INTERACTIONS OF CLEAN AND SULFUR-MODIFIED REACTIVE METAL SURFACES WITH AQUEOUS VAPOR AND LIQUID ENVIRONMENTS: A COMBINED ULTRA-HIGH VACUUM/ELECTROCHEMISTRY STUDY

DISSERTATION

Presented to the Graduate Council of the University of North Texas in Partial Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

Tien-Chih Lin, B.S., M.S.
Denton, Texas
May, 1998

Corrosion has been one of the long-standing problems in the industry. It is particularly important to gain a fundamental understanding of interfacial chemical reaction pathways governing corrosion and passivation at surfaces of iron or nickel-based materials in aqueous environments.

The focus of this research is to explore the molecular-level interactions between reactive metal surfaces and aqueous environments by combined ultra-high vacuum/electrochemistry (UHV-EC) methodology. The objectives of this work are to understand (1) the effects of sulfate ions on the passivity of metal oxide/hydroxide surface layer, (2) the effects of sulfur-modification on the evolution of metal oxide/hydroxide surface layer, and (3) the effects of sulfur adsorbate on cation adsorption at metal surfaces.

A consistent method for the quantitative analysis of the Fe(2p) and O(1s) core level XPS spectra has been developed and successfully applied to the analysis of thin iron oxide films. XPS analyses of the iron oxide films formed by O2 exposures in UHV reveal that the films are predominantly trilayers of FeO, Fe3O4 and FeOOH phases.

Iron electrodes passivate in a borate buffered electrolyte. The presence of sulfate ions leads to enhanced anodic dissolution of iron, along with an increased hydroxylation
of the surface film. Pitting of the iron surface is observed. Exposure to sulfate results in
inhibited passivation of iron in pure borate.

The presence of sulfur on an iron surface leads to the enhanced anodic dissolution
in a borate electrolyte. The iron dissolution current is found to vary in a non-linear
manner with sulfur coverage. XPS data reveal that an abrupt change in the anodic
dissolution current and in the surface composition at 64% of sulfur coverage. Sulfur
adsorbed on nickel inhibits the NiO formation, which results in the enhanced nickel
dissolution in aqueous solutions. The adsorption of lead is enhanced by as much as
1200% when the nickel is modified by a monolayer of sulfur.
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# TABLE OF CONTENTS

| LIST OF TABLES | vi |
| LIST OF FIGURES | vii |

## Chapter

1. INTRODUCTION ................................................................. 1

1.1. Corrosion and Passivation ........................................... 3
1.2. Adsorbate-Modified Metal Surfaces ................................ 5
1.3. Combined Ultra-High Vacuum/Electrochemistry (UHV-EC) .... 7
   1.3.1. Apparatus ......................................................... 7
   1.3.2. Methodology .................................................... 8
   1.3.3. X-ray Photoelectron Spectroscopy .......................... 9
   1.3.4. Potential Sweep Methods .................................... 13
1.4. Chapter References .................................................. 14

2. A CONSISTENT METHOD FOR QUANTITATIVE XPS PEAK ANALYSIS
   OF THIN OXIDE FILMS ON CLEAN POLYCRYSTALLINE IRON
   SURFACES ................................................................. 19

2.1. Introduction ............................................................ 19
2.2. Experimental ........................................................... 22
2.3. Quantitative XPS Peak Analysis .................................... 24
2.4. Results and Discussion ............................................... 27
   2.4.1. The XPS Fe(2p) Shake-up Satellite Features ................. 27
   2.4.2. Atomic sensitivity factors (ASF) of Fe(2p) and O(1s) .... 29
   2.4.3. Quantitative XPS Analysis of Thin Oxide films formed by O
           Exposure in UHV ................................................. 34
2.5. Conclusions ............................................................. 41
2.6. Chapter References .................................................. 42

3. POLYCRYSTALLINE IRON ELECTRODES IN BORATE AND
   SULFATE MEDIA ............................................................ 45

3.1. Introduction ............................................................ 45
3.2. Experimental ........................................................... 47
LIST OF TABLES

| Table 2.1. | Curve fitting results and parameters for Fe(2p) and O(1s) XPS spectra of Fe₃O₄ powder sample | 31 |
| Table 2.2. | The results of quantitative XPS analysis of iron oxide film grown by different oxygen exposures | 36 |
| Table 2.3. | Curve fitting parameters for XPS Fe₂p₃/₂ spectra and oxide film composition as a function of oxygen exposure | 37 |
| Table 3.1. | Surface composition as determined by XPS of iron in borate buffer | 52 |
| Table 3.2. | Surface composition as determined by XPS of iron in borate buffer contaminated with 0.05M sulfate ions | 60 |
| Table 4.1. | Composition of the surface overlayer on a 100% sulfur-saturated iron surface as a function of emersion potential from a borate buffer of pH 8.4 | 85 |
| Table 4.2. | Results of XPS analysis of Inconel 600 | 96 |
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1.</td>
<td>Schematic polarization curve of anodic metal dissolution in solutions</td>
</tr>
<tr>
<td>Figure 1.2.</td>
<td>Adsorbates (A) act as site-blockers in UHV and hinder the formation of adsorbed oxygen (Oₐ) via water dissociation</td>
</tr>
<tr>
<td>Figure 1.3.</td>
<td>Schematic of the apparatus for combined ultrahigh vacuum and electrochemistry (UHV-EC) methodology</td>
</tr>
<tr>
<td>Figure 1.4.</td>
<td>Schematic representation of the x-ray photoelectron process for a carbon atom</td>
</tr>
<tr>
<td>Figure 2.1.</td>
<td>XPS Fe(2p) spectra of clean Fe, oxidized Fe by 10⁴ L of O₂ exposure and Fe₃O₄ powder sample. (S = Shake-up Satellite, II and III indicate the oxidation state of Fe)</td>
</tr>
<tr>
<td>Figure 2.2.</td>
<td>XPS Fe(2p) spectra of (a) electrochemically modified Fe²⁺-rich electrode and (b) electrochemically modified Fe³⁺-rich electrode. The Fe electrode was cycled 8 times (-1.4V to 0.9V vs. Ag/AgCl, 50mV/sec) in borate buffer and emersed at -1.4V to produce Fe²⁺-rich oxides. The Fe³⁺-rich oxide was produced by 2 linear scan and the Fe electrode was emersed at 0.9V</td>
</tr>
<tr>
<td>Figure 2.3.</td>
<td>XPS Fe(2p) and O(1s) spectra of Fe₃O₄ powder sample</td>
</tr>
<tr>
<td>Figure 2.4.</td>
<td>XPS Fe(2p) and O(1s) spectra of polycrystalline iron as a function of oxygen exposures. The spectra were recorded at 60° take-off angle. (d is the thickness of oxide overlayer)</td>
</tr>
<tr>
<td>Figure 2.5.</td>
<td>The oxides growth as a function of oxygen exposures at the pressure of 10⁻⁷ torr. The thickness of oxide film was calculated by assuming an inelastic mean free path of 2.0 nm for the Fe(2p) photoelectron in the oxide film</td>
</tr>
<tr>
<td>Figure 3.1.</td>
<td>(a) Cyclic voltammogram of a clean iron electrode in borate buffer pH 8.4. (b) Cyclic voltammogram of an iron electrode in a solution of 0.05 M Na₂SO₄ in borate buffer pH 8.4.</td>
</tr>
</tbody>
</table>
This electrode was previously cleaned to atomic level in UHV, cycled in borate 16 times and emersed at 0.9 V. (c) Same as in Figure 3.1b, except second exposure to sulfate, see text for details.

Figure 3.2. XPS spectra of iron in borate buffer, corresponding to the experiments described in Table 3.1. (1) 8 cyclic scans, emersed at -1.4V. (2) 16 cyclic scans and 2 linear scans, emersed at 0.9V. (3) 16 cyclic scans and 1 linear scan, emersed at 0.9V. (4) Held at 0.5V for 10 minutes, emersed at 0.5V. (5) 16 cyclic scans and 2 linear scans, emersed at 0.9V. All other experimental conditions as described in Table 3.1.

Figure 3.3. (a) XPS spectrum of the Fe(2p) and O(1s) regions, of an Fe electrode after 16 cyclic scans and 2 linear scans in the borate buffer pH 8.4. (b) XPS spectrum of the Fe(2p) and O(1s) region after the electrode in Figure 3.3a was subjected to 5 cyclic scans and 2 linear scans in a borate solution containing 0.05 M Na$_2$SO$_4$. (c) XPS spectrum of an iron electrode cleaned in UHV and scanned directly in a borate solution containing 0.05M Na$_2$SO$_4$. The number of scans was the same as in Figure 3.3a.

Figure 3.4. XPS spectra of iron in borate buffer contaminated with 0.05M sulfate ions, corresponding to the experiments described in Table 3.2. (1) Iron with passive film, cycled in sulfate, emersed at 0.9V. (2) Same as (1) but second exposure to sulfate. (3) Clean iron cycled in sulfate, emersed at -1.4V. (4) Iron with passive film, cycled in sulfate at more noble potentials, emersed at 0.9V. (5) Same as (4) but second exposure to sulfate. All other experimental conditions as given in Table 3.2.

Figure 3.5. Cyclic voltammogram of a clean Fe electrode in a borate solution containing 0.05 M Na$_2$SO$_4$.

Figure 3.6. Cyclic voltammogram of an iron electrode cycled in borate 16 times and emersed at 0.9 V, then cycled in the borate solution containing 0.05 M sulfate at more noble potentials.

Figure 3.7. (a) Cyclic voltammogram of an Fe electrode in borate buffer pH 8.4 after corroding in sulfate followed by cleaning in UHV. (b) Same as Figure 3.7a except that the electrode had been corroded twice in sulfate followed by cleaning in UHV. The dotted lines I, II and III correspond to the peak potentials of
the most noble anodic peak in Figures 3.1, 3.7a and 3.7b respectively ................................................................. 66

Figure 4.1. Percentage of sulfur saturation (proportional to relative XPS S(2p)/Fe(2p) intensity) of the iron surface as a function of exposure time to H₂S at a dosing pressure of $6 \times 10^{-10}$ torr .......................... 77

Figure 4.2. XPS of the Fe(2p) region before and after exposure to H₂S at a dosing pressure of $1 \times 10^{-8}$ torr for 50s ................................................................. 78

Figure 4.3. (a) Linear scan voltammograms of sulfur covered iron surfaces in borate buffer (pH = 8.4). (b) same as (a) but at higher sulfur coverages ................................................................. 80

Figure 4.4. Variation of the iron dissolution current as a function of sulfur Coverage ........................................................................................................................................... 82

Figure 4.5. XPS of the S(2p) region. (a) After dosing with H₂S at a dosing pressure of $1 \times 10^{-8}$ torr for 50s. (b) After one linear scan in borate buffer (pH = 8.4) and emersing at +0.9V. (c) After partially sputtering away the oxide/hydroxide overlayer, grown as described in (b). (d) After partial electrochemical reduction of the oxide / hydroxide overlayer (grown as described in (b)), by holding the electrode at -1.4V for 10 min ....................................................... 83

Figure 4.6. XPS of the Fe(2p) and O(1s) regions after emersing the Fe electrode from a borate electrolyte (pH 8.4) at +0.9V (a) Of a clean Fe surface. (b) Of a Fe surface that was totally saturated with S by dosing at a pressure of $6 \times 10^{-10}$ torr ................................................................. 87

Figure 4.7. Surface component ratios as a function of sulfur saturation ................................................. 88

Figure 4.8. Pictorial representation of the growth of the passivation layer on iron. (a) At low S coverage. (b) At high S coverage ............................................. 91

Figure 4.9. Polarization curves of (a) clean Inconel 600 and (b) sulfur-covered Inconel 600 in borate buffer (pH=8.4) ................................................................. 94

Figure 4.10. Polarization curves of (a) clean Inconel 600 and (b) sulfur-covered Inconel 600 in acetate buffer (pH=4.4) ................................................................. 96

Figure 5.1. The amount of lead adsorbed on the sulfur-modified nickel surface from 0.001M Pb(NO₃)₂ solution as a function of number of rinses .............................. 108
Figure 5.2. XPS Pb(4f) spectra of adsorbed lead on clean and sulfur-modified nickel surfaces. The adsorption of lead was done by immersing the nickel electrodes into (a) 0.01M and (b) 0.001M Pb(NO₃)₂ solutions for 5 seconds

Figure 5.3. XPS Ni(2p₃/₂) and O(1s) spectra of clean and sulfur-modified nickel surfaces oxidized by water vapor exposure. The peak at 855.4 eV is a combination of the feature of Ni(OH)₂ and the satellite feature of NiO (see experimental section for details)

Figure 5.4. XPS results of the adsorption of lead on nickel surfaces as a function of immersion time. (a) The amount of sulfur on the nickel surface before and after immersion. (b) The amount of oxidized nickel species on clean and sulfur-modified surfaces. (c) The amount of lead on clean and sulfur-modified surfaces

Figure 5.5. Results of XPS analysis for nickel oxidation and lead adsorption on the sulfur-modified nickel surface as a function of immersion time

Figure 5.6. Open-circuit potential of clean and sulfur-modified nickel surfaces as a function of immersion time in 0.1M NaNO₃ solution (solid line) and in a solution of composition 0.001M Pb(NO₃)₂, 0.1M NaNO₃ (dashed line)

Figure 5.7. XPS Ni(2p₃/₂) spectra of clean nickel electrodes (a-b) and sulfur-modified nickel electrodes (c-d) after 20 minutes of immersion in the 0.1M NaNO₃ solution with and without Pb²⁺

Figure 5.8. A schematic representation of the reaction rate of the two partial reactions that occur on nickel surfaces in nitrate solution based on the mixed potential theory (MPT)
CHAPTER 1

INTRODUCTION

Fundamental processes at the interface between reactive metal surfaces and the aqueous vapor and liquid environments are of practical importance for many industrial and environmental applications. Such processes include the dissolution of metals, formation of oxide or hydroxide films, corrosion/passivation, adsorption of ionic species, and catalytic reduction of organic contaminants. Among them, corrosion has been a long-standing problem in the electric power industry. Particularly, the problem of intergranular stress corrosion cracking (IGSCC) is significant in both nuclear and conventional fossil fuel power plants. Therefore, a fundamental understanding of interfacial chemical reaction pathways governing corrosion and passivation at surfaces of iron or nickel-based materials in aqueous environments is particularly important. Such knowledge can provide practical insight in improved methods for corrosion inhibition and prevention.

Aqueous/solid interactions involving reactive metals (e.g. Fe, Ni) typically occur concurrent with or subsequent to the formation of an oxide or oxide/hydroxide overlayer. The modification of reactive metal surfaces with certain adsorbates (e.g. sulfur) has been shown to alter or hinder the process of surface oxidation/hydroxylation. This alternation or inhibition of surface oxide/hydroxide formation can significantly influence the fundamental interfacial properties of reactive metals. Understanding the
interactions of adsorbate-modified reactive metal surfaces with aqueous environments on a molecular level will not only permit the design of better corrosion inhibitors, but also lead to a better ability to predict and model complex interfacial properties. Such ability will also be beneficial to the design of improved catalytic materials, enhanced ionic filtration systems, and innovative electrode materials with novel chemical and electrochemical properties.

Combined ultra-high vacuum/electrochemistry (UHV-EC) methodology is used in this study to investigate the effects of surface composition and contamination on corrosion at the metal/solution interface. The UHV-EC method allows accurate modeling of chemical/electrochemical interactions at the interface between metal surface and the electrolyte solution. This is precisely the area of interest for corrosion and IGSCC in particular. IGSCC involves the stress-induced rupture of the protective oxide scale, exposure of the fresh metal at the crack tip to the solution, and metal dissolution at the crack tip. This problem may be initiated by the segregation of internal impurities to grain boundaries, leading to a catalyzed intergranular corrosion. In order to address such phenomena effectively, it is necessary to understand the relationship between the composition of a surface or grain boundary, and its electrochemical behavior in the aqueous environments of interest. The UHV-EC methodology allows us to explore such phenomena at the molecular level under realistic yet controlled conditions. The objectives of this work are to obtain detailed understanding of the following:

1. The effects of sulfate ions on the passivity of metal oxide/hydroxide surface layer.
(2) The effects of sulfur modification on the evolution of oxide/hydroxide surface layer.

(3) The effects of sulfur adsorbate on cation adsorption at metal surfaces.

This chapter is devoted to a discussion of the basic concepts and mechanisms of corrosion and passivation, the role of adsorbed sulfur on reactive metal surfaces, and the experimental aspects of UHV-EC methodology. In chapter 2, a consistent method for quantitative XPS peak analysis is developed and applied to the analysis of iron oxide films formed by oxygen gas exposure in UHV. The effects of sulfate ion on the passivation and corrosion of polycrystalline iron have been investigated and included in chapter 3. Chapter 4 contains the studies of sulfur effects on the corrosion of iron and alloy 600 in aqueous solutions. Finally, a study of lead adsorption on clean and sulfur-modified nickel surfaces is presented in chapter 5.

1.1. Corrosion and Passivation

Corrosion is an electrochemical phenomenon. Its fundamental step is anodic dissolution of an atom of metal. The metal atom dissolves as an ion into the solution, injecting electrons into the electrode. Such electrons enable a cathodic reaction to occur, such as oxygen reduction or hydrogen evolution. The pair of reactions (anodic and cathodic) is coupled not only by electrons flowing in the metal but also through conductance in the solution. Nevertheless, most practical corrosion processes are inhibited by the formation of a protective layer, usually an oxide. This passivation phenomenon can be defined in terms of the characteristic current-potential curve as seen in Figure 1.1. The passivation potential \( E_p \) is usually associated with the potential...
Figure 1.1. Schematic polarization curve of anodic metal dissolution in solutions.

corresponding to the maximum current on the curve. Below the $E_p$, the electrode

corroses at a relatively high rate. This region is defined as the active state. The current

(i.e., corrosion rate) decreases above the $E_p$ despite a higher driving force for corrosion

(i.e., high anodic polarization). This corrosion resistance above $E_p$ is defined as passivity

and is mainly due to the formation of a passivating oxide/hydroxide film.

The passive oxide film naturally formed on metals is often thin and fragile,

therefore its breakdown can result in unpredictable localized forms of corrosion,

including pitting $^{46-48}$, intergranular corrosion and stress corrosion cracking $^{49}$. Certain

anion impurities in the aqueous environment, such as halide ($\text{Cl}^-$, $\text{I}^-$, $\text{Br}^-$), sulfate ($\text{SO}_4^{2-}$)

and perchlorate ($\text{ClO}_4^-$) ions can induce the breakdown of oxide films on metals $^{15,46}$. In
the conventional model, the mechanism of this impurity-induced corrosion can be presented as follows:

\[
M + A^{n-}_{(aq)} \rightarrow MA + ne^{-} \tag{1-1}
\]

\[
MA \rightarrow MA_{(aq)} \tag{1-2}
\]

\[
MA_{(aq)} \rightarrow M^{n+}_{(aq)} + A^{n-}_{(aq)} \tag{1-3}
\]

An anion impurity \((A^{n-})\) reacts with the metal \((M)\) to form a soluble salt \((MA)\). The salt \((MA)\) is then dissolved in the aqueous solution and further dissociated into oxidized metal ion \((M^{n+})\) and the original anion impurity \((A^{n-})\). However, it has been found that corrosion at grain boundaries can occur even in situations where the aqueous solution is relatively free of corrosive anion species. Therefore, it is obvious that the conventional model shown in Equations (1-1) to (1-3) cannot be applied for the grain boundary corrosion. In many cases, pitting and intergranular stress cracking are induced not by impurities in the aqueous environment, but by internal impurities (e.g. sulfur) segregated to grain boundaries. Studies have shown a correlation between sulfur segregation to the grain boundaries of ferrous alloys and the extent of intergranular stress corrosion cracking observed in aqueous environment.

### 1.2. Adsorbate-Modified Metal Surfaces

Impurity segregation to a grain boundary, as to an external surface, is driven by the availability of surface sites with favorable bonding configuration. The situation at a grain boundary is then expressive of the situation at a surface covered with a monolayer...
of relevant adsorbate. Therefore, studies of adsorbate-modified surfaces provide a model for probing the behavior of impurity at grain boundaries. The effects of adsorbates, like halides and sulfur, on the reactivities of non-noble transition metal surfaces toward water \((H_2O)\) and other species have been investigated under UHV and aqueous conditions. As shown in Figure 1.2, such so-called “site-blocker” adsorbates on a metal surface can block the formation of adsorbed oxygen \((O_a)\) via water dissociation and slow down the initial oxidation process under UHV environments. In aqueous solution, adsorbed sulfur \((S_a)\) inhibits the formation of passivating materials on iron and a variety of iron/nickel alloys surfaces, resulting in enhanced anodic dissolution without losing the sulfur adsorbates and change in their oxidation state. The adsorbed sulfur, though nominally electronegative, is...
close to zero-valent on these metal surfaces \(^{38,42,63-65}\). In fact, work function measurements show that sulfur-metal bonds at nickel \(^{64}\) and iron \(^{63}\) surfaces involve merely \(-0.04\) electron charge transfer. The relatively covalent nature of sulfur-metal bonds may be due to the difficulty in localizing a charge at a metallic surface. This hypothesis is supported by the fact that iodine (I\(_a\)) adsorbed at a metallic surface is zero-valent \(^{66}\), but is in an ionic state when adsorbed on an oxide surface \(^{67}\). It has been reported that adsorbed zero-valent iodine (I\(_a\)) on a palladium (Pd) surface also significantly enhances anodic dissolution without change in the surface coverage and oxidation state of adsorbate \(^{66}\). However, it is not understood whether this effect is due to inhibition of water dissociation, or to some other factors.

