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Influence of anode material on current yield during ferrate(VI) production by anodic iron dissolution
Part II: Current efficiency during anodic dissolution of white cast iron to ferrate(VI) in concentrated alkali hydroxide solutions

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The dependence of the current efficiency for the oxidation of a white cast iron anode to ferrate(VI) ions in 14 M NaOH was measured in the region of bubble induced convection for the temperature range 10 to 50 °C. Using a white cast iron anode the highest current yield obtained after 3 h of electrolysis was 55% at a current density of 8 mA cm^{-2} and a temperature of 20 °C. The anode was activated by cathodic prepolarization. The iron concentration in low oxidation states contained in the post electrolysis solution increased with temperature over the whole temperature range studied. This concentration was almost 10 times higher than in the case of grey cast iron reported earlier. The dependence of ferrate(VI) current yield on the hydroxide concentration was studied in the range 5 to 16 M. The optimum concentration was found to be 14 M. The quasisteady state anodic polarization curve of white cast iron anode in the transpassive potential region was measured. This shows the start of oxygen evolution occurring at higher potentials compared to grey cast iron.

1. Introduction

In Part I [1] previously published results [2–5] for ferrate(VI) production by anodic dissolution of undefined iron anode were discussed. On the basis of these results a grey cast iron was used as an anode [1]. The current yields obtained for grey cast iron were not in agreement with previously published data [2–5], which implies, that a different anode material was used in [2–5]. Therefore, in this study, white cast iron was used. White cast iron contains carbon only in the form of iron carbide [6] in contrast to grey cast iron which contains carbon mainly in the form of graphite with the iron carbide content lower than 0.8 wt. % C with respect to the anode material weight [1]. The presence of iron carbide Fe_3C in white cast iron may significantly influence current yields for the electrochemical production of ferrate(VI).

Previous results show different influences of the electrolyte concentration on the ferrate(VI) current yield. Haber [2] and Pick [3] reported that the current yield increases with NaOH concentration in a range from about 14.5 to 18.5 M. Toušek [4] found the optimum electrolyte concentration to be 14.3 M. The experimental conditions used in [4] were: a current density of 6 mA cm^{-2}, a temperature of 30 °C and an electrolysis duration of 60 min. The anode material was an unspecified cast iron.

For this study white cast iron has been used instead of grey cast iron [1] and mild steel [5]. The use of white cast iron anode may help in explaining the influence of different forms of carbon (graphite particles, iron carbide) in the anode material on the current yields for ferrate(VI) and in clarifying the nature of the unpublished anode materials used in previous studies [2–4].

2. Experimental details

Chemicals and analytical methods used during this study were identical to those used in [1]. The apparatus used was also described in detail in [1]. The anolyte volume was, in the present case, 110 ml. The anode had the following composition: 3.16 wt % C, 0.44 wt % Mn and 0.036 wt % Ni, the remainder being Fe. According to [6], in white cast iron the prevailing carbon compound is Fe_3C and carbon is not present in the form of graphite.

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3. Results

3.1. *Influence of electrolyte concentration on ferrate*(*VI*) *current yield*

The NaOH concentration was varied in the range from 6 to 16 M. The current yield was measured using anodic current densities (c.d.'s) varying from 2 to 27 mA cm^{-2}. The temperature of the electrolyte was kept at 20 °C. In Fig. 1 the dependency of the ferrate(VI) current yield on the electrolyte concentration is given. The best NaOH concentration is 14 M (Fig. 1). This finding is in close agreement with the value of 14.3 M reported by Toušek [4]. At all electrolyte concentrations the dependencies shown in Fig. 1 exhibit a maximum in the ferrate(VI) current yield. At 14 M a c.d. of 8 mA cm^{-2} provided the highest current yield, 55%, for 20 °C.

The ratio of the total iron to Fe(VI) shown in Fig. 2 exhibits a minimum value of 1.00 at the above mentioned optimum conditions for ferrate(VI) production (14 M NaOH, 8 mA cm^{-2} and 20 °C). For other NaOH concentrations the ratio of total iron to Fe(VI) decreased continuously with increasing current density.

