M A S S A C H U S E T T S I N S T I T U T E O F T E C H N O L O G Y

3.014 Materials Laboratory
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LABORATORY 3: Electrochemical Corrosion
Gibbs Free Energy, Anodic Corrosion & the EMF Series

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Objectives

• Learn about **galvanic (anodic) corrosion** and the driving force that causes galvanic corrosion of a metal.

• Understand the connection between **a change in Gibbs free energy** and the **cell potential (emf)** in an **electrochemical** or **corrosion reaction.**

• Appreciate the **active (anodic)** and **noble (cathodic)** behavior of a selection of common metals.

• Explore the effectiveness of **sacrificial anodes** in corrosion control and prevention.

Materials and Equipment

Ag, Al, Au, Co, Cu, Fe, Mg, Ni, Pb, Pt, Zn and brass foils
1018-steel cylinder
Piece of scrap iron
Darkened (sulfidized) silver object
220-grit silicon carbide abrasive paper
NaCl (rocksalt) powder
$NaHCO_3$ (sodium bicarbonate) powder
De-ionized water
Digital voltmeters, ammeters
Digital power supply
Digital thermometer
Stopwatch
Two electrochemical cells
Magnetic stirrer and heater

Background

Corrosion is a trillion-dollar problem worldwide, most commonly associated with metals and alloys, but also affecting ceramic and polymeric materials. Corrosion is generally divided into

three categories: high-temperature gaseous (dry) corrosion (oxidation, sulfidation); aqueous (electrochemical) corrosion; and biological corrosion (attack by microbes). In this laboratory we will investigate the second of these, aqueous electrochemical corrosion of metals and alloys.

Corrosion involves **chemical reactions**, in which the original material reacts with a chemical agent, to form a new compound or to dissolve into the chemical agent, in both cases involving charge transfer. **Corrosion** in aqueous solutions is an electrochemical reaction that involves charge transfer, either *oxidation*, involving loss of electrons; or *reduction* involving gain of electrons. As shown in fig. 1, corrosion is a metal dissolution process, with metal atoms being converted to metal ions and going into solution.
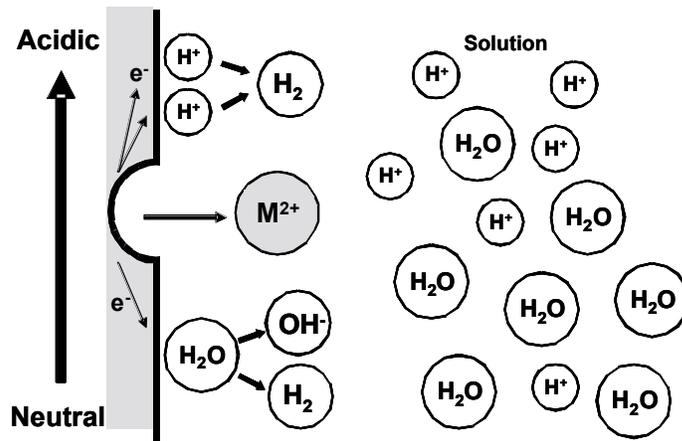

Fig. 1 Electrochemical attack of a metal surface immersed in an aqueous medium (after Fontana and Greene[1]).

The products of the reaction depend on the pH $(= -\log[H^+])$ of the aqueous solution, which is a measure of the H^+ hydrogen ion concentration. Notice the dissolution involves the transfer of charge, in this case electrons. At the metal surface, neutral metal atoms are *oxidized* to positive metal ions in what is known as an oxidation or anodic reaction:

<u>Oxidation or Anodic Reaction</u>

$$M \rightarrow M^{n+} + ne^-$$ (1)

(*e.g.* $Fe \rightarrow Fe^{2+} + 2e^-$, $Zn \rightarrow Zn^{2+} + 2e^-$)

The corresponding reduction reactions depend on the nature of the environment, particularly the pH. Typical reduction, or cathodic, reactions are:

<u>Reduction or Cathodic Reactions</u>

Hydrogen
$2H^+ + 2e^- \rightarrow H_2$ (acidic solutions) (2a)

Oxygen

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(acidic solutions)} \tag{2b}$$

$$O_2 \text{ (dissolved)} + 2H_2O + 4e^- \rightarrow OH^- \quad \text{(neutral/basic solutions)} \tag{2c}$$

Water

$$2H_2O + 2e^- \rightarrow H_2 + OH^- \text{ (neutral/basic solutions)} \tag{2d}$$
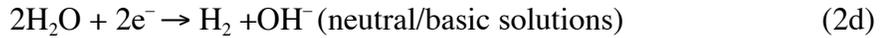
Corrosion measurements are quantified by constructing a corrosion cell (an electrochemical cell, Fig. 2) in which the oxidation and reduction reactions generally take place at separate electrodes in the cell, which develop an electrical potential difference between them. The (open circuit) cell potential is a measure of the tendency of a metal to corrode. When the two electrodes are in electrical contact, an electrical circuit is formed in which electron current flows through the electrical connection between the electrodes and a corresponding ion current flows through the electrolyte between the electrodes. The current flow is a measure of the corrosion taking place at the anode.

