

Electrochemical Passivation of Iron in NO_3^- , SO_4^{2-} , and ClO_4^- SolutionsVladislava M. Jovanovic[†] and Norman Hackerman*

Department of Chemistry, Rice University, 6100 Main Street, Houston, Texas 77005

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Electrochemical passivation of iron was studied in NO_3^- , SO_4^{2-} , and ClO_4^- solutions of different pH values. Passivation potential of iron in NO_3^- and ClO_4^- was similar for any pH examined, while in SO_4^{2-} it was more anodic. Passive current was lowest in NO_3^- ($10 \pm 2 \mu\text{A}/\text{cm}^2$), in SO_4^{2-} was in the range of 40–60 $\mu\text{A}/\text{cm}^2$ while in ClO_4^- passive current of 30–50 $\mu\text{A}/\text{cm}^2$ was reached only at 600–800 mV. After passivation, the properties of passivated iron are similar in NO_3^- and SO_4^{2-} but differ in ClO_4^- . In the latter, the passive region is shorter by 200–300 mV. The transpassive potential in ClO_4^- is 1.2 V vs SCE and independent of pH, but shifts anodically with decrease in ClO_4^- concentration. The transpassive potential in NO_3^- and SO_4^{2-} is higher, O_2 evolution starts, and the potential shifts cathodically with increase of pH. At the transpassive potential in ClO_4^- , a black substance forms which dissipates in acidic solutions and is stable in strong alkaline solutions. Microphotographs of anodically polarized iron in these solutions show no pits, only uniform corrosion over the whole electrode surface. We assume that the rapid increase of anodic current at transpassive potential in ClO_4^- is due to oxidation of iron and iron oxides from the passive film to hexavalent iron.

Introduction

Electrochemical passivation of iron has been intensively studied in various solutions and with pH values from acidic through neutral to alkaline. If iron is anodically polarized starting from the corrosion potential, anodic dissolution of metal increases following a Tafel $E-\log i$ function up to the passivation potential (E_p). At this point it is believed that some sort of protective film completely covers the metal surface, inhibiting it from further rapid metal oxidation. Continued anodic polarization leaves the iron passive throughout a potential range of as much as 1 V.

Various models have been suggested for the nature of this film. They range from an oxygen layer adsorbed on the surface to iron oxides like magnetite or a mixture of magnetite and hematite.^{1,2} The oxide film model is more widely accepted. This passive layer on iron can be of nanometer thickness and can pass electrons readily.

However, when

$$E_{\text{tp}} \approx 1.5 - 0.06\text{pH} \quad (\text{V vs SCE})$$

is reached, the current increases rapidly. This transpassive potential (E_{tp}) is that for oxygen evolution on the passive iron surface. It includes an overpotential of about 0.5 V. This easily distinguishes the film on iron from the insulating oxide which covers aluminum, titanium, and other metals. In the latter case, the potential must rise several volts before any current passes and then it is an ionic current.

To return to the case of iron, both the passivation and transpassive potential depend on pH and both shift cathodically with increase of pH. This is certainly true for anodic polarization of iron in NO_3^- and SO_4^{2-} solutions.

While there are many papers describing passivation of iron in nitrate and sulfate solutions,^{3–8} only a few are concerned with iron in perchlorate solutions.^{9–11} In the latter, the behavior of iron on anodic polarization is somewhat different. The passive region is shorter by 200–300 mV and passive currents are higher by several tens of $\mu\text{A}/\text{cm}^2$. Furthermore, the reaction at the end of the passive region is not oxygen evolution. The increase of current has been ascribed to pitting caused by perchlorate anions.^{12,13}

We studied the electrochemical passivation of iron by anodic polarization in solutions of nitrates, sulfates, and perchlorates and for the latter also found a rapid increase of current at about 1.2 V. However, we do not think that the reason is pitting since we found no pits in either acid or alkaline solution. We will provide a different reason for the rapid increase of anodic current at 1.2 V in the presence of ClO_4^- .

Experimental Section

Iron rod (Johnson Matthew, Puratronic 99.99%), mechanically buffed with emery paper of decreasing grain size, was used as the working electrode throughout all experiments. The rod was sealed by pressure and epoxy in a Teflon holder so that only the working surface was exposed to the solution. The electrode was mounted vertically in the cell. The counter electrode was a Pt wire, and the reference electrode was a double junction saturated calomel electrode (SCE). Therefore, all potentials herein are versus SCE. The experiments were performed in a standard three compartment three-electrode cell at room temperature.