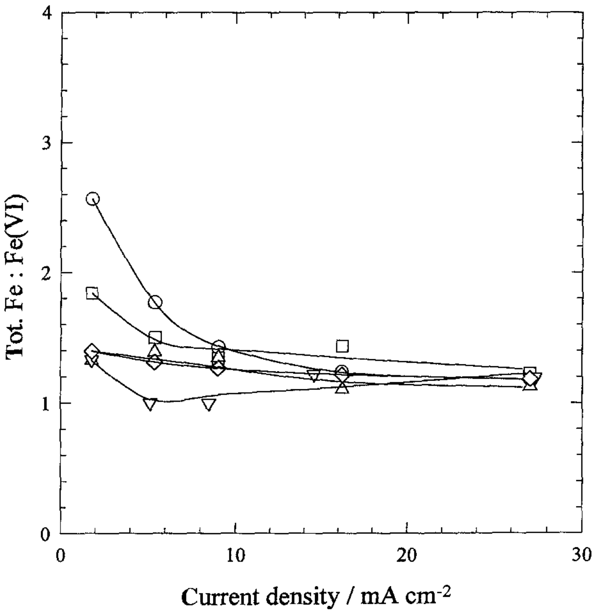

Fig. 2. Dependence of ratio of total anolyte iron concentration after electrolysis to the concentration of Fe(VI) on c.d. at 20 °C, electrolysis duration 180 min and various concentrations of NaOH: (○) 5, (□) 8, (△) 12, (▽) 14 and (◇) 16 M.

3.2. *Dependence of ferrate*(*VI*) *current yield on electrolyte temperature and anodic current density*

The temperature of the electrolyte was varied between 10 and 50 °C and the anodic c.d. from 1 to 34 mA cm^{-2}. The results are shown in Fig. 3. The highest current yield occurs at a temperature of 20 °C.

The location of the maximum in current yields changes with temperature. The current yield was 45% at 10 °C with 1 mA cm^{-2}, 47% (15 °C, 2 mA cm^{-2}), 55% (20 °C, 8 mA cm^{-2}), 44% (30 °C, 5 mA cm^{-2}), 26% (40 °C, 5 mA cm^{-2}) and 16% (50 °C, 5 mA cm^{-2}).

The dependence of the ratio of the total iron to Fe(VI) concentration on the current density (corresponding to Fig. 3) is shown in Fig. 4. At 20 °C and a c.d. of 8 mA cm^{-2} a global minimum ratio of 1.00 was found. These conditions also correspond to the highest ferrate(VI) current yield. The temperature of 30 °C exhibits the minimum value of the ratio of total iron to Fe(VI) at a c.d. of 11 mA cm^{-2}. For temperatures outside this range (from 20 to 30 °C) the ratio of total iron to Fe(VI) decreases continuously for the whole current density range studied (from 1 to 34 mA cm^{-2}). The concentration of iron in low

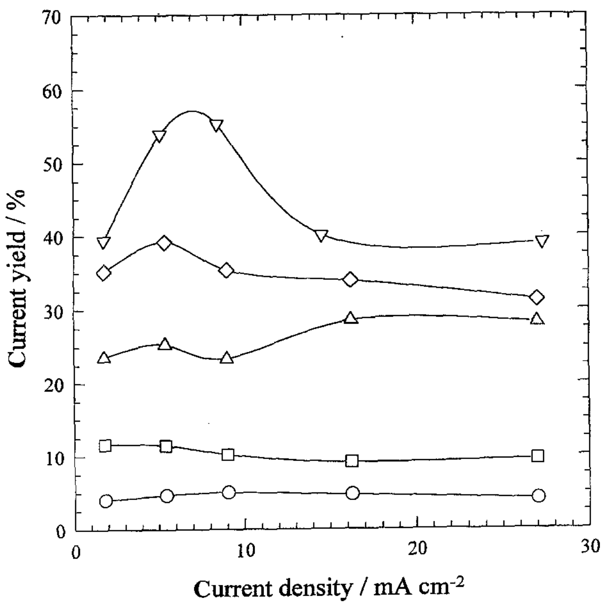

Fig. 1. Dependence of ferrate(VI) current yield on c.d. at 20 °C, electrolysis duration 180 min and various concentrations of NaOH: (○) 5, (□) 8, (△) 12, (▽) 14 and (◇) 16 M.

