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Electrochemical generation of ferrate
Part I: Dissolution of an iron wool bed anode

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The preparation of ferrate by the anodic dissolution of iron in 10 M NaOH using a membrane cell with an iron wool anode is described. It is shown that the current efficiency drops from an initial value of 45–60% to ~25% during a 2–3 h electrolysis. This is shown to be due to a change in the iron anode surface, probably the composition, structure and/or thickness of surface films. The influence of cell current as well as NaOH concentration and temperature on the current efficiency is described. The kinetics of the reactions of ferrate with water, alcohols and phenol have also been investigated and it is shown that some organics (methanol, ethanediol and phenol) undergo complete oxidation to CO_2 and H_2O even at room temperature.

1. Introduction

At the present time, there is considerable interest in the development of new technology for the disinfection and removal of trace organic materials from potable water supplies and also the removal of organics from aqueous process streams prior to recycle or discharge into natural waters. Much of the driving force results from the perceived need to discontinue the use of chlorine and chlorine derivatives for such purposes. Both direct and indirect electrochemical processes have been described which avoid chlorine as an intermediate. For indirect electrolytic processes, as well as procedures based on the addition of chemical oxidizing agents, it is essential that after treatment, the water does not contain unwanted chemicals resulting from the treatment process. Hence, the favoured oxidizing agents have included oxygen, ozone and hydrogen peroxide; the former is not harmful and, indeed, is an essential component of environments which support life while ozone and hydrogen peroxide are considered to decompose only to oxygen and/or water. All may be made by electrolysis.

Another strong oxidizing agent which could meet the environmental requirements is ferrate (as the sodium or potassium salt). Iron is normally an innocuous element in the environment. Moreover, a product from oxidation in neutral or alkaline solution is normally insoluble ferric hydroxide. This can behave as a very efficient flocculating agent before it is removed by filtration, thus aiding further the water treatment process. Several papers have already discussed the application of ferrates in water and effluent treatment; for example, it has been shown that ferrate can remove toxic organic molecules such as nitrosamines [1], phenol [2] and nitrilotriacetic acid [3], as well as inorganic ions such as cyanide [4], destroy viruses [5] and bacteria [6] and act as a biocide [7]. Such water treatment procedures can also lead to the simultaneous removal of metal ions precipitated with the $Fe(OH)_3$ as it forms [4, 6].

Ferrate is usually prepared in strongly alkaline media where it is recognized to be quite stable at room temperature. Solid sodium and potassium ferrate are also quite stable but there are differing opinions about the stability of ferrate in near neutral aqueous media [8, 9], presumably because of the influence of impurities. In acidic and weakly alkaline solutions, ferrate is very unstable and it is clear that the mechanism and kinetics of the ferrate/water reaction are complex. Moreover, the decomposition of ferrate is catalysed by transition metal species including solid $Fe(OH)_3$. It is, therefore, possible to envisage approaches to water and effluent treatment based on (a) the addition of a solid ferrate salt to a neutral solution or (b) dosing the water or effluent with a strongly alkaline solution of ferrate.

As a strong oxidizing agent (the standard potential for the $FeO_4^{2-}/Fe(OH)_3$ couple is +0.72 V vs SHE [10]), ferrate has also attracted the attention of organic chemists. It has, for example, been used for the oxidation of alcohols [9, 11] and carbohydrates [12] and conversion of alcohols to aldehydes or ketones can be selective. The mechanism has been studied and it has been proposed that the initial attack occurs at a C–H bond α to the OH group [9].

Ferrate can also be prepared electrolytically by the anodic dissolution of iron in strongly alkaline solution, often 14–19 M NaOH. Indeed, the reaction was first reported in 1841 [13] and hence it was one of the earliest electrochemical preparations. It has been reinvestigated at intervals [14–26] but, in general, the yields are poor and the electrolysis is limited to a low current density. It is recognized that the evolution of oxygen always competes with the formation of ferrate and that the relative rates of these competing reactions depend on the composition of the passivating films on the surface of the iron anode. Hence, pretreatments of the iron surface to remove existing oxide layers, for example, cathodic polarization [15] and acid etching [23] have been recommended. It is also common for the yield of ferrate to drop with electrolysis time and techniques such as current reversal [15] and a.c. modulation of the current [16, 26] have been proposed in order to maintain the higher initial current efficiency.

In this paper we report the preparation of ferrate in an electrolytic cell with a three dimensional anode fabricated from a bundle of iron wool; three-dimensional electrodes are known to be suited to electrolyses which occur at low current density [27]. An objective was to develop a high yield route at an acceptable current density to the synthesis of ferrate solution which could be used directly for water or effluent treatment. It was, therefore, desirable to avoid the addition of chloride [21, 22] (which opens up the possibility for the formation of chlorinated organics) or the use of an a.c. current [26] (which was considered impractical). It was considered advantageous to use the minimum sodium hydroxide concentration compatible with the chemistry of the system and most experiments reported here involve 10 M NaOH; this is significantly lower than those used in most papers referenced above. Indeed, some experiments are reported with even lower NaOH concentrations. A factor in the choice of alkali concentration is the stability of the ferrate in homogeneous solution and, therefore, the kinetics of the ferrate/water reaction as a function of sodium hydroxide concentration were also considered. Finally, the reaction of ferrate with dilute solutions of alcohols and phenol were investigated.

