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Electrochemical production of ferrate(VI) using sinusoidal alternating current superimposed on direct current. Pure iron electrode

K. BOUZEK[1], L. FLOWER[2], I. ROUŠAR[1†] and A. A. WRAGG[2]

[1]*Institute of Chemical Technology, Department of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic;*

[2]*University of Exeter, School of Engineering, North Park Road, Exeter, EX4 4QF, UK*

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Abstract

The current yield for the anodic oxidation of a pure iron (99.95%) electrode to ferrate(VI) ions in 14 M NaOH between 30 and 60 °C using a sinusoidal alternating current (a.c.) at amplitudes in the range 38–88 mA cm^{-2} and frequencies in the range 0.5 mHz to 5 kHz superimposed on direct current (d.c.) of 16 mA cm^{-2} was measured under conditions of bubble induced convection in a batch cell. The current yield for ferrate(VI) synthesis exhibited a complex dependence on temperature and a.c. frequency, but generally a maximum was observed in a frequency range 2–50 Hz depending on the a.c. amplitude. A global maximum current yield after 180 min of electrolysis of 33% was reached at the following conditions: a.c. amplitude of 88 mA cm^{-2}, a.c. frequency of 50 Hz and temperature of 40 °C. At the optimum conditions the highest d.c. electrolysis yield was 23%. Thus, operation with the a.c. component leads to an increase in the yield by 43% with respect to d.c. electrolysis alone.

1. Introduction

In the first part of this series [1] previously published results [2–13] concerned with ferrate(VI) production by anodic dissolution of iron were discussed. In agreement with [10, 11] significant differences in the behaviour of grey and white cast iron electrodes were also found using a superimposed a.c. component [1]. Although grey cast iron exhibits a yield maximum in the a.c. frequency range 5 mHz to 0.5 Hz, depending on the amplitude, white cast iron shows highest ferrate(VI) yield in the frequency range 0.5 to 5 Hz. For grey cast iron a pronounced maximum in the yield against a.c. frequency relationship was observed. Using a white cast iron a complex relationship showing one maximum and two minima was found. The white cast iron behaviour is close to that of mild steel [9]. The difference between grey cast iron and the other studied electrode materials was explained as being due to the presence of graphite in the grey cast iron structure and, consequently, on the surface [10–12]. This hypothesis was verified by reference to galvanodynamic polarization curves presented earlier [1].

The differences in the current yield for direct current (d.c.) electrolysis using white cast iron and pure iron anodes were explained [12] in terms of the different passivating properties of the surface oxihydroxide layers; these are strongly dependent on the iron carbide (Fe_3C) content of the anode material.

The present work employed pure iron (99.95 wt %) to offer elucidation of the influence of both the content and form (graphite particles or Fe_3C particles) of the carbon in the working electrode material on the properties of the oxihydroxide layer covering its surface and, consequently, on the current yield.

2. Experimental details

Chemicals, analytical methods, apparatus and experimental techniques are described elsewhere [1]. The cell parameters, anode material composition and structure are discussed in [12].

[†] Deceased

The d.c. current density component was 16 mA cm^{-2} in all cases. A wide range of a.c. component frequencies, 0.5 mHz to 5 kHz, and amplitudes (peak-to-peak), 38–88 mA cm^{-2}, were applied and temperature was varied in the range 30–60 °C. The current yield was calculated with respect to d.c. current electrolysis, the reasons for this being discussed in detail in [1]. The average accuracy of the data was ±1% (absolute).

3. Results

3.1. *Dependence of ferrate(*VI*) current yield on a.c. frequency and amplitude*

The ferrate(VI) yields as a function of a.c. frequency are presented for an a.c. amplitude of 63 mA cm^{-2} in Figure 1. For comparison the current yields for d.c. only are shown in the same Figure.

