Quantitative Electrochemistry

Introduction

What is the relationship between the quantity of electricity and the extent of a chemical reaction in an electrochemical process?

Concepts

- Electrolysis
- Electrical charge (coulombs)
- Current (amperes)
- Faraday constant (coulombs per mole)

Background

The principles governing the amount of product obtained in electrolysis were developed by Michael Faraday in his 1834 paper entitled "On Electrical Decomposition." The terms he defined are still used today to describe electrochemical cells (electrode, cathode, anode, electrolyte, etc.). Michael Faraday also laid out the mathematical relationship between the quantity of electricity and the amount of a substance produced in electrolysis.

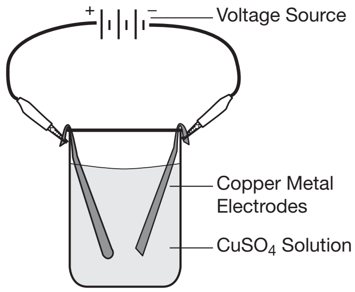
- The amount of a substance deposited on each electrode in an electrolytic cell is directly proportional to the quantity of electricity passed through the cell.
- The quantity of an element deposited by a given amount of electricity depends on its chemical equivalent weight.

Faraday's work in electrochemistry has been honored in the name of the *Faraday constant*, a fundamental physical constant corresponding to the charge in coulombs of one mole of electrons. In this experiment, the value of the Faraday constant will be determined by measuring the amount of copper obtained in an electroplating reaction.

Electroplating is the process of depositing a metal on the surface of a conductor by passing electricity through a solution of metal ions. Figure 1 shows a basic diagram of an electrolytic cell for a "copper-plating" reaction. The electrodes are copper metal. Oxidation of copper metal to copper(II) ions occurs at the anode, and reduction of copper(II) ions to copper metal occurs at the cathode.

Anode reaction (oxidation)

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$



Cathode reaction (reduction)

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Figure 1. Basic Diagram of an Electroplating Cell.

The change in mass at each electrode depends on the reaction time and the current. The coulomb (C) is the fundamental unit of electrical charge, and the charge on the electron is equal to 1.602×10^{-19} C. Current is measured in amperes, where one ampere (A) is equal to the flow of one coulomb of charge per second (1 A = 1 C/sec). The flow chart in Figure 2 shows the steps involved in calculating the amount of a substance produced in electrolysis.

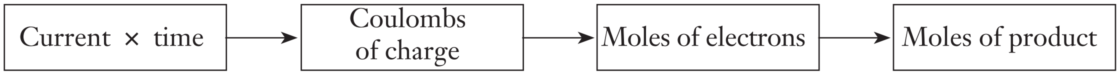


Figure 2. Flow Chart for Electrolysis Calculations.

Materials (for each student group)

Copper strips, 1 cm × 10 cm, 2
Copper(II) sulfate solution, $CuSO_4$, 1 M, 80 mL
Distilled water and wash bottle
Ammeter (0.2 to 1.0 A)
Alligator cords with clips, 3
Balance, centigram or milligram precision
Batteries, D-cell, 4, or power supply
Battery pack (to connect batteries in series)
Beaker, 150-mL
Clock or timer
Forceps
Paper towels
"Rinse" beaker containing distilled water*
"Rinse" beaker containing isopropyl alcohol or acetone*
Scissors
Steel wool or sandpaper

**Several groups of students may share alcohol and water rinse beakers.*

**Place several 400-mL rinse beakers containing 200 mL isopropyl alcohol or acetone in convenient locations for students to share. Water rinse beakers are also needed.*

Safety Precautions

Isopropyl alcohol is a flammable organic solvent; avoid contact with flames and heat. Copper(II) sulfate solution is toxic by ingestion and is a skin and eye irritant. Avoid contact with eyes and skin. Metal pieces may have sharp edges—handle with care. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the lab. Please review current Safety Data Sheets for additional safety, handling, and disposal information.

Procedure

1. Connect four D-cell (1.5 V) batteries in series using a battery pack or battery holders. *Note:* The battery pack consists of a molded plastic sleeve that will hold four batteries. The pack includes metal plates that may be placed at either end to connect the batteries to the electrochemical cell.

