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

by

Digby D. Macdonald
Kalliopi Aligizaki, Mohammed Al-Rifaie,
EunAe Cho, Monika Gomez,
Jun Liu, Sue Liu, and Elzbieta Sikora

Center for Advanced Materials
Pennsylvania State University
University Park, PA 16802
ddm2@psu.edu

Department of Energy
Environmental Science Program

Grant No. DE-FG07-97ER62515
(Project 60219)

Outline

1. Introduction
2. Objectives
3. Development of Corrosion Mechanisms
4. Passive film on Metals
   - Tungsten
   - Iron
   - Aluminum
   - Nickel
   - Fe-20Cr Steel
5. Electrochemical Emission Spectroscopy
6. Crack propagation studies
7. Summary and Conclusions
8. Publications and Presentations

1. Introduction

- DOE currently stores about 253 million liters of high-level nuclear waste at the Hanford Reservation in Washington.

- The waste consists of a concentrated solution of NaOH, $NaNO_3$, $NaNO_2$, and NaCl, with other species such as $NaSO_4$, $NaHPO_4$, $NaAlO_2$, and NaF also being present.

- Additionally, various radioactive species and "sludge", comprising a mixture of precipitated salts, are also present in the system.

- The temperature of the waste is typically 95°C – 97°C and the pH (25°C) is greater than 12.

- The waste is stored in a variety of single walled and doubled wall tanks manufactured from ASTM A537-Cl. 1, ASTM A515-Gr. 60, or ASTM A516-Gr. 60 steel.

- The single walled tanks were not stress relieved after welding, and hence contain weld heat-affected zones (HAZs) that are susceptible to stress corrosion cracking (SCC) and/or hydrogen-induced fracture (HIC). Some of the single walled tanks are suspected to be leaking due to corrosion-induced penetrations of the walls.

2. Objective

The principal goals of this project are:

- To devise advanced electrochemical emission spectroscopic (EES) methods for monitoring the corrosion of carbon steel in simulated DOE liquid waste.

- 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.

The work that is being carried out has three components:

- Basic research to define corrosion mechanisms
- Technology development through devising and developing new corrosion sensors.
- Technology transfer (realized by exposing potential manufacturers to the sensor technologies developed in this program, principally through Penn State University's Intellectual Property Office).

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 and in devising new corrosion monitoring techniques.

3. Development of corrosion mechanisms

- A new law, based on the Point Defect Model (PDM) for the growth and breakdown of passive films, 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 (HFM).
- We have used tungsten, rather than iron, for this analysis, because the passive film on tungsten is a pure oxygen vacancy conductor (for which the theory for thickness transients is currently developed) and because experimental data are available for this metal from our previous work.
- The theory is currently being applied to iron.
- According to the PDM, the rate of change of the thickness of the barrier oxide layer on a metal substrate under anodic conditions can be written in the form:

$$\frac{dL}{dt} = ae^{-bL} - c$$

Physicochemical processes that occur within a barrier layer on a metal surface during growth of a barrier oxide layer according to PDM.

metal	barrier layer	solution
1) $m + V_M^{\chi'} \overset{k_1}{=} M_M + v_m + \chi e'$		4) $M_M \overset{k_4}{=} M^{\delta+} + V_M^{\chi'} + (\delta - \chi)e^-$
2) $m \overset{k_2}{=} M_i^{\chi+} + v_m + \chi e^-$		5) $M_i^{\chi+} \overset{k_5}{=} M^{\delta+} + (\delta - \chi)e^-$
3) $m \overset{k_3}{=} M_M + \frac{\chi}{2} V_O^{\cdot\cdot} + \chi e^-$		6) $V_O^{\cdot\cdot} + H_2O \overset{k_6}{=} O_O + 2H^+$
	7) $MO_{\chi/2} + \chi H^+ \overset{k_7}{=} M^{\delta+} + \frac{\chi}{2} H_2O + (\delta - \chi)e^-$	

The steady state thickness of the film is:

$$L_{ss} = \frac{(1-a)}{\varepsilon}V + \left(\frac{2.303n}{a_3K} - \frac{\beta}{\varepsilon}\right)pH + \left(\frac{1}{\alpha_3 K}\right)\ln\left(\frac{k_3^0}{k_7}\right)$$

The equation predicts that:

- For a given pH, the steady state film thickness varies linearly with applied voltage.
- For a given voltage, L_{ss} varies linearly with pH, and for a given voltage and pH the thickness is controlled by the ratio of the rate constants for the generation of oxygen vacancies at the metal/film interface.

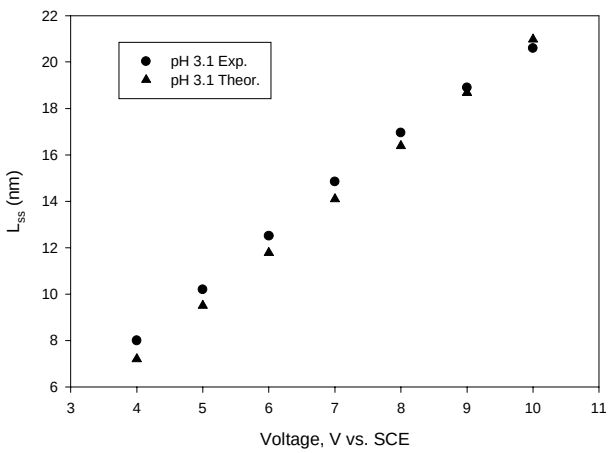
The transient in film thickness is:

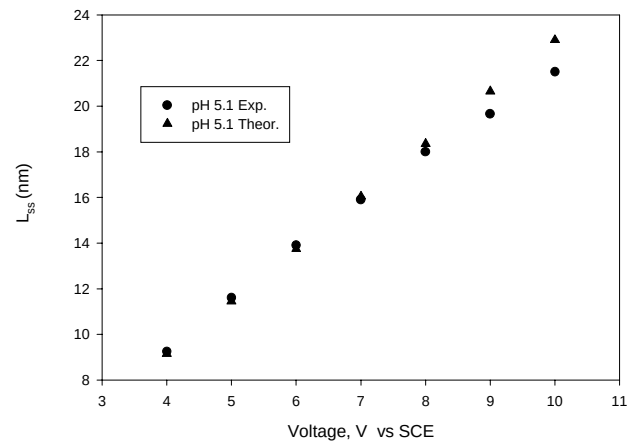
$$L(t) = L_0 + \frac{1}{b}\ln\left[\left(\frac{a'}{c}\right)e^{-bL_0}\left(e^{bct} - 1\right) + 1\right] - ct$$

The transient in film thickness is a combination of a linear relationship and a logarithmic function.