2. Experimental details

Voltammetric experiments were carried out in a three electrode, two compartment glass cell. The working electrode was a disc of an iron alloy (>98% Fe, 0.94% Mn, 0.31% Si, 0.20% C) from Goodfellow Metals; its diameter was 5 mm and it was surrounded by a polypropylene sheath. Prior to experiments, it was polished sequentially with 1, 0.3 and 0.05 μm alumina powder (Buehler) on a felt pad (Buehler) and then washed well with water. The counter electrode was a Pt spiral and the reference electrode was Hg/HgO in 10 M NaOH, separated from the working electrode by a Luggin capillary.

Preparative electrolyses were carried out in the flow cell shown in Fig. 1(a). It was constructed from four blocks of polypropylene 270 mm × 100 mm × 10 mm. The centre two formed the electrolyte compartments and were machined so that there were entry and exit zones where the channel broadened slowly. The current collectors were stainless steel plates, 100 mm × 60 mm, sunk into one of the outer blocks, with an electrical contact through the block. The cathode was an iron wool bundle against the current collector. The separator was a Nafion^{TM} 350 cation permeable membrane and the gaskets were cut from a Viton^{TM} sheet. The cell was sealed via 16 bolts.

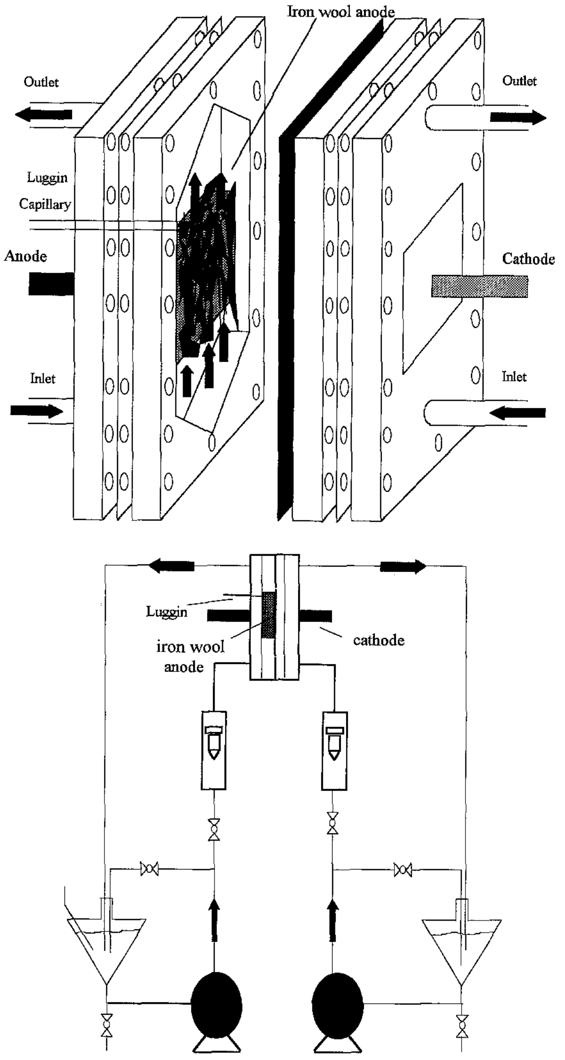

Fig. 1. Sketch of (a) membrane flow cell with iron wool anode and (b) flow circuit used for the preparation of ferrate by the dissolution of iron wool in concentrated aqueous sodium hydroxide.

The anode was made from iron wool (>99.5% Fe, 0.08% C) supplied by BDH Ltd; 36 g of the iron wool was worked into a uniform pad 60 mm × 100 mm × 10 mm and fitted into the anolyte channel so that it was adjacent to the anode current contact plate. The cell performance was found to be very sensitive to the uniformity and thickness of this iron wool electrode. The membrane was protected from the iron wool with a sheet of coarse polymer mesh. The catholyte was an aqueous NaOH solution with the same concentration as used in the anolyte.

The flow circuit is shown in Fig. 1(b). The anolyte and catholyte each had a 1 dm^3 glass reservoir, a Totton pump type NDP 14/2 (2 $dm^3 min^{-1}$), and a 0.2–1.5 $dm^3 min^{-1}$ flow meter, type GTF 2ASS from Flowbits. The electrolyses generally used 0.45 dm^3 of anolyte and catholyte and the electrolyte flow rates were generally 0.8 $dm^3 min^{-1}$. The cell connectors were supplied by Nalgene and were Soltube Quick-Disconnect fittings 6175 with 1/4 inch internal diameter.

The voltammetric experiments used a Hi Tek potentiostat, type DT2101, and pulse generator, type PPR1 and responses were recorded on a Gould series 60000 *X-Y* recorder. Constant current electrolyses were controlled with a Powerline power supply. U.v. visible spectra were recorded in 2 mm glass cuvettes using a Philips PU8730 spectrometer.

