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THE ANODIC OXIDE FILM ON IRON IN NEUTRAL SOLUTION

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Abstract—The composition of the anodic passive oxide film on iron in neutral solution has been investigated by cathodic reduction, chemical analysis and ellipsometry. The cathodic reduction using a borate solution of pH 6.35 containing arsenic trioxide as inhibitor estimates iron in the film to be all iron (III), indicating that no magnetite layer is present. Oxygen in the film is estimated from the ellipsometric thickness to be in excess of the stoichiometric ferric oxide, suggesting the presence of bound water. The average composition is represented as $\text{Fe}_2\text{O}_3 \cdot 0.4 \text{H}_2\text{O}$, in which hydrogen may be replaced partly with iron-ion vacancy. The anodic oxide film is composed of an inner anhydrous ferric oxide layer, which thickens with the potential and an outer layer of hydrous ferric oxide whose thickness depends on the condition of passivation and environment.

The anodic oxide film formed in the oxygen-potential region has also been measured by cathodic reduction, and it is found that the film retains nearly constant thickness above a critical potential where transpassive dissolution begins to occur.

Résumé—La composition des films passifs d'oxyde anodique engendrés sur le fer dans une solution neutre a été étudiée par réduction cathodique, analyse chimique et ellipsométrie. La réduction cathodique avec une solution au borate de pH 6,35 contenant du trioxyde d'arsenic comme inhibiteur, prouve que le fer présent dans le film est entièrement sous forme de fer (III), ce qui indique qu'il n'y a aucune couche de magnétite. A partir de l'épaisseur ellipsométrique, on estime que l'oxygène présent dans le film est en excès par rapport à l'oxyde ferrique stœchiométrique, ce qui suggère la présence d'eau liée. La composition moyenne est représentée par la formule $\text{Fe}_2\text{O}_3 \cdot 0,4 \text{H}_2\text{O}$, dans laquelle l'hydrogène peut être substitué partiellement par une lacune ion-fer. Le film d'oxyde anodique est composé d'une couche d'oxyde ferrique anhydre interne, qui épaissit avec le potentiel et d'une couche externe d'oxyde ferrique hydraté dont l'épaisseur dépend des conditions de passivation et de l'environnement.

Le film d'oxyde anodique formé dans la région du potentiel de l'oxygène a aussi été mesuré par réduction cathodique et on trouve que le film conserve une épaisseur presque constante au-dessus d'un potentiel critique où une dissolution transpassive commence à se manifester.

Zusammenfassung—Die Zusammensetzung anodischer, passiver Oxydfilme auf Eisen in neutralen Lösungen ist mittels kathodischer Reduktion, chemischer Analyse und Ellipsenmessung untersucht worden. Die kathodische Reduktion, welche eine borsäure Lösung von pH 6,35 mit einem Arsenitrioxyd Gehalt als Inhibitor enthält, führt zu der Schätzung, dass das Eisen in dem Film völlig Eisen (III) ist und zeigt an, dass keine magnetische Schicht vorhanden ist. Sauerstoffgehalt wird in dem Film nach Ellipsenmessungsstärke höher als das stöchiometrische Eisenoxyd geschätzt und lässt auf Vorhandensein von gebundenem Wasser schliessen. Die durchschnittliche Zusammensetzung wird als $\text{Fe}_2\text{O}_3 \cdot 0,4 \text{H}_2\text{O}$ gegeben, in welcher Wasserstoff teilweise mit Eisenionen Leerstellen ersetzt werden kann. Der anodische Oxydfilm setzt sich aus einer inneren, anhydrischen Eisenoxyschicht zusammen, welche mit der Spannung dicker wird, und einer Aussenschicht von wasserhaltigem Eisenoxyd, dessen Stärke von den Umständen der Passivierung und Umgebung abhängt.

Per anodische Oxydfilm, der in der Sauerstoff-Potential Region gebildet wurde, ist auch mit kathodischer Reduktion gemessen worden, und es wurde gefunden, dass der Film über ein kritisches Potential hinaus, wo transpassive Lösung beginnt, fast konstante Stärke beibehält.

1. INTRODUCTION

FOR THE composition of anodic passive oxide films on iron in aqueous solution a composite layer model comprising inner magnetite and outer ferric oxide has been suggested from thermodynamic considerations¹ and cathodic reduction experiments² of the film. In a previous paper,³ however, we demonstrated by means of cathodic reduction combined with ellipsometry that the anodic oxide film on iron in neutral

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solution is a layer of partially hydrated iron (III) oxide rather than a composite layer of magnetite and ferric oxide.