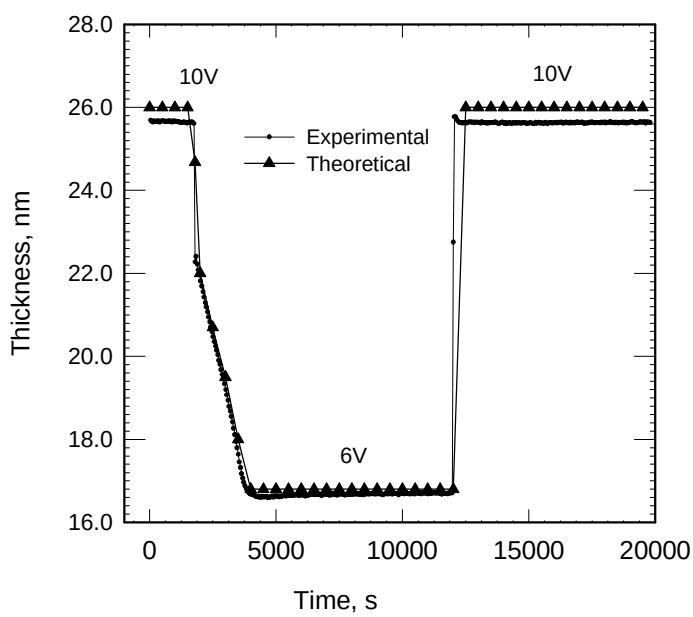
4. Studies on metals

4.1 Tungsten





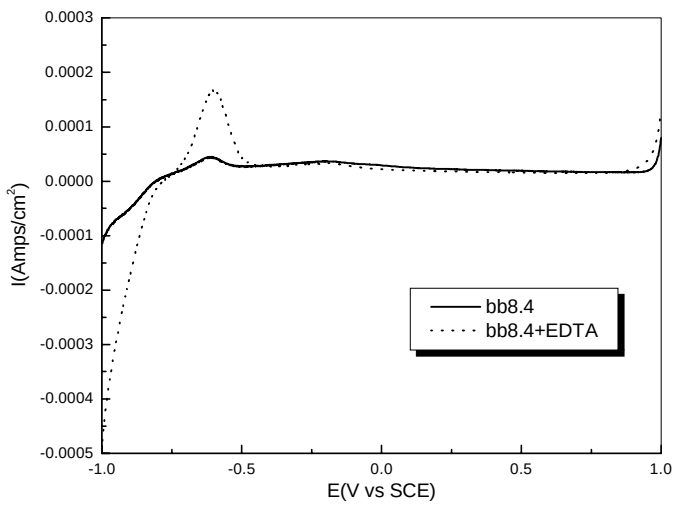
Steady state thickness vs. voltage in phosphate buffer solution.

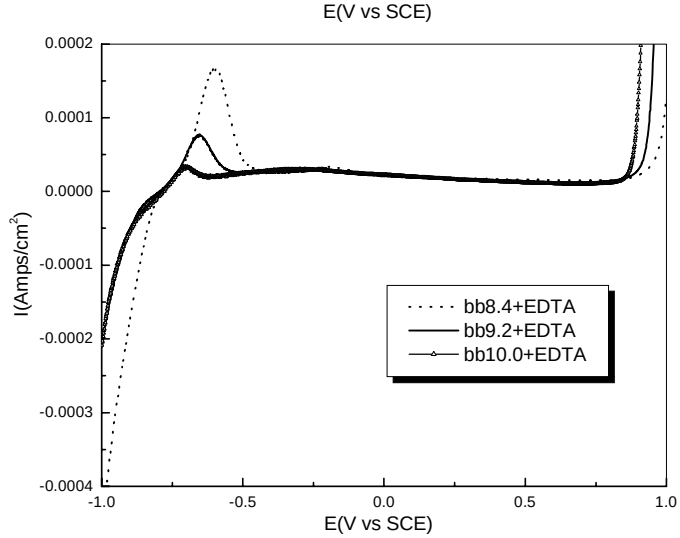


Transients in the thickness of the passive film on tungsten in phosphate buffer solution as voltage is stepped from 10 V_{SCE} to 6V_{SCE} and back to 10 V_{SCE}.

4.2 Iron

- The passive film on iron has a bilayer structure comprising a defective Fe_3O_4 inner layer (the "barrier" layer), which grows directly into the metal and a γ-Fe_2O_3 outer layer that forms by precipitation.
- The present work is based on the hypothesis that EDTA, which chelates the iron cations that are ejected from the barrier layer, should be effective in preventing the formation of the outer layer.





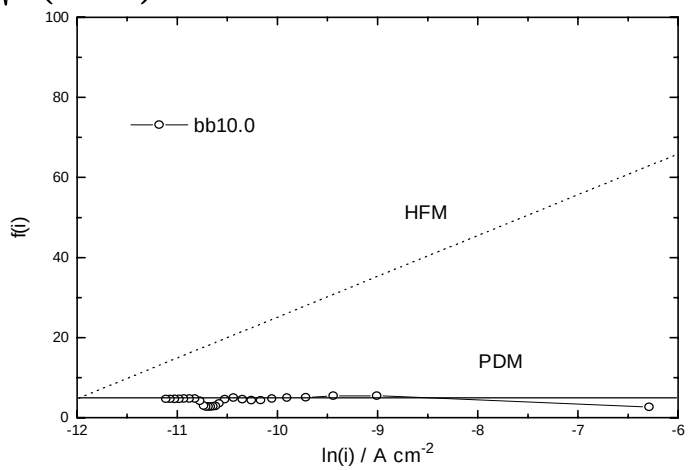
Polarization curves in borate buffer solution with and without 0.01M EDTA, and as a function of pH.

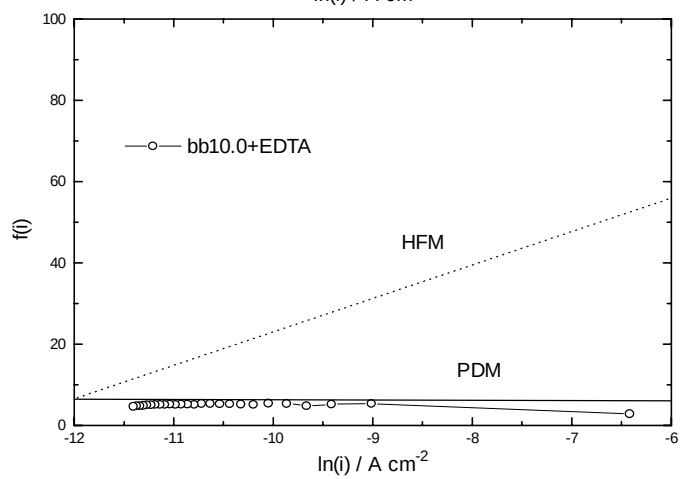
Diagnostic Criteria

Diagnostic criteria based on current transient data measured under potentiostatic conditions have been employed to distinguish between the PDM and the HFM.

HFM: $$\sqrt{\frac{-i'}{i(i-\delta)}} = \left(\frac{1}{\chi F}\sqrt{\frac{\Omega RT}{aV}}\right)\ln i - \left(\frac{1}{\chi F}\sqrt{\frac{\Omega RT}{aV}}\right)\ln A$$

PDM: $$\sqrt{\frac{-i'}{i(i-\delta)}} = \sqrt{\frac{a_2 \varepsilon \Omega}{RT}}$$



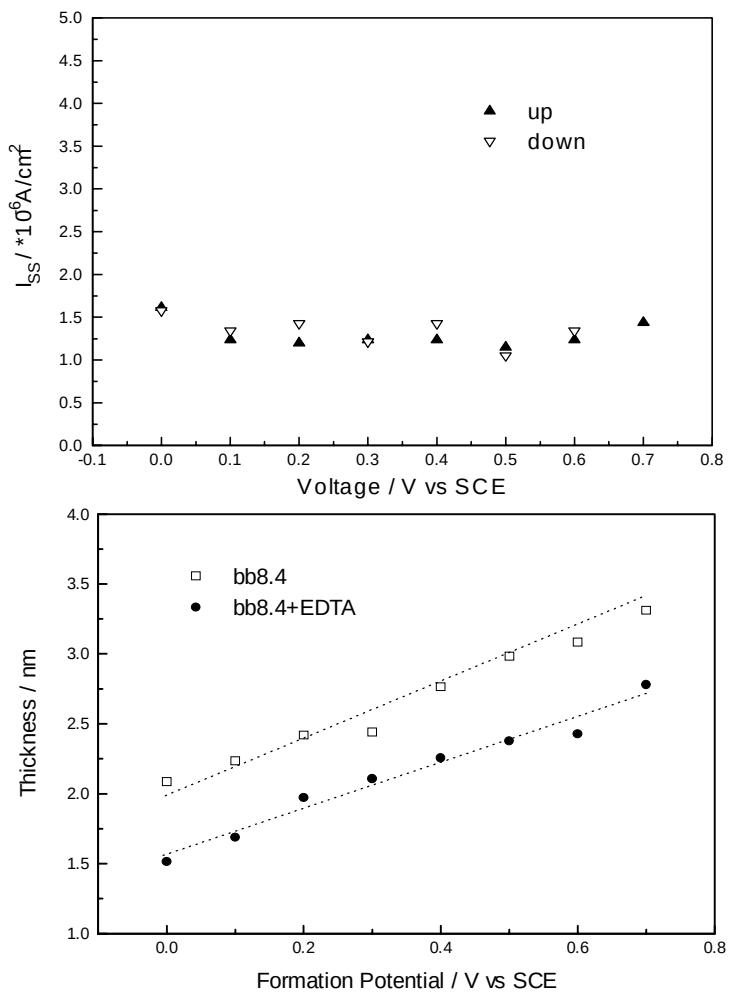


Diagnostic test for the growth mechanism for the passive film in borate buffer solution with and without EDTA.