Using a pure iron electrode, the peak yield was observed in the a.c. frequency range 2–50 Hz. The highest yield after 180 min of electrolysis, 33%, was obtained at an a.c. amplitude of 88 mA cm^{-2}, a frequency of 20 Hz and a temperature 40 °C. This represents an increase of 43% compared to d.c. electrolysis (23%). The maximum increase in yield, 106% with respect to d.c. electrolysis alone, was found at an a.c. amplitude of 88 mA cm^{-2}, a frequency of 50 Hz and a temperature of 30 °C. It was generally observed that the influence of the a.c. component increased with decreasing temperature. The relatively low d.c. current yield at 60 °C is known to be caused by decomposition of ferrate(VI) and not by passivation of the working electrode surface.

It is shown in Figure 2(a), that the peak value of the ferrate(VI) yield shows a different dependence on a.c. component amplitude at different temperatures. In most cases the highest yield was reached at 50 °C, see Figure 2(a), the only exception being the highest studied a.c. amplitude, 88 mA cm^{-2}, for which the optimum temperature was 40 °C.

It is apparent from Figure 1 that the superimposed a.c. component not only caused a maximum in the current yield against a.c. frequency, but also a minimum

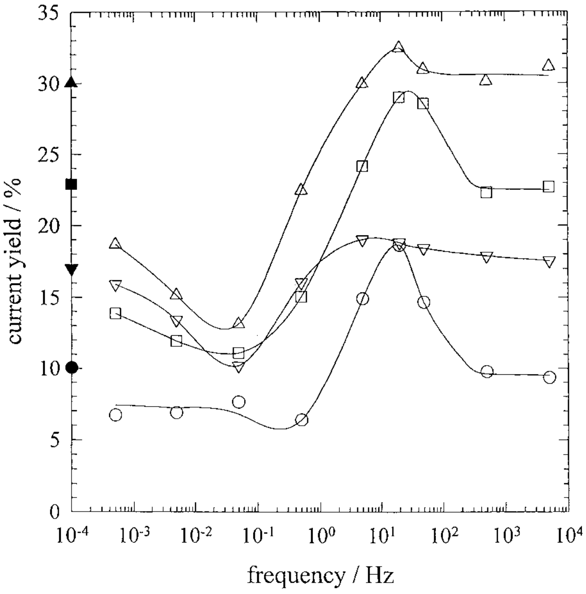

Fig. 1. Current yield for ferrate(VI) at various a.c. frequencies and a.c. amplitude of 62.7 mA cm^{-2} superimposed on d.c. current density of 16.0 mA cm^{-2}. Duration of electrolysis 180 min, temperature: (○) 30 °C, (□) 40 °C, (△) 50 °C and (▽) 60 °C. Filled symbols: d.c. electrolysis.

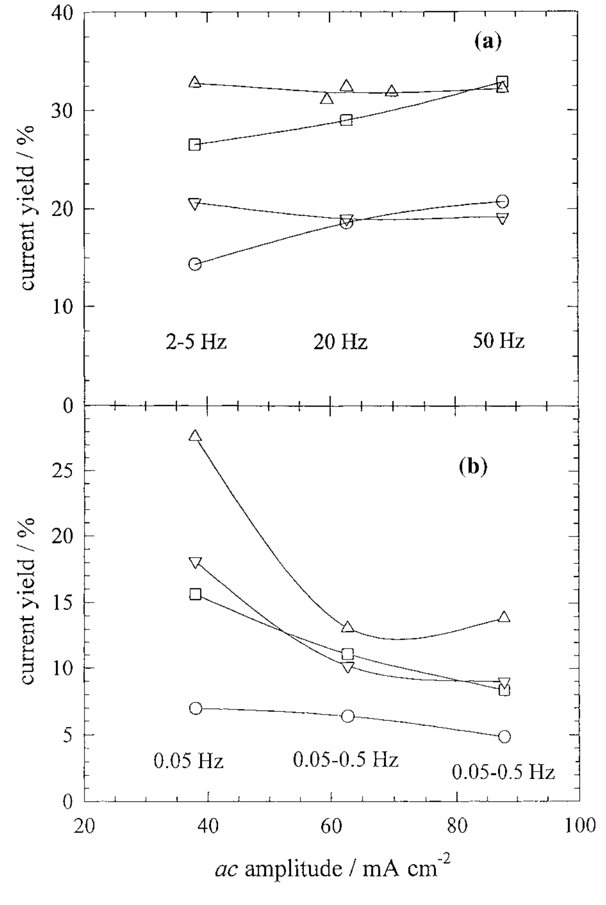

Fig. 2. Current yield for ferrate(VI), at the a.c. frequency providing (a) highest (b) lowest ferrate(VI) current yield at various a.c. amplitudes superimposed on a d.c. current density of 16.0 mA cm^{-2}. Duration of electrolysis 180 min, temperature: (○) 30 °C, (□) 40 °C, (△) 50 °C and (▽) 60 °C. The inserted numbers show the a.c. frequency used in the corresponding amplitude range.