1.3. Combined Ultra-High Vacuum/Electrochemistry (UHV-EC)

The UHV-EC methodology is used to study the effects of surface chemical composition on susceptibility to IGSCC in aqueous environments. This approach combines electrochemical and UHV measurements without intermediate sample exposure to atmosphere. This allows a direct correlation between the surface composition of a metal and its electrochemical behavior in a specific aqueous environment. This is the region of interest in IGSCC, where stress rupture of the oxide scale exposes fresh metal to the electrolyte solution at the crack tip.

1.3.1. Apparatus. The combined UHV-EC apparatus used in this research is shown schematically in Figure 1.3. The system is similar to published designs \(^{68}\) and consists of an UHV analytical system, an antechamber for the electrochemical cell, and a sample introduction chamber. The UHV system is equipped with a dual anode x-ray
source, an ion-sputtering gun, and a hemispherical energy analyzer for x-ray photoelectron spectroscopy (XPS). The design of the electrochemical cell is also included in Figure 1.3. The cell is composed of an Ag/AgCl reference electrode and a platinum counter electrode. The working electrode (sample) is attached on a transfer rod and positioned above the cell. A potentiostat is used to perform polarization and voltammetry measurements.

1.3.2. Methodology. The sample is cleaned in UHV by alternating cycles of argon ion ($\text{Ar}^+$) sputtering and annealing in the UHV system chamber. Adsorbate-modified sample surfaces are also prepared in this chamber by controlled exposure to the
vapor. Sample surface composition is then characterized by XPS under UHV. This is followed by sample transfer from UHV to the evacuated (high vacuum) electrochemical chamber, which is isolated from the UHV chamber by a gate valve. The electrochemical chamber is then pressurized with ultrapure nitrogen gas (drawn from the vapor over a liquid nitrogen cylinder). The pressure in the electrochemical chamber is maintained at about 3 psi above atmosphere by an adjustable high-pressure leak valve. The electrochemical cell is then introduced into the chamber and filled with electrolyte solution so that the meniscus of the solution in the cell wets the sample surface. This design allows electrochemical experiments to be performed without wetting the sample edges and backside, which have not been subjected to UHV sputter-anneal cleaning procedures. The transfer rod is electrically isolated by Teflon seals and acts as electrical contact to the sample as the working electrode.

Following electrochemical measurements, the electrolyte is flushed out of the cell. The cell and then the sample surface are rinsed with argon purged millipore water. This procedure removes physisorbed salts on the sample surface upon emersing the sample from the electrolyte. Rinsing is accomplished using the inlet and drain valves at the base of the cell to change the solution. After electrochemical studies are carried out, the procedure is reversed to transfer the sample back to the UHV environment. The sample surface is then characterized by XPS to study the effects of electrochemistry on the sample surface.

1.3.3. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), was
developed for analytical use in the 1960s, largely due to the pioneering work of Kai Siegbahn and his research group. Important achievements in that period of time include the development of better electron spectrometers, the realization that electron binding energies are sensitive to the chemical state of the atom, and the finding that the technique is surface sensitive. This surface sensitivity, combined with quantitative and chemical state analysis capabilities has made XPS one of the most broadly used surface analysis techniques today. XPS is the least destructive of all the electron or ion spectroscopy techniques, and can detect all elements except hydrogen and helium across the periodic table.

Surface analysis by XPS is accomplished by irradiating a sample with monoenergetic soft x-ray and analyzing the energy of the detected electrons. Mg Kα (1253.6 eV) and Al Kα (1486.6 eV) x-rays are usually used. The photoelectron process is schematically shown in Figure 1.4. A photon of sufficiently high energy (i.e. x-ray) can ionize an atom, producing an ejected free electron which is known as the photoelectron. The kinetic energy (KE) of the photoelectron depends on the energy of the photon (hv) expressed by the photoelectric law:

\[ KE = hv - BE - \phi_s \]  

(1-4)

where BE is the binding energy of the atomic orbital from which the photoelectron originates and \( \phi_s \) is the work function for spectrometer (a constant energy pre-determined for a given electron analyzer). All of photoelectron spectroscopy is based on Equation (1-4). Since hv and \( \phi_s \) are known, BE can be determined by a measurement of KE. The
XPS spectrum is obtained as a plot of the number of detected electrons versus the kinetic energy. Using Equation (1-4), a BE scale can be substituted for the KE scale.

Each element has a unique set of binding energies. The spectrum from a mixture of elements is approximately the sum of the peaks of the individual constituents. Thus, XPS can be used to identify and determine the surface composition. Variations in the elemental binding energies (the chemical shifts) originate from differences in the chemical potential and polarizability of compounds can be used to identify the chemical state of elements.70
Electrons in XPS can travel only short distance through solids before losing energy in collision with atoms. This inelastic scattering process is the reason for the surface sensitivity of XPS. Only the photoelectrons ejected from atoms close to the surface can escape unscattered and appear as the XPS peaks. Since most photoelectrons have kinetic energies in the range of 50 – 1500 eV, the mean free paths of these electrons are on the order of 4 – 20 Å (0.4 – 2 nm) based on the "universal curve" (the curve shows the mean free path of electrons for inelastic scattering in solids as a function of the kinetic energy of the emitted electron) \(^7\). Electrons originating from deeper have less chances of escaping unscattered and mostly end up in the background at lower KE after the XPS peak.

While the photoelectron is leaving the atom, the other electrons respond to the hole being created. The responses, known as "final state effects", often lead to additional features in the XPS spectrum \(^7\). An effect that always occurs is the relaxation of the surrounding electrons towards the hole. This allows the outgoing photoelectron to carry greater KE (i.e. the BE determined is lower). This indicates that the electronic state of the photoionized atom (the final state) may be different from that of the initial state (usually the atomic ground state). Nevertheless, the relaxation effects are usually neglected to simplify the interpretation of BE shifts. Spin-orbit splitting results from a coupling of the spin of the unpaired electron left behind in the orbital from which its partner has been photoejected with the angular momentum of that orbital, giving two possible different energy final states (spin up or spin down). It occurs for all levels except s levels, which has no orbital angular momentum (being spherical), turning single-
peaks into doublet peaks. For instance, the region of Fe(2p) in a XPS spectrum consists of a doublet of Fe(2p1/2) and Fe(2p3/2). Some elements, particularly the transition metals, have unpaired electron spins in their valence levels. The coupling of the unpaired electron remaining after the photoemission process will couple to any unpaired spin in the valence levels, and create an ion with several possible final state configurations and as many energies. This is called multiplet splitting.

While a core-electron is being ejected, there is a finite probability that a valence electron will be simultaneously excited to a state that is a few electron volts above the ground state. In this shake-up process, the KE of the emitted photoelectron is reduced, with the difference corresponding to the energy difference between the ground state and the excited state. This results in the formation of a “shake-up satellite” peak a few electron volts lower in KE (higher in BE) than the main peak. The displacements and relative intensities of these shake-up satellites can sometimes be useful in identifying the chemical state of an element. After the photoemission process is over, the core-hole left behind can eventually be filled by an electron dropping into it from another orbital. The energy released may be sufficient to eject another electron. This is called Auger electron emission. When doing XPS the allowable Auger process peaks are superimposed on the spectrum, and they can be used as an additional means of element analysis.

1.3.4. Potential Sweep Methods. Potential sweep techniques consist of a group of electroanalytical methods in which information can be derived from the measurement of current as a function of applied potential under conditions that encourage polarization of a working electrode. Usually the potential is varied linearly with time at a constant
The simplest potential sweep method is called linear sweep voltammetry (LSV). In this experiment, the potentiostat sweeps the cell potential from an initial potential to a final potential and measures the current that results. LSV is usually performed to observe either oxidation or reduction, based on the choice of scan direction. Cyclic voltammetry (CV) is another potential sweep technique. In this technique, the potentiostat applies a linear sweep of a programmed potential range which reverses at some point in potential and monitors the current as a function of applied potential. The major difference between LSV and CV is that both oxidation and reduction reactions can be observed in CV.

1.4. Chapter References


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CHAPTER 2

A CONSISTENT METHOD FOR QUANTITATIVE XPS PEAK ANALYSIS OF THIN OXIDE FILMS ON CLEAN POLYCRYSTALLINE IRON SURFACES

2.1. Introduction

The formation of Fe oxide thin films has been the subject of intensive study in corrosion science\textsuperscript{1-10}. X-ray photoelectron spectroscopy (XPS) has proven to be a powerful method for the study of oxidation processes\textsuperscript{11} as well as for the analysis of surface films formed by a variety of treatments\textsuperscript{12,13}. However in common with other transition metals, a significant problem in the detailed analysis of Fe XPS spectra arises from their complex nature. Spin-orbit splitting, multiple oxidation states and satellite structure complicate the quantitative analysis of Fe(2p) spectra – particularly the determination of relative Fe\textsuperscript{2+} and Fe\textsuperscript{3+} concentrations\textsuperscript{14}. This problem has been addressed in part through the use of x-ray excited valence band spectra in comparison with band structure calculations\textsuperscript{15}. Other studies have pointed out the justification for use of a different full width half maximum (FWHM) and secondary electron background of the Fe\textsuperscript{0} component in constructing simulated spectra from separate Fe\textsuperscript{0}, Fe\textsuperscript{2+} and Fe\textsuperscript{3+} components\textsuperscript{1,16,17}.

An important issue, which is unresolved by the above approaches, concerns the independent determination of relative Fe\textsuperscript{2+} and Fe\textsuperscript{3+} concentrations within the analyzed region. The uncertainty in depth distribution and consequent signal attenuation is always
a complicating factor. However, even in films of known homogeneity or extreme thinness, the actual decomposition of the Fe(2p) spectrum into Fe$^{2+}$ and Fe$^{3+}$ components is still uncertain. In addition to the complexity of the peak fitting process, which can be overcome by modern computer software, the validity and consistency of methods for quantitative XPS peak analysis are also important issues which have been discussed in the literature. Recent studies of ultra thin films formed by the exposure of Fe to O$_2$ under ultra-high vacuum (UHV) conditions have shown that small changes in FWHM values assigned to Fe$^{2+}$ and Fe$^{3+}$ component spectra result in significant variations in calculated Fe$^{2+}$/Fe$^{3+}$ relative concentrations.

In this chapter, we demonstrate a different approach for the fitting of experimental spectra in order to determine Fe$^{2+}$/Fe$^{3+}$ ratios. This approach involves a more detailed and explicit consideration of Fe$^{2+}$ and Fe$^{3+}$ shake-up satellite features in the Fe(2p) spectrum. In this study, the Fe$^{2+}$ and Fe$^{3+}$ shake-up satellites are found at binding energies approximately 5-8 eV higher than the respective main core (2p) lines (Figure 2.1), which is in agreement with the values reported by Brundle et al. In addition, we report the relationship between Fe$^{2+}$, Fe$^{3+}$ FWHM values and Fe$^{2+}$/Fe$^{3+}$ concentration ratios.

Experimental methods and XPS quantitative analysis are detailed in section 2.2 and 2.3, respectively. In section 2.4, we demonstrate the importance of the XPS Fe(2p) shake-up satellite features for an independent measurement of Fe$^{2+}$/Fe$^{3+}$ relative concentration by comparing the Fe(2p) spectra of an Fe$^{2+}$-rich oxide film to that of an Fe$^{3+}$-rich oxide film. Then the method of obtaining atomic sensitivity factors (ASF) for
Figure 2.1. XPS Fe(2p) spectra of clean Fe, oxidized Fe by $10^4$ L of O$_2$ exposure and Fe$_3$O$_4$ powder sample. (S = Shake-up Satellite, II and III indicate the oxidation state of Fe).

Fe(2p) and O(1s) from an Fe$_3$O$_4$ sample is delineated. Finally, using Fe$^{2+}$/Fe$^{3+}$ relative concentrations and ASFs for Fe(2p) and O(1s) by methods outlined above, we investigate the growth of thin oxide films on a polycrystalline iron substrate by exposure to O$_2$ in
UHV. A significant result of this study is the finding that Fe$^{2+}$ or Fe$^{3+}$ FWHM values increase with relative Fe$^{2+}$ or Fe$^{3+}$ content, reflecting the multiple nature of both Fe$^{2+}$ and Fe$^{3+}$ chemical environments within the oxide film. In addition, the binding energy (BE) of the Fe$^{2+}$ and Fe$^{3+}$ peaks systematically change with the surface oxide compositions. Apparently, these results are due to changes in relaxation energy with changes in the surrounding environment.

2.2. Experimental

A powder sample of Fe$_3$O$_4$ (Aesar, 97%) was used as received. The Fe$_3$O$_4$ sample serves as a standard for obtaining empirical atomic sensitivity factors (ASF) of Fe(2p) and O(1s). The ASF is a scale factor for computing atomic concentration of an element from its spectral peak intensity. Fe$_3$O$_4$ powder was ground with a mortar and pestle to expose fresh surfaces and pressed into an indium foil (Goodfellow, 99.999%) for analysis. To reduce the amount of physisorbed water, the Fe$_3$O$_4$ sample was left in UHV overnight before examination. This process reduces the amount of water, but does not eliminate the OH content in the powder sample. The iron oxyhydroxide phase, formed from the reaction of Fe$_3$O$_4$ and H$_2$O, is rather stable in UHV. Polycrystalline iron was obtained as a high purity foil (Puratronic 99.998%) from Aesar. The iron sample was cleaned in UHV by argon ion bombardment (2.3keV) at room temperature followed by annealing the sample to ~ 950K. This process was repeated to drive out bulk impurities, particularly sulfur and nitrogen. The XPS spectrum of the atomically clean iron surface was then obtained.
Experiments were performed in a turbo-molecularly pumped stainless steel UHV system which has been described in chapter 1 (see Figure 1.3). The base pressure of the system was $2 \times 10^{-10}$ torr after bake-out. XPS spectra were recorded using unmonochromatized Mg Kα radiation operated at 15kV and 300W with a hemispherical electron energy analyzer in the constant pass energy mode at 50 eV. The x-ray angle of incident is 54.7° relative to the analyzer axis. The sample was mounted so that the angle between the sample surface normal and the analyzer axis (the take-off angle) could be varied from 0° (the analyzer axis perpendicular to the surface) to ~ 90°. The analyzer was calibrated by referencing the Fe(2p$_{3/2}$) peak position for clean iron to 706.75 eV. The polycrystalline iron foil, with tantalum wires spot-welded on both edges of the foil, was mounted on a manipulator. The temperature was monitored by a chromel-alumel thermocouple spot-welded on the back of the sample. All experiments were carried out at room temperature (~ 298K) in this study.

In the gas-phase oxidation experiments, clean iron surfaces were oxidized by dosing O$_2$ gas (99.999%) into the UHV chamber through a precision leak valve (doser). Chamber pressure was then increased and maintained at constant pressure ($10^{-7}$ torr for 10L ~ 50L exposure, $10^{-6}$ torr for 250L ~ 1000L exposure, and $10^{-5}$ torr for 10$^4$L exposure) by adjusting the leak rate. Exposures are reported in terms of time and background pressure (1 L = $10^{-6}$ Torr • s). Chamber pressure was measured by a nude ion gauge calibrated for dinitrogen and mounted out of line-of-sight from the sample. Exposures reported here have not been corrected for different O$_2$/N$_2$ ion gauge sensitivities or flux to the sample.
Combined Ultrahigh Vacuum/Electrochemical (UHV-EC) methods were utilized to expose iron samples to aqueous solution and for the subsequent transfer back to the UHV analysis chamber without exposure to air. The details of this experimental setup have been presented in Figure 1.3. Electrochemical experiments were carried out using a Pine Instruments AFRDE5 potentiostat. Electrode potentials are reported with respect to an Ag/AgCl (0.01M NaCl) reference electrode. The oxide films were grown by extensively cycling the iron electrode between −1.4V and +0.9V in borate buffer solution. The iron oxide films emersed at hydrogen evolution potential (−1.4V) and at noble potential (+0.9V) were characterized by XPS. The borate buffers used in this study were 0.075M H$_3$BO$_3$ (Spectrum Chemical) containing 0.01875M Na$_2$B$_4$O$_7$ (Aldrich). The pH of the buffer was 8.4. All solutions were prepared from Millipore grade water and purged with argon. All chemicals were reagent grade and used as received.

2.3. Quantitative XPS Peak Analysis

Peak fitting of XPS spectra was performed using commercially available software, ESCA tools developed by Surface/Interface Inc. and utilized as a toolbox in the MATLAB environment. The first important step for obtaining quantitative information from XPS spectra is the correction of secondary electron background. Several background removal methods have been proposed and used in the literature. Among these, the Shirley (non-linear) background subtraction is one of the most widely used and was adopted in this study. It has been demonstrated that the Shirley background subtraction is the most effective method in fitting the short energy range (10 - 50 eV) found in typical core level XPS spectra. However, to measure the area of
spectral peaks correctly, the energy range of the spectrum (i.e. $E_{\text{max}}$ and $E_{\text{min}}$) needs to be determined and fixed in a manner consistent for comparing different spectra of the same element.

As shown in Figure 2.1, the satellite feature of Fe$^{3+}(2p_{1/2})$ is located at binding energy higher than 730 eV and is obscured by both inelastic background and the O(KVV) Auger line. After removing the inelastic background from the spectrum, the satellite feature of Fe$^{3+}(2p_{1/2})$ still cannot be separated from the O(KVV) Auger line. Therefore, the Fe(2p) spectra were fitted over the range 700 – 730 eV, and the fitted spectrum consists of a weighted spectrum (background corrected) of pure iron for Fe$^0$, doublets for both Fe$^{2+}$ and Fe$^{3+}$, a doublet for Fe$^{2+}$ shake-up satellite, and a single Fe$^{3+}(2p_{3/2})$ shake-up satellite. The fitted features of the Fe$^{2+}$ and Fe$^{3+}$ shake-up satellites then serve as guides to initial guesses for peak heights of the Fe$^{2+}$ and Fe$^{3+}$ main features. The intensities of the shake-up features provide an independent and qualitative determination of relative Fe$^{2+}$/Fe$^{3+}$ concentrations, and therefore place bounds on the values of relative concentration derived from fitting the main spectral features. It should be pointed out that there is a range of reported energy differences between Fe$^{2+}$/Fe$^{3+}$ satellites and main features in the Fe(2p) spectrum. Therefore, the relative satellite features serve as approximate rather than exact guides as to the position of the main peaks. The O(1s) spectrum is composed of three peaks which correspond to the signals from oxygen in the oxide ($O^2-$) at 529.7 eV, oxygen in hydroxyl group (OH$^-$) at 531.2 eV, and water (H$_2$O) at 532.4 eV.
The background corrected XPS spectra were fitted by constructing the parameter-controlled Gaussian/Lorentzian (G/L ratio is 0.75) peaks for different chemical states of the element. The parameters used to define a single peak include binding energy (BE), full width at half maximum (FWHM) and peak height (H). For doublet features, peak to peak separation (PS) and peaks height ratio (HR) determined from the background corrected spectrum were incorporated and fixed during the fitting process. Any of the peak parameters can be individually fixed to a preset value or left free to vary during the computer fitting process. Like any other fitting process of a set of non-linear equations, the results of fitting may vary significantly with different sets of initial preset values of the parameters. Thus the initial set of peaks is given and modified manually until the fitted and experimental spectra are close to each other. The spectrum was then fitted by the computer program. However, to prevent obtaining the irrational results for Fe$^{2+}$ and Fe$^{3+}$, the BE and FWHM are never allowed to vary together within a computer fitting routine. Therefore the spectrum was first fitted with fixed BE and allowing the FWHM and H free to vary. After getting an improved fitting result, the spectrum was fitted again with fixed FWHM and allowing the BE and H free to vary. This process was repeated until the best fit was obtained.