Steady-State Properties

- The steady-state current density does not depend on the applied potential, which is diagnostic of the principal defects being oxygen vacancies and/or iron interstitials. This is consistent with the n-type character of passive iron.
- The film thickness can be estimated from the well-known "parallel plate" expression, as

$$Lss = \frac{\varepsilon\varepsilon_0 A}{C}$$

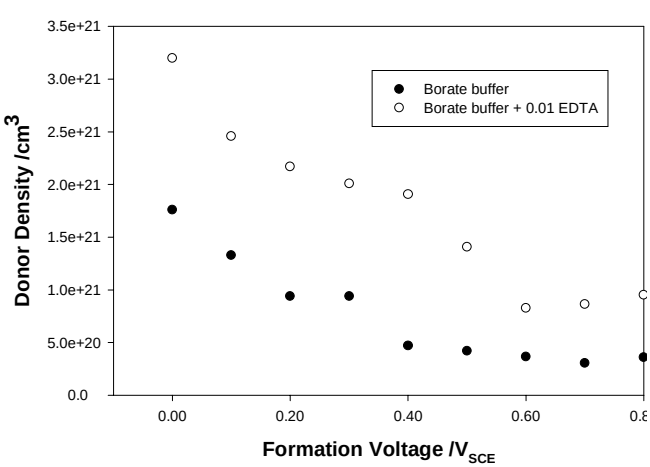


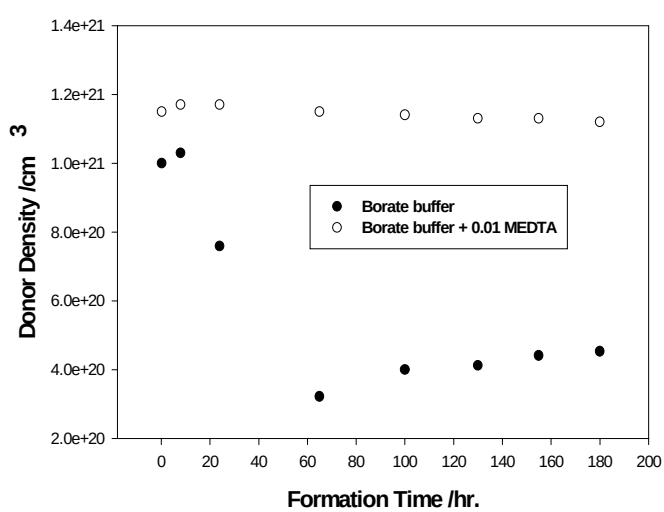
Plots of stead state current and film thickness as a function of applied voltage in borate buffer solution.

Semiconductive Properties

- The donor density decreases with increasing formation potential, which is in agreement with the prediction of the PDM. Also, the passive film formed on iron in borate buffer solution with EDTA is more defective than that formed in the absence of EDTA.

- The donor density in the passive film on iron with EDTA decreases slightly with increasing formation time. Without EDTA, it initially decreased with time, while at times greater than 60 hours it slowly increases with time, but still remains well below the N_D value obtained in the presence of EDTA.





Donor density as a function of passive film formation time at a formation voltage of 0.4 VSCE (a), and as a function of formation voltage at a formation time of 24 hours (b) with and without 0.01M EDTA.

4.3 Aluminum

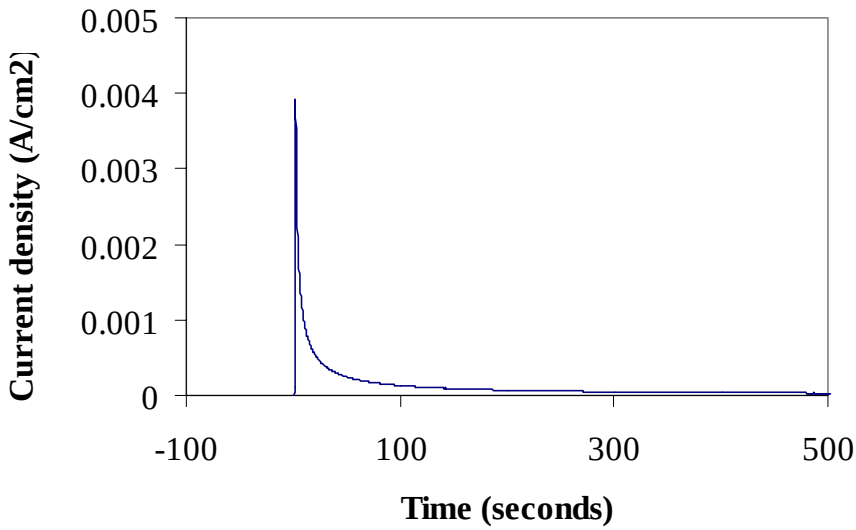
Goal: Assess the relative merits of the Point Defect Model and the High Field Model in describing the kinetics of film growth on metals.

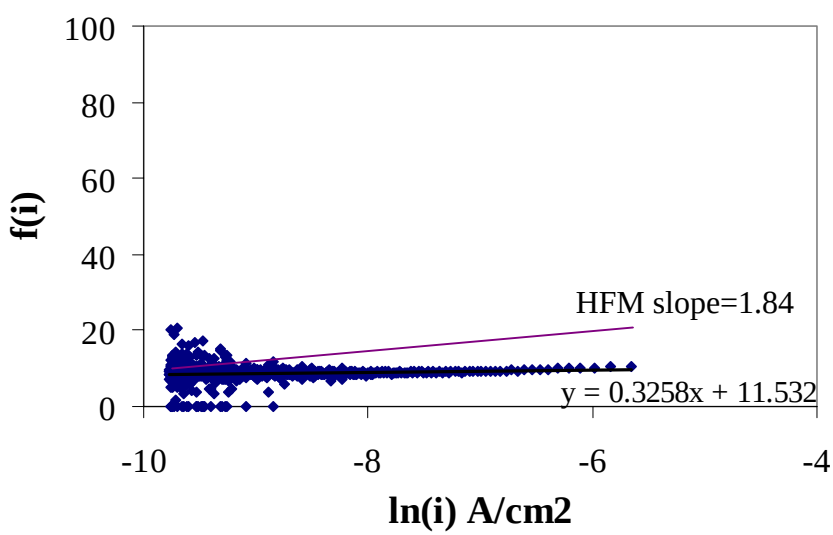
Aluminum was chosen because:

- It is an excellent substrate upon which to test anodic oxidation mechanisms
- It has a single oxidation state (+3)
- Passive film dissolves at a convenient rate in most aqueous electrolytes
- It may be anodized at very high voltages without significant interference from oxygen evolution

Potentiostatic current transients at applied potentials of 1V, 2V, 3V, 4V, 5V, 6V, 7V versus the OC potential.