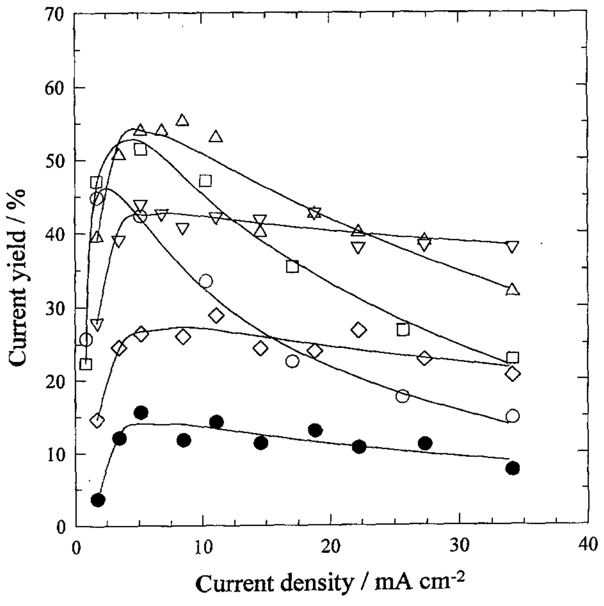

Fig. 3. Dependence of ferrate(VI) current yield on c.d. at electrolysis duration 180 min, concentration 14 M NaOH and various temperatures: (○) 10, (□) 15, (△) 20, (▽) 30, (◇) 40 and (●) 50 °C.

oxidation states in the solution after electrolysis was determined as $0.29 \pm 0.05\,\mathrm{g\,Fe\,dm^{-3}}$ (10 °C), $0.43 \pm 0.09\,\mathrm{g\,Fe\,dm^{-3}}$ (15 °C), $0.8 \pm 0.3\,\mathrm{g\,Fe\,dm^{-3}}$ (20 °C), $1.2 \pm 0.5\,\mathrm{g\,Fe\,dm^{-3}}$ (30 °C), $1.2 \pm 0.2\,\mathrm{g\,Fe\,dm^{-3}}$ (40 °C) and $2.0 \pm 0.4\,\mathrm{g\,Fe\,dm^{-3}}$ (50 °C). These values were reached after passing a charge of about $200\,\mathrm{C\,cm^{-2}}$ at 30 °C. With decreasing temperature the charge necessary for reaching the constant value of concentration of iron in lower oxidation states decreased. For 10 °C a charge of about $90\,\mathrm{C\,cm^{-2}}$ was enough to reach the constant value of iron in lower oxidation states than Fe(VI).

3.3. *Dependence of ferrate(VI) current yield on electrolysis duration in 14 M NaOH*

The dependency of the ferrate(VI) current yield on electrolysis duration was studied in the temperature range 10 to 50 °C and at c.d.'s of 5, 18 and $34\,\mathrm{mA\,cm^{-2}}$. The results are shown in Fig. 5. The optimum c.d. and the optimum duration of electrolysis varies with temperature, as shown in Fig. 5.

At a temperature of 10 °C the highest ferrate(VI) current yield, 42%, for a c.d. of $5\,\mathrm{mA\,cm^{-2}}$ was reached after 180 min of electrolysis in 14 M NaOH. At a c.d. of $18\,\mathrm{mA\,cm^{-2}}$ a maximum current yield of 27% was reached after 70 min and at a c.d. of $34\,\mathrm{mA\,cm^{-2}}$ a current yield of 20% was reached after 6 min of electrolysis.

At 20 °C the optimum c.d. was $5\,\mathrm{mA\,cm^{-2}}$, but the highest ferrate(VI) current yield, 63%, was reached after 60 min electrolysis at this temperature. This was also the highest ferrate(VI) current yield obtained in this study. This result corresponds with the maximum current yield reported by Toušek [4], who reached a ferrate(VI) current yield of 67% using a

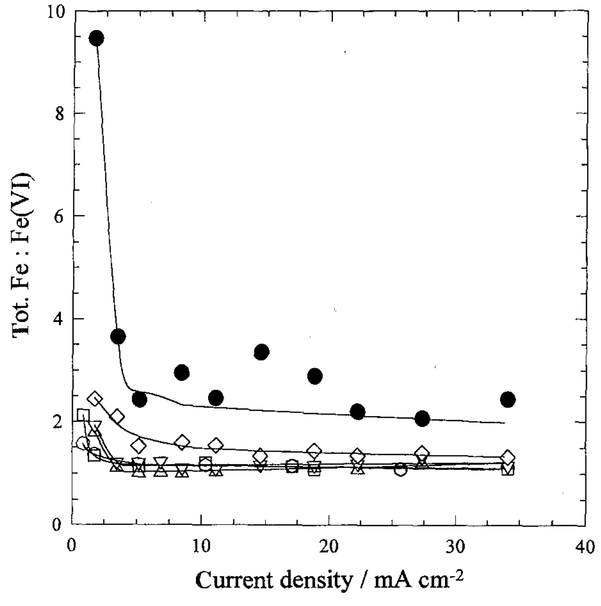

Fig. 4. Dependence of ratio of total iron concentration in the anolyte after electrolysis to the concentration of Fe(VI) on the c.d. at electrolysis duration 180 min, concentration 14 M NaOH and various temperatures: (○) 10, (□) 15, (△) 20, (▽) 30, (◇) 40 and (●) 50 °C.