Solutions were prepared with water from a Milli-Rho/MilliQ system. The sodium hydroxide was BDH AnalaR grade. The standard ferrate solution was prepared by the addition of 1.622 g (10 mmole) of anhydrous ferric chloride to a solution of 14% NaClO in 10 M NaOH. The mixture was then stirred vigorously at room temperature until no further solid was dissolving and the absorbance at 505 nm reached a steady state. A small amount of solid was filtered off, dried and weighed (0.096 g) and the concentration of ferrate in solution after making up to one litre (9.4 mM) was calculated assuming that the red/brown solid was Fe_2O_3 and all the other Fe(III) had been converted to FeO_4^{2-}. The solution of ferrate was deep purple and in the presence of the large excess of hypochlorite, it was stable indefinitely. The spectrum of this solution was found to have a visible spectrum identical to that reported by Carrington *et al.* [28] and Wood [10] for the sodium ferrate in sodium hydroxide solution. The major absorption peak occurs at $\lambda_{max} = 505$ nm with an extinction coefficient, $\epsilon_{max} = 1070\ dm^3\ mol^{-1}\ cm^{-1}$.

3. Results and discussion

3.1. *Stability of ferrate in sodium hydroxide solutions*

The solutions of sodium ferrate in 10 M NaOH were prepared by electrolysis (see below); their visible spectra were identical to that of a solution prepared chemically and also reported in the literature [10, 28]. The absorbance at the wavelength of the peak at 505 nm was used to monitor the decomposition of the ferrate. Figure 2 shows the decrease in the absorbance of a ferrate solution, initially 10 mM ferrate in 10 M NaOH, at 297 K. It can be seen that the decay in absorbance was very slow, occurring over many days and that the plot of $\ln A_t/A_{t=0}$ against t was linear confirming that the reaction

$$4FeO_4^{2-} + 10H_2O \longrightarrow 4Fe(OH)_3 + 3O_2 + 8OH^-$$

was first order in ferrate. The rate constant was $7.2 \times 10^{-7}\ s^{-1}$ and the half life of the ferrate in these conditions was about 270 h. The $Fe(OH)_3$ appeared to be formed as large particles on the surface of the glass optical cell.

This experiment was repeated at a series of temperatures up to 333 K. As expected the stability of the ferrate decreased substantially with increasing temperature (the half life was only ~2.5 h at 333 K) but the decay in absorbance remained first order in ferrate. At all temperatures, however, the solution colour change was from dark purple to colourless and the $Fe(OH)_3$ is formed on the glass of the optical cell. An Arrhenius plot is shown as an inset to Fig. 2 and the energy of activation estimated from the slope was 99 kJ mol^{-1}. The rate constants determined in this way were all ~10 lower than those reported by Tousek [19] for ferrate decomposition in 19 M NaOH although the energies of activation are similar. The differences suggest impurities in the chemicals used in the earlier study.

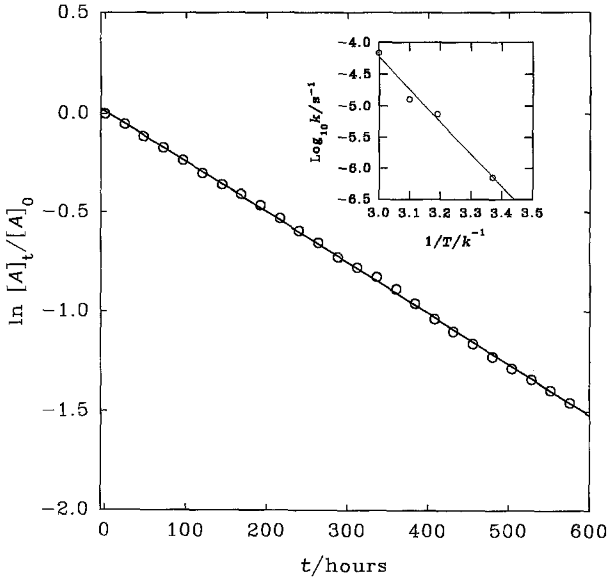

Fig. 2. Plot of $\ln[A]_t/[A]_0$ against t for a solution of ferrate, initially 10 mM, in aqueous 10 M NaOH solution at 298 K. $[A]_t$ is the absorbance of the solution at 505 nm at time, t and $[A]_0$ is the absorbance of the solution at $t = 0$. The inset shows an Arrhenius plot for the rate constant for the ferrate/water reaction (taken from the slopes of $\ln[A]_t/[A]_0$ against t plots) as a function of temperature.

