

FKA195: Nanoscale Science & Technology: Thin Films & Materials.

Lab Demo *Electroplating*

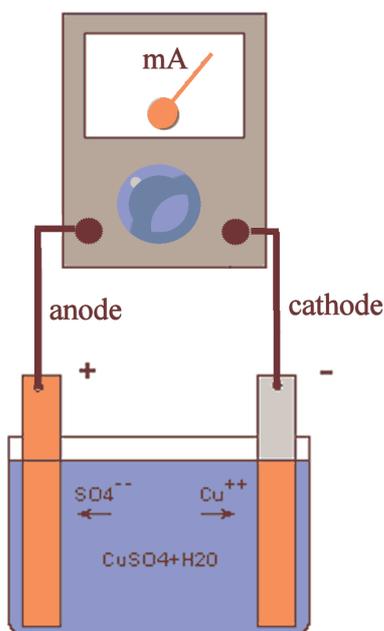
1. Introduction

Electroplating is achieved by passing an electrical current through a solution containing dissolved metal ions and the metal object to be plated.

The Baghdad Battery is an artifact from between 250 BC Centuries: 4th century BC- 2nd century BC; it is a device found in Baghdad, Iraq which is believed to be a crude battery used for electroplating.

Italian chemist, Luigi Brugnatelli was the first to invent (modern) electroplating in 1805 when he electrodeposited gold by using the Voltaic pile, discovered by his colleague Alessandro Volta several years earlier. Luigi Brugnatelli's was ordered by Napoleon Bonaparte not to continue on his experiments. Braking the order, Luigi Brugnatelli published his work in the Belgian Journal of Physics and Chemistry, "I have lately gilt in a complete manner two large silver medals, by bringing them into communication by means of a steel wire, with a negative pole of a voltaic pile, and keeping them one after the other immersed in ammoniuret of gold newly made and well saturated".

Usually there is an anode (positively charged electrode), which is the source of the material to be deposited; the electrochemistry which is the medium through which metal ions are exchanged and transferred to the substrate to be coated; and a cathode which is the substrate (the negatively charged electrode) to be coated.



Plating is done in a plating bath which is usually a non-metallic (plastic) tank filled with electrolyte which contains the metal to be plated in the ionic form.

The anode is connected to the positive terminal of a power supply. The anode is usually of the metal to be deposited on the cathode, the electrically conducting "substrate" to be plated. This is connected to the negative terminal of the power supply. The power supply should be stable, with minimum of ripple noise as well as designed to provide a steady bias current which independent of changing loads (resistance of the bath) during deposition.

When a dc current is applied between the cathode and anode, the positive metal ions from the solution will move towards the negative cathode and will precipitate their. To replenish for these deposited ions, the metal from the anode will be dissolved in the solution thus balancing the ionic concentration.

In the case of some materials such as Au, the anode is made of material that does not dissolve in the electrolyte, such as titanium (the anode is not sacrificial). The plated Au comes out of the solution in an oxidation-reduction reaction, where one material gives up electrons (gets oxidized) and the other material gains electrons (gets reduced).

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Metals which are possible to deposit from aqueous solutions are marked by green color. Elements with yellow color are only possible to deposit in combination with some other elements (alloy plating). Elements such as Ti and Al can only be deposited from organic electrolytes, while other metals such as Mg, Nb, Ta, and W can only be plated from molten salt electrolytes (at 700°C and above).

Faraday's Laws of Electroplating state:

1. The weight of a material deposited at an electrode is proportional to the amount of current passed through the cell.
2. The weights of different materials deposited at an electrode by the same amount of current are proportional to their equivalent weights.

Equivalent weight in an oxidation-reduction reaction is the molar weight of the compound / algebraic change in oxidation number of the atom that is oxidized or reduced. Say, if Fe valency (oxidation number) goes from +2 to +3, the change is +1. Therefore equivalent weight of FeCl₂ as a reducing agent is equal to 1 mole or 126.8 g. In some reactions Fe (+2) is reduced to Fe (0). The equivalent weight of is then 76.0 g which is = molar weight/change in valency.

Some background:	
1 Coulomb	= 1 Ampere × 1 second
Charge of 1 electron	= 1.602 × 10 ⁻¹⁹ Coulomb
Charge of 1 mole of electrons =	
1.602 × 10 ⁻¹⁹ Coulomb/electron × 6.022 × 10 ²³ electrons/mole	
=	96485 Coulombs/mole
=	1 Faraday

In other words, 1 Faraday of charge is equivalent to one mole of electrons passed from cathode to anode.