The solutions used were HClO_4 , HNO_3 , and H_2SO_4 or 1 M NaClO_4 , NaNO_3 , and Na_2SO_4 in a pH range between 0 and 3.00, as well as 1 M NaClO_4 solutions with pH values of 5.86 and 9.00–14.00. Also, NaOH solutions with pH between 11.00 and 14.00 were used. Thus, the only cations present were H^+ and Na^+ . The solutions were prepared using triply distilled water and analytical grade reagent and were maintained oxygen-free by bubbling argon gas through the solution.

[†] Permanent address: ICTM Department of Electrochemistry, University of Belgrade, Njegoseva 12, P.O. Box 815, 11001 Belgrade, Yugoslavia. E-mail: vlad@elab.tmf.bg.ac.yu. Present address: Chemistry Department, Rice University, Houston, TX 77005. Fax: (713) 285 5155. E-mail: vladjov@ruf.rice.edu.

After immersion of the electrode in the solution, the corrosion potential (E_{cor}) was followed for 60 min by which time it reached a steady state. Then the electrode was anodically polarized from 0.25 V cathodic to the corrosion potential up to 2.0 V, at a sweep rate of 1 mV/s.

Potential/time decay for passivated iron, as a criterion for the character of the passive film, was followed by switching off the potentiostat immediately after polarization of iron at a chosen potential. In NO_3^- solutions it was possible to do so immediately after anodic polarization to 2.0 V, while in SO_4^{2-} and ClO_4^- solutions potential/time decay could be followed only after 1 and 2 h, respectively, of potentiostatic polarization at 1.0 V. This value was chosen as it is in the passive region for all solutions.

The concentration of Fe^{3+} was followed by chronopotentiometry using a Pt wire as the working electrode and currents of a few tens of $\mu\text{A}/\text{cm}^2$.

Results

Anodic polarization of iron was examined in nitric acid, sulfuric acid, and perchloric acid of pH values between 0 and 3. These pH values were achieved by tenfold dilution of the starting solution of pH = 0 and therefore these solutions were without adjusted ionic strength and with decreasing concentration of the corresponding anion. Solutions of the same pH values but with ionic strength adjusted to 1 were prepared with the sodium salt of the anion corresponding to the acid in question.

Before anodic polarization, the corrosion potential of iron in each solution was followed to its steady value. Solutions containing NO_3^- or ClO_4^- showed more anodic values at given pH than those containing SO_4^{2-} anions (Figure 1a). The E_{cor} in all solutions, other than those with NO_3^- , shifted 60–80 mV cathodic per unit pH increase (Figure 1b). Adjusting the ionic strength did not affect the E_{cor} .

With NO_3^- and ClO_4^- at any pH examined, E_p is similar (300 ± 30 mV) (Figure 2a). With SO_4^{2-} the passivation potential is more positive, i.e., for pH = 0 it is 400 ± 30 mV (Figure 2a). This is probably caused by the formation of slightly soluble basic FeSO_4 that precipitates or is incorporated in the passive film. In any of the solutions, the E_p shifts about 100 mV cathodically with unit increase of pH as is shown for HNO_3 in Figure 2b.

In the passive region, however, iron behavior is similar in NO_3^- and SO_4^{2-} solutions but differs in ClO_4^- solutions. In the former, passive currents are consistently in the range of $10 \pm 2 \mu\text{A}/\text{cm}^2$ in NO_3^- and $40\text{--}60 \mu\text{A}/\text{cm}^2$ in SO_4^{2-} from the passive to transpassive potential. Continued anodic polarization in NO_3^- and SO_4^{2-} at pH = 0 showed a large current increase at 1.5 V with intensive oxygen evolution (Figure 2a). This potential is also cathodically shifted by about 60 mV per pH unit. Figure 2b presents such behavior for NO_3^- but similar results are obtained in SO_4^{2-} .