Borate buffer solution
[0.50 kmol/m^3 H_3BO_3/0.05 kmol/m^3 $Na_2B_4O_7$],
pH=6.9, V=7 V_{SCE}.





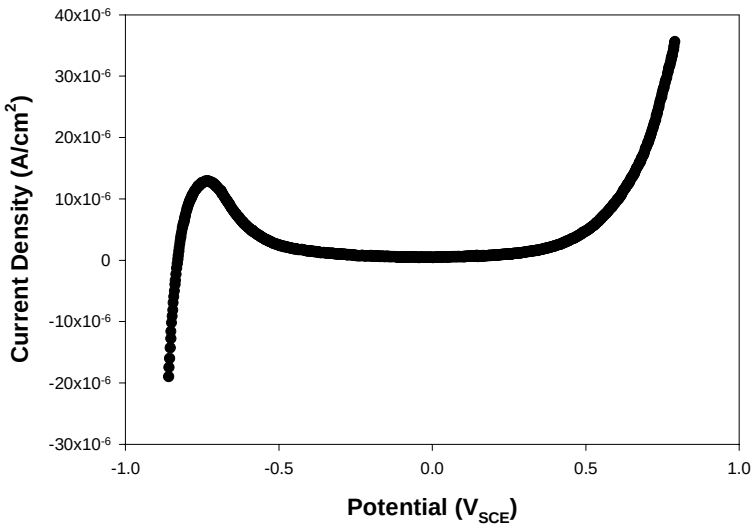
Diagnostic criteria

Slope according to PDM = **0**

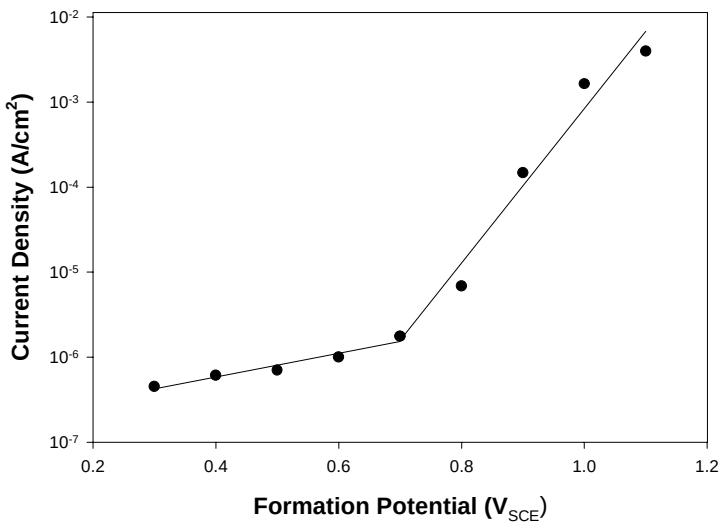
Slope according to HFM = $\frac{1}{\chi \cdot F}\sqrt{\frac{\Omega \cdot R \cdot T}{\alpha \cdot \Delta V}}$ =**1.84**

4.4 Nickel

Nickel is used extensively in structural alloys, both as an alloy base and as an alloying element in austenitic stainless steels. In this study, we have explored the semiconductive properties of the passive film formed on nickel in borate buffer solution, with particular emphasis on the upper end of the passive potential range.

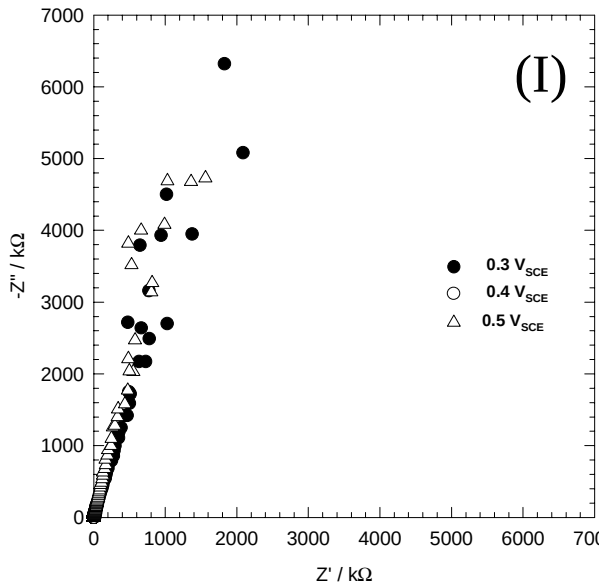


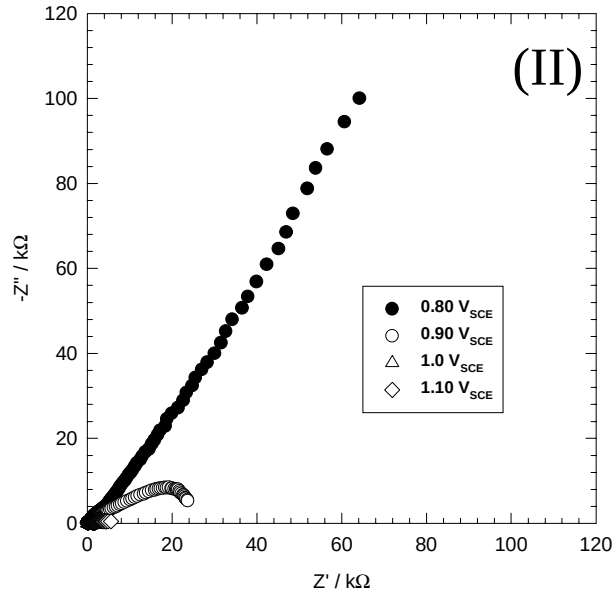
Potentiodynamic polarization curve for Ni in borate buffer solution.



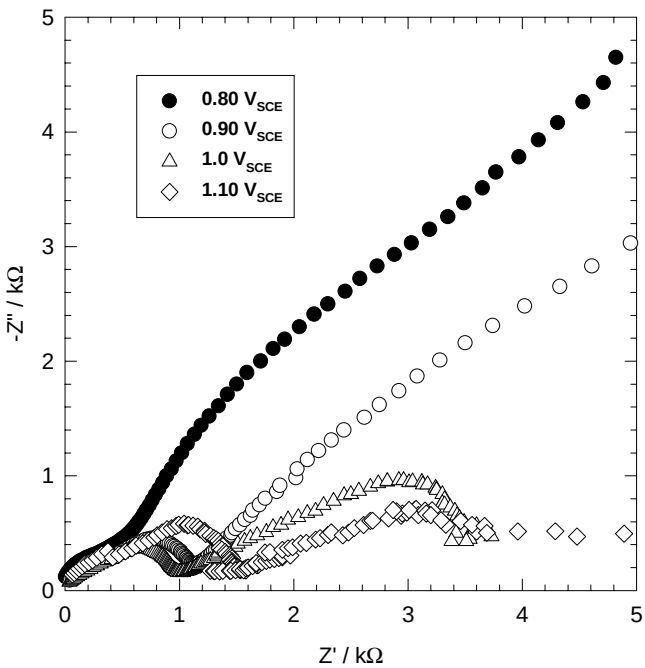
Dependence of the steady state passive current density on the passive film formation potential.

Impedance measurements





Impedance spectra for passive nickel in borate buffer solution (pH=8.4) as a function of potential, in Region (I) and in Region (II).