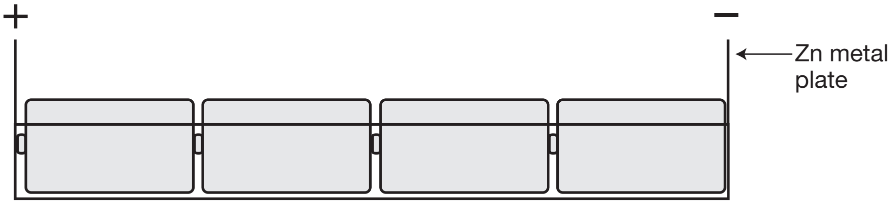


Figure 3. Battery Pack with Four D-Cells in Series.

2. Obtain two 1 cm × 10 cm strips of copper metal. Using scissors, round off the top edge of one of the copper strips. *The copper strip with the rounded edge will be used as the anode in this experiment.*
3. Polish the copper strips with steel wool or sandpaper and wipe clean with a paper towel.
4. Rinse each copper strip with a gentle stream of distilled water from a wash bottle, and pat dry.
5. Holding the metal strips with forceps, dip each copper electrode into a beaker containing isopropyl alcohol or acetone. Remove the copper strips and allow to air dry.
6. When the copper strips are dry, measure and record the mass of each electrode. *Remember that the strip with the rounded edge is the anode.*
7. Obtain about 80 mL of 1 M copper(II) sulfate in a 150-mL beaker and place the two copper electrodes upright in the beaker. Be sure that the electrodes do not touch each other.
8. Set up the electroplating apparatus (Figure 4): Using alligator clips, connect the anode to the positive lead on the battery pack, and the cathode to the positive lead on the ammeter.

9. Check the apparatus, then connect the negative lead of the ammeter to the negative lead of the battery pack. *Record the initial time.*

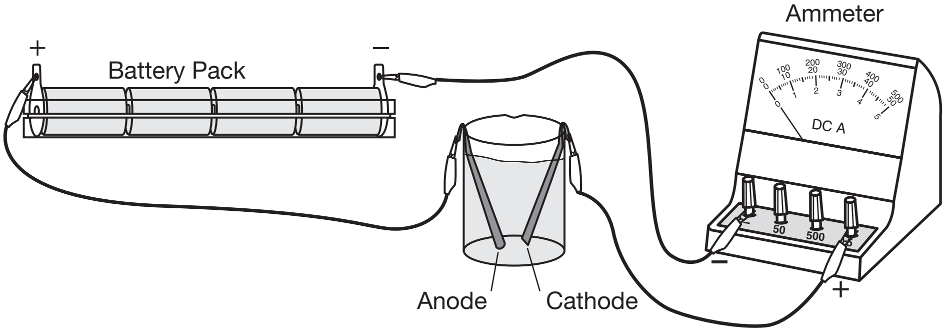


Figure 4. Electroplating Apparatus.

10. Bend the tops of the electrodes over the sides of the beaker to hold the electrodes in position. Read the current on the ammeter for a few seconds. The current will depend on the distance between the electrodes.
11. Move the electrodes closer together or farther apart as necessary to obtain a stable current in the range 0.6–0.7 A. The maximum current is usually obtained with the electrodes about 1–2 cm apart. *Do not allow the electrodes to touch.* After adjusting the electrodes, try not to move the electrodes during the electrolysis, because this will affect the current flow.
12. Measure and record the current at one minute intervals throughout the electrolysis reaction.
13. Continue electrolysis for 18–20 minutes, as time permits. *Record the final time at the end of the electrolysis reaction.*
14. Disconnect the alligator clips from the electrodes and gently remove the electrodes from the beaker.
15. Using forceps, carefully dip each electrode into a beaker of distilled water and then into a beaker of isopropyl alcohol or acetone to rinse the electrodes. Place the electrodes on a paper towel and allow to air dry. Do not wipe the surfaces of the electrodes!
16. When the copper strips are dry, measure and record the mass of each electrode. Remember that the strip with the rounded edge is the anode.
17. Consult your instructor concerning disposal of the copper(II) sulfate solution and the copper electrodes.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. Excess copper(II) sulfate solution may be rinsed down the drain with excess water according to Flinn Suggested Disposal Method #26b. Save the copper metal strips for future use. The copper strips may be cleaned by dipping them quickly in 6 M nitric acid. Rinse thoroughly with distilled water and with alcohol. Allow to air dry.