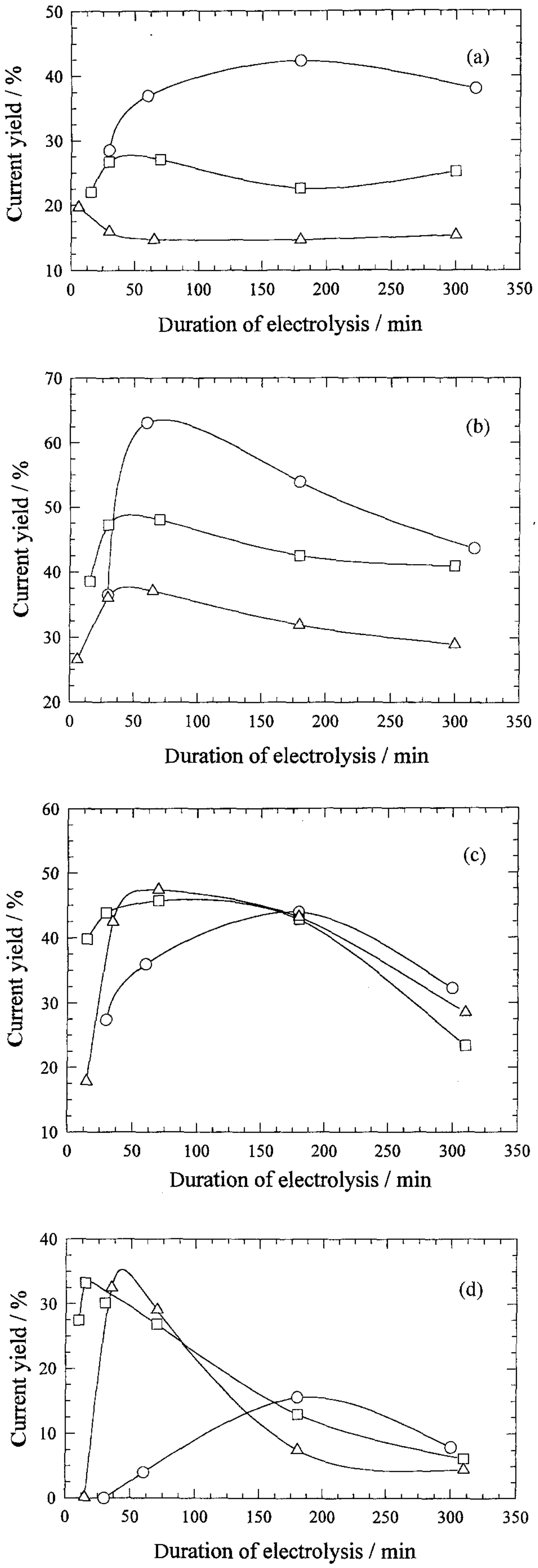

Fig. 5. Dependence of ferrate(VI) current yield on electrolysis duration in 14 M NaOH, at various c.d.: (○) 5, (□) 18, and (△) $34\,\mathrm{mA\,cm^{-2}}$ at 10 (a), 20 (b), 30 (c) and 50 °C (d).