Although E_p for iron in NO_3^- and ClO_4^- solutions is about the same, the properties of the passivated iron are different. With ClO_4^- , following the initial current decrease at E_p , the lowest current of $30\text{--}50 \mu\text{A}/\text{cm}^2$ is reached only at 600–800 mV (Figure 2a). At 1.2 V the current increases rapidly but without noticeable oxygen evolution (Figure 2a). Instead, a black substance forms on the electrode surface and a black-brown stream of very fine particles flows from the electrode, coloring the solution. These particles dissipate on moving through the acidic solution, but leave it colorless. The lower the pH of the perchlorate, the larger the quantity of the substance formed, the more intense the flow of the black-brown stream from the electrode, and the less noticeable is oxygen evolution. The

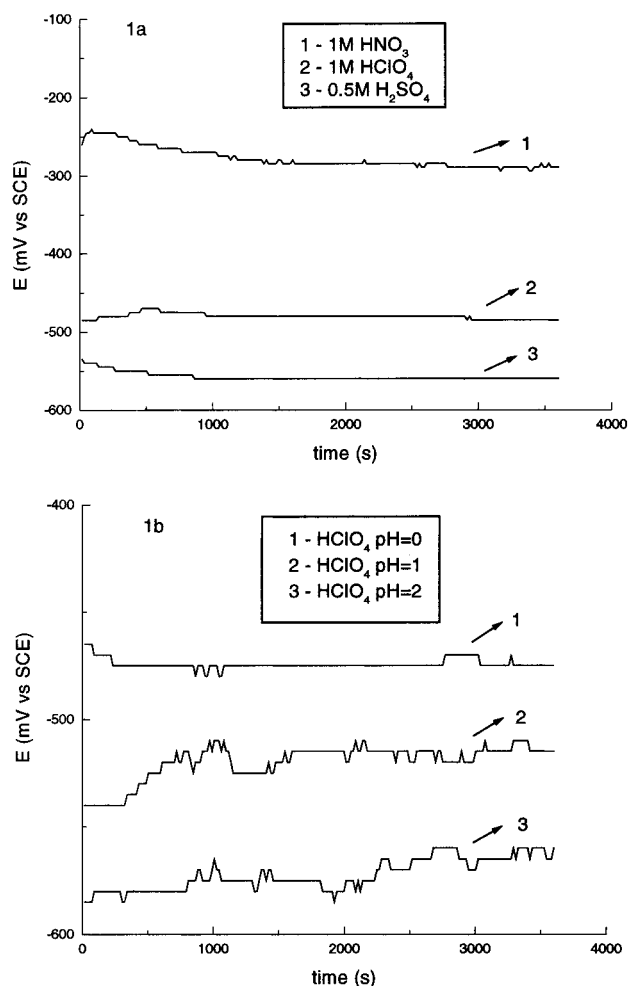


Figure 1. Corrosion potentials of Fe in (a) 1 M HNO_3 , 1 M HClO_4 , and 0.5 M H_2SO_4 solution and (b) HClO_4 solutions of pH = 0, pH = 1, and pH = 2.

thermodynamic potential for oxygen evolution in 1 M acid is 0.985 V vs SCE. However, at this potential, iron is covered with passive film in 1 M acid. There is an overpotential and oxygen evolution starts at 1.5 V vs SCE. Thus, at 1.2 V the potential for O_2 evolution on passive iron in 1 M ClO_4^- is not reached, but with the formation of the black material the electrode is no longer passive. So, oxygen evolves in parallel with the formation of the black substance. If more of the black substance forms the less noticeable is oxygen evolution.

The E_p in NO_3^- (Figure 2b) as well as in SO_4^{2-} solutions, as already noted, depends only on pH and shifts cathodically with increase in pH. In ClO_4^- solutions E_p is about 1.2 V and is not influenced by the pH from 0 to 14. However, E_p depends on the concentration of ClO_4^- and shifts anodically with its decrease.

So, in all of the solutions without adjusted ionic strength, there is an anodic shift of E_p as $[\text{ClO}_4^-]$ decreases (Figure 3a). Also, in contrast to the other acids, in HClO_4 even at pH = 2 it is difficult to passivate iron. On the other hand, in those solutions with adjusted ionic strength, with the same $[\text{ClO}_4^-]$ there is no shift of E_p as is shown in Figure 3b for the solutions of pH 0, 3, 5.86, 9, and 12. So, the same value of 1.2 V for E_p was recorded during anodic polarization of iron not only in acidic solutions of 1 M NaClO_4 but also in this solution with the measured pH of 5.86.

