JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 679–684

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

K. BOUZEK, I. ROUŠAR†

Prague Institute of Chemical Technology, Department of Inorganic Technology, 16628 Prague 6, Czech Republic

Received 20 February 1996; revised 30 September 1996

The dependence of the current efficiency for the oxidation of a pure iron (99.95%) anode to ferrate(VI) ions in 14 M NaOH was measured in the region of bubble induced convection for the temperature range 20 to 50 °C. The highest current yield obtained after 180 min electrolysis was 60% at a current density of 2.3 mA cm^{-2} and a temperature of 30 °C. The same current yield was found at a current density of 4.5 mA cm^{-2} and a temperature of 40 °C. The dependence of the ferrate(VI) current yields on the NaOH concentration in the electrolyte solution was studied in the range 12 to 17 M. The optimum concentration was found to be 16 M. The quasistationary anodic polarization curve of pure iron in the transpassive potential region was measured. Apparent oxygen evolution starts at a potential 110 mV higher than for white and grey cast iron anodes.

1. Introduction

In the first two parts of this series grey [1] and white [2] cast iron were used as anode material. These materials contain part of their carbon as graphite and part as iron carbide or as iron carbide (Fe_3C) only, respectively. The current yields obtained for these two materials differed considerably.

The literature review [3–9] was provided in [1]. Most recently the electrochemically ferrate(VI) production was studied by Denvir and Pletcher [10] using a three-dimensional anode. These authors also studied the influence of anode composition on electrochemical ferrate(VI) generation [11]. They found that increasing carbon content in the anode material in the range 0.08 to 0.9 wt% has a positive influence on the yield obtained.

There are two possible reasons for the differences between current yields found by different authors [1–9]. These are the differences in the anode material composition and the analytical method used for the estimation of ferrate(VI) content in the anolyte [2]. The use of a pure iron anode (99.95%) represents one limiting material composition; these new experiments together with the previously obtained results for grey [1] and white [2] cast iron may clarify the influence of the material composition on the ferrate(VI) current yield.

2. Experimental details

Chemicals, analytical methods, as well as the apparatus are described elsewhere [1]. The anolyte volume was 90 ml. The anode material was Fe of 99.95 wt% purity containing less than 0.005 wt% C, 0.0048 wt% Ni and 0.0003 wt% Mn. All carbon in the anode material was in the form of iron carbide Fe_3C. The anode was activated by cathodic prepolarization for 30 min at a current density (c.d.) of 20 mA cm^{-2} before the start of the experiment. (For details, see [9])

3. Results

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

The concentration of the NaOH in the electrolyte was varied in the range 12 to 17 M. The current yield was measured using an anodic c.d. of 4.4 mA cm^{-2} and temperatures of 20 and 40 °C. In Fig. 1 the dependence of the ferrate(VI) current yield on the electrolyte concentration after 180 min of electrolysis is given, showing a maximum yield, for both studied temperatures at 16 M NaOH, of 28% and 63% at 20 and 40 °C, respectively.

The ratio of the total iron to Fe^{6+} concentration in the anolyte shown in Fig. 2 decreases progressively over the whole NaOH concentration range studied at 20 °C. At 40 °C the ratio exhibits a flat minimum at a NaOH concentration of 15 M.

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

The temperature of the electrolyte was varied between 20 and 50 °C and the anodic c.d. was varied in