in the frequency range 50 mHz to 0.5 Hz, an exception being the lowest studied a.c. amplitude of 38 mA cm^{-2}. The current yields found in this frequency range are lower in comparison with the yields for d.c. electrolysis. From Figure 2(b) it seems that this difference increases with increasing a.c. amplitude and temperature.

The dependence of the concentration of iron in oxidation states lower than Fe^{6+} (difference between the concentration of the total iron and Fe^{6+}) in the anolyte after 180 min of electrolysis on the a.c. frequency exhibits a marked increase in the a.c. frequency range corresponding to the lowest current yield. A second maximum occurs at the frequency providing the highest yield. The relevant concentrations in the a.c. frequency range corresponding to the minimum and maximum in the ferrate(VI) yield varies with a.c. amplitude and temperature as shown in Table 1.

3.2. *Dependence of ferrate(VI) current yield on electrolysis duration*

The dependence of current yield on electrolysis duration using an a.c. component amplitude of 63 mA cm^{-2} and frequencies corresponding to the maximum (20 Hz) and minimum (0.05 Hz) ferrate(VI) yields is shown in Figures 3 and 4. In all cases studied the maximum yield was reached after 30 min. The highest current yield of 50% was reached at 50 °C. This is an increase in yield of 12% with respect to d.c. electrolysis. It follows from Figure 3 that the influence of the a.c. component at 20 Hz increases with decreasing temperature. At 0.05 Hz the current yield was generally lower when compared to d.c. electrolysis.

Interesting information is also provided by the dependence of the concentration of iron in lower oxidation states in the anolyte on electrolysis time, shown for 20 Hz in Figures 5(a) and for 0.05 Hz in Figure 5(b). At 20 Hz the concentration approaches a nearly limiting value shortly after the start of electrolysis. At 30 °C this value remains approximately constant for 180 min. At 40 and 50 °C this period is shortened considerably and varies in the range 30 to 60 min.

Table 1. Dependence of the difference between the concentration of the total iron and Fe^{6+} in the anolyte a.c. frequency providing minimum and maximum ferrate(VI) yield at various amplitude and temperature, 14 M NaOH, electrolysis duration 180 min.

Amplitude/mA cm^{-2}		ΣFe − Fe^{6+}/g dm^{-3}			
		30 °C	40 °C	50 °C	60 °C
38.0	minimum	0,075	0,200	0,751	2,340
	maximum	0,119	0,297	1,061	3,051
62.7	minimum	0,053	0,218	0,620	1,739
	maximum	0,254	0,450	1,120	2,541
87.9	minimum	0,076	0,232	0,597	1.247
	maximum	0,470	0,460	1,165	2,650

