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Potential decay behavior of iron in dilute nitric acid

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Abstract Potential-time decay curves were used to investigate the passivation of iron in dilute nitric acid solutions of different concentrations. The effect of sulfate ions on the decay curves was also examined. It was observed that the decay curves formed an almost flat potential segment ending after reaching the Flade potential (the potential at the end of the plateau). The duration of the plateau was a function of both the initial holding potential and the acid concentration. The addition of sulfate ions affected the decay duration without interfering with the Flade potential. This is worth noting in view of the well-known dependence of the open-circuit potential decay on both pH and on the constituents of the solution.

Key words Flade potential · Anodic passivation · Passive film · Potential-time decay curve

Introduction

Iron is known to undergo passivation in nitric acid solutions. However, this process occurs in a complicated manner. Bonhoeffer and coworkers [1] proposed that this passivation of iron is mainly due to the formation of nitrous acid by reaction of iron with nitric acid. It was found that the level of nitrous acid increases after iron has been passivated, and this is believed to interfere with the reduction of the passive film.

Evans [2] suggested that NO_2 is the cause of passivity of iron in nitric acid solutions. He assumed that NO_2 accumulates at the electrode and initiates the oxide film formation on the metal. Along with NO and HNO_2 ,

NO_2 is one of the products of the reduction of nitric acid. Moreover, it may be generated alternatively by the decomposition of HNO_2 .

Uhlig and O'Connor [3] demonstrated that ferric acid, H_2FeO_4 or a hexavalent iron compound related to it, is formed at anode sites when iron reacts with HNO_3 . They assumed that chemisorbed ferric acid can reduce the tendency of the metal surface to react, making it passive.

Using the mechanism of iron dissolution, some investigators [4] concluded that passivation of iron in nitric acid proceeds via reaction of an FeOH^+ intermediate with adsorbed NO_2 to give Fe^{3+} , which is a constituent of the passive film.

We aim to examine iron behavior in more dilute nitric acid by means of potential decay curves, and to establish to what extent a small amount of sulfate ions may interfere with the anodic passivation process carried out in dilute nitric acid solutions. This method has been used in the past [5, 6] to characterize the activation of iron from the passive state. The technique is not affected by potential ohmic resistance, which complicates polarization measurements.

We have found that sulfate ions influence the duration of the decay curves without causing any change in the value of the Flade potential. This fact is in contrast to the reported dependence of the open-circuit breakdown of the passive film on the constituents of the solution [6–9].

Experimental

Iron specimens from Johnson Matthey (Puratronic, 99.9985%) were mounted on Teflon (with epoxy resin to prevent crevice corrosion) and placed in a glass cell that provides connection with three electrodes. The Versastat (potentiostat/galvanostat, EG&G Princeton Applied Research) was used for the measurements. The reference electrode was a saturated calomel electrode connected to the cell by a salt bridge and a Luggin probe. The counter-electrode consisted of a Pt gauze placed in a compartment separated by a frit

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Table 1 Equivalent conductivity of HNO₃ solutions at 18 °C (from [10])

Concentration (mol/l)	10 ⁻³	10 ⁻²	10 ⁻¹	1
Conductivity (Ω ⁻¹ m ² equiv ⁻¹)	375	368	350	310

in order to avoid contamination of the solution by the products formed on the counter-electrode.

