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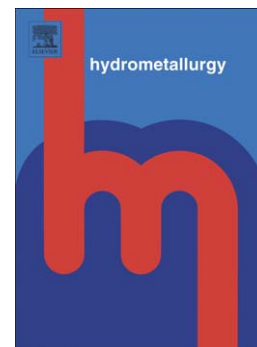
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Suchun Zhang, Michael J. Nicol

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An Electrochemical Study of the Reduction and Dissolution of Ilmenite in Sulfuric Acid Solutions

Suchun Zhang and Michael J. Nicol *

A.J. Parker Centre, Murdoch University, Perth, Australia, WA6150
(*author for correspondence, Fax: +61 8 93606343, Email: nicol@murdoch.edu.au)

Abstract

Electrochemical techniques have been used to investigate the reduction and dissolution of two different ilmenite samples in 450 g L^{-1} sulfuric acid solutions at elevated temperatures. The results have shown that the dissolution rate of ilmenite ($FeTiO_3$) is low at potentials above about 0.3 V at which potentials the dissolution of ilmenite and the reduction of hematite (if present in the ilmenite sample) are the main reactions. At more negative potentials the dissolution of ilmenite increases simultaneously with reduction of ilmenite to trivalent titanium. These observations are consistent with those predicted from thermodynamic data. Hematite has a higher dissolution rate under reductive conditions than ilmenite. Studies of the effect of temperature on the dissolution of ilmenite at low potentials such as 0 V have shown that in the temperature range of 65-95°C, the activation energy is about 50 kJ mol^{-1} and this together with the high ratio of the charge passed to metals dissolved suggests that the rate of the non-reductive dissolution reaction is not significant under these conditions.

Keywords: Ilmenite; Dissolution; Reduction; Electrochemistry; Sulfuric acid

1. Introduction

Ilmenite ($FeTiO_3$) is one of the primary global sources of titanium dioxide which is extensively used in paints, paper, porcelain, plastics and fibres. The ilmenite minerals of greatest importance are those from the relatively rare massive deposits, which often occur in association with oxides such as hematite or magnetite, and the more widely occurring titaniferous beach sand deposits, which have resulted from natural erosion and concentration processes (Temple, 1966). There are two industrial methods which have been developed for making titanium dioxide pigment from ilmenite minerals, namely:

(a)   Pyrometallurgical methods, which include the smelting process in which ilmenite is carbothermically reduced in a DC plasma/electric arc furnace to cast iron and a slag rich in titanium (Mohanty and Smith, 1993; Mackey, 1994; Welham and Williams, 1999), or the roasting process in which iron is reduced to either metallic or ferrous state and removed by subsequent accelerated corrosion and/or acid leaching to obtain a synthetic rutile (Becher et al., 1965; Chen and Huntoon, 1977). The upgraded high grade titanium products are subjected to the sulfate or chloride process (see below) to produce pigment titanium dioxide.

(b)   Hydrometallurgical methods, which include leaching of ilmenite with hydrochloric acid (Lanyon et al., 1999; Ogasawara et al., 2000; Lasheen, 2005) or sulfuric acid both under atmospheric or pressure leaching conditions to dissolve iron in order to obtain synthetic rutile or

titanium dioxide pigment (Kataoka and Yamada, 1973; Kulling et al., 1979; Toromanoff and Habashi, 1985; Jayasekera et al., 1995; Charnet, 1999).

The sulfate process in which ilmenite minerals are directly dissolved by heating with concentrated sulfuric acid at 150-180°C is the first step in the commercial production of pigment-grade titanium dioxide (Barksdale, 1966). In the process, iron is removed by reducing ferric ions in the solution to the ferrous state with scrap iron followed by selective crystallization of ferrous sulfate below 15°C. After suitable adjustment the remaining solution rich in titanium is boiled to precipitate the titanium oxide. The precipitate is heated to about 1000°C to drive off contained water which allows the formation of very fine crystals of raw white pigment (Mackey, 1994). Large quantities of waste iron sulfate and dilute sulfuric acid are produced in the process. The advantages of the sulfate process are low capital investment and low energy consumption. Thus, it accounts for about 40% of world production for pigment titanium dioxide (Adams et al., 1997; Kamala et al., 2006). In response to increasing environmental pressures, numerous investigations have been carried out and innovative techniques developed to improve the process (Welham and Llewellyn, 1998; Kretschmer and Derler, 2004; Smith, 2004). Recently, a process has been described for reductive dissolution of ilmenite in sulfuric acid media (Roche et al., 2004; Stuart et al., 2007). It involves leaching of ilmenite minerals in the presence of reductants such as scrap iron in concentrated sulfuric acid of 400-700g L^{-1} at temperatures of less than 110°C, or gaseous reduction of ilmenite minerals to reduce the ferric ions to ferrous state at about 700°C followed by leaching in strong sulfuric acid. The dissolution of ilmenite minerals in sulfuric acid solutions is significantly accelerated under reductive conditions. However, despite the industrial importance of the sulfate route for ilmenite dissolution for producing pigment TiO$_2$ there has been surprisingly little published on the kinetics and mechanisms of the dissolution of ilmenite in strong sulfuric acid (Barton and McConnel, 1979; Han et al., 1987; Liang et al., 2005; Sasikumar et al., 2007).

Ilmenite is a p-type semiconductor with the electrical conductivity ranging from 0.016 to 0.38 ohm^{-1} cm^{-1} depending on the crystal orientation of ilmenite and hematite content (Ishikawa, 1958). Thus, electrochemical studies on ilmenite minerals could provide useful information for the mechanisms and kinetics of the dissolution of ilmenite in acid solutions. However, limited information has been published on electrochemical processes associated with the reduction ilmenite, due possibly to the difficulty in obtaining pure samples of the mineral.
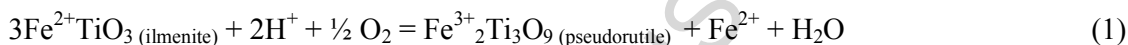
Fig. 1 shows a published Eh-pH diagram for the Ti-Fe-H$_2$O system at 25°C (Kelsall and Robbins, 1990). It is apparent from the diagram that reductive dissolution of ilmenite to form Fe^{2+} and Ti^{3+} is possible at pH values higher than required for oxidative dissolution, which also occurs at pH values higher than required for non-oxidative dissolution (normally pH<0). Reductive dissolution of Fe$_2$O$_3$ is also predicted which may have kinetic benefits for ilmenite dissolution.

