Kinetics of $\text{H}_2\text{O}_2$ reaction with oxide films on carbon steel

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Abstract

The nature of carbon steel surfaces in 0.01 M borate solutions (pH 10.6) have been characterized using a range of electrochemical techniques and ex situ analyses such as Raman and Auger spectroscopy. Their subsequent behaviour on exposure to $10^{-3}$ M $\text{H}_2\text{O}_2$-containing solutions has also been studied. The anodically oxidized carbon steel surfaces have been characterized according to three regions: (I) the potential range $< -0.5$ V (vs SCE), when the surface is active and covered by $\text{Fe}^{II}/\text{Fe}^{III}$ oxide/hydroxide; (II) the potential range $-0.5$ V to $-0.0$ V when the surface is passivated by an outer layer of $\text{Fe}^{III}$ oxide/hydroxide over the inner layer of $\text{Fe}^{II}/\text{Fe}^{III}$ oxide/hydroxide; and (III) potentials $>0$ V when further growth of the underlying layer appears to lead to minor film breakdown/restructuring. The addition of $\text{H}_2\text{O}_2$ to films grown in the passive region or above (II and III) leads initially to a degradation of the outer layer allowing increased growth of the inner layer. Subsequently, the outer passivating layer is repaired and passivity re-established. These changes appear to be confirmed by Raman spectroscopy.

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1. Introduction

Many of the operational and safety issues of nuclear power plants stem from the effects of radiation on the oxidation or corrosion kinetics of construction materials. Of particular...
concern are the effects of chemically reactive species produced by the radiolysis of reactor water. Exposed to ionizing radiation (e.g., $\alpha$, $\beta$ and $\gamma$-radiation), water decomposes to yield a range of chemically reactive species [1].

$$\text{H}_2\text{O} \rightarrow \cdot\text{OH}, \text{e}^{\text{aq}}, \text{H}, \text{HO}_2^{-}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}^+$$

(1)

While the concentrations of these primary radiolysis products may be limited by their rapid recombination, low steady state concentrations are rapidly achieved. However, these pseudo steady-state concentrations are easily affected by reaction with dissolved impurities or immersed surfaces.

Since water radiolysis produces both highly oxidizing and reducing species, it could dominate the redox condition in nuclear reactor coolant water [2,3]. This can strongly influence the corrosion kinetics of materials in contact with the water. For a potentially reactive material such as carbon steel, the redox condition is established by the interactions between reactive radiolysis products and the steel surface, and the corrosion products produced by these reactions. Since the surface area to water volume ratio in nuclear reactor circuits is large, consumption of a radiolysis product (such as $\text{H}_2\text{O}_2$) during corrosion can influence the concentrations of other radiolysis species by disturbing the steady-state balance between them. $\text{H}_2\text{O}_2$ can also decompose on various surfaces,

$$2\text{H}_2\text{O}_2 \leftrightarrow \text{O}_2 + 2\text{H}_2\text{O}$$

(2)

The kinetics of this reaction are not well characterized but will strongly depend on the composition and structure/morphology of the oxide produced by corrosion. Corrosion also produces soluble metallic species which can react with water radiolysis products [4].

$$\text{Fe}^{2+}(\text{aq}) + \cdot\text{OH}, \text{H}_2\text{O}_2, \text{or O}_2, \cdot\text{H}, \text{e}^{\text{aq}}, \text{or } \cdot\text{O}_2^- \rightarrow \text{Fe}^{3+}(\text{aq})$$

and consequently interfere with the steady-state balance between radiolytic species besides producing metallic species (Fe$^{3+}$) which could influence the composition of the corroding surface. The production of Fe$^{3+}$ in the vicinity of the corroding steel could lead to its passivation since the solubility of iron oxides/hydroxides decreases in the order [5–7]:

$$\text{Fe(OH)}_2 \ll \text{FeOOH} < \text{Fe}_3\text{O}_4 < \text{Fe}_2\text{O}_3$$

An attempt to represent this synergistic circuit is shown in Fig. 1.