The computer program, ESCA Tools, uses an iterative non-linear least-squares fitting process in order to modify the peak parameters until the deviation between the synthesized peak and the experimental XPS spectrum is minimized. The goodness of the fit is determined by the $\chi$ (chi) value available from the program. Ultimately, peak areas were obtained from the program and used as a measure of the peak intensity.
The atomic sensitivity factors (ASF) of Fe(2p) and O(1s) are needed to calculate the distribution of possible iron oxide phases. The ASF is defined as a scale factor, which can be used to calculate atomic concentration (N) of an element from the spectral peak intensity (I). The calculation is given by the equation, \( N = I / \text{ASF} \), where \( N \) is the concentration of that element within the surface region. If we consider a XPS peak from each of two elements (A and B), then the quantitative relationship between these two elements can be given as:

\[
\frac{N_A}{N_B} = \frac{I_A}{I_B} \times \frac{\text{ASF}_B}{\text{ASF}_A}
\]

It has been shown that the published ASFs have quite high levels of deviation and inconsistency due in part to the difference between the true peak area measurement and the use of background subtraction method. Thus it is necessary to obtain ASFs for Fe(2p) and O(1s) from an iron oxide sample of known composition. The O(1s) ASF was arbitrarily assigned to 1.00 to simplify the calculations. The factor for Fe(2p) was then determined by correlating the XPS Fe(2p) and O(1s) spectra of the known sample.

2.4. Results and Discussion

2.4.1. The XPS Fe(2p) Shake-up Satellite Features. An important question in simulating Fe(2p) spectra is the determination of binding energies and FWHM values for Fe\(^{2+}\) and Fe\(^{3+}\) components. A comparison of Fe(2p) spectra of an Fe\(^{2+}\)-rich oxide (Figure 2.2a) to that of an Fe\(^{3+}\)-rich oxide (Figure 2.2b) illustrates the utility of shake-up satellite features in providing an independent and qualitative estimate of Fe\(^{2+}\) to Fe\(^{3+}\) relative concentration. This is of particular concern in quantitative analyses, since even small
Figure 2.2. XPS Fe(2p) spectra of (a) electrochemically modified Fe$^{2+}$-rich electrode and (b) electrochemically modified Fe$^{3+}$-rich electrode. The Fe electrode was cycled 8 times (-1.4V to 0.9V vs. Ag/AgCl, 50mV/sec) in borate buffer and emersed at -1.4V to produce Fe$^{2+}$-rich oxides. The Fe$^{3+}$-rich oxide was produced by 2 linear scan and the Fe electrode was emersed at 0.9V.
changes in the FWHM of the Fe\textsuperscript{2+} and Fe\textsuperscript{3+} components of calculated spectra can lead to large changes in the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} relative concentration\textsuperscript{1}.

Figure 2.2 shows the curve fitting of XPS Fe(2p) spectra of iron oxide films grown by cycling in borate buffer solution and emersed at hydrogen evolution potential (−1.4V) and at noble potential (+0.9V). The spectra clearly show that the surface oxide film composition of the Fe sample emersed at −1.4V is Fe\textsuperscript{2+}-rich (Figure 2.2a), while the sample emersed at +0.9V is more rich in Fe\textsuperscript{3+} (Figure 2.2b). Details of film formation and characterization will be reported later in chapter 3\textsuperscript{33}.

We have found that the binding energies of shake-up satellite peaks of Fe\textsuperscript{2+}(2p\textsubscript{3/2}) and Fe\textsuperscript{3+}(2p\textsubscript{3/2}) are 714.5 eV and 719 eV, respectively, which are in agreement of the published values\textsuperscript{20}. After subtracting the intensity due to metallic Fe from both Fe(2p) spectra, the Fe\textsuperscript{2+}-rich oxide film (Figure 2.2a) shows negligible additional intensity at 719 eV. In contrast, the 719 eV region of the Fe\textsuperscript{3+}-rich oxide film (Figure 2.2b) can only be fitted by the assignment of additional Fe\textsuperscript{3+}(2p\textsubscript{3/2}) shake-up satellite peak at 719 eV. As shown in Figure 2.2, the satellite features provide a qualitative guide concerning the relative Fe\textsuperscript{2+}/Fe\textsuperscript{3+} concentrations in the oxide film. This information then serves as an independent (though approximate) check on Fe\textsuperscript{2+}/Fe\textsuperscript{3+} relative concentrations obtained from main peaks.

2.4.2. Atomic sensitivity factors (ASF) of Fe(2p) and O(1s). The Fe\textsubscript{3}O\textsubscript{4} powder sample serves as a standard for obtaining Fe(2p) and O(1s) empirical ASFs. Shown in Figure 2.3 are the curve fitting of XPS Fe(2p) and O(1s) spectra of Fe\textsubscript{3}O\textsubscript{4}. The quantitative results and parameters of the fit are listed in Table 2.1. Since the Fe\textsubscript{3}O\textsubscript{4}
Figure 2.3. XPS Fe(2p) and O(1s) spectra of Fe₃O₄ powder sample.
Table 2.1. Curve fitting results and parameters for Fe(2p) and O(1s) XPS spectra of Fe$_3$O$_4$ powder sample

<table>
<thead>
<tr>
<th></th>
<th>Fe$<em>{2p</em>{3/2}}$</th>
<th>Fe$<em>{2p</em>{3/2} \text{ satellites}}$</th>
<th>Fe$<em>{2p</em>{1/2}}$</th>
<th>Fe$<em>{2p</em>{1/2} \text{ satellite}}$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$^{2+}$ Fe$^{3+}$</td>
<td>Fe$^{2+}$ Fe$^{3+}$</td>
<td>Fe$^{2+}$ Fe$^{3+}$</td>
<td>Fe$^{2+}$ Fe$^{3+}$</td>
<td></td>
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<tr>
<td>B. E.</td>
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<td>169.9 298.9</td>
<td>169.7 669.6</td>
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<table>
<thead>
<tr>
<th></th>
<th>O(1s)</th>
<th>Total</th>
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<tr>
<td></td>
<td>O$^{2-}$ OH$^{-}$ H$_2$O</td>
<td>(O$^{2-} + \text{OH}^{-}$)</td>
</tr>
<tr>
<td>B. E.</td>
<td>529.7 531.2</td>
<td>532.4</td>
</tr>
<tr>
<td>Height</td>
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<td>75.1</td>
</tr>
<tr>
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<td>1.6</td>
</tr>
<tr>
<td>Area</td>
<td>1479.0 501.3</td>
<td>136.8</td>
</tr>
</tbody>
</table>

powder was used as received, the powder may trap some lattice H$_2$O or react with H$_2$O vapor to form surface iron oxyhydroxide phases (FeOOH) in the air. Thus, a mixture of Fe$_3$O$_4$ and FeOOH with perhaps some H$_2$O is a reasonable model to be assumed first for the powder sample. Also, in order to apply our method of XPS quantitative analysis, we have to assume the sample is a homogeneously mixed oxide containing Fe$_3$O$_4$ and FeOOH phases.

As listed in Table 2.1 and shown in Figure 2.3, there is a small amount of H$_2$O in the Fe$_3$O$_4$ sample. The O(1s) signal due to H$_2$O (B.E = 532.4 eV) $^{19,29-31}$ was not used in
the calculation of ASF determination since the H₂O is neither in the Fe₃O₄ phase nor in
the FeOOH phase. The amount of O²⁻ and OH were used to determine the concentration
of Fe³⁺ in both FeOOH and Fe₃O₄ phases, and the concentration of Fe²⁺ in the Fe₃O₄
phase. Then the ASF for Fe(2p) can be calculated from the total Fe(2p) intensity and the
total Fe (Fe²⁺ and Fe³⁺) concentration obtained from the O(1s) spectrum.

From the quantitative results of O(1s) spectrum in Table 2.1 and the pre-assigned
O(1s) ASF = 1.00, the atomic concentrations (arbitrary unit) of O²⁻ and OH⁻ can be
calculated, and they are 1479.0 and 501.3, respectively. Based on the stoichiometry of
FeOOH,
\[ N(\text{Fe}^{3+})_{\text{FeOOH}} = N(\text{O}^{2-})_{\text{FeOOH}} = N(\text{OH}^-)_{\text{FeOOH}} = 501.3 \] (2-2)

Therefore, the atomic concentration of O²⁻ in Fe₃O₄ can be calculated,
\[ N(\text{O}^{2-})_{\text{Fe₃O₄}} = N(\text{O}^{2-})_{\text{total}} - N(\text{O}^{2-})_{\text{FeOOH}} = 1479.0 - 501.3 = 977.7 \] (2-3)

Again, based on the ideal stoichiometry of Fe₃O₄,
\[ N(\text{Fe}^{3+})_{\text{Fe₃O₄}} = \frac{1}{2} N(\text{O}^{2-})_{\text{Fe₃O₄}} = 488.9 \] (2-4)
\[ N(\text{Fe}^{2+})_{\text{Fe₃O₄}} = \frac{1}{4} N(\text{O}^{2-})_{\text{Fe₃O₄}} = 244.4 \] (2-5)

Finally, the total atomic concentration of Fe and Fe²⁺/Fe³⁺ ratio can be obtained as
follows,
\[ N(\text{Fe})_{\text{total}} = N(\text{Fe}^{3+})_{\text{FeOOH}} + N(\text{Fe}^{3+})_{\text{Fe₃O₄}} + N(\text{Fe}^{2+})_{\text{Fe₃O₄}} = 1234.6 \] (2-6)
\[ \frac{N(\text{Fe}^{2+})}{N(\text{Fe}^{3+})} = \frac{244.4}{(488.9+501.3)} = 0.25 \] (2-7)

Before using these results, obtained only from the O(1s) spectrum, to determine the ASF
for Fe(2p), it is necessary to check if the proposed sample model (Fe₃O₄ + FeOOH) is
valid. From the quantitative results of Fe(2p) spectrum in Table 2.1, the Fe²⁺/Fe³⁺ ratio,
can be calculated using the peak intensities of Fe$^{2+}$ and Fe$^{3+}$ in either Fe$^{2+}$/$Fe^{3+}$ feature. The Fe$^{2+}$/Fe$^{3+}$ ratio (0.25) obtained from the Fe(2p) spectrum is in close agreement of the ratio (0.25) calculated independently from the O(1s) spectrum. This indicates that the proposed sample model (Fe$_3$O$_4$ + FeOOH) is correct. In spite of the fact that air-exposed iron oxide samples are covered with a thin layer of Fe$_2$O$_3$, and small amounts of iron hydroxide phases (Fe(OH)$_2$ and Fe(OH)$_3$) might possibly be present, our results clearly show that the amounts of Fe$_2$O$_3$ and iron hydroxides are quite small and can be neglected in the ASF analysis. Ultimately, the Fe(2p) ASF can be obtained as follows,

$$\text{ASF}_{\text{Fe}(2p)} = \frac{I_{\text{Fe}(2p)}}{N_{\text{Fe}(2p)}} = \frac{3332.8}{1234.6} = 2.70$$ (2-8)

We are aware of that small amount of indium oxide may add some intensity to the O(1s) peak. However, the results of further investigation have shown that an 150% change of In/Fe ratio causes less than 10% of ASF deviation for Fe(2p), which means that the O(1s) signal contributed from indium oxide is negligible.

The published ASFs$^{21}$ of Fe(2p) and O(1s) are 2.957 and 0.711, respectively. These values are relative factors of the assigned F(1s) ASF = 1.00 and are strictly applicable when the spherical capacitor type electron energy analyzer is equipped with a Physical Electronics Omnifocus III lens$^{21}$. Comparing our empirical ASFs for Fe(2p) and O(1s) with these published values, there is a 35% difference on the calculated Fe/O relative concentration. It has been noted that the use of published ASFs for a homogeneous sample will normally provide quantitative results with about 10-20% error$^{21}$. For heterogeneous samples, like the iron oxide/hydroxide samples used in this study,
applying these published ASFs for quantitative analysis will result in even larger error because the microscopic character of the heterogeneous system influences the quantitative results. In addition, first row transition metals, such as iron, have widely varying efficiency for the formation of photoelectron. Thus, an ASF determined on one chemical state for a transition metal may not be valid for another chemical state. Because of these reasons and the fact that the instrumental setup (electron energy analyzer) used in this study is configured differently, a 35% deviation between published ASF values and our empirical sensitivity factors is expected.

2.4.3. Quantitative XPS Analysis of Thin Oxide films formed by O2 Exposure in UHV. Figure 2.4 shows the Fe(2p) and O(1s) spectra of a polycrystalline iron sample recorded at 60° take-off angle, as a function of oxygen exposures. The detailed quantitative analysis was done under the assumption of that the oxide film grown by O2 exposure is a homogeneously mixed oxide film containing only FeOx, Fe3O4 (if present) and FeOOH phases. Also, the possibility of other phases (Fe2O3 and iron hydroxides) might be present in the oxide films was ignored for simplification. The results of quantitative analysis for the oxidized iron surfaces are detailed in Table 2.2. The relative atomic concentrations of Fe0, Fe2+, Fe3+, O2− and OH− were first calculated from their intensities by applying the ASFs of Fe(2p) and O(1s) obtained in this study. Then, the concentration of FeOOH was determined from the total amount of OH− associated with the same amount of Fe3+ and O2−. After accounting for Fe3+ in FeOOH phase, the remaining Fe3+ (if present) was used to estimate the concentration of Fe3O4. The ratio of Fe3+:Fe2+:O2− is 2:1:4 based on the ideal stoichiometry of Fe3O4. Finally, the
Figure 2.4. XPS Fe(2p) and O(1s) spectra of polycrystalline iron as a function of oxygen exposures. The spectra were recorded at 60° take-off angle. (d is the thickness of oxide overlayer).
Table 2.2. The results of quantitative XPS analysis of iron oxide film grown by different oxygen exposures

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<tr>
<th>Oxygen Exposure</th>
<th>Atomic Concentration (Arbitrary Unit)</th>
<th>FeOOH</th>
<th>FeO4</th>
<th>FeOx</th>
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<tbody>
<tr>
<td></td>
<td>Fe⁺⁺⁺⁺</td>
<td>Fe⁺⁺⁺</td>
<td>Fe⁺⁺</td>
<td>O⁻⁻</td>
</tr>
<tr>
<td>10L</td>
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<td>109.9</td>
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<td></td>
<td>[FeOOH] = 111.8</td>
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<td></td>
</tr>
<tr>
<td>25L</td>
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<td>824.0</td>
<td>151.9</td>
<td>877.1</td>
</tr>
<tr>
<td></td>
<td>[FeOOH] = 157.2</td>
<td>[FeO₄] = 0.0</td>
<td>[FeOₓ] = 824.0</td>
<td></td>
</tr>
<tr>
<td>50L</td>
<td>424.1</td>
<td>772.8</td>
<td>173.9</td>
<td>948.0</td>
</tr>
<tr>
<td></td>
<td>[FeOOH] = 174.9</td>
<td>[FeO₄] = 0.0</td>
<td>[FeOₓ] = 772.8</td>
<td></td>
</tr>
<tr>
<td>250L</td>
<td>261.0</td>
<td>880.1</td>
<td>431.2</td>
<td>1176.0</td>
</tr>
<tr>
<td></td>
<td>[FeOOH] = 223.7</td>
<td>[FeO₄] = 103.8</td>
<td>[FeOₓ] = 776.3</td>
<td></td>
</tr>
<tr>
<td>1000L</td>
<td>153.9</td>
<td>691.4</td>
<td>484.0</td>
<td>1122.0</td>
</tr>
<tr>
<td></td>
<td>[FeOOH] = 224.7</td>
<td>[FeO₄] = 129.7</td>
<td>[FeOₓ] = 561.7</td>
<td></td>
</tr>
<tr>
<td>10000L</td>
<td>139.6</td>
<td>685.3</td>
<td>527.7</td>
<td>1192.0</td>
</tr>
<tr>
<td></td>
<td>[FeOOH] = 262.7</td>
<td>[FeO₄] = 132.5</td>
<td>[FeOₓ] = 552.8</td>
<td></td>
</tr>
</tbody>
</table>
concentration of FeO\(_x\) was calculated from the remaining Fe\(^{2+}\) and O\(^{2-}\), and the \(x\) value is the ratio of O\(^{2-}\)/Fe\(^{2+}\). Based on the results in Table 2.2, the composition of the iron oxide films formed by different O\(_2\) exposures was determined and listed in Table 2.3 with some important fitting parameters.

Thickness of the oxide films were determined according to

\[
\frac{I_{\text{OX}}}{I_{\text{METAL}}} = K \left[ \exp \left( \frac{d}{\lambda_{\text{OX}} \cos \theta} \right) - 1 \right] \tag{2-9}
\]

where \(d\) is the thickness of the oxide film, \(\lambda_{\text{OX}}\) is the electron attenuation length (EAL) of the Fe(2p) photoelectrons for the oxide overlayer and is assumed to be the same as the EAL for the Fe substrate in this study, \(\theta = 60^\circ\) is the take-off angle measured with respect

<table>
<thead>
<tr>
<th>Oxygen Exposure</th>
<th>Fe(^{2+}) (2p(_{3/2}))</th>
<th>Fe(^{3+}) (2p(_{3/2}))</th>
<th>Oxide Film Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E.</td>
<td>FWHM</td>
<td>B.E.</td>
</tr>
<tr>
<td>10L</td>
<td>709.2</td>
<td>3.8</td>
<td>711.7</td>
</tr>
<tr>
<td>25L</td>
<td>709.3</td>
<td>3.8</td>
<td>711.6</td>
</tr>
<tr>
<td>50L</td>
<td>709.3</td>
<td>3.8</td>
<td>711.4</td>
</tr>
<tr>
<td>250L</td>
<td>709.7</td>
<td>3.6</td>
<td>711.3</td>
</tr>
<tr>
<td>1000L</td>
<td>709.7</td>
<td>3.2</td>
<td>711.3</td>
</tr>
<tr>
<td>10000L</td>
<td>709.7</td>
<td>3.1</td>
<td>711.3</td>
</tr>
</tbody>
</table>
to the surface normal, $I_{OX}$ and $I_{METAL}$ are the spectral peak intensity of the Fe(2p) band from the oxide overlayer and the substrate, respectively, and $K$ is a normalization parameter which can be calculated from

$$K = \frac{n_{OX} \lambda_{OX}}{n_{METAL} \lambda_{METAL}}$$  (2-10)

where $n_{OX}$ and $n_{METAL}$ are the atomic density of the oxide overlayer and the substrate, respectively, and $\lambda_{METAL} = 2.0$ nm determined by using the general model of Seah and Dench$^{34}$ is the EAL for the substrate. The atomic densities for Fe, FeO, Fe$_3$O$_4$ and FeOOH were obtained from the literature$^{35}$. The oxide overlayer atomic density ($n_{OX}$) was then estimated based on the composition of oxide film presented in Table 2.3. The calculated oxide thickness as a function of O$_2$ exposure is presented in Figure 2.4. The thickness of oxide film grown by $10^4$ L O$_2$ exposure is 2.93 nm. For comparison, the thickness of the natural oxide film on iron formed in air is $3.4 \pm 0.7$ nm$^{36}$. A variety of other algorithms have been proposed for the determination of overlayer thickness by XPS. The detailed comparison of these algorithms has been reported by Fulghum$^{37}$ and will not be discussed in this study.

In all the O(1s) spectra (Figure 2.4) small amounts of OH were detected, which indicates that there is a small amount of H$_2$O contamination in the ambient environment. The mass spectroscopy analysis of the residual gas in our UHV chamber shows the existence of water even at the pressure lower than $1 \times 10^{-9}$ torr.

Based on the results obtained in this study, an oxide growth model can be proposed as follows. At low O$_2$ exposure ($10$L to $50$L), the oxide film consists of an iron
oxide of FeO-like composition (FeOx) grown as the nucleating oxide and a thin film of FeOOH on the top. Other studies have also confirmed the formation of FeO in the initial stages of oxide growth. The formation of Fe³⁺ states was detected even at 10L O₂ exposure. This result has also been reported in UV photoelectron spectroscopy (UPS) studies. Also, the calculated atomic concentrations of Fe³⁺ and OH⁻ are almost equal (±1%) in the oxide films formed by 10L, 25L and 50L oxygen exposure (see Table 2.2). These facts lead us to believe that most of the detected Fe³⁺ is associated with the formation of FeOOH in our study. By the time 250L of O₂ has been delivered to the iron surface, Fe₃O₄ starts to grow. With the increasing O₂ exposure, Fe₃O₄ and FeOOH continue to grow, and coexists with FeOₙ and until the oxide growth saturates. Similar models have been proposed for the oxide film grown by exposure to pure O₂ gas on iron. Figure 2.5 is a graphic representation of the proposed oxide growth model by incorporating the oxide thickness information into the quantitative results of surface oxide composition.

In Table 2.3, as the O₂ exposure increases, the BE of Fe²⁺(2p₃/2) shifts to higher energy and the corresponding FWHM decreases. On the contrary, the BE of Fe³⁺(2p₃/2) shifts to lower energy and the corresponding FWHM increases. The rationale for these changes can be given as follows. At low O₂ exposure, the oxide films consist of only FeOₙ (Fe²⁺) and FeOOH (Fe³⁺). The BE of Fe²⁺ and Fe³⁺ are 709.3 eV and 711.6 eV, respectively. When Fe₃O₄ (Fe³⁺:Fe²⁺ = 2:1) starts to grow and FeOOH (Fe³⁺) is still growing at higher O₂ exposure, the overall BE of the Fe³⁺ component is shifted to lower energy (711.3 eV) and the peak is broadened from 2.4 eV to 3.3 eV. This suggests that
Figure 2.5. The oxides growth as a function of oxygen exposures at the pressure of $10^{-7}$ torr. The thickness of oxide film was calculated by assuming an inelastic mean free path of 2.0 nm for the Fe(2p) photoelectron in the oxide film.