0021-891X

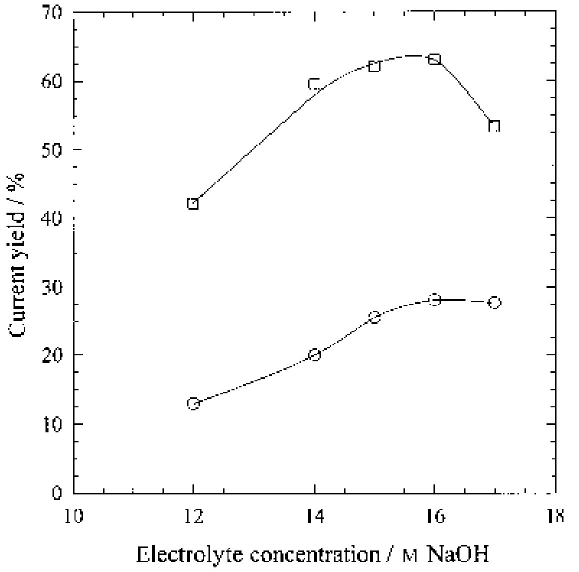

Fig. 1. Dependence of ferrate(VI) current yield on electrolyte concentration at c.d. 4.4 mA cm^{-2}. Duration of electrolysis: 180 min; temperature: (○) 20 °C and (□) 40 °C.

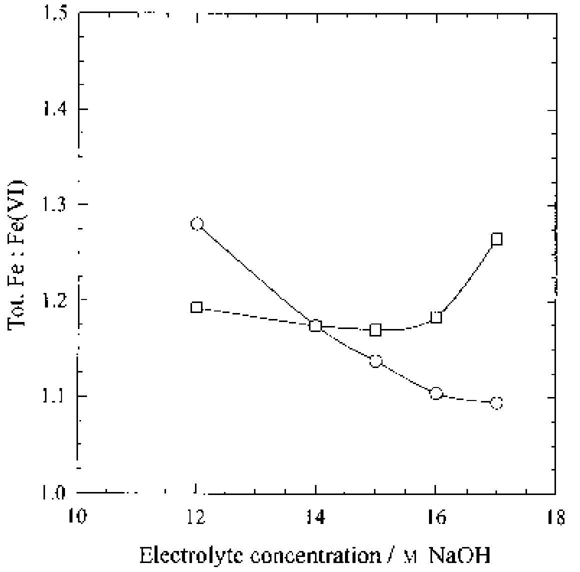

Fig. 2. Dependence of ratio of total iron to Fe^{6+} content in anolyte on electrolyte concentration at c.d. 4.4 mA cm^{-2}. Duration of electrolysis: 180 min; temperature: (○) 20 °C and (□) 40 °C.

the range 0.8 to 66.1 mA cm^{-2}. The results are shown in Fig. 3. The optimum electrolyte temperature was between 30 and 40 °C.

The location of the maximum current yield depends on the temperature. The maximum current yield was 39% for 20 °C at 0.8 mA cm^{-2}, 60% for 30 °C at 2.3 mA cm^{-2}, 60% for 40 °C at 4.5 mA cm^{-2} and 52% for 50 °C at 6.5 mA cm^{-2}.

The ferrate(VI) current yield does not differ considerably when comparing 16 M and 14 M NaOH. The shape of the dependence of the current yield on the c.d. is the same for both concentrations. There is an increase in the current yield of about 4% for 16 M NaOH in comparison with 14 M NaOH. This difference remains nearly constant throughout whole c.d. range studied.

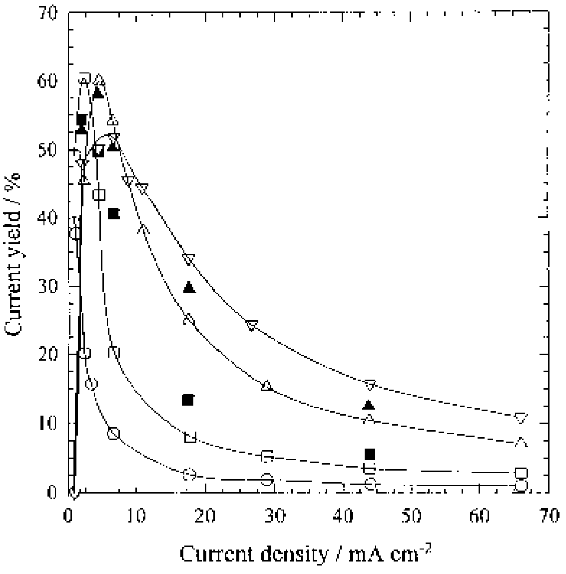

Fig. 3. Dependence of ferrate(VI) current yield on anodic c.d. Duration of electrolysis: 180 min; temperature: (○) 20 °C, (□) 30 °C, (△) 40 °C and (▽) 50 °C; *open* symbols correspond to 14 M, *filled* to 16 M NaOH.