Fig. 1 here

McConnel (1978) carried out a preliminary study of the electrochemical behaviour of synthetic and natural ilmenites in various concentrations of H$_2$SO$_4$ at temperatures of 20°C and 40°C using cyclic voltametric and potentiostatic techniques. He reported that applied potentials less than the rest potential significantly increase the rate of dissolution of ilmenite in sulfuric acid solutions while there appeared to be little influence of potentials positive to the rest potential on the rate. No selective dissolution of either iron or titanium from ilmenite was observed at all potentials studied. It was suggested that the electrode processes may occur in the solid state.

Andriamanana et al (1984) studied the electrochemical behaviour of several natural ilmenites in 1 M sulfuric acid by cyclic voltammetry with a carbon paste electrode. They concluded that the oxidation state of the metal ions in $FeTiO_3$ are Fe^{II} and Ti^{IV}, and that small amounts of Fe^{III} and excess Ti^{IV} can occur in natural ilmenite samples.

White et al (1994) performed an electrochemical study of an ilmenite sample high in Fe^{III} in 0.1 M NaCl solution in the pH range from 1 to 7, and concluded that anoxic weathering of ilmenite proceeds by release of Fe^{II} to solution coupled with the formation of oxidized surface products. For pure ilmenite, Fe^{II} release does not involve a redox reaction. However, reductive dissolution can occur if ilmenite forms partial solid solutions with hematite. The anodic oxidation of ilmenite results in formation of passivating surface oxidation products (most likely pseudorutile). The reactions involved could be expressed by the following equations

$$3Fe^{2+}TiO_{3\ (ilmenite)} + 2H^+ + \tfrac{1}{2}\,O_2 = Fe^{3+}{}_2Ti_3O_{9\ (pseudorutile)} + Fe^{2+} + H_2O \qquad (1)$$

and

$$Fe^{2+}TiO_3 + 2H^+ = TiO_{2\ (rutile)} + Fe^{2+} + H_2O \qquad (2)$$

The present study is part of a more extensive investigation into the kinetics of the dissolution of ilmenite in sulfuric acid solutions and focuses on the role of potential in controlling the kinetics.

2. Experimental

2.1. Materials

Two ilmenite samples were used in this study. A massive ilmenite sample, obtained from a geological specimen collection at Murdoch University, was analysed using XRD and SEM/EDS techniques at the BHP Billiton Technology Centre. The analytical and mineralogical results show that the sample was a coarse granular ilmenite interspersed with oriented laths of titaniferous hematite. The ilmenite in the sample was analysed as 48% TiO_2, 50% Fe_2O_3 and 2.5% MgO, while the titaniferous-hematite analysed as 17% TiO_2 and 82% Fe_2O_3. Most of the experiments were conducted with a powdered sample of ilmenite sand from a local producer. The sample was also mineralogically and chemically analysed at the former BHP Billiton Technology Centre in Newcastle, NSW and the results are given in Table 1. Its particle size is between 53-63 μm, with a specific gravity of 4.3-4.6. Its estimated stoichiometry is $0.16Fe_2O_3 \cdot 0.65FeO \cdot TiO_2$ based on chemical analysis. It is worth noting that about 1/3 of total iron exists in the ferric state, though the hematite is only a minor component in the sample according to the results of the mineralogical analysis shown in Table 1.

Table 1 here

All chemicals used in this study were of analytical grade, except ferric sulfate which was of laboratory grade. De-ionized water from a Millipore Milli-Q system was used.

2.2. Preparation of ilmenite working electrodes

Electrodes for electrochemical studies were fabricated at Murdoch University using the massive ilmenite sample which was cut using a diamond saw into pieces 5 mm square and 8 mm thick. These samples were attached to stainless steel rods with conducting silver epoxy, and

subsequently coated with an insulating Araldite epoxy resin. The electrode surfaces were polished with P2400 grade SiC waterproof paper and rinsed with Milli-Q water before each electrochemical measurement.

For the powdered ilmenite, a carbon paste electrode was prepared by mixing fine pure graphite, spectroscopic grade liquid paraffin and ilmenite powder in a ratio of 3:3:12 (by mass) into a homogeneous paste and tightly filling a 2.7 mm deep, 7 mm diameter cavity of a special holder electrode made of Araldite epoxy resin. The surface was smoothed and excess material removed using a spatula (Nicol and Miki, 2005). The area of the ilmenite in the carbon paste used for calculation of current density was roughly estimated to be about 0.14 cm^2 and its estimation is given in the Appendix.

2.3. Apparatus and procedure

Electrochemical studies were conducted using the following experimental techniques:

1) Open circuit potential measurements;

2) Linear potential sweep cyclic voltammetry;

3) Potentiostatic current-time transients.

Electrochemical instrumentation and experimental procedures were similar to those described previously (Zhang and Nicol, 2003). Unless otherwise stated, all electrochemical experiments were carried out in 20 mL oxygen free solutions containing 450 g L^{-1} sulfuric acid with or without addition of ferrous sulfate and/or ferric sulfate in the temperature range of 60-95 ^{o}C using ilmenite electrodes rotated at 200 rpm. The potential scan rate was set 5 mV s^{-1}. All the potentials were measured against a silver/silver chloride (3 M KCl solution) reference electrode (0.197 V against the standard hydrogen electrode (SHE)) but are reported here with respect to SHE. A platinum rotating disk electrode of 2 mm diameter was also utilised.

For potentiostatic experiments, constant potentials were applied to the ilmenite electrode in oxygen free concentrated sulfuric acid for several hours. The current passed through the cell was recorded and the electric charge was obtained by integration of the current-time transient. The current-time transients obtained during these experiments (not shown in this study) revealed that the current decayed with time initially and then maintained a relatively steady value throughout the experiment at each of potentials. The average charge passed through the electrode was calculated by dividing the integrated charge by the ilmenite surface area and the time. After each experiment, the solution was analysed for titanium and iron, and the average dissolution rates of iron and titanium during the period of the experiment were calculated in a similar fashion.

