

## Passivity of Iron

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The nature of the “passive” oxide film on iron has been the subject of investigation since Schonbein and Faraday (1,2) first developed the theory of a protective oxide skin. It is now generally accepted that passivity is due to the presence of a thin oxide film 1-4 nm thick which isolates the metal surface from a corrosive aqueous environment. This paper will provide a brief historical perspective of the developments in understanding the nature of the passive oxide film.

As pointed out in previous surveys (3-5), early work dealing with the electrochemistry of iron was done in acid solution, but over the last 30 years studies have been carried out mainly in neutral buffered solution. A major impetus for work in neutral solutions came from the research of Nagayama and Cohen (6) using a pH 8.4 sodium borate-boric acid buffer solution. They considered that in the passive region iron is covered by a thin film of cubic oxide of the  $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  type, the same type of film that is formed by the reaction of clean iron with oxygen or dry air. Other compositions and structures were proposed for the passive film, some involving the inclusion of hydrogen (7,8) or the presence of water (9). In fact, the composition of the passive film on iron depends on the type of electrochemical treatment for forming the film and the nature of the solution in which it is formed. There may even be problems with passivation of iron in pH 8.4 borate buffer if the anodic treatment allows the dissolution of substantial amounts of  $\text{Fe}^{2+}$ . In such a situation,  $\text{Fe}^{2+}$  ions in solution may anodically deposit on the surface to give an outer  $\gamma\text{-FeOOH}$  layer (10).

Some of the most important developments over the past 30 years in the study of passivity have been the use and application of surface analytical techniques, scanning probe microscopy and synchrotron radiation studies. For example, Auger electron spectroscopy (11, 12), Mössbauer spectroscopy (13-15), secondary ion mass spectrometry (16-18), extended X-ray absorption fine structure (4, 19) and surface enhanced Raman spectroscopy (20) have been used to obtain detailed, although sometimes contradictory, information regarding the composition of the passive film on iron. However, taking into account the possibility of  $\text{Fe}^{2+}$  deposition, and the fact that films formed at lower potentials are unstable in air (21), the data in general support the duplex, cubic oxide structure proposed by earlier workers (4, 6, 22, 23).

More recent studies have used in-situ and ex-situ scanning tunneling microscopy (24) and synchrotron X-ray scattering and X-ray absorption near-edge spectroscopy to study passive films (5, 25, 26) and artificial iron oxide films (27) in borate buffer solutions. In-situ STM at intermediate potentials after passivating at high potentials showed the same lattice on a large number of areas (24). The structure is consistent with a  $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  structure of the passive film and the results refute the suggestion of a highly disordered or amorphous passive film. X-ray scattering data (5, 25) are consistent with a spinel oxide ( $\gamma\text{-Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4$ , or related structure) and inconsistent with other crystalline bulk oxides, hydroxides or oxyhydroxides. However, the data demonstrate that neither  $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ , nor any

combination of these phases can adequately describe the experimental results. A new spinel phase with a fully occupied oxygen lattice, octahedral site occupancy of  $80\pm 10\%$ , tetrahedral site occupancy of  $66\pm 10\%$  and an octahedral interstitial site occupancy of  $12\pm 4\%$  is proposed (5). The passive film according to this model is therefore related to  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ , but has notable different occupancies of octahedral, tetrahedral, and interstitial sites. This detailed structure of the oxide formed in borate buffer underscores the progress that has been made over the last 160+ years to improve our understanding of the nature of passive films.

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