The BE of Fe$^{3+}$ in the Fe$_3$O$_4$ environment is lower than its corresponding value in the FeOOH environment. Unlike FeOOH, the Fe$^{3+}$ is partially surrounded by Fe$^{2+}$ in the Fe$_3$O$_4$ environment, which may cause the lowering of its BE by the decreasing of the relaxation energy. Shirley $^{38,39}$ and Sherwood $^{40}$ has shown that the relaxation energy varies with electronegativity of the nearest neighbour atoms, coordination number, geometry and formal oxidation state. Usually, the relaxation energy is expected to increase with increasing formal oxidation state, and decrease when the atom is surrounded by especially electronegative atoms. Using a similar analogy, the Fe$^{2+}$ in Fe$_3$O$_4$ should have higher BE than its corresponding value in FeO$_x$. Correspondingly, the BE of Fe$^{2+}$ shift to higher energy (709.7 eV) when Fe$_3$O$_4$ starts to grow. This would lead
one to expect an increase in FWHM of the Fe$^{2+}$ peak due to the overlap of two Fe$^{2+}$ peaks (for FeO and Fe$_3$O$_4$) separated by ~0.4 eV. However, the Fe$^{2+}$ FWHM is narrowing (from 3.8 eV to 3.1 eV) instead of broadening as expected. This can be explained by the fact that the rate of decrease (from 81.6% to 58.3%) of relative FeO$_x$ concentration is faster than the rate of increase (from 0% to 14.0%) of relative Fe$_3$O$_4$ concentration. In addition, approximately only one third of Fe content in Fe$_3$O$_4$ is Fe$^{2+}$. Therefore, the overall Fe$^{2+}$ feature is shifted to higher energy on account of the increase in the relative concentration of Fe$_3$O$_4$. However, the FWHM of Fe$^{2+}$ decreases due to the decrease in FeO$_x$ relative concentration.

Another interesting observation is that the $x$ value for FeO$_x$ increases from 0.78 to 1.00 as the O$_2$ exposure increases from 10L to 50L. This shows that the oxygen-deficient FeO phases are formed during the initial stage of the oxidation process. At the O$_2$ exposures higher than 50L, Fe$_3$O$_4$ starts to grow, the value of $x$ drops to ~ 0.7 and stays constant. This could be due to the oxidation of FeO to form Fe$_3$O$_4$. By examining both the curve fitting results of thin oxide films (Table 2.3) and the results of Fe$_3$O$_4$ compound (Table 2.1), we conclude that the BE and FWHM of Fe$^{2+}$ or Fe$^{3+}$ changes with the relative content of Fe$^{2+}$ or Fe$^{3+}$ in the oxide phases, indicating the multiple nature of both Fe$^{2+}$ and Fe$^{3+}$ chemical environments within the oxide phases.

2.5. Conclusions

A consistent method for the quantitative determination of Fe$^{2+}$/Fe$^{3+}$ stoichiometry from XPS spectra has been developed and successfully applied to the analysis of iron oxide films formed by O$_2$ gas exposure in UHV. The shake-up satellite features of
Fe(2p) have been found to serve as an indication of relative Fe$^{2+}$/Fe$^{3+}$ content. This has been used to ensure the accuracy and consistency of the fitting results. The atomic sensitivity factors (ASF) of Fe(2p) and O(1s), 2.70 and 1.00 respectively, were determined from a standard Fe$_3$O$_4$ powder sample. The validity and consistency of the process of obtaining these ASFs have been presented in this chapter. The oxide films formed by low O$_2$ exposure consist of predominantly FeO$_x$ and a thin layer of FeOOH, the latter due to ambient background contamination. At higher exposure a trilayer oxide of FeO, Fe$_3$O$_4$ and FeOOH is formed. The multiple nature of Fe$^{2+}$ and Fe$^{3+}$ chemical environments within an oxide film has been delineated in this study. Further investigation is needed to apply this method to more complicated system, e.g. the alloy-oxygen-water system. Also, a comparative study of different background correction methods for the iron-oxygen-water system would be useful for improving the process of XPS quantitative analysis.

2.6. Chapter References


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(23) ESCA Tools™; 4.6 ed.; Surface/Interface Inc.: Mountain View, California, 1995.

(24) MATLAB; 4.2c 1 ed.; The Mathworks Inc.: Natick, Massachusetts, 1995.


(40) Sherwood, P. M. A. *J. C. S. Faraday II* 1976, 72, 1791.
CHAPTER 3

POLYCRYSTALLINE IRON ELECTRODES IN BORATE AND SULFATE MEDIA

3.1. Introduction

Corrosion and passivation of iron and its alloys has been studied extensively\(^1\)-\(^{29}\). However, in spite of the numerous studies published, a great deal remains to be understood about these processes. There is no clear consensus on the nature of the passive film formed on iron in borate media, especially regarding the hydroxylation, or lack thereof, of these films\(^1\),\(^{10}\)-\(^{23}\). The effect of surface morphology of iron on the electrochemical behavior has been, to the best of our knowledge, largely unexplored after some early reports by Wieckowski\(^24\).

Methods like surface enhanced Raman spectroscopy (SERS) and high resolution x-ray absorption near-edge spectroscopy (XANES) have been combined, \textit{in-situ}, with electrochemical measurements to study the growth of passive films on iron in borate media\(^{18}\)-\(^{22}\). Combined Ultrahigh Vacuum/Electrochemical studies (UHV-EC) enable the exposure of iron or its alloys to corroding/passivating agents in aqueous solution and transfer to a UHV analysis chamber without exposure to air and its associated contaminants\(^25\). Such studies are not strictly \textit{in-situ}, and sample surfaces can undergo structural or compositional changes during transfer\(^25\). However, due to the lack of air exposure in this methodology, it is one of the most accurate methods (besides the \textit{in-situ} spectroscopic methods cited above), to characterize a surface that has been exposed to

45
electrolytes at noble potentials. UHV-EC methodology also permits electrochemistry measurements to be carried out on surfaces in extremely well characterized initial states.

UHV-EC studies of iron in borate media have been reported earlier. In these earlier studies, Auger spectroscopy was used to characterize the films formed on iron. Some details about the overlayer like hydroxide to oxide content, or oxidation states of the iron in the film are not easily obtained by Auger spectroscopy. The UHV-EC studies carried out by Wieckowski and coworkers have shown that the Auger spectra and depth profiles of iron surfaces cleaned in UHV and exposed to borate buffer vapor are identical to those obtained by cathodic reduction of an iron surface that has been immersed at rest potential in the borate buffer. This suggests that a thin oxide film is formed on exposure to buffer vapor. However, the same study shows that this thin oxide film does not obscure the effects of emersing the electrode at more noble potentials; i.e., electrodes subjected to various electrochemical experiments and emersed at more noble potentials show different Auger spectra and depth profiles. Other reports in the literature where UHV techniques like X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) were utilized, either involved exposure to air during transfer from the electrochemical cell and/or considerable time lapse between insertion of the sample into the UHV chamber and surface analysis.

Our UHV-EC studies involve the use of XPS to characterize the nature of the surface films formed on iron in borate/sulfate media at a variety of applied potentials and conditions. Our interest in sulfate stems from results of earlier works which have shown that it has a detrimental effect on the corrosion resistance of iron. Sulfate is a
common environmental contaminant in reactor water and certain other industrial
environments. SERS studies have shown that sulfate ions will induce corrosion at iron
surfaces. The results reported here are in general agreement with those of the previous
study. In addition, our results suggest an effect with general consequences for
corrosion in aqueous environments: corrosion due to an environmental contaminant may
lead to inhibited passivation even after that contaminant and resulting corrosion products
have been removed. We have evidence for the formation of hydroxylated overlayers on
iron at all potentials in borate solutions with and without sulfate. Our XPS studies
indicate that the hydroxylated layer is thicker when grown in the presence of sulfate ions.
Further, we have observed that iron surfaces corroded in sulfate, sputtered and annealed
in UHV and subsequently exposed to a borate electrolyte show a trend of increasingly
positive potentials for the oxidation peaks in the cyclic voltammograms. Increased
anodic current in the passive region is also observed. In view of the fact that the surface
chemical composition prior to exposure to the borate solution is verified to be identical
by XPS, this difference in electrochemical behavior is attributed to variation of surface
roughness.

3.2. Experimental

Polycrystalline iron foil (Aesar, Puratronic 99.998%) was used. Electrical contact
was established by spot welding Tantalum wires on one side of the foil. The borate
buffers utilized in this study were of the composition 0.075M H$_3$BO$_3$ (Spectrum
Chemical), 0.01875M Na$_2$B$_4$O$_7$ (Aldrich). The pH of the buffer was 8.4. Experiments in
sulfate media were performed in solutions of 0.05M Na$_2$SO$_4$ (Mallinckrodt) made up in
the borate buffer listed above. All chemicals were of analytical grade and used as received. All solutions were prepared in millipore grade water and purged with argon.

Electrochemical experiments were carried out using a Pine Instruments AFRDE5 potentiostat, with data output to a Hewlett Packard 7046B XY recorder. Electrode potentials are with respect to Ag/AgCl (0.01M NaCl) reference electrode. Cyclic voltammograms were acquired at a scan rate of 50 mV/s and linear scans at 10 mV/s.

Cleaning of the foil in vacuum was done by alternating cycles of argon ion bombardment (2.3 keV) at room temperature and annealing the sample to temperatures ~950K. This serves to drive out bulk impurities like nitrogen and sulfur. The surface was then examined by X-ray Photoelectron Spectroscopy (XPS). This process was repeated till XPS spectra showed the presence of only metallic iron.

XPS spectra were acquired using unmonochromatized Mg Kα radiation from a dual anode x-ray source in conjunction with a hemispherical analyzer in the constant pass energy mode at 50 eV pass energy. The details of the system are described in chapter 1. All XPS data presented in this study were acquired with the sample surface at an angle of 90° with respect to the analyzer axis. Fitting of XPS data was accomplished using commercially available software, ESCA Tools\(^{35}\) in a MATLAB environment\(^{36}\). A detailed account of fitting XPS spectra has been presented in chapter 2. The Shirley background subtraction method was adopted in this study as, it has been shown to be the most effective method for fitting the short energy range found in typical core XPS spectra\(^{37}\). Fitting of Fe (2p) spectra was done over the binding energy range 700-730 eV.

Binding energies for Fe\(^{2+}\)(2p\(_{3/2}\)) and Fe\(^{3+}\)(2p\(_{3/2}\)) were assigned to 709.7 and 711.3 eV.
respectively \(^{38,39}\). The binding energies for the shake up satellites of \(\text{Fe}^{2+}(2p_{3/2})\) and \(\text{Fe}^{3+}(2p_{3/2})\) were assigned to 714.5 eV and 719 eV respectively \(^{40,41}\). O(1s) binding energies corresponding to oxide, hydroxide and water species were assigned at 529.7 eV and 531.2 eV and 532.4 eV respectively \(^{38,39}\). Different FWHM values in the range 2.5-3.5 eV were used for \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\). The assignment of different values of FWHM to \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) is based on the work reported in chapter 2 which involved a systematic study of iron oxide films grown by exposure of a polycrystalline iron surface to oxygen gas in UHV \(^{40}\). In chapter 2, we have demonstrated that the FWHM of \(\text{Fe}^{2+}\) or \(\text{Fe}^{3+}\) changes as a function of the relative content of \(\text{Fe}^{2+}\) or \(\text{Fe}^{3+}\) in the oxide phase, indicating that both \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) are present in a multiplicity of chemical environments \(^{40}\). Other studies have pointed out the justification for the use of different FWHM values and the use of secondary electron background of the pure iron (\(\text{Fe}^0\)) component in constructing simulated spectra from separate \(\text{Fe}^0\), \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) components \(^{39,42,43}\).

The oxygen to iron ratios were obtained using empirical atomic sensitivity factors of 2.7 for Fe(2p) and 1.00 for O(1s). The empirical atomic sensitivity factors were obtained by XPS analysis of a standard sample of Fe\(_2\)O\(_4\) powder. The published sensitivity factors for Fe(2p) and O(1s) are 2.957 and 0.711 respectively \(^{38}\). These published values are strictly applicable when the spherical capacitor type electron energy analyzer is equipped with a Physical Electronics Omnifocus III lens \(^{38}\). The apparatus used in this study is configured differently. Even though our sensitivity factors do not differ greatly from the published values, use of the published atomic sensitivity factors listed above \(^{38}\) led to erroneous iron to oxygen ratios for known iron oxide phases. Hence
empirical sensitivity factors for Fe(2p) and O(1s) in our experimental set up had to be
determined. XPS signals obtained for boron and sulfur in this study were weak.
Therefore, empirical atomic sensitivity factors for boron and sulfur in our experimental
setup are difficult to determine. Estimates of the relative amount of boron or sulfur
compared to Fe have been obtained using published atomic sensitivity factors for boron
and sulfur^38.

3.3. Results and Discussion

3.3.1. Iron in Borate Buffer. Figure 3.1a shows a cyclic voltammogram of
crystalline iron in the de-aerated borate buffer. The general shape of the cyclic
voltammogram is similar to those observed by Wieckowski and others^24. As the cyclic
voltammogram of Fe in borate solutions has been discussed extensively in previous
literature reports, a detailed account will not be given here^4,8,9,19,42. The anodic peak
corresponding to the dotted line in Figure 3.1a is typically assigned to the oxidation of
Fe^{2+} to Fe^{3+}, while the shoulder that is situated negative to this peak is typically assigned
to oxidation of metallic Fe to Fe^{2+}^42. Table 3.1 shows the chemical composition of the
surface that has been extensively cycled between -1.4 and 0.9V as a function of emersion
potential. Figure 3.2 shows the XPS spectra associated with each of the experiments
described in Table 3.1. The emersion and rinsing procedure is described in the
experimental section. The surface composition of the Fe sample emersed and rinsed at -
1.4V is more rich in Fe^{2+}, while the sample emersed at 0.9V is richer in Fe^{3+}. This
demonstrates the sensitivity of the experimental set up to emersion potential.

Hydroxylation is evident irrespective of whether the sample is emersed at hydrogen
Figure 3.1. (a) Cyclic voltammogram of a clean iron electrode in borate buffer pH 8.4. (b) Cyclic voltammogram of an iron electrode in a solution of 0.05 M Na₂SO₄ in borate buffer pH 8.4. This electrode was previously cleaned to atomic level in UHV, cycled in borate 16 times and emersed at 0.9 V. (c) Same as in Figure 3.1b, except second exposure to sulfate, see text for details.
Table 3.1. Surface composition as determined by XPS of iron in borate buffer

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Emersion Potential</th>
<th>Fe(0)/Fe total</th>
<th>Fe^{II}/Fe^{III}</th>
<th>O^2-/Fe^{III}</th>
<th>OH^-/Fe^{III}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>8 cyclic scans</td>
<td>-1.4V</td>
<td>0.24</td>
<td>2.88</td>
<td>1.23</td>
</tr>
<tr>
<td>2.</td>
<td>16 cyclic scans and 2 linear scans  &amp; a b</td>
<td>0.9V</td>
<td>0.20</td>
<td>0.65</td>
<td>1.33</td>
</tr>
<tr>
<td>3.</td>
<td>16 cyclic scans and 1 linear scan a</td>
<td>0.9V</td>
<td>0.20</td>
<td>0.58</td>
<td>1.27</td>
</tr>
<tr>
<td>4.</td>
<td>Holding at 0.5V for 10 minutes</td>
<td>0.5V</td>
<td>0.16</td>
<td>0.49</td>
<td>1.26</td>
</tr>
<tr>
<td>5.</td>
<td>16 cyclic scans and 2 linear scans  &amp; a b c</td>
<td>0.9V</td>
<td>0.21</td>
<td>0.85</td>
<td>1.35</td>
</tr>
</tbody>
</table>

a The scan limits are -1.4V to 0.9V. b The scan limits for the linear scan are -0.9V to 0.9V. c The electrode was corroded twice in sulfate, cleaned in UHV prior to this run.

evolution potentials or at noble potentials. Boron was detected by XPS in all cases. In a previous study where boron was detected by Auger analysis after emersing the sample at negative potentials, it was suggested that the boron could be in a reduced state. A broad XPS peak for boron centered around a binding energy of 192.5 eV (not shown) suggests that the boron is in the oxidized form, possibly a mixture of borax and boric acid from the electrolyte. A similar boron XPS signal was obtained for the sample emersed at +0.9V. Seo and Scharifker, using ex-situ AES and XPS respectively, have also reported the detection of boron in surface films grown on iron. Therefore the borate we observe may be adsorbed on the surface of the oxide or incorporated during the cycling process, but is not likely to be an artifact created by faulty rinsing procedure. As explained in the Experimental Section, a precise estimation of the amount of borate
Figure 3.2. XPS spectra of iron in borate buffer, corresponding to the experiments described in Table 3.1. (1) 8 cyclic scans, emersed at -1.4V. (2) 16 cyclic scans and 2 linear scans, emersed at 0.9V potential. (3) 16 cyclic scans and 1 linear scan, emersed at 0.9V. (4) Held at 0.5V for 10 minutes, emersed at 0.5V. (5) 16 cyclic scans and 2 linear scans, emersed at 0.9V. All other experimental conditions as described in Table 3.1.
incorporated is not possible. However, using published sensitivity factors for boron, the B/Fe atomic ratio was found to be between 0.11-0.33. Wieckowski has indicated that cycling the iron electrode in borate extensively, leads to a memory effect, specifically, Auger analysis of an iron electrode that had been cycled in borate followed by electrochemical reduction of the oxide for 5 min at -1.4V, revealed the presence of iron oxide $^{24}$. As no attempt was made in our studies to completely reduce the oxide, a considerable amount of it remains following emersion at -1.4V. Using the equilibrium potentials for the Fe-H$_2$O system at pH 8.4 as a guideline $^{44,45}$, and using the ratios of various iron and oxygen species obtained by XPS analysis, we attempted to arrive at the most reasonable composition of surface species that reflect these ratios. It must be pointed out that these XPS atomic ratios have been obtained using a model that assumes that the surface region probed is a homogeneous mixture of oxide and hydroxide phases. In films formed by corrosion, situations frequently arise where the outer regions of the film differ in composition from the inner regions of the film $^{46}$. In addition, magnetite (Fe$_3$O$_4$) and iron oxyhydroxide (FeOOH) are frequently non-stoichiometric. In light of the above factors, no attempt has been made at to obtain a precise quantitative analysis. Instead in this paper, only the most probable combinations of various oxide and hydroxide phases are suggested. The following approach was adopted to arrive at an approximate picture of the surface composition, both for the iron surfaces exposed only to the borate electrolyte and for the iron electrodes exposed to a sulfate containing borate electrolyte which is presented in the next section. The hydroxide signal was typically assigned to a mixture of FeOOH, Fe(OH)$_2$ or Fe(OH)$_3$ in varying amounts depending on
the emersion potential. The amount of oxidized iron (Fe$^{2+..3+}$) present in hydroxide was
then subtracted from the total amount of Fe$^{2+..3+}$. The XPS signal for oxygen in
oxyhydroxide would be expected to overlap with oxidic oxygen (oxygen in the binding
energy region attributed to oxide). After accounting for oxygen in the oxyhydroxide if
present, the ratio of the remaining Fe$^{2+..3+}$ and oxidic oxygen were determined. The
nature of the iron oxide was then determined by the species that has a Fe/O ratio similar
to the remaining Fe$^{2+..3+}$/oxidic oxygen ratio. For the electrode that is emersed at -1.4V
(Table 3.1, expt. 1), the OH is most probably associated with Fe(OH)$_2$. The oxide phase
present is largely FeO. Some Fe$^{3+}$ is also detected. This could be associated with some
remaining Fe$_3$O$_4$ in the outer regions of the film. Alternatively, this Fe$^{3+}$ could be
associated with Fe$^{2+}$ in a mixed Fe$^{2+}$, Fe$^{3+}$ hydroxide. There is still a considerable excess
of oxidic oxygen that may be attributed to the borate species, as the XPS signal for
oxygen in borate would be expected to overlap with the oxygen from the various iron
oxides. For the sample emersed at 0.9V, the most likely composition appears to be Fe$_3$O$_4$
with the hydroxide being accounted for by a mixture of Fe$^{2+}$ and Fe$^{3+}$ hydroxides or by a
mixture of Fe(OH)$_2$ and FeOOH, as suggested by Devine $^{19-21}$ and more recently by Flis
$^{44}$. Borate once again accounts for some of the excess oxidic oxygen. There is no major
difference in the XPS atomic ratios irrespective of whether the iron electrode is cycled
extensively followed by one final linear scan to the emersion potential of 0.9V or if after
the same number of cyclic scans, more than one linear scan is performed with a final
emersion potential of 0.9V (see expts. 2 and 3 of Table 3.1 and expts. 2 and 3 of Figure
3.2).
If the oxide is grown by holding the iron electrode in borate electrolyte at 0.5 V for 10 minutes, there is an increase in the amount of Fe\textsuperscript{3+} detected. The composition suggested by the XPS atomic ratios, once again is revealed to be Fe\textsubscript{3}O\textsubscript{4} with either a mixture of FeOOH and Fe(OH)\textsubscript{2} or a mixture of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} hydroxides accounting for the hydroxide.