Anodic polarization of iron in 1 M NaClO_4 solutions with pH from 9 to 14 again gave the E_p of 1.2 V as can be seen in

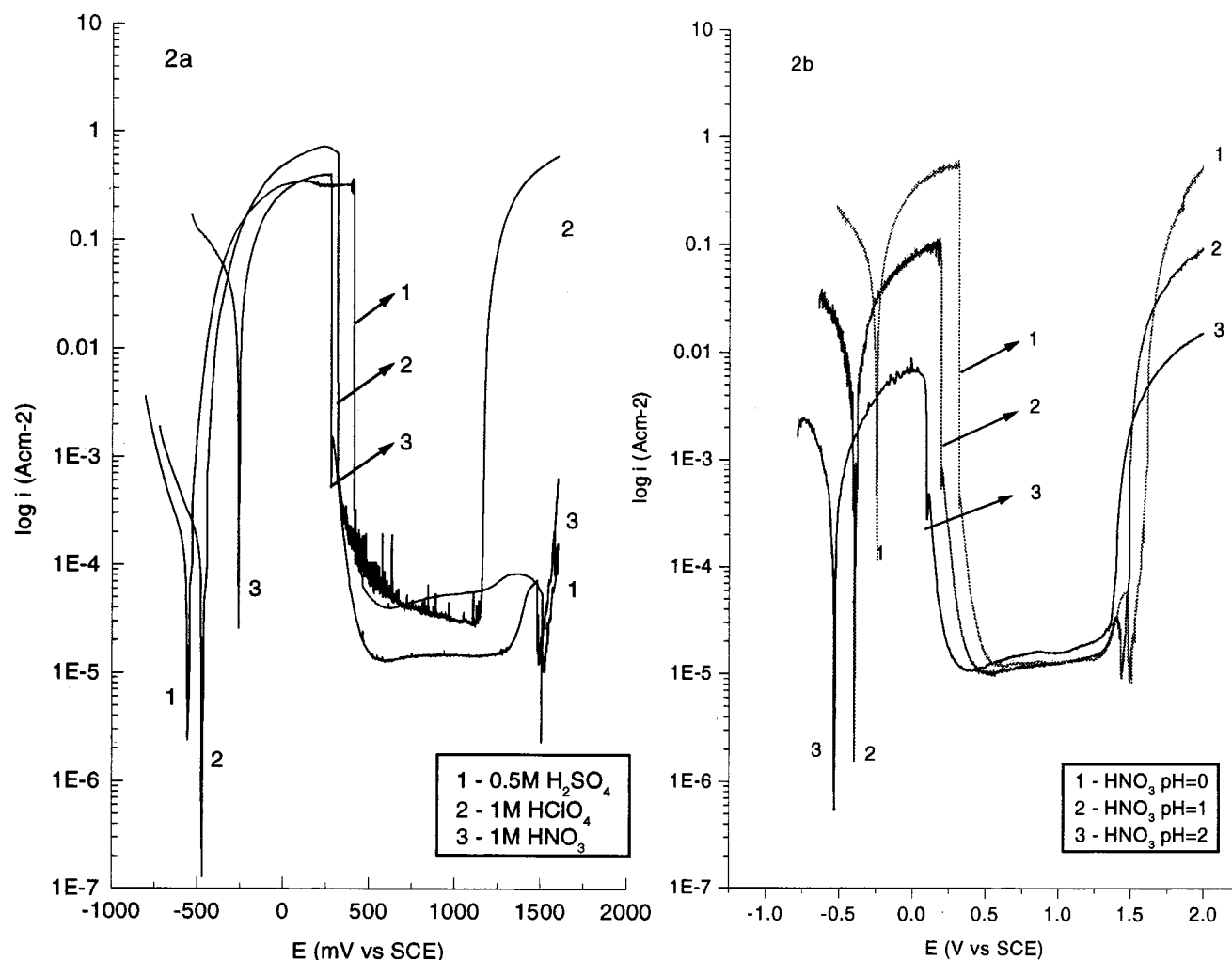


Figure 2. Anodic polarization curves of Fe in (a) 0.5 M H_2SO_4 , 1 M HClO_4 and 1 M HNO_3 solutions (sweep rate 1 mV/s) and (b) HNO_3 solutions (without adjusted ionic strength) of pH = 0, pH = 1, and pH = 2 (sweep rate 1 mV/s).

Figure 3b for pH of 9 and 12. This time, though, the black particles were bigger and did not dissolve but precipitated and with time turned to a black-brown gelatinous mass leaving the solution colorless. Oxygen evolution was much more intense in alkaline solutions than in acidic solutions. This is because in alkaline solutions the potential for oxygen evolution at iron passive surface is reached before 1.2 V, before the formation of the black substance. When iron was anodically polarized in 1 M NaClO_4 of pH = 12 (Figure 3b), oxygen evolution started at ~ 0.7 V, about the same potential as on platinum or iron in sodium hydroxide solution of the same pH. However, the black substance formed at 1.2 V as it did in all ClO_4^- solutions. If iron is polarized in sodium hydroxide (pH = 9–14) without ClO_4^- anions, only oxygen evolution occurred at approximately the same potentials as on platinum but without the formation of black-brown material on iron.

