath. Electrolyses were carried out with large disc anodes (diameters 60 mm) in a small glass batch cell with a glass sinter separating the anode from a platinum anode; the anolyte volume was $\sim 20\,\text{cm}^3$ and the anolyte was stirred with a slow stream of nitrogen. Prior to experiments, all the iron alloy disc electrodes were polished sequentially with 1, 0.3 and 0.05 μm alumina powder on a felt pad (Buehler) and then washed well with deionised water. The iron, steels and related alloys used in this work were obtained either from Goodfellow Metals or from British Steel and they had the following compositions:

Iron: Fe > 99.5%, C 0.08%
Alloy A: Fe > 99.7% C 0.04%, Mn 0.26%, others <0.05%
Alloy B: Fe > 98%, C 0.16%, Mn 0.75%, Si 0.21%, others <0.03%
Alloy C: Fe > 98%, C 0.20%, Mn 0.94%, Si 0.31%, others <0.03%
Alloy D: Fe > 98%, C 0.65%, Mn 0.78%, Si 0.22%, Cr 0.35%, others <0.05%
Alloy E: Fe > 96.5%, C 0.90%, Mn 1.30%, Cr 0.50%, W 0.50%, V 0.2%, others <0.02%
Alloy F: Fe > 96.5%, C 0.22%, Mn 1.41%, Si 0.97%, others <0.04%
Alloy G: Fe > 96.5%, C 0.25%

Current efficiencies were determined by measuring the absorbance of the anolyte at 505 nm [10].

