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Project Title: **Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste**

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60219 - Development of Advanced Electrochemical Emission Spectroscopy for Monitoring
Corrosion in Simulated DOE Liquid Waste

Pennsylvania State University

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OBJECTIVE

Objective of this project is to develop and use Electrochemical Emission Spectroscopy (EES) and other electrochemical techniques as in situ tools for exploring corrosion mechanism of iron and carbon steel in highly alkaline solutions and for continuously monitoring corrosion on structural materials in DOE liquid

waste storage system. In particular, we will explore the fundamental aspects of the passive behavior of pure iron since breakdown of passivity leads to localized corrosion.

RESEARCH PROGRESS

This report summarizes work after 2 years of a 3-year project.

During the past eight decades the passive film on iron has been the subject of numerous investigations [1-7] aimed at developing a detailed understanding of the film growth mechanisms, the film structure and composition as well as reduction of iron oxides that form on the surface. In most of this work, the results of galvanostatic reduction experiments have been interpreted by assuming the presence of a two-layer film consisting of an inner layer of magnetite (Fe_3O_4) and an outer layer of maghemite ($\gamma\text{-Fe}_2\text{O}_3$). However, it was found [7], that the reduction of thin, single layers of Fe_2O_3 also takes place in two stages, so the observation of a two-stage reduction does not necessarily imply a bilayer structure. Other reduction experiments combined with ellipsometry favored the idea of a passive film on iron consists of an inner barrier layer of maghemite and an outer deposit layer of a porous hydroxide. Photoelectrochemical experiments revealed that the iron hydroxide layer deposited on the passive film decreased a photocurrent response [8]. However, secondary-ion mass spectroscopy (SIMS) measurements did not confirm an existence of hydroxide on the passive film [9]. Experiments using in situ scanning tunneling microscopy (STM) support an idea of a passive film on iron with a crystalline structure resembling maghemite. It was observed that presence of chelating agent (EDTA) in test solution can hinder the formation of the precipitated layer [10], and enhanced cathodic reduction of the passive film on iron in alkaline solution [11].

Electrochemical studies were carried out in a three-electrode PTFE electrochemical cell. The counter electrode was a Pt wire and all potentials were measured against a saturated calomel electrode (SCE). The working electrode was a pure iron wire (99.99%) with a diameter of 1 mm.

All experiments were performed at ambient temperature (22-25°C) in pH 8.4 borate buffer, with and without an addition of 0.01 M EDTA. The solution was deaerated with N_2 . Prior to all experiments, the samples were cathodically polarized at $-1.0 V_{\text{SCE}}$ for 5 min. to remove the air formed film. Then the potential was stepped to different formation potentials, ranging from $0.0 V_{\text{SCE}}$ to $0.9 V_{\text{SCE}}$.

Electrochemical experiments were performed using a Schlumberger/Solartron 1286 Electrochemical Interface, The capacitance of the interface was recorded with a Schlumberger/Solartron 1250 Frequency Response Analyzer using an excitation voltage of 10 mV (peak-to-peak), and an applied frequency of 1 kHz. The current output was usually amplified with a differential amplifier (Tektronix Model AM 502) prior to interfacing with the FRA.

Photoelectrochemical experiments were carried out using a monochromatic 150 W xenon lamp in combination with a 1/8 monochromator. The light was modulated (30 Hz) by using an electronic shutter driven directly by the FRA.

On cyclic voltammograms of Fe in borate buffer solution with and without EDTA, the active dissolution current is higher, and the passive current is lower in the presence of EDTA. In potentiostatic experiments, in the presence of EDTA, the current decay is slower than without EDTA (suggesting lower film formation rate). From potentiodynamic and galvanostatic reduction experiments, it was observed that the reduction in borate buffer solution with EDTA is much faster than in the absence of EDTA and resulting in obtaining a more active metal surface.

From capacitance, C, measurements of the passive films formed on iron in borate buffer solution with and without EDTA, it was observed that C^{-2} vs. V profiles (Mott-Schottky plots) were characterized by the presence of two linear regions. These regions are attributed to the existence of two donor levels described as Fe^{+2} located in a spinel oxide structure, the shallow level should correspond to Fe^{+2} in tetrahedral positions, and the deep donor level to Fe^{+2} in octahedral positions. Additionally, it was observed that the passive films formed on iron in borate buffer solution is less defective than those formed in the presence of

EDTA. It was also found that the space charge layer thickness of the passive film on iron formed in borate buffer with EDTA was lower than for the films formed without EDTA.

Crystal structures of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are closely related, both being based on spinel structure with a unit cell containing 32 oxide ions with 16 octahedral and 8 tetrahedral interstices [12]. Magnetite is an "inverse" spinel with 8 tetrahedral and 8 octahedral interstices filled by Fe^{3+} , and the other 8 octahedral interstices are filled by Fe^{2+} . In maghemite the 24 interstices are occupied at random by $21\frac{1}{3}$ Fe^{3+} ions. A ratio of Fe^{2+} defects in octahedral position to those in tetrahedral position as a function of formation voltage was calculated from Mott-Schottky plots. It was observed that for the films formed in the presence of EDTA the calculated ratio is close to 2 (like in Fe_3O_4), whereas for films formed without EDTA that ratio is much lower. These finding may suggest that EDTA hinders formation of an outer layer on iron in borate buffer solution. Another interesting observation is an effect of EDTA on donor density as a function of film formation time. Concentration of Fe^{2+} defects in tetrahedral and octahedral positions in passive films formed at 0.4 V SCE in the presence of EDTA is almost constant in time (experiment was discontinued after 10 days). In the absence of EDTA the concentration of Fe^{2+} defects in tetrahedral positions decreases with time.

