

Project Summary Report (Project ID Number 60219)

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

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Research Objective

The principal goals of this project are to develop advanced electrochemical emission spectroscopic (EES) methods for monitoring the corrosion of carbon steel in simulated DOE liquid waste and to develop a better understanding of the mechanisms of the corrosion of metals (e.g. iron, nickel, and chromium) and alloys (carbon steel, low alloy steels, stainless steels) in these environments. During the first two years of this project, significant advances have been made in developing a better understanding of the corrosion of iron in aqueous solutions as a function of pH, on developing a better understanding of the growth of passive films on metal surfaces, and on developing EES techniques for corrosion monitoring. This report summarizes work on beginning the third year of the 3-year project.

Research Progress and Implications

A new rate law for the growth of a passive film on a metal surface has been derived. The new law, which is based on the Point Defect Model (PDM) for the growth and breakdown of passive films [1], is found to account for the transient in thickness of the anodic film on tungsten in phosphate buffer, under voltage cycling, much more accurately than does the High Field Model. We have used tungsten, rather than iron, for this analysis, because the passive film on W is a pure oxygen vacancy conductor (for which the theory for thickness transients is currently developed) and because experimental data are available from our previous work [2]. The theory is currently being applied to iron, but the required experimental data were not available at the time of preparation of this report.

The temporal change in thickness of the passive film on tungsten in phosphate buffer solution (pH = 1.5) as the potential is cycled from 10 V_{SCE} to 6 V_{SCE} and back to 10 V_{SCE} is shown in Figure 1 [2]. The experimental data were calculated from measured capacitance data and by assuming that the film could be modeled as a parallel plate capacitor with a dielectric constant of 35 [2]. However, the parallel plate model is not entirely appropriate, because a sharp drop occurs in the calculated “thickness” as the potential is stepped from 10 V_{SCE} in the negative direction. We previously [2] attributed this sudden decrease in apparent thickness to an artifact associated with a change in the space charge capacitance, an interpretation that was confirmed by also monitoring the change in thickness using optical reflectance measurements (no sudden change in thickness was detected using this latter technique). Excellent agreement is obtained between theory and experiment, which further supports the validity of the Point Defect Model. Finally, it is important to note that the High Field Model, which has been used for more than seventy years to describe the growth of anodic oxide films on metals, is unable to account for any of the data shown in Figure 1.

Although the passive state of iron has been extensively studied in the past, considerable disagreement exists as to the nature and composition of the passive film that forms on the metal surface. This previous work has shown that the passive film formed on iron in borate buffer solutions has a bilayer structure comprising a defective inner Fe₃O₄ layer (the “barrier” layer, which grows directly into the metal) and an outer γ -Fe₂O₃ layer that forms by precipitation. The outer layer effectively screens the barrier layer from optical interrogation and also significantly modifies the electrochemical response of the surface. However, general agreement exists that the passivity of iron is primarily due to the barrier layer. Accordingly, the present work is based on the hypothesis that EDTA (ethylene diammine tetra acetic acid), which chelates the iron cations that are ejected from the barrier layer, should be effective in preventing the formation of the outer layer. If so, then the barrier layer alone may be investigated to provide a much more accurate account of the passive state. Our current work clearly shows that EDTA in borate buffer solutions effectively prevents the formation of the outer layer. Finally, passivation is enhanced by higher pH values of the solution.

The PDM (Point Defect Model), not the HFM (High Field Model), gives a better account of the kinetics of film growth. Furthermore, steady state polarization data show that the passive film on iron is an n-type semiconductor, due to a preponderance of oxygen vacancies and/or iron interstitials. Mott-Schottky analysis further confirms that the passive film formed on iron is an n-type semiconductor. The donor density of the barrier layer decreases and the steady state thickness increases linearly with increasing film formation potential, in agreement with the prediction of the PDM. Recent in situ X-ray diffraction studies by Toney, et. al. [3] also concluded that the passive film on iron is a “highly defective spinel oxide with a high concentration of vacancies and interstitials”. However, these workers did not specify the exact nature of the defects. From the present work, we conclude that the dominant defects must be oxygen vacancies, which are generated by growth of the barrier layer into the metal, and Fe (II) interstitials, because of the n-type electronic character of the film. Cation vacancies cannot contribute substantially to the electronic structure, because they should impart p-type character.

A high fidelity method for measuring electrochemical emission data on carbon steel (AISI 1018: C 0.16, Mn 0.79, S 0.018, P 0.006, Fe balance) in alkaline solutions has been developed as a means of monitoring general corrosion and pitting corrosion of carbon steel in simulated DOE waste storage systems and to develop a better understanding of the mechanisms of corrosion of metals (iron) and alloys (carbon steel) in these environments. The initial goal was to demonstrate that noise data can yield corrosion rates that are of engineering relevance and can be used for estimating the integrated damage (loss of wall thickness). EES measurements are performed at the corrosion potential, making this monitoring technique more relevant to the actual conditions than is linear polarization, for example. The time domain data were transformed through Fast Fourier Transformation into the frequency domain, and power spectral densities (PSDs) were then calculated. An important quantity, the “noise resistance” (R_n), defined as the ratio of the standard deviations of the current and voltage fluctuations over a given time [4,5], was employed to derive the corrosion current densities and penetration corrosion rates shown in Figure 2. These data are in reasonable accord with data in the literature for similar systems.