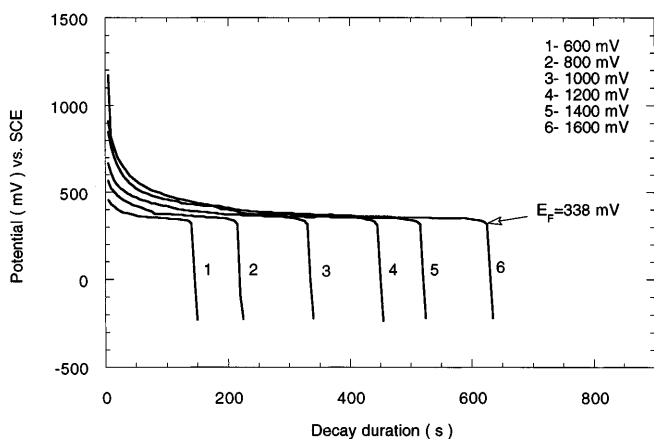
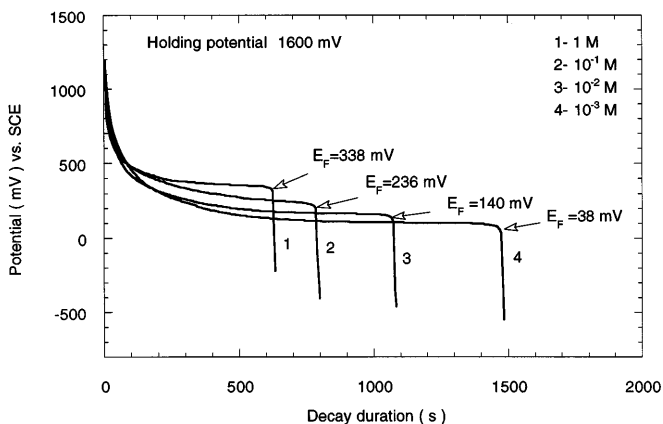
The specimens were prepared by polishing with emery papers and washing with redistilled water before immersion in the solutions. Oxygen was removed from the solution by sparging with an argon stream for 1 h both before the immersion of the specimens and during the experiment. The concentrations of nitric acid solutions were 1 M, 10⁻¹ M, 10⁻² M, and 10⁻³ M. The equivalent conductivities of the solutions are listed in Table 1 [10].

All solutions were prepared by mixing redistilled water and 69 wt% nitric acid (Fisher Scientific). The experiments were performed at room temperature, in the presence or absence of 10⁻⁴ M sodium sulfate. The working electrode was set and held initially for 5 min at various potentials ranging from 0.6 V to 1.6 V. The potentiostat was then switched off and the open-circuit potential decay was followed as a function of time.

Results and discussion

The open-circuit potential-time decay curves obtained in 1 M nitric acid solutions are presented in Fig. 1. It can be seen that the potential, after an initial exponential drop related to the discharge of the double layer, decays in an almost flat line ending after reaching the Flade potential. Similar curves were also recorded in less concentrated acid. Figure 2 shows the dependence of Flade potential on the concentration of the acid. It can be observed that the value of Flade potential shifts about 100 mV in the cathodic direction with decreasing acid concentration.

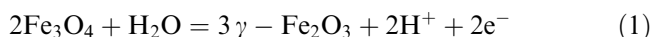
This fact is not in agreement with the generally accepted change of potential by 59 mV per unit pH. We should mention that our experiments were carried out in unbuffered solutions. In such solutions, the pH in the vicinity of the electrode differs from the one in the bulk

**Fig. 1** Decay curves of iron passivated in 1 M HNO₃ for 5 min at different holding potentials. E_F denotes Flade potential**Fig. 2** Decay curves of iron passivated for 5 min in different HNO₃ concentrations

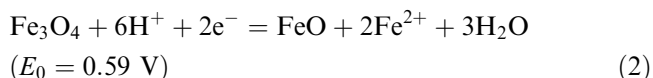
solution. This may be the reason for such difference. However, certain authors have also reported similar or somewhat different values [5, 11, 12].

The potential arrest is usually attributed to the reductive dissolution of the passive film. During this reduction, ferric species from the passive film are transformed into ferrous ions, which go into solution. After conversion of potentials to the hydrogen scale, it was found that the Flade potential is close to the value 0.58 V in 1 M HNO₃ (pH = 0). Attempts have been made to show that at pH = 0, γ -Fe₂O₃, Fe₃O₄ and FeOOH electrodes have almost the same potential, which lies in the region near the Flade potential [13, 14]. Thus it can be assumed that at a potential 0.58 V the structure of the passive film is similar to that of one of or a mixture of the above-named oxides.

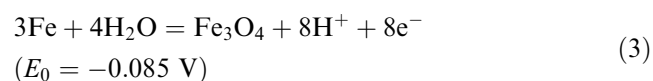
Wagner [15] has found that the value 0.58 V corresponds to a potential of iron-deficient magnetite whose composition is halfway between Fe₃O₄ and Fe₂O₃. Gohr and Lange [16] and Vetter [17] have suggested that the Flade potential is determined by the following reaction:



Uhlig [6] proposed a layer of chemisorbed atomic and molecular oxygen on the surface and described the Flade potential as an oxygen adsorption potential. If we consider the equilibrium system Fe-H₂O to interpret the results, we can see that the value 0.58 V is close to the standard potential of the electrochemical reaction:



According to this reaction, Fe₃O₄ is reduced to Fe²⁺ and FeO, which rapidly dissolves in the acid. On the other hand, thermodynamically, Fe₃O₄ begins to form at about -0.085 V according to the reaction:



There is therefore, within a potential range -0.085 to 0.58 V (pH = 0), competition between the formation of the magnetite and its dissolution in the acid. This suggests that the electrode surface is partially covered by a magnetite layer in this potential region. When the electrode potential reaches the Flade potential, it should become completely covered. Accordingly, the Flade potential can be seen as the higher limit of a potential region related to the passive layer stability depending on the pH at which experiments are conducted. The discrepancies between the passivation potential and the reactivation potential, observed during many measurements, are mainly due to the ohmic drop between electrodes and to the irreversible character of the passive layer formation and dissolution [18]. When the iron electrode is polarized at potentials more anodic than the Flade potential, a magnetite layer may be covered by or converted into a nonstoichiometric higher oxide [19].

Different passive film structure models have been suggested [20–22]. Vetter [23] proposed that the passive film is composed of two kinds of oxide layer. The magnetite layer was considered to be the inner part, with Fe_2O_3 forming the outer part. This model was, however, proved true mainly in neutral solutions [24–27]. It is unlikely in acidic environments, where the passive layer is very thin compared to those formed in neutral or alkaline media. Considering also their mutual miscibility, it seems acceptable to say that there is not a real phase boundary between these two oxides, but probably a cubic array of oxygen with a gradually lower concentration of iron from the metal to the solution interface.

With increasing pH, the passive film becomes progressively more hydrated. The hydrated oxide may result from oxidation of ferrous ions during passivation [25]. It may also be due to the dissolution and precipitation of ferric ions during formation of the layer [28] or to the chemisorption of water at the oxide electrolyte interface. Thus, the magnetite layer may be covered by an FeOOH layer. Mossbauer studies [29] carried out in acidic and neutral nitrate solutions have shown that α - and γ - FeOOH are formed on magnetite.

Effect of initial holding potential

Another important result is the influence of the holding potential on the Flade potential and on the duration of the decay. It was found that the initial holding potential does not affect the value of the Flade potential (Fig. 1). It was observed that the decay lasts longer with higher initial holding potential (Fig. 3). This can be explained by the fact that at potentials more anodic than the Flade potential, the passive film grows to a greater thickness [30, 31]. The film formed at less positive passive potentials is thinner than the one produced at more positive passive potentials. Therefore, for the latter, complete reduction is slow.

The driving force for oxide dissolution is the potential difference across the Helmholtz layer [32]. Both

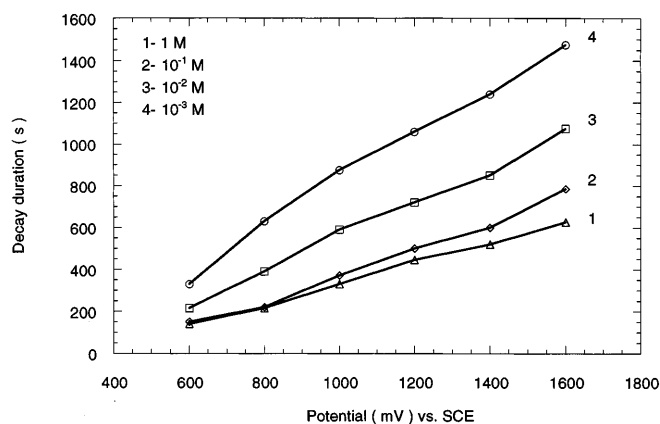


Fig. 3 Influence of holding potential on the decay duration for different HNO_3 concentrations

the oxide film and the base metal dissolve during reductive dissolution. The dissolution process implies transfer of metal ions to the oxide phase followed by ion diffusion through the oxide, transfer through the oxide solution interface, and finally hydration of the ions in the solution [33]. It is the pH of the solution which controls the dissolution process in the absence of interfering ions. It follows that the rate of reductive dissolution will decrease with increasing pH in acidic environments. Consequently, the film thickness will increase with increasing pH [25, 34]. This explains why the duration of the decay is longer with decreasing acid concentration (Fig. 3). Similar trends were obtained in sulfuric acid (1 M, 0.5 M) [4] (P. Mutombo and N. Hackerman, unpublished results). One can thereby conclude that anodic passivation of iron may occur in a similar manner in both environments. However, the rates of cathodic processes are higher in nitric acid than in sulfuric acid. The oxidizing species in the latter is hydrogen ion, whereas nitrate, nitrite and eventually hydrogen ions are oxidizing species in the former.