![Fig. 1. Schematic illustration of the synergistic interactions between water radiolysis and the corrosion of carbon steel.](image)

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To develop a quantitative understanding of this synergistic behaviour, and hence develop a predictive capability of the effects of radiation on steel corrosion kinetics, a detailed understanding of the interactions between surface oxide films and water radiolysis products is required. As a first step, we have been studying the mechanism and kinetics of the reaction of H$_2$O$_2$ with various iron hydroxide/oxide films on carbon steel. While the results presented here are confined to room temperature in the presence of chemically added H$_2$O$_2$, experiments at higher temperatures and in the presence of gamma irradiation are underway. In the study presented in this paper, iron oxide/hydroxide films were grown potentiostatically on carbon steel and characterized with electrochemical impedance spectroscopy (EIS). The H$_2$O$_2$ reaction with the characterized oxide films were then followed by corrosion potential, $E_{CORR}$, and EIS measurements as a function of exposure time to H$_2$O$_2$. Ex situ Raman spectroscopy and Auger spectroscopy were used to characterize the oxides/hydroxides.

2. Experimental

2.1. Electrochemical system

A standard three-electrode cell, consisting of a carbon steel (CS) working electrode, a reference electrode and a counter electrode, was used for all experiments. The working electrode was a 10-mm (in diameter) A516 Gr70 carbon steel (CS) disc, set in resin so that only the flat front face was exposed to the solution. Prior to each experiment, this electrode was manually polished with 600 and 800 grit silicon carbide papers, and polishing residue removed by sonication in an acetone/methanol mixture for 5 min. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum mesh. All potential measurements were made with, and are quoted against, a saturated calomel reference electrode (SCE).

A Solartron model 1240 potentiostat and 1252 frequency response analyzer were used in all electrochemical measurements. Corrware™ and Corrview software (supplied by Scribner and Associates) was used to control experiments and analyze data. Electrochemical Impedance Spectroscopy (EIS) was performed by applying a 10 mV sinusoidal potential waveform at an open circuit potential over the frequency range 10 kHz to 10$^{-2}$ Hz.

2.2. Solutions

Experiments were conducted at room temperature in Ar-purged 0.01 M borate (Na$_2$B$_4$O$_7$) with the pH adjusted to 10.6 with NaOH (unless otherwise stated). Solutions were prepared with water purified using a NANOpure Diamond UV ultrapure water system from Barnstead International to remove organic and inorganic impurities. Prepared in this manner, the water had a resistivity of 18.2 MΩ cm.

A hydrogen peroxide stock solution was prepared by adding an appropriate amount of concentrated H$_2$O$_2$ (30% in the weight percentage) to the electrolyte solution to bring the H$_2$O$_2$ concentration to a desired value in the range of 10$^{-4}$ to 10$^{-2}$ mol dm$^{-3}$ (M).

2.3. Experimental procedure

The experimental procedure used to study the interaction of electrochemically grown oxide films with H$_2$O$_2$ is presented schematically in Fig. 2. All experiments were preceded...
by a cathodic cleaning of the electrode at a potential of $-1.1 \text{ V}$ for 300 s. After cathodic cleaning, an iron oxide film was grown potentiostatically at a potential in the range $-0.7 \text{ V}$ to $+0.4 \text{ V}$ for 1 h, while monitoring the current (Step 1). The $E_{\text{CORR}}$ of the oxide covered CS electrode was then allowed to relax for $\sim 20 \text{ min}$ to a pseudo steady-state value (Step 2), and the electrode/solution interface characterized by EIS (Step 3). The reaction of the oxide films with $\text{H}_2\text{O}_2$ was initiated by adding $\text{H}_2\text{O}_2$ to the electrolyte solution, to bring the $\text{H}_2\text{O}_2$ concentration to $10^{-3} \text{ M}$. The progress of the reaction was monitored by measuring $E_{\text{CORR}}$ (Step 4), and recording EIS spectra at various reaction times (Step 5).

Cyclic voltammetry, from the cathodic cleaning potential to various anodic limits at a scan rate of $5 \text{ mV s}^{-1}$, was also conducted as a function of pH, temperature, electrode rotation speed and the number of scan cycles.

2.4. Surface analysis

Ex situ Raman spectra of the carbon steel electrode surfaces were acquired before and after the reaction with $\text{H}_2\text{O}_2$ with a Renishaw Model 2000 Raman Spectrometer. The $633 \text{ nm}$ line of a $10 \text{ mW}$ HeNe laser was focused on the specimen by an Olympus microscope with a $50 \times$ magnification objective lens. Auger electron spectroscopy (AES) analyses were performed with a primary electron beam voltage of $3 \text{ kV}$, and the electron beam used to generate Auger electron spectra was at $5 \text{ kV}$. The AES system is computer controlled with provision for in-situ Ar-ion sputtering. All the samples were sputtered with $3 \text{ keV Ar}^+ \text{ ions}$ for $1 \text{ min}$ to remove the surface contamination due to air-handling before the AES measurement for each sample began [8].