The dependence of the ratio of the total iron to Fe^{6+} concentration in the anolyte after electrolysis at c.d.s corresponding to Fig. 3 is shown in Fig. 4(a). This dependence exhibits a global minimum of 1.07 at 30 °C and 4.5 mA cm^{-2}, close to the highest ferrate(VI) current yield. At 20 °C the ratio of the total iron to Fe^{6+} shows a decreasing trend over the whole c.d. range studied. With increasing temperature the minimum value appears at conditions corresponding to the maximum in the ferrate(VI) yields.

The difference between the total iron and Fe^{6+} concentration (concentration of iron in oxidation states lower than Fe^{6+}) in the anolyte after electrolysis shown in Fig. 4(b) tends to reach a limiting value increasing with the temperature. At 50 °C the difference increased over the whole c.d. range studied. The differences found using a 16 M NaOH solution were generally higher than in the case of 14 M NaOH, but the shape of the dependence on the c.d. did not differ.

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

From the dependence of ferrate(VI) current yield on electrolysis duration for temperatures of 20 to 50 °C and current densities of 4.4 and 44.0 mA cm^{-2} shown in Fig. 5 it follows that the time at which the maximum yield was found generally decreased with increasing temperature. On the other hand the current yield peak value increased with increasing temperature in the temperature range studied. Using 16 M NaOH the dependence of ferrate(VI) current yield on electrolysis duration follows almost the same curve as for 14 M NaOH.

From the dependence of the ratio of total iron to Fe^{6+} content in the anolyte shown in Fig. 6(a) it follows that the electrolysis duration after which the

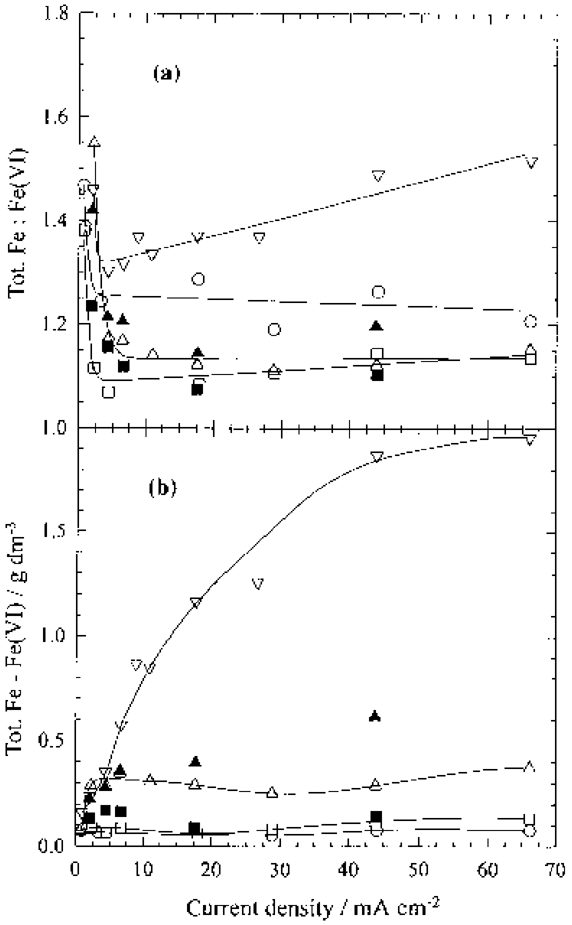

Fig. 4. (a) Dependence of ratio of total iron to Fe^{6+} content in the anolyte on anodic c.d.; (b) dependence of difference between total iron and Fe^{6+} content in the anolyte on anodic c.d. Duration of the electrolysis (in both cases): 180 min; temperature: (○) 20 °C, (□) 30 °C, (△) 40 °C and (▽) 50 °C; *open* symbols correspond to 14 M, *filled* to 16 M NaOH.

