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

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Current efficiency for the oxidation of a grey cast iron anode to ferrate(VI) in 14 M NaOH was measured in the region of bubble induced convection. The maximum current yield, obtained after 180 min of electrolysis, had a value of 11% at a current density of 32 mA cm^{-2} and a temperature of 20 °C. The ferrate(VI) current yield increased throughout the whole current density range under study (from 1 to 36 mA cm^{-2}). The iron anode was activated by cathodic prepolarization. The iron concentration in lower oxidation states in the solution after electrolysis was constant within experimental error over the whole temperature range under study. The quasisteady state anodic polarization curve for grey cast iron in the transpassive potential region was measured. This anodic polarization curve was shifted to more negative potential, at the same current density, compared to the potential of the mild steel anode.

1. Introduction

The formation of ferrate(VI) ions by the anodic oxidation of iron in concentrated hydroxide solutions was first observed in 1841 by Poggendorf [1]. This problem was later studied in more detail by Haber [2] and Pick [3]. They found that a necessary condition for the formation of ferrate(VI) is that the pH of the solution used as an electrolyte should be at least 14. Haber [2] and Pick [3] used 40 and 50 wt % solutions of NaOH or KOH. According to Pick [3] the ferrate(VI) current yields were better in NaOH solutions than in KOH; the current yield generally increased with the hydroxide concentration in the concentration range (40 to 50 wt % of NaOH or KOH) and temperature range (30 to 70 °C) under study. The current yield also increased with the carbon content in the iron used; the ferrate(VI) current yields were 15% for raw iron, 27% for steel and 50% for cast iron at a current density of 1 mA cm^{-2} and a NaOH concentration of 16.5 M. Cathodic polarization was the best pretreatment of the anode prior to oxidation [2, 3]. In the work described in [1–3] an unspecified cast iron anode was used.

The study of electrochemical generation of ferrate(VI) was later continued by Grube and Gmelin [4], Toušek [5], Venkatadri *et al.* [6] and Beck *et al.* [7]. Ferrate(VI) production using a mild steel anode was reported by us in a previous study [8]. The influence of iron anode pretreatment on the ferrate(VI) current yield and a proposed mechanism of the formation of ferrate(VI) was also given.

The results for mild steel [8] exhibited a different behaviour compared to data published by Toušek [5], who used an unspecified cast iron anode. The maximum ferrate(VI) current yield of 40% was reached at a current density of 2 mA cm^{-2}, a temperature of 30 °C and a duration of the electrolysis of 3 h [8]. In comparison to this, Toušek [5] reported a higher ferrate(VI) current yield, 65%. The dependence of the ferrate(VI) current yield on the current density given by Toušek [5] also exhibited a slower decrease after reaching a maximum value at the current density of 4 mA cm^{-2}, compared to data published for mild steel [8]. The optimum current densities reported in [3, 5, 8] are relatively close to each other (1, 4 and 2 mA cm^{-2}, respectively). Only Grube and Gmelin [4] are reporting a much higher current density providing the highest ferrate(VI) current yield, namely 13 mA cm^{-2}. The reason may be the difference in temperature. Whereas the results obtained in [3, 5, 8] were obtained in a temperature range of 20 to 30 °C, Grube and Gmelin [4] used a temperature of 60 °C. It will be shown later, that higher temperature influences the results more at lower than at higher current densities.

The dependence of ferrate(VI) current yield on current density at a constant duration of electrolysis, as reported in [8], shows qualitative agreement with the corresponding dependence published by Toušek [5]. The differences in the current yields reported by Haber [2], Pick [3], Toušek [5] and in [8] are probably caused by the different anode materials. The other reason for discrepancies is the different analytical

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method used for the estimation of the ferrate(VI) concentration by Haber [2], Pick [3] and Grube and Gmelin [4], who estimated only the total iron concentration in the anolyte and recalculated it as the concentration of ferrate(VI). It was shown in [5, 7, 8] that the anolyte after electrolysis also contains iron compounds in lower oxidation states than Fe(VI). The aim of this work is to estimate the optimum electrolysis conditions for ferrate(VI) production using a grey cast iron anode and to explain differences in the previously published results.