In order to be sure that this behavior is connected with perchlorate anion, the iron was anodically polarized in HNO_3 of pH = 0 containing 1 M NaClO_4 . Again, anodic current increased rapidly from that in the passive region at 1.2 V. Again, a black substance was formed and a black-brown stream flowed from the surface. At 0.1 or 0.01 M NaClO_4 in HNO_3 of pH = 0, neither of these phenomena occurred. Moreover, the polarization curve had the same shape as in HNO_3 alone at pH 0 (Figure 4). Anodic polarization curves for iron in sodium salts of other reduced oxychlorates in HNO_3 of pH = 0 also had the same shape as in the HNO_3 alone. Similar experiments repeated in

H_2SO_4 solutions containing ClO_4^- ions showed the same results as for HNO_3 solutions with ClO_4^- ions. It should be mentioned, however, that in these mixed solutions less of the black substance was formed.

Potential/time decay recorded immediately after anodic polarization of iron in nitrate solution shows that there is still passive film on the electrode and the time for decay increases with pH (Figure 5a). With ClO_4^- , the potential drops almost immediately to the corrosion value, showing no evidence of a passive film. In these solutions potential/time decay curves require at least 2 h of potentiostatic polarization of iron (Figure 5b). The time for decay is very short and decreases with increase in pH. The short time for decay together with the necessity for longer polarization (passivation) for following potential/time decay and higher passive currents indicate that iron passivated in ClO_4^- solutions has a less effective passive film. This is in accordance with polarization measurements (Figure 3a) which show that with increasing the pH of HClO_4 solution, passive currents are less stable and it is difficult to passivate iron.

Discussion

The results described show that passive film breakdown before reaching the oxygen evolution potential in strongly acid solution is related to the presence of ClO_4^- . The E_{tp} is independent of the pH of the solution because either the reaction that takes place does not involve hydroxide ions or the pH in

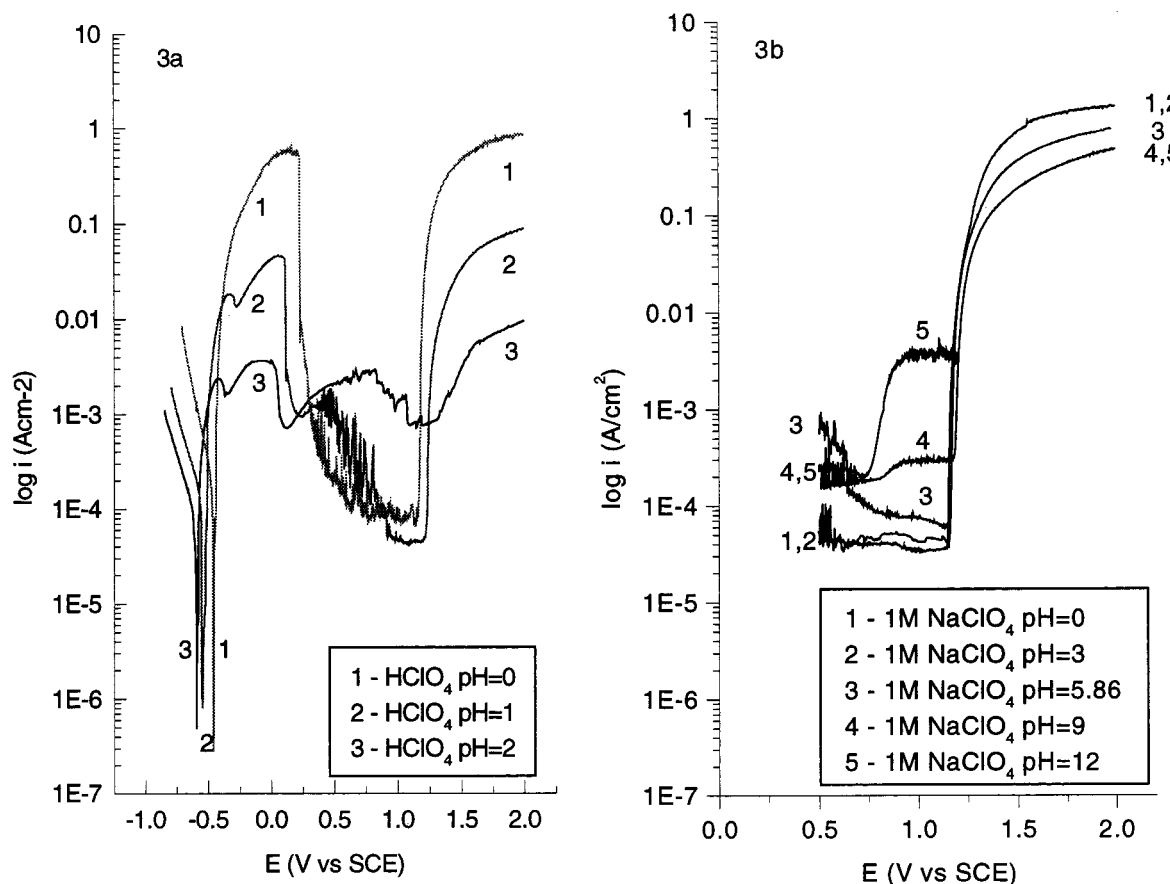
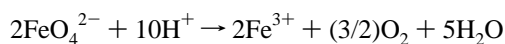