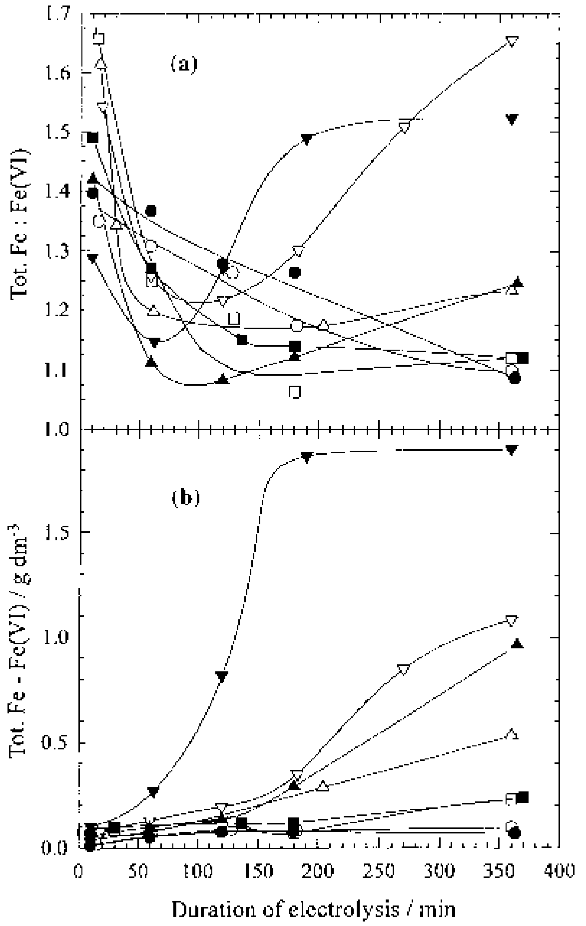

Fig. 6. (a) Dependence of ratio of total iron to Fe^{6+} content in the anolyte on electrolysis duration; (b) dependence of difference between total iron and Fe^{6+} content in the anolyte on electrolysis duration. Electrolyte (both cases): 14 M NaOH; temperature (○) 20 °C, (□) 30 °C, (△) 40 °C and (▽) 50 °C; *open* symbols refer to c.d. 4.4 mA cm^{-2}, *filled* symbols refer to c.d. 44.0 mA cm^{-2}.

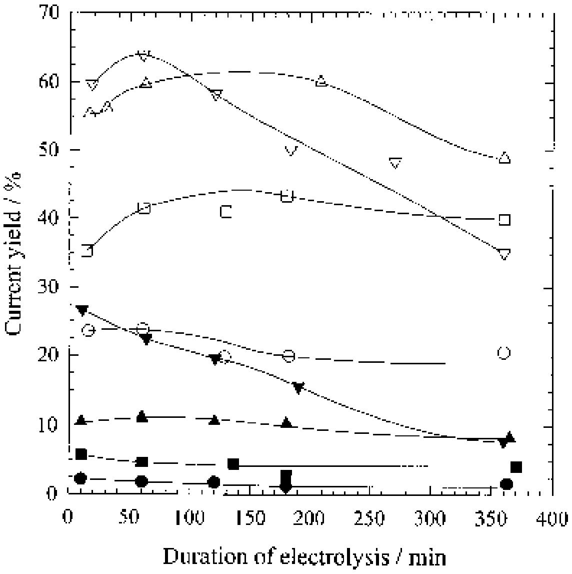

Fig. 5. Dependence of ferrate(VI) current yield on electrolysis duration in 14 M NaOH, temperature: (○) 20 °C, (□) 30 °C, (△) 40 °C and (▽) 50 °C; *open* symbols refer to c.d. 4.4 mA cm^{-2}, *filled* symbols refer to the c.d. 44.0 mA cm^{-2}.

minimum ratio value was observed decreased with increasing temperature and c.d. At 20 °C the ratio decreased with increasing time of electrolysis over the whole time interval studied. At 50 °C the minimum was reached after 120 and 60 min of electrolysis at current densities of 4.4 and 44.0 mA cm^{-2}, respectively.