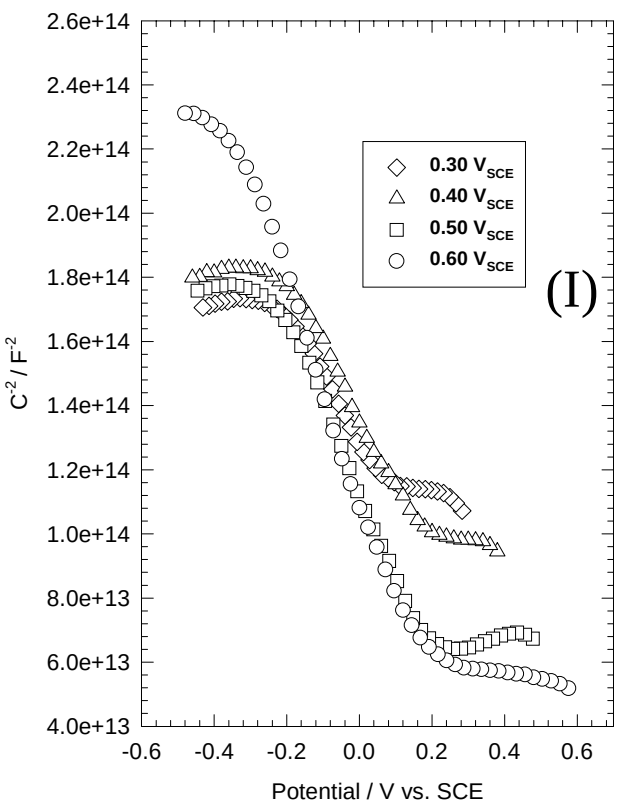


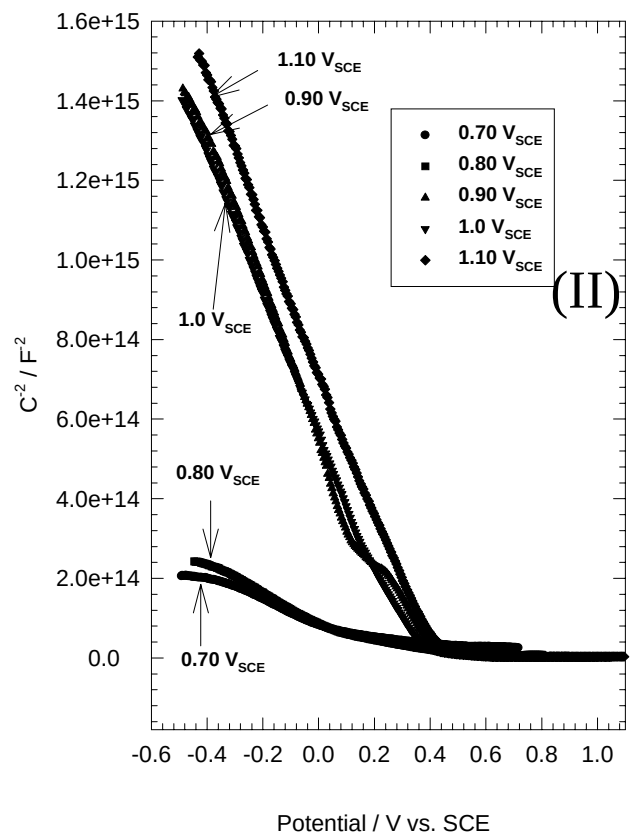
Expanded view of impedance spectra for Region (II).

Capacitance measurements

According to Mott-Schottky theory, the space charge capacitance of a p-type semiconductor is given by Equation:

$$\frac{1}{C^2} = \frac{-2}{\hat{\varepsilon}\varepsilon_o e N_A A^2}\left(V - V_{fb} - \frac{kT}{e}\right)$$





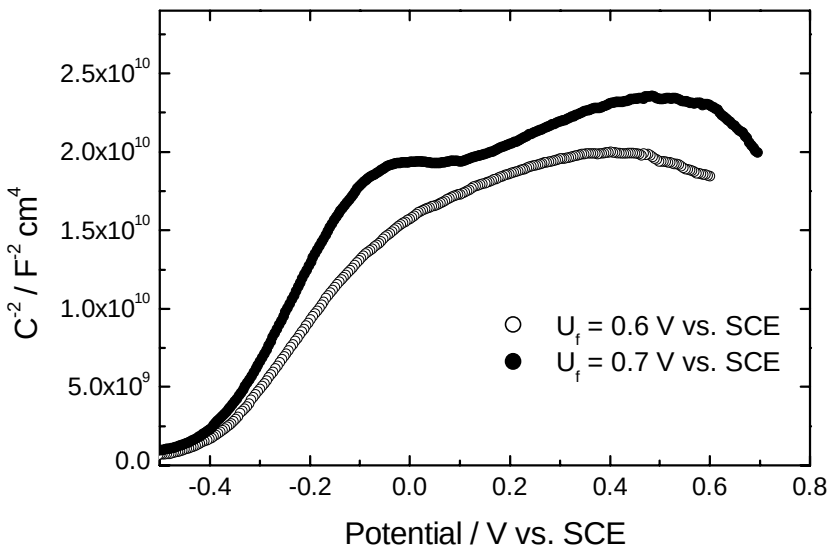
Mott-Schottky plots for passive nickel in borate buffer solution (pH=8.4) as a function of potential in Region (I) and Region (II).

4.5 Fe-Cr Alloys

- Excellent corrosion resistance of stainless steels is due to a passive film formed on their surface.
- Corrosion resistance of stainless steels depends on structure, composition and electronic properties of passive film.
- Ionic movements in the passive film are coupled with conduction of electrons and/or holes in the film.
- Electronic structure and properties are responsible for corrosion resistance, i.e. film breakdown and pitting initiation.
- Electronic structure of the passive film on stainless steels remains far from clear.
- The objectives are to characterize the electronic structures of the passive film on Fe-20Cr according to the formation potential of the passive film by in situ Mott-Schottky analysis, and hence to understand the detailed mechanism of physical and electronic structural changes of the passive film.

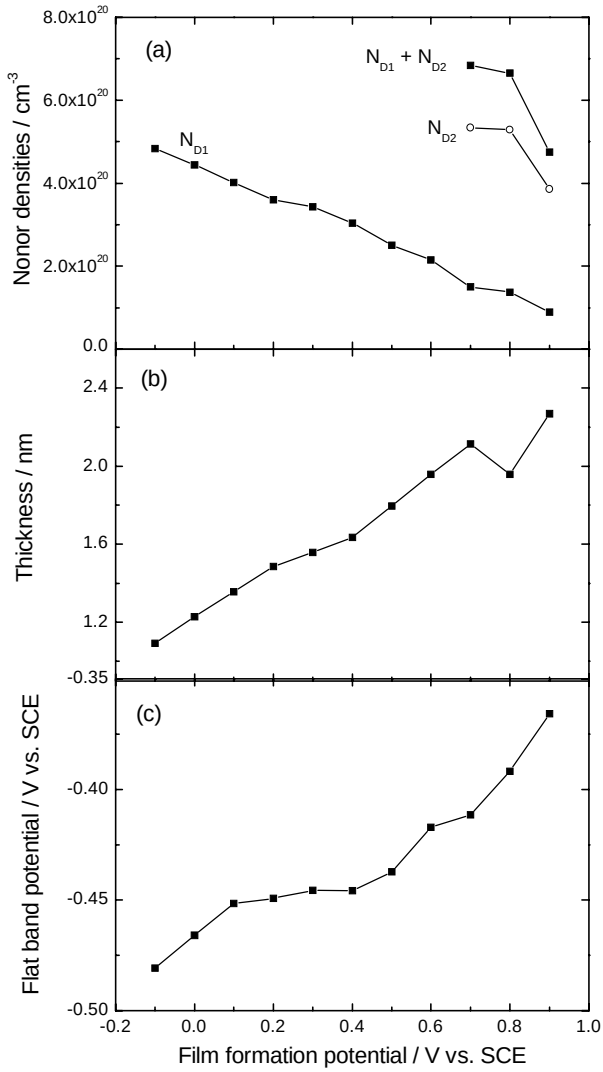
Mott-Schottky Plots at Passive and Transpassive Potentials

- n-type characteristics at all film formation potentials (-0.1 to 0.9 V vs. SCE)
- Passive film formed at passive potentials exhibits one linear region while that formed at transpassive potential revealed two linear regions; N_{D1} for shallow donors at lower potentials and N_{D2} for deep donors at higher potentials.
- The deep donors (N_{D2}) can be induced by ionization of deep donors at high potentials possibly indicating the presence of Cr^{6+}.