Figure 3. Anodic polarization curves of Fe in (a) HClO₄ solutions (without adjusted ionic strength) of pH = 0, pH = 1, and pH = 2 (sweep rate 1 mV/s) and (b) 1 M NaClO₄ solutions of pH = 0, pH = 3, pH = 5.86, pH = 9, and pH = 12 (sweep rate 1 mV/s).

the double layer in all cases examined is about the same. The latter is due to the congregation of negative ions and oriented dipoles adjacent to the anode.

The value of E_{tp} , and its independence of pH, as well as the anodic shift with decrease of ClO₄⁻ concentration are consistent with other work.^{12,13} However, their explanation, as already noted, is based on pitting caused by ClO₄⁻. Microphotographs of our electrodes either anodically polarized to 2.0 V or potentiostatically polarized at different potentials from 1.2 to 2.0 V vs SCE showed no pits, only uniform corrosion over the whole electrode surface. The solutions were checked for Cl⁻, which might be a product of ClO₄⁻ reduction, or present as impurity in the solution. Addition of 0.1 M silver nitrate did not produce a precipitate. Moreover, if the increase of current at 1.2 V was due to pitting, then during potentiostatic polarization at this potential a constant increase of current would be seen. In this work, during potentiostatic polarization of iron at any potential from 1.2 to 2.0 V, current changed up to some limiting values that remained essentially constant. Finally, the black substance that spreads over the whole electrode surface, and the black-brown stream flowing from the surface, even with potentiostatic polarization of the electrode, is not characteristic of pitting. Therefore, the rapid increase of current at transpassive potential is not the consequence of pitting but, according to us, of oxidation of iron and iron oxide from passive film to hexavalent iron, FeO₄²⁻.

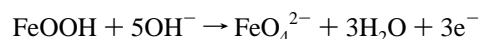
Ferrate ion is stable in strong alkaline solution but in neutral and acidic solutions decomposes according to the equation¹⁴



We followed the concentration of Fe³⁺ by chronopotentiometry

in acidic ClO₄⁻ solutions. The increase in cation concentration was recorded in colorless solutions, when the black substance dissolved completely, in comparison with the solutions colored by fine particles of the black material immediately after polarization. In alkaline solutions (maximum 1 M) the black precipitate with time turned into a black-brown gelatinous mass as ferric ions in the solutions of pH higher than 2 readily hydrolyze and form colloidal gels.

Beck et al.¹⁵ and Bouzak et al.¹⁶ discussed further oxidation of Fe(III) oxide layer on iron to Fe(VI) species parallel with O₂ evolution in the concentrated hydroxide solutions in the region of transpassive anodic oxidation.



Uhlig and O'Connor¹⁷ considered ferric acid or related higher valence iron compound to be responsible for passivity of iron in concentrated nitric acid. They demonstrated it by immersing an Fe electrode in NaOH solution, placed in one compartment of H-cell, and electrically short circuited with Pt electrode immersed in concentrated HNO₃ solution in another compartment of the cell. Purple reaction product streamed off the Fe electrode accompanied by oxygen evolution.