This paper presents additional evidence that indicates more clearly all the iron to be ferric in the anodic oxide film, estimates the average composition of the film, and proposes a model that consists of an inner layer of anhydrous ferric oxide and an outer hydrous ferric oxide. Furthermore, the paper provides information on the anodic oxide film formed in the oxygen-potential region.

2. EXPERIMENTAL TECHNIQUE

The materials, apparatus and methods were essentially the same as those in previous papers.^{3,4} The specimen was a polycrystalline iron of 99.9% purity in the form of sheet $50 \times 10 \times 1$ mm, annealed and electropolished before measurement. The solutions were mixtures of 0.15 N boric acid and 0.15 N sodium borate with or without sodium hydroxide, their pH being from 5.45 to 10.45. They were de-aerated practically completely by purified nitrogen gas before transfer into the 60-ml glass cell.

The specimen surface free from oxide films was made by cathodic reduction as reported previously,³ and the anodic oxide film was formed on it by potentiostatic oxidation for 1 h. The film was then cathodically reduced and the solution was analysed for iron as a function of cathodic charge.

All the measurements were carried out at $25 \pm 1^\circ\text{C}$. Potentials are referred to the saturated calomel electrode.

The notation used is as follows. L is the film thickness measured by ellipsometry, E the potential referred to sce, i_a and i_c the anodic and the cathodic cd, Q_a and W_{Fe}' the amount of charge passed and of iron dissolved during anodic oxidation, Q_f the charge of oxide film estimated as $Q_f = Q_a - Q_{\text{Fe}}$ where Q_{Fe} is the charge equivalent to W_{Fe}' (valid except in the oxygen-potential region), Q_c and Q_{Fe} the amount of charge passed and of iron reductively dissolved from the film during cathodic reduction, $W_{\text{Fe(max)}}$ the maximum amount of iron reductively dissolved from the film, W_{Fe}^T the calculated amount of iron in the film from Q_f assuming iron (III), and Q_c° the cathodic charge required for the induction period of reductive dissolution of the film.

3. RESULTS AND DISCUSSION

Cathodic reduction behaviour

Effect of current density. The anodic oxide film was formed by 1-h potentiostatic oxidation at +0.85 V in the solution of pH 8.42 with the anodic charge $Q_f = 7.39$ mC/cm², equivalent to iron (III), $W_{\text{Fe}}^T = 1.425$ $\mu\text{g}/\text{cm}^2$. It was then cathodically reduced at various constant cds in the same solution and the amount of iron W_{Fe} reductively dissolved from the film was measured as a function of cathodic charge Q_c .

The results are shown in Fig. 1, where a potentiostatic reduction curve at -0.90 V is also shown for comparison. The broken line indicates the calculated curve for reductive dissolution of ferric oxide at 100% current efficiency by the reaction $\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e} \rightarrow 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$.

The current efficiency estimated from the linear part of the W_{Fe}/Q_c curves at this pH is not 100% but about 80%, independent of the cd. The maximum amount of iron dissolved from the film, $W_{\text{Fe(max)}}$, is seen however to depend on the cd. It increases with decreasing cd, but $W_{\text{Fe(max)}} = W_{\text{Fe}}^T$ is not attainable in this solution even at very small cd.

FIG. 1. Effect of current density on the cathodic reduction of anodic oxide film represented by potential E and amount of iron W_{Fe} reductively dissolved from the film as a function of cathodic charge Q_c , $W_{\text{Fe(max)}}$ being the maximum amount of iron from the film and W_{Fe}^T the amount of iron calculated from anodic charge Q_f of the film assuming iron (III).

The film was formed at $+0.85 \text{ V(sce)}$ and reduced at various current densities in 0.15 N boric-borate solution of $\text{pH } 8.42$.