2.4. Chemical analyses

The titanium content in solution was analysed by spectrophotometry. Solutions were diluted, re-acidified and the peroxy compound formed by addition of hydrogen peroxide. The absorbance of the resulting orange complex was measured at 400 nm with an Agilent 8453 Spectrophotometer. Beer's law was obeyed for titanium concentrations up to 50 ppm and an absorbance of 0.8. Total iron in solution was measured using atomic absorption spectrometry.

In the following sections all reduction potentials and the free energy change of reactions were calculated using HSC software (Roine, 2002).

3. Results and discussion

In order to understand the reductive dissolution of ilmenite in strong sulfuric acid, the electrochemistry of both a massive impure ilmenite sample and a particulate pure concentrate was studied.

3.1. Massive ilmenite electrode

3.1.1. Open circuit potentials

Fig. 2 shows the open-circuit potentials of the massive ilmenite electrode and a platinum electrode measured in 450 g L^{-1} sulfuric acid solutions with and without Fe^{2+} and Fe^{3+} ions at 60°C. The potential in the equimolar Fe^{2+}/Fe^{3+} solution is as expected for this couple (E^o=0.77 V, at 25 ^{o}C in non-complexing media) as evidenced by an identical potential of a platinum electrode under these conditions. The potential of the ilmenite electrode in sulfuric acid solution alone is lower than that in the equimolar Fe^{2+}/Fe^{3+} solution and gradually increases with time. This could be interpreted in term of more rapid or selective dissolution of Fe^{III} than Fe^{II} from the mineral. The potential of the ilmenite electrode in acid solution containing 20 g L^{-1} Fe^{2+} is also higher than that of the platinum electrode, again suggesting the more rapid dissolution of Fe^{III} from the mineral. The measurements of the open circuit potentials suggest that the potential of the ilmenite is likely determined by that of the Fe^{3+}/Fe^{2+} couple at the mineral surface. This could therefore be a relatively rapid means of determining the Fe^{III}/Fe^{II} ratio in the mineral.

Fig. 2 here

3.1.2. Linear sweep voltammetry

A typical linear sweep voltammogram in a negative direction from the open circuit potential is given in Fig. 3. Cathodic currents can be observed at potentials below the rest potential and the rate of the cathodic reaction(s) increases significantly below about -0.2 V. The first small cathodic peak at about 0.65 V is obviously due to a transient process, probably involving the reduction of Fe^{III} to Fe^{II} either in solution or in the solid phase (see below)

$$Fe^{3+} + e = Fe^{2+} \qquad\qquad E^o = 0.69 \text{ V (1 M } H_2SO_4 \text{ at } 25^oC) \qquad (3)$$

The second cathodic peak at about 0.1 V is possibly associated with the reduction of the mineral to Ti^{III} in a reaction such as

$$2FeTiO_3 + 6H^+ + 2e = Ti_2O_3 + 3H_2O + 2Fe^{2+} \qquad E^o = \text{-0.10 V at } 60^oC \qquad (4)$$
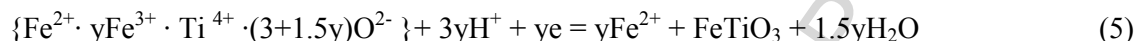
Fig. 3 here

3.1.3. Coulometric/dissolution studies

The ilmenite electrode was potentiostatted at various potentials negative to the rest potential for periods of up to several hours and the current measured as a function of time. The solution was subsequently analysed for iron and titanium. The results are shown in Fig. 4 as plots of the average dissolution rate as a function of potential. Also shown is the average charge passed (in faraday cm^{-2} s^{-1}).

Fig. 4 here

It is apparent that under these conditions of acidity, temperature and time, the dissolution rates of iron are about 3 to 5 times those of titanium at least for the first few hours. It is interesting to note that the rate of iron dissolution is almost identical to that calculated from the charge passed for a process involving reduction with one electron per iron, such as

$$\{Fe^{2+} \cdot yFe^{3+} \cdot Ti^{4+} \cdot (3+1.5y)O^{2-}\} + 3yH^+ + ye = yFe^{2+} + FeTiO_3 + 1.5yH_2O \tag{5}$$

or

$$Fe_2O_3 + 6H^+ + 2e = 2Fe^{2+} + 3H_2O \qquad\qquad E^o = 0.75 \text{ V at } 60^oC \tag{6}$$

Fig. 5 here

Fig. 5 shows the surface of the ilmenite electrode after 13000 seconds at 0.1 V in a solution of 450 g L^{-1} H_2SO_4 at 60^oC. It suggests that hematite is more reactive in this potential region as could be expected from the thermodynamic data shown in Fig. 1. These experimental results suggest that the main reactions involved during the reductive dissolution of this ilmenite sample in the potential region from 0.5 V to 0 V are summarized in Eqs. (5) and (6) together with the non-oxidative dissolution of stoichiometric ilmenite.

$$FeTiO_3 + 4H^+ = Fe^{2+} + TiO^{2+} + 2H_2O \qquad\qquad \Delta G^o = 32.44 \text{ kJ mol}^{-1} \text{ at } 60^oC \tag{7}$$

At lower potentials, reductive dissolution of the ilmenite (Eq. (8)) may occur, as evidenced by the higher rate of dissolution and the ratio of the charge passed to the iron dissolved at a potential of -0.15 V as shown in Fig. 4.

$$FeTiO_3 + 6H^+ + e = Fe^{2+} + Ti^{3+} + 3H_2O \qquad\qquad E^o = -0.29V \text{ at } 60^oC \tag{8}$$
$$= 0.06V \text{ at } 60^oC, [Fe^{2+}]=[Ti^{3+}]=1mM$$

A more extensive study may reveal more details on the mechanism but this was not carried out with this sample which was not pure ilmenite.

The effect of temperature on the average dissolution rates (over a period of 2 to 4 hours depending on temperature) of iron and titanium in 450 g L^{-1} sulfuric acid at an applied potential of 0 V in the range of temperature from 60 to 95 ^oC is shown in Fig. 6 together with the average charge passed.

Fig. 6 here

As expected, the rates of dissolution of both iron and titanium increase with increasing temperature. The higher dissolution rate of iron than that estimated from the charge passed at temperatures above 70 ^oC is possibly due to non-reductive dissolution of hematite and/or ilmenite at the higher temperatures. An apparent activation energy of 44 kJ mol^{-1} can be calculated based on the rates of titanium dissolution. Given that this value is probably a combination of values for both reductive and non-reductive dissolution, it is not appropriate to comment on its magnitude.