In the case of AgNO₃, 1 mole of Ag (107.9 g) of Ag is deposited when 1 Faraday of charge passes from anode to cathode. In the case of CuSO₄, 1/2 mole of Cu (31.8 g) of Cu is deposited when 1 Faraday of charge goes through the system. In the case of AgCl₃, 1/3 mole of Au or 65.7 g of Au is deposited when 1 Faraday of charge goes through the bath.

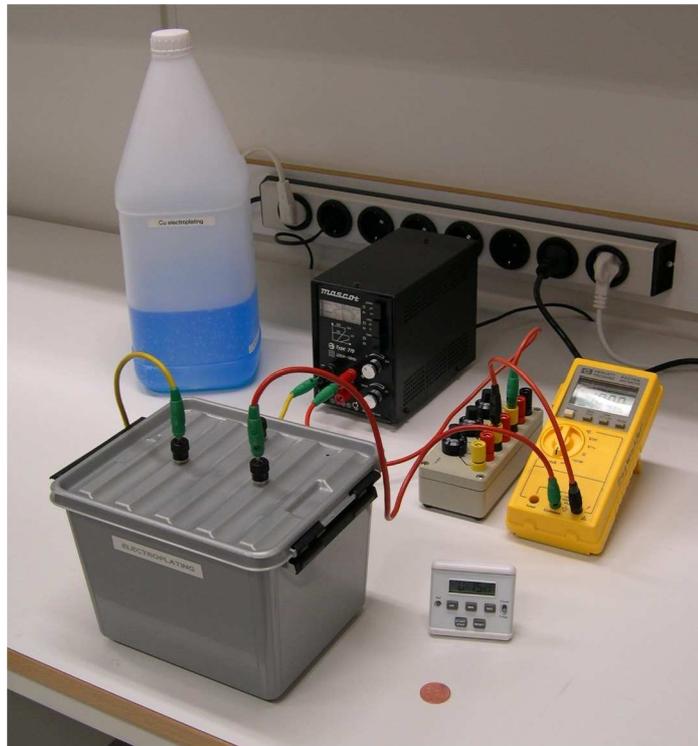
Thus 1 A-h of current through a CuSO_4 solution will make plating according to the following:

$$1 \text{ A-h} = 3600 \text{ A s} = 3600 \text{ Coulomb} = (3600 / 96485) = 0.0373 \text{ Faraday}$$

Since 1 Faraday is equivalent to 31.8g of deposited Cu, 0.0373 Faraday will deposit ~1.2 g of Cu.

Based on the mass of the metal deposited, the thickness of the thin film can be calculated if the area and density of the deposited material is known (the latter can be slightly different from the bulk values found in the handbooks). The bulk density of Cu is $\approx 8.9 \text{ g/cm}^3$

2. The electrolytic cell



The simple electroplating system consist of:

- Plastic bath (electrolytic cell) ($\approx 3\text{l}$)
- Power supply (0-30V)
- Multimeter
- Variable resistor (0-10 $\text{k}\Omega$)

3. Electroplating of Cu.

For electroplating with Cu we will use the following solution:

- 1.8 M H_2SO_4
- 0.25 M CuSO_4
- 1 mM NaCl
- 44 μM Polyethyleneglycol (PEG) (average molecular weight = 6000)

Anode is made of copper braid (Cu-cable wires).

To fasten a sample to be plated, we will use the crocodile clamp.

In the lab demo, we will electroplate Cu on a Si wafer with a thin film of Ag (deposited by PVD somewhere else). An exercise consists in calculating thickness of the deposited Cu film by measuring the current through the cell and the time of deposition (5-10 min).

Various qualitative questions may be asked during the demonstration, based on this PM, like:

- What would happen if we changed the direction of the dc current after the deposition?
- Suggest an experiment of measuring the molecular weight of Cu and other metals.
- What are the advantages and drawbacks of electroplating? Do you think it can be used in nanotechnology? Suggest possible realization.
- What parameters does the resistance of the solution depend on? Would it decrease or increase if we put more salt (CuSO_4) in water?
- What would happen if we left the current switched on for a much longer period of time (hours and days, may be)?
- Which metals you know are electroplated on a large scale?
- There is a third electrode assumed to be used in the electrolytic cell. Do you know why?
- What is the mole of electrons? What is its charge?
- What is the purpose of variable resistor which we connect in series to the cell? Can it be taken away?
- How is it possible to electroplate insulating materials?