Effect of pH. The anodic oxide film, formed at $+0.655 \text{ V}$ in the solution of $\text{pH } 8.42$ with $Q_f = 6.27 \text{ mC/cm}^2$ and $W_{\text{Fe}}^T = 1.210 \mu\text{g/cm}^2$, was cathodically reduced at a constant cd of $5.6 \mu\text{A/cm}^2$ in the solutions of various pH . Figure 2 gives the results. The current efficiency is seen to increase with decreasing pH towards its limit of 100% , which is attained at $\text{pH } 6.35$. $W_{\text{Fe(max)}}$ also increases with decreasing pH . Figure 3 shows the pH dependence of the ratio, $W_{\text{Fe(max)}}/W_{\text{Fe}}^T$, as well as the current efficiency, η , wherein the suggestion is made that $W_{\text{Fe(max)}}$ would become equal to W_{Fe}^T at solution pH less than 6.35 .

Experimentally, however, W_{Fe} continues to increase and exceeds W_{Fe}^T , though closer examination reveals that the rate, dW_{Fe}/dQ_c differs before and after W_{Fe} exceeds W_{Fe}^T . This is probably due to the dissolution of underlying iron, which would occur at an appreciable rate in acid solution. To confirm the dissolution of iron from its bare surface, comparison was made of the rate of increase of dissolved iron in the final stage of cathodic reduction with the rate of dissolution of the iron having no surface oxide under the same condition of cathodic current and pH . Figure 4 gives the result, which shows the same rate of iron dissolution for the two cases. Therefore, we attribute the excess amount of W_{Fe} over W_{Fe}^T to the dissolution of metallic iron, which immediately follows the reductive dissolution of the film.

FIG. 2. Effect of solution pH on the cathodic reduction of anodic oxide film represented by E/Q_c and W_{Fe}/Q_c curves. Curve 1 is for pH = 6.35, 2 for pH = 7.45, 3 for pH = 8.42, 4 for pH = 9.37, 5 for pH = 10.05 and 6 for pH = 10.45. The film was formed at +0.655 V(sce) at pH 8.42 and reduced at $5.6 \mu\text{A}/\text{cm}^2$ at various pH in 0.15 N boric-borate solution.

FIG. 3. Current efficiency η and ratio $W_{Fe(max)}/W_{Fe}^T$ in the cathodic reduction of anodic oxide film as a function of solution pH: data corresponding to those in Fig. 2.

FIG. 4. Comparison in the rate of iron dissolution between the final stage of cathodic reduction of the film-covered iron and the cathodic polarization of the bare iron in 0.15 N boric-borate solution of pH 6.35, showing them to be identical. The film was formed at +0.655 V(sce) at pH 8.42 and reduced at $5.6 \mu\text{A}/\text{cm}^2$ at pH 6.35; the bare iron was polarized cathodically at $5.6 \mu\text{A}/\text{cm}^2$ at pH 6.35.

Cathodic reduction for analysing the anodic oxide film

The results mentioned above have led us to assume that cathodic reduction in the solution of pH 6.35, if performed without any dissolution of iron substrate, would enable the total amount of iron in the film to be measured by analysing the solution

FIG. 5. Effect of various inhibitors on the cathodic reduction of anodic oxide film in 0.15 N boric-borate solution at pH 6.35. $\circ$ = without inhibitor. Δ = 1.3×10^{-2} mol/l pyridine, ∇ = 3×10^{-2} mol/l HCHO, $\square$ = 1×10^{-4} mol/l NaCl. The film was formed at +0.655 V(sce) at pH 8.42 and reduced at $5.6 \mu\text{A}/\text{cm}^2$ at pH 6.35 with or without inhibitor.

for dissolved iron ion, and it follows that if the total amount of iron $W_{\text{Fe(max)}}$ thus measured is equal to W_{Fe}^{T} calculated from the anodic charge Q_f assuming iron (III), then all the iron in the film must be in the form of iron (III).

This was examined by using the solution of pH 6.35 but containing various inhibitors. Figure 5 gives some results, in which pyridine, formaldehyde and sodium chloride are seen to inhibit, although not completely, the dissolution of the iron substrate. The best inhibitor we found is arsenic trioxide, dissolved as HAsO_2 or AsO_2^- in neutral solution. Figure 6 shows, for arsenic trioxide inhibition, the cathodic reduction curves of the films formed at pH 8.42 and pH 10.30 with the same Q_f and hence the same W_{Fe}^{T} . W_{Fe} is seen to increase with Q_c , initially very slowly, indicating

FIG. 6. Cathodic reduction of anodic oxide film in 0.15 N boric-borate solution of pH 6.35 containing 4×10^{-4} mol/l As_2O_3 as inhibitor, showing establishment of $W_{\text{Fe(max)}} = W_{\text{Fe}}^{\text{T}}$.