In Fig. 6(b) the dependence of the difference between the total iron and Fe^{6+} concentration after electrolysis is shown. This shows for 14 M NaOH at 20 °C and both current densities (4.4 and 44.0 mA cm^{-2}) a trend to a limiting difference value. After a certain time of electrolysis is exceeded, a strong increase in the difference values starts. The time interval after which the increase in the difference value starts increases with decreasing temperature and c.d.. At 20 °C an increase was not observed, even after 360 min of electrolysis for both studied c.d. On the other hand, at 50 °C and a c.d. of 4.4 mA cm^{-2} the increase starts after 120 min of electrolysis and at 44.0 mA cm^{-2} the initial trend to a limiting difference value is almost impossible to observe.

Using 16 M NaOH the values of the difference in concentrations were generally higher compared to the 14 M NaOH solution, but the dependence again followed the same shape.

3.4. *Quasisteady state polarization curves in the transpassive potential region*

Polarization curves were measured galvanostatically using the procedure described in [1]. The typical potential–charge curves for grey and white cast iron and for the case of the pure iron are shown in Fig. 7. The values of the quasisteady state anode potentials for all studied current densities correspond to the same charge passed, namely $0.4 \pm 0.1\,\mathrm{C\,cm^{-2}}$. This charge corresponds, within inherent error, to the first maximum on the potential–charge curve [1, 2, 9], shown in Fig. 7, for all studied current densities. The resulting polarization curve is shown in Fig. 8. The quasisteady state anodic polarization curve is shifted by about 110 mV to more anodic potentials when compared to the polarization curves measured for grey and white cast iron [1, 2].

4. Discussion

Figure 1 shows that the maximum ferrate(VI) current yield was reached for 16 M NaOH. The optimum concentration of NaOH is higher compared to the previously found optimum of 14 M for white cast iron [2, 6]. On the other hand this value is in agreement with the results obtained in [3–5], where no definition of the anode material was given. In [2] it was suggested that the reasons for the differences in the current yields obtained by different authors studying the influence of electrolysis parameters (e.g. c.d., electrolyte concentration and temperature) may be the different anode composition, especially the content and form of carbon in the anode material used, or the analytical method used for the estimation of the ferrate(VI) content. The results obtained in the present study and in [1, 2] support both these theories.

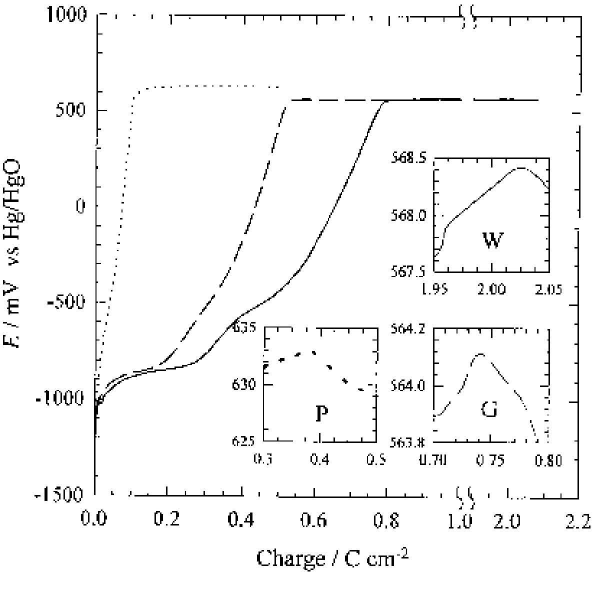

Fig. 7. Dependence of anode potential on charge passed after cathodic prepolarization Temperature: 20 °C, electrolyte concentration: 14 M NaOH: (——) white cast iron anode at c.d. $0.4\,\mathrm{mA\,cm^{-2}}$, (- - - -) grey cast iron anode at c.d. $0.3\,\mathrm{mA\,cm^{-2}}$ and (·········) pure iron anode at c.d. $0.4\,\mathrm{mA\,cm^{-2}}$. The inserted plots show the first maximum on the charge–potential plot: this potential was used as the potential corresponding to the studied c.d. in the quasisteady state polarization curve. W means white cast iron, G means grey cast iron and P means pure iron, the axis of plots are identical with corresponding axes of main plot.

