Name:______________________________Date:______________Class:_______________

Student Worksheet

Electro-deposition of Copper on a Filter Template for Growing Nanowires

Introduction

Safety

This lab makes use of a strong base solution (sodium hydroxide) and a volatile organic solvent (acetone). All these chemicals must be handled with care. Safety eyewear (full chemical goggles, not safety glasses) and nitrile gloves (not latex gloves) must be worn when handling these chemicals. Acetone should be handled under a fume hood if available, or in an area with good circulation, avoiding direct inhalation of the vapor.

This lab is designed to introduce you to the electroplating process of growing nanowires. Nanowires are nanoscale (1x10-9) objects that have large length to width ratios that can be greater than 20 to 1. That have a wide range of applications such as vehicles for drug delivery and biological sensors. This experiment will use an electro plating process to transfer metal ions in a solution to a template to produce nanowires. The electric field in the solution carries these ions and deposits them onto an electrode. In this experiment, an anode (platinum strip) will be used in a solution of copper sulfate. Copper will be plated out onto the pores of a filter at the cathode. You will discover how nanowires can be created to further understand the reduction-oxidation process, Ohm's law, and the mechanism of metal electroplating.

Question: What are the redox reactions at the anode and cathode?

Reduction reaction for Cu at cathode: $CuSO_4 \rightarrow ?$

Oxidation reaction for Cu^{2+} at anode: $Cu^{2+} + ? \rightarrow ?$

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Materials

- Copper sulfate electrolyte solution
- Whatman alumina membrane filters (20 nm pore size, 25mm diameter)
- Copper tape
- Platinum-coated electrode
- Nail polish
- 10 ml 1.0 M sodium hydroxide
- 10ml 1.0M ethanol

Equipment

- Safety goggles
- Nitrile gloves
- One pair of tweezers
- Power supply or battery (6.0-9.0 volts, capable of passing 0.60-1.0 amps)
- Two connecting wires with alligator clips
- 16-18 gauge copper wire
- Beakers – 25-mL; 50-mL; 250mL
- Vial
- pipet
- Cotton swaps
- Plastic container to hold filter
- Hot stir plate
- Cardboard square (approx. 15 cm on a side)
- Ammeter or multimeter
- Stopwatch
- Optical microscope

Procedure:

First period.

1. Cut the copper tape into pieces about 6 to 8 cm in length.
2. Place the Whatman aluminum oxide filter near the end of one side of the tape. Apply nail polish as an insulator to cover the edge of the filter and half of the tape on both sides and along the edges.
3. Pour 150 ml of the copper plating solution into 250 ml beaker. Place a stirring magnet in the beaker and put it on the stirrer/hot plate.
4. Connect the copper tape to one alligator clip. Make sure the unpainted portion of the tape does not touch the solution. This tape acts as a cathode (negative electrode, which attracts positive charges (cations)). The other alligator clip attaches to a platinum metal plate as an anode (positive electrode, which attracts negative charges (anions)).
5. Connect the cathode to the negative (minus) pole on the power source, using an alligator clip.
6. Connect the anode to the negative (minus) pole on the ammeter or multimeter. This is usually black in color. Prepare to start timing.
7. Connect the positive (plus) pole on the ammeter (usually red in color) to the positive terminal of the power source. Start timing *immediately* when this connection is made.

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8. Check to see that the ammeter is measuring a current of around 500 milliamps (mA) or less. If no current is flowing, check your connections and try again.
9. Turn the hot plate on, adjust the temperature to warm and observe the experiment for 10 minutes or as advised by your instructor.
10. Record the current (in milliamps) every minute in your notebook. At the end of the deposition, record the total time that current has flowed (in seconds).
11. Take the sample out of the plating bath and rinse it with water. Save the sample in a plastic container.

Second period.
To observe and measure the nanowires, you will release the nanowires from the filter and examine the wires under an optical microscope, or if available, a scanning electron microscope.

To prepare the sample for microscopy, do the following:
1. Use acetone or nail polish remover to remove the nail polish from the filter.
2. Place the sample into a 25 ml beaker and pipet 15 ml ethanol, and leave it for 1 hour
3. Transfer the sample to a vial and separate the deposited nanowires using a sonicator or vigorous stirring.
4. Remove a small amount of liquid, which contains suspended nanowires, and place on a glass microscope slide, or if an SEM is available, an SEM sample stub. Let the liquid dry for one hour.
5. Now the nanowires can be further observed under the optical microscope or SEM. You will measure the lengths of the 20-30 nanowires using the stage micrometer, and obtain an average wire length to compare with their predictions.
6. If insufficient numbers of nanowires are released using the ethanol, the alumina filter may be dissolved to release all the wires. To dissolve the filter, place the filter in 5 mL of 1..0M NaOH and leave for at least 20 minutes. Allow the wires to settle under gravity, pipette up a few drops from the bottom of the suspension, and transfer to a microscope slide. Repeat step 5.