The films were formed at +0.655 V(sce) at pH 8.42 (○) and 10.30 (●), and reduced at $5.6 \mu\text{A}/\text{cm}^2$ at pH 6.35.

an induction period that depends on the pH of film formation, then at 100% current efficiency until a sudden drop in the rate occurs, and finally reaching W_{Fe}^{T} . The sudden drop in the current efficiency, which also corresponds to a break in the E/Q_c curve, is probably due to the cathodic reduction of HAsO_2 or AsO_2^- , which occurs on the bare part of the surface forming a protective film of arsenic on it, while the reductive dissolution of the film is still taking place on the oxide-covered part of the surface.

From the results shown in Fig. 6, it is made clear that all the iron ions in the film are in the state of iron (III) with a negligibly small amount of iron (II). Furthermore, the above results lead us to recommend the use of boric-acid-sodium-borate solution of pH 6.35 with As_2O_3 of 4×10^{-4} mol/l for the estimation of iron in the anodic oxide film by means of cathodic reduction.

Anodic oxide films in the oxygen potential region

By making use of the solution recommended above we measured the anodic oxide film formed in the oxygen-potential region; the film in this region had not yet been

made clear. The anodic oxide film was formed by 1-h potentiostatic oxidation in the solutions of pH 7.45, 8.42 and 9.37, and the solution was then analysed for iron to estimate the anodic dissolution in this potential region. After changing the solution to the solution of pH 6.35 containing As_2O_3 the film was cathodically reduced and the amount of iron in the film was estimated.

Figure 7 gives the results. Immediately above the onset potential of oxygen evolution, the anodic oxide film appears to thicken. However, above a critical potential, where transpassive dissolution begins to occur, the anodic oxide film ceases to thicken and maintains a nearly constant thickness independent of the potential. The onset of transpassive dissolution of iron is at about +1.3 V, which potential appears to be independent of the solution pH.

FIG. 7. Anodic oxide film and transpassive dissolution of iron as a function of potential in the oxygen-evolution region, Q_t being the anodic charge equivalent to iron in the film estimated by cathodic reduction and W'_{Fe} the amount of iron dissolved during 1-h potentiostatic anodic oxidation. $\circ \bullet$ = pH 7.45, $\triangle \blacktriangle$ = pH 8.42, $\square \blacksquare$ = pH 9.37.

We notice that in a potential region where the anodic oxide film loses its passivating property the film thickness does not increase with rise of the potential. This fact can be explained by a mechanical theory of film breakdown previously proposed by one of the authors (N. S)⁶, which has described thermodynamically the existence of a critical thickness above which the anodic oxide film breaks as a result of mechanical deformation due mainly to the high electrostriction pressure.

Composition of anodic oxide films

Figure 8 shows the film thickness L measured by ellipsometry and the anodic charge Q_t by coulometry of the anodic oxide films formed by 1-h potentiostatic oxidation at various potentials in the solutions of various pH. Both L and Q_t are seen to increase with the potential but appear not to depend on the solution pH at which the film is formed.

FIG. 8. Film thickness L estimated by ellipsometry and anodic charge Q_f estimated by coulometry as a function of potential in the passivity region.

Iron was potentiostatically oxidized for 1 h in 0.15 N boric-borate solutions of various pH. $\circ \bullet = \text{pH } 7.45$, $\triangle \blacktriangle = \text{pH } 8.42$, $\square \blacksquare = \text{pH } 9.37$, $\nabla = \text{pH } 10.45$.

Since all the iron ions in the film are iron (III), as established above, the amount of iron in the film can be estimated from the anodic charge Q_f . Furthermore, from the ellipsometric film thickness L we can estimate the amount of oxygen in the film, assuming an fcc lattice of oxygen with lattice constant $4.16 \text{ \AA}$,⁶ which gives the number of oxygen atoms for unit thickness, $n_0 = 5.56 \times 10^{14} \text{ oxygen/\AA} \cdot \text{cm}^2$. Calculation was thus made based on the data shown in Fig. 8 assuming the surface roughness factor to be 1.00.

TABLE 1. IRON AND OXYGEN IN ANODIC OXIDE FILMS ESTIMATED FROM Q_f AND L .