Previous studies in the literature have indicated that hydroxides are observed in the passive film grown in a borate medium, when the iron electrode was passivated by stepping to low potentials \textsuperscript{12,13,19-21}. Hydroxides have also been observed by potential cycling through the active region \textsuperscript{18} or when iron oxide/hydroxide films have been grown by deposition on other metal substrates \textsuperscript{47}, but not when the film was grown by stepping to positive potentials \textsuperscript{14,15,22}. This study, confirms that hydroxides are formed when the electrode is swept through the active region and demonstrates that the hydroxide is Fe\textsuperscript{2+} rich when the electrode is emersed at -1.4 V and contains significantly higher fractions of Fe\textsuperscript{3+} when emersed at more noble potentials.

The XPS spectra of iron samples after electrochemistry in borate showed no evidence for the presence of sulfur in the region between 161 and 163 eV where the S(2p) signal would be expected on a clean iron or an iron oxide surface \textsuperscript{38}. This shows that once the bulk sulfur is driven out by cleaning in UHV as described in the experimental section, cycling the electrode in pure borate buffer does not induce any further segregation of sulfur.

**3.3.2. Iron in Sulfate Containing Media.** Figure 3.1b shows the cyclic voltammogram of an iron electrode (previously cycled in borate buffer as in expt. 2 of
Table 3.1) in borate buffer containing 0.05M Na₂SO₄ and emersed at 0.9V. It can be seen that there is enhanced anodic current when compared to Figure 3.1a. The same iron electrode, after being sputtered and annealed in UHV to get rid of the corrosion products formed, was cycled in borate to build up the oxide and then once again cycled in the borate solution containing 0.05M sulfate. The cyclic voltammogram obtained was as shown in Figure 3.1c. The cyclic voltammogram shows enhanced anodic dissolution and also a difference in the shape of the current voltage profile at potentials more noble than 0V. In other words, when the cyclic voltammogram shown in Figure 3.1b was recorded, it was the first exposure of that particular iron sample to sulfate. Figure 3.1c represents a scan obtained on the second exposure of the iron sample to sulfate. As the surface chemical composition of the sample prior to sulfate exposure is the same in both cases as verified by XPS, a difference in surface chemical composition cannot account for the difference in the electrochemical response. We attribute this difference in electrochemical behavior to a difference in surface roughness/morphology after the first exposure to sulfate. Prolonged exposure to sulfate caused a visible decrease in surface reflectivity of the sample that was not restored by UHV cleaning. We have found these effects to be reproducible on different polycrystalline iron samples.

Figure 3.3a shows the XPS spectrum of the Fe(2p) and O (1s) regions after 16 cyclic scans and 2 linear scans of the clean iron electrode in borate and emersed at 0.9V on the second linear scan. Following XPS analysis, this electrode was subjected to 5 cyclic scans and 2 linear scans in borate solution containing 0.05M sulfate and emersed at 0.9V on the second linear scan. The XPS spectra obtained after this experiment is shown
Figure 3.3. (a) XPS spectrum of the Fe(2p) and O(1s) regions, of an Fe electrode after 16 cyclic scans and 2 linear scans in the borate buffer pH 8.4. (b) XPS spectrum of the Fe(2p) and O (1s) region after the electrode in Figure 3.3a was subjected to 5 cyclic scans and 2 linear scans in a borate solution containing 0.05 M Na₂SO₄. (c) XPS spectrum of an iron electrode cleaned in UHV and scanned directly in a borate solution containing 0.05M Na₂SO₄. The number of scans was the same as in Figure 3.3a.
in Figure 3.3b. It is clear that emersion from the sulfate contaminated borate solution at 0.9V leads to a considerable attenuation of the metallic iron signal when compared to emersion at the same potential in pure borate solution. A considerable increase in the magnitude of the OH peak relative to the oxide peak is also evident. It could be argued that the increased hydroxide observed in Figure 3.3b results from precipitation of iron hydroxides over and above the hydroxides already formed by voltammetric experiments in the sulfate free borate electrolyte. Figure 3.3c is the XPS spectra of the iron and oxygen regions of an electrode, sputtered and annealed in UHV and directly subjected to 16 cyclic scans and 2 linear scans in the borate solution contaminated with sulfate, followed by emersion at 0.9V after the second linear scan. The number of scans and the sequence of scans in Figure 3.3c is hence the same as in Figure 3.3a, enabling a more direct comparison of the effect of added sulfate on surface composition. Once again the attenuation of the metallic iron signal and the very pronounced growth of the hydroxide signal are evident. This shows that a thicker overlayer grows in the presence of sulfate at noble potentials, irrespective of whether the Fe is scanned directly in sulfate contaminated solutions or after preliminary overlayer growth in a pure borate solution. An enhancement of the ratio of hydroxide to oxide is also evident. It is also clear that the water content of the films shown in Figures 3.3b and 3.3c (where the surface was cycled in sulfate) is increased when compared to the film formed after cycling in borate (Figure 3.3a). Table 3.2 shows the XPS atomic ratios of various iron and oxygen species after exposure to borate electrolytes containing sulfate under various conditions. Figure 3.4 shows the XPS spectra associated with each of the experiments listed in Table 3.2. From
Table 3.2. Surface composition as determined by XPS of iron in borate buffer contaminated with 0.05M sulfate ions

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Emersion Potential</th>
<th>Fe(0)/Fe_{total}</th>
<th>Fe^{II}/Fe^{III}</th>
<th>O^{2-}/Fe^{II,III}</th>
<th>OH/Fe^{II,III}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Iron with passive film\textsuperscript{a}, cycled in sulfate (-1.4V~0.9V)</td>
<td>0.9V</td>
<td>0.15</td>
<td>0.63</td>
<td>1.32</td>
<td>0.77</td>
</tr>
<tr>
<td>2. Iron with passive film, cycled in sulfate (-1.4V~0.9V)\textsuperscript{b}</td>
<td>0.9V</td>
<td>0.05</td>
<td>0.32</td>
<td>0.94</td>
<td>0.79</td>
</tr>
<tr>
<td>3. Clean iron, cycled in sulfate (-1.4V~0.9V)</td>
<td>-1.4V</td>
<td>0.47</td>
<td>4.48</td>
<td>1.46</td>
<td>0.71</td>
</tr>
<tr>
<td>4. Iron with passive film\textsuperscript{a}, cycled in sulfate (-0.5V~0.9V)</td>
<td>0.9V</td>
<td>0.12</td>
<td>0.48</td>
<td>1.24</td>
<td>0.43</td>
</tr>
<tr>
<td>5. Iron with passive film, cycled in sulfate (-0.5V~0.9V)\textsuperscript{c}</td>
<td>0.9V</td>
<td>0.13</td>
<td>0.54</td>
<td>1.38</td>
<td>0.79</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The passive oxide film was grown by cycling iron electrode in borate as described in Table 3.1. \textsuperscript{b} Same as Expt. 1, but second exposure to sulfate. \textsuperscript{c} Same as Expt. 4, but second exposure to sulfate.

Table 3.2 (expts. 1 and 2) it is evident that sulfate exposure leads to an increase in the OH/Fe ratio compared to that obtained by cycling the electrode in borate buffer (expt. 2 of Table 3.1). We attribute this increase in hydroxide to the increased precipitation of Fe(OH)\textsubscript{2} and Fe(OH)\textsubscript{3}. Precipitation of iron hydroxides as by-products of pitting corrosion has been discussed in the literature\textsuperscript{48}. After accounting for Fe, present in hydroxide phases, the ratios of the remaining oxidized iron to oxide suggest that the oxide present is Fe\textsubscript{3}O\textsubscript{4}. The XPS spectrum of the sulfur region shows a peak at binding energy centered at 169 eV (not shown). This is in the region assigned in the literature to...
Figure 3.4. XPS spectra of iron in borate buffer contaminated with 0.05M sulfate ions, corresponding to the experiments described in Table 3.2. (1) Iron with passive film, cycled in sulfate, emersed at 0.9V. (2) Same as (1) but second exposure to sulfate. (3) Clean iron cycled in sulfate, emersed at -1.4V. (4) Iron with passive film, cycled in sulfate at more noble potentials, emersed at 0.9V. (5) Same as (4) but second exposure to sulfate. All other experimental condition as given in Table 3.2.
S(2p) in Fe₂(SO₄)₃. We attribute this peak to the presence of sulfate salts. Iron sulfate salts are known to be soluble in water. The presence of sulfate in the film could be either due to some excess that was not rinsed off, or due to sulfate salts being incorporated in the oxide. Using the published atomic sensitivity factor for S(2p), the S/Fe ratio was found to be 0.08 (±0.01).

XPS analysis of a clean Fe sample, cycled in borate to build up the oxide and cycled in the borate solution contaminated with sulfate for the second time is shown in expt. 2 of Table 3.2 and expt. 2 of Figure 3.4. Once again, compared to the surface after emersion from a pure borate solution, there is a considerable increase in the hydroxide species after emersion from sulfate. A considerable increase in the Fe³⁺ species when compared to the experiment carried out in sulfate free borate solution was also observed. The increase in Fe³⁺ species relative to the Fe²⁺ species is more pronounced than after the first exposure to sulfate (Table 3.2, expt. 1 and Figure 3.4, expt. 1). The increased Fe³⁻ content suggests that some Fe₂O₃ could have formed in addition to Fe₃O₄. XPS analysis showed the presence of sulfate that suggests the presence of iron sulfate on the surface.

If the passive film on iron was grown by holding the electrode at 0.5V for 10 minutes and then subsequently scanned in a borate buffer solution contaminated with 0.05M sulfate as described above, anodic dissolution was once again observed (not shown). This shows that the method used to grow the protective oxide appears to have no bearing on its behavior in a borate solution contaminated with sulfate under the conditions described above.
Figure 3.5 shows the cyclic voltammogram of a clean iron surface cycled between -1.4V and 0.9V and emersed at -1.4V in a borate electrolyte containing sulfate. No passivation is observed and anodic current is enhanced when compared to those obtained in pure borate buffer solution. The results of XPS analysis are presented in expt. 3 of Table 3.2. Compared to emersion at the same potential in borate (expt. 1 of Table 3.1), it is clear that emersion in sulfate at this negative potential leads to a considerable increase in the metallic iron signal. It could be argued that the anodic dissolution observed in Figures 3.1b and 3.1c is caused by reduction at negative potentials in the sulfate containing solutions, of the protective film formed in borate, resulting in corrosion of the exposed iron. However, we have observed as shown in Figure 3.6, that if an iron electrode, sputtered and annealed in UHV, cycled in borate to develop the protective oxide film, is then scanned in a borate solution containing 0.05M sulfate between potential limits where reduction of the oxide film is not expected, enhanced anodic dissolution (when compared to the case shown in Figure 3.1a) along with crossing of anodic and cathodic traces is observed. Table 3.2, expt. 4 and Figure 3.4, expt. 4 show the results of XPS analysis after this experiment. XPS results of a subsequent repetition of this experiment are shown in Table 3.2, expt. 5 and Figure 3.4, expt. 5. In this case too, enhanced anodic dissolution was observed in the sulfate solution (not shown), and it was more pronounced than shown in Figure 3.6. The atomic ratios of iron and oxygen species in both cases indicate a mixture of Fe$^{2+}$ and Fe$^{3+}$ hydroxides and a mixture of Fe$_3$O$_4$ and Fe$_2$O$_3$. The excess oxidic intensity after accounting for these species is attributed to the presence of sulfate and borate entities.
Figure 3.5. Cyclic voltammogram of a clean Fe electrode in a borate solution containing 0.05 M Na$_2$SO$_4$.

Figure 3.6. Cyclic voltammogram of an iron electrode cycled in borate 16 times and emersed at 0.9 V, then cycled in the borate solution containing 0.05 M sulfate at more noble potentials.
3.3.3. Effect of Sulfate Exposure on the Behavior of Iron in Borate Buffer.

As described above, cycling an iron electrode in a sulfate containing solution leads to corrosion of the iron sample. We have observed that repeated exposure to sulfate containing solutions affects the ability of iron to passivate in a borate medium even after the iron electrode is sputtered and annealed in UHV and verified by XPS to be free of corrosion products.

Figure 3.1a shows the cyclic voltammogram of an iron electrode that has never been exposed to sulfate media. Provided that the iron electrode was never exposed to sulfate ions, this cyclic voltammogram was obtained reproducibly after cleaning the iron sample in UHV. Figure 3.7a shows the cyclic voltammogram obtained in borate after corroding once in a sulfate containing solution and cleaning in UHV. By corroding in sulfate, we mean that the iron covered with a protective oxide (grown in borate electrolyte) was subjected to 5 cyclic scans and 2 linear scans and emersed on the second linear scan at 0.9V in a sulfate containing solution (same conditions described in Figure 3.3b). Similarly, Figure 3.7b shows the cyclic voltammogram in a borate buffer of an iron electrode that had been corroded twice in a sulfate containing solution, followed by extensive cleaning in UHV prior to exposure to borate. There is a clear increase in anodic current in the cyclic voltammograms shown in Figure 3.7 when compared to Figure 3.1a. The dotted lines in this figure labeled I, II and III correspond to the peak potential of the most noble peak in Figures 3.1, 3.7a and 3.7b respectively. They serve to point out a trend, namely that the features on the anodic scan are shifted to more noble potentials indicating that passivation is no longer facile.
Figure 3.7. (a) Cyclic voltammogram of an Fe electrode in borate buffer pH 8.4 after corroding in sulfate followed by cleaning in UHV. (b) Same as Figure 3.7a except that the electrode had been corroded twice in sulfate followed by cleaning in UHV. The dotted lines I, II and III correspond to the peak potentials of the most noble anodic peak in Figures 3.1, 3.7a and 3.7b respectively.
The composition of the surface in borate after recording the cyclic voltammogram shown in Figure 3.7b is shown in expt. 5 of Table 3.1. A considerable increase in Fe$^{2+}$ species is evident, as is a slight increase in OH, compared to the other entries in this table. This would be expected if there were less of the FeOOH species traditionally associated with the passive film and more of the precursor Fe(OH)$_2$\cite{3,4,9}. Wieckowski has reported that cyclic voltammograms obtained for polycrystalline iron and Fe(100) show differences in the baseline current in the anodic part of the cyclic voltammogram\cite{24}. It is possible that corrosion and pitting in sulfate leads to the exposure of different faces on the polycrystalline iron, thereby leading to shift in features and increased anodic current.

3.4. Conclusions

Iron electrodes passivate in a borate buffered electrolyte. The protective oxide grown in the borate medium does not offer the electrode protection against corrosion when the electrode is scanned in sulfate containing borate media. Corrosion in sulfate leads to an increased hydroxylation of the surface as shown by XPS analysis. Exposure to sulfate results in inhibited passivation in pure borate solutions even if the sample is sputtered and annealed in UHV to atomically clean iron prior to exposure to borate. Such effects are not observed on a surface that has not been exposed to sulfate. The corrosion in sulfate apparently causes a change in surface roughness and/or morphology of the iron substrate. This change in surface roughness or morphology affects the behavior of the iron substrate on subsequent exposure to sulfate media. Additionally, this changed surface morphology affects the ability of iron to passivate in borate, even when all the surface contaminants have been removed by cleaning in UHV.
3.5. Chapter References


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CHAPTER 4

THE PROMOTION OF ANODIC DISSOLUTION OF POLycRYSTALLINE IRON
AND INCONEL 600 ALLOY SURFACES BY ADSORBED SULFUR

4.1. Introduction

The presence of internal impurities like sulfur is known to have a deleterious effect on the corrosion resistance of ferrous alloys and steels in aqueous environments. Marcus and coworkers, and Baer and coworkers, have extensively studied the effect of sulfur on a variety of metals and alloys. In all these studies the presence of sulfur, whether on the surface, included in the alloy, or in solution was found to enhance anodic dissolution of the metal (alloy) surface. While these studies were carried out in acidic solutions or in calcium nitrate solutions, we have chosen to carry out our iron studies in a mildly alkaline medium, akin to those commonly found in many Pressurized Water Reactor (PWR) systems. The studies of Inconel 600 (an alloy with composition of Ni72/Cr16/Fe8) were carried out in both mildly alkaline and mildly acidic medium for comparison.

The possible relationship between the observed electrochemical behavior of sulfur-modified surfaces and intergranular stress corrosion cracking (IGSCC) has been pointed out in the literature. Briefly, the stress fracture of the protective oxide can expose the substrate, including grain boundaries, to the aqueous environment. Studies have shown a correlation between sulfur segregation to the grain boundaries of ferrous
alloys and the extent of IGSCC observed in aqueous solution \(^1,8,9\). Moreover, such IGSCC has been shown to occur within a narrow well-defined range of potentials \(^1\). This suggests that IGSCC is controlled by the anodic dissolution of the sulfur-modified grain boundary surface within the active region of the surface. The chemical response of a sulfur-modified iron or alloy surface in aqueous solution is therefore of interest in gaining a more fundamental insight into the complex phenomenon of IGSCC.

The use of ultrahigh vacuum-electrochemistry (UHV-EC) methodology enables the preparation and characterization of surfaces in UHV that cannot be prepared by conventional bench top methods \(^10\). We have used this methodology to prepare metallic iron and Inconel 600 alloy surfaces modified with varying coverages of adsorbed sulfur, thus modeling a sulfur-contaminated grain boundary exposed to solution. It must be pointed out that the sulfur-modified surface is briefly exposed to \(\text{H}_2\text{O}\) vapor immediately prior to immersion in solution. However, previous studies of non-noble transition metal surfaces suggest that this does not significantly obscure the effect of sulfur on electrochemical behavior \(^2-9\).

We have used UHV-EC methodology to obtain a fundamental understanding of the effect of adsorbed sulfur on the polarization behavior of a polycrystalline iron surface in a mildly alkaline borate buffered solution. We have investigated the effects of systematically increased sulfur coverage on the electrochemical response of iron in a borate buffer of pH 8.4. Varying sulfur surface coverages were obtained by varying the exposures of atomically clean iron to \(\text{H}_2\text{S}\) gas at \(\approx 330\text{K}\). This reaction, under UHV conditions, results in the formation of sulfur ad-atoms without hydrogen adsorption \(^11,12\).
The surface was examined by X-ray Photoelectron Spectroscopy (XPS) prior and subsequent to polarization. XPS spectra of iron and sulfur indicate that no bulk FeS is formed at any sulfur coverage, i.e., iron remains essentially zero-valent. This is similar to the behavior observed for sulfur adsorbed on nickel surfaces as reported by Hardegree 13. We have observed that increasing the adsorbed sulfur coverage, leads to enhanced anodic dissolution of iron, although passivation is ultimately observed at noble potentials at all sulfur coverages. Furthermore, the iron dissolution current is found to increase in a non-linear manner with increased sulfur coverage of the surface. The current is found to increase more rapidly for sulfur coverages exceeding 64% saturation. XPS analysis of the surface overlayer after electrochemical polarization experiments reveals some interesting features. There is a rather sudden change in the ratios of hydroxide to oxide and Fe\(^{2+}\) to Fe\(^{3+}\) content of the surface film for sulfur coverages exceeding \(\approx 64\%\) sulfur saturation. Increasing the sulfur coverage leads to thicker overlayers on the iron surface as determined by the relative amounts of metallic iron to oxidized iron from XPS spectra. The effect on XPS spectra of emersing the electrode at various potentials along the polarization curve at constant sulfur coverage has also been examined.

We have also found that while the presence of adsorbed sulfur on the surface of polycrystalline iron in a borate buffer of pH 8.4 greatly enhances anodic dissolution, adsorbed sulfur has a minimal effect on the electrochemical response of Inconel 600 in the same solution. However, in an acetate buffer of pH 4.4, the presence of sulfur on Inconel 600 leads to an enhancement of anodic current. XPS quantitative analysis of the Inconel 600 surface before and after polarization in acetate medium suggests an enhanced
segregation of chromium (Cr) to the surface after polarization. A similar XPS analysis of Inconel 600, prior and subsequent to polarization in borate suggests that there is no increase in the amount of surface chromium after polarization.