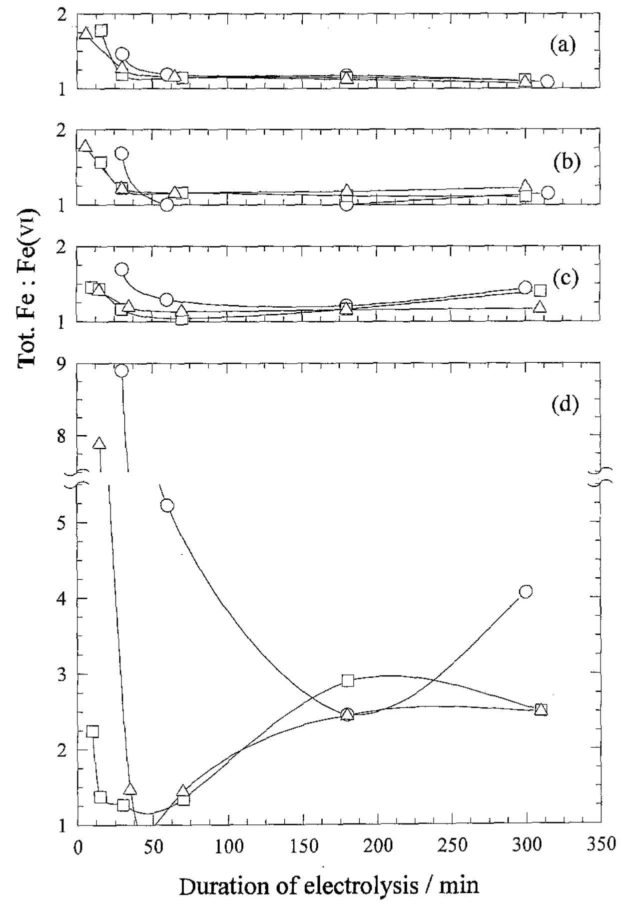

Fig. 6. Dependence of ratio of total anolyte iron concentration after electrolysis to the concentration of Fe(VI) on electrolysis duration in 14 M NaOH, at various c.d.: (○) 5, (□) 18 and (△) 34 mA cm^{-2} and at 10 (a), 20 (b), 30 (c) and 50 °C (d).

c.d. of 5.6 mA cm^{-2}, a temperature of 20 °C and an electrolysis duration of 60 min.

At 30 °C a maximum ferrate(VI) current yield of 47% was reached at a c.d. of 34 mA cm^{-2} and maximum ferrate(VI) current yield of 46% at a c.d. of 18 mA cm^{-2}. In both cases the electrolysis duration was 70 min. The maximum current yield of 44% at a c.d. of 5 mA cm^{-2} was reached after 180 min of electrolysis. The shapes of the dependencies of the ferrate(VI) current yield on the electrolysis duration are very close for all c.d.'s at 30 °C.

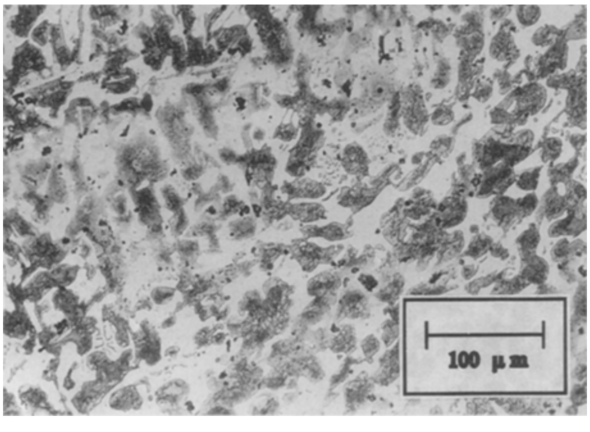

Fig. 7. The microstructure of the white cast iron anode material. The dark fields represent pearlite, the white fields represent Fe$_3$C iron carbide.

At a temperature of 50 °C the differences between the lowest (5 mA cm^{-2}) and the higher c.d.'s (18 and 34 mA cm^{-2}) are most significant. The maximum ferrate(VI) current yield 33% was reached at the c.d. of 18 mA cm^{-2} and for an electrolysis duration of 15 min.

The dependence of the ratio of the total iron to Fe(VI) concentration in the anolyte after electrolysis on the c.d. corresponding to Fig. 5 is shown in Fig. 6. At the lowest temperature of 10 °C (Fig. 6(a)) the ratio decreases over the whole range of electrolysis duration. At temperatures of 20 and 30 °C the ratio increases slightly at electrolysis duration longer than 60 min. The ratio changes significantly at 50 °C; after 30 min of electrolysis and at a c.d. 5 mA cm^{-2} the ratio is 8.95. The minimum ratio, 2.49, was reached after 180 min. At the higher c.d.'s (18 and 34 mA cm^{-2}) the dependencies differ only in the region of short electrolysis durations (less than 30 min). Both dependencies exhibit minima at electrolysis duration of 60 min. After reaching the minimum a relatively strong increase of the ratio with electrolysis time occurs.