THE FILMS WERE FORMED AT CONSTANT POTENTIAL IN 0.15 N BORIC-BORATE SOLUTION OF pH FROM 7.45 TO 10.45. VALUES OF Q_f AND L ARE THE AVERAGES OF SEVERAL MEASUREMENTS. N_{Fe} AND N_0 ARE THE NUMBERS OF IRON AND OXYGEN ATOMS, AND x THE EXCESS OF OXYGEN REPRESENTED AS $\text{Fe}_2\text{O}_{3+x}$ OR $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

E_a V	Q_f mC/cm^2	N_{Fe} no/cm^2	L $\text{\AA}$	N_0 no/cm^2	N_0/N_{Fe}	x $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
-0.2	3.50	0.73×10^{16}	22.5	1.25×10^{16}	1.71	0.43
-0.1	3.95	0.82	25.0	1.39	1.70	0.39
0	4.30	0.89	27.0	1.50	1.69	0.38
0.1	4.68	0.98	29.5	1.64	1.68	0.36
0.2	4.97	1.04	32.0	1.78	1.71	0.43
0.3	5.35	1.11	34.0	1.89	1.70	0.39
0.4	5.72	1.19	36.5	2.03	1.71	0.42
0.5	6.04	1.25	39.0	2.17	1.74	0.46
0.6	6.37	1.33	41.5	2.31	1.74	0.48
0.7	6.75	1.40	43.7	2.43	1.74	0.47
0.8	7.15	1.49	46.0	2.56	1.72	0.44
Mean					1.71	0.42

Table 1 gives the results of calculation. It is evident that oxygen in the film is in excess of stoichiometric anhydrous ferric oxide. For the film to be stoichiometric and electrically neutral the excess oxygen has to be associated with proton to form partially hydrated ferric oxide, the average composition of which is given by $\text{Fe}_2\text{O}_3 \cdot 0.4 \text{H}_2\text{O}$ or $\text{Fe}_2\text{O}_3 \cdot 1.4 \text{FeOOH}$.

Hydrogen in the film has been measured to be represented as $\text{Fe}_2\text{O}_3 \cdot 0.2 \text{H}_2\text{O}$ by Yolken, Kruger and Calvert⁷ and as $\text{Fe}_2\text{O}_3 \cdot 1.99 \text{H}_2\text{O}$ by Kudo, Shibata, Okamoto and Sato.⁸

Non-stoichiometric excess oxygen

The anodic oxide films formed in the solutions of various pH but at the same potential of +0.655 V with the same Q_f were cathodically reduced galvanostatically using the solution of pH 8.42. Figure 9 gives the results, which reveals that the solution pH of film formation has no influence on the film except for the induction period appearing in the initial stage of the reductive dissolution of the film. Figure 10 shows more closely the induction period, wherein the charge Q_o° required for the induction period is estimated by extrapolation; Q_o° is not affected by the cd and pH of the cathodic reduction, as observed in Figs. 1 and 2. During the induction period both L and W_{Fe} remain nearly constant at their initial values, suggesting that Q_o° is non-faradaic.

FIG. 9. Effect of solution pH of film formation on the anodic oxide film appearing in the initial stage of its cathodic reduction.

The films were formed at +0.655 V(sce) at various pH ($\circ$ = pH 7.45, $\triangle$ = pH 8.42, $\square$ = 9.37, ∇ = 10.45) and reduced at $5.6 \mu\text{A}/\text{cm}^2$ at pH 8.42 in 0.15 N boric-borate solution.

Since Q_o° is much larger than a simple electrical double-layer charge, we assume a capacitive charge due to sorption and desorption of proton,⁷ which may be written

where $\text{O}_{\text{ex}}^{2-}$ is the excess oxygen ion not associated with proton. It follows then that the concentration of $\text{O}_{\text{ex}}^{2-}$ increases with the pH as well as the potential. Figure 11

FIG. 10. Detail of the induction stage of cathodic reduction of anodic oxide film in terms of film thickness L and amount of iron W_{Fe} as a function of cathodic charge Q . The film was formed at $+0.85$ V(sce) at pH 8.42 and reduced at $5.6 \mu\text{A}/\text{cm}^2$ at pH 8.42 in 0.15 N boric-borate solution.

