Electrochemistry course
ACME Faculty, EHVE course
B.Sc. Studies, II year, IV semester

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Electrodeposition. Electroless plating.

Electrochemical series

(standard half-cell potentials vs SHE)

Li^+/Li	-3.045 V	$AgCl/Ag$	+0.222 V
Ca^{2+}/Ca	-2.864 V	$Hg_2Cl_2/2Hg$	+0.268 V
Na^+/Na	-2.711 V	Cu^{2+}/Cu	+0.338 V
Mg^{2+}/Mg	-2.370 V	$I_2/2I^-$	+0.536 V
Al^{3+}/Al	-1.700 V	MnO_4^-/MnO_4^{2-}	+0.558 V
SO_4^{2-}/SO_3^{2-}	-0.932 V	Fe^{3+}/Fe^{2+}	+0.771 V
Zn^{2+}/Zn	-0.763 V	Ag^+/Ag	+0.799 V
Cr^{3+}/Cr	-0.744 V	Pt^{2+}/Pt	+0.963 V
Fe^{2+}/Fe	-0.441 V	Cl_2/Cl^-	+1.358 V
Ni^{2+}/Ni	-0.234 V	Au^{3+}/Au	+1.498 V
Pb^{2+}/Pb	-0.126 V	MnO_4^-/Mn^{2+}	+1.531 V
H_3O^+/H_2	0.000 V	F_2/F^-	+2.866 V

Metallic coatings - applications

Formation of metallic coatings on various materials has plenty of applications:

- Anticorrosion protection – coating material with tight layer of metal that does not corrode (or to a negligible extent);
- Higher resistance to abrasion/grinding and for better surface quality – *e.g.* engine pistons/cylinders;
- Strengthening or smoothing surface (decreasing surface porosity/coarseness);

Metallic coatings - applications

- High luster of the surface – *e.g.* specifically for headlights reflectors;
- Decorative – when the given material (polymeric for instance) should look premium, like metal for instance (e.g. plating with chromium or gold);
- Introduction of catalytic layer (supporting reaction processes at the surface) or chemically resistive one;
- ...and many more, *e.g.* increasing hardness/durability.

Electroplating

- A special case of electrolysis is **electroplating**. It consists in carrying out an electrolysis with an electrode, on which the substance in question (usually metal) can deposit (initially forms a crystal nucleus) as a layer (thus the name – plating).
- It is one of simpler and better methods to cover one metal with the other (sometimes also non-metal or metal compound).
- Amount of the plated substance can be calculated/designed the same way as in the typical electrolysis.

Electroplating

- With the means of electroplating lot of things can be produced like nails (zinc plating), coins (nickel or copper plating), roofing tiles (zinc plating), computer cases (aluminum), car, ship or train car bodies, *etc.*

- Decorative items as well – jewelry, cutlery, car bumpers, wheel rims (chromium plating), *etc.*

What can be plated with metal?

Usually one divides materials by the type of the base for plating. These are:

- Metals and their alloys;
- Single crystals of elements or compounds (*e.g.* Si, SiO_2, GaAs);
- Ceramics and glass;
- Polymers and plastics;
- Material of biological origin.

Issues with the material choice

When choosing material for plating on, one has to pay attention to the following issues:

- Size and shape of the object – defines what technology is required to produce element;
- Technology of layer deposition – if it is electroplating, base has to conduct electricity well; it is also possible to use electroless plating.

Issues with the material choice, cont'd

- Reactivity between the base and the coating – they should not form galvanic cells, which would cause corrosion;
- Matching base and coating – if layer would adhere properly to the base;
- What temperatures and their differences would the product be a subject to (or to any other unusual conditions).

Electroplating process

It consists in carrying out the electrode reaction:

$A^+ + e^- \rightarrow A$

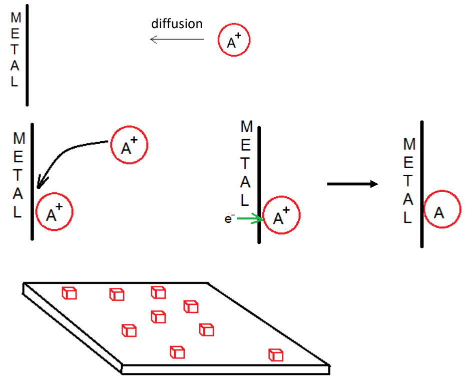
Object that conducts electricity to be coated is immersed in the so-called electroplating bath (electrolyte with additives) that contains ions of the metal A, which will form a layer.

Metalized object has to be connected as a cathode (as a chemical equation indicates).