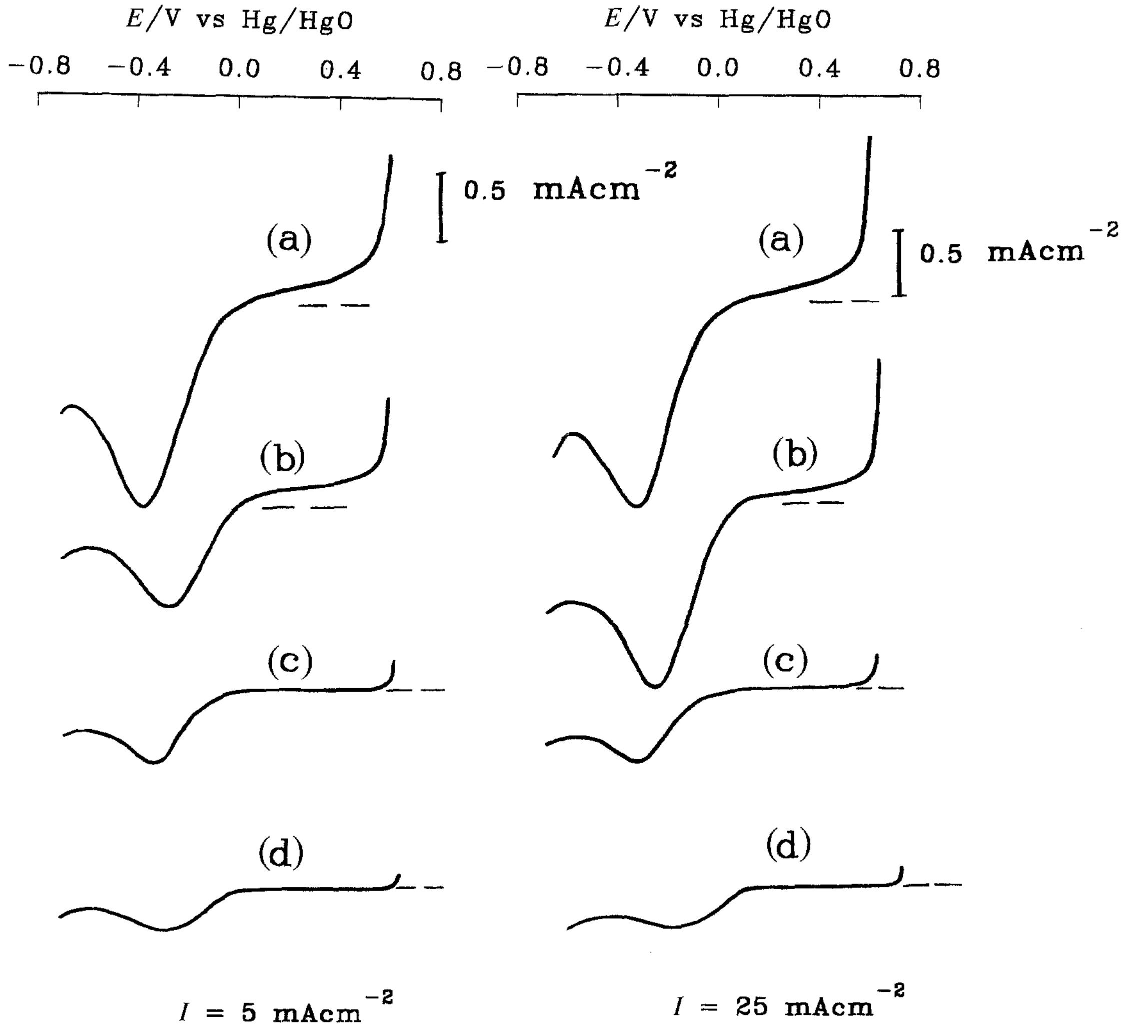

Fig. 1. Current/potential curves to monitor the formation of ferrate during a constant current pulse for 20 s. The iron alloys were pretreated by passing the same current density for 100 s and then dispersing the ferrate formed during this pretreatment with a fast stream of nitrogen. The current densities are shown on the figure and the alloys were (a) E (C 0.90%) (b) D (C 0.65%) (c) C (C 0.20%) and (d) A (C 0.04%). Temperature 298 K. Potential scan rate 250 mV s^{-1}.

3. Results and discussion

In the previous paper [8], it was confirmed that, in 10 M NaOH, the dissolution of iron to give ferrate occurs on a surface passivated with an oxide/hydroxide film and in a potential region where oxygen evolution is always a competing reaction. Moreover, it was shown that the size of the cathodic reduction peak for ferrate was a convenient way to compare the current efficiencies for ferrate formation during different constant current pulses immediately prior to the voltammogram. This technique was therefore used to investigate the influence of the anode composition on the relative rates of ferrate formation and oxygen gas evolution. In all experiments, the following procedure was followed: (a) a constant current, usually the same value as used in (c), was passed for 100 s to ensure that the surfaces were fully covered by a pseudo steady state film of oxide/hydroxide, (b) a fast stream of nitrogen was passed for a few seconds to remove from the vicinity of the electrode surface all the ferrate formed, (c) ferrate was formed using a constant current for 20 s, and (d) the electrode potential was immediately scanned from + 600 mV to −700 mV vs Hg/HgO at 250 mV s^{-1} and the current/potential curve recorded. Figure 1 reports the current/potential responses for two series of experiments using four alloys and current densities of 5 and 25 mA cm^{-2}. While in all experiments, a cathodic peak for the reduction of ferrate was observed, the peak current densities varied strongly with the different anode alloys. Indeed, with a current density of 5 mA cm^{-2} and at alloy E (C content 0.9%) the ferrate reduction peak was some five times larger than that at alloy A (carbon content 0.04%). Moreover, it can be seen that the trends were the same with both current densities for the ferrate generation. In fact, the peaks were all slightly larger at the higher current density reflecting a higher rate (although probably not current efficiency) of generation of ferrate. Two other features of the curves should be noted. First, at the positive potential limit for these scans, + 600 mV, there was a significant anodic current for alloys D and E but not alloys A or C. Secondly, the peak potential for ferrate reduction also varied slightly between −280 mV (alloy D) and − 400 mV vs Hg/HgO (alloy E).

Figure 2 shows a plot of the peak current density for

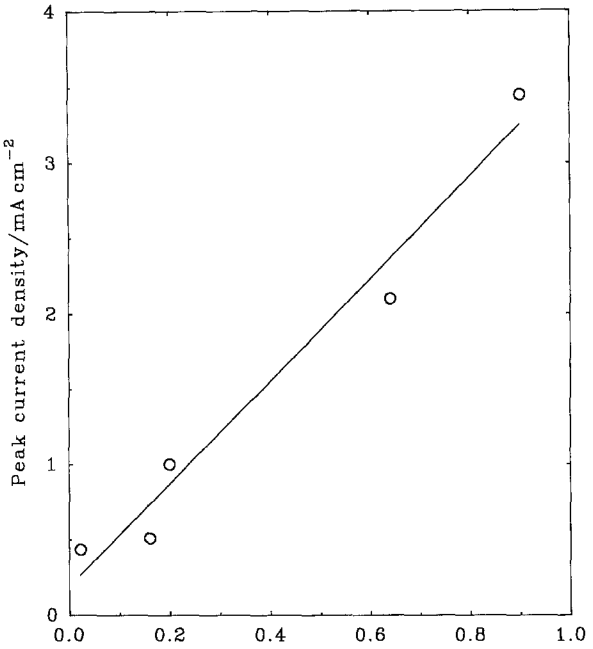

Fig. 2. Plot of peak current density for the reduction of the ferrate formed during a constant current pulse ($5\,\mathrm{mA\,cm^{-2}}$ for 20 s) against the carbon content of the iron alloy.

