Electrochemistry: Electroplating, Coloring, and Etching of Metals

Goals

- Explore the properties of an electrolytic cell by studying the electroplating of Zn and Cu electrodes
- Examine the oxidation-reduction reactions of copper when exposed to heat treatment and chemical dip
- Compare the oxidizing and reducing strengths of copper, aluminum, and zinc and various etching agents

Introduction.

Redox chemistry occurs in two types of electrochemical cells: electrolytic in which a voltage source provides the electrical energy that produces chemical change; and galvanic, in which the chemical reaction proceeds spontaneously without an external source of electrical energy. In the most common galvanic cell, a lead storage battery, a spontaneous chemical reaction generates the potential needed to start our cars. Charging the battery is an electrolytic process that reserves the direction of this reaction. In *electroplating*, another electrolytic process, a metal ion is reduced to its elemental form to form a *plate* or surface coating on the cathode, the negative terminal of the voltage source; e.g., a battery. The electroplating bath contains the metal ion to be reduced as well as other ions to support the flow of current during electrolysis. Simultaneous with deposition of a metal film on the cathode, oxidation occurs at the other electrode surface, the anode which is connected to the positive terminal of the voltage source. The oxidation reaction may involve the anode itself or a component of the electroplating bath. Figure 1 contains a schematic drawing of an electroplating apparatus.

Many industries rely on electroplating processes. Jewelry makers electroplate silver and gold on less expensive metals. Inexpensive gold rings cause fingers to turn green when the thin gold plate on copper wears away and exposes the more reactive metal. Similarly tin cans are made by electroplating thin layers of tin onto iron. The less reactive tin surface protects the underlying iron against corrosion by the food product in the can. Corrosion is the spontaneous oxidation of a metal includes the formation of rust from the structural iron in bridges and automobiles. Zinc is plated on structural iron to protect it from corrosion and the formation of rust. Electroplating will explored in this lab with zinc and copper electrodes in a zinc sulfate solution.

Deliberate exposure of a metal to oxidizing or corrosion conditions can be used to produce desirable colors or a *patina* on its surface. The patina may be produced by chemical treatment because of its beauty or to reproduce the appearance that an object would have acquired over a long, slow exposure to atmospheric conditions. The coloring of metals by changing their surface appearance will be explored in this lab by exposing copper to heat treatment and a chemical dip.

Finally, students will compare oxidizing agents, called etchants, and their reactivity with copper, aluminum, and zinc. Etching procedures, similar to those used in industrial

fabrication, will be used to make three simple decorative pieces that can be used as jewelry or as plates for printing.

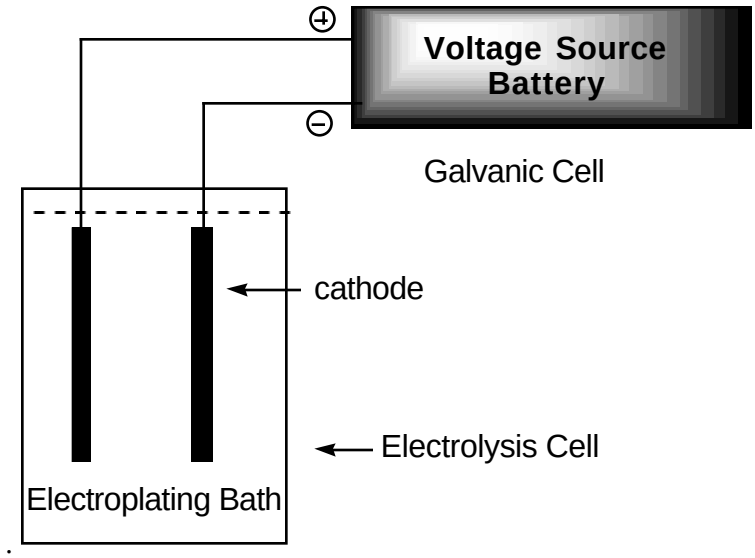

Figure 1. Schematic of Electroplating Apparatus

Experimental. The experiments below do not need to be completed in the sequence given.

A. Electroplating.

1. Obtain a microwell plate (6 wells) along with a cover that has two slits cut over each of the wells. These slits will be used to hold the electrodes.
2. Obtain small pieces of copper and zinc sheet to be used as electrodes and weigh each. Insert the two metal electrodes into the slits over one of the wells and bend the strips of metal to hold them securely in place
3. Half-fill the well in the microplate with 0.5 M zinc sulfate ($ZnSO_4$). Place the cover on the well plate so that the electrodes are submerged in the zinc sulfate solution, which serves as the electroplating bath.
4. Attach the copper electrode to the negative terminal of a 9-volt battery and the zinc to the positive terminal. Allow the reaction to proceed for 1 or 2 minutes while you observe. Then disconnect the wires and examine the electrodes. Record your observations.
5. Carefully remove the electrodes, rinse with distilled water and acetone (taking care not to get acetone on the microplate which dissolves in this solvent), dry, and weigh each electrode.
6. Repeat the experiment (steps 4-6) with new solutions pieces of weighed copper and zinc. In this case, connect the copper to the positive terminal of the battery.

Part B. Coloring of Copper using Heat Treatment and Chemical Dips.