4.2. Experimental

The electrode materials used were 0.5 mm thick polycrystalline iron foil (Aesar, Puratronic 99.998%) and 0.1 mm thick Inconel 600 foil (Ni72/Cr16/Fe8). Tantalum wires were spot welded on one side of the foil in order to establish electrical contact. A chromel alumel thermocouple was also spot-welded on the same side to monitor sample temperature. Care was taken to ensure that this side of the foil was kept away from solution contact while carrying out electrochemical experiments. The composition of borate buffer (pH = 8.4) used in this study was 0.0375M H₃BO₃ (Spectrum Chemical), 0.0094M Na₂B₄O₇ (Aldrich). The acetate buffer (pH = 4.4) was of 0.1M strength, prepared by mixing appropriate amounts of sodium acetate (Fisher) and acetic acid (EM Science). The chemicals listed were of analytical grade and used as received. Millipore water was used to prepare the solutions, and all solutions were purged with argon before use.

Electrochemical studies were carried out with a Pine Instruments AFRDE5 potentiostat, and the data was collected by a Hewlett Packard 7046B XY recorder. All electrode potentials reported in this study are with respect to an Ag/AgCl (0.01M NaCl) reference electrode. All voltammograms were recorded at 5mV/s.

Foils were cleaned in UHV by alternating cycles of argon ion bombardment (2.3keV, 300K) and annealing to ≈900K. This cleaning regimen was repeated until the
surfaces were observed to be devoid of impurities by XPS. Sulfur was adsorbed on the surface by directional dosing of H\textsubscript{2}S gas (electronic grade), through a stainless steel doser tube. Except where indicated, dosing on iron was performed by maintaining a pressure during dosing of \( \approx 6 \times 10^{-10} \) torr for varying durations. Dosing of H\textsubscript{2}S on Inconel 600 surface was carried out at a pressure of \( 5 \times 10^{-9} \) torr for 600 seconds. The temperature of the sample was \( \approx 330 \)K. Dosing at this temperature has been shown to lead to the presence of adsorbed sulfur and not adsorbed HS or H\textsubscript{2}S\textsuperscript{11,12}. The sample was then examined by XPS to check for adsorption of sulfur and verify the absence of adsorption of any oxygen containing species that could be introduced through the gas doser.

Following this, the sample was taken into the antechamber to perform electrochemical experiments. The electrochemical cell used was conceptually similar in design to those reported previously \textsuperscript{10}, and has been described in chapter 1. After recording of voltammograms, the sample was emersed from the solution under controlled potential and rinsed 6 times with Ar-purged millipore water. Potential control was maintained during the rinsing procedure. Following this, the chamber was evacuated by a turbomolecular pump to pressures of \( \approx 10^{-6} \) torr, and rapidly transferred back to the UHV chamber.

XPS analysis was performed using unmonochromatized Mg K\textalpha radiation from a dual anode X-ray source in combination with a hemispherical analyzer. Spectra were acquired using constant pass energy of 50 eV. Deconvolution of XPS data was accomplished by using ESCA tools \textsuperscript{14} in a MATLAB environment \textsuperscript{15}. The Binding Energies for Fe\textsuperscript{2+}(2p\textsubscript{3/2}) and Fe\textsuperscript{3+}(2p\textsubscript{3/2}) were assigned to 709.7 and 711.4 eV respectively.
Spectra were calibrated by referencing the observed Fe(2p\textsubscript{3/2}) binding energy for a clean iron surface to 706.75 eV. The binding energies for the oxide and hydroxide species corresponding to O(1s) were assigned to 529.6 and 531.1 eV respectively. The binding energies for pure Ni(2p\textsubscript{3/2}), Ni\textsuperscript{2+}(2p\textsubscript{3/2}), pure Cr(2p\textsubscript{3/2}) and Cr\textsuperscript{3+}(2p\textsubscript{3/2}) were assigned to 852.3, 855.1, 574.1 and 576.4 eV respectively. Detailed procedures for deconvolution of core-level spectra are discussed in chapter 2.

### 4.3. Poly crystalline Iron Studies

#### 4.3.1. Dosing of Iron Surfaces with Sulfur in UHV.

Figure 4.1 shows the variation of sulfur surface coverage (proportional to the S(2p)/Fe(2p) XPS intensity ratio) as a function of exposure to H\textsubscript{2}S at \approx 330K and a dosing pressure of 6\times10^{-10} torr. At higher exposures, no further increase in sulfur coverage is observed, indicating that the surface is saturated. This means that no further adsorption of sulfur is possible because all available surface sites are occupied. The fractional surface coverage was determined by measuring the relative S(2p)/Fe(2p) intensity ratios, and assigning 100\% saturation to the maximum value at which the ratios leveled off (see Figure 4.1). A possible shortcoming to this procedure is that a bulk sulfide layer might conceivably form and increase in thickness without a corresponding change in relative S/Fe XPS intensity. This situation has been observed, for example, in the reaction of Cl\textsubscript{2} with iron surfaces. However, the transition from a sulfur ad-layer to a bulk sulfide phase (either FeS or FeS\textsubscript{2}) is accompanied by significant shifts in the Fe(2p\textsubscript{3/2}) and S(2p\textsubscript{3/2}) binding energies to higher and lower values, respectively. As shown in Figure 4.2, no binding energy change was observed in the Fe(2p) spectrum upon H\textsubscript{2}S exposure. Similarly, no change
Figure 4.1. Percentage of sulfur saturation (proportional to relative XPS S(2p)/Fe(2p) intensity) of the iron surface as a function of exposure time to H₂S at a dosing pressure of $6 \times 10^{-10}$ torr.
Figure 4.2. XPS of the Fe(2p) region before and after exposure to H$_2$S at a dosing pressure of $1 \times 10^{-8}$ torr for 50s.

was observed in S(2p) binding energy (not shown). XPS spectra taken at glancing take-off angle (not shown) also displayed no shift in Fe(2p$_{3/2}$) and S(2p$_{3/2}$) binding energies.

The constancy of Fe(2p$_{3/2}$) and S(2p$_{3/2}$) binding energies as a function of sulfur exposure indicates that there is little or no Fe-S charge transfer in the sulfur ad-layer, up to saturation coverage. Similar behavior has been reported for H$_2$S on nickel by Hardegree $^{13}$. On the basis of work function measurements $^{13}$, the charge transfer from sulfur to nickel has been reported as only 0.04 electrons for S/Ni(100). Work function changes of a similar magnitude have been reported by Panzner et al. $^{19}$ for segregated
sulfur on single crystal and polycrystalline iron surfaces. These results indicate that at sub-monolayer coverages, the adsorbed sulfur is in a significantly less ionic state than in the corresponding bulk sulfides. Our XPS data, as well as other XPS, Auger, and inter-atomic work function data indicate that the sulfur ad-atoms on iron are much less ionic than the corresponding sulfide phases.

4.3.2. Effect of Sulfur Coverage on the Electrochemical Response of Iron.

Figures 4.3a and 4.3b show the polarization curves of iron in a borate buffer of pH 8.4 as a function of increasing sulfur coverage. It can be seen that the potential region over which iron shows dissolution behavior is not affected by the presence of adsorbed sulfur. Sulfur adsorption does, however, affect the polarization response in several ways. Firstly, increasing the sulfur coverage results in increased anodic dissolution current. At 100% of saturation coverage, the anodic dissolution current has increased by more than a factor of 10 when compared to a bare iron surface. It could be argued that hydrogen permeation into iron might lead to enhanced currents. However, temperature programmed desorption studies (TPD) of polycrystalline iron surfaces dosed with H₂S at ≈ 300K show that hydrogen adsorption on the iron surface does not occur under these conditions. Therefore, there is no hydrogen adsorption during H₂S exposure under our experimental conditions. A second feature of interest in these polarization curves is that while two anodic features are clearly delineated at sulfur coverages up to 33% of saturation, at higher coverages the two features begin to overlap, and the feature located at the more noble potential starts to appear as a shoulder on the larger peak located at the more active potential. On the basis of rotating ring disk studies and in-situ surface
enhanced Raman spectroscopy studies on a sulfur-free iron surface in a borate buffer of pH 8.4, the first feature on the voltammogram has been assigned largely to the dissolution of Fe to an Fe$^{2+}$ species, possibly Fe(OH)$_2$. In this potential range, Fe$_3$O$_4$ formation from Fe and Fe(OH)$_2$, and some FeOOH formation is reported. The second feature
at the more noble potential is associated with the conversion of Fe$^{2+}$ to Fe$^{3+}$, possibly due
to FeOOH formation or a mixed Fe$^{2+}$, Fe$^{3+}$ hydroxide from precursor species like
Fe(OH)$_2$. This could involve oxidation of Fe$^{2+}$ species that are in the film and/or in the
solution. Based on our XPS data, we believe that similar transitions may
be associated with these features even on a sulfur-covered iron surface. A third
interesting trend that is evident from examining Figures 4.3a and 4.3b is that by looking
at the relative peak heights of the two features, up to sulfur coverages of about 64%, the
first peak appears to grow at a faster rate, while at higher coverages the second feature
appears to grow faster. On the basis of calculations from our XPS data that will be
discussed below, there is evidence to show that Fe$^{3+}$ content in the film increases in the
potential region of the second wave and also increases with increasing sulfur coverage.
The XPS data demonstrate that there is a real growth of the second anodic peak with
increasing sulfur coverage and that this is not an artifact created by sloping baselines
associated with the polarization curves. This indicates that at sulfur coverages below
64% the dissolution of iron is greatly enhanced by the presence of sulfur while the
subsequent oxidation of Fe$^{2+}$ to Fe$^{3+}$ is not as greatly affected. At sulfur coverages >
64%, the rate of oxidation of Fe$^{2+}$ to Fe$^{3+}$ increases significantly.

Figure 4.4 shows the variation of the peak current associated with the first anodic
feature as a function of sulfur coverage. It is clear that the peak current does not vary
linearly with sulfur coverage. It is also clear from Figure 4.4 that at coverages of sulfur
exceeding 64% saturation, the current rises more rapidly with increasing coverage than at
the lower coverages. Baer has reported a similar acceleration of the corrosion of iron in a
Figure 4.4. Variation of the iron dissolution current as a function of sulfur coverage.

55 weight percent Ca(NO$_3$)$_2$ solution, when sulfur content exceeds a threshold value. However, in that case, above the threshold coverage (0.7 monolayer), the corrosion rate was independent of sulfur content. As is clear from Figure 4.4, no leveling off of the corrosion current is observed below saturation coverage. As the XPS data in Figure 4.2 does not indicate any bulk FeS formation at higher sulfur dosage, the change in the polarization curve cannot be attributed to the formation of FeS on the surface.

4.3.3. XPS Results. Figure 4.5 shows the XPS spectrum of the S(2p) region at various stages of the experiment. Figure 4.5a shows the sulfur region after exposure of
Figure 4.5. XPS of the S(2p) region. (a) After dosing with H₂S at a dosing pressure of 1 x 10⁻⁸ torr for 50 s. (b) After one linear scan in borate buffer (pH = 8.4) and emersing at +0.9 V. (c) After partially sputtering away the oxide/hydroxide overlayer, grown as described in (b). (d) After partial electrochemical reduction of the oxide/hydroxide overlayer (grown as described in (b)), by holding the electrode at -1.4 V for 10 min.
the iron surface to H₂S, but prior to solution electrochemistry. XPS of the S(2p) region after polarization in borate buffer and emersing at +0.9V (Figure 4.5b) reveals no sulfur signature. This was found to be the case at all initial surface coverages of sulfur. However after partial sputtering of the oxide (Figure 4.5c), or reduction of the oxide by cycling the electrode back to -1.4V and holding the electrode at that potential for 10 minutes (Figure 4.5d), the S(2p) peak starts to reappear. This indicates that the oxide/hydroxide phase has grown on top of the underlying sulfur layer at all initial surface coverages of sulfur. The intensity of the sulfur signal in Figures 4.5c and 4.5d appears reduced when compared to Figure 4.5a. While this could indicate partial desorption of the sulfur from iron, it is also possible that the oxide remaining on the surface attenuates the signal from the underlying sulfur. As we do not have depth profiling capabilities at present, we were unable to quantify the sulfur present after the polarization experiment. Electrochemical reduction did not lead to total reduction of the oxide, so we were unable to use this method to accurately quantify sulfur by subsequent XPS analysis. As has been reported earlier by Wieckowski, if iron is subjected to cyclic voltammetry in borate buffer, a "memory effect" exists, in that total reduction of the iron oxide grown on the surface is not observed.

Marcus has shown by the use of radioactivity measurements, that for sulfur adsorbed on a nickel surface, no desorption of sulfur occurs for electrodes polarized in an acidic medium and emersed in the active region or at the active-passive transition. However, for nickel electrodes emersed in the passive region, partial desorption of sulfur is observed. Baer has reported that most of the sulfur remains on the surface of iron
after subjecting the iron electrode to electrochemical studies in Ca(NO₃)₂. Based on our current data, we cannot rule out partial desorption of sulfur in the passive region but we have no evidence to indicate that it does occur.

Table 4.1 shows the composition of the surface overlayer (as determined by XPS analysis) formed on an iron surface that is totally saturated with sulfur, as a function of the emersion potential from a borate electrolyte. The ratio of Fe²⁺ species to Fe³⁺ species decreases at the more positive emersion potentials. The overlayer thickness (as indicated by the ratio of the XPS signals of metallic iron to the total iron), increases at the more noble emersion potentials. At -0.8V, the hydroxide/oxide ratio is high, possibly due to the presence of Fe(OH)₂ species, assuming that the oxidation processes that occur on the sulfur-covered iron surface are similar to those occurring at a sulfur-free iron surface.

The high Fe²⁺ content of the films formed when the electrode is emersed at this potential (-0.8V), suggests that Fe(OH)₂ is the most likely species. There is a slight dip in the hydroxide/oxide ratio for surfaces emersed at -0.4V. This could be on account of the fact

### Table 4.1. Composition of the surface overlayer on a 100% sulfur-saturated iron surface as a function of emersion potential from a borate buffer of pH 8.4

<table>
<thead>
<tr>
<th>Emersion Potential</th>
<th>Fe²⁺ /Fe³⁺</th>
<th>Fe(0) /Fe(total)</th>
<th>OH⁻ / O²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.8V</td>
<td>3.01</td>
<td>0.28</td>
<td>0.49</td>
</tr>
<tr>
<td>-0.4V</td>
<td>2.31</td>
<td>0.21</td>
<td>0.40</td>
</tr>
<tr>
<td>+0.1V</td>
<td>1.01</td>
<td>0.09</td>
<td>0.54</td>
</tr>
<tr>
<td>+0.9V</td>
<td>0.64</td>
<td>0.04</td>
<td>0.53</td>
</tr>
</tbody>
</table>

a Sulfur dosing was done at ~1.5 × 10⁻⁸ torr for 50s.
b Potentials are with respect to Ag/AgCl (0.01 M NaCl).
that in this potential range some conversion of Fe(OH)$_2$ to Fe$_3$O$_4$ is possible. For surfaces emersed at +0.1V and +0.9V, the hydroxide content has increased again. According to the literature, the conversion of Fe(OH)$_2$ and Fe$_3$O$_4$ to Fe$^{3+}$ containing hydroxides occurs over this potential range. These processes account for the increase in hydroxide content at these potentials.

Adsorbed sulfur significantly affects the thickness and composition of the oxide/hydroxide surface layer formed during the polarization experiments. XPS data of the Fe(2p) and O(1s) regions are shown in Figure 4.6 for iron electrodes emersed at +0.9V. Figure 4.6a corresponds to spectra obtained for a clean iron electrode and Figure 4.6b to those obtained on a iron electrode that was totally saturated with sulfur. The data indicate that for the sulfur-covered iron surface there is an increase in hydroxyl content of the film and also the film is thicker as indicated by the attenuation of the metallic iron signal. Thickness of the oxide/hydroxide films were computed according to

$$I = I_0 \exp\left(-\frac{d}{\lambda \cos \theta}\right)$$

(4-1)

where $d$ is the thickness of the oxide film, $\lambda = 2$ nm is an electron attenuation length of the Fe(2p) photoelectrons and is determined by using the general model of Seah and Dench, $\theta = 0^\circ$ is the take-off angle in this study, and $I$ and $I_0$ are the spectral peak intensity of the metallic substrate of the Fe(2p) band for the oxidized iron sample and the clean iron sample, respectively. The thickness of oxide/hydroxide films grown on clean iron and sulfur-saturated iron surfaces under our experimental conditions are 6.39 nm and 9.17 nm, respectively. For comparison, the thickness of the natural oxide film on iron formed in air is $3.4 \pm 0.7$ nm.
Figure 4.6. XPS of the Fe(2p) and O(1s) regions after emersing the Fe electrode from a borate electrolyte (pH 8.4) at +0.9V (a) Of a clean Fe surface. (b) Of a Fe surface that was totally saturated with S by dosing at a pressure of $6 \times 10^{-10}$ torr.
Figure 4.7 shows the surface layer component ratios as a function of surface sulfur saturation for iron surfaces emersed at +0.9V from borate buffer. At surfaces where sulfur coverage is < 64%, the \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio is \( \approx 1.1 \) with some scatter. At higher coverages of sulfur, there is a considerable drop in the \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio. Similarly the

![Graph showing surface component ratios as a function of sulfur saturation.](image)

**Figure 4.7.** Surface component ratios as a function of sulfur saturation.
hydroxide to oxide ratio increases at coverages higher than 64% though not in as
pronounced a manner as the Fe$^{2+}$/Fe$^{3+}$ ratio. The fact that the OH does not increase as
much is not surprising given the data in Table 4.1, from which it is clear that OH is
present on the surface at all emersion potentials. However, the fact that there is an
increase in OH content along with an increase in Fe$^{3+}$ content over the same range of
sulfur coverages indicates that there could be enhanced FeOOH formation at these
coverages or enhanced formation of Fe$^{3+}$ containing hydroxides. The sharp increase in
the OH$^-$/O$^{2-}$ ratio in Figure 4.7 argues against enhanced FeOOH formation. The
electrochemical data in Figure 4.3 also indicate an enhancement of the wave associated
with Fe$^{3+}$ formation as mentioned earlier. From Figures 4.6 and 4.7, it is also evident that
the overlayer thickness increases as a function of sulfur coverage as shown by the
attenuation of the metallic iron signal when compared to the total iron signal. Baer has
reported that a thicker oxide grows on sulfur-covered iron surfaces on exposure to
Ca(NO$_3$)$_2$ when compared to pure iron. These data in conjunction with the polarization
data shown in Figures 4.3 and 4.4 all point to the fact that at coverages of sulfur $>$64% a
transition occurs that leads to different electrochemical behavior and different surface
composition as a result.

4.3.4. Discussion. For the case of adsorbed sulfur on nickel that is polarized in
H$_2$SO$_4$ solution, Marcus has suggested that as long as sulfur is present on the nickel
surface, passivation is blocked because H$_2$O or OH adsorption on the surface is blocked.
He has suggested that as some of the sulfur desorbs (as determined by radioactivity
measurements), the sites vacated by sulfur are now free for water or OH adsorption,
leading to passivation. As mentioned above, it is not clear at the present time if any desorption of sulfur occurs in our experiments. Hence we are unable to determine if partial sulfur desorption is a necessary condition for FeOOH formation. However, this simple model proposed for nickel cannot explain why a thicker overlayer is formed on iron in a borate electrolyte in the presence of adsorbed sulfur. Also it cannot explain why a transition in behavior is observed when sulfur coverage exceeds 64% of saturation.

In the active region, anodic current is proportional to the corrosion rate. As mentioned earlier in this section, the potential range over which anodic dissolution occurs is not altered by the presence of sulfur on the surface. However, the anodic current increases. This indicates that sulfur could lower the activation barrier for iron dissolution. Another factor that could also contribute to enhanced anodic current and explain the abrupt changes in behavior at coverages greater than 64% sulfur saturation is discussed below. Figure 4.8 shows a pictorial representation of overlayer formation at different sulfur coverages. There are two competing processes that contribute to overlayer growth. The first process occurs in areas of the iron surface that are sulfur free. At such sites, direct surface growth of the passivating FeOOH (or a mixed Fe$^{2+}$-$^{3+}$ hydroxide) occurs. The second process occurs in the areas that are sulfur covered. At sulfur covered sites, the near surface Fe$^{2+}$ that is generated during the initial dissolution could get oxidized further to Fe$^{3+}$ oxides and hydroxides and precipitate on top of the sulfur. Support for such a growth mechanism is provided by the XPS data presented above in Figure 4.5, where it is shown that the oxide/hydroxide phase ultimately grows over the underlying sulfur at all sulfur coverages. At low surface coverages of sulfur as
shown in Figure 4.8a, the direct growth of the oxyhydroxide phase is more facile. At higher sulfur coverages as shown in Figure 4.8b, vacant sites would be limited or unavailable. Hence direct formation of surface oxides and hydroxides would be difficult. The oxides and hydroxides would have to grow predominantly by oxidation and reprecipitation of the near surface Fe$^{2+}$ species generated by dissolution. There is increased iron dissolution to begin with at the higher sulfur coverages as indicated in
Figure 4.3. As a result, there is a higher concentration of Fe$^{3+}$ formed by subsequent oxidation of the Fe$^{2+}$. There is also increased hydroxide species associated with this Fe$^{3+}$ as suggested by the XPS data in Figure 4.6.