A 1 mM ferrate solution in 1 M NaOH was prepared by dilution of the anolyte from the electrolysis cell with water and, again the absorbance was monitored as a function of time. The decay in absorbance now occurs on a quite different timescale and the half life of the ferrate was only some 180 s. The plot of absorbance versus time was no longer exponential and there was initially a clear trend for the rate of reaction to increase with time. Towards the end of the reaction, the solution was yellow/orange and the absorbance at 505 nm began to increase again. When the spectra were recorded as a function of time, see Fig. 3, it was apparent that another different species was being formed. Early in the experiment, the purple ferrate solution was characterized by absorbance peaks at 505 and 780 nm and there was also some absorption below 375 nm. As the reaction proceeds in 1 M NaOH, the visible absorption peaks decreased but a new and strong absorbance was observed in the u.v. which tailed into the visible region and gave a growing contribution to the absorbance at 505 nm. Moreover, no $Fe(OH)_3$ was formed on the glass walls of the optical cell. We therefore believe that the $Fe(OH)_3$ was being formed as a colloid or very fine suspension throughout the solution and this was the cause of the orange colouration of the solution. The large change in the rate constant (a factor of ~5000) for ferrate decomposition for a tenfold decrease in sodium hydroxide concentration implies strongly a change in mechanism. The increase in the rate of decomposition with time was compatible

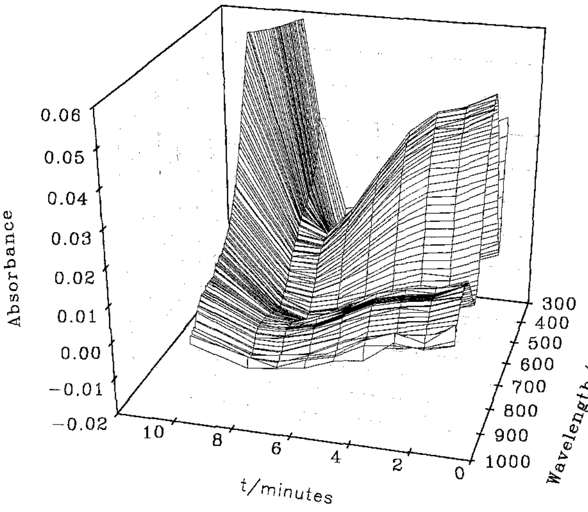

Fig. 3. Spectra of a solution initially 1 mM ferrate in 1 M aqueous NaOH as a function of time.

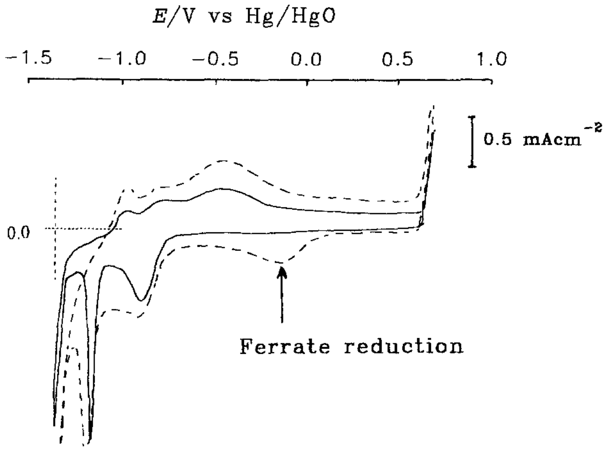

Fig. 4. Cyclic voltammograms for an iron disc electrode in 10 M NaOH at 298 K. The solid line shows the response when the potential is held at +650 mV for 30 s before the potential scan while the dashed line shows the voltammogram when the positive limit is +700 mV. Potential scan rate 250 mV s^{-1}.

with an autocatalytic reaction scheme where the high surface area $Fe(OH)_3$ acts as a heterogeneous catalyst. The catalysis of the ferrate/water reaction by transition metal species including $Fe(OH)_3$ has previously been suggested [9].

A few experiments were carried out by dissolving solid sodium ferrate in water. Initially, the ferrate appeared to be stable as a neutral solution but, again, once a small amount of $Fe(OH)_3$ was formed, decomposition suddenly became rapid. The 'initial' time during which the ferrate appeared stable was variable but it is clear that the oxidation of many organic compounds should be possible in these conditions.

Clearly, a requirement for a successful electrosynthesis of ferrate is that the cell design must allow a timescale for the electrolysis which is much less than the half life of the ferrate in the electrolysis conditions. This determined the selection of a cell with a high surface area anode to give a high rate of conversion. Moreover, the kinetics reported above clearly indicate that concentrated NaOH is essential and 10 M NaOH, close to room temperature, were potentially useful conditions for electrolysis. On the other hand, the complex kinetics of the ferrate/water reaction offer several windows of opportunities to carry out rapid reactions of ferrate with organic molecules. For example, reaction between ferrate (added as a solid) and organics in neutral media should be possible.