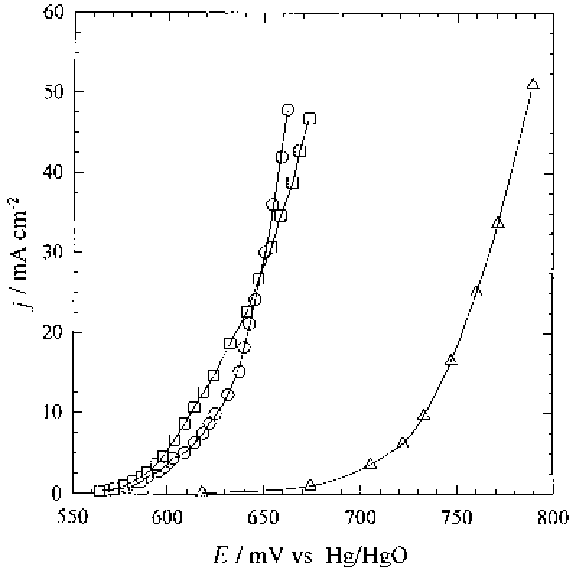

Fig. 8. Quasisteady state polarization curve. Temperature: 20 °C, 14 M NaOH: (○) white cast iron, (□) grey cast iron and (△) pure iron anode.

The main differences between published data [1–9] are caused by the different anode material composition. Both this study and [2] show that the optimum NaOH concentration in the anolyte decreases with increasing iron carbide (Fe_3C) content in the anode material. The reasons for this behaviour are the different properties (porosity, compactness etc.) of the oxy-hydroxide layer covering the electrode surface during ferrate(VI) synthesis for anode materials with different iron carbide content. It was shown in [2] that the iron carbide particles suppress the passivating properties of the oxy-hydroxide layer, probably through local disintegration of this surface layer, thus enabling the anode material to be continuously dissolved and oxidized. If the iron carbide content is low, the surface layer is more compact and a higher NaOH concentration is necessary to break down the more compact surface oxy-hydroxide layer and to allow the anode dissolution.

The same reason applies to the different temperatures providing the highest ferrate(VI) yields found in the present study and in [2, 6, 9] using anode materials with different composition. Using the anode material with low iron carbide content (pure iron, present study) the optimum temperature was found to vary between 30 and 40 °C. Using an anode with high iron carbide content (white cast iron [2]) the temperature of 20 °C provided the highest ferrate(VI) yield after 180 min electrolysis. This difference is also explained by the increasing OH^- ion activity with increasing electrolyte temperature. The more compact oxy-hydroxide surface layer formed with decreasing iron carbide content in the anode material requires higher hydroxide solution temperature to break down its passivity. This theory agrees well with the experimental results of the present study and in [2, 6, 9] showing a decrease in the optimum electrolyte temperature with increasing iron carbide content in the anode material.

The different stability of the oxy-hydroxide surface layer buildup on the material with different iron carbide content also explains the difference in the ferrate(VI) yield against current density found for pure iron, see Fig. 3, and white cast iron [2]. The lower current density providing highest ferrate(VI) yield in the case of pure iron, as well as the sharper decrease in the yield for greater current densities are explained by the buildup of the thinner, more compact passive layer on the pure iron anode surface when compared to the white cast iron anode.