It is known that corrosion rate or anodic current decreases substantially once the passive film begins to form. It is also believed that phases formed by dissolution and reprecipitation are not as protective as oxides or hydroxides formed in place on the surface. If this is true, then at higher sulfur coverages where the passivating layer grows primarily by reprecipitation, the anodic current observed before the onset of passivation would be expected to be higher as the over layer is not as protective. This, when compounded with the possible lower activation barrier to iron dissolution on a sulfur-covered surface could explain the much higher anodic currents observed at higher sulfur levels on the surface.

Another possibility is that this transition in behavior could originate from sulfur occupying different sites on the iron at higher coverages. This could lead to the changes in the rate of various oxidation and dissolution processes that are evident from the polarization curves. On a polycrystalline iron surface such as the one used in our experiments, such effects are difficult to identify, but studies on single crystal iron planned for the future could shed light on the nature of surface sites occupied by iron as a function of sulfur coverage.

As has been pointed out above, sulfur segregation to grain boundaries of ferrous alloys is believed to influence the extent of IGSCC. Studies like the one presented above, and reported by others that make use of the UHV-EC methodology enable the
modeling of the response in aqueous media of a surface that has sulfur at the grain boundaries. As in the previous studies \(^8,9\), this study has shown that sulfur when present at the surface of iron, leads to enhanced anodic dissolution and the presence of a thicker overlayer. However, this study helps to draw attention to the fact that sulfur could affect the IGSCC or general corrosion of ferrous alloys in different ways and to different extents depending on the aqueous medium to which the sulfur-covered iron surface is exposed. To be more specific, this study reveals that the finer details of the electrochemical response of sulfur-covered iron and the chemical composition of the resulting overlayer are very dependent on the electrolyte medium. In the previous studies \(^8,9\), the iron dissolution current in Ca(NO\(_3\))\(_2\) was found to be independent of sulfur coverage above the threshold coverage of 0.7 monolayer. Also, below the threshold coverage of sulfur, the dissolution current was found to essentially similar to that observed for pure iron \(^8,9\). In contrast, in this study, an increased dissolution current for iron is observed at all sulfur coverages, with a more rapid increase in dissolution current above 64% of sulfur saturation coverage. Also in this study, the changing ratios of surface components in the overlayer have been described as a function of increased sulfur coverage. Increased overlayer thickness is attributed specifically to an increase in Fe\(^{3+}\) containing hydroxides. This serves to point out that continued studies of this nature are important to develop a broader understanding at a fundamental level of the role of sulfur or any other impurity in IGSCC and in corrosion of ferrous alloys in general.
4.4. Inconel 600 Studies

4.4.1. Effect of Sulfur in Borate Buffer. Figure 4.9 shows polarization curves for Inconel 600 in borate buffer of pH 8.4. Figure 4.9a shows the polarization curve for a clean Inconel 600 surface. Two features are present in the anodic region at 0.67V and 0.9V. Bench top experiments of a nickel electrode in borate buffer do not show these features on the first anodic scans. The presence of such features on nickel in alkaline media on subsequent polarization scans have been reported. These have been

Figure 4.9. Polarization curves of (a) clean Inconel 600 and (b) sulfur-covered Inconel 600 in borate buffer (pH=8.4).
attributed to mixtures of Ni\(^{3+}\) containing hydroxides, oxides and oxyhydroxides based on \textit{in-situ} UV-Visible spectroscopy at these potentials\(^{28}\). It is possible that such species could be forming on the Inconel 600 surface. Another possible explanation would be the formation of spinels (general formula \(\text{AB}_2\text{O}_4\))\(^{29}\). However, Pourbaix diagrams for the Ni-Cr-Fe system suggest that iron nickel spinels are not stable at the potentials at which the peaks are observed in Figure 4.9a, even though a pH of 8.4 is favorable for spinel formation\(^{29}\). Spinels containing chromium and nickel are stable under acidic conditions\(^{29}\), which is not the case in the polarogram shown in Figure 4.9a. Figure 4.9b shows the polarization response in borate buffer of pH 8.4 for a sulfur-covered Inconel 600 surface. It is evident that in contrast to the pronounced effect that sulfur has on the electrochemical response of iron shown in Figure 4.3, the presence of sulfur on Inconel 600 surface does not lead to a pronounced increase in the anodic dissolution current.

Results of XPS analysis of the Inconel 600 surface prior and subsequent to polarization under various conditions are shown in Table 4.2. Experiments 1 and 2 are for polarization in borate medium. It is clear that in contrast to the iron surface described above, the presence of sulfur on the Inconel 600 surface does not greatly affect the hydroxide content of the film after polarization. Both in the presence and absence of adsorbed sulfur, the surface is rich in nickel after polarization in the borate electrolyte.

\textbf{4.4.2. Effect of Sulfur in Acetate Buffer.} Figure 4.10a represents the polarization response of a clean Inconel 600 surface in acetate buffer of pH 4.4. In Figure 4.10b, the polarization response of a sulfur-covered Inconel 600 surface in acetate buffer is shown. It is obvious that there is an enhanced anodic current in the region of
Table 4.2. Results of XPS analysis of Inconel 600

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ni/Cr Initial</th>
<th>Adsorbed S</th>
<th>Ni/Cr [Ox]a</th>
<th>OH⁻/O₂⁻</th>
<th>Electrolyteb</th>
<th>Emersion Potentialc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.75</td>
<td>No</td>
<td>4.00</td>
<td>1.28</td>
<td>Borate</td>
<td>1.0V</td>
</tr>
<tr>
<td>2</td>
<td>2.81</td>
<td>Yes</td>
<td>3.84</td>
<td>1.3</td>
<td>Borate</td>
<td>1.0V</td>
</tr>
<tr>
<td>3</td>
<td>2.64</td>
<td>No</td>
<td>1.25</td>
<td>0.81</td>
<td>Acetate</td>
<td>0.7V</td>
</tr>
<tr>
<td>4</td>
<td>2.44</td>
<td>Yes</td>
<td>0.95</td>
<td>0.87</td>
<td>Acetate</td>
<td>0.7V</td>
</tr>
<tr>
<td>5</td>
<td>3.69</td>
<td>No</td>
<td>1.95</td>
<td>0.96</td>
<td>Acetate</td>
<td>0V</td>
</tr>
<tr>
<td>6</td>
<td>3.39</td>
<td>Yes</td>
<td>1.00</td>
<td>1.86</td>
<td>Acetate</td>
<td>0V</td>
</tr>
</tbody>
</table>

a These are ratios obtained after polarization. b See text for composition. c Potentials are with respect to Ag/AgCl (0.01M NaCl).

Figure 4.10. Polarization curves of (a) clean Inconel 600 and (b) sulfur-covered Inconel 600 in acetate buffer (pH=4.4).
potentials between -0.4V and 0V. Hence from Figures 4.9 and 4.10 it is clear that the effect of sulfur on the aqueous corrosion of Inconel 600 is dependent on the composition of the solution. Experiment 3 in Table 4.2 shows the surface composition of Inconel 600 that was polarized in acetate and emersed at 0.7V. It is evident that subsequent to polarization in acetate, the concentration of chromium at the surface increases.

Experiment 4 shows the results of a sulfur-covered Inconel 600 surface that was polarized in acetate under similar conditions as in Experiment 3. It is clear once again that the surface content of chromium increases after polarization. Experiments 5 and 6 show results of XPS analysis done on sulfur-free and sulfur-covered Inconel 600 that was polarized in acetate buffer but emersed at 0V. The XPS results indicate that both in the presence and absence of sulfur on the Inconel 600 surface, polarization in acetate buffer results in enhanced levels of chromium in the surface film.

It is also evident from the data presented in Table 4.2 that by cleaning the surface of Inconel 600 in UHV (as described in the experimental section) after polarization in borate buffer, it is possible to reproducibly obtain a surface where the initial ratio of Ni/Cr is of the order of 2.8. However, after polarization in acetate, the UHV cleaning regimen leads to surfaces that are nickel rich but the ratio of Ni/Cr is not reproducible. The reasons for this are unclear at the present time. However, irrespective of the exact value of the Ni/Cr ratio prior to polarization, whenever the Inconel 600 surface is subjected to potentiodynamic scanning in the acetate medium, the surface undergoes a transformation from being nickel rich to a surface that has enhanced chromium content.
4.5. Conclusions

The presence of sulfur on a polycrystalline iron surface leads to enhanced anodic
dissolution in a borate electrolyte. The region of potentials over which anodic dissolution
is observed remains similar to that observed on a sulfur-free iron surface. The two anodic
peaks observed in borate buffer for a sulfur-free iron surface are observed when sulfur
saturation on the iron surface is less than 33%. At higher coverages, the two features
start to merge. For sulfur coverages less than 64%, the anodic peak associated largely
with iron dissolution at the more active potential grows faster than the second feature at
more noble potentials. At sulfur coverages higher than 64%, the second peak in the
voltammogram associated largely with formation of the Fe$^{3+}$ species grows faster. The
current associated with the first peak in the voltammogram is found to increase in a non-
linear manner with sulfur coverage. XPS data indicate that a marked increase in Fe$^{3+}$
concentration as well as hydroxide concentration in the overlayer occurs at sulfur
coverages exceeding 64% saturation. The XPS data in conjunction with the polarization
data suggest enhanced formation of Fe$^{3+}$ containing hydroxide phases at higher
coverages. XPS data indicate that there is residual sulfur on the surface after polarization
in solution. The presence of sulfur inhibits the formation of the passive film observed on
sulfur-free surfaces $^{20,22,26}$. Instead a film that is rich in Fe$^{3+}$ hydroxides which are less
efficient at passivation is formed. A second possible effect is that the presence of
adsorbed sulfur significantly lowers the activation barrier for iron dissolution, and this
effect may be enhanced at higher coverages due to the occupation of a lower symmetry
site.
The effect of sulfur on the anodic dissolution of Inconel 600 in the borate buffer is minimal. The presence of adsorbed sulfur causes a pronounced increase of the anodic dissolution current of Inconel 600 in an acetate buffer of pH 4.4. XPS analysis shows that in acetate medium there is an enhanced chromium content of the surface film after polarization. An increase in chromium content is not observed after polarization in borate buffer. Hence the differences in behavior of Inconel could be a result of differences in chemical identities of surface species. To sum up, the results presented above show that the effect of sulfur on the corrosion of metals and their alloys in a particular aqueous medium is very dependent on the nature of the alloy or metal. In addition it is also clear that for a particular alloy, the effect of adsorbed sulfur is very dependent on the composition of the solution in which corrosion is investigated. XPS analysis show that these differences in behavior stem from differences in the nature of chemical species present on the surface of the alloy or metal.

4.6. Chapter References


(14) ESCA Tools™; 4.6 ed.; Surface/Interface Inc.: Mountain View, California, 1995.


CHAPTER 5

THE ADSORPTION OF LEAD ON CLEAN AND SULFUR-MODIFIED NICKEL SURFACES IN AQUEOUS ENVIRONMENTS

5.1. Introduction

The phenomenon of adsorption of metal cations from aqueous solution onto solid substrates is a subject of long standing and considerable interest, mainly because of its environmental implications. The adsorption of cations at substrate surfaces is known to either enhance or inhibit certain electrochemical reactions. Better understanding of such effects is very important to a number of different fields, including the design of environmental electrocatalysts, corrosion inhibition and the deposition of thin films for microelectronic applications. This work is part of a larger effort to understand the chemical and electronic information concerning essentially surface-modified materials in aqueous environments. Until recently, most such studies were carried out on high surface area colloidal systems, due to the detection limits of electrochemistry and in-situ spectroscopy methods. The use of systems with such complex geometry inhibits the detailed characterization of substrate/adsorbate and adsorbate/adsorbate interactions. In this study, we have used combined ultrahigh vacuum/electrochemistry (UHV-EC) methodology to gain such detailed information on well-characterized metal surfaces in aqueous solution.
The underpotential deposition (UPD) of lead on a gold electrode has been shown to have a significant effect on the reduction of nitrobenzene. It has also been reported that the adsorption of Pb\(^{2+}\) inhibits electroless nickel deposition. In addition, lead, one of the contaminants in the secondary side system of Pressurized Water Reactor (PWR) steam generators, has been suspected as being responsible for enhancing stress corrosion cracking (SCC) on the nickel-based alloys. The results of corrosion studies in the open literature are still inconclusive on the mechanism of this lead-induced SCC. Sulfur is also known to have destructive effects on the corrosion resistance of nickel and iron alloys. Studies have shown that sulfur inhibits the oxide formation and enhances anodic dissolution of the metals (or alloys) in aqueous solution. This effect of sulfur preventing metal passivation has been related to the sulfur-enhanced SCC. It is therefore of interest to gain more fundamental insight into the influence of Pb\(^{2+}\) on clean and sulfur-adsorbed nickel surfaces at the molecular level.

Combined ultrahigh vacuum/electrochemistry (UHV-EC) methodology provides the means to prepare and modify sample surfaces in UHV before the surfaces are subjected to electrochemistry in aqueous solution. We have used UHV-EC methodology to prepare atomically clean nickel surfaces and sulfur-covered nickel surfaces for electrochemical measurements under various conditions. Sample transfer necessitates a brief vapor exposure of the UHV-prepared surface immediately prior to immersion into or emersion from the aqueous environment. The effect of such exposures on the electrochemical behavior of reactive metal systems (e.g., Fe) may be negligible under certain circumstances but has not been explored in detail. We present
evidence (*vide infra*) that the vapor induced oxide/hydroxide overlayer dissolves at short times after immersion and before the growth of an oxide/hydroxide layer in solution.

The open-circuit potential (OCP), also known as mixed potential or corrosion potential in a corrosive environment, of the electrochemical system was measured to characterize the *in-situ* electrochemical behavior of adsorbate-modified surfaces after immersion. We have observed that the adsorbed sulfur shifts the OCP of nickel about 150 mV more negative (less noble) in NaNO₃ electrolyte solution. Such shift correlates with *ex-situ* XPS measurements of the evolution of the oxide/hydroxide surface layer as a function of immersion time. This is consistent with previous observations based on voltammetric and corrosion studies, in which adsorbed sulfur obstructs the passivating process on nickel surfaces. This is also similar to the behavior of sulfur on iron surfaces reported in our previous study. However, this sulfur-induced shift of OCP is reduced to 30 mV when a trace amount of Pb²⁺ is present in the electrolyte solution. This suggests that the Pb²⁺ has a substantial effect on the oxidation of sulfur-covered nickel surfaces in the solution.

The sample surface was examined by x-ray photoelectron spectroscopy (XPS) prior and subsequent to electrochemical treatments and measurements. Analysis of XPS spectra indicates that adsorbed sulfur on nickel enhances the adsorption of Pb²⁺ by at least 400%. The binding energy of Pb(4f₇/₂) for Pb²⁺ adsorbed on sulfur-modified nickel is 0.3 eV more positive than that on clean nickel. This binding energy shift demonstrates that Pb²⁺ interacts with pre-adsorbed sulfur on nickel surface. XPS results have also shown that sulfur inhibits the formation of NiO (a critical oxide phase for passivation)
and enhances hydroxylation $^{13,27,28}$. The hydroxide film grown on sulfur-modified nickel is found to be thinner when Pb$^{2+}$ is present in the solution. It suggests that the adsorption of lead retards the oxidation of sulfur-modified nickel surfaces. The amount of lead adsorption as a function of immersion time has also been investigated. These results have provided a fundamental understanding of the adsorption process at a solid/liquid interface, and the time scales over which these processes occur.

5.2. Experimental

5.2.1. Materials and Reagents. Polycrystalline nickel foil (Aesar, Puratronic, 99.994%) was used as the electrode material. Tantalum wires were spot-welded on both edges of the foil to establish electrical contact. The sample temperature was monitored by a chromel-alumel thermocouple spot-welded on the back of the electrode. All experiments were carried out at room temperature (~298 K). Reagent grade Pb(NO$_3$)$_2$ (Alfa Aesar) and NaN0$_3$ (Spectrum Chemical) were used as received. All solutions were prepared from Millipore grade water and purged with argon before use.

5.2.2. Sample Preparation. The nickel foil was cleaned under vacuum by argon ion bombardment (2.3 keV) at room temperature followed by annealing the foil to ~700K. This cleaning process was repeated until XPS showed the presence of only metallic nickel without impurities. Sulfur-modified nickel surfaces were obtained by directional dosing of H$_2$S (electronic grade) gas. H$_2$S dosing was performed by maintaining a background pressure of 5 x 10$^{-9}$ torr during dosing for 30 seconds, which resulted in saturation coverage. Exposures are reported in terms of time and background
pressure \((1 \text{L} = 10^{-6} \text{torr} \cdot \text{s})\). Higher exposures of \(\text{H}_2\text{S}\) were also performed to confirm that no more sulfur could be adsorbed.

5.2.3. Lead Adsorption and OCP Measurements. Lead adsorption experiments were carried out by immersing clean and sulfur-modified nickel electrodes in both 0.01M and 0.001M \(\text{PbNO}_3\) solutions for various durations. The OCP measurements were carried out using an ORION 420A pH/mV meter. Electrode potentials reported here are referenced to an Ag/AgCl (0.01M NaCl) electrode. The potential of our Ag/AgCl reference electrode was 0.1V (vs. SCE). The potential was measured right after the electrode was immersed into 0.1M NaNO\(_3\) (pH = 5.9) or 0.1M NaNO\(_3\) containing 0.001M PbNO\(_3\) (pH = 4.8) electrolyte solution. In the current configuration of our electrochemical cell, use of a luggin capillary is not feasible. Therefore a high concentration of supporting electrolyte (0.1M NaNO\(_3\)) is needed to minimize resistance between reference and working electrodes. The measured potentials were recorded by an IBM PC-compatible computer at intervals of 5 seconds to a total of 20 minutes.

5.2.4. XPS Analysis. XPS spectra were acquired using unmonochromatized Mg K\(\alpha\) radiation operated at 15 kV and 300 W in conjunction with a hemispherical electron energy analyzer in the constant pass energy mode at 50 eV. The x-ray angle of incidence is 54.7\(^\circ\) relative to the analyzer axis. The sample was mounted so that the angle between the analyzer axis and sample surface normal (take-off angle) could be varied from 0\(^\circ\) to ~90\(^\circ\). Peak fitting of XPS spectra was accomplished using commercially available software, ESCA tools, developed by Surface/Interface Inc. \(^{29}\) and utilized as a toolbox in the MATLAB environment \(^{30}\). Shirley (non-linear) background subtraction \(^{31}\) was used
in this study as it has been shown to be the most effective method for fitting the short energy range found in typical core XPS spectra \(^{32}\). Spectra presented in this study were calibrated by referencing the observed Ni(2p\(_{3/2}\)) binding energy for a clean nickel surface to 852.3 eV \(^{33}\). The Ni(2p\(_{3/2}\)) spectra were fitted over the range of 845 – 865 eV. The binding energies of Ni\(^{2+}\)(2p\(_{3/2}\)) for Ni(OH)\(_2\) were assigned at 855.4 eV \(^{34}\). The main Ni\(^{2+}\)(2p\(_{3/2}\)) feature associated with NiO is situated at 853.5 eV with an intense satellite peak at 855.4 eV \(^{35}\). In this study, only one peak at 855.4 eV was used in the fitting scheme to represent a combination of the main feature of Ni(OH)\(_2\) and the satellite feature for NiO. We have found it necessary to include a small peak at 854.3 eV in all the spectra to obtain better fitting results. The intensity of this feature does not vary with the film composition (oxide/hydroxide ratio). Hence, this might be an artifact due to the fitting method used in this study. The assignment of this feature is not fully understood at this point. A combined satellite feature for Ni\(^{2+}\)(2p\(_{3/2}\)) was assigned between 861.1 and 861.3 eV based on the composition of the oxide/hydroxide film \(^{34,35}\). The binding energies of O(1s) for nickel oxide, hydroxide and lattice water (if present) were assigned at 529.1, 530.8 and 532.4 eV, respectively \(^{32,34}\). The Pb(4f) spectra were fitted over range of 132 – 148 eV. The binding energies of Pb(4f\(_{7/2}\)) and Pb(4f\(_{5/2}\)) for adsorbed Pb\(^{2+}\) species were observed at 138.2 (±0.2) and 143.2 (±0.2) eV, respectively. Detailed assignments of the Pb(4f) binding energies will be discussed in the results and discussion section. The XPS Peak fitting routine used in this study \(^{36}\) has been described in chapter 2.
5.3. Results and Discussion

5.3.1. The Adsorption of Lead on Nickel Surfaces. The amount of Pb\textsuperscript{2+} adsorbed onto clean and sulfur-modified nickel surfaces after various immersion durations was determined by calculating the Pb/Ni intensity ratio from XPS data. After emersing from dilute Pb(NO\textsubscript{3})\textsubscript{2} solution, the sample surface was covered not only by chemically adsorbed Pb\textsuperscript{2+} but also by an appreciable amount of Pb(NO\textsubscript{3})\textsubscript{2} salt. Therefore, adequate rinsing is required to ensure the removal of physisorbed salt layers\textsuperscript{16}. Figure 5.1 shows the amount of lead left on the sulfur-modified nickel surface as a function of increasing number of rinses. Each rinse was done by immersing the lead-adsorbed sample surface into deionized water for exactly 10 seconds. As Figure 5.1 demonstrates,

![Figure 5.1](image)

Figure 5.1. The amount of lead adsorbed on the sulfur-modified nickel surface from 0.001M Pb(NO\textsubscript{3})\textsubscript{2} solution as a function of number of rinses.
most of the loosely-bound Pb(NO₃)₂ salt was rinsed off after 4 rinses. A procedure of 4 rinses was therefore used throughout this study.