Mott-Schottky plot for the passive film formed on Fe-20Cr at passive (0.6 V_{SCE}) and transpassive (0.7 V_{SCE}) potential in dearetate buffer solution at room termperature

Effects of Film Formation Potential on Semiconducting Properties of the Passive Film



- With increasing film formation potential:
  - Donor density decreases
  - Film thickness and flat band potential increase
- These results are in a good agreement with the prediction of PDM.
- The dominant defects of the passive film on Fe-20Cr formed in pH 8.5 buffer solution are oxygen vacancies and Fe and/or Cr interstitials, because of the observed n-type semiconducting properties.

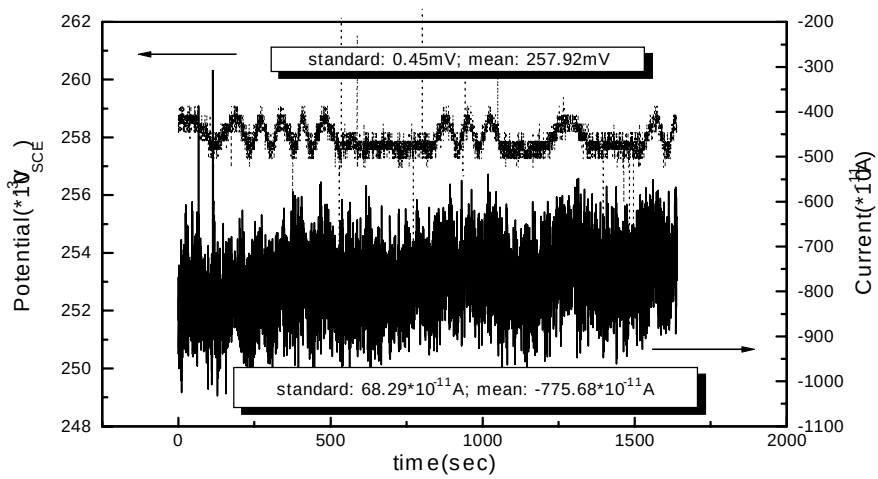
5. Electrochemical Emission Spectroscopy

- A high fidelity method for measuring electrochemical emission data on carbon steel 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.

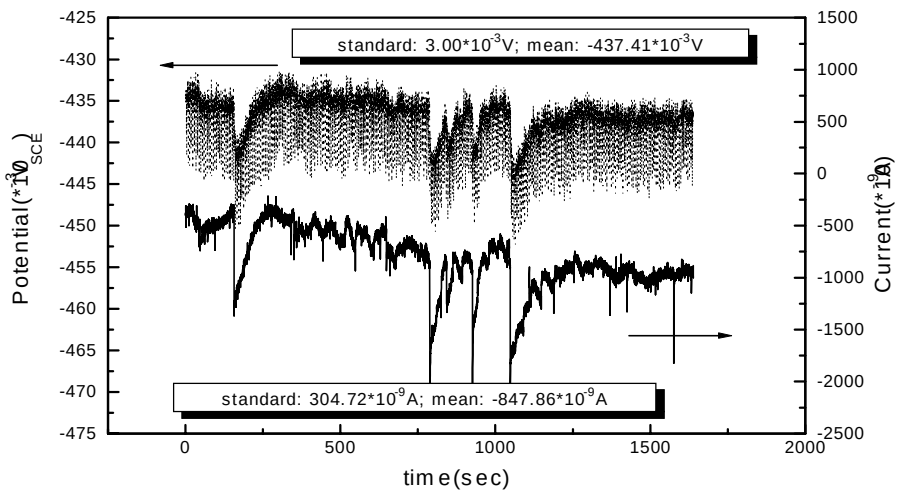
- The general measurement scheme of Electrochemical Emission Spectroscopy is to simultaneously monitor current fluctuations between two identical electrodes of the metal and/or alloy of interest that are maintained at the same potential by a zero resistance ammeter (ZRA) and voltage fluctuations of the current-carrying electrodes by using a reference electrode (RE)/high impedance voltmeter.

Typical traces of electrochemical voltage and current, as a function of time, are shown for general corrosion (seven days after immersion) and pitting corrosion (one day after immersion) of AISI 1018 carbon steel in 1M NaOH and 0.5M NaCl solutions, respectively.

Simultaneous fluctuations of voltage and current were observed in both cases.



General Day7 Transients



Pit Day1 Transients

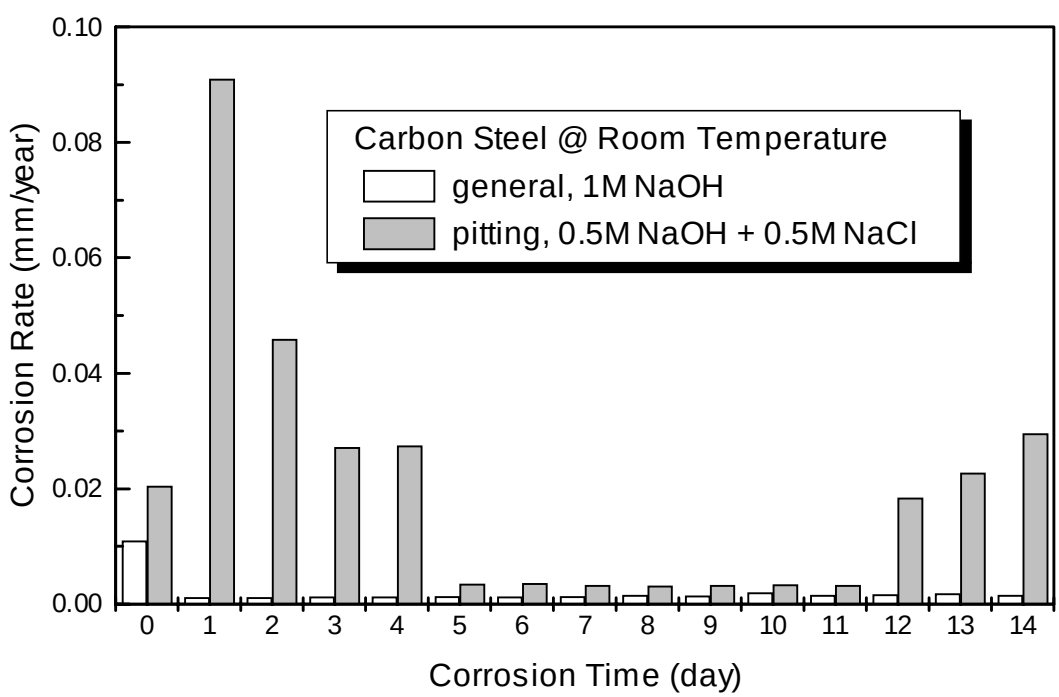
Potential and current transients for carbon steel in NaOH and NaOH+NaCl solutions after 7 day and 1 day immersion.