3. Results and discussion

3.1. Cyclic voltammetry

Two sets of voltammograms recorded in Ar-purged $0.01 \text{ M}$ borate buffer solution at pH 10.6 and room temperature are shown in Fig. 3: (Panel a) shows the influence of scan cycle and (Panel b) shows the influence of electrode rotation rate on the first scan. The primary purpose of performing these scans was to provide a basis for interpreting the potentiostatic film growth and EIS experiments. Fig. 4 summarizes the thermodynamic possibilities for iron oxide/hydroxide reactions within the potential range investigated, based on the data.
CVs were also recorded as a function of pH, rotation speed, anodic potential limits and temperature.

On the first cycle, five indistinct peaks are observed, which is not surprising considering the thermodynamic possibilities. Similar, but slightly different behaviour is observed at lower [11,12] and higher [13] pH values. Subsequent cycles, performed without repreparing the electrode surface, show a decrease in general reactivity but the development of a distinct anodic peak, A3/A3', and two cathodic peaks, C1 and C2, Fig. 3a.

Fig. 3. Cyclic voltammograms recorded on a carbon steel electrode in Ar-purged, 0.01 M borate solution at pH 10.6 and 25 °C at a scan rate of 5 mV/s: (a) CVs obtained on various scan cycles (no rotation); and (b) CVs of the first scan cycle obtained with various electrode rotation speeds. The arrows in (b) indicate the direction of change with an increase in rotation speed.

Vertical lines: $E^\text{eq}$

$pH = 10.6, 25^\circ C$

- $\alpha$-FeOOH
- $\gamma$-FeOOH
- $\text{Fe}^{3+}(\text{aq})$
- $\text{Fe}^{2+}(\text{aq})$

Fe
- Fe$_3$O$_4$
- Fe(OH)$_2$
- Fe(OH)$_3$
- Fe$_2$O$_3$
- Fe$_2$(OH)$_4$
- Fe$^{3+}$(aq)
- Fe$^{2+}$(aq)

Fig. 4. Schematic of equilibrium potentials (vs SCE) for redox reactions possible on carbon steel. The short vertical lines indicate the equilibrium potentials for given redox pairs at pH 10.6 and 25 °C. The curvy lines indicate potential non-electrochemical processes such as dissolution and phase transformations.

by Misawa [9,10]. CVs were also recorded as a function of pH, rotation speed, anodic potential limits and temperature.

On the first cycle, five indistinct peaks are observed, which is not surprising considering the thermodynamic possibilities. Similar, but slightly different behaviour is observed at lower [11,12] and higher [13] pH values. Subsequent cycles, performed without repreparing the electrode surface, show a decrease in general reactivity but the development of a distinct anodic peak, A3/A3', and two cathodic peaks, C1 and C2, Fig. 3a.
The shoulder at $\sim –0.9\ V$ (A1 in Fig. 2a) is only observed on the first cycle, and can be attributed to the reoxidation of H absorbed in the electrode during the cathodic cleaning prior to the first scan [13]. The broad anodic peak (A2) in the potential range $–0.9\ V$ to $–0.6\ V$ encompasses the active metal dissolution region within which the formation of Fe(OH)$_2$, Fe$_3$O$_4$ and the conversion of Fe(OH)$_2$ to $\alpha$-FeOOH become thermodynamically possible, Fig. 4. Depending on the scan rate, this peak was partially resolved. The commonly accepted mechanism for dissolution [14–20],

$$Fe + OH^- \rightarrow [Fe(OH)_{ads} + e] \rightarrow FeOH^+ + 2e$$ \hspace{1cm} (3) 

$$FeOH^+ + OH^- \rightarrow Fe(\text{OH})_2$$ \hspace{1cm} (4)

acknowledges the importance of intermediate oxidation states of Fe (Fe$^3$). As written, dissolution precedes Fe(OH)$_2$ formation on the surface. However, at pH 10.6, the potential for the anodic formation of Fe(OH)$_2$ from Fe is low ($–0.973\ V$ vs SCE), and the equilibrium between the Fe$^{II}$ species ($Fe^{2+} \leftrightarrow Fe(OH)^+ \leftrightarrow Fe(OH)_2 \leftrightarrow Fe(OH)_3^–$) in the aqueous phase should be fast. Hence, Fe(OH)$_2$ formation could be rapid, and dissolution could proceed via adsorbed Fe(OH)$_2$ species which could alternatively be transformed into an Fe(OH)$_2$ film [21].