Effect of sulfate ions

The effect of the addition of 10^{-4} M Na_2SO_4 to nitric acid is shown in Figs. 4 and 5. From the former, it can be seen that the Flade potential is the same as in solutions without sulfate. Similar results were also obtained in more concentrated acid solutions. This indicates the non-interference of SO_4^{2-} ions on the passivation process in nitric acid. In the presence of sulfates there should be an increase in Fe^{2+} concentration in solutions due to enhanced iron dissolution. In contrast to earlier publications [7, 12], this increase of Fe^{2+} ions does not cause a shift in the Flade potential in the cathodic direction. We think that the reason why the shift does not happen is probably because the addition of sulfates to nitric acid solutions leads to the decrease of the pH in the vicinity of the electrode. Lower pH should cause a shift of the Flade potential in the anodic

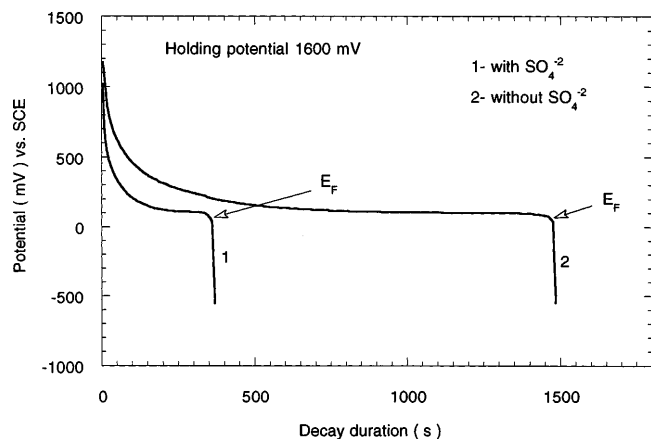


Fig. 4 Decay curves of iron passivated for 5 min in 10^{-3} M HNO_3 with and without 10^{-4} M SO_4^{2-} ions

direction. If the effect of higher Fe^{2+} content is balanced by the effect of lower pH, the resulting Flade potential will remain constant. Figure 5 expresses the difference in the decay duration between nitric acid solutions without and with sulfate ions as a function of initial holding potentials. It can be seen that sulfate ions have a greater effect on the duration of the decay in less concentrated acid than in more concentrated acid. The difference in the decay duration grows with increasing initial holding potential. The effect of holding potential is particularly important in the more dilute solution.

Polarization measurements have been conducted in order to verify the sulfate effect on passivation of iron in nitric acid solutions (Figs. 6 and 7). It appeared that sulfate retarded the passivation of iron by inducing a shift of the passivation potential in the anodic direction. The passive current was found to be higher in the presence of sulfates. The potential shift and the current increase were very notable in the less concentrated acid solution.

These findings can be explained by the ability of sulfate ions to activate the passive film. The activation

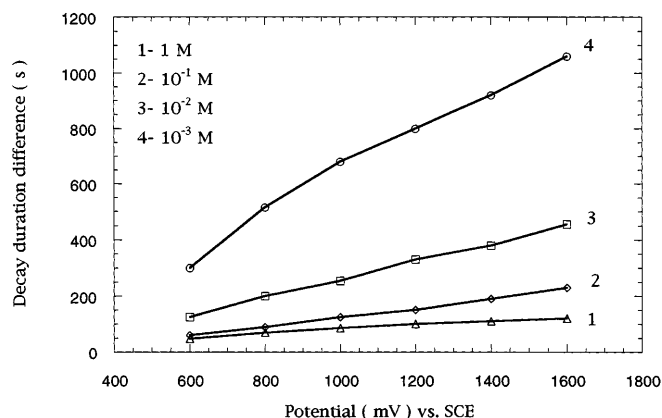


Fig. 5 Influence of holding potential on the decay duration difference for different HNO_3 concentrations containing 10^{-4} M SO_4^{2-} ions