Tips

- This experiment can be completed in a typical 50-minute lab period. Set up and demonstrate a model apparatus to help students prepare for lab. This experiment is not intended as an introductory level experiment in electrochemistry. Students should have a good working knowledge of the language of electrochemistry (electrode, cathode, anode, etc.) and the signs of the electrodes. Students should also be familiar with the definitions and units used in electrical measurements (volts, current, charge, etc.).
- Both the copper electrodes and the copper sulfate solution may be recycled and reused by several lab sections. In our testing, we used the copper electrodes about 3–4 times without any problems—sand and polish well before each use. (The anode may become too thin after repeated use.) It may, in fact, be beneficial to reuse the electrodes from class to class. Bending and cutting a metal produces defects or stress areas in the crystal structure. Stress areas in the metal willcreate potential differences and may cause uneven plating or the growth of dendritic crystals that do not adhere well to the electrode. Repeated use removes these stress areas.

- The amount of copper gained or lost at each electrode depends on the current and the time of electrolysis. The current, in turn, depends on the voltage and the resistance of the cell, which is difficult to control. DC power supplies, if available, give better results than batteries, because the voltage can be adjusted to give a higher and more stable current. The highest, stable voltage we could achieve using four D-cell batteries in series (6 V) was about 0.7 A. At this current level, an electrolysis time of 20 minutes is recommended to give accurate results. If power supplies and/or milligram balances are available, the electrolysis time may be reduced to 15 minutes without sacrificing precision. A maximum current of about 1 A is recommended if a power supply will be used.
- The electrolytic cell and the ammeter are set up in series. The total resistance of the circuit is equal to the sum of the resistances supplied by each component. Some sources recommend adding sulfuric acid to the electrolysis solution (making it 1 M in $CuSO_4$ and 1 M in H_2SO_4) to decrease the resistance of the cell. We tested this modification and found that it did not improve accuracy.
- In general, the batteries can only be used by two classes before they have been drained of power and must be replaced. A large, 6-V lantern battery may be used instead of 4 D-cells. The 6-V batteries cost more, but they will also last longer.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Constancy, change, and measurement
Content Standards: Grades 9–12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, chemical reactions, interactions of energy and matter
Content Standard E: Science and Technology
Content Standard G: History and Nature of Science, historical perspective

Sample Data *(Student data will vary.)*

Mass of Anode (Initial)	*2.62 g*
Mass of Cathode (Initial)	*3.03 g*
Mass of Anode (Final)	*2.36 g*
Mass of Cathode (Final)	*3.30 g*
Time (Initial)	*9:05*
Time (Final)	*9:25*
Total Electrolysis Time	*20 min*

Record current at 1 minute intervals:

Time	Current	Time	Current	Time	Current	Time	Current
1 min	*1.00 A*	**6 min**	*0.65 A*	**11 min**	*0.65 A*	**16 min**	*0.65 A*
2 min	*0.45 A*	**7 min**	*0.60 A*	**12 min**	*0.65 A*	**17 min**	*0.65 A*
3 min	*0.69 A*	**8 min**	*0.65 A*	**13 min**	*0.63 A*	**18 min**	*0.63 A*
4 min	*0.68 A*	**9 min**	*0.63 A*	**14 min**	*0.63 A*	**19 min**	*0.63 A*
5 min	*0.68 A*	**10 min**	*0.63 A*	**15 min**	*0.65 A*	**20 min**	*0.65 A*

Sample Calculations and Analysis *(Student answers will vary.)*

1. *Mass gain at cathode* = *3.30 g* − *3.03 g* = *0.27 g*
Mass loss at anode = *2.36 g* − *2.62 g* = *−0.26 g*
Moles of copper gained at cathode = *0.27 g/(63.55g/mole)* = *0.0042 moles Cu*

$$\text{Moles of copper lost at anode} = 0.26\text{ g}/(63.55\text{ g/mole}) = 0.0041\text{ moles Cu}$$