3.4. *Quasi-steady state polarization curves in the transpassive potential region*

The quasi-steady state polarization curve of white cast iron anode was measured galvanostatically using the setup described elsewhere [1]. The white cast iron does not include any graphite in the structure (Fig. 7) as does the grey cast iron, but includes a greater amount of Fe$_3$C particles. The typical potential–charge curves for white cast iron and grey cast iron are shown

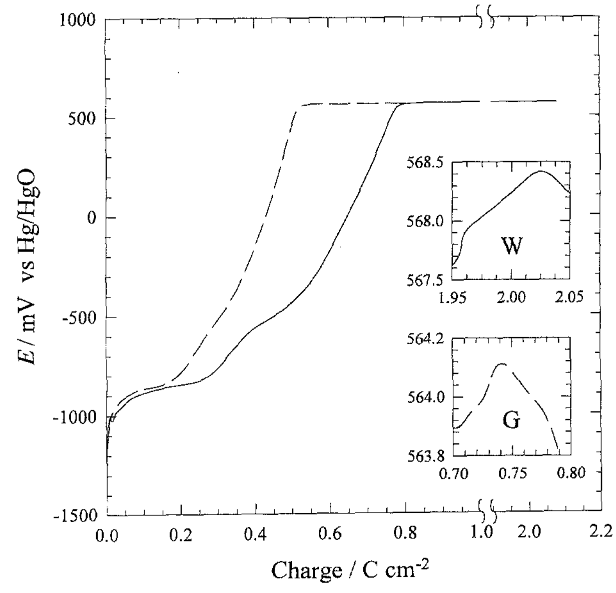

Fig. 8. Dependence of anode potential on charge passed after cathodic prepolarization, temperature 20 °C, electrolyte concentration 14 M NaOH: (—) white cast iron anode at c.d. 0.4 mA cm^{-2}, (- - -) grey cast iron anode at c.d. 0.3 mA cm^{-2}. The inserted plots show the first maximum on the charge–potential plot; this potential was used as the potential corresponding to the studied current density in the quasi-steady state polarization curve. W = white cast iron, G = grey cast iron. Plot axes are identical with corresponding axes of main plot.

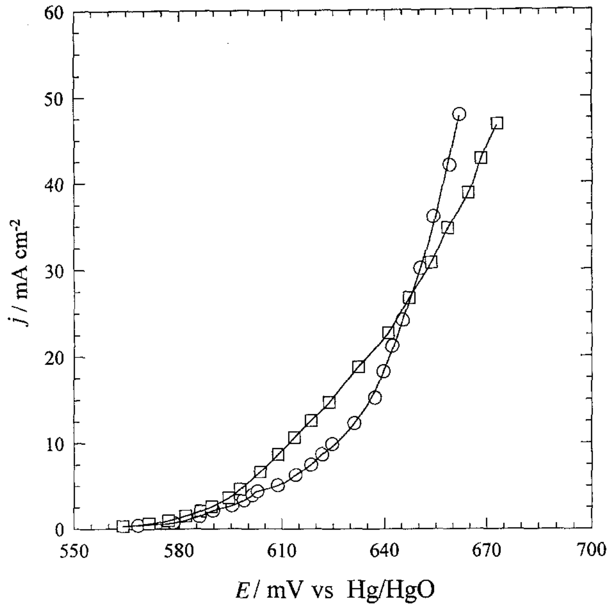

Fig. 9. Quasisteady state polarization curve at 20 °C with 14 M NaOH: (○) white cast iron anode, (□) grey cast iron anode.

in the Fig. 8. All anode potentials for white cast iron were measured after passing a charge of $2.1 \pm 0.6\,\mathrm{C\,cm^{-2}}$ after activation by cathodic prepolarization. This charge corresponds to the first maximum on the potential–charge dependence described in [1]. The resulting polarization curves are shown on Fig. 9. Up to $27\,\mathrm{mA\,cm^{-2}}$ the polarization curve for white cast iron is shifted positively in comparison with the polarization curve for grey cast iron. This shift of the polarization curve may reflect the slower oxygen evolution reaction on the surface of the white cast iron anode in comparison to that on the graphite particles involved in the grey cast iron anode.