Evidence at lower [11,12] and higher [13] pH values shows that active dissolution is suppressed by Fe(OH)$_2$ and/or Fe$_3$O$_4$ formation. This could account for the increase in current observed on rotating electrodes over the potential range $–0.9\ V$ to $–0.6\ V$, Fig. 3b. Within the active region, enhanced permeation of H into the steel has been observed [17,22], indicating the catalysis of water reduction via the intermediates involved in active dissolution (Fe/Fe$^I$, Fe$^I$/Fe$^{II}$) or on the surface of an Fe$_3$O$_4$ (Fe$^{II}$/Fe$^{III}$) film. Catalysis of H$_2$ evolution by mixed metal cation oxidation states is well documented [23].

Experiments recorded as a function of electrode rotation rate, Fig. 3b, show peak A2 ($–0.9\ V$ to $–0.6\ V$) and peak A4 ($–0.4\ V$ to $–0.1\ V$) are related, and involve, at least partially, soluble species. The current in region A2 increases with electrode rotation rate indicating an increase in production of soluble Fe$^{2+}$. If dissolution occurs in competition with the formation of an Fe(OH)$_2$ film, an increase in rotation rate would also decrease the amount of Fe(OH)$_2$ formed on the surface. In contrast, the current in region A4 decreases with increasing rotation rate indicating that the anodic process is partially avoided by either the convective removal of Fe$^{2+}$ or the decreased availability of Fe(OH)$_2$. These observations, as well as the increase in current and the shift in peak position to more negative potentials observed with increasing pH (not shown), allow us to attribute peak A4 to the oxidation of Fe$^{II}$ species (Fe$^{2+}$, Fe(OH)$_2$) to $\alpha$-FeOOH. The equilibrium potential for the conversion of Fe(OH)$_2$ to $\alpha$-FeOOH lies at a much more negative potential, indicating that the kinetics of this anodic process are slow. These claims are consistent with the claims of Guzman et al. [24] and Hugot–LeGoff [10], who observed a current peak for this reaction at $–0.75\ V$ in 1 M NaOH, and with the results of Ohtsuka et al. [25] who showed that the anodic oxidation of soluble Fe$^{II}$ species resulted in the formation of a partially hydrated FeOOH (or Fe(OH)$_3^–$) layer.

On subsequent voltammetric cycles, Fig. 3a, the currents in region A2 and A4 are considerably reduced, a feature attributable to the formation of Fe$_3$O$_4$. Fe$_3$O$_4$ can form either directly from Fe or via the conversion of Fe(OH)$_2$, since both of these reactions become thermodynamically feasible at the negative potential end of region A2. That Fe$_3$O$_4$ is formed around these potentials, and subsequently present over the whole potential range
scanned, has been demonstrated by Raman Spectroscopy [13]. It was also shown that Fe$_3$O$_4$ was not fully reduced on the cathodic scan, even at the cathodic limit of $-1.2$ V in $1$ M NaOH [13], and using light absorption measurements, that repetitive scanning lead to the accumulation of irreducible products on the electrode surface [11,12].

A similar accumulation of magnetite would account for the suppression of the current in the active region A4 on our second scan and also for the enhancement of the anodic process A3/A3' at $\sim -0.5$ V. With scan cycle, the charge associated with peak A3/A3' and the sum of the charges associated with peaks C1 and C2 increase together and are equal, indicating that the species formed anodically (A3/A3') are completely reduced (at C1 and C2). This anodic peak separates into two peaks (hence, the notation A3/A3') when the scan rate is reduced to $0.167$ mV/s, confirming that two anodic processes are involved. CVs to various anodic potential limits (results not shown) show that peaks C1 and C2 are associated with anodic processes A3' and A3, respectively.