As a second reason for differences in the optimum electrolysis temperature found by different authors (e.g. present study and [3, 4]) the ferrate(VI) analysis method used was mentioned above. The total iron analysis used in [3, 4] does not distinguish between the oxidation stages of the iron in the anolyte solution. It follows from Figs 3 and 4 that, upon recalculating the total iron to Fe^{6+} concentration, the current yield for pure iron increased with temperature within the experimental error. For example, at the c.d. of $4.4\,\mathrm{mA\,cm^{-2}}$ using ferrate(VI) analysis we obtained the following current yields: 16, 43, 60 and 50% for 20, 30, 40 and 50 °C, respectively. Using the assumption that all iron in the anolyte is present in the oxidation stage Fe^{6+} the following current yields were obtained: 20, 46, 68 and 69% for the respective temperatures. The total iron analysis leads to overestimation of the ferrate(VI) current yields by approximately 7 to 15%. Also the temperature providing the highest ferrate(VI) current yield is shifted to higher values. Using the Fe^{6+} analysis the optimum temperature was found to be 40 °C. Using total iron analysis an optimum temperature of 50 °C was found. This is explained by the more intensive dissolution of the oxy-hydroxide layer on the anode surface at higher temperature which results in higher total iron concentration. The increasing temperature also enhances the rate of a proposed chemical step in the ferrate(VI) formation mechanism [9]. On the other hand, the increasing temperature also increases the ferrate(VI) decomposition rate [12]. But the decomposition can not be identified by the total iron analysis. This is the reason for the high optimum c.d. ($13\,\mathrm{mA\,cm^{-2}}$ at 60 °C) reported by Grube and Gmelin [5] and the optimum temperature of 70 °C reported by Pick [4]. Comparing the current yield obtained by Haber [3] and Pick [4] and the yield obtained in this study, it is possible to conclude that both Haber and Pick used a relatively pure iron.

The dependence of current yield on electrolysis duration shown in Fig. 5 also supports the suggestions introduced in the previous paragraphs. From Fig. 5 it follows that an increase in temperature enhances the current yield at the beginning of the electrolysis. With increasing temperature, the time of electrolysis after which ferrate(VI) decomposition prevails over the positive influence of the increasing temperature decreases. The ratio, see Fig. 6(a), and the difference, see Fig. 6(b), of the total iron and Fe^{6+} content in the anolyte indicates enhancement of the ferrate(VI) decomposition by an apparent increase at higher temperatures and electrolysis duration over 60 to 180 min. The increasing anodic current density supports the tendency to passivation of the anode surface and enhances oxygen evolution. Therefore, at the higher c.d. ($44.0\,\mathrm{mA\,cm^{-2}}$) the ferrate(VI) current yield is lower compared to the lower c.d. ($4.4\,\mathrm{mA\,cm^{-2}}$) and decreases throughout the time of electrolysis studied and no maximum current yield is observed.

The suggestion that the differences in ferrate(VI) yield between the pure iron, mild steel and white cast iron are caused by different iron carbide contents resulting in disintegration of the surface passive oxy-hydroxide layer agrees well with the three stage ferrate(VI) formation mechanism introduced in [9]. The charge used during the initial period after finishing cathodic prepolarization for the intermediate product formation corresponds to the charge necessary for reaching the first maximum on the plot of anode potential against charge passed (Fig. 7). As shown in Table 1, this charge increases with increasing iron carbide content in the anode material, which indicates the formation of a thicker, more porous and less protective surface oxy-hydroxide layer.

This theory also explains the differences on the plots of anode potential against charge passed shown in Fig. 7. Formation of the thin, compact surface oxy-hydroxide layer on the pure iron anode requires a relatively small charge; therefore the oxidation steps on the potential against charge plot corresponding to this process ($E = -850\,\mathrm{mV}$ and $E = -530\,\mathrm{mV}$) are almost not apparent at pure iron when compared to the white cast iron anode. The fast passivation is also the reason for the shift of the pure iron quasi-steady state polarization curve by 110 mV to a more positive potential compared to the white cast iron (Fig. 8). This is supported by the limiting concentration of iron in the oxidation state lower than Fe^{6+} in the anolyte, which was found to be $0.8\,\mathrm{g\,dm^{-3}}$ (for white cast iron at 20 °C) [2] and $0.08\,\mathrm{g\,dm^{-3}}$ (for pure iron at the same temperature) (Fig. 4(b)).