- The noise resistance is defined as the ratio of the standard deviations of the current and voltage fluctuations over a given time:

$$i_{corr} = \frac{b_a b_c}{2.3(b_a + b_c)R_n} = \frac{B}{R_n} \approx \frac{0.22}{R_n}$$

The penetration corrosion rate is then derived as:

$$\delta = \frac{i_{corr} V_m}{nF}$$



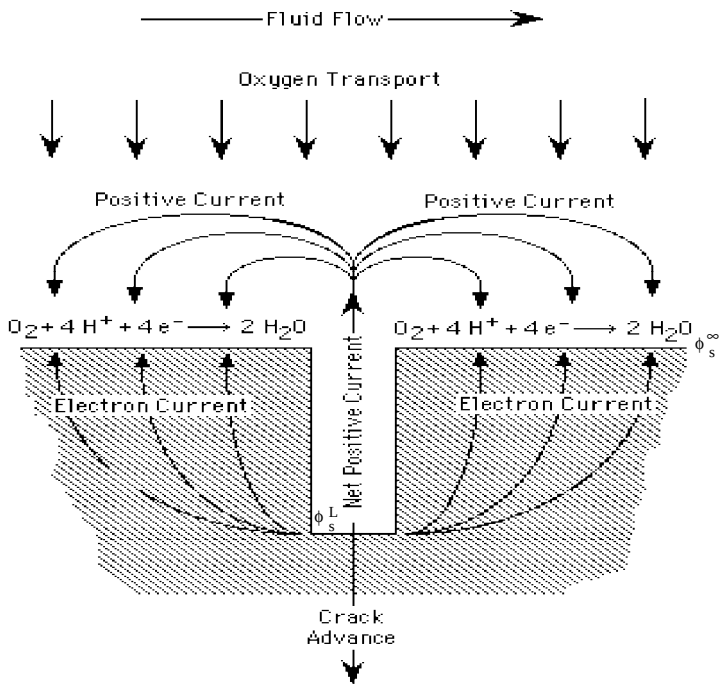
Penetration corrosion rates for general corrosion and pitting corrosion of carbon steel at room temperature.

6. Crack Propagation Studies

Objectives:

- To explore Electrochemical Emission Spectroscopy (EES) as a means of characterizing crack propagation in AISI 4340 steel in NaOH solution.

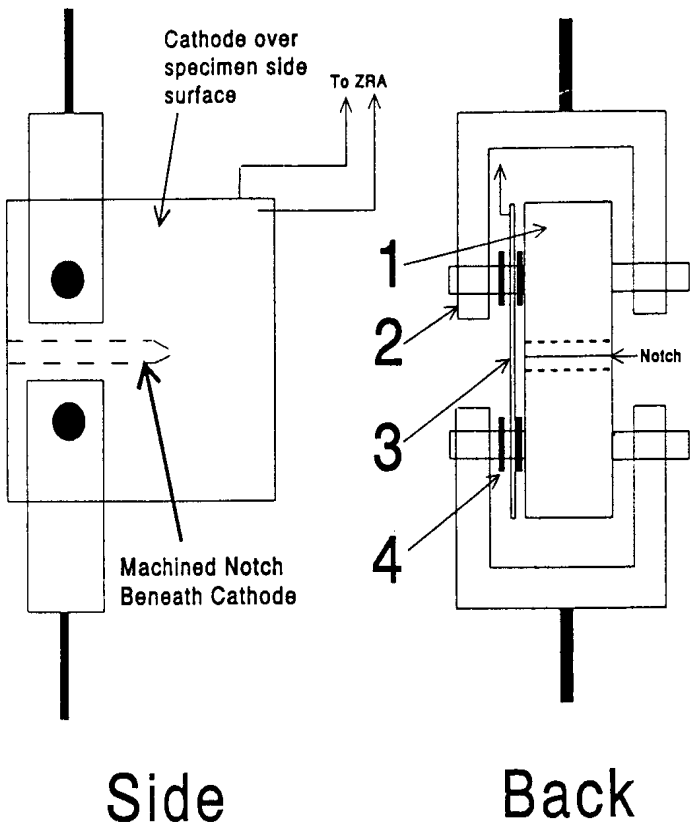
- To understand the mechanism of caustic cracking with particular emphasis of resolving key mechanistic issues:
  - Anodic dissolution *vs*. hydrogen embrittlement;
  - Crack advance via discrete events *vs*. continuous propagation.



Schematic of the origin of the coupling current in stress corrosion cracking.

Experimental Method

- The C (T) fracture mechanics specimen is coated with PTFE to inhibit the cathodic reduction of oxygen on the specimen surface.
- The electron current flows from the crack tip to the side cathodes via a zero resistance ammeter, which is used for its measurement

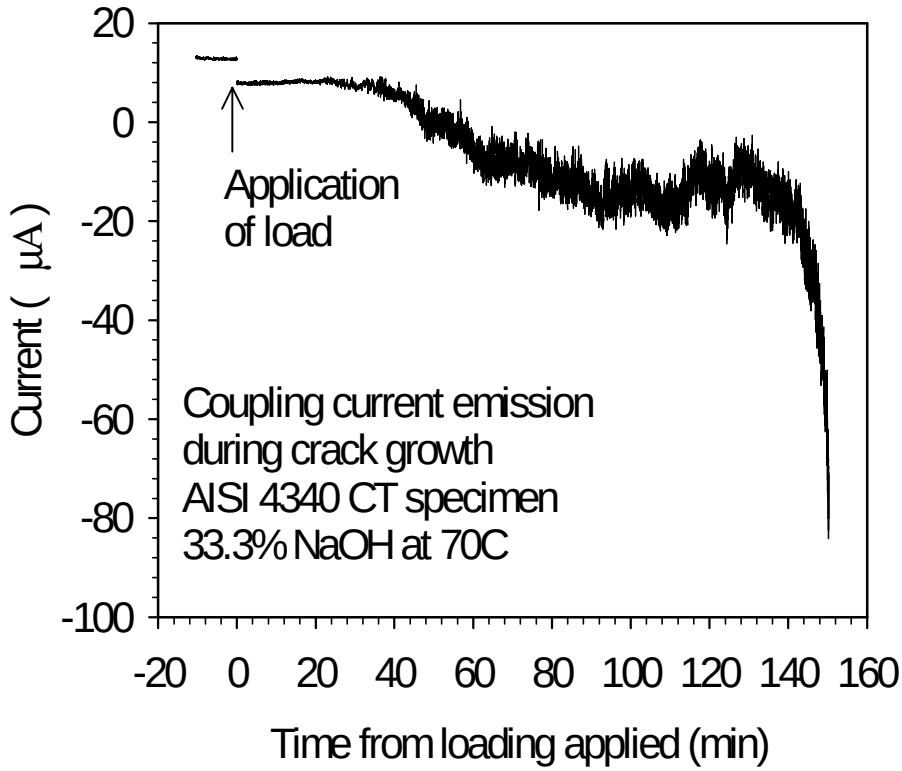


1. Specimen; 2. Clevis; 3. Cathode; 4. PTFE Washer

Specimen configuration used in detecting and measuring the coupling current flowing from a crack to the external metal surface.

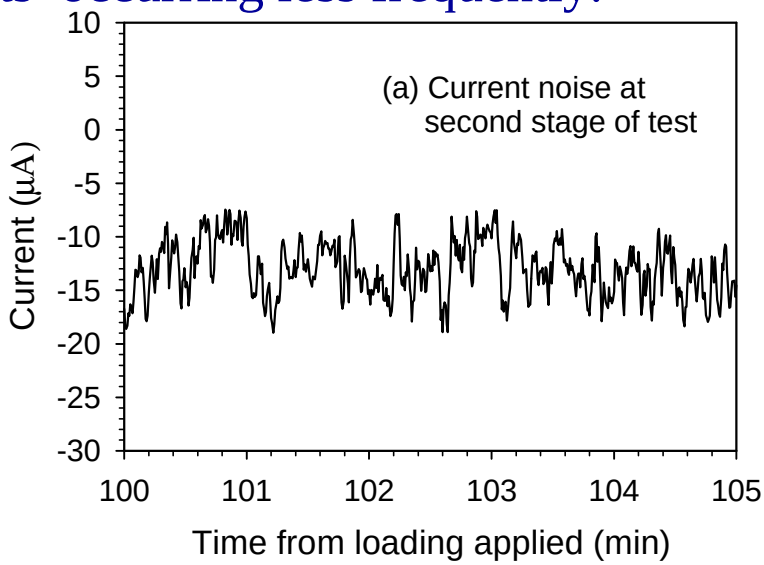
- Positive current flows though the solution from the crack tip to an external cathode, and the negative current flows though the ZRA from the crack tip to the surface, during crack propagation (as shown in the figure).