The sharpness of oxidation peak A3 suggests a rapid reaction to produce an insulating surface layer which would account for the suppression of the current in region A4 after the first cycle. Based on equilibrium potentials (Fig. 4), and the stability of Fe$_2$O$_3$, the conversion of Fe$_2$O$_4$ $\rightarrow$ $\gamma$-Fe$_2$O$_3$ is the most likely reaction. With continuous cycling, the increase in size of anodic peak A3 is consistent with the accumulation of Fe$_2$O$_4$ on successive cycles and its oxidation (at least partially) to $\gamma$-Fe$_2$O$_3$. The oxidation of Fe$_3$O$_4$ to $\gamma$-Fe$_2$O$_3$ should be rapid since both oxides have similar crystallographic structures. Both phases possess an O$^{2-}$ sub lattice which is cubic close-packed (ccp), and Fe$^{II}$/Fe$^{III}$ cations occupy similar octahedral and tetrahedral lattice sites [26]. Since peak A3/A3' also lies above the equilibrium potential for the conversion of Fe(OH)$_2$ to $\gamma$-FeOOH, this reaction could account for the anodic current associated with A3'. The assignment of the anodic processes, A3/A3', to the formation of $\gamma$-Fe$^{III}$ species ($\gamma$-Fe$_2$O$_3$ and $\gamma$-FeOOH) is consistent with the claims of Devine et al. [27,28] who investigated the passive films using in-situ surface-enhanced Raman spectroscopy. They suggested that the passive films formed at low passive potentials ($-0.4$ V at pH 8.4) consist of Fe(OH)$_2$ + Fe$_3$O$_4$ and/or $\gamma$-Fe$_2$O$_3$ (or $\gamma$-FeOOH), whereas at higher passive potentials (0.1 V at pH 8.4) $\gamma$-FeOOH is predominant.

Peaks C1 and C2 are attributed to the reduction of $\gamma$-FeOOH (C1) and $\gamma$-Fe$_2$O$_3$ (C2) to Fe$_3$O$_4$. Both these reduction processes can lead to the production of soluble Fe$^{II}$ but the production of significant amounts of soluble iron is unlikely at pH 10.6. Stratmann et al. [26] have shown by XRD that the reduction of $\gamma$-FeOOH to Fe$_3$O$_4$ occurs based on XRD and magnetic force measurements [26].

Finally, a very shallow additional anodic process (A5) is observed over the potential range 0–0.4 V, which could be attributed to the conversion of Fe$_3$O$_4$ to $\gamma$-FeOOH, as suggested by the equilibrium potential in Fig. 4. This assignment is consistent with the findings of Devine et al. [27,28] who observed Raman peaks associated with $\gamma$-FeOOH for passive films formed at high passive potentials. For an increase in current to be observed in this potential region passivation must either be incomplete or some film breakdown or restructuring must occur. Given the large number of phases and interconversion reactions possible it is not clear what causes this. One possibility is that volume changes accompanying field- or stress-assisted dehydration processes (e.g., $\gamma$-FeOOH to Fe$_2$O$_3$) lead to a temporary loss of passivation. The decreasing significance of this process on successive cycles is consistent with either an increasingly thick or comprehensively protective passive film.
3.1.1. Summary of anodic processes

Based on these observations three distinct regions of behaviour as a function of increasing potential can be specified: (I) \( E < -0.5 \text{ V} \); (II) \(-0.5 \text{ V} < E < 0.0 \text{ V} \); and (III) \( E > 0.0 \text{ V} \) (Fig. 5). In region I, anodic oxidation leads to dissolution as \( \text{Fe}^{2+} \) and the formation of oxides/hydroxides in the \( \text{Fe}^{II} \) and \( \text{Fe}^{III} \) oxidation states. This is the active region for steel and oxides, such as \( \text{Fe}_2\text{O}_4 \), while partially protective, are conductive and able to support cathodic reactions (e.g., the reduction of \( \text{H}_2\text{O} \)).

The beginning of region II is marked by the sharp peak at \( \approx -0.5 \text{ V} \), indicating the formation of \( \gamma\)-\( \text{Fe}_2\text{O}_3 \) and \( \gamma\)-\( \text{FeOOH} \) species. Since \( \text{Fe}^{III} \) oxides/hydroxides are very insoluble, this marks the onset of passivity although the properties of this layer appear to vary with \( E \) and pH as can be appreciated by a comparison of our results to those of Schmucki et al. (pH 8.4 [11,12]) and Hugot–Le Goff (pH 14 [13]).

In region III, film breakdown/restructuring accompanied by the anodic oxidation of \( \text{Fe}_3\text{O}_4 \) to \( \gamma\)-\( \text{FeOOH} \) appears to occur.