In agreement with the recent findings of Edgemon, Danielson, and Bell [6], general corrosion on carbon steel in simulated waste systems is characterized by random fluctuations in current and potential. In passive systems, the fluctuations tend to decrease in frequency and magnitude with time as the passive film forms on the metal surface. In general, lower corrosion rates were associated with lower mean currents and smaller fluctuations in the current. Also, as shown by Legat [7], the correlation dimension and the maximum Lyapunov exponent of the electrochemical noise shows that localized corrosion is generated by a deterministic chaotic process, whereas uniform corrosion is a random (stochastic) process. Our study demonstrates that Electrochemical Emission Spectroscopy (EES) is a feasible, *in situ* technique for monitoring the corrosion of carbon steel in highly alkaline solutions of the type that exist in liquid waste facilities. Our future research will focus on general and pitting corrosion in different solutions and at higher temperatures. We will try to establish the link between the deterministic model (Point Defect Model, PDM [8]) and the “noise” due to metastable pitting.

We have now initiated the crack propagation studies that were scheduled for the final year of this program. The composition of DOE waste consists mainly of sodium salts with a high pH(>12). Accordingly, failure of the carbon steel storage tank by caustic cracking must be considered as one of principal threats to tank integrity. The emphasis in this part of our work is on exploring fundamental aspect of the caustic cracking mechanisms by using electrochemical emission spectroscopy (EES) to ascertain the dimension of the brittle micro fracture events that occur during crack propagation. Methods are currently being developed to measure the electrochemical emissions from growing cracks in the high strength, low alloy steel that was chosen to represent heat affected zones adjacent to welds in DOE storage tanks. A computer-based data acquisition system with a fast, multi-channel A/D board and a large buffer is being used to record the current and potential vs. time at a sampling frequency of 4 Hz. The loading and crack propagation measuring systems have been developed and are currently being assessed for accuracy. All specimens have been prepared and the first experiment is scheduled to begin during the week of February 28, 2000. These experiments are designed to provide fundamental information on the mechanisms of crack propagation.

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Planned Future Activities

Work will continue over the third year on all aspects of the program outlined above, with emphasis on EES and in particular on the ability of this method to monitor general corrosion rates and to discern the mechanism of stress corrosion cracking. Our theoretical work on passivity and on predicting localized corrosion damage will also continue, because it provides the basis for interpreting the experimental data and for estimating tank service life.

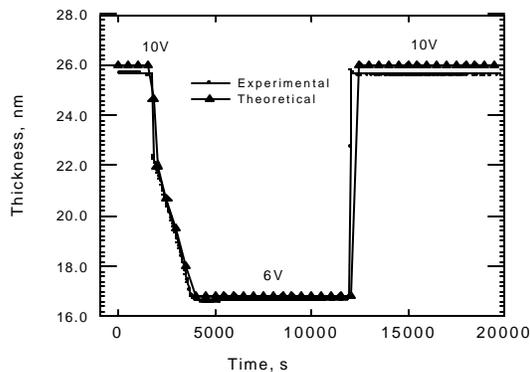


Figure 1. Transients in the thickness of the passive film on tungsten in phosphate buffer solution as the voltage is stepped from 10 V_{SCE} to 6 V_{SCE} and back to 10 V_{SCE} . The experimental values were measured using high frequency (1 kHz) capacitance. The theoretical values were calculated using Equation (4) and the parameter values given in Ref. 3. Note that allowance has been made for the sudden drop in thickness upon stepping the voltage from 10 V_{SCE} to 6 V_{SCE} , which is an artifact due to charging of the space charge capacitance. $pH = 1.5$.

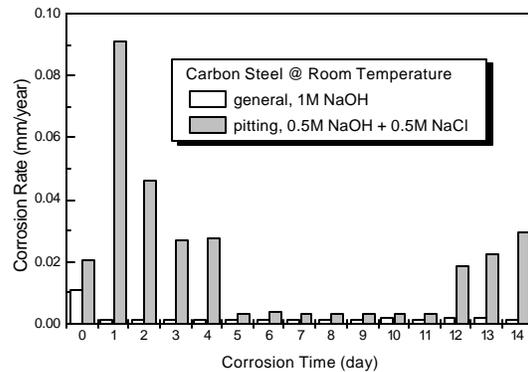


Figure 2. Comparison of penetration corrosion rates for general corrosion and pitting corrosion of carbon steel at room temperature.