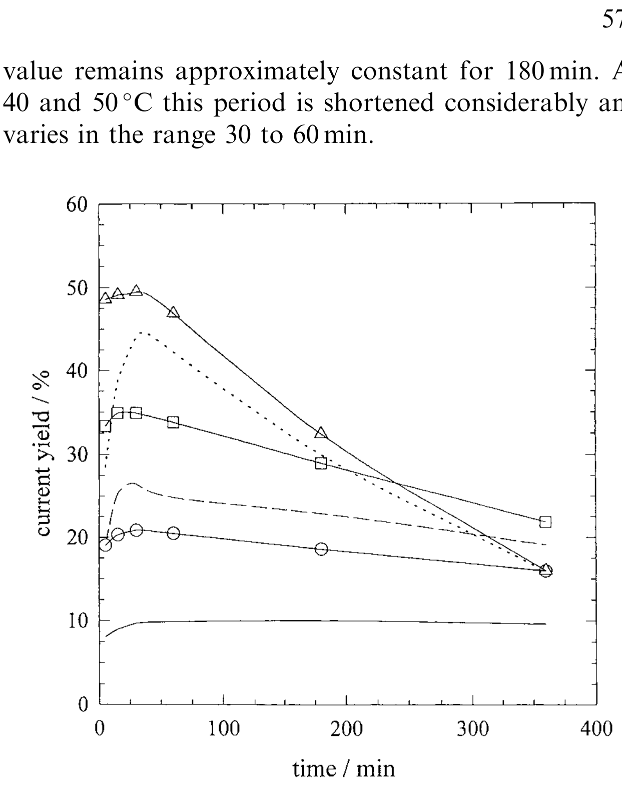

Fig. 3. Dependence of ferrate(VI) current yield on electrolysis duration, a.c. frequency of 20 Hz, amplitude of 62.7 mA cm^{-2} and temperature: (○) 30 °C, (□) 40 °C and (△) 50 °C; (——) refers to d.c. electrolysis at 30 °C; (– – – –) refers to d.c. electrolysis at 40 °C and (······) refers to d.c. electrolysis at 50 °C.

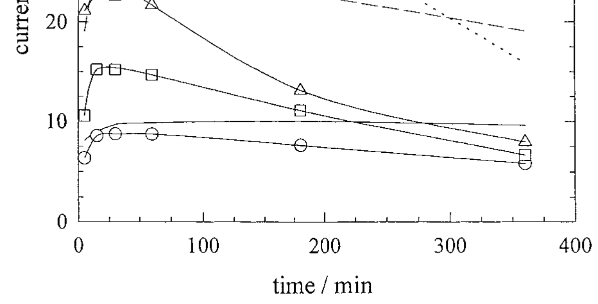

Fig. 4. Dependence of ferrate(VI) current yield on electrolysis duration, a.c. frequency of 0.05 Hz, amplitude 62.7 mA cm^{-2} and temperature: (○) 30 °C, (□) 40 °C and (△) 50 °C; (——) refers to d.c. electrolysis at 30 °C; (– – – – –) refers to d.c. electrolysis at 40 °C and (······) refers to d.c. electrolysis at 50 °C.

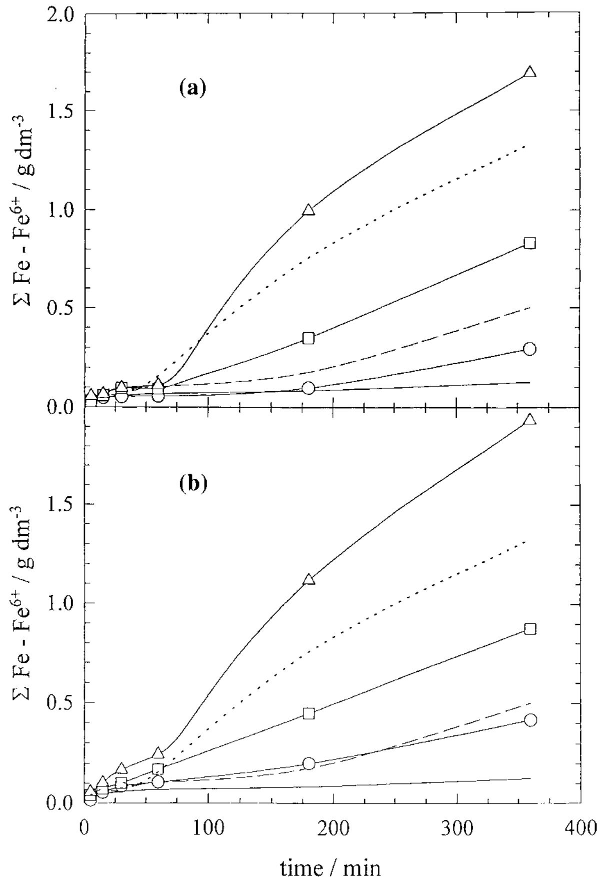

Fig. 5. Dependence of difference between total iron and Fe^{6+} concentrations in the anolyte on electrolysis duration, a.c. frequency of (a) 20 Hz and (b) 0.05 Hz, amplitude 62.7 mA cm^{-2} and temperature: (○) 30 °C, (□) 40 °C and (△) 50 °C; (——) refers to d.c. electrolysis at 30 °C, (– – – –) refers to d.c. electrolysis at 40 °C and (······) refers to d.c. electrolysis at 50 °C.