3.2. *Synthesis of ferrate in a cell with an iron wool anode*

The corrosion of iron has, of course, been widely studied [29–32] and it is also well known that complex oxide/hydroxide chemistry occurs during polarization of iron in 10 M NaOH. Figure 4 illustrates the voltammetry of iron when the potential is scanned through the passive region to positive potentials where oxygen evolution occurs. The interpretation of this complex voltammetry is not the purpose of this work. Here, it is suffice to note the appearance of the additional reduction peak, $E_p = -300$ mV vs Hg/HgO when the positive potential limit is extended by 50 mV from 650 to 700 mV. This peak is due to the reduction of ferrate [23, 33] as may be confirmed by adding ferrate to the solution. The voltammetry also clearly confirms that ferrate will only be formed at potentials where oxygen gas evolution is a competing reaction. In this system, the current efficiency for ferrate formation must be expected to be a strong function of many parameters including potential (or current density), temperature as well as the history and composition of the passivating oxide layer (see later). It is also not surprising that the yield is influenced by ions likely to cause pitting (e.g., chloride) [21, 22].

Figure 5 reports a plot of ferrate concentration in the anolyte versus time for an electrolysis carried out in a membrane flow cell with a bed electrode fabricated by packing the central part of the anolyte chamber with iron wool. The anolyte was 10 M NaOH at room temperature and the cell current was 1 A corresponding to a superficial or 'membrane' current density of 17 mA cm^{-2}. It can be seen that the ferrate concentration builds up with time and reached 10 mM within 3 h. As expected from the kinetic data above, no $Fe(OH)_3$ formation was observed and there was no evidence for decomposition of the ferrate within the anolyte stream. On the other hand, it was also clear that the ferrate concentration does not increase linearly with time. Since this was not due to the homogeneous decomposition of the ferrate (this was confirmed by switching off the electrolysis, when the absorbance at 505 nm was effectively constant), the ratio of ferrate/oxygen formed at the anode must have decreased with time.

Figure 6 shows data from a series of similar electrolyses carried out at different cell currents; the results are presented as plots of overall current efficiency versus time. In the case of the experiment described above for 1 A, the current efficiency was initially

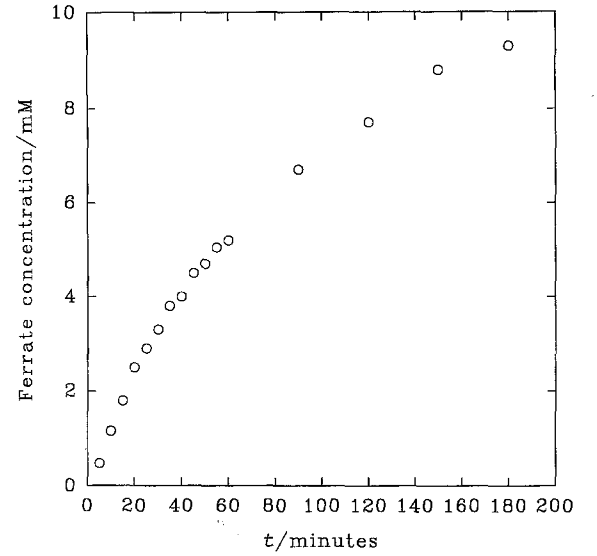

Fig. 5. Concentration of ferrate in the anolyte as a function of time during an electrolysis with a current of 1 A in the membrane flow cell with an iron wool anode. Anolyte: 10 M NaOH. Temperature 298 K.

almost 50% but tends to a value around 20% after ~2 h. In fact, the incremental current efficiency was close to 20% throughout the second half of this electrolysis. On increasing the cell current to 5 A, the current efficiency started at ~15% but showed only a small drop to ~10% during the electrolysis period. It should, however, be noted that although the current efficiency is lower at the higher cell current, the rate of production of ferrate is significantly higher at 5 A. With a cell current of 0.4 A, the trend was the same as 1 A although the current efficiencies were slightly lower. On the other hand, at the lowest current, 0.2 A, the behaviour was different. There was a delay before ferrate begins to form. We do not believe that Fe(IV) or Fe(V) intermediates are ever stable in these conditions and it must be concluded that initially, the anode surface conditions are inappropriate for the formation of Fe(VI). Almost certainly, the anode potential was not sufficiently positive for ferrate to be formed and oxygen evolution is the dominant reaction.

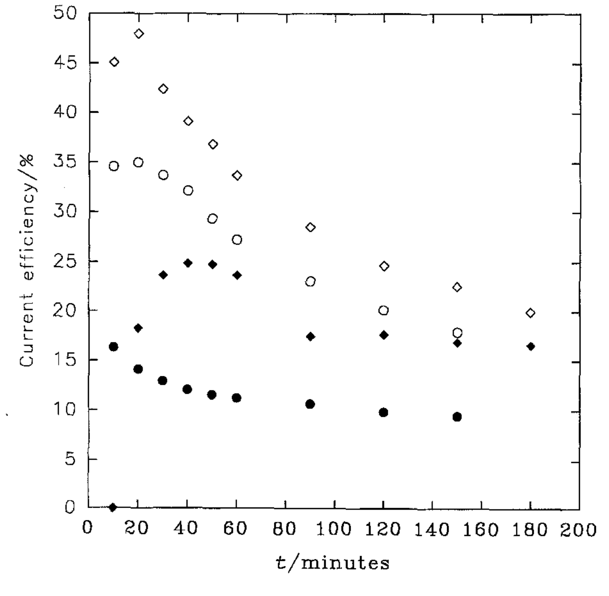

Fig. 6. Current efficiency as a function of time for a series of electrolyses in the membrane flow cell with the iron wool anode. Anolyte: 10 M NaOH. Temperature 298 K. Cell currents: (●) 5, (◇) 1, (○) 0.4 and (◆) 0.2 A.