Personnel

Digby D. Macdonald (Principal Investigator).

Elzbieta Sikora (Research Associate), 9/30/97 – 12/31/99

Sue Liu (Research Associate), 9/15/99 – present.

Jun Liu, Graduate Student, 9/30/97 – present.

Mohammed Al-Rifaie, 9/30/97 – May 31, 1999. Tuition and stipend were supported by the University of Kuwait.

Monika Gomez, 8/30/99 – present. Tuition and stipend are being provided by COLCIENCIAS/LASPAU-Fulbright, programs in Colombia.

Publications and Presentations

Papers in press or in print:

1. D. D. Macdonald, "Passivity-the Key to Our Metals-Based Civilization", *Pure Appl. Chem.*, **71**(6), 951-978 (1999).
2. G. R. Engelhardt and D. D. Macdonald, "Modeling of Corrosion Fatigue Chemistry in Sensitized Stainless Steel in Boiling Water Reactor Environments", *CORROSION/2000*, Orlando, FL, March, 2000, Paper No. 00227 (NACE International, Houston, TX).

3. Sikora, E and D. D. Macdonald, "Electrochemical and Photoelectrochemical Study of Passive Films on Iron Formed in the Presence of EDTA", Proc. Int. Symp. Hon. Prof. Norio Sato: Passivity and Localized Corrosion, Electrochemical Society, Princeton, N.J., in press (1999).
4. Macdonald, D. D and D. F. Heaney, "Sequence of Events in the Breakdown of Passivity on Stainless Steels", Proc. Int. Symp. Hon. Prof. Norio Sato: Passivity and Localized Corrosion, Electrochemical Society, Princeton, N.J., in press (1999).
5. Sikora, J, E. Sikora, and D. D. Macdonald, "Nature of the Passive Film on Tungsten", Proc. Int. Symp. Hon. Prof. Norio Sato: Passivity and Localized Corrosion, Electrochemical Society, Princeton, N.J., in press (1999).

Papers in preparation:

1. M. Al Rafie and D. D. Macdonald, "On the Transients in the Thickness of Anodic Passive Films on Metals", J. Electrochem. Soc., in preparation (2000).
2. E. Sikora and D. D. Macdonald, "The Passivity of Iron in the Presence of EDTA. I. General Electrochemical Behavior", Corros. Sci., in preparation (2000).
3. Jun Liu and D. D. Macdonald, "The Passivity of Iron in the Presence of EDTA. II. The Defect and Electronic Structures of the Barrier Layer", Corros. Sci., in preparation (2000).
4. S. Liu and D. D. Macdonald, " A Review of Caustic Cracking of Carbon Steel", Corrosion, in preparation (2000).

Conference Presentations:

1. Sikora, E and D. D. Macdonald, "Electrochemical and Photoelectrochemical Study of Passive Films on Iron Formed in the Presence of EDTA", Proc. Electrochem. Soc. 197th Meeting, **99-2**, Abstr. 484 (1999).
2. Sikora, J, E. Sikora, and D. D. Macdonald, "Nature of the Passive Film on Tungsten", Proc. Electrochem. Soc. 197th Meeting, **99-2**, Abstr. 490 (1999).
3. D. D. Macdonald and M. Al-Rifaie, "New Rate Law for the Anodic Growth of Passive Films", Proc. Electrochem. Soc. 198th May 14-19, 2000, Toronto, Canada,
4. J. Liu and D. D. Macdonald, "The Passivity of Iron in EDTA-Containing Solutions", Proc. Electrochem. Soc. 198th Meeting, May 14-19, 2000, Toronto, Canada,
5. D. D. Macdonald, "Mechanistic Analysis by Electrochemical Impedance Spectroscopy", Proc. Electrochem. Soc. 198th Meeting, May 14-19, 2000, Toronto, Canada,
6. D. D. Macdonald, "Fundamental Aspects of Passivity Breakdown", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.
7. D. D. Macdonald, M. Al-Rifaie, and G. R. Engelhardt, "Transient Growth and Reduction of Anodic Oxide Films on Metal Surfaces", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.
8. D. D. Macdonald, "Mechanistic Analysis by Electrochemical Impedance Spectroscopy", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.
9. D. D. Macdonald and G. R. Engelhardt, "The Deterministic Prediction of Localized Corrosion Damage", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.

Degrees Granted

The following degrees were granted to students who worked on this project over the past year:

1. Mohammed Al-Rifaie, Ph.D., "Identification of Point Defects Within Passive Films", May 1999. Present address: Assistant Professor, Department of Mechanical Engineering, University of Kuwait, Kuwait. Dr. Al-Rifaie was partially supported (stipend and academic fees) by the University of Kuwait.
2. Jun Liu, M.S., "Electrochemical Studies on the Passive Film on Iron", March 2000. Mr. Liu is continuing on this program for his Ph.D. degree.