3.3. *Dependence of electrode potential on current density for different a.c. frequencies*

It was shown previously [1] that vital information, which helps explain the influence of a.c. superimposed on d.c. on ferrate(VI) current yield, is provided by the potential versus current density relationships at the various a.c. frequencies. These current–potential plots, after 180 min electrolysis at an amplitude of 63 mA cm^{-2} and 50 °C, are shown in Figure 6 for a.c. frequencies of 5 mHz, 50 mHz, 20 Hz and 100 Hz corresponding, according to Figure 1, to the increase in current yield at frequencies lower than the global minimum at 50 mHz, to the global current yield minimum, to the global maximum and to the range without influence of the a.c. on the yield, respectively. The inserts show the individual curves and the main plot shows the total picture for comparison. All these galvanodynamic polarization curves were measured in anolyte containing 0.40 to 0.69 g dm^{-3} Na_2FeO_4.

The range of variation of working electrode potential decreases with increasing a.c. frequency. At frequencies of 5 and 50 mHz a ferrate(VI) reduction wave of halve-wave potential −30 mV occurs on the polarization curves.

4. Discussion

Two main overall reactions occur on the anode surface: (i) iron dissolution and subsequent oxidation and (ii) oxygen evolution. Although iron oxidation is the desired reaction, oxygen evolution represents the main anodic reaction.

Several reaction mechanisms for ferrate(VI) formation have been proposed (e.g., in [5, 13]). These are based on the reaction of the anode material with OH^- ions thus forming a surface oxide layer. On the pure iron surface the formation of FeOOH occurs and subsequently, according to [5], this is directly oxidized to FeO_4^{2-}. According to our previous results [13] the external surface of oxide layer formed by FeOOH dissolves forming FeO_3^{2-}. Further oxidation proceeds, probably in the liquid phase near the working electrode surface. Alternatively, during continuous anodic polarization FeOOH, together with $Fe(OH)_2$, covering the working electrode surface, may undergo so called 'ageing' [16]. Ageing represents conversion of these compounds into Fe_3O_4, Equation 1. This phase represents a barrier against electrode bulk material dissolution:

$$2FeOOH + Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O \qquad (1)$$

Introduction of superimposed alternating current hinders or, in optimal cases, avoids protective oxide layer formation (Equation 1) taking place under steady state anodic polarization. Alternating current, on the other hand, may cause reduction of the final and/or intermediate electrolysis products during the cathodic part of its period. An optimum therefore has to be found providing cathodic polarization sufficiently long to stop (or at least minimize) protective layer formation and, at the same time, to avoid final or intermediate product reduction to proceed to a significant extend.

This is in good agreement with the plot of ferrate(VI) yield against a.c. frequency for various temperatures shown in Figure 1. This plot exhibits a distinct maximum in the frequency range 2–50 Hz depending on the a.c. amplitude. The frequency of the yield maximum represents the optimum for each individual a.c. amplitude. The yield minimum in Figure 1, on the other hand, represents an opposite situation. At this frequency most