The capacitance behavior of passive films formed on iron in borate buffer solution (at -0.2 V SCE for 20 min) was also studied by adding Cl^- and EDTA to the borate buffer solution after first measuring the C-2 vs. V profiles in pure borate buffer. It was easily observed that an addition of EDTA to pure borate buffer solution results in change in of the slope of the Mott-Schottky plot. The change of the slope indicates the adsorption on the film surface followed by the changes in the capacitance behavior. Further addition of Cl^- ions does not change capacitance behavior. Contrary, an addition of EDTA to chloride containing borate buffer solution changes the slope of the Mott-Schottky plots. This may be an indication that the adsorption of EDTA on passive films on iron in borate buffer solution is stronger than the adsorption of Cl^- ions.

Preliminary results from photoelectrochemical experiments showed that in the presence of EDTA photocurrent response is increased, thereby confirming that EDTA is effective in removing precipitated layer.

We have also started electrochemical experiments on nickel in borate buffer solution (pH 8.4). Ni exhibits passive behavior in potentials between -0.1 V_{SCE} and 0.7 V_{SCE} . Passive film on nickel is known to behave as a p-type semiconductor [13]. However, our results showed an interesting feature of passive films formed on nickel in borate buffer solution; depending on concentration of the employed solution (borate buffer with pH 8.4 can have different concentration), the films showed either n-type behavior or p-type behavior in potential range between 0.1 V_{SCE} and 0.5 V_{SCE} . These findings suggest that the dissolution kinetics of passive film on nickel in borate buffer may have a significant effect on its electronic properties.

We have now initiated our research on assessing the feasibility of using electrochemical noise techniques to monitor the corrosion of carbon steel in highly alkaline solutions of the type that exist in liquid waste facilities. The important issue is that iron in contact with highly alkaline solutions is electrochemically quiescent (in contrast to iron in contact with acid), in that the noise in both the current and voltage is very small. It is possible that extraordinary measures will be required to obtain accurate noise data. Thus, in the first task, we have reviewed the background knowledge in this field [Electrochemical Emission Spectroscopy (EES) and Electrochemical Noise Measurements (ENMs)] to ascertain what innovations will be required in order to produce an effective monitoring technology. The general measurement scheme is to simultaneously monitor current fluctuations between two identical electrodes of the metal of interest that are maintained at the same potential by a zero resistance ammeter (ZRA) and voltage fluctuations of the current-carrying electrodes by using a reference electrode (RE)/high impedance voltmeter. The measurements are performed at the corrosion potential, making this monitoring technique more relevant to the actual conditions that exist in the system than, for example, linear polarization, which requires a significant perturbation of the potential and current from those that exist under open circuit conditions. Measured values of electrochemical voltage and current, as a function of time, are transformed through Fourier transformation into the frequency domain, and power spectral densities (PSDs) are then calculated. Historically, an important quantity has been the "noise resistance" (R_n), defined as the ratio of the standard deviations of the current and voltage fluctuations over a given time [14,15]. Another

important quantity has been the spectral noise resistance (R_{sn}), derived from the PSDs of the current and voltage fluctuations. In Legt's paper [16], the correlation dimension and the maximum Lyapunov exponent of electrochemical noise was used to show that localized corrosion is generated by a deterministic chaotic process whereas uniform corrosion is a random process. Our future research will focus on the case of pitting corrosion and we will try to establish the link between the deterministic model (Point Defect Model, PDM [17]) and the "noise" due to metastable pitting. A recent study of electrochemical current noise on aluminum microelectrodes [18] indicates a possible mechanism of noise generation, which is based on the physical process of fluctuations in the widths of cracks or pores in the outer part of the passive oxide film.

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FUTURE WORK

- 1) To continue our work on studying the passivity of metals in alkaline solutions including investigation of electrochemical behavior of Ni and Cr;
- 2) To study photoelectrochemical behavior of Fe;
- 3) To set up the test loop for measuring the electrochemical noise from carbon steel and pure iron in borate buffer and sodium hydroxide solutions;
- 4) To measure and analyze the electrochemical noise data;
- 5) To link the PDM and the origin of electrochemical noise (in the case of pitting corrosion) in these systems, and
- 6) To assess the potential of EES for monitoring the corrosion rate of iron in alkaline environments.

PUBLICATIONS

Passive Films on Iron Formed in the Presence of EDTA

E. Sikora and D.D. Macdonald,

presented on 8th International Symposium on Passivity of Metals and Semiconductors, Jasper, Canada, May 9-15, 1999.

Electrochemical and Photoelectrochemical Study of Passive Films Formed on Iron in the Presence of EDTA

E. Sikora and D.D. Macdonald,

submitted for International Symposium in Honor of Professor Norio Sato: Passivity and Localized Corrosion, Electrochemical Society Meeting, October 1999.