3.2. Ilmenite powder – carbon paste electrode

3.2.1. Linear sweep voltammetry

The linear sweep voltammograms shown in Fig. 7 indicate very little current on the carbon paste electrode in the potential range of –0.4 to 1.2 V in the absence of ilmenite. Attachment of powdered ilmenite sand to the surface of the paste resulted in large currents in this potential range. Fig. 8 shows the result of successive sweeps under the similar conditions as Fig. 7. The voltammograms in Figs. 7 and 8 are clearly different from that in Fig. 3 and presumably reveal the voltametric characteristics of the ilmenite mineral. These results are similar to those previously published (Andriamanana et al., 1984).
It was found that cyclic voltammograms with and without rotation of the electrode were similar, and that the current with rotation (200 rpm) of the electrode were slightly lower than those with a stationary electrode in sulfuric acid solutions (not shown in this paper), suggesting the involvement of soluble species in the reactions.

Fig. 7 here

Fig. 8 here

During the negative scan there are two cathodic peaks at about 0.6 V and 0 V, while on the reverse positive sweep two anodic peaks are observed at about 0.2 V and 0.77 V. The peaks at about 0.6 V and 0.77 V are characteristic of the redox reaction of the Fe^{3+}/Fe^{2+} couple . This could involve reduction of hematite (Eq. (6)) and/or the Fe^{III} component in the mineral (Eq. (5)) as the sand sample does contain small amounts of hematite. The cathodic peak at about 0 V could, as suggested above (Eq. (4)), be associated with the reduction of ilmenite. The anodic peak at 0.2 V could be due to the oxidation of Ti^{III} to Ti^{IV} species such as

$$TiO^{2+} + 2H^+ + e = Ti^{3+} + H_2O \qquad\qquad E^o = 0.046 \text{ V at } 60^oC \qquad\qquad (9)$$

$$2TiO^{2+} + H_2O + 2e = Ti_2O_3 + 2H^+ \qquad\qquad E^o = 0.24 \text{ V at } 60^oC \qquad\qquad (10)$$

Reaction (10) is more likely given that, at a rotating disk, soluble Ti^{3+} ions will not be available for oxidation during the subsequent positive going scan.

3.2.2. Coulometric/dissolution studies

Constant potentials negative to the rest potential were applied to the ilmenite powder-carbon paste electrode at 60^oC for 7 to 14 hours (depending on applied potential) in 450 g L^{-1} sulfuric acid and the cathodic currents recorded. On completion of the run, dissolved iron and titanium in the resulting solutions were analysed to calculate the average dissolution rate of the ilmenite powder. The results of these experiments are given in Fig. 9, which shows that the rate of dissolution and reduction of the ilmenite at potentials above 0.3 V is low while it is much higher at 0 V. This result is consistent with the voltametric studies and with the Eh-pH diagram shown in Fig. 1. The rate of dissolution of iron is almost equal to the charge passed through the electrode at 0.3 V and 0.5 V. The slightly higher dissolution rates of titanium than those of iron are probably due to the difficulty of analysis of the trace amounts (4 to 7 mg L^{-1}) of titanium at the higher potentials by the peroxide/spectrophotometric method. The results at 0 V show that the ratio of the rate of iron dissolution to that of titanium is about 1.5, and that the average

charge (measured in faradays) involved is approximately equal to the sum of the molar dissolution rates of iron and titanium.

The effect of temperature on the rates of dissolution of the ilmenite powder also was investigated by applying a constant potential of 0 V to the carbon paste-ilmenite electrode in sulfuric acid solutions at various temperatures for several hours. The results are shown in Fig. 10 and Table 2.
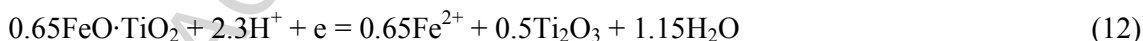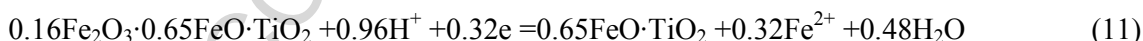
Fig. 9 here

Fig. 10 here

Table 2 here

It is apparent that the dissolution rate of the ilmenite powder at 0 V increases with increasing temperature and that the dissolution rate of iron is about 1.5 times that of titanium at all temperatures. The sum of rates of dissolution of iron and titanium at each temperature was calculated to be approximately equal to the average number of faradays passed through the electrode. In addition, the ratio of the electric charge to the rate of iron dissolution is about 1.5 for all temperatures investigated while the corresponding ratio is above 2 for titanium and it appears to decrease with increasing temperature. An activation energy of about 50 kJ mol^{-1} was calculated which is similar to that obtained using the massive ilmenite electrode, but much lower than published values of about 90 kJ mol^{-1} for freely dissolving of ilmenite under similar conditions (Han et al., 1987; McConnel, 1978). The above experimental observation that iron dissolves more quickly than titanium at 0 V apparently agrees with that in published studies on Fe-Ti bearing minerals in natural weathering environments (White et al., 1994).

Given the composition of ilmenite sand sample as $0.16Fe_2O_3 \cdot 0.65FeO \cdot TiO_2$, one could possibly expect the following reactions to occur at potentials below that for the reduction of ilmenite to Ti^{III}.

$$0.16Fe_2O_3 \cdot 0.65FeO \cdot TiO_2 + 0.96H^+ + 0.32e = 0.65FeO \cdot TiO_2 + 0.32Fe^{2+} + 0.48H_2O \qquad (11)$$

$$0.65FeO \cdot TiO_2 + 2.3H^+ + e = 0.65Fe^{2+} + 0.5Ti_2O_3 + 1.15H_2O \qquad (12)$$

$$0.5Ti_2O_3 + 3H^+ = Ti^{3+} + 1.5H_2O \qquad (13)$$

Reactions (11) + (12) + (13) would predict a ratio of 1.36 for the charge to the iron dissolved and a ratio of 1.32 for the charge to the titanium dissolved, i.e. a ratio of 0.67 for the charge to total iron plus titanium dissolved. The higher observed ratio could be due to a loss in current efficiency as a result of evolution of hydrogen at 0 V given the elevated temperature and concentrated acid used. It is also possible that, as suggested in Section 3.2.1 above, that Ti_2O_3 is produced (reaction (12)) which only partially dissolves in the solution. This could account for both the low current efficiency and the low ratio of titanium dissolved relative to iron. The greater rate of dissolution of iron compared to titanium could also possibly be due to a degree of selective dissolution of iron by way of reactions such as