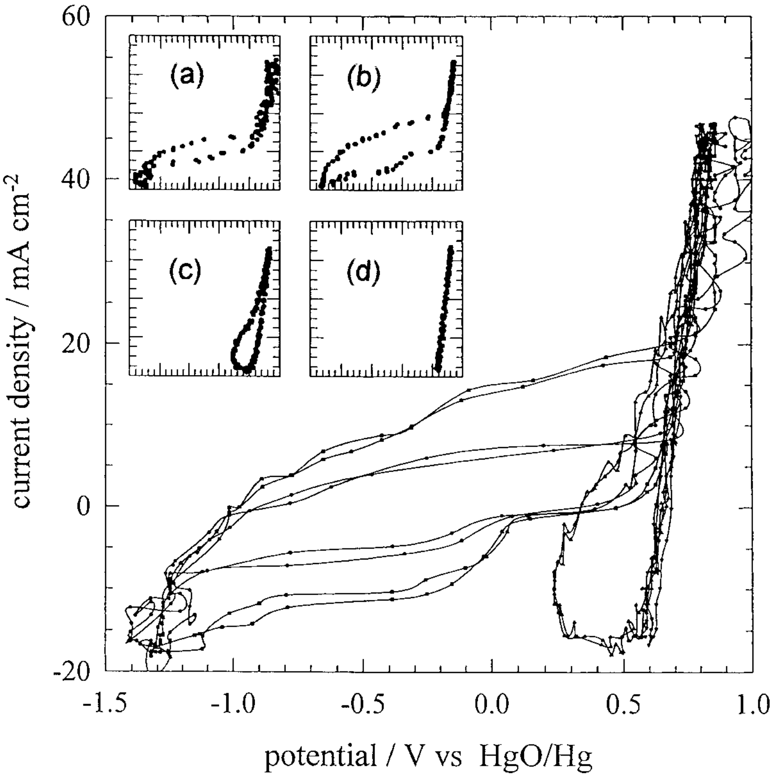

Fig. 6. Dependence of working electrode potential on current density, temperature 50 °C, d.c. current density 16.0 mA cm^{-2}, a.c. amplitude of 62.7 mA cm^{-2}, the inserts show individual curves and the main plot the total picture for comparison; the axis scales are identical, a.c. frequencies: (a) 0.005 Hz, (b) 0.05 Hz, (c) 20 Hz and (d) 100 Hz, after 180 min electrolysis. Reference electrode HgO/Hg in 14 M NaOH.

of the cathodic charge is used to reduce final and intermediate products.

This behaviour is well supported by the polarization curves of Figure 6. The peak potential of ferrate(VI) reduction on a stationary iron cathode has a value of approximately −70 mV vs HgO/Hg electrode [17]. At a yield maximum frequency (20 Hz) the working electrode potential does not reach the potential of ferrate(VI) reduction during the cathodic period. All cathodic charge was, as also observed in the case of white cast iron [1], used for surface restructuring and/or the reduction of oxygen adsorbed on the electrode surface. This oxygen reduction leads to a local increase in pH near the electrode surface thus enhancing ferrate(VI) production.

At the a.c. frequency providing minimum yield (50 mHz) the charge during the cathodic sweep is used mainly for the reduction iron in different oxidation stages. The polarization curves at frequencies of 5 mHz and 100 Hz show behaviour almost identical with that for white cast iron [1].

The chemical reaction of the surface oxihydroxide layer with hydroxyl ions causing dissolution and increased film porosity, together with enhanced ferrate decomposition, is a reason for the lower yield dependence of the a.c. amplitude at the two higher temperatures (50 °C and 60 °C). Chemical reaction also explains the increase in yield peak value with temperature shown in Figures 3 and 4. The relatively short time of electrolysis (30 min) in which the maximum yield was reached, as well as the high temperature providing the highest ferrate(VI) yields, corresponds to a thin, relatively compact and stable passive layer.

In the case of mild steel [9] and white cast iron [1] iron carbide is present in the working electrode material. Under anodic polarization this reacts readily with hydroxyl ions probably forming ferrate(III):

$$Fe_3C + 18OH^- \rightarrow 3FeO_2^- + CO_3^{2-} + 9H_2O + 13e^- \qquad (2)$$

This continuous process is responsible for the local disruption of the protective passive layer and the formation of a thick, porous oxide layer enhancing ferrate formation. Thus using white cast iron [1], the yield peak value was reached after 60 to 180 min electrolysis.

With increasing iron carbide content its dissolution becomes more intensive. Nevertheless, the mechanism of ferrate formation, as well as the oxygen evolution kinetics, in principle, remain identical. It follows that the dependence of ferrate formation current yield on a.c. frequency and amplitude exhibits identical main features. This agrees with results of the present work and those of [1, 9].

The influence of the iron carbide content on surface oxide layer passivation properties is confirmed by comparison of the data in Table 1 in the present work and that of Table 2 in [1]. Using white cast iron the concentration of iron in lower oxidation states is apparently higher than when using pure iron.