4. Discussion

The dependence of the ferrate(VI) current yield on the current density at a temperature of 20 °C with different electrolyte concentrations shown in Fig. 1 confirms that the optimum concentration of NaOH in the electrolyte is 14 M as found by Toušek [4]. Haber [2] and Pick [3] reported an increasing current efficiency for the production of ferrate(VI) with increasing electrolyte concentration within the concentration range from about 14.5 to 18.5 M. A possible explanation for this difference may be the overestimation of the ferrate(VI) production due to the recalculation of the content of iron in lower oxidation states to ferrate(VI). Haber [2] and Pick [3] analysed the total iron content in the anolyte after electrolysis and considered the value as a ferrate(VI) concentration. All other calculations were based on these values. Compared to this Toušek [4] used the chromite method [7] for analysis, which enabled him to estimate the real concentration of ferrate(VI). The ratio of the total iron to the Fe(VI) content in the anolyte after electrolysis depends on the c.d., temperature and electrolyte concentration (see Fig. 2). For 20 °C the amount of iron in lower oxidation states increased in the electrolyte concentration range 14 to 16 M and consequently the ratio increased from 1.330 to 1.396 at a c.d. of $2\,\mathrm{mA\,cm^{-2}}$, a temperature of 20 °C and an electrolysis duration of 180 min. At a c.d. of $9\,\mathrm{mA\,cm^{-2}}$ (the other conditions being the same) the ratio of total iron to Fe(VI) increased from a value of 1.049 to 1.264. Using the total iron analysis approach for a c.d. of $2\,\mathrm{mA\,cm^{-2}}$ and an electrolyte concentration of 14 M would give a ferrate(VI) current yield of 52%, and 49% at an electrolyte concentration of 16 M instead of the correct values of 39% and 35%, respectively. At $9\,\mathrm{mA\,cm^{-2}}$ and an electrolyte concentration of 14 M would give a current yield of 58% and 45% at an electrolyte concentration of 16 M instead of the correct values of 55% and 35% respectively. These numbers show that using the 'total iron analysis' leads to an overestimation in the ferrate(VI) current yields. Direct recalculation of the data in [3] is not possible, because in the case of Pick [3] the electrolysis was 48 h at a c.d. of $1\,\mathrm{mA\,cm^{-2}}$, which is outside the duration of the present experiments. Another important factor influencing the ratio of the total iron to Fe(VI) is the electrolyte temperature, see Fig. 4. Pick [3] does not report the temperature at which he carried out the experiments. The temperature in the work of Toušek [4] was 30 °C. Due to the incomplete data in [3] it is not possible to predict the amount of iron in the lower oxidation state contained in the anolyte after electrolysis and to calculate the exact value of the ferrate(VI) concentration and thus the real ferrate(VI) current yield. Also the use of anode material with different carbon and carbide content may influence the current yields considerably, as shown in [1] and in this study.

The dependence of the ferrate(VI) current yield on electrolyte temperature is also influenced by errors connected with the use of the total iron analysis. Haber [2] and Pick [3] reported that the ferrate(VI) current yield increased with electrolyte temperature in a range from 5 to 70 °C. Toušek [4] found 20–25 °C as an optimal temperature range. In this study the optimal electrolyte temperature was 20 °C (see Fig. 3). It is also necessary to mention the differences in the anode materials used by different authors. Using a mild steel anode [5] the ferrate(VI) current yield at the optimal c.d. was, within experimental error, almost the same at 20 °C (c.d.: $5\,\mathrm{mA\,cm^{-2}}$) and 30 °C (c.d.: $5\,\mathrm{mA\,cm^{-2}}$), the respective values being 40 and 38%. Higher temperatures were not reported. Compared to this, white and grey cast iron [1] exhibit highest current yield at 20 °C (54% and 9%, respectively). At 30 °C the optimum current yield decreased (44% and 7% for white and grey cast iron, respectively).

The increase in the ratio of the concentration of the total iron to the Fe(VI) in the anolyte after electrolysis at the low current densities shown in Fig. 4, together with the location of the maximum on the dependency of the ferrate(VI) current yield–current density at all the studied temperatures, supports the theory introduced in [5] concerning the periods of electrochemical ferrate(VI) formation. At low current density and with electrolysis duration of 180 min only the first period is completed. The second period is completed at a current density leading to the maximum current yield at the given temperature. After exceeding this current density the current yield begins to decrease. This corresponds to the start of the third period of ferrate(VI) formation which represents the passivation of the anode surface and the consequent decrease in the current yield towards zero. The ratio of the total iron to Fe(VI) decreases continuously at temperatures of 10, 40 and 50 °C. It corresponds again to the above-mentioned theory of electrochemical ferrate(VI) formation periods [5]. The concentration of the intermediate products (i.e., iron present in the lower oxidation states) remains nearly constant. The possible increase in the concentration of iron in the lower oxidation states at longer duration of the electrolysis is probably caused by the decomposition of ferrate(VI).

The suggested theory does not explain the minimum value in the relationship of the ratio of total iron to Fe(VI) against current density at temperatures 20 and 30 °C and at c.d.'s of 8 and 11 mA cm^{-2}, respectively. These minima have not been explained until now. The increase in c.d. corresponding to the minimum value in the ratio shows the possibility that a minimum value also exists at other temperatures than 20 and 30 °C, but for the higher temperatures this minimum did not lie within the studied c.d. range. The same minimum value of the ratio at a c.d. of about 20 mA cm^{-2} and at temperatures of 20 and 30 °C was also observed using mild steel [5]. In [5] the increase in the ratio was explained as due to experimental error.