Perchloric acid, although one of the strongest acids, when diluted is not a very strong oxidizing agent.¹⁸ However, in combination with nitric or sulfuric acid, perchloric acid has been used for oxidation of organic materials.^{18,19} Reduction of perchlorates yields chloride ions.^{20,21} IR and XPS techniques show that ClO₄⁻ anions are not adsorbed on iron oxides.²² Therefore, in ClO₄⁻ solutions adsorption of water dipoles and/or hydroxide anions on the electrode surface is likely enabled. Also, according to Walrafen,²³ ClO₄⁻ ions are strong structure

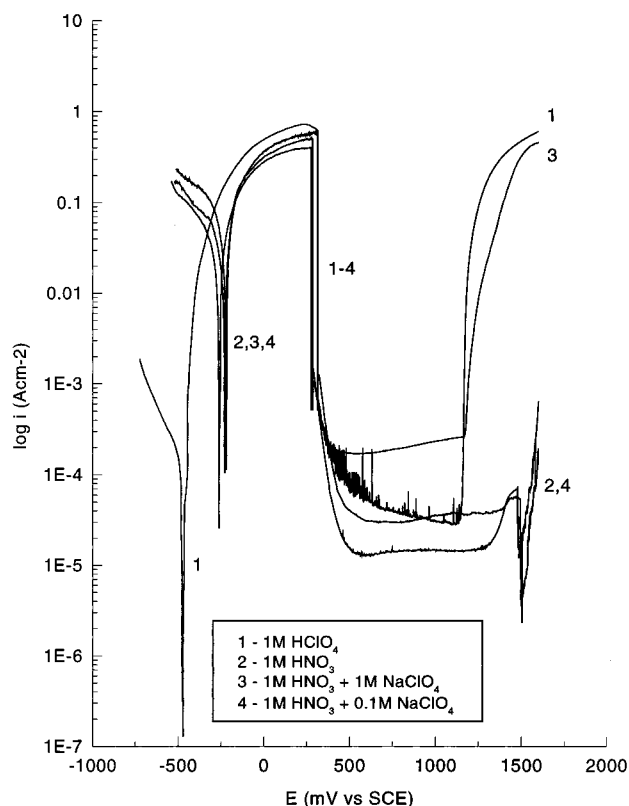


Figure 4. Anodic polarization curves of Fe in 1 M HClO₄, 1 M HNO₃, 1 M HNO₃ + 1 M HClO₄, 1 M HNO₃ + 10⁻¹ M HClO₄ (sweep rate 1 mV/s).

breakers and do not hydrate appreciably. Addition of these anions to the solutions of H₂O (HDO or D₂O) produces pronounced splitting of OH (or OD) stretching contours from H₂O (HDO or D₂O) and this splitting increases with ClO₄⁻ concentration.²³ This leads to an increase in OH⁻ concentration. Thus, it is possible that in ClO₄⁻ solutions a very high pH interfacial fluid is established so that in the solution of these anions double layer and electrode/electrolyte interface are populated more with OH⁻ ions than in NO₃⁻ or SO₄²⁻. This may be the reason for previously mentioned difficulties in passivating iron in ClO₄⁻ solutions. This may also be the reason for the very short potential/time decay in ClO₄⁻ as well as the shorter time for decay to corrosion potential with increasing pH in this solution, as in that case the concentration of OH⁻ ions in electrode/electrolyte interface increases.

On the other hand, ClO₄⁻ anions must participate in the reaction because under our experimental conditions (pH of the solution, anions used) the formation of black precipitate (ferrate) occurs only in their presence. The dependence of the trans-passive potential on ClO₄⁻ concentration and its anodic shift with the decrease of this concentration also mean that these anions participate in the reaction. When iron is anodically polarized they are electrostatically attracted toward the electrode surface and accumulate in the electrode/electrolyte interface. At 1.2 V the double layer is populated with enough ClO₄⁻ ions and at a high enough pH to provide for the oxidation of iron oxide in the passive film to ferrate.