2. Experimental details

2.1. *Chemicals*

A solution of 14 M NaOH, at 20 °C, was used in all experiments. NaOH (Spolana Neratovice) contained the following maximum impurities (wt %): Cl 0.008, Ag 0.002, Fe 0.002, Al 0.002, PO_4^{3-} 0.005, and Ca^{2+} 0.001.

2.2. *Analytical methods*

The content of ferrate(VI) was determined by the chromite method, which is suitable for solutions that are not appreciably contaminated by other oxidants [9, 10]. The total Fe content, including possible solid precipitates dispersed in the solution, was determined by the Zimmermann–Reinhardt method.

2.3. *Apparatus*

The electrolyser is shown schematically in Fig. 1. Two polymethylmethacrylate glass frames formed the anodic and cathodic compartments separated by a PVC diaphragm (D) 4 cm in width and 13 cm in height, of porosity 43.4% and medium pore size 28 μm (Eilenburger Chemie-Werk GmbH, FRG). The diaphragm thickness was 1 mm. The gasket was made of nonvulcanized rubber. The cast iron plates serving as the electrodes closed the electrode compartments from the outer sides. The iron electrodes were in the form of a plate 5 mm thick of dimensions 18 cm × 7.3 cm. The active electrode surface area was 55.4 cm^2. The anode had the following composition: 3.43 wt % C, 0.58 wt % Mn and 0.045 wt % Ni, rest being Fe. According to [11], the grey cast iron contains carbon mainly in the form of graphite (at least 2.63 wt % C with respect to the anode material weight) and only approximately up to 0.8 wt % C with respect to anode material weight in the form of iron carbide (Fe_3C).

Thermostated water was fed to the reverse face of the anode. This enabled control of temperature during electrolysis in the range 10 to 60 °C. The influence of the polymethylmethacrylate used for the frames forming the electrolyser walls on the current yields (e.g., the problem of extraction of soluble organic compounds into the solution) was negligible [8]. A Hg/HgO electrode in the same NaOH solution served as a reference. The anolyte volume was 92 ml.

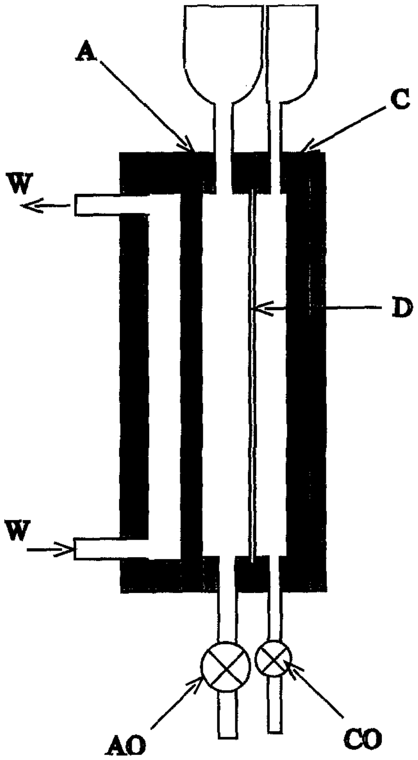

Fig. 1. Scheme of the electrolyser: (A) anode, (C) cathode, (D) diaphragm, (AO) anolyte outlet, (CO) catholyte outlet and (W) thermostating water feed.

3. Results

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

The dependence of the ferrate(VI) current yield on current density at constant duration of electrolysis, 180 min, is shown in Fig. 2. The current density was varied in the range 2 to 36 mA cm^{-2}. The temperature was varied in the range 20 to 50 °C. From Fig. 2 it follows that the ferrate(VI) current yield increases over the studied current density range. The temperature of 20 °C provides the highest current yield, 11%, which was obtained at a current density of 32 mA cm^{-2}. With increasing temperature the ferrate(VI) current yield decreases and at 50 °C it becomes only about 3% at a current density of 27 mA cm^{-2}.