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2. $$\text{Moles of electrons at anode} = 0.0041\text{ moles Cu} \times \frac{2\text{ moles of }e^{-}}{\text{mole of Cu}} = 0.0082\text{ moles }e^{-}$$

$$\text{Moles of electrons at cathode} = 0.0042\text{ moles Cu} \times \frac{2\text{ moles of }e^{-}}{\text{mole of Cu}} = 0.0084\text{ moles }e^{-}$$

3. $$\text{Average current} = 0.65\text{ A }(0.65\text{ C/sec})$$

$$(0.65\text{ C/sec}) \times 1200\text{ sec} = 780\text{ C}$$

4. $$\frac{780\text{ C}}{1.60 \times 10^{-19}\text{ C/electron}} = 4.9 \times 10^{21}\text{ electrons}$$

5. $$\text{At the anode: } \frac{780\text{ C}}{0.0082\text{ moles}} = 9.5 \times 10^{4}\text{ C/mole}$$

$$\text{At the cathode: } \frac{780\text{ C}}{0.0084\text{ moles}} = 9.3 \times 10^{4}\text{ C/mole}$$

6. $$\text{Percent error} = \frac{|\text{ Literature value } - \text{ Experimental value }|}{\text{Literature value}} \times 100$$

$$\text{Faraday constant} = 9.65 \times 10^{4}\text{ C/moles.}$$

Both the anode and the cathode gave excellent results (1–4% error) for the value of the Faraday. If the copper formed at the cathode does not adhere well to the metal surface, the mass gain at the cathode will be less accurate than the mass loss at the anode. (That's why it is important not to wipe the surfaces of the electrodes—see step 15 in the Procedure.) Competing reduction of water during the electroplating reaction may give rise to hydrogen gas at the cathode. This would make the anode results more accurate. (Oxygen generation at the anode is less likely.)

Materials for *Quantitative Electrochemistry* are available from Flinn Scientific, Inc.

Catalog No.	Description
C0182	Copper Strips, 6/pkg.
C0246	Copper(II) Sulfate Solution, 1 M, 500 mL
I0020	Isopropyl Alcohol, Reagent, 4 L
S0128	Steel Wool, 16/pkg.

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.

Quantitative Electrochemistry Worksheet

Data Table

Mass of Anode (Initial)	
Mass of Cathode (Initial)	
Mass of Anode (Final)	
Mass of Cathode (Final)	
Time (Initial)	
Time (Final)	
Total Electrolysis Time	

Record current at 1 minute intervals:

Time	**Current**	**Time**	**Current**	**Time**	**Current**	**Time**	**Current**
1 min		**6 min**		**11 min**		**16 min**	
2 min		**7 min**		**12 min**		**17 min**	
3 min		**8 min**		**13 min**		**18 min**	
4 min		**9 min**		**14 min**		**19 min**	
5 min		**10 min**		**15 min**		**20 min**	

Post-Lab Calculations *(Show all work on a separate sheet of paper.)*

1. Calculate the change in mass for both the anode and the cathode. Divide the change in mass by the atomic mass of copper to determine the *moles of copper* lost or gained at the anode and cathode, respectively.
2. Multiply the number of moles of copper by two to find the *moles of electrons* transferred at each electrode during electrolysis.
3. Determine the average current during the electrolysis procedure. Multiply the average current by the time of electrolysis in seconds to calculate the *coulombs of charge* passed through the cell.
4. Divide the total coulombs of charge by the charge on an electron (1.60×10^{-19} C/electron) to determine the *number of electrons* passed through the cell during electrolysis.
5. Divide the coulombs of charge passed through the cell (Question #3) by the moles of electrons transferred to each electrode to calculate the *Faraday constant*, $\mathcal{F}$ (coulombs of charge per mole of electrons).
6. Look up the literature value of the Faraday constant and calculate the *percent error* in the experimental value for both the anode and the cathode. Which electrode gave more accurate results? Suggest a possible reason for any difference in accuracy.