Table 1. Current efficiency for the formation of ferrate as a function of sodium hydroxide concentration and temperature in the membrane cell with an iron wool anode

[NaOH] /M	*Temperature* /K	*Current efficiency** /%
10	273	59
	293	45
	333	35
5	293	37
2	293	2
1	293	1
0.1	293	0

* Current efficiency after 300 s.
Cell current 1 A; temperature ~300 K.

Overall, it is clear that, in general, the trend was for a high initial current efficiency for ferrate formation but this decayed with continued electrolysis. In further experiments, it was shown that simply changing the anolyte did not recreate the conditions for a high current efficiency. On the other hand, thorough acid washing of the iron wool between electrolyses allowed the rerun of the above experiments. Hence, we believe that the current efficiency reflects the composition and perhaps structure or thickness of the oxide films on the iron surface. Certainly, after the electrolysis, a black layer was seen on the iron wool and its original metallic appearance was recovered by a thorough acid wash. It is, therefore, not surprising that control techniques which reduce oxide on the iron surface (e.g., current reversal) [15], have been reported to be effective in maintaining the initial, high current efficiency. Some preliminary experiments confirmed this possibility was applicable to three dimensional anodes.

Current efficiencies for electrolyses carried out at 1 A at a series of temperatures and sodium hydroxide concentrations are reported in Table 1. The values reported are 'initial current efficiencies' after 300 s. In general, although the values were lower, the trends were the same after longer electrolysis. For example, the current efficiencies after 150 min were 20, 17 and 15% at temperatures of 298, 313 and 333 K, respectively. Clearly, the use of a lower temperature has a small advantage. The results in Table 1 also confirm that a high concentration of NaOH was essential but, interestingly, the major change in electrolysis performance occurred below 5 M. None of these trends are determined by decomposition of the ferrate in homogeneous solution (cf. the electrolysis time of 300 s with the half lives for ferrate reported in Section 3.1). Although previously reported, the very low yield of ferrate in 1–2 M NaOH is perhaps surprising. It does seem that the properties of passivating film on iron are very sensitive to both temperature and hydroxide concentration and that ferrate is only formed when the thickness, composition and/or structure fall within a narrow range. It is tempting to interpret the

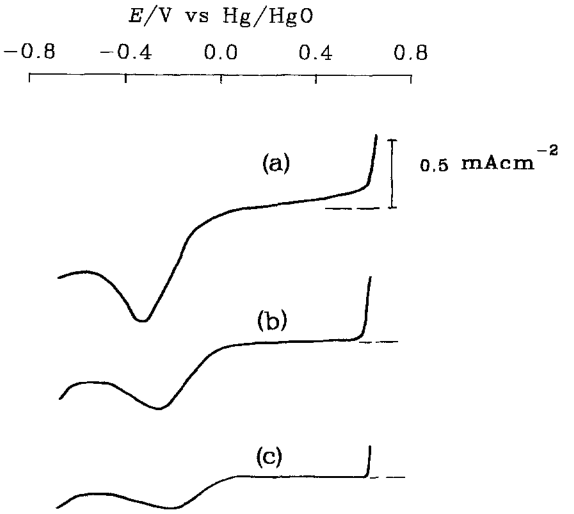

Fig. 7. Linear potential scans recorded at 250 mV s^{-1} for an iron disc electrode in 10 M NaOH after a current density of 5 mA cm^{-2} had been passed for 20 s. Immediately prior to the experiments, the electrode had been conditioned by passing a current density of 5 mA cm^{-2} for (a) 10 s, (b) 100 s and (c) 1000 s and the ferrate formed during the conditioning was then dispersed with a stream of nitrogen for a few seconds. Temperature 298 K.

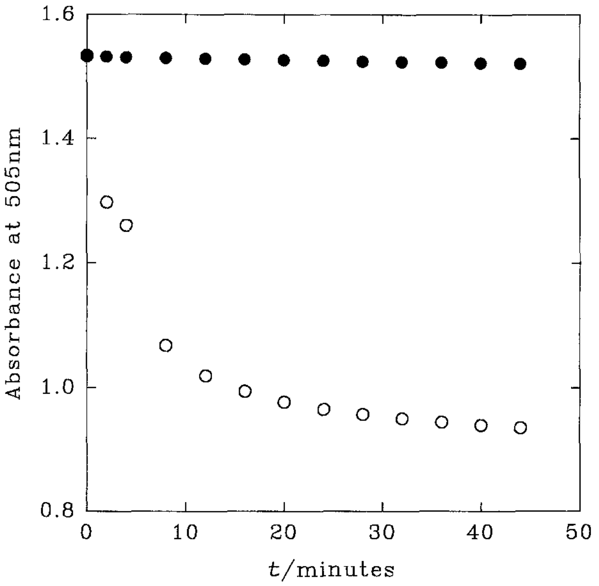

Fig. 8. Plots of absorbance versus time for solutions initially (●) 7.2 mM ferrate in 10 M NaOH (○) 0.5 mM C_2H_5OH + 7.2 mM ferrate in 10 M NaOH. Temperature 298 K.

differences at short times to slow changes in the oxide film after the potential of the iron anode was taken into the very positive region for ferrate generation. A few experiments sought to investigate the influence of the packing and thickness of the iron wool anode; it was clear that a good current efficiency was favoured by a dense but uniform packing which filled the whole electrolyte channel.