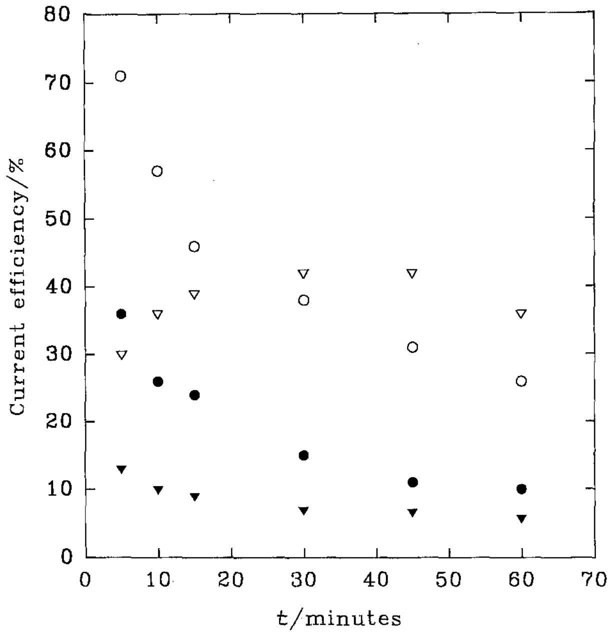

Fig. 3. Plots of current efficiency for the formation of ferrate versus time for alloy E (C 0.90%) in a cell with flat plate electrodes. Anolyte: 10 M NaOH. Temperature: 298 K. Current densities: (▽) 0.5, (○) 1, (●) 5 and (▼) $25\,\mathrm{mA\,cm^{-2}}$.

ferrate reduction against the percentage carbon in the alloy and it can be seen that there appears to be a good linear correlation. Visual observation also supported the trend shown by voltammetry. At alloys D and E, the purple ferrate ion could clearly be seen by eye to accumulate at the anode surface during the constant current pulses. The ferrate was only poorly visible at alloys A and B. The other major elements found in most of the alloys are silicon and manganese, but there was no correlation between the percentage of these elements and the rate of formation of ferrate. Nor was it possible to discern the factor leading to the change in peak potential for the reduction of ferrate although this shift presumably follows a change in property of the oxide/hydroxide layer. It was found that the peak potential for ferrate reduction occurred at about +100 mV at Pt and about − 400 mV vs Hg/HgO at vitreous carbon and hence it is certainly an electron transfer reaction which is sensitive to cathode material.

The alloys were supplied in a form which made them suitable only as two dimensional electrodes. Hence, electrolyses were carried out at flat plate electrodes using a low, constant current density. Figure 3 shows plots of current efficiency against time for a series of electrolysis carried out at the silver steel (alloy E) at room temperature with an anolyte which was 10 M NaOH; the current density was varied between 0.5 and $25\,\mathrm{mA\,cm^{-2}}$. The highest current efficiencies are obtained at $1\,\mathrm{mA\,cm^{-2}}$. Initially, in this electrolysis the current efficiency was as high as 70% although it dropped quite rapidly and after an hour had dropped to ~30%. This decrease in efficiency occurs in all electrolyses and seems to result from changes in the corrosion film on the iron or steel surface [10 and references therein]. With the lowest current density ($0.5\,\mathrm{mA\,cm^{-2}}$), the current efficiency for ferrate formation initially increased with time and this must have reflected a change in the anode surface layer which improves the selectivity of the desired reaction; the current efficiency reaches more than 40% before decaying slowly. With current densities greater than $1\,\mathrm{mA\,cm^{-2}}$, the current density always dropped with time and the current efficiency was lower with increasing current density. It should be noted, however, that the rate of ferrate formation was highest at $25\,\mathrm{mA\,cm^{-2}}$. Figure 4 compares the performance of

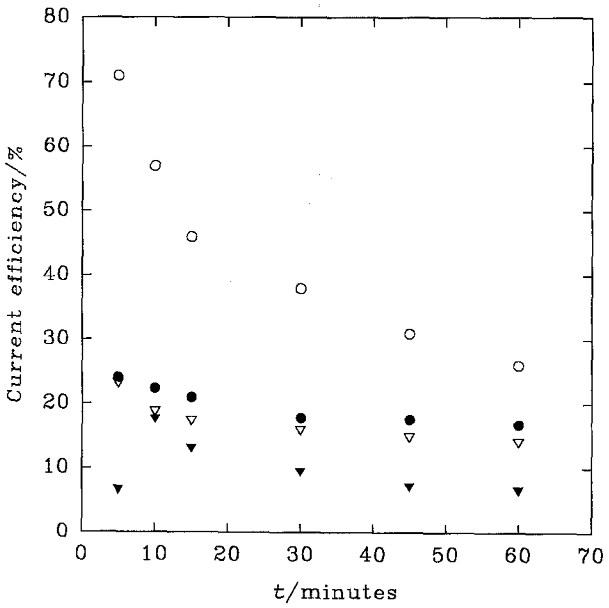

Fig. 4. Plots of current efficiency for the formation of ferrate versus time for four iron alloys in a cell with flat plate electrodes. Current density: $1\,\mathrm{mA\,cm^{-2}}$. Anolyte: 10 M NaOH. Temperature: 298 K. The alloys are: (○) E (C 0.90%), (▽) F (C 0.22%), (●) G (C 0.25%) and (▼) Fe (C 0.08%).