Minor differences in the frequencies giving peak current yields, optimum temperatures and a.c. amplitudes follow from the influence of iron carbide on the surface oxihydroxide layer properties. A thicker layer requires higher electrical charge to undergo the necessary changes and this results in a decreasing optimum frequency (pure iron: 2 to 50 Hz, mild steel: 5 Hz [9], white cast iron: 0.5 to 5 Hz [1]). The same also applies in the case of different temperatures providing the highest ferrate(VI) yield: pure iron 50 °C, mild steel yields increase in temperature range 20–30 °C [9], and white cast iron 20 °C [1]. With increasing iron carbide content lower temperature is sufficient to break down the electrode passivity. Low temperature also assures a low ferrate(VI) decomposition rate. Therefore, the temperature providing the highest yield decreases with increasing iron carbide content.

Different behaviour may be observed in the case of the a.c. frequency providing minimum current yield. This is independent of the a.c. amplitude over a certain range, (Fig. 2(b)). With white cast iron [1] this range was found to be wider.

The electrical charge passed during the a.c. cathodic period is several times lower compared to that of the anodic period. Thus, even ferrate(VI) and its intermediates production proceeds with lower current efficiency compared to that of theirs reduction, the charge passed during cathodic part of a.c. period is insufficient to provide theirs complete reduction. With increasing a.c. amplitude the ratio between the charges in the anodic and cathodic a.c. periods decreases (e.g., amplitude $38\,\mathrm{mA\,cm^{-2}}$ *45.4*, $48\,\mathrm{mA\,cm^{-2}}$ *12.3* and $88\,\mathrm{mA\,cm^{-2}}$ *3.3*). Above a certain a.c. amplitude the ferrate ion concentration adjacent to the working electrode surface reaches zero during the cathodic period and the yield minimum frequency begins to increase with increasing a.c. amplitude. Because of the higher ferrate surface concentration in the case of white cast iron and the thick and porous oxihydroxide layer covering its surface, the value of a.c. amplitude giving zero surface concentration is higher. This is confirmed by the content of iron in lower oxidation states showing a local maximum in this a.c. frequency range. At two lower temperatures this maximum increases with a.c. amplitude (Table 1). An opposite trend at temperatures of 50 and 60 °C is probably caused by homogeneous ferrate decomposition. This also explains the second maximum appearing at the a.c. frequency of the yield maximum. The same also applies in the case of white cast iron [1].

The tendency of the concentration of iron in lower oxidation states against electrolysis duration to reach a limiting value, shown for the first 60 min of electrolysis in Figure 5, corresponds well to the previous postulation concerning the stages of ferrate(VI) production using d.c. [13]. Initially, an increase in concentration of iron in lower oxidation states during the first 30 min corresponds to a first period of intermediate product formation. The following 30 min, during which the concentration of intermediates remains constant corresponds to the second period of continuous ferrate production. Increase in the concentration value (Fig. 5) after a certain time, depending on the temperature (180 min for 30 °C and 60 min for 40–50 °C), corresponds to the last (third) period, characterised by increasing electrode surface passivation and homogeneous ferrate(VI) decomposition.

Comparing the yield peak value for a.c. for white cast iron [1], to d.c. electrolysis at 30 °C and after 180 min, a decrease of 8% was observed. An increase of 70% was observed in the case of mild steel [9] at this temperature. In the present study pure iron shows an increase in the peak yield value at 30 °C of 106%. This sequence corresponds well to the decrease in iron carbide content in the working electrode materials. These results suggest that the ferrate current yield achieved using white cast iron approaches a value no longer limited by surface passivation, but by the kinetics of the two competing reactions (oxygen evolution and ferrate formation) and/or homogeneous ferrate decomposition only. As such its value cannot be significantly exceeded without significant changes in the electrode reaction kinetics.

The behaviour of the iron carbide on the anode surface in concentrated NaOH is illustrated in Figure 7 which shows a white cast iron microstructure together with the surface morphology scan. These Figures confirms that during anodic polarization in 14 M NaOH the Fe_3C phase in the white cast iron readily dissolves and breaks down the passive layer. Grey cast iron [1] behaves differently because of the presence of inert graphite in its structure. Different electrochemical reactions proceed at the two different parts of the electrode surface, or, at least, their kinetics differ. This makes the problem much more complex.