Record Your Observations.

Measurements

	Ampere (mA)	Second (s)	Coulombs	Charge
Current				
Mean Current				
Time				
Mole electron				

Analysis.

The calculation is done in the following steps. First, calculate the amount of charge that has passed through the solution, and convert to the number of charged ions. The quantity of electricity that has passed through a solution is equal to the current (for example, 500 mA = 0.500 amps) multiplied by the total time that the electrolysis is conducted (for example, 5 minutes = 300 seconds.

The amount of charge is given in coulombs.

Number of coulombs C = Amperes (A) $\times$ seconds (s)

If you ran the current for 5 minutes (300 seconds), then the calculation would be

0.5A $\times$ 300 s = 150 coulomb

This can be converted to electronic charges as follows:

Number of electron charge $e^{-} = \frac{150\ Coulomb}{1.602 \times 10^{-19}} = 9.36 \times 10^{20}$

A convenient unit in electrochemistry is the Faraday (or *mole electron)*, defined as the amount of charge (in coulombs) represented by one mole of electrons. This can be calculated by the following.

$$\frac{1.602 \times 10^{-16}}{e^{-}} Coulomb \times \frac{6.022 \times 10^{23}}{mole\ e-} e^{-}$$

$= \frac{96{,}485\ \text{Coulomb}}{mole\ e^{-}}$ = 1 Faraday= 1 mole electron

So for our example of 150 Coulombs we can convert to the number of Faraday:

Number of Faraday = $\frac{1\ mole\ e^{-}}{1} \times \frac{150\ Coulomb}{96485\ coulomb} \times \frac{1\ mole\ of\ Cu}{2\ mole\ of\ e^{-}}$

This tells us how many moles of copper that this much charge will react with. The last term tells us that two moles of electrons are required to react with one mole of Cu^{2+}, since the copper ion is doubly positive charged.

The result of this equation is 0.0000773 mole of Cu. That is, our 150 coulombs of charge will react with 0.0000773 moles of copper during the electro-plating process. This amount of copper will be electro-deposited at the cathode and into the pores of the filter that we are using as a deposition template. The filter pores are cylindrical, so the deposited copper nanowires will be too. We know the diameter of the pores (and resulting wires) from the filter manufacturer, but nanowire length will depend on how much copper we deposit.

To predict the size of nanowires, we'll need to know the total volume of copper deposited. Using the molecular weight for Cu (63.5 g/mole) and the mass density (89.6g/cm^3) we can calculate the mass and the volume of the deposited copper in our example.

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Mass of Cu deposit:

$$= \frac{0.0007773\ mole\ of\ Cu}{1} \times \frac{63.5\ g}{1\ mole\ of\ Cu} = 0.04936 \text{ g of copper deposited in this example.}$$

Then the total volume of Cu deposited in this example is

$$\text{Volume (cm}^3\text{)} = \frac{Mass\ (g)}{Density\ (g/cm^3} = \frac{0.04936\ g}{89.6\ g/cm^3} = 5.5089 \times 10^{-4} cm^3 = 0.55089 \text{ mm}^3$$

This total volume of copper will be formed into many nanowires. To calculate the nanowire length for this example, assume the following:

a. Each filter is 25mm in diameter, so total filter face area can be calculated (what is the formula you will use?).
b. Each filter has a porosity of 50%, meaning the half face area is made up of pores that copper will deposit into. So the total pore area is equal to 0.5 x the filter face area.
c. Assuming the copper plates evenly inside the pores, the expected length of each nanowire will be:

$$L = \frac{(total\ volume\ deposited)}{(Total\ pore\ area\ available)}$$

Now, repeat this analysis using your actual measured values for mean current (in amperes) and deposition time (in seconds). You may use all other assumptions used in the above example.

Data Analysis Table	Diameter (mm)	Thickness (µm)	Area (mm^2)	Volume (cm^3)	Mass (g)
Anodisc					
Nanowires					
Copper deposited					
Predicted Nanowire Length					
Mean measured length					
Difference					

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Step by step calculations.

1. What is the volume of copper deposited in the pores of the filter template after the deposition is complete, using the measured value of current?

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2. What is the predicted length of the copper nanowires deposited in the 20 nm diameter pores?

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3. When you measure at least 20 of the nanowires that you made under a microscope, what is the mean length?

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4. What is the difference between the predicted and measured values? Calculate the difference using the following formula:

$$\%\ \text{Difference} = \frac{\text{Measured value} - \text{predicted value}}{\text{predicted value}} \times 100$$

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