$$FeTiO_3 + 2H^+ = Fe^{2+} + TiO_2 + H_2O \qquad (14)$$

$$2FeTiO_3 + 6H^+ + 2e = Ti_2O_3 + 2Fe^{2+} + 3H_2O \qquad (15)$$

The results of these experiments suggest that the rate of non-reductive dissolution by a reaction such as

$$0.16Fe_2O_3 \cdot 0.65FeO \cdot TiO_2 + 3.3H^+ = 0.16Fe_2O_3 + TiO^{2+} + 0.65Fe^{2+} + 1.65H_2O \qquad (16)$$
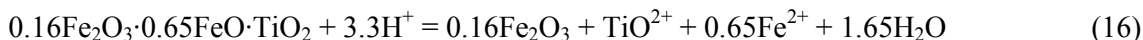
can not be significant under these conditions. It is worth noting that the dissolution rate of titanium in the ilmenite powder-carbon paste electrode at 0 V is similar to the rate of dissolution of titanium from the massive ilmenite electrode at the same potential.

4. Conclusions

The dissolution rate of ilmenite ($FeTiO_3$) is low at potentials above about 0.3 V where the free dissolution of ilmenite and the reductive dissolution of hematite (if present in the ilmenite sample) are the main reactions. At more negative potentials the dissolution of ilmenite increases substantially due to reduction of the titanium in ilmenite to the trivalent state. These observations are consistent with those predicted from the thermodynamic data. The hematite phase in the mineral has a higher dissolution rate under reductive conditions than the ilmenite. In the temperature range of 65-95°C a low activation energy of about 50 kJ mol^{-1} was obtained at low potentials in 450 g L^{-1} H_2SO_4 and this together with the high ratio of the charge passed to metals dissolved suggests that the rate of the non-reductive dissolution reaction is not significant under these conditions.

Acknowledgements

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Appendix - Estimation of area of exposed ilmenite particles

The CPE holder electrode has a cylindric cavity of 2.7 mm depth (H) and 7 mm diameter. The cavity was filled with 0.255 g of carbon paste-ilmenite powder mixture (ilmenite : graphite : paraffin oil = 12:3:3 by weight).

Mass ilmenite W_i = 0.255 *12 / 18 =0.17 g

The specific gravity of ilmenite is p = 4.3-4.6 g cm^{-3}. Assume 4.5 g cm^{-3}.

Volume of ilmenite in paste V_i = W_i/p = 0.0378 cm^3.

The mean particle size (d) of ilmenite is 58 μm. Assuming the particles are cubes of side 58 μm, the number of ilmenite particles is

N_i =V_i / d^3 = W_i / (p*d^3)

Assuming that ilmenite in the paste is evenly dispersed in the cavity, the number of ilmenite particles in the surface layer of thickness d is

N_p = N_i / (H/d) = N_i d / H

Assuming that the ilmenite particles are oriented parallel to the surface of the electrode, the maximum exposed surface area (S) of the ilmenite particles is

S = N_p d^2 = N_i d^3 / H = Wi / (p*H) = 0.14 cm^2.

Table 1
Chemical and mineralogical analyses of ilmenite sand

Species	Wt%	Mineral	Wt%
Total Ti	30.3	Ilmenite	95.2
Total Fe	33.9	leucoxene	3.10
Fe_2O_3	15.9	Rutile	0.13
FeO	29.3	Hematite	0.32
SiO_2	0.38	Mg_Chromite	0.42
Al_2O_3	0.42	Ti_Magnetite	0.47
Cr_2O_3	0.27	Titanite	0.07
MgO	0.92	Zircon	0.06
V_2O_5	0.19	Ferro_clay	0.17
MnO	1.31	Kaolinite	0.03
ZrO_2	0.13	Quartz	0.04

Table 2
Effect of temperature on the mean rates of dissolution (10^{-10} mol cm^{-2} s^{-1}) of Ti and Fe and electrical charge (10^{-10} faraday cm^{-2} s^{-1}) in 450 g L^{-1} H_2SO_4 at 0 V.

Temp. ^oC	Rate Fe	Rate Ti	Charge	Fe/Ti	Charge/Fe	Charge/Ti	Charge/(Fe+Ti)
60	29	19	50	1.5	1.7	2.6	1.04
75	45	28	68	1.6	1.5	2.4	0.93
85	75	63	142	1.2	1.9	2.3	1.03
95	180	120	256	1.5	1.4	2.1	0.85
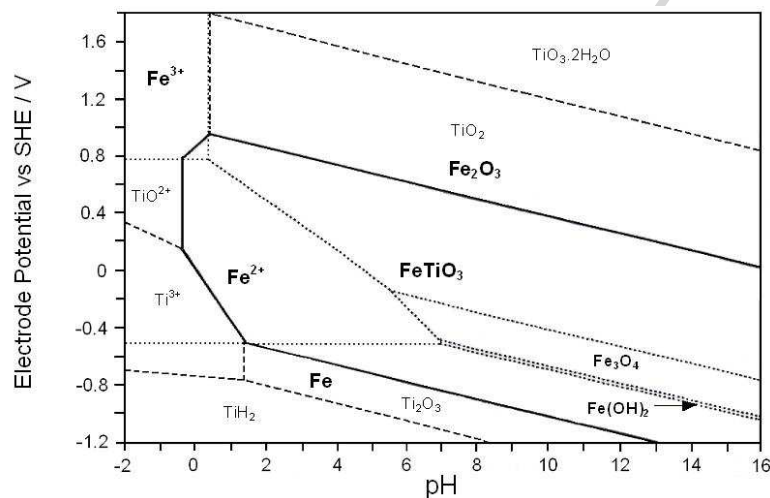
Fig. 1   Eh-pH diagram of the Ti-Fe-H_2O system at 25 ^{o}C, (excluding Ti^{2+} ions) considering TiO_2 (c, hydrated), Ti_2O_3 (c, hydrated) and Fe_2O_3 as the solid titanium oxide and Fe^{III} phases, and for 0.1 and 0.01 dissolved iron and titanium activities, respectively. (Solid line refers to the stability area of $FeTiO_3$.) (after Kelsall and Robbins, 1990)
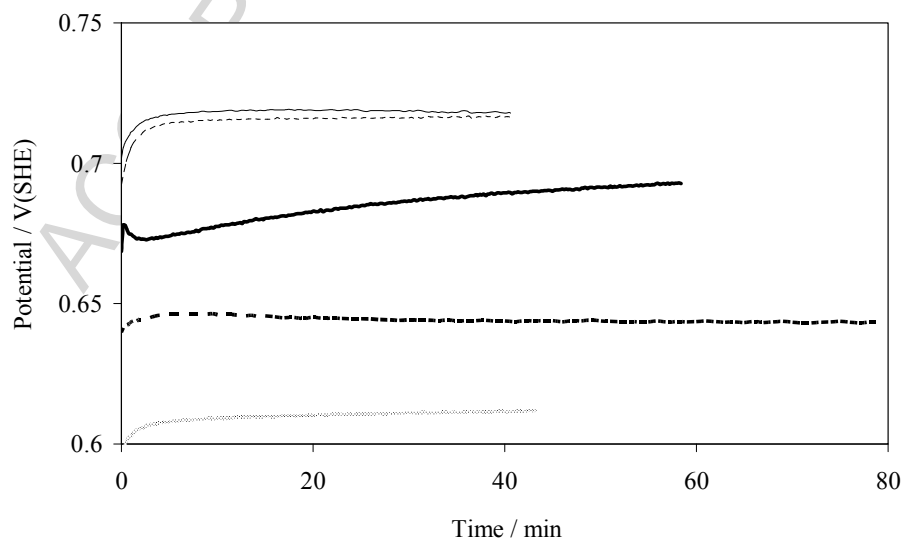