Figure 5.2 shows the fitted Pb(4f) XPS spectra of clean and sulfur-modified nickel surfaces which had been subjected to 5 seconds immersion in different concentration of Pb(NO₃)₂ solutions. It is evident that pre-adsorbed sulfur on the nickel surface dramatically enhances lead uptake from the solution. The Pb(4f₇/₂) binding energy of 138.1 eV suggests that the adsorbed lead species on clean nickel surface are Pb²⁺ in the hydroxide environment. Based on the Pb/Ni intensity ratio, the degree of lead uptake is increased when the solution has higher concentration of Pb²⁺. However, the effect of sulfur-enhanced lead adsorption is more prominent in the dilute Pb²⁺ solution. The enhancement of lead adsorption due to adsorbed sulfur is ~250% in 0.01M Pb²⁺ solution compared to ~400% in 0.001M Pb²⁺ solution for an immersion time of 5 seconds. These results indicate that the lead adsorption is controlled both by the possibility of interaction of Pb²⁺ ions with the surface and by the specific chemical interaction between sulfur adatoms on the surface and the nearby Pb²⁺ ions in the solution. On clean nickel surfaces, the amount of lead adsorbed from a higher concentration of Pb²⁺ solution is larger than that from a lower concentration of Pb²⁺ solution. This is simply because the higher concentration of Pb²⁺ increases the possibility of interaction of Pb²⁺ ions with the surface. Nevertheless, the adsorption of lead on sulfur-modified nickel surfaces does not seem to be significantly affected by Pb²⁺ concentration, indicating that the amount of Pb²⁺ adsorbed is related to available sulfur.
Figure 5.2. XPS Pb(4f) spectra of adsorbed lead on clean and sulfur-modified nickel surfaces. The adsorption of lead was done by immersing the nickel electrodes into (a) 0.01M and (b) 0.001M Pb(NO$_3$)$_2$ solutions for 5 seconds.

In Figure 5.2 the binding energies of Pb(4f$_{7/2}$) and Pb(4f$_{5/2}$) for adsorbed lead cations on sulfur-modified nickel surface were shifted to 138.4 and 143.3 eV, respectively. These two values are 0.3 eV higher than the Pb(4f) binding energies for lead adsorbed on the clean nickel surface. This binding energy shift in the XPS Pb(4f)
spectra is consistent and reproducible in all the experiments. It is direct evidence of sulfur-lead interaction. The change in Pb\(^{2+}\) binding energy for clean vs. sulfur-covered nickel surfaces is significant. In view of the high reactivity of lead with H\(_2\)O vapor, one might expect to observe a Pb(OH\(_2\))-like surface upon emersing regardless of Pb/surface interaction. The 0.3 eV difference in binding energy for sulfur-covered nickel vs. clean nickel is evidence that Pb\(^{2+}\) ions interact strongly with sulfur sites on nickel.

The shift of Pb(4f) to higher binding energies for the Pb\(^{2+}\)/S/Ni system suggests strong final state effects in the XPS spectrum, as observed for other Pb\(^{2+}\) system. Sulfur is more polarizable than oxygen, and the substitute of a S-Pb bond for an O-Pb bond in the cation nearest neighbor environment should lead to a larger polarization of the system’s final state in response to the creation of a core hole. It has also been shown that the final state relaxation energy increases with decreasing electronegativity of the nearest neighbor atoms for the same coordination number, geometry and formal oxidation state. Sulfur is less electronegative than oxygen. The S-Pb\(^{2+}\) interaction leads to a higher relaxation energy for the Pb(4f) core hole than the O-Pb\(^{2+}\) interaction. Therefore, the binding energy of Pb\(^{2+}\)(4f) increases because of the higher relaxation energy. Further studies are required to explore in detail how Pb\(^{2+}\) ions are coordinated with both sulfur adatoms and hydroxyl groups.

5.3.2. Lead Adsorption and Nickel Oxidation as a Function of Immersion

**Time.** XPS analysis reveals that clean and sulfur-modified nickel surfaces prepared in UHV are oxidized by water vapor before immersing into the solution. This is due to the reactive nature of nickel metal. Although the pre-formed nickel oxide/hydroxide can be
reduced in the solution by applying a negative potential \(^{38,39}\), this procedure was not performed in order to avoid electrodeposition of lead. Figure 5.3 shows the XPS Ni(2p\(_{3/2}\)) and O(1s) spectra of nickel and sulfur-modified nickel surfaces oxidized by exposure to water vapor above the electrochemical cell. On the clean nickel surface the film was composed of NiO and Ni(OH)\(_2\). The film formed on sulfur-modified nickel

\[\text{Clean Ni} \quad \text{S-Modified Ni}\]

\[
\begin{array}{c}
\text{Ni(2p}_{3/2}\text{)} \\
\text{Counts} \\
865 \quad 860 \quad 855 \quad 850 \quad 845
\end{array}
\]

\[
\begin{array}{c}
\text{Ni(OH)}_2^* \\
\text{NiO} \\
\text{Ni}^0
\end{array}
\]

\[
\begin{array}{c}
\text{Ni(2p}_{3/2}\text{)} \\
\text{Counts} \\
865 \quad 860 \quad 855 \quad 850 \quad 845
\end{array}
\]

\[
\begin{array}{c}
\text{Ni(OH)}_2^* \\
\text{NiO} \\
\text{Ni}^0
\end{array}
\]

\[
\begin{array}{c}
\text{O(1s)} \\
\text{Counts} \\
535 \quad 534 \quad 533 \quad 532 \quad 531 \quad 530 \quad 529 \quad 528 \quad 527 \quad 526 \quad 525
\end{array}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{Oxide}
\end{array}
\]

\[
\begin{array}{c}
\text{O(1s)} \\
\text{Counts} \\
535 \quad 534 \quad 533 \quad 532 \quad 531 \quad 530 \quad 529 \quad 528 \quad 527 \quad 526 \quad 525
\end{array}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{Oxide}
\end{array}
\]

**Figure 5.3.** XPS Ni(2p\(_{3/2}\)) and O(1s) spectra of clean and sulfur-modified nickel surfaces oxidized by water vapor exposure. *The peak at 855.4 eV is a combination of the feature of Ni(OH)\(_2\) and the satellite feature of NiO (see experimental section for details).
surface consisted of Ni(OH)$_2$ and only a trace amount of NiO. It is clear that sulfur inhibits the formation of NiO. It has been reported that $S_{ads}$ blocks the complete dissociation of H$_2$O and therefore prevents the formation of O$_{ads}$ on metal surfaces.\textsuperscript{40}

A series of experiments were performed to investigate the processes of lead adsorption and nickel oxidation in aqueous solution at different time scales. The results are presented in Figure 5.4. As shown in Figure 5.4a, prior to any vapor exposure or immersion procedure the amount of sulfur put on nickel surface did not vary significantly for all the experiments. After water vapor exposure, the S/Ni$^0$ ratio increases because the oxide/hydroxide overlayer attenuates the signal of underlying Ni substrate more than that of the sulfur adatoms. The S/Ni$^0$ ratio increases with longer immersion time.

In Figure 5.4b the Ni$^{n+}$/Ni$^0$ intensity ratio represents the relative amount of oxidized nickel species left on the surface after emersion and subsequent rinsing procedure. After water vapor exposure, the oxide/hydroxide film formed on clean nickel is observed to be thicker than the film on sulfur-covered nickel. As shown in Figure 5.3, the film formed on sulfur-covered nickel is mostly Ni(OH)$_2$ while a mixture of NiO and Ni(OH)$_2$ is formed on clean nickel surfaces. On clean nickel the dissolution of oxide/hydroxide film occurs right after immersion. After 30 seconds of immersion the film reaches a point where net oxide/hydroxide layer thickness starts to increase but not in a significant manner. On the sulfur-modified nickel surface, the hydroxide film dissolves between 5 and 30 seconds and starts growing again at a steady pace after an immersion time of 30 seconds. Eventually, the amount of oxidized nickel on both surfaces approaches the same level after an immersion time of 20 minutes. An obvious
Figure 5.4. XPS results of the adsorption of lead on nickel surfaces as a function of immersion time. (a) The amount of sulfur on the nickel surface before and after immersion. (b) The amount of oxidized nickel species on clean and sulfur-modified surfaces. (c) The amount of lead on clean and sulfur-modified surfaces.
concern in UHV-EC studies of reactive surfaces has been the unavoidable exposure of the sample to water vapor above the electrochemical cell \(^{13-15,41}\). It has been argued in the literature that significant surface changes could occur during the time that elapses between sample exposure and immersion or between sample emersion and transfer of the sample to the analysis chamber \(^{16}\). The results in Figure 5.4 demonstrate that the *ex-situ* nature of this technique does not significantly obscure the result of reactions occurring on reactive metal surface in the solution. Studies of iron surfaces have reported similar conclusions \(^{13-15,41}\). The results in Figure 5.4 indicate that this is due at least part to the dissolution of some or all of the vapor-induced surface film immediately upon immersion in solution at OCP.

Figure 5.4c shows the increase of lead adsorption on sulfur-modified nickel surface with immersion time. The amount of lead adsorbed on the clean nickel surface is considerably less than on the sulfur-covered surface, and is not affected by the immersion time. The enhancement of lead adsorption by sulfur increases from 400% to 1200%, for immersion times ranging from 5 seconds to 20 minutes. Using the published atomic sensitivity factors (ASF) for Pb(4f) and S(2p), which are 8.329 and 0.666 respectively \(^{33}\), the relative atomic concentrations (N) of lead and sulfur can be calculated from the measured intensities (I). The calculation is given by the equation, \( N = I / \text{ASF} \). The quantitative relationship between lead and sulfur can be given as:

\[
\frac{N_{\text{pb}}}{N_{\text{s}}} = \frac{I_{\text{pb}}}{I_{\text{s}}} \times \frac{\text{ASF}_{\text{s}}}{\text{ASF}_{\text{pb}}} \]

(5-1)
With the assumption of sulfur and lead are uniformly distributed in the film, the amount of adsorbed lead was found to be 25% to 40% of the total amount of sulfur, as the immersion time increases from 5 seconds to 20 minutes. Use of the assumption mentioned above results in a slight overestimation of the lead to sulfur concentration ratio owing to the fact that the intensity of sulfur is attenuated by adsorbed lead.

For the Pb-S-Ni system, the correlation between lead adsorption and nickel oxidation/dissolution as a function of immersion time is presented in Figure 5.5. The XPS intensity ratios in Figure 5.5 are presented with error bar of ±1.5% estimated from the quantitative analysis of XPS spectra of well-characterized sulfur-covered nickel surfaces. Based on the values of Pb/Ni ratio (Figure 5.5a), 70% of the total lead uptake occurs in the first 30 seconds of immersion. Thereafter, adsorption slowly increases. During the last 10 minutes, only 3% of the total lead adsorption occurs on the surface. As shown in Figure 5.5b, the dissolution of nickel hydroxides is observed after an immersion time of 5 seconds. The lowest Ni^{n+}/Ni° ratio is observed at immersion time of 30 seconds. Then the oxidized nickel species increases in a linear fashion because of sulfur-enhanced oxidation. In Figure 5.5c, the Pb/Ni^{n+} ratio represents the change of the relative amount of adsorbed lead and oxidized nickel. The abrupt increase of Pb/Ni^{n+} ratio at 30 second is the result of both the dissolution of nickel hydroxides and increasing uptake of lead. The Pb/Ni^{n+} ratio decreases for immersion times between 10 and 20 minutes. This can be explained by the fact that at this stage the oxidation of nickel still occurs during the last 10 minutes while the adsorption of lead has stopped.
5.3.3. OCP Measurements. The results of OCP measurements as a function of immersion time are presented in Figure 5.6. It is evident that sulfur has a significant effect on the reactions that occur at the nickel/liquid interface. The OCP for sulfur-covered nickel is found to be \(\sim 150\) mV more negative than that of the clean nickel in 0.1M NaNO\(_3\) solution (pH = 5.9). The shift of OCP towards negative (or active) potentials is interpreted as a surface associated with a higher rate of oxidation (or oxidation).
As shown in Figure 5.6, when trace amounts of Pb\(^{2+}\) (0.001M) are present in the same solution (pH decreases to 4.8), the OCP of a sulfur-modified nickel surface is only ~30 mV more negative than that of a clean nickel surface. This indicates that the presence of Pb\(^{2+}\) reduces the corroding effect of sulfur on nickel. A Pb\(^{2+}\)-induced decrease of sulfur-enhanced corrosion of nickel is also evident from the XPS data. Four Ni(2p\(_{3/2}\)) spectra acquired after the OCP measurements (Figure 5.6) are presented in

**Figure 5.6.** Open-circuit potential of clean and sulfur-modified nickel surfaces as a function of immersion time in 0.1M NaNO\(_3\) solution (solid line) and in a solution of composition 0.001M Pb(NO\(_3\))\(_2\), 0.1M NaNO\(_3\) (dashed line).
Figure 5.7. Based on the Ni\(^{n^+}/Ni^0\) and Ni(OH)\(_2\)/NiO intensity ratios, the presence of Pb\(^{2+}\) on clean nickel electrode does not affect either the nickel oxidation or the

**Figure 5.7.** XPS Ni(2p\(_{3/2}\)) spectra of clean nickel electrodes (a-b) and sulfur-modified nickel electrodes (c-d) after 20 minutes of immersion in the 0.1M NaNO\(_3\) solution with and without Pb\(^{2+}\).
oxide/hydroxide film composition as shown in Figure 5.7a and 5.7b. However, the
adsorption of Pb\(^{2+}\) on the sulfur-modified nickel electrode is found to retard nickel
oxidation resulting in a film with relatively less amount of Ni(OH)\(_2\) (Figure 5.7c and
5.7d). Another interesting observation in Figure 5.6 is that, during the first 5 minutes of
immersion, the OCP of a clean nickel electrode in a Pb\(^{2+}\) containing NaNO\(_3\) solution is
more positive than the electrode in a Pb\(^{2+}\) free NaNO\(_3\) solution. After 5 minutes of
immersion, the OCP of a clean nickel electrode in a Pb\(^{2+}\) containing NaNO\(_3\) solution is
more negative than the electrode in a NaNO\(_3\) solution. This can be explained by the fact
that lead adsorption occurs at the early immersion time. The adsorbed Pb\(^{2+}\) inhibits the
nickel oxidation, which results in a more positive OCP (less corrosive). Once the nickel
oxide/hydroxide overlayer covers the adsorbed lead at a later immersion time, the OCP of
the nickel oxide/hydroxide surface changes with the pH of solution. The Pb\(^{2+}\) containing
NaNO\(_3\) solution has lower pH (more corrosive) than the Pb\(^{2+}\) free NaNO\(_3\) solution.
Therefore, the OCP of a nickel electrode should be more negative when the electrode is
in Pb\(^{2+}\) containing NaNO\(_3\) solution at a later immersion time.

Based on the principle of charge neutrality, the total rate of oxidation reactions
must equal the rate of reduction reactions on a conducting surface where these reactions
occur simultaneously. In other words, the net anodic oxidation current must equal the net
cathodic reduction current to avoid accumulating charge in the electrode. The anodic
reaction for the system of nickel electrode in the nitrate solution is the oxidation of
nickel,

\[
Ni \rightarrow Ni^{2+} + 2e^{-}
\]  

(5-2)
The cathodic reaction involved was found to be the reduction of $\text{NO}_3^-$,
\[
\text{NO}_3^- + 3\text{H}^+ + 2e^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O} \quad (5-3)
\]
As the solutions used in this study were always deaerated by purging with argon gas, the reduction of dissolved oxygen is minimized and can be neglected. Also, hydrogen evolution cannot be involved because the calculated reduction potential of this reaction at the pH of our electrolyte (i.e. pH 4.8 to 5.9) is more negative than the nickel reduction \(^{42}\).

According to the mixed potential theory (MPT) \(^ {24}\), the OCP for our system should be located between the reduction potentials of the two reactions involved. The reduction potentials \(^ {42}\) of reactions relevant to this system are -0.257 V (SHE) for the reduction reaction of $\text{Ni}^{2+}$ to $\text{Ni}$, and 0.588 V (SHE, pH=5.9) or 0.685 V (SHE, pH=4.8) for the reduction of $\text{NO}_3^-$ with an assumption of $[\text{NO}_3^-]/[\text{HNO}_2] = 10^6$. In Figure 5.6 the measured OCPs are observed in the range of -0.330 to -0.105 V (0.012 to 0.237 V vs. SHE).

In Figure 5.8, the OCP of the system is depicted schematically as a function of the polarization curves for the nickel oxidation and $\text{NO}_3^-$ reduction half reactions. The rate of nickel oxidation, expressed as anodic current ($i_a$) increases as the potential becomes more anodic (i.e. from left to right). After passing a certain potential (active/passive transition potential) the current decreases as the passivating oxide/hydroxide layer starts to form. The rate of nitrate reduction, expressed as cathodic current ($i_c$) increases as the potential moves in cathodic direction (i.e. from right to left). At high cathodic overpotential, a diffusion-limited plateau is reached. In this case the oxidation of nickel is more likely to be kinetically limited because the nickel oxide/hydroxide surface layer
formed on the nickel can kinetically hinder further oxidation. The reduction of nitrate is limited by the diffusion of NO$_3^-$ ions towards sample surface (i.e. diffusion control). When a nickel electrode is immersed in the nitrate solution, the starting potential is usually more negative than the final equilibrium OCP because of the higher rate of both oxidation and reduction reactions (Figure 5.6). Eventually, the potential shifts in anodic direction until the equilibrium OCP is achieved. Furthermore, when the nickel oxidation is enhanced by sulfur adatoms on the surface, the measured OCP should be more negative to maintain the net current of zero (Figure 5.8). It is in agreement with the observation of sulfur-enhanced corrosion of nickel $^{25,26}$.

5.3.4. Sulfur-Induced Lead Adsorption. Based on the observations of this study, a model of sulfur-induced lead adsorption on nickel electrode is proposed as
follows. Before the immersion, a thin film of nickel hydroxide is formed on the sulfur-modified nickel electrode by water vapor exposure. The Pb$^{2+}$ ions interact with sulfur adatoms through the thin hydroxide layer formed right after the electrode is immersed in the solution. Between immersion time of 5 to 30 seconds, more Pb$^{2+}$ ions are attracted by sulfur while the hydroxide film starts to dissolve into the solution. Then the process of lead adsorption continues at a slower rate with increasing nickel oxidation and nickel hydroxide formation. After 10 minutes of immersion, nickel hydroxide starts to grow over the adsorbed lead. Ultimately, the nickel hydroxide film is thick enough to block the sulfur-induced lead adsorption.

5.4. Conclusion

The effect of sulfur on lead adsorption and nickel oxidation in aqueous solution has been investigated by UHV-EC. Pre-adsorbed sulfur was found to enhance the adsorption of lead on nickel electrode. The enhancement of lead adsorption on sulfur-modified nickel increases from 400% to 1200% relative to clean nickel as the immersion time increases. Based on XPS analyses and OCP measurements, this sulfur-induced lead adsorption was found to retard the sulfur-enhanced corrosion on nickel electrode at OCP. However, further studies are needed to explore the passivating characteristics of the lead-adsorbed nickel hydroxide film in a corroding environment. We have also demonstrated that the combined UHV-EC methodology can be used effectively to probe the processes of lead adsorption and nickel oxidation at the solid/liquid interface. According to our observations, most of the lead adsorption on sulfur-modified nickel surface takes place during the first 30 seconds of immersion. After 10 minutes of immersion, the amount of
adsorbed lead reaches the maximum as the adsorption of lead stops due to the formation of thicker nickel hydroxide film that blocks the interaction between the sulfur adatoms and Pb\textsuperscript{2+} ions. More detailed structural information of this Ni-S-Pb-OH system is essential for a better understanding of the adsorption process. However, due to the limitation of the techniques used in this study, it cannot be provided here and will be investigated in the future.

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