ELECTROCHEMICAL CELL
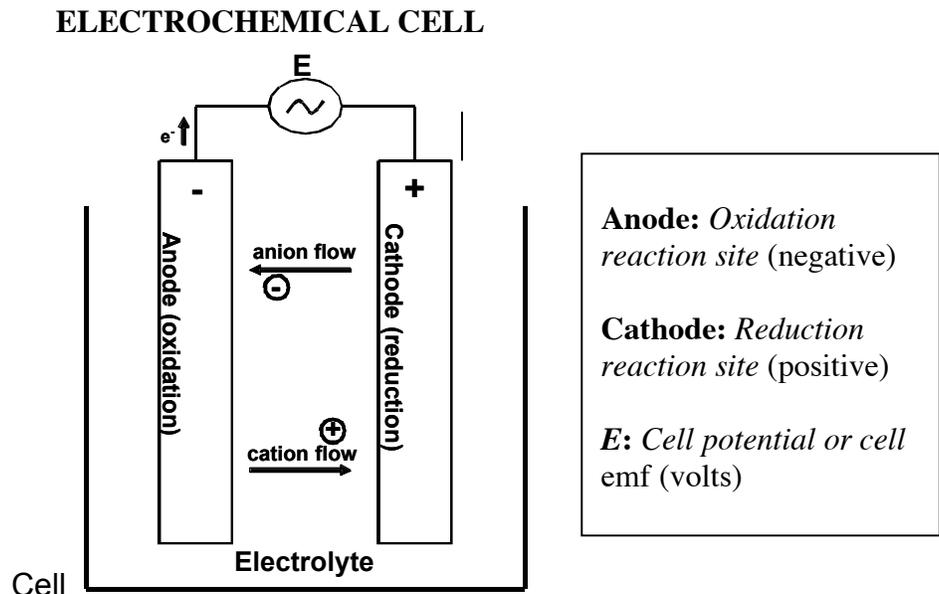
Fig. 2. An electrochemical cell.

Relationship between Gibbs Free Energy and the Cell Potential[1,2]

One can assert the tendency of a metal to corrode from thermodynamic considerations. The change ΔG in Gibbs free energy for the corrosion reaction predicts whether or not a corrosion reaction occurs spontaneously; it does so spontaneously if $\Delta G < 0$. The change in free energy can be calculated from a measurement of the cell potential E. The maximum amount of electrical energy (or work done) that can be delivered by an electrochemical cell in a given state is $n\text{F}E$, which is equivalent to the change in Gibbs free energy

$$\Delta G = -n\text{F}E, \tag{1}$$

where n is the number of moles of *electrons* exchanged in an electrochemical reaction, F is Faraday's constant (96,485 C /mol), and E is the cell potential (in volts) for the cell in a given state. For cell conditions in a standard state,

$$\Delta G^0 = -n\text{F} E^0 \tag{2}$$

where E^0 represents the standard-state electrochemical cell potential, and ΔG^0 represents the Gibbs free energy change for constituents in their standard states. The standard Electromotive Force (emf) series for metals shown in most text books[1,2] registers values for E^0.

How the cell potential varies with cell conditions is established by the *Nernst equation*. The Nernst equation codifies the fundamental relationship in electrochemical reactions that expresses the electrochemical cell potential in terms of reactants and products of the reaction. It can be derived based on Gibbs free energy criterion for chemical reactions.[2] For a general chemical reaction, the change in Gibbs free energy is related to the activities of the reactants and products of reaction, as follows:

$$\Delta G - \Delta G^0 = \text{RT} \ln (a_{products} / a_{reactants}), \text{ or} \tag{3}$$

$$\Delta G - \Delta G^0 = 2.303 \text{ RT} \log_{10} (a_{products} / a_{reactants}), \tag{4}$$

where ΔG and ΔG^0 represent changes in the free energy of products and reactants in non-standard and standard states, respectively; R is the gas constant (8.314 J/mol·K), T is the temperature in Kelvins, and the qunatities $a_{products}$ and $a_{reactants}$ are the activities (roughly related to concentration) of products and reactants, respectively.

Eqns (3) and (4) establish the Nernst equation (5,6), which relates the cell potential, in any state, to the cell potential in a standard state and to the products and reactants of the electrochemical reaction.

$$E - E^0 = -(2.303 \text{ RT}/n\text{F}) \log_{10} (a_{products} / a_{reactants}), \text{ or} \tag{5}$$

$$E = E^0 - (2.303 \text{ RT}/n\text{F}) \log_{10} (a_{products} / a_{reactants}) \tag{6}$$

Though the thermodynamic aspect is useful in determining the relative tendencies of metal reactivity (or corrosion), in practical situations the kinetics of a corrosion reaction are important in governing the extent to which a metal corrodes, that is, the rate of corrosion. The corrosion rate is proportional to corrosion current (this relationship will be the subject of study next semester). Thus, a definite way of knowing if a metal in a given environment is corroding is to make a current measurement.