The dependency of the ferrate(VI) current yield on the duration of electrolysis at different c.d.'s and temperatures also supports the suggested theory of the three periods of ferrate(VI) formation. The optimum electrolysis duration remains nearly constant at all temperatures for all c.d.'s used in this study. There are only two exceptions. The first is the c.d. of 34 mA cm^{-2} at 10 °C, where the maximum was not detected, and the second the c.d. of 5 mA cm^{-2} at 20 °C, where the maximum shifted from 180 min to 60 min. At these conditions the ferrate(VI) current yield was 63%. This was the highest current yield obtained during the present study. The dependency for 50 °C shown in Fig. 5(d) exhibits a strong decrease in current yield after the maximum, compared to the other temperatures. The reason for this is probably an increase in ferrate(VI) decomposition rate with temperature. This corresponds with the relatively strong increase in the ratio of total iron to Fe(VI) after reaching a minimum value shown in Fig. 6(d). At temperatures below 50 °C this increase is much less apparent, see Fig. 6(a)–(c).

The quasisteady state polarization curve for the white cast iron (see Fig. 9) shows an increase in potential compared to that measured for the same c.d.'s using the grey cast iron electrode [1] in the potential range up to 642 mV vs Hg/HgO electrode or in the c.d. range up to about 20 mA cm^{-2}. The lower anode potential for the grey cast iron anode is probably due to the lower overvoltage of the oxygen evolution on graphite in the 14 M NaOH, compared to the mild steel or white cast iron anode covered by the oxo-hydroxide passive layer. The lower anode potential for a given c.d. means that more oxygen is evolved and less ferrate(VI) formed. The grey cast iron contains 3.43 wt % C, but at least 2.63 wt % C in the form of graphite particles and up to 0.8 wt % C as Fe_3C. The white cast iron contains 3.16 wt % C, all in the form of Fe_3C. The mild steel contains only 0.08 wt % of carbon, all as Fe_3C. To estimate more exactly the influence of carbon (graphite or Fe_3C), a pure iron anode should be used. The use of pure iron help to explain the influence of the anode material on all the electrolysis parameters and may help to elucidate and explain the discrepancies in the results obtained by different authors.

On the basis of present results one of the main factors influencing the ferrate(VI) current yield is the iron carbide content in the anode material. The iron carbide content probably influences the structure of the oxo-hydroxide layer build up on the anode surface during anodic polarization. Comparing the charges necessary to reach the first potential maximum after cathodic prepolarization gives: mild steel [5] 1.8 ± 0.2 C cm^{-2}; grey cast iron 0.65 ± 0.04 C cm^{-2}, white cast iron 2.1 ± 0.6 C cm^{-2}. The charge for grey cast iron is the lowest. This means that part of the anode surface is formed by graphite particles, which need almost no charge. From Fig. 8 it follows that, after the change in polarity, at least one charging step at constant potential corresponds to the formation of the oxo-hydroxide layer on the electrode surface. This charging step is more pronounced for white cast iron than for grey cast iron. The increase in the charge necessary to reach the first potential maximum is probably caused by the different nature of the oxo-hydroxide layer on the anode surface. From the increase in charge it follows that the surface layer on the white cast iron electrode is not so readily passivated as mild steel. Therefore more intensive dissolution of the electrode material is possible and the ferrate(VI) current yields are higher.

The present results correspond with the results published by Toušek [4]. The unspecified electrode material used by Toušek was probably white cast iron.

5. Conclusion

The dependence of the current efficiency for the oxidation of an iron anode to ferrate(VI) ions in 14 M NaOH was measured in the region of bubble-induced convection using a white cast iron anode. A current yield of 55% for a c.d. of 8 mA cm^{-2} at 20 °C was attained after 180 min of electrolysis. A current yield of 63% was reached for a c.d. of 5 mA cm^{-2} at 20 °C and after 60 min of electrolysis. The optimal concentration of NaOH electrolyte was found to be 14 M. These results support the theory about the influence of the graphite particles and iron carbide Fe_3C in the anode material on the ferrate(VI) current yield during the electrochemical synthesis of ferrate(VI) using direct current [1]. The iron carbide content in the anode material considerably influences the ferrate(VI) current yield. The presence of iron carbide on the surface probably changes the properties of the oxo-hydroxide layer covering the anode surface. This layer, in the presence of iron carbide particles, is probably less dense, more disordered or more porous, which means that it is more active and therefore supports the formation of ferrate(VI) ions.

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