1. Cleaning the Copper. Obtain at least 3 pieces of copper. Clean the surfaces by rubbing each piece with the metal cleaner provided. Wash the surface with detergent and rinse well with water. Immediately proceed with the coloring methods.

2. Heat coloring
   a. Carefully note the color and the luster of the copper.
   b. Using tongs, hold the copper in the flame of a Bunsen burner for 2-5 minutes until you notice a distinct color change.
   c. Remove the metal from the flame, let it cool, and examine the surfaces. Record the colors and textures of the surface, particularly in comparison to the unheated copper.

3. Chemical Dip Coloring of Copper using <u>Liver of Sulfur</u> (a mixture of K_2S, S, and $K_2S_2O_3$). Solutions of liver of sulfur are often used to produce an antique look to copper, silver, and gold objects. Dip a piece of copper into the liver of sulfur (in the hood).
   a. After the copper has changed to a desired color, remove it with plastic tongs. Wash the pieces in cold water, then hot water, and allow them to dry.
   b. Compare the surface coloring of the treated piece with the original and record your observations.

<u>Part C. Etching of Copper, Zinc, and Aluminum</u>

1. Evaluation of Reactions.

In this part of the experiment, students will compare reagents (*etchants*) for etching (oxidizing) metal surface. The following equations describe the possible reactions of the three reagents:

a. Nitric acid (Any brown gas produced is NO_2 formed from oxidation of NO, eqt 2):

b.

$$NO_3^- + 4\,H^+ + 3\,e^- \longrightarrow NO + 2\,H_2O \qquad (1)$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \qquad (2)$$

c. Stannous Chloride:

$$2Sn^{2+} \longrightarrow Sn_{(s)} + Sn^{4+} \qquad (3)$$

Such simultaneous oxidation-reduction of the same material is called disproportionation.

d. Ferric chloride may undergo one of two reactions:

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad (4)$$

$$Fe^{3+} + 3e^- \longrightarrow Fe_{(s)} \qquad (5)$$

Obtain three test strips each of the three metals. Sequentially dip (instructor will demonstrate) one test strip of metal into a small amount of the three reagents. After a few

minutes (or less if reaction is apparent), remove the test strip from the reagent and note any change appearance of the metal or of the reagent solution to indicate reaction. Based on your results and before proceeding further with the experiment, indicate the product of all reactions observed in your notebook.

2. Preparation of three etched decorative metal pieces.

In this part of the experiment, students will prepare three decorative pieces. Parts of the metal surfaces will be protected from the etchant by materials called resists. The parts of the metal covered by the resist will not be oxidized. Consequently, if the resist is applied as a design, exposure to an etchant will oxidize only the exposed metal so that, at the end of the etching process, the design is a part of the metal surface.

a. Selecting the metals and etchants. At least two different metals and two different etchants must be used to prepare the three decorative pieces. Use the results obtained with the small metal strips to select the combinations most appealing to you

b. Drawing the designs. Water-insoluble ink and a polymer, similar to those used in the microelectronics industry, will be used as the resists in this lab. Two types of metal pieces will be available for each of the three metals:

i) One type has a protective coating on one surface and bare metal on the reverse surface; a design can be drawn on the metal surface with ink, which serves as the resist. Note that nitric acid reacts with this ink so this process cannot be used with this etchant. The etchant will oxidize the metal not covered by the resist design.

ii) The second type has a protective polymer coating on both sides; a design can be scratched through this surface with a needle. Alternatively a Q-type dipped in isopropanol or acetone can be used to dissolve the resist to make more dramatically large lines. The etchant in this case will oxidize the metal exposed by drawing through the resist.

Etching the metal. Pour a small portion of the etchant into a small beaker. Using plastic tong to dip the metal piece containing the design into it. Carefully monitor the each reaction. When you are satisfied with the depth of the etch, remove the metal from the etchant and wash with water. Remove the resists by washing the ink away

Discussion and Conclusions.

A. Electroplating.

Discuss your observations. Show equations for the reactions occurring at each electrode for each experiment. Support your conclusions with data from the weights and appearances of the electrodes.

B. Coloring of copper using chemical treatment and a chemical dip

1. Write chemical equations to account for the two copper compounds formed from heating the metal in air.

2. Write a chemcial equation to account for the reaction occurring between the Cu and S in the liver of sulfur solution.

C. Etching of Cu, Zn, and Al with HNO_3, $FeCl_3$, and $SnCl_2$.

1. Prepare a table in your notebook to summarize the results of from the metal test strips and three reagents. Include the metal strips, the products for each reaction, and a balanced chemical equation.
2. Discuss the relative strength of the three metals as reducing agents. Support your conclusions with your experimental observations.

3. Discuss the relative strengths of the three etchants as oxidizing agents. Support your conclusions with your experimental observations.

4. Include the three decorative metal pieces in your notebook. Use them to discuss the relative merits of each combination to produce jewelry. Consider the safety and convenience of each etchants in recommending which combination would be most suitable for a home shop or studio.

The experiments here are adapted from ones developed by Professor Patricia S. Hill, Department of Chemistry, Millersville University, Millersville, PA 17551 for her course: *The Molecular Basis of Color and Form: Chemistry and Art.*