3.2. Potentiostatically formed iron oxide films

3.2.1. Current behaviour during potentiostatic film growth

The current–time and the charge (\( Q \))-time behaviour observed during film growth at various applied potentials, \( E_{\text{APP}} \), in regions I, II and III are shown in Fig. 6. At the three highest potentials, \(-0.15 \text{ V} \) (in region II), \( 0.1 \text{ V} \) and \( 0.4 \text{ V} \) (in region III), three regions of current-time behaviour are observed, Fig. 6a. The potential dependence of the current is small initially (<2 s), suggesting a predominantly chemically-controlled anodic dissolution process through a rapidly grown \( \text{Fe(OH)}_2 \) layer whose thickness varies with potential to maintain an electric field across the film almost independent of potential. The subsequent
faster decay in current (2 s to \( \sim 10\) s) could represent a potential-dependent transformation of this layer to Fe\(_3\)O\(_4\), and/or the anodic formation of a partially protective layer of Fe\(_3\)O\(_4\) from the underlying steel. For \( t > 20\) s the slope of the log \( i \) vs log \( t \) approaches \( \sim -1 \) for applied potentials \( > -0.15\) V. This is consistent with the field-assisted growth of an outer passive layer of Fe\(_{11}\) oxide/hydroxide, since, in all cases, the applied potential is more positive than the position of peak A3/A3' (Fig. 3). Slightly further growth of the underlying layer is also likely. This rapid initial formation of an underlying Fe\(_{II}/Fe_{III}\) layer followed by the suppression of its growth by the formation of a passivating outer layer is best appreciated from the \( Q-t \) plots in Fig. 6b.

At the two lower values of \( E_{\text{APP}} \) (–0.7 and –0.55 V), region I, the current eventually switches to a cathodic value at long times. At –0.55 V, prior to switching to a negative current (at \( \sim 2000\) s), the log \( i \) – log \( t \) plot is similar to those observed at higher potentials suggesting a similar film growth process. Since this applied potential is still more positive than the equilibrium potentials for Fe\(_3\)O\(_4\)/\( \gamma\)-Fe\(_2\)O\(_3\) and Fe(OH)$_2$/\( \gamma\)-FeOOH it is possible some growth of one, or both, of these phases occurs. However, the eventual switch to a cathodic current indicates passivation is incomplete, since electron transfer to sustain H\(_2\)O reduction is possible. At –0.7 V, the anodic formation of a passive \( \gamma\)-Fe\(_2\)O\(_3\) film is not possible and the current rapidly becomes cathodic (at \( \sim 70\) s) indicating H\(_2\)O reduction is sustained on a conducting Fe\(_3\)O\(_4\) surface. The ensuing cathodic current is greater at –0.7 V than at –0.55 V, as expected.

3.2.2. Corrosion potential (\( E_{\text{CORR}} \)) measurements before H\(_2\)O\(_2\) addition

Prior to the addition of H\(_2\)O\(_2\), the potentiostatically grown films were allowed to relax on open circuit for 20 min. As indicated by the three vertical lines in Fig. 5, \( E_{\text{CORR}} \) relaxed to one of three values, depending on the potential applied during film growth. For films grown at potentials \( <-0.7\) V, \( E_{\text{CORR}} \) achieves a value of –0.8 V (line A) consistent with an electrode covered by Fe(OH)$_2$/Fe\(_3\)O\(_4\) in the active region I. For films grown at potentials \( > -0.15\) V (in region II), \( E_{\text{CORR}} \) relaxes to \( \sim -0.4\) V (line C) consistent with a passive surface covered by an inner layer of Fe\(_3\)O\(_4\) and a passive outer layer of \( \gamma\)-Fe\(_2\)O\(_3\) and possibly some \( \gamma\)-FeOOH. For films grown at –0.25 V (in region II, Fig. 5), \( E_{\text{CORR}} \) reaches \( \sim -0.6\) V (line B), which is very close to the equilibrium potential for the reaction.
Fe$_3$O$_4$/$\gamma$-Fe$_2$O$_3$ suggesting the presence of both these phases in contact with the aqueous solution, i.e., a condition of partial passivation.

3.3. Interaction of the oxide films with H$_2$O$_2$

3.3.1. Corrosion potential

Following relaxation on open circuit, $10^{-3}$ M of H$_2$O$_2$ was added to the electrolyte solution: the responses of $E_{\text{CORR}}$ for films grown at $-0.25$ V (after relaxation to $\sim -0.6$ V) and 0.1 V (after relaxation to $\sim -0.4$ V) are shown in Fig. 7. Similar responses are obtained for films grown in potential regions I and II. $E_{\text{CORR}}$ increases sharply on H$_2$O$_2$ addition, and then changes more gradually to achieve a steady-state value, $(E_{\text{corr}})_{\text{SS}}$. This steady-state value of $\sim 0.05$ V is the same irrespective of whether the original film was grown at a potential in region I, II or III. Since $(E_{\text{CORR}})_{\text{SS}}$ is in the passive region this suggests that peroxide addition leads to surface passivation irrespective of the initial surface composition.