Several further series of experiments were carried out in order to demonstrate the role of surface films and their conditions of formation on the current efficiency for ferrate. Using a stationary and polished Fe disc in 10 M NaOH, the following sequence was followed: (i) a reproducible film was established on the iron surface by applying a constant potential or passing a constant current density for a defined period, (ii) a fast stream of nitrogen gas was used to disperse from the anode surface all the ferrate formed during this conditioning phase, (iii) a constant potential or a constant current for a short period was used to form ferrate on the preconditioned surface, and (iv) a potential sweep through the range where the reduction of ferrate occurs was used to estimate the relative amounts of ferrate formed during (iii). Figure 7 illustrates the results from such experiments. It shows the current/potential responses to the scans following preconditioning of the surface with a current density of 5 mA cm^{-2} for various periods followed by generation of ferrate at the same current density for 20 s. It can be conclusively seen that the peak for the reduction of ferrate decreased as the conditioning period was increased. This is akin to the loss in current efficiency with electrolysis time but shows conclusively that the decrease in yield occurs even in a short timescale experiment with well defined and reproducible surfaces and hence confirms that the loss in current efficiency is indeed due to a surface effect. Such experiments, of course assume that the cathodic peak current density reflects the concentration of ferrate close to the anode. It should be noted that Beck *et al.* [23] have reported that ferrate ion reduction on iron is complicated by chemical reactions between ferrate and the iron; we have not observed evidence for such chemical processes and, in any case, would suggest that such complications would not greatly influence the interpretation of relative peak heights where the differences are substantial.

3.3. *Oxidation of alcohols by ferrate*

For the destruction of organics in waters, the complete oxidation to CO_2 and H_2O is often desirable. Hence, a series of reactions of alcohols with a large excess of ferrate was studied. The experiments followed the procedure: (i) a solution ~10 mM ferrate in 10 M NaOH, prepared electrolytically in the membrane cell with the iron wool anode, was cooled and mixed with a solution of the alcohol (concentration chosen so that in the mixed solution, its concentration was 0.5 or 1.0 mM) in 10 M NaOH, (ii) this solution was placed in the spectrometer and the absorbance at 505 nm was monitored with time, and (iii) when the absorbance reached a steady value, the solution was filtered to remove the $Fe(OH)_3$ formed and the absorbance was checked at intervals to ensure that no further reaction was occurring. A typical set of absorbance/time plots, in fact those for ethanol are shown in Fig. 8. The total change in ferrate concentration allows an estimate of the extent of oxidation of the alcohol while the rate of change in the absorbance permits an estimate of the kinetics of the reactions.

The results are summarized in Table 2. It can be seen that, with methanol, ethanediol and phenol, complete oxidation to CO_2 and H_2O occurs. With the larger alcohols, there is significant oxidation but the reaction does not go to completion and there must be partially oxidized organics in the final solution. It can be seen that, in these conditions, the rates

Table 2. Data from the reactions between alcohols and phenol and excess ferrate in 10 M NaOH at room temperature

Alcohol	*[alcohol]* /mM	*[ferrate]*/mM		*Reaction timescale** /s	*Extent of oxidation/e⁻ per alcohol molecule*	
		Initial	*Final*		*Experimental*	*Complete oxidation*
CH_3OH	0.5	11.5	10.5	180	6	6
	1.0	11.5	9.6	420	6	
C_2H_5OH	0.5	7.2	5.7	360	9	12
C_3H_7OH	0.5	8.3	6.3	900	12	18
$C_2H_5CH(OH)CH_3$	0.5	10.2	7.3	1245	14	24
$C_2H_5C(OH)(CH_3)_2$	0.5	9.7	8.0	1560	10	30
$(CH_2OH)_2$	0.5	11.3	9.7	720	10	10
C_6H_5OH	0.5	11.0	5.3	1685	34	28

* Time to 50% change in ferrate concentration.

of reaction are fast; with the straight chain alcohols, the rate of oxidation decreases with increasing number of carbons in the skeleton and the secondary and tertiary alcohols are oxidized only more slowly. The oxidation of phenol was complete after a few hours and, in general, the timescale of the other reactions is less than 2 h.