Table 1. Charge necessary to reach this first potential maximum after cathodic prepolarization at 20 °C

Anode material carbon content / wt. %	*First potential maximum charge* / $\mathrm{C\,cm^{-2}}$	*Reference*
pure iron < 0.005	0.4 ± 0.1	present study
mild steel 0.08	1.8 ± 0.2	5
white cast iron 3.16	2.1 ± 0.6	2

After finishing of the primary surface layer formation a second period of ferrate(VI) production starts. During the second period ferrate(VI) production, together with anode surface passivation, takes place. With increasing Fe_3C content in the anode the passivation process is decelerated and the second period lasts longer. This is apparent from the comparison of Fig. 5 in the present study and in [2]. During this period the concentration of iron in oxidation states lower than Fe^{6+} in the anolyte remains nearly constant.

The third ferrate(VI) production period is characterized by the passivated anode surface at which ferrate(VI) production almost ceases and only oxygen is evolved. This results in a decrease in the ferrate(VI) yield. During the second and third ferrate(VI) formation periods ferrate(VI) decomposition proceeds simultaneously with the electrode reactions.

A very important condition is the presence of all carbon in the electrode material in the form of iron carbide. If a part of the carbon is present in the form of graphite, which forms a separate phase, the behaviour of the anode changes radically (grey cast iron [1]). In the presence of ferrate ions oxygen evolution on the graphite particles has a lower overvoltage compared to the pure iron passivated surface. This leads to a shift of the quasisteady state polarization curve to less positive potentials when compared to pure iron and to a decrease in the ferrate(VI) yields by enhancement of the parasitic oxygen evolution reaction. The same shift to less anodic potentials was observed using white cast iron. In this case the shift is caused by the oxy-hydroxide layer covering the anode surface, which has poor protecting properties, high porosity and a greater specific electrode surface, which results in higher ferrate(VI) yields. This explanation is in agreement with the theory introduced in [1, 2].

5. Conclusion

The results of this study together with [1] and [2] lead to the following conclusions for the case of pure iron, mild steel and white cast iron as anode materials in ferrate(VI) production. The difference between these materials is in the passivating properties of the oxy-hydroxide layer covering the anode surface. A compact and stable surface layer is almost insoluble, that means, it protects the anode material against further dissolution. The tendency to form such a compact layer is highest for pure iron. Higher temperature (30 to 50 °C depending on the electrolysis conditions) or higher electrolyte concentration is necessary to support dissolution in this case. With increasing iron carbide (Fe_3C) content in the anode material the porosity and local faults in the surface layer increase. For a high iron carbide content a relatively high current yield during a long electrolysis time can be expected, even at a low temperature (20 °C). If the carbon is present partially in the form of graphite in the anode material (grey cast iron), the enhancement of the anodic oxygen evolution side reaction on the graphite particles present at the anode surface is dominant and the current yield decreases dramatically at all temperatures.

References

[1] K. Bouzek and I. Roušar, *J. Appl. Electrochem.* **26** (1996) 919.

[2] K. Bouzek, I. Roušar and M. A. Taylor, *ibid.* **26** (1996) 925.

[3] F. Haber, *Z. Elektrochem.* **7** (1900) 215.

[4] W. Pick, *ibid.* **7** (1901) 713.

[5] G. Grube and H. Gmelin, *ibid.* **26** (1920) 153.

[6] J. Toušek, *Coll. Czech. Chem. Comm.* **27** (1962) 914.

[7] A. S. Venkatadri, H. H. Bauer and W. F. Wagner, *J. Electrochem. Soc.* **121** (1974) 249.

[8] F. Beck, R. Kaus and M. Oberst, *Electrochim. Acta* **30** (1985) 173.

[9] K. Bouzek and I. Roušar, *J. Appl. Electrochem.* **23** (1993) 1317.

[10] A. Denvir, D. Pletcher, *ibid.* **26** (1996) 815.

[11] A. Denvir, D. Pletcher, *ibid.* **26** (1996) 823.

[12] W. F. Wagner, J. R. Gump, E. N. Hart, *Anal. Chem.* **24**(9) (1952) 1497.