3.3.2. EIS as a function of exposure time to H$_2$O$_2$

EIS spectra obtained on films grown at $-0.15$ V (region II) and $+0.1$ V (region III) before and after various exposure times to $10^{-3}$ M H$_2$O$_2$ are shown in Fig. 8. The time-dependent behaviour of the spectra reflects that of $E_{\text{CORR}}$: a rapid initial change on addition of H$_2$O$_2$, followed by a slower and smaller change with time. An electrical equivalent circuit involving two parallel RC circuits in series [29–31] was found to most adequately fit the spectra. Such a circuit is consistent with the presence of a dual layer film grown potentiostatically as illustrated in Fig. 9. In this circuit $\tau_2(=R_2(CPE)_2)$ represents charge transfer processes within the inner Fe(OH)$_2$/Fe$_3$O$_4$ layer, and $\tau_1(= R_1(CPE)_1)$ defect migration processes in the outer passive Fe$_2$O$_3$/FeOOH layer. Analysis according to this circuit yields the parameter values given in Table 1. The parameter, $P_{\text{CPE}}$ in Table 1 is the exponent defining the nature of the constant phase element, CPE, used to fit the circuit. A value

![Fig. 7. Time dependent behaviour of $E_{\text{CORR}}$ on oxide-covered carbon steel following the addition of $10^{-3}$ M H$_2$O$_2$: Films Grown for 1 h at $-0.25$ V (after relaxation to $\sim -0.6$ V) and at 0.1 V (after relaxation to $\sim -0.4$ V).](image-url)
Fig. 8. Electrochemical impedance spectra of carbon steel electrodes covered with potentiostatically grown oxide films. The films were grown at $-0.15\,\text{V}$ and $0.10\,\text{V}$, allowed to relax for 20 min and then exposed to a solution containing $10^{-3}\,\text{M}\,\text{H}_2\text{O}_2$. The EIS spectra were taken at exposure times of 1.4 h, 4 h and 8.5 h.

Fig. 9. Schematic representation of the anodically grown dual layer film and the electrical equivalent circuit used in EIS analyses: films grown at $-0.15\,\text{V}$ and 0.1 V.
of $P_{\text{CPE}}$ approaching 1 defines CPE as effectively a capacitance. For CPE₂, $P_{\text{CPE2}}$ is always $>0.8$ and CPE₂ was taken to be a capacitance. For CPE₁, $P_{\text{CPE1}}$ often exceeded 1 and in those cases a value $= 1$ was fixed when performing the fit. Again, CPE₁ was assumed to be a capacitance in subsequent discussions.

Table 1
Fitting Parameters of the Equivalent Circuit Analysis of the EIS Results

<table>
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<th>Film Growth Potential</th>
<th>Exposure time to $\text{H}_2\text{O}_2$</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_2$ (Ω cm$^2$)</th>
<th>CPE$_2$ (F/cm$^2$)</th>
<th>$P_{\text{CPE2}}$</th>
<th>CPE$_1$ (Ω cm$^2$)</th>
<th>$P_{\text{CPE1}}$</th>
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<td>133</td>
<td>1.0E4</td>
<td>2.0E-5</td>
<td>0.82</td>
<td>1.5E5</td>
<td>2.6E-4 0.88</td>
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<td>4.7E4</td>
<td>1.1E-4</td>
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Fig. 10. Film resistances and capacitances obtained by fitting to the electric equivalent circuit in Fig. 9: (a) the inner layer; and (b) the outer layer.
Fig. 10a shows the resistance of the inner oxide layer ($R_2$) increases sharply on $H_2O_2$ addition, and then decreases very slightly with time. This is mirrored by an accompanying sharp initial decrease in $C_2$ followed by a subsequent slow increase. This combination is consistent with a sudden thickening of the inner $Fe^{II}/Fe^{III}$ oxide/hydroxide layer which must involve further oxidation of the steel surface driven by $H_2O_2$ reduction. By contrast, Fig. 10b, the resistance of the outer layer ($R_1$) initially decreases slightly before steadily increasing over the subsequent 8 h exposure period. This increase in $R_1$ is accompanied by a steady decrease in capacitance ($C_1$). The initial decrease in $R_1$ indicates that $H_2O_2$ addition initially leads to a more defective outer layer, thereby initially allowing growth of the inner layer. However, with time, the steady increase in $R_1$ (and decrease in $C_1$) indicates a slow repassivation process. The slight decrease in $R_2$ accompanying this slow increase in $R_1$ is consistent with growth of the outer layer via conversion of the inner layer; i.e., $Fe_3O_4/Fe(OH)_2$ conversion to $Fe_2O_3/FeOOH$. It is likely that the increase in the outer layer resistance (and corresponding decrease in capacitance) reflects a combination of film thickening (at the expense of the inner layer) and defect annealing.