As already mentioned, the most widely accepted structure of passive film on iron is one in which the inner layer is semiconducting magnetite Fe₃O₄ covered by a very thin outer layer of hematite Fe₂O₃.²⁴ According to Mutombo and Hackerman,⁸ these layers are not strictly separated. Magnetite contains Fe²⁺, the radius of which is larger than that of Fe³⁺ so that the

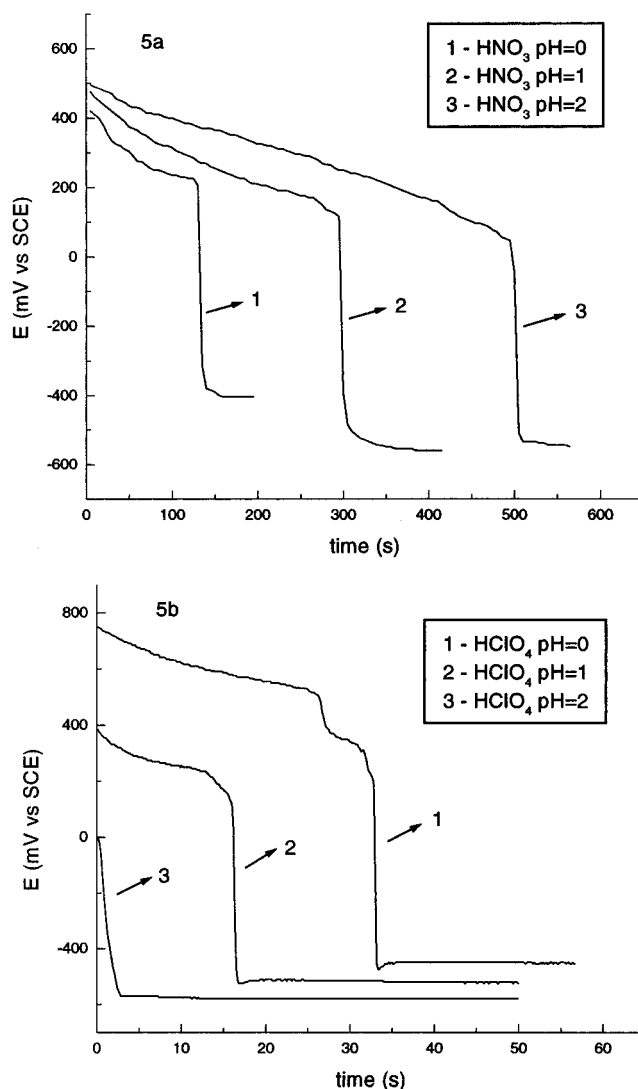
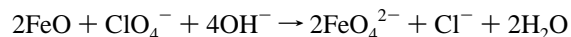


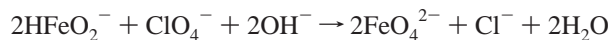
Figure 5. Potential/time decay curves for passivated Fe in (a) HNO₃ solutions of pH = 0, pH = 1, and pH = 2 and (b) in HClO₄ solutions of pH = 0, pH = 1, and pH = 2 (3).

Fe²⁺-O bond is longer and thus weaker than the Fe³⁺-O bond.²² These bonds thus make magnetite more susceptible to dissolution. Note though, in this study the actual composition is not a principal concern. Rather it is the availability of Fe^{II} or Fe^{III} in the passive film that is important. These can be converted to Fe^{VI} by a known reaction. This stems from the likelihood of high concentrations of OH⁻ and ClO₄⁻ at the anodically polarized iron surface. Therefore, in the presence of ClO₄⁻ and OH⁻ ions the following reaction may well be taking place:



The same reaction goes on in NO₃⁻ or SO₄²⁻ solutions containing sufficient ClO₄⁻ ions. However, in these solutions the extent of ferrate formation is lower due to the competition for the interface by the host anions. Furthermore, nitric acid and nitrates react with iron on immersion so that the reduced ions are also present in the solution.^{26,27} Sulfates adsorb on iron oxide as well²² and form a sparingly soluble compound with iron. Both, NO₃⁻ and SO₄²⁻ contrary to ClO₄⁻ can complex Fe(III) ions.²⁸ Due to this the electrode surface area available for OH⁻ and ClO₄⁻ is less than in simple ClO₄⁻ solutions. Therefore, in these mixed solutions the formation of ferrate is less extensive.

Oxidation of iron oxide to ferrate by ClO_4^- causes breakdown of the passive film and iron is corroded at a higher rate giving rise to increased anodic current. Being now in contact with strong alkaline double layer, iron dissolves giving HFeO_2^- species^{29,30} that are further oxidized to ferrates by ClO_4^- ions according to the equation



The products of ClO_4^- reduction may include Cl^- ions, but addition of AgNO_3 showed no sign of a AgCl precipitate. Thus the concentration of Cl^- is below 10^{-5} M. The reason could be that ferrate, a strong oxidizing agent, might oxidize the Cl^- .

The oxygen evolution, as already noted, proceeds in parallel, but is less intense the more intense the ferrate formation.

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