Laboratory Experiments[3]

1. GALVANIC CELL POTENTIAL & GALVANIC SERIES

Construct a galvanic cell between two dissimilar metals in "artificial seawater," a 3 wt% solution of sodium chloride (NaCl) in de-ionized water. Measure the cell electromotive force (emf), or potential, between a copper metal strip and every other metal strip, in turn. Designate the copper strip as the positive electrode (*cathode*) for all measurements, and change the metal strip at the other electrode from the available set.

Establish a galvanic series by ordering the examined metals according to their cell emfs with respect to copper. Place the more *cathodic* (noble) metals at the top and more *active* metals at the bottom.

Calculate the Gibbs free energy changes from the measured cell potentials.

The galvanic series can be set up for any given electrolyte. It may differ drastically from tabulated galvanic series or emf series and values in textbooks that refer to a measurement under normalized conditions for given electrolytes and concentrations.

Lessons to be learned: Galvanic, or two-metal, corrosion occurs when two metals are coupled together through a conducting solution The galvanic series predicts which metal is more *anodic* (active) or *cathodic* (noble) in galvanic corrosion.

2. TIME DEPENDENCE OF CELL POTENTIAL

Construct a galvanic cell with a **zinc-copper** couple in synthetic sea water. Measure the cell potential as a function of time over a period of at least 20 minutes. We will use a Solartron potentiostat for this part of the experiment. Make **copper** the *cathode*.

Reclean first the zinc electrode and then the copper electrode and note any effect on the cell potential.

Lessons to be learned: Reaction products formed on the electrode surfaces can affect the measured cell potential over time.

3. SILVER CLEANING

Prepare a 5% sodium bicarbonate (baking soda) solution in a 200 mL beaker. Take a piece of aluminum foil, crumple and stress it a bit to damage the native passivating oxide layer, thereby exposing the base metal. Wrap a tarnished silver item (jewelry) with the foil and place the foil-wrapped item into the bottom of the beaker. Heat the solution for 1 h at 70 $^{\circ}$C.

Lessons to be learned: Two different metals placed in electrical contact in an electrolyte comprise a *galvanic element*. The result is the oxidation and dissolution of the less noble metal. The more noble metal, covered with an oxide or some other similar tarnish layer (such as a

sulfide), can be reduced to the bare metal again if the cell potential is high enough, as it is for this case.

4. ELECTRODE SIZE EFFECTS ON CORROSION POTENTIAL AND CURRENT

Construct a cell with a piece of **brass** (*cathode*) and piece of **zinc** (*anode*). Measure the emf and cell current for brass and zinc for different electrode areas. Choose, for example, two sets of electrodes that differ in area by a factor of 4.

Lessons to be learned: Current in an electrochemical cell is proportional to electrode area and is a measure of corrosion rate. The cell potential is independent of the area of the electrode.

5. SACRIFICIAL ANODES

A. *Zinc as a sacrificial anode*
Prepare a galvanic couple between a piece of **1018 steel** or **iron** as an *anode* and **copper** as a *cathode*. Measure the emf of and current through the cell. Add to the cell a third electrode (**zinc** electrode). Connect current meters simultaneously between the copper and the steel/iron, copper and zinc, and steel/iron and zinc electrodes. Note any change in the corrosion current through the steel/iron anode, and comment on the relationship among the three currents you measure.

B. *(Biased) scrap steel or iron as a sacrificial anode*
Prepare a galvanic couple between a piece of **1018 steel or iron** as an *anode* and a **copper** strip as a *cathode*. Measure the emf of and current through the cell. Add a piece of **scrap steel or iron** as a third electrode. Insert a *DC* power supply into the circuit with the third electrode *negative* relative to the initial steel or iron electrode (and therefore more electronegative). Record the applied voltage and the corresponding diminishment the current flowing through the initial steel material to be protected, until a negligible current flows between cathode and the piece to be protected, indicating control of corrosion of this piece of steel.

Lessons to be learned: Sacrificial anodes can be configured biased or unbiased to protect materials that would otherwise be subjected to corrosion currents.

The principle is known as cathodic protection and was first employed in 1824 for the Royal Navy by Sir Humphrey Davy, who succeeded in protecting copper components of naval vessels using iron sacrificial anodes.

References

1. Mars G. Fontana and Norbert D.Greene, *Corrosion Engineering*, 2rd ed. (McGraw-Hill, NY, 1984), pp. 297-304.

2. H. H . Uhlig, *Corrosion and Corrosion Control*, 2nd ed. (Wiley, New York, 1971) pp. 18-21.

3. E.C. Subbarao, D. Chakravorty, M. F. Merriam, V. Raghavan and L. K. Singhal, *Experiments in Materials Science*, Ch. 14 (McGraw-Hill, NY, 1961), pp. 90-97; 210

Additional Reading

J. Wulff, *et al*., *Structure and Properties of Materials*, Vol. **II**: *Thermodynamics of Structure* (Wiley, NY, 1966) pp. 159-179.

J.C. Scully, *The Fundamentals of Corrosion*, 3rd ed. (Pergamon, NY, 1990).