### 3.4. Surface analyses

All the surface analyses were ex situ analyses, and, hence subject to air-exposure prior to analysis. However, the films formed at the high potentials ($>-0.2$ V) are relatively inert with the surface already oxidized predominantly to the $Fe^{III}$ state, and careful handling of the samples under low oxygen environments should have minimized any changes prior to the surface analyses.

SEM images of the carbon steel surfaces potentiostatically-oxidized at $E_{APP} > -0.15$ V showed no significant differences in the surface morphology. No significant changes were observed due to exposure to $H_2O_2$. The atomic ratio $O/Fe$ determined by AES, is shown as a function of sputtering time for specimens preoxidized at $+0.4$ V (Fig. 11). The profile for a specimen preoxidized in air at room temperature (stored in a desiccator for a few days) is

![Figure 11](image-url)
also shown for comparison. The solid horizontal lines are the expected O/Fe ratios for three oxide/hydroxide phases. The ratio at the specimen surface (short sputtering time) shows the high Fe$^{III}$ content of the surface and suggests a mixed Fe$\textsubscript{2}$O$\textsubscript{3}$/c-FeOOH composition. For deeper film depths (longer sputtering times) the composition of the film changes confirming its dual layer nature. The height of the shoulder in the depth profile suggests the inner layer is predominantly Fe$\textsubscript{3}$O$\textsubscript{4}$.

The Raman spectrum of a specimen preoxidized at +0.4 V appears to confirm the AES analysis since small peaks attributable to Fe$\textsubscript{3}$O$\textsubscript{4}$ are observed, Fig. 12. The peaks are very weak on such a smooth surface. Other oxides/hydroxides were likely present, but in insufficient quantity to be detected by Raman spectroscopy. While the variation observed between different areas of the same sample is relatively large, there appears to be a measurable increase in the Raman scattering peak for Fe$\textsubscript{3}$O$\textsubscript{4}$ as a result of exposure to H$_\textsubscript{2}$O$_\textsubscript{2}$ of a specimen preoxidized at +0.4 V. This is consistent with the claim (above) that exposure to H$_\textsubscript{2}$O$_\textsubscript{2}$ leads initially to a degradation of the passive layer leading to growth of the inner layer.

4. Conclusions

Based on voltammetric experiments the anodic oxidation behaviour of carbon steel in borate solutions (pH 10.6) can be divided into three distinct regions: (I) the potential region $<$$-0.5$ V, when the surface is active and partially covered by Fe(OH)$_\textsubscript{2}$/Fe$\textsubscript{3}$O$\textsubscript{4}$; (II) the potential region $-0.5$ V to $-$0 V, when the surface is passivated with an outer layer of Fe$_\textsubscript{2}$O$_\textsubscript{3}$/γ-FeOOH over the inner Fe$^{II}$/Fe$^{III}$ oxide/hydroxide layer; and (III) the potential region $>0$ V, within which the further conversion of Fe$_\textsubscript{3}$O$_\textsubscript{4}$ to γ-FeOOH can cause some restructuring and slight film breakdown.

Potentiostatic, EIS and AES experiments yield results consistent with a film comprised of a dual layer structure with an outer layer of Fe$^{III}$ oxide/hydroxide over an inner layer of Fe$^{II}$/Fe$^{III}$ oxide/hydroxide. Both AES and Raman spectroscopy indicate the inner layer is predominantly Fe$\textsubscript{3}$O$\textsubscript{4}$. 

![Ex situ raman spectra obtained with films grown at 0.4 V: the lower spectrum is for a film not exposed to H$_\textsubscript{2}$O$_\textsubscript{2}$ while the upper spectrum is for a film exposed to $10^{-3}$ M H$_\textsubscript{2}$O$_\textsubscript{2}$. The lines indicate the main Raman shifts (in cm$^{-1}$) expected for Fe$_\textsubscript{3}$O$_\textsubscript{4}$ and γ-Fe$_\textsubscript{2}$O$_\textsubscript{3}$ [13,32].](image)
Addition of $10^{-3}$ M $\text{H}_2\text{O}_2$ leads first to a degradation of the outer passivating layer allowing a thickening of the inner layer. This is then followed by the slow repair of the outer layer as its Fe$^{III}$ content steadily increases with time. A stronger signal for Fe$_3\text{O}_4$ in the Raman spectrum is consistent with an inner layer thickening.

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References


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