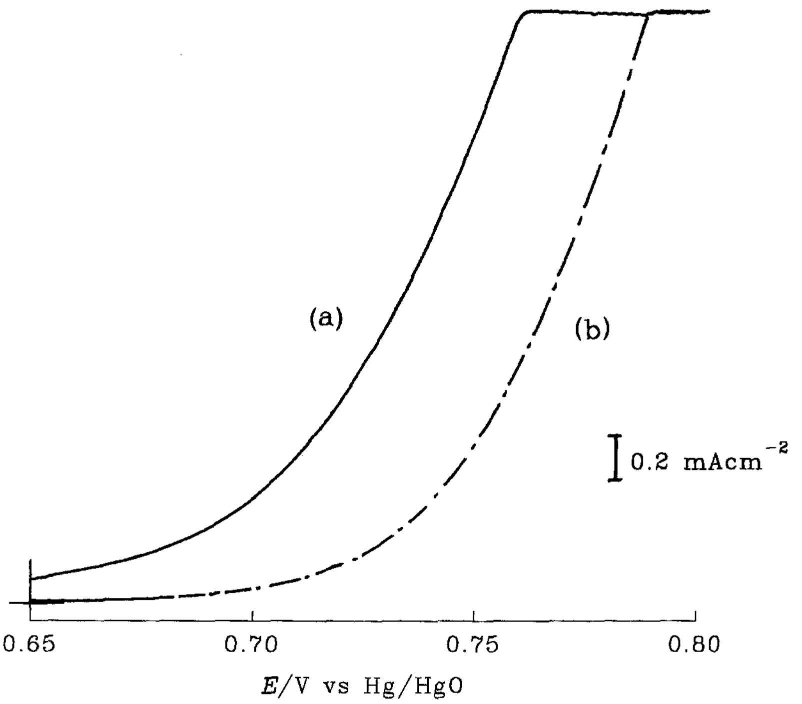

Fig. 5. Current potential curves (a) alloy E (C 0.90%) and (b) alloy A (C 0.04%). The alloys were pretreated by passing 5 mA cm^{-2} for 1000 s and then dispersing the ferrate formed during this pretreatment with a fast stream of nitrogen. Temperature 298 K. Potential scan rate 2.5 mV s^{-1}.

four alloys in electrolyses carried out at 1 mA cm^{-2}. These clearly confirm that the current efficiency was higher for the alloys with a high carbon content although, unfortunately the current efficiencies always decreased with time.

The current efficiency for ferrate formation could increase due either to an increase in rate of iron dissolution or a decrease in the rate of oxygen evolution. To distinguish these possibilities, current/potential curves were recorded after the alloys had been pretreated to form a passive layer by passing a current of 5 mA cm^{-2} for 1000 s and dispersing the ferrate formed with a fast stream of nitrogen. Figure 5 reports current/potential curves for alloy A (C 0.04%) and alloy E (C 0.90%). It can be seen that at all potentials in the range of interest, the current density was significantly higher at alloy E, clearly confirming that the improved current efficiency for ferrate formation results from an increased rate of iron dissolution.

It is interesting to speculate why the alloys with high carbon content dissolves more readily to form ferrate in the strongly alkaline medium. The alloys used in this study all have a low nonferrous metal content and such carbon steels are produced for their improved mechanical properties, including hardness and strength [11]. Moreover, it is generally accepted that their corrosion resistance in many media is lower. Even as anodes in electrolytic cells, we are aware of a quite different system, a neutral aqueous phosphate buffer, where mild steel (alloy B) dissolves much less readily than a stainless steel (similar to alloy D) [12]. Such information, however, relates to conditions of active corrosion or, more commonly, those where the surface is passivated. Ferrate formation occurs in a transpassive regime. The structure of the carbon steels consists of two phases. At low carbon contents, iron and iron carbide coexist. The structure is made up of many small grains and the crystals of iron carbide are found at the inter-grain boundaries. As the carbon content is increased above 0.5%, the two phases which coexist are iron carbide and a solid solution of iron and iron carbide [11] and more complex structures (e.g., laminar arrangements of the phases are found). It should, however, be noted that the current efficiency for ferrate appears to increase smoothly through such structural changes. It has been proposed that the separation into two phases creates the possibility of local corrosion cells but it must be recognized that, in the electrolysis cell, the iron alloy is covered with an oxide/hydroxide layer and it is more likely that the carbon modifies the properties of this layer. For example, perhaps the carbide ion is able to create pits in the oxide/hydroxide layer.

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