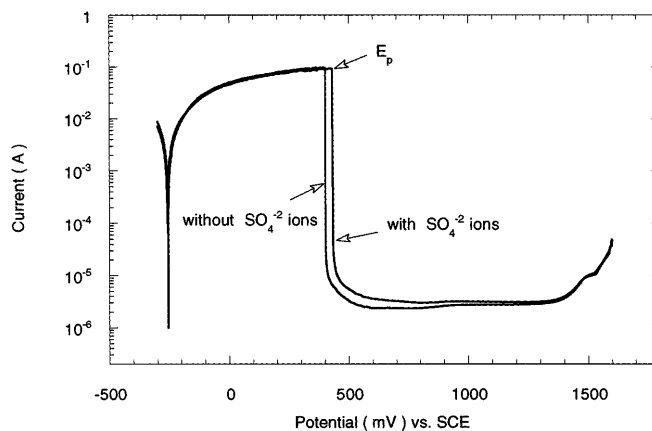


Fig. 6 Polarization curves of iron after 1 h of immersion in deaerated 1 M HNO_3 with and without 10^{-4} M SO_4^{2-} ions, scan rate 1 mV/s. E_p denotes passivation potential

depends on the concentration of both SO_4^{2-} ions and passivating species [35, 36]. SO_4^{2-} ions may displace nitrate ions from the metal surface and subsequently may be adsorbed or incorporated in the passive film, initiating defects. It has been reported [37–39] that hydrous iron oxides may provide in acid solution a fixed positive charge and hence act as an anion-selective layer. Generally, the fixed charge arises from the acid-base dissociation of surface hydroxyl groups on hydrated metal oxides. The adsorption of anions on the metal oxides is governed by the surface charge density. The latter is associated with the difference between the pzc (potential of zero charge) of the oxide and the pH of the solution. Considering the pzc of iron oxides, i.e., 6.5–6.7 for Fe_3O_4 , 6.1–8 for FeOOH and 8.3–9.3 for Fe_2O_3 [40, 41], it follows that the positive surface charge will increase with decreasing pH. When anions are adsorbed on or incorporated in the oxide film, the positive charge is altered, and subsequently the film becomes cation-selective. A cation-selective film should be

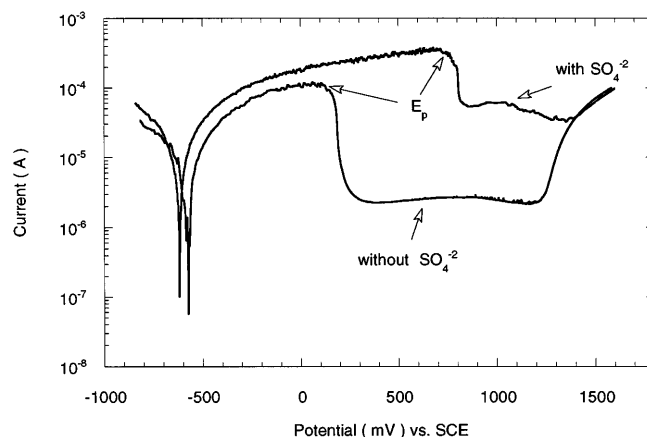


Fig. 7 Polarization curves of iron after 1 h of immersion in deaerated 10^{-3} M HNO_3 with and without 10^{-4} M SO_4^{2-} ions, scan rate 1 mV/s. E_p denotes passivation potential

permeable to hydrogen ions and other cations. Cation selectivity of the film facilitates depassivation processes when the potentiostat is turned off. It follows that sulfate adsorption should enhance reductive dissolution of the passive film in comparison with the behaviour of a defect-free film in nitrate solution. In concentrated nitric acid solutions, more sulfate ions are needed in order to affect the passive film because of higher positive charge on the oxide surface.

Conclusions

1. Potential decay curves of iron in dilute nitric acid exhibit a plateau which corresponds to the reductive dissolution of the passive film.
2. It is assumed that the passive film in acidic nitrate solutions can be related to the magnetite covered by or fully converted into a higher nonstoichiometric oxide. In less acidic solutions, a layer of α - or γ -FeOOH may be present on the magnetite.
3. The addition of sulfate ions mainly influences the duration of the decay curves without interfering with the Flade potential. This suggests the similarity between passivation of iron in dilute nitric acid solutions and in sulfuric acid alone. The effect of sulfate ions on the duration of the decay may be ascribed to their adsorption on or incorporation in the oxide film. This leads to the acceleration of reductive dissolution by hydrogen ions.

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