The corresponding dependence of the ratio of the total iron to Fe(VI) content in the anolyte after 3 h of electrolysis is shown in Fig. 3. The ratio of the total iron to Fe(VI) decreases with increasing current density in the range 2 to 36 mA cm^{-2}. The ratio decreases considerably up to about 25 mA cm^{-2}, for example, at a current density of about 2 mA cm^{-2} the ratio is 2.74, 4.32, 2.21 and 5.40 for temperatures of 20, 30, 40 and 50 °C, respectively. At higher current densities the values become similar for all temperatures, for example, at a current density of 36 mA cm^{-2} the ratio is 1.09, 1.13, 1.21 and 1.35 for temperatures of 20, 30, 40 and 50 °C, respectively. The iron concentration in low oxidation states contained in the solution after electrolysis was determined at 0.26 ± 0.04 g Fe dm^{-3} at 20 °C, 0.20 ± 0.04 g Fe dm^{-3} at 30 °C, 0.22 ±

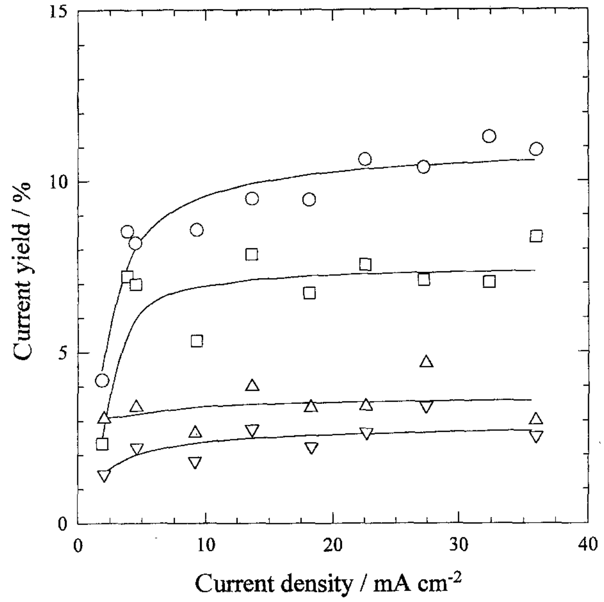

Fig. 2. The dependence of ferrate(VI) current yield on current density at a duration of electrolysis of 180 min in 14 M NaOH and various temperatures: (0) 20, (□) 30, (△) 40 and (▽) 50 °C.

0.08 g Fe dm^{-3} at 40 °C and 0.25 ± 0.05 g Fe dm^{-3} at 50 °C. These values were reached after a charge of about 200 C cm^{-2} was passed.

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

The dependence of the ferrate(VI) current yield on the duration of electrolysis was studied at temperatures of 20 and 30 °C, and at current densities of 2, 9, 18 and 27 mA cm^{-2}. The dependence of current yield on the duration of the electrolysis is shown for the temperature of 20 and 30 °C in Fig. 4. For all current densities, and times of electrolysis longer than 200 min, the experimental points follow almost the same curve.

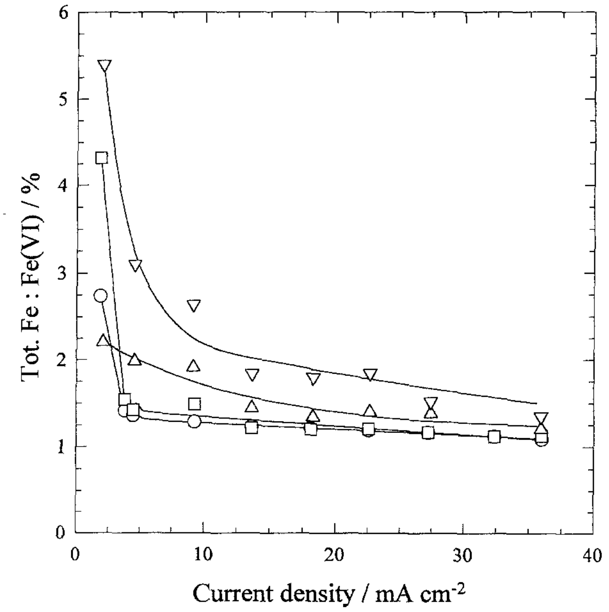

Fig. 3. The dependence of the ratio of total iron concentration in the anolyte after electrolysis to the concentration of Fe(VI) on the current density at a duration of electrolysis of 180 min in 14 M NaOH and various temperatures: (○) 20, (□) 30, (△) 40 and (▽) 50 °C.