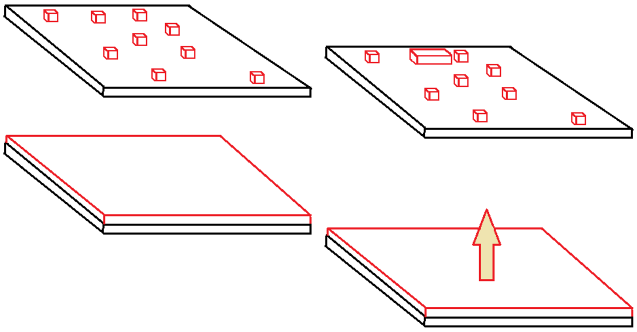
Electroplating process - steps

1. Transport of an ion to the base (diffusion);
2. Adsorption to the surface of an object;
3. Acceptance of electron by an adsorbed ion;
4. Nucleation of crystal structure;
5. Nucleus growth (insular structure);
6. Coalescence of nuclei (tight layer formation);
7. Layer thickness growth.

Electroplating process - steps



Electroplating process - steps



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Issues with electroplating

Selection of appropriate plating conditions is the main issue of electroplating, *e.g.*:

- Current density and time of plating (layer thickness affects all its properties considerably);

  $m = M·I·t/(F·z)$
- Composition of the electroplating bath – introduction of proper additives like pH regulation (buffered solutions), or those increasing smoothness of the surface (usually organic additives like citrates);

Issues with electroplating

- Hydrogen evolution issues – effect in the formation of rough and non-homogenous layers;
- Formation of poorly adherent layers in case of the improperly prepared/cleaned/degreased surface;
- Dendrites formation on the improperly prepared surfaces;
- Stabilization against hydrolysis;
- Maintaining high conductivity of the electrolyte;
- Complexation of ions of the plated metal.

Electroplating methods

During constant current plating – when the enforced current is constant over time – it often allows for gas bubbles nucleation and thus formation of the rough surface (or dendrites growth);

It is also possible to plate with the pulsed plating method. Current is flowing through the cell in short pulses with the determined current density. Short pulse precludes (or hinders considerably) nucleation of gas bubbles – yielding smoother surface finish as a result.

Surface preparation before electroplating

It is important that surface for plating should be prepared adequately (cleaned) – for better adhesion of the layer. There are few processes to do that:

- mechanical scrubbing/brushing to remove corrosion products, for instance (stripping outer layer);
- degreasing (emulsion, chemical, ultrasonic, *etc.*);
- polishing – various types (prevents dendrites growth);
- etching – to remove corrosion products.

Electroless plating, or how to gild the rose

Often it is required to plate metal layer on the dielectric material.

Most of the plastics, ceramics and biologically-derived materials are dielectrics.

Electroless plating

Electroless plating is carried out in a very similar way to that of the typical electroplating, although after the surface cleaning additional surface treatment is required. Electrically conducting layer is deposited on the surface (so-called surface activation), which then enables the object to the rest of the process (layer thickness growth). There are few methods to obtain the conductive layer.

Direct metal plating

Employing palladium sublayers: One of the methods of conducting sublayer formation consists in immersing the object in a colloidal palladium solution where palladium molecules are closed in stabilizers (polymers or tin compounds). Subsequently, colloid is adsorbed at the surface (pre-treated) and upon the formation of the catalyst grains stabilizer is rinsed away.

Direct metal plating

Employing polymeric sublayers: Deposition of manganese compounds (MnO_2 for instance) on the base, followed by coating it with monomer and then polymerizing this monomer. During the polymerization manganese compounds presence affect the process to produce polymer in the conducting form (*e.g.* polypyrrole, polythiophene, PEDOT). It is possible to plate metal on a surface with the conducting polymer sublayer.

Direct metal plating

Employing carbonic/graphitic sublayers: Deposition of colloidal graphite from the solution (aqueous one for instance). This graphite is crystalline and adhere well to the surface. In the same time it is electronically conducting and enables electroplating.

Electroless plating

Electroless plating is a base for an electronics industry, as this is the main production method of the printed circuit boards (vias - connection between layers of a board, paths, *etc.*).

Calculations

Zinc electroplating of the roof tiles with the surface of 4200 cm^2 (35x120 cm) is carried out in the galvanic bath. There are 100 tiles and the layer thickness should be 40 µm. Calculate the current needed to perform this process in 5 minutes. Calculate what current density it would be (A/cm^2).

Zin density is 7.13 g/cm^3.

Calculations

How long does it take to carry out the copper electroplating of the printed circuit board inner surface of the vias (ø1 mm) in the galvanic bath, where current is 10 A, PCB has 1 mm thickness, there are 100x50 vias, and a copper layer thickness should be of 50 µm?

Copper density is 8.96 g/cm^3.