

Environmental Management Science Program

Project ID Number 60219

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

Dr. Digby D. MacDonald
Pennsylvania State University
517 Deike Building
University Park, Pennsylvania 16802
Phone: 814-863-7772
E-mail: ddm2@psuvm.psu.edu

June 1, 1998

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

Dr. Digby D. MacDonald, Pennsylvania State University

Research 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 mechanisms 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 and Implications

This report summarizes work after 1 year 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 have been interpreted by assuming the presence of a two-layer film consisting of an inner layer of Fe_3O_4 and an outer layer of $\text{g-Fe}_2\text{O}_3$. This is based on a frequently reported observation of two reduction waves in galvanostatic and potentiodynamic experiments. Those two waves (or peaks) are generally attributed to reduction of first, the outer layer and then second, the inner layer to form soluble Fe^{+2} [8-9]. An alternative explanation can be found in the proposal that the film is a single layer of $\text{g-Fe}_2\text{O}_3$. In this case, the two reduction waves are believed to be the reduction of Fe_2O_3 first to Fe_2^+ and then to Fe^0 [10,11].

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. The wire was embedded in a two component epoxy resin and mounted in a PVC holder. The samples were mechanically polished with 1200 grit emery paper and with 0.3 mm Al_2O_3 , then rinsed and sonicated in distilled water.

All experiments were performed at ambient temperature (22 – 25°C) in pH 8.4 borate buffer (0.075 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, 0.3 M H_3BO_3), which was deaerated with N_2 during the measurements. Prior to all experiments, the samples were cathodically polarized at -1.0 V SCE for 5 min. to remove the air formed film. Then the potential was stepped (within 0.02 s) to different formation potentials (ranging from 0.0 V to 0.6 V). The potential was maintained constant until a steady-state was achieved (typically between 24 and 48 hr).

In some experiments, 0.01 M EDTA was added to the solution in order to hinder the formation of the precipitated layer. Formation of passive films consisting only of barrier layer, is vital to our experiments since the current models describing passivity breakdown take into account the existence of only the barrier layer.

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. On reverse scanning, the current recorded in borate buffer with EDTA becomes cathodic at more noble potentials (around 0.0 V SCE) whereas without EDTA the current becomes cathodic at potentials around -0.2 V SCE . In potentiostatic experiments, in the presence of EDTA, the current decay is slower than without EDTA (suggesting lower film formation rate), but after approximately 15 hr the passive current on Fe is lower than that in the solution without EDTA. In order to study the influence of EDTA in hindering the formation of the outer layer, galvanostatic and potentiodynamic reduction

curves were measured. The samples were passivated for 60 hr at 0.6 V SCE. In galvanostatic reduction experiments, the reduction current density was -25 mA/cm^2 . In the case of potentiodynamic measurements, the potential sweep rate was -1 mV/s . Particularly from the potentiodynamic curves, it is obvious that the film reduction process in borate buffer solution occurs in two steps – as reported several times in the literature, which can be attributed to the $\text{Fe}^{+3}/\text{Fe}^{+2}$ reduction in the outer $\text{g-Fe}_2\text{O}_3$ layer as well as in the inner Fe_3O_4 part of the film. The potentiodynamic curve recorded in borate buffer with EDTA solution displays only one reduction peak suggesting the reduction (and hence the existence) of only a single layer passive film.

It is well known that passive films on most metals and alloys exhibit a semiconducting behavior. Therefore, in recent years a variety of experimental techniques have been applied to studying the electronic properties of passive films. The most common in situ method for probing the electronic properties of passive film is (besides photoelectrochemistry) Mott-Schottky analysis (capacitance measurements).

In Mott – Schottky experiments, the specimens are passivated for at least 24 hr at different formation potentials and the imaginary part of the impedance (Z'') at 1 kHz is recorded as a function of the potential. The interfacial capacitance, C , is obtained from $C = -1/wZ''$. According to Mott – Schottky theory, the space charge capacitance of a semiconductor is given by a well know equation [12] where $C-2$ is inversely proportional to the donor concentration (for an n-type semiconductor). Thus, for $C-2$ vs. V profiles which display linear part, the calculation of the number of defects (which serve as charge carriers) in the passive film is straightforward.

Assuming that the capacitance of the Helmholtz layer can be neglected, $C = C_{sc}$.

$C-2$ vs. V profile recorded for passive film formed on Fe in borate buffer solution with and without EDTA show non-linear behavior. The observed nonlinearity can be due to several phenomena, such as an inhomogeneous doping profiles, the presence of deep states, and the presence of surface states, which become ionized as the Fermi potential changes. The ionized states then contribute to the measured charge. The doping concentration can be determined from the slope of the linear part of the curve in the relevant potential range. It is obvious that the passive film formed on iron in borate buffer solution is less defective than that formed in the presence of EDTA. This phenomenon may be due to the lower thickness of the passive films formed in borate buffer solution with EDTA, because of the higher dissolution rate of the film. The donor densities calculated for all formation potentials for passive films formed on iron decrease with increasing voltage (over the range of 8.8 to $5.2 \cdot 10^{20} \text{ cm}^{-3}$). The Mott-Schottky plots were also measured as a function of a potential sweep rate. For two different potential sweep rates 1 mV/s and 0.2 mV/s the recorded $C-2$ vs. V profiles were virtually the same.

Steady – state thicknesses of the films formed at different potential were calculated from the measured capacitance. The results display a linear dependence between the film thickness and formation voltage above 0.4 V SCE . Film thickness for formation potentials below 0.4 V SCE is constant and equals 2.3 nm . This result may suggest the existence of an additional capacitance, C_{add} , which is smaller than that of oxide, (C_{ox}). Accordingly, for potentials more negative than 0.4 V SCE this additional capacitance governs the overall measured capacitance, C ($1/C = 1/C_{add} + 1/C_{ox}$). EIS measurements seem to confirm this hypothesis; for films formed below 0.4 V SCE there is an additional capacitive loop observed in the impedance locus at high frequencies.

1. P. Southworth, A. Hamnet, A.M. Riley and J.M. Sykes, *Corr.Sci.*, 28, 1139 (1988).
2. N. Sato, T. Noda and K. Kudo, *Electrochim. Acta*, 19, 471 (1974).
3. M. Nagayama and M. Cohen, *J.Electrochem. Soc.*, 109, 781 (1962).
4. B.D. Cahan and C. T. Chen, *J. Electrochem. Soc.*, 129, 474 (1982).
5. U. Stimming in *Passivity of Metals and Semiconductors*, Elsevier, Amsterdam (1983).
6. U. Konig, P. Meisterjahn, J.W. Schultze, *Werkstoffe u. Korrosion*, 42, 179, (1991).
7. P. Schmuki, S. Virtanen, A. Davenport and C. Vitus, *J. Electrochem. Soc.*, 143, 574 (1996).
8. D. Rahner and W. Forker, *Z. Phys. Chem.*, 18, 344 (1978).
9. S. Haruyama and T. Tsuru, *Corr. Sci.*, 13, 275 (1976).
10. K. Ogura and T. Majima, *Electrochim. Acta*, 25, 1361 (1978).
11. K. Ogura and K. Sato, *Electrochim. Acta*, 27, 857 (1980).
12. S.R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, (1980).

Planned Activities

In the future, we intend to continue our work on studying the passivity of metals in alkaline solutions including investigation of the electrochemical behaviors of Ni and Cr. This task will continue during next year.