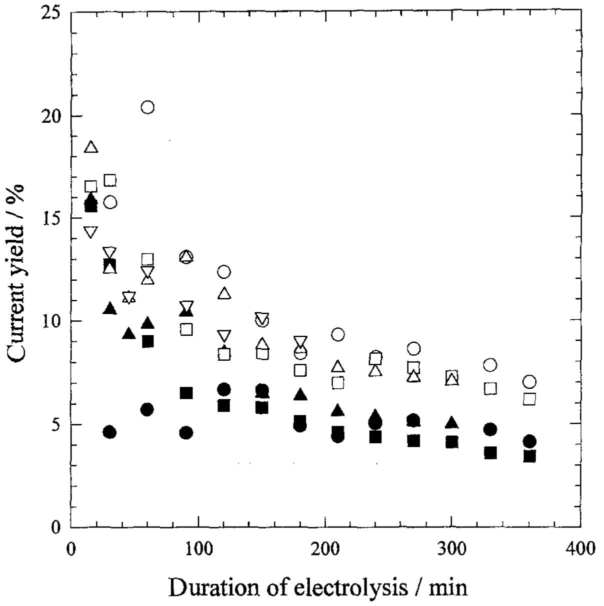

Fig. 4. The dependence of the ferrate(VI) current yield on the duration of electrolysis in 14 M NaOH and at various current densities: (○) 2, (□) 9, (△) 18 and (▽) 27 mA cm^{-2}. Open symbols: 20 °C, filled symbols: 30 °C.

At 20 °C the current yield reaches its highest values at the start of electrolysis. At 30 °C the situation is almost the same. The differences in the current yields between the experiments carried out at different electrolyte temperatures and current density decrease with increasing current density.

3.3. *The quasi-steady state polarization curves in the transpassive potential region*

Polarization curves were measured galvanostatically using the procedure described in [8]. The anode was prepolarized cathodically at a current density of 20 mA cm^{-2} for 10 min before the measurement of each point on the curve. The quasisteady state anode potential corresponding to the current density was defined as the first maximum on the potential–charge curve, which was the most easily reproducible potential at all current densities. The maximum on the anode potential–charge dependence is due to the decrease in the anode surface activity with increasing anodic charge passed at the anode surface. Thus, all quasisteady state potential values correspond to approximately the same charge passed, namely 0.65 ± 0.04 C cm^{-2}. The resulting curve is shown in Fig. 5. The quasisteady state anodic polarization curve is shifted to more negative potentials, approximately by 100 mV, compared to the potential of the mild steel anode at 25 °C at the same current density [8].

4. Discussion

The dependence of the ferrate(VI) current yield on temperature and anodic current density at constant electrolysis duration increases over the whole current density range under study (1–36 mA cm^{-2}). This is

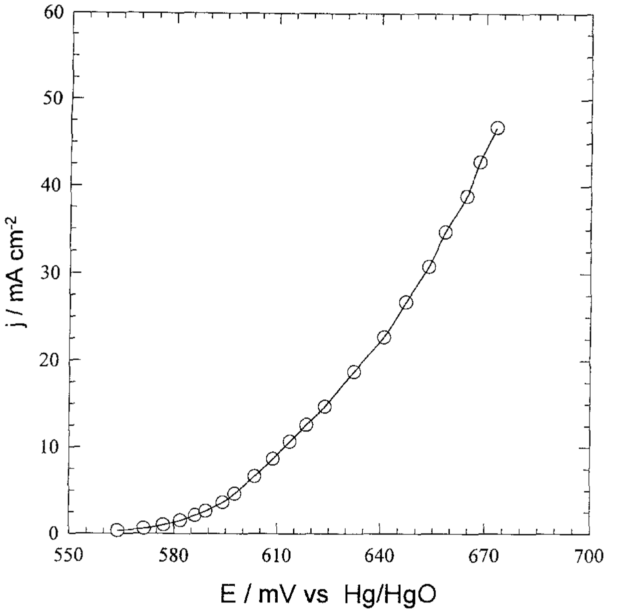

Fig. 5. Quasisteady state polarization curve on grey cast iron anode (at least 2.63 wt % C as graphite particles, up to 0.8 wt % C in the form of Fe_3C), temperature 20 °C and electrolyte concentration 14 M NaOH.

not in agreement with data reported previously by Toušek [5] for a cast iron anode and with our previous data for a mild steel anode [8], where the ferrate(VI) current yield reached a maximum at current densities of 4 and 2 mA cm^{-2}, respectively, and after which it decreased to zero. The differences between the mild steel and grey cast iron anodes may be explained by the influence of the material composition. The major part of the carbon in grey cast iron is present in the form of graphite (at least 2.63 wt %).