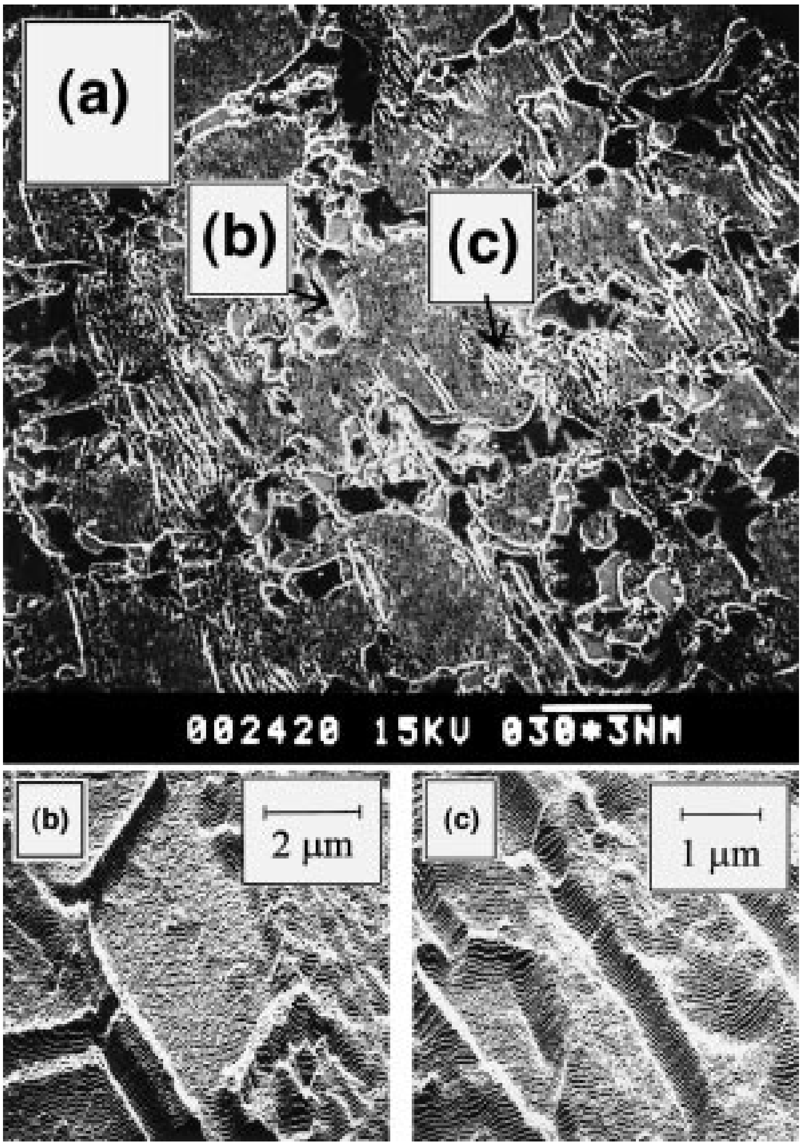

Fig. 7. (a) White cast iron microstructure after 10 min anodic polarization at 10 mA cm^{-2} in 14 M NaOH; (b) and (c) surface morphology scan showing preferential iron carbide particle dissolution.

5. Conclusion

The present study has confirmed previous theories [1, 10–12] concerning the influence of surface heterogeneity and iron carbide content in the working electrode material on ferrate(VI) current yield. With grey cast iron the heterogeneity of the electrode surface is caused by part of the carbon content being present in the form of graphite [1]. In the case of white cast iron surface heterogeneity results from appreciable amounts of Fe_3C being present in the material structure. From the comparison of results obtained using white cast iron [1] and pure iron electrodes a positive influence of iron carbide on the ferrate(VI) yield is apparent. Comparing white and grey cast iron it is clear that, as well as differences in composition, the electrode material structure is one of the parameters exerting a crucial influence on the current yield.

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