Fig. 2   Open circuit potentials of rotating ilmenite and platinum electrodes in 450 g L^{-1} H_2SO_4 solutions containing various concentrations of iron at 60 ^{o}C. (——) ilmenite, (——) ilmenite (10 g L^{-1} Fe^{2+} + 10 g L^{-1} Fe^{3+}), (-----) platinum (10 g L^{-1} Fe^{2+} + 10 g L^{-1} Fe^{3+}), (▬▬▬) ilmenite (20 g L^{-1} Fe^{2+}), (·········) platinum (20 g L^{-1} Fe^{2+}).
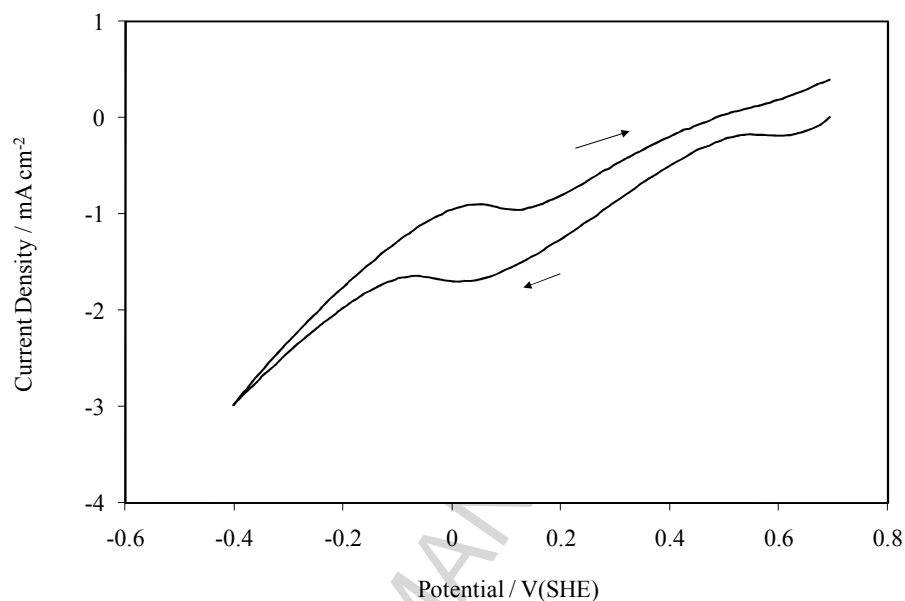
Fig. 3 Linear sweep voltammogram (5 mV s^{-1}) of an ilmenite electrode in 450 g L^{-1} H$_2$SO$_4$ solution at 60°C. Sweep started in negative direction from the open circuit potential (0.72 V) and reversed at -0.4 V.
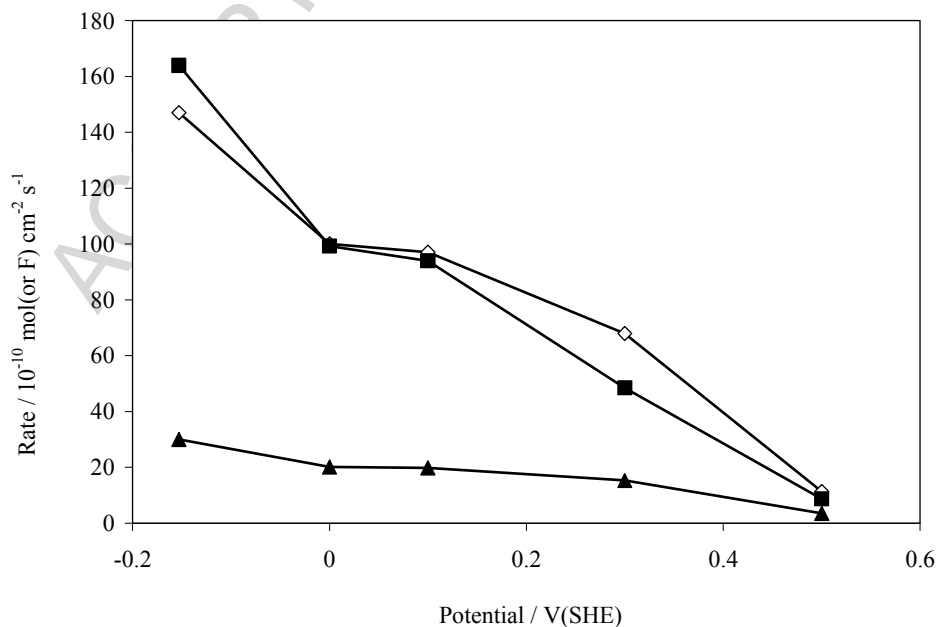
Fig. 4 Potentiostatic dissolution of an ilmenite electrode in 450 g L^{-1} H$_2$SO$_4$ solution at various potentials at 60°C.(▲) Ti, (◊) Fe, (■) Charge.
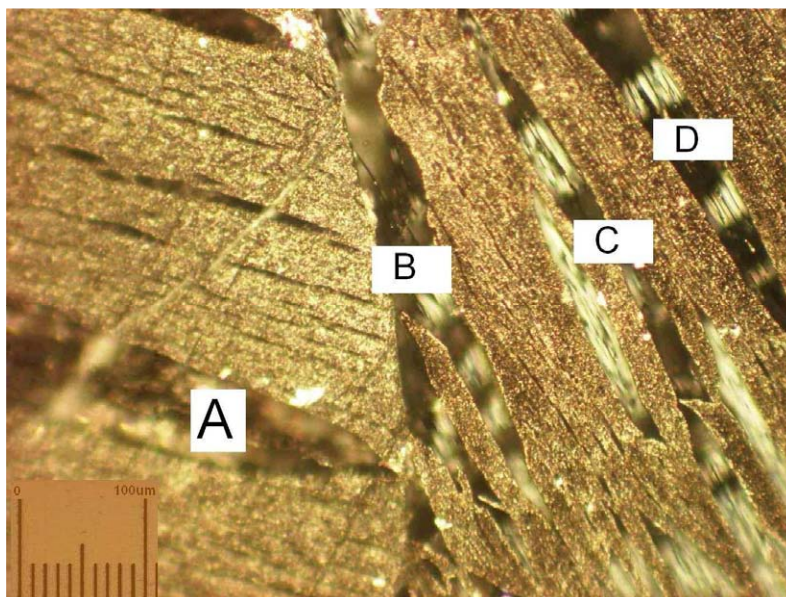