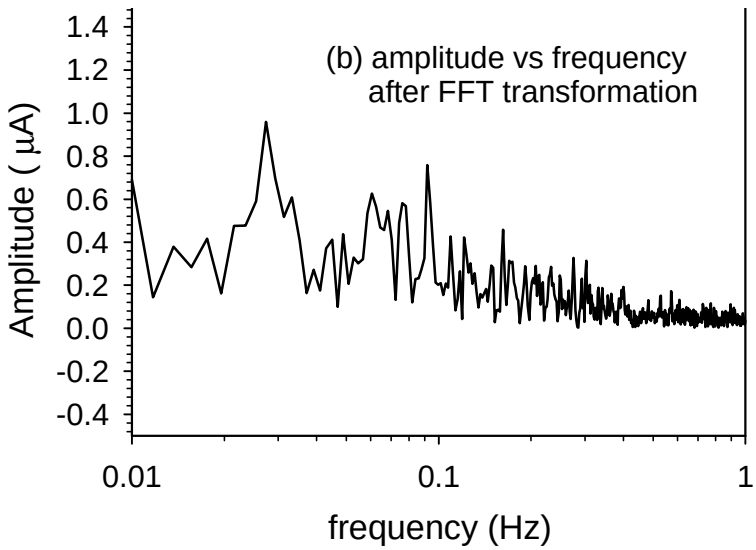
- Cathodic reaction occurs predominantly on the external surfaces, as postulated in the CEFM.



Measurement of coupling current emission vs. time during crack propagation for AISI 4340 steel in 33.3% (wt.) NaOH solution at 70°C.

- Semi chaotic (but periodic) pulses observed in the coupling current between the specimen and external cathodes during SCC are attributed to the overlap of many micro cracks propagating simultaneously along grain boundaries, with larger events occurring less frequently.





Details of the current noise (a), and its amplitude *vs.* frequency (b) after FFT transformation during the second stage in the fracture history of AISI 4340 CT specimen in 33%(wt.) NaOH solution at 70°C.

7. Summary and Conclusions

- The mechanism(s) of corrosion of metals, including iron, tungsten, and aluminum, and low and high alloy steels (e.g., Fe-20Cr) in the passive state have been explored. We have derived an entirely new rate law for the growth of the barrier oxide layer on a metal surface within the framework of the Point Defect Model.

- The new rate law successfully accounts for transient data in the thickness of the passive film on tungsten in phosphate buffer solution, as measured in response to both positive and negative potential steps, which were measured in previous studies.

- The passive film formed anodically on nickel in borate buffer solution in both the passive and transpassive regions is found to be p-type, corresponding to a preponderance of metal vacancies (over oxygen vacancies and nickel interstitials) in the barrier layer. However, at high anodic potentials, some n-type character was detected by Mott-Schottky analysis, which is probably due to the presence of free charge carriers (electrons) from the evolution of oxygen at the barrier layer /solution interface.

- Analysis of transient current data for the growth of the passive films on iron, aluminum, and tungsten, obtained under potentiostatic conditions further supports the validity of the Point Defect Model in describing the passive states on these metals. 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 transient data.

- In agreement with the recent findings of Edgemon, Danielson, and Bell, general corrosion on carbon steel in simulated liquid waste systems is characterized by random fluctuations in the coupling current between identical specimens and in the corrosion potential measured against a reference electrode.

- In passive systems (e.g. carbon steel in alkaline solution), 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 coupling currents and smaller fluctuations in the current.

- As shown by Legat, the correlation dimension and the maximum Lyapunov exponent of the electrochemical noise reveals that localized corrosion is a deterministic chaotic process, whereas uniform corrosion is a random (stochastic) process.

- Electrochemical Emission Spectroscopy (EES) is an effective, in situ technique for monitoring the corrosion rate of carbon steel in highly alkaline solutions of the type that exist in liquid waste facilities. The noise signature exhibited by general corrosion is significantly different and is easily distinguished from that for localized corrosion in this system.

- Our current work is attempting to establish the link between the deterministic model (Point Defect Model, PDM) and the "noise" due to metastable pitting. A recent study by Isaacs and Herbert of electrochemical current noise on aluminum microelectrodes indicates a possible mechanism of noise generation, which is based on fluctuations within cracks or pores in the outer part of the passive oxide film.

- Positive current is found to flow from the crack to an external cathode during stress corrosion cracking in AISI 4340 steel in concentrated sodium hydroxide solution at 70°C. The coupling current contains noise, the amplitude and mean value of which increases with crack growth rate.

- Semi chaotic (but periodic) pulses observed in the coupling current between the specimen and external cathodes during SCC are attributed to the overlap of many micro cracks propagating simultaneously along grain boundaries. The discrete events are apparently hydrogen induced, and hence the mechanism of caustic cracking of AISI 4340 steel is considered to be hydrogen embrittlement.

8. Publications and Presentations

1. 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).
6. E. Sikora and D. D. Macdonald, “The Passivity of Iron in the Presence of EDTA. I. General Electrochemical Behavior”, J. Electrochem. Soc., submitted (2000).

2. Papers in preparation

1. D. D. Macdonald, G. R. Engelhardt, and M. Al-Rifaie, “On the Transients in the Thickness of Anodic Passive Films on Metals”, J. Electrochem. Soc., in preparation (2000).
2. 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”, J. Electrochem. Soc., in preparation (2000).
3. S. Liu and D. D. Macdonald, “ A Review of Caustic and Nitrate Cracking of Carbon Steel”, Corrosion, in preparation (2000).
4. E. Sikora and D. D. Macdonald, “The Electrochemistry and Electronic Character of the Passive State on Nickel”, Electrochim. Acta, in preparation (2000).

3. 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.

4. External Collaborations

- Significant collaboration has occurred between Professor Macdonald and Dr. George R. Engelhardt at SRI International in developing various theoretical aspects of the work described in this work. Prior to joining SRI, Dr. Engelhardt was a Research Associate at the Center for Advanced Materials, which was directed by Professor Macdonald. Importantly, Dr. Engelhardt is the Principal Investigator on a DOE/NERI project at SRI that seeks to develop deterministic methods for predicting localized corrosion damage high-level nuclear waste canisters. A high level of synergism exists between our research program and that of Dr. Engelhardt.

- The work described above on the passivity of Fe-20Cr alloy is being performed by Ms EunAe Cho as part of the requirements for a Ph. D. degree from Korea Advanced Institute of Science and Technology (KAIST). Ms Cho is spending four months in our laboratory as a Visiting Scholar. The Korea Science and Engineering Foundation (KOSEF) are meeting all salary and travel costs associated with Ms Cho's stay at Penn State University.

- Finally, Ms Monika Gomez-Duran from Universidad Industrial de Santander in Colombia is studying for her M.S. degree in Materials Science at Penn State University. Her thesis work is concerned with the generation of coupling current during the fracture of sensitized Type 304 SS in the presence of partially reduced sulfur species. All stipend and travel costs, and academic fees, are covered by COLCIENCIAS/LASPAU.