4. Conclusions

The membrane cell with an anode fabricated from iron wool allows the convenient preparation of ferrate at a reasonable rate and current efficiency in 10 M NaOH. While ferrate may also be prepared in 5 M NaOH, in 1 M NaOH the yield is negligible. Although the rate of the homogeneous decomposition of ferrate also increases in importance very rapidly as the [NaOH] concentration is decreased, this is not the explanation of the decay in electrolysis performance. The change in product from ferrate to oxygen must therefore result from differences in the chemistry of the iron oxide surface films on the anode with NaOH concentration. It is also clear that the surface of the iron anode changes during electrolysis and initial current efficiencies of up to 60% drop to ~25% during a couple of hours. We have found that thorough acid washing is a suitable procedure to reverse this unwanted change and also confirmed the earlier conclusion [15] that current reversal would maintain a higher current efficiency even in the three dimensional anode cell.

Ferrate is shown to react with both alcohols and phenol, giving significant extents of oxidation in a timescale of less than 1 h. With methanol and ethanediol complete oxidation to CO_2 and H_2O is observed in <20 min. Phenol also oxidizes completely but takes longer. Others have reported oxidation of organics and inorganics as well as the destruction of viruses and bacteria [1–6, 9, 11, 12] and we therefore believe that ferrate could be used effectively as a water treatment reagent. The electrolytic preparation avoids contamination of the ferrate by chloride but scale up would necessitate careful selection of conditions.

Acknowledgement

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References

[1] R. Bartzatt and D. Nagel, *Archives Environ. Health* **46** (1991) 313.
[2] T. D. Waite and M. Gilbert, *J. Water Pollution Control Fed.* **50** (1978) 543.
[3] J. D. Carr, P. B. Keller and A. T. Ericson, *Environ. Sci. Technol.* **15** (1981) 184.
[4] N. Neveux, N. Aubertin, R. Gerardin and O. Evrard, *in* 'Chemical Water and Wastewater Treatment III' (edited by R. Klute and H. H. Hahn), Springer Verlag, Berlin (1994).
[5] T. Schink and T. D. Waite, *Water Res.* **14** (1980) 1705.
[6] R. K. Murmann and P. R. Robinson, *ibid.* **8** (1974) 543.
[7] J. Fagan and T. D. Waite, *Environ. Sci. Technol.* **17** (1983) 123.
[8] T. Ernst, M. Wawrzenczyk, M. Cyfert and M. Wronska, *Bull. Acad. Polonaise Sci.* **27** (1979) 773.
[9] D. G. Lee and H. Gai, *Can. J. Chem.* **71** (1993) 1394.
[10] R. H. Wood, *J. Am. Chem. Soc.* **80** (1958) 2038.
[11] R. J. Audette, J. W. Quail and P. J. Smith, *Tetrahedron Lett.* **39** (1971) 279.
[12] J. N. BeMiller, V. G. Kumari and S. D. Darling, *ibid.* **40** (1972) 4143.
[13] J. C. Poggendorf, *Pogg. Ann.* **54** (1841) 372.
[14] F. Haber, *Z. Elektrochem.* **7** (1900) 215.
[15] W. Pick and F. Haber, *ibid.* **7** (1901) 713.
[16] G. Grube and H. Gmelin, *ibid.* **26** (1920) 153.
[17] *Idem, ibid.* **26** (1920) 459.
[18] G. Grube, *ibid.* **33** (1927) 389.
[19] J. Tousek, *Coll. Czech. Chem. Comm.* **27** (1962) 908 and 914.
[20] A. S. Venkatadri, H. H. Bauer and W. F. Wagner, *J. Electrochem. Soc.* **121** (1974) 249.
[21] J. P. Deininger (Olin), *US Patent 4 435 256* (1984).
[22] J. P. Deininger and R. L. Dotson (Olin), *US Patent 4 435 257* (1984).
[23] F. Beck, R. Kaus and M. Oberst, *Electrochim. Acta* **30** (1985) 173.
[24] A. A. Kamnev and B. B. Ezhov, *Soviet Electrochem.* **24** (1988) 1027.
[25] K. Bouzek and I. Rousar, *J. Appl. Electrochem.* **23** (1993) 1317.
[26] *Idem, Electrochim. Acta* **38** (1993) 1717.
[27] D. Pletcher and F. C. Walsh, *in* 'Electrochemistry for a Cleaner Environment' (edited by J. D. Genders and N. L. Weinberg), The Electrosynthesis Co., Lancaster, NY (1992).
[28] A. Carrington, D. Schonland and M. R. C. Symons, *J. Chem. Soc.* (1957) 695.
[29] J. O'M. Bockris, B. E. Conway, E. Yeager and R. E. White (eds), 'Comprehensive Treatise of Electrochemistry', Vol. 4, Plenum Press, New York (1981).
[30] O. J. Murphy, *in* 'Electrochemistry in Transition from the 20th to the 21st Century' (edited by O. J. Murphy, S. Srinivasan and B. E. Conway), Plenum, New York (1992) p. 521.
[31] R. D. Armstrong and I. Baurhoo, *J. Electroanal. Chem.* **34** (1972) 41.
[32] *Idem, ibid.* **40** (1972) 325.
[33] A. S. Venkatadri, W. F. Wagner and H. H. Bauer, *Anal. Chem.* **43** (1971) 1115.