The low ferrate(VI) current yields reached using a grey cast iron anode are probably caused by the presence of graphite. It can be assumed that the enhancement of the ferrate(VI) decomposition is caused by graphite particles dispersed in the electrolyte or held on the anode surface. The influence of graphite particles on ferrate(VI) current yield by the following decomposition reaction may be explained as a catalytic action of the graphite particles.

$$2FeO_4^{2-} + 5H_2O \longrightarrow 2Fe(OH)_3 + \frac{3}{2}O_2 + 4OH^- \qquad (1)$$

Another explanation for the increase in the ferrate(VI) decomposition rate is that the presence of the graphite particles also leads to an increase in the solid–liquid interface area by the graphite particles released from the anode. According to [12] the increase in the interface area causes an increase in the ferrate(VI) decomposition rate. However, there is no evidence based on experimental data for an increase in ferrate(VI) decomposition rate. Even at high temperature (50 °C) the concentration of iron in the lower oxidation states remains almost constant and the ratio of total iron to ferrate(VI) concentration in the anolyte decreases over the whole current density range under study (Fig. 3). Moreover, the increase in the ratio compared to that for the mild steel anode [8] is not sufficiently high to explain the very low level of the ferrate(VI) current yields. Therefore the enhancement of the decomposition of the ferrate(VI) by graphite may represent only a partial explanation for the decrease in current yield. The rate of the decomposition of ferrate(VI) also does not explain the difference in the dependence of ferrate(VI) current yield on current density (Fig. 2) and duration of electrolysis (Fig. 4) compared to the previously published data [5, 8].

The effect of graphite particles may be explained as the effect of the heterogeneous composition of the anode surface of which one part is formed by iron

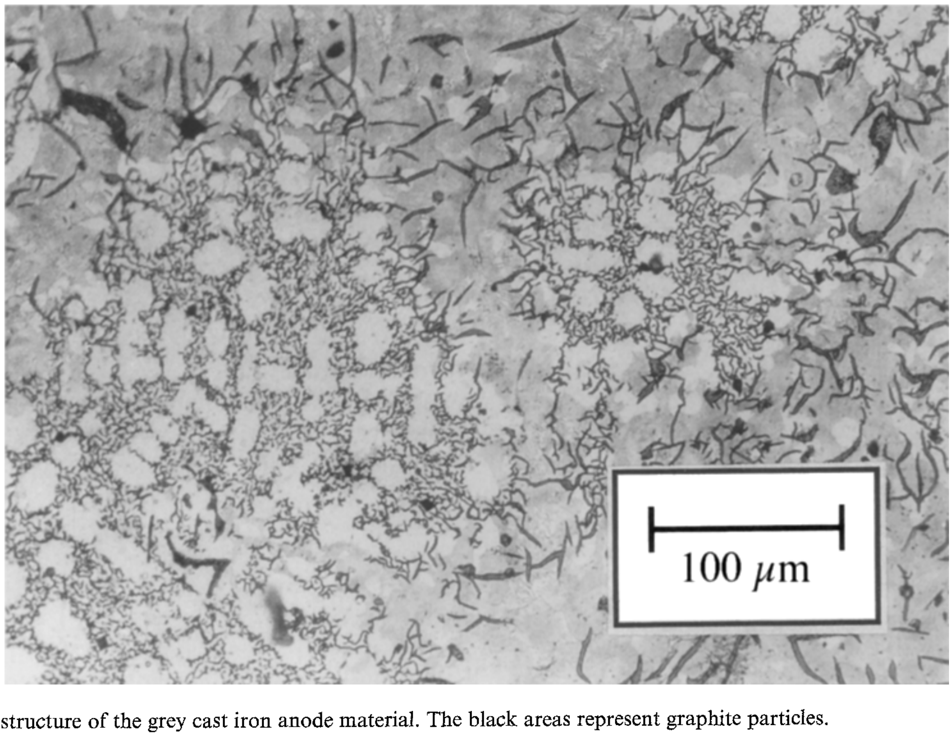

Fig. 6. The microstructure of the grey cast iron anode material. The black areas represent graphite particles.

covered by a passive layer and the other by graphitic carbon. The percentage of the surface area constituted by the graphite particles is relatively high. The microstructure of the electrode used in this study is illustrated in Fig. 6. The black areas represent graphite particles [11]. To evaluate the portion of the surface area formed by graphite particles is not possible due to the fact that during the electrolysis the iron is continuously dissolving, but the graphite particles are partially oxidized and partially removed from the surface by gas bubbles at irregular intervals. The portion of the electrode surface formed by graphite particles therefore changes with time. This is also a reason for the lower reproducibility of the data obtained in this study compared to that obtained for mild steel [8].

On the surface of the graphite particles the overvoltage for the evolution of oxygen in 14 M NaOH electrolyte is probably lower than that on the passivated iron surface. Thus, at a given current density the average potential of the anode is lower, compared to the potential of the mild steel [8]. This theory is supported by the quasisteady state polarization curves measured for grey cast iron (Fig. 6), which shows a decrease in the anode potential compared to mild steel at 25 °C [8] in the range 25 to 280 mV for a given current density.

This shift in the anode potential may also be the reason for the shape of the dependence of the ferrate(VI) current yield on the anodic current density, which does not exhibit a maximum and increases continuously (Fig. 2). This may be explained as a consequence of the lower anode potential leading to slower passivation of the anode surface and enabling ferrate(VI) production at longer electrolysis durations or at higher current densities, compared to the mild steel [8].

Figure 4 shows the dependence of ferrate(VI) current yield on the duration of electrolysis at different current densities. At both electrolyte temperatures the ferrate(VI) current yield differs, at a duration of electrolysis up to 180 min, for different current densities. At electrolysis durations of more than 200 min the current yield at the lowest current density exceeds the current yield reached at highest current density. At the temperature of 30 °C this is more apparent.

This behaviour may be explained by the mechanism of ferrate(VI) formation reported previously [8]. According to this theory the ferrate(VI) formation on iron proceeds in three steps: (i) formation of the intermediate products – ferrate(VI) current yield is zero, (ii) ferrate(VI) formation and simultaneous passivation of the anode surface – the ferrate(VI) current yield has a maximum value, which decreases with continuous passivation of the surface, and finally (iii) the surface passivation reaches such a degree that almost only oxygen is evolved on the anode surface – the ferrate(VI) current yield again decreased to zero. For low current densities it takes a longer time to complete the first period of ferrate(VI) production than at higher current densities. The first ferrate(VI) production period is characterized by the charge used for the production of the necessary amount of the intermediate products. This is more apparent with increasing temperature when the solubility of intermediate products increases and subsequently the charge necessary for their formation increases. On the other hand at lower current density it also takes a longer time to complete the passivation of the anode surface to such a degree that almost only oxygen is produced. The complementary factor is that at higher current density the anode potential is also higher. The increase in anode potential enhances the rate of surface passivation.

5. Conclusion

The dependence of current efficiency for the oxidation of an iron anode to ferrate(VI) was measured in 14 M NaOH using a grey cast iron anode (3.43 wt % C). The maximum current yield of 11% was found at a current density of 32 mA cm^{-2} and a temperature of 20 °C. Comparing this current yield with previously published results for anodes made from undefined cast iron [5] and a mild steel (0.08 wt % C) [8] the current yield reached here is very low. Also the dependence of the ferrate(VI) current yield on the current density for grey cast iron anode is different from that found for the undefined cast iron [5] and mild steel anodes [8]. The quasisteady state polarization curve measured in the transpassive potential region using grey cast iron electrode in 14 M NaOH shows a shift to more negative potentials in comparison to the polarization curve measured using mild steel. These differences are explained as a consequence of the carbon being present in the form of graphite particles in the grey cast iron electrodes. These graphite particles form a significant part of the anode surface.

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