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Fig. 5   Photomicrograph of the surface of a massive ilmenite electrode after application of a potential of 0.1 V for 13000 seconds in a 450 g L^{-1} H$_2$SO$_4$ solution at 60°C. Areas of A, B, C and D indicate corrosion of hematitic lamellae.
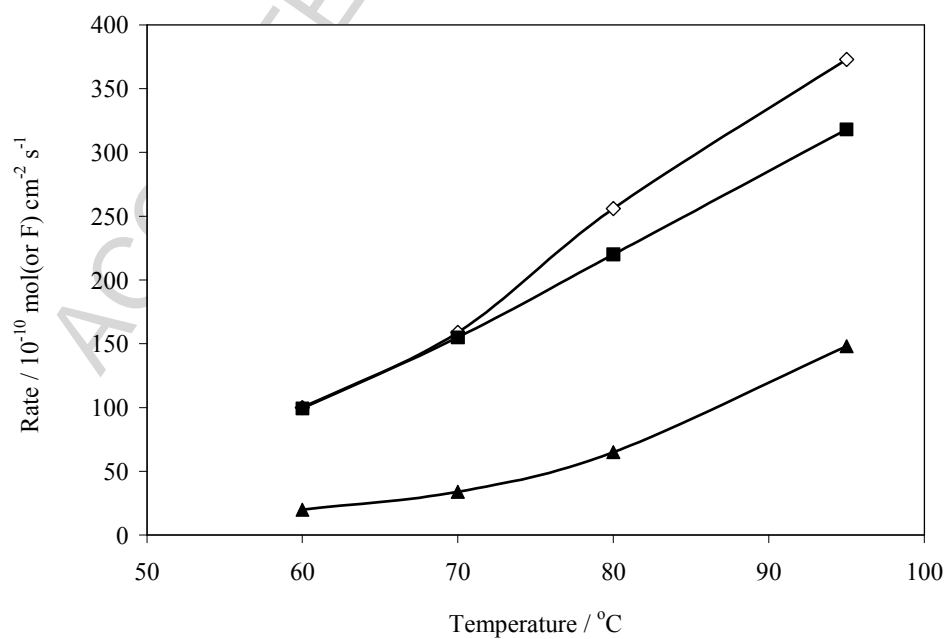
Fig. 6   Effect of temperature on the rate of dissolution of a rotating ilmenite electrode at an applied potential of 0 V in 450 g L^{-1} H$_2$SO$_4$ solutions. (▲) Ti, (◊) Fe, (■) Charge.
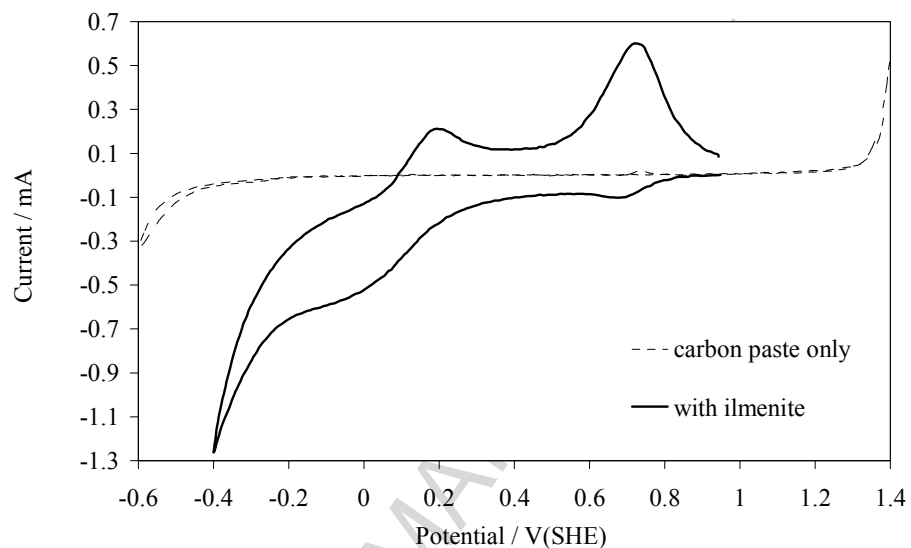
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Fig. 7   Linear sweep voltammograms of a carbon paste electrode without and with ilmenite powder pressed onto the surface in 450 g L^{-1} H$_2$SO$_4$ at 60°C. Sweeps commence in a negative direction from the rest potentials.
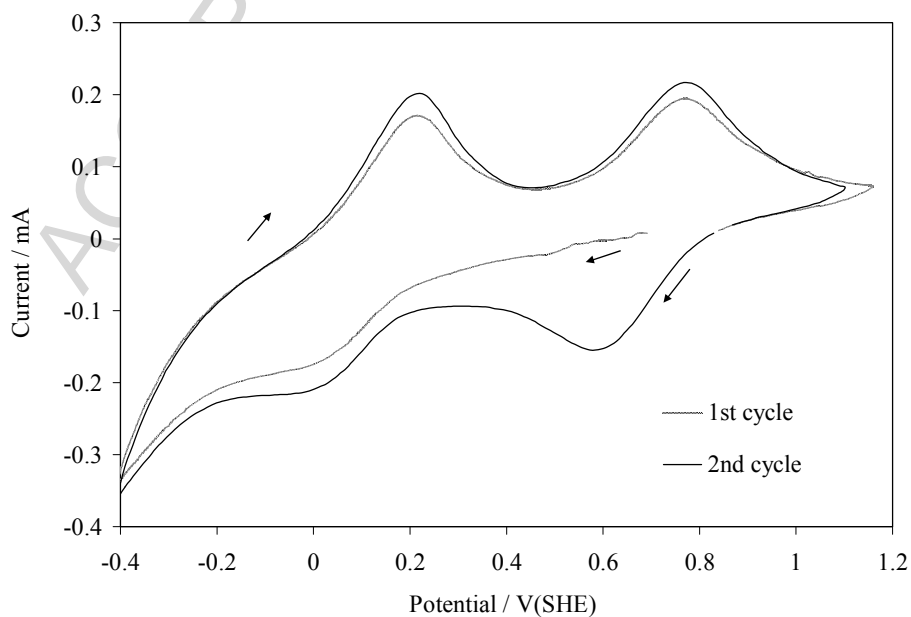