FIG. 11. Non-stoichiometric excess oxygen in anodic oxide film represented by ratio Q_c^0/Q_t as a function of potential and solution pH of film formation, Q_c^0 being the charge for the induction stage of cathodic reduction. $\circ$ present work; $\square$ from results by Nagayama and Cohen.² The films were formed potentiostatically for 1 h in 0.15 N boric-borate solution, at several potentials at pH 8.42 and at several pH values for potential $+0.655$ V(sce).

gives the ratio Q_o°/Q_t as a function of pH and potential, which is in qualitative agreement with the assumption that Q_o° corresponds to O_{ex}^{2-} .

The excess oxygen ion not associated with proton makes the film non-stoichiometric, and the extent of non-stoichiometry may be estimated from Q_o° ; the ratio of O_{ex}^{2-} to Fe^{3+} in the film is $(3/2) \cdot (Q_o^\circ/Q_t)$.

Film thickness depending on the speed of passivation

The thickness of anodic oxide films on iron depends not only on the potential of anodic oxidation but also on the speed at which the potential is set by potentiostat

FIG. 12. Effect of the speed of passivation on the thickness of anodic oxide film represented by anodic charge Q_t as a function of potential.

The films were formed potentiostatically in 0.15 N boric-borate solution of pH 7.45 with transition times of 1–2 s and 8–10 s for potential setting.

jumping over the active dissolution region. As shown in Fig. 12, the slower the speed of setting the potential, then the film becomes thicker even for the same duration of anodic oxidation. This is caused by anodic deposition of ferric oxide from ferrous ion dissolved from the metal in the active potential region, the amount of which increases with decreasing speed of passivation.

It is therefore reasonable to assume that the film consists of two layers, one whose thickness depends on the potential and the other whose thickness is determined by the anodic oxidation of ferrous ion in the solution¹⁰⁻¹² rather than by the anodic oxidation of metallic iron.

4. A MODEL OF THE ANODIC OXIDE FILM

From the present results and the results in previous papers^{3,4} we can make a model of the anodic oxide film on iron, which is schematically represented in Fig. 13. The

FIG. 13. Model of the anodic oxide film on iron and distribution of space charge, potential ϕ , and bound water. The inner layer is anhydrous ferric oxide with negative space charge and the outer layer is hydrous ferric oxide with bound water.

inner layer is anhydrous ferric oxide probably containing some amount of excess oxygen depending on the potential, and its thickness is determined by the potential. The outer layer is of hydrous ferric oxide containing bound water, the thickness of which is rather independent of the potential; this would grow to a considerable bulk in the presence of ferrous ion in the solution. The boundary between the layers, of course, will not be distinct, through the layers diffusing into each other.

The metal in contact with the semiconducting anhydrous or hydrous oxide, when polarized anodically, causes the accumulation of a negative charge in the space-charge layer in the oxide, the thickness of which, as represented by the Debye length, increases with decrease of the concentration of relatively free charge carriers, *ie* electrons and protons. Bound water in the oxide may serve as donor of electrons as well as protons. Protons will diffuse out of the space-charge layer leaving excess oxygen ions, which pull iron ions from the metal. At very high anodic field, most of the space charge will consist of excess oxygen ions because of depletion of free electrons. The potential profile across the film has been discussed in a previous paper,³ in which the inner layer is an electrically and ionically limiting barrier layer across which most of the anodic overvoltage develops.

5. CONCLUSIONS

A solution is recommended for the cathodic reduction to estimate the amount of iron in the film; this is a sodium-borate-boric-acid mixture of pH 6.35 containing arsenic trioxide as inhibitor.

Iron in the film is all ferric and oxygen is in excess of stoichiometric ferric oxide; hence hydrogen may be associated with excess oxygen to form bound water. The average composition is given by $\text{Fe}_2\text{O}_3 \cdot 0.4 \text{H}_2\text{O}$ or $\text{Fe}_2\text{O}_3 \cdot 1.4 \text{FeOOH}$.

Any excess oxygen not associated with hydrogen makes the composition non-stoichiometric; this increases with potential and with solution pH.

The film may be divided into two layers, an inner layer of anhydrous ferric oxide which thickens with increase of potential, and an outer layer of hydrous ferric oxide whose thickness depends on the solution environment. It is across the inner layer in which most of the overpotential develops.

The thickness of the film formed in the oxygen-evolution region ceases to increase and becomes potential-independent above a critical potential where the film loses its passivating property and transpassive dissolution of iron occurs.

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