Fig. 8   Cyclic voltammogram of a rotated (200 rpm) electrode consisting of a mixture of carbon paste and ilmenite powder in 450 g L^{-1} H$_2$SO$_4$ at 60°C. Sweep initiated in a negative direction from the rest potential.
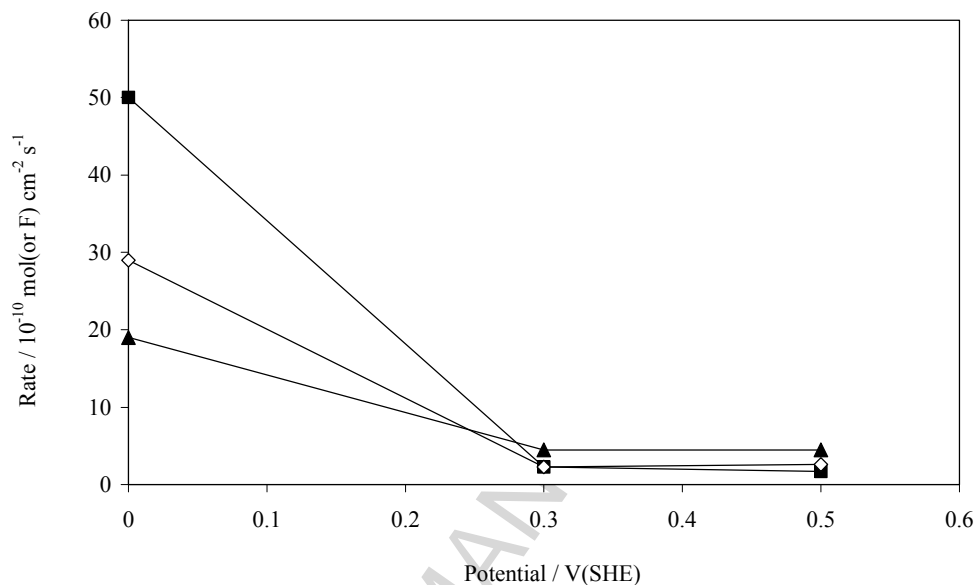
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Fig. 9   Dissolution of ilmenite powder in a carbon paste electrode in 450 g L^{-1} H$_2$SO$_4$ at 60 ^{o}C and various potentials. (▲) Ti, (◊) Fe, (■) Charge
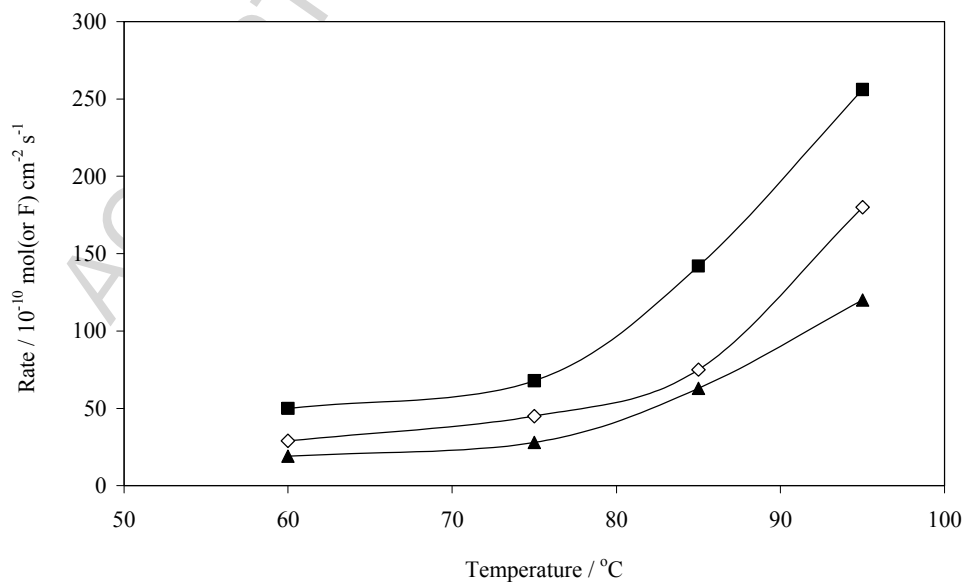

Fig. 10   Effect of temperature on the dissolution of ilmenite powder in a carbon paste electrode in 450 g L^{-1} H$_2$SO$_4$ at 0 V. (▲